University of Nairobi

Assessment of Heavy Metals Pollution Using XRF Spectrometry– A Case Study of Kilimapesa Hill Gold Mines Processing Plant area, Narok County

By

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A thesis submitted in partial fulfilment of the requirements for the award of Master of Science degree in Nuclear Science at the University of Nairobi

2020

Declaration

I hereby declare that this thesis is my own original work and has not been presented for award of any degree or qualification in any other institution of higher learning.

Lynda Kanguha Wamere - S56/5961/2017

Signature………………………...   Date……………………………

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Dedication

This work is dedicated to my husband and family for their support and encouragement. They are a support system in my scholarly pursuits.

Acknowledgement

I thank the Almighty God, for the opportunity afforded me to do this research, and for blessing me with sound health during the whole period of working on this project.

I want to thank my supervisors; Mr Michael J. Mangala and Dr Geoffrey O. Okeng'o for their support and direction in the course of putting this work together. I also want to acknowledge with thanks, Mr Simon K. Bartilol, the Chief Technologist, Institute of Nuclear Science, and Mr Justus J. Okonda, Ph.D student and Laboratory In charge, Department of Physics, for their guidance and assistances in the laboratory work.

Lastly, but not least, my sincere appreciation, to the Nuclear Power & Energy Agency (NuPEA), formerly Kenya Nuclear Electricity Board (KNEB), under the Ministry of Energy & Petroleum for awarding me the sponsorship to pursue this master's degree program.

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Abbreviations

AAS	-	Atomic Absorption Spectroscopy
AMD	-	Acid Mine Drainage
ANOVA	-	Analysis of Variance
ARD	-	Acid Rock Drainage
CF	-	Contamination Factor
CRM	-	Certified Reference Method
DNA	-	Deoxyribonucleic acid
EDXRF	-	Energy Dispersive X-ray fluorescence
EMCA	-	Environmental Management Regulations and Coordination Act
EPA	-	Environmental Protection Agency
FP	-	Fundamental Parameters
GPS	-	Global Positioning System
IAEA	-	International Atomic Energy Agency
ICP	-	Inductively Coupled Plasma
ICP-MS	-	Inductively Coupled Plasma Mass Spectroscopy
INAA	-	Instrumental Neutron Activation Analysis
MCA	-	Multi-Channel Analyser
NAA	-	Neutron Activation Analysis
NEMA	-	National Environmental Management Authority
NEX CG	-	Cartesian Geometry software
PE	-	Polyethylene
PLI	-	Pollution Load Index
RPF-SQX	-	Rigaku Profile Fitting analytical software
SDD	-	Silicon Drift Detector
TXRF	-	Total Reflection X-Ray Fluorescence
UNEP	-	United Nations Environmental Program
US EPA	-	United States Environmental Protection Agency
WHO	-	World Health Organization
XRF	-	X-Ray Fluorescence

Chemical symbols

Al	-	Aluminium
Au	-	Gold
As	-	Arsenic
Ba	-	Barium
C	-	Carbon
Cd	-	Cadmium
Cr	-	Chromium
Cu	-	Copper
Fe	-	Iron
FeS_2	-	Pyrite
Ga	-	Gallium
Hg	-	Mercury
H_2SO_4	-	Sulphuric acid
HNO_3	-	Nitric acid
Mg	-	Magnesium
Mn	-	Manganese
Mo	-	Molybdenum
Na	-	Sodium
Ni	-	Nickel
Pb	-	Lead
Se	-	Selenium
Sn	-	Tin
Ti	-	Titanium
U	-	Uranium
V	-	Vanadium
Zn	-	Zinc

Abstract

Metal mining processes in general, cause environmental heavy metal pollution over time. Extraction and processing of metals, therefore, comes with the responsibility of ensuring that any of by-products are treated before disposal as requirement. This study determined the levels of heavy metal concentrations; cadmium, arsenic, chromium, mercury, lead, copper and zinc in environmental samples, in order to assess the extent of heavy metal pollution in Kilimapesa Gold mine processing plant in Narok County. A total of forty-one (41) samples, from nineteen (19) sites, namely; nine (9) sub-surface soils, eight (8) sediments, fourteen (14) Sodom apple (*Solanum incanum*) leaves and ten (10) water samples, from the nearby river streams were analysed for heavy metal content. The sediments, soils and plants samples were dried, crushed, sieved and made into thin pellets for analysis using the EDXRF spectrometer available at the Department of Physics, University of Nairobi. Gallium was added to the water samples as an internal standard, mixed before analysis for heavy metal content, using the TXRF spectrometer at the Ministry of Petroleum and Mining Laboratories. The metals concentrations levels in water samples (mg/l) were distributed as follows; Cd ($<$ 4.4), Hg ($<$ 1.0), As ($<$ 1.5), Cr ($<$ 6.5 - 391), Zn ($<$ 3.0 -187), Ni ($<$ 4.0 - 830), Pb ($<$ 3.0) and Cu ($<$ 1.1 - 470). The highest concentrations were recorded at the confluence of the river streams; this could be due to an accumulation of sediments at the convergence point. The levels in soil samples (mg/kg) were; Cd ($<$ 3.00), Hg ($<$ 1.9-23.5), As (14.6 – 935), Cr (111 - 406), Zn (61.5-156), Ni (24.4-164), Pb (26.6-148) and Cu (42.3-174. The variations of the metals concentration levels in Sodom apple (*Solanum incanum)* samples (mg/kg) were; Cd ($<$ 3.0), Hg ($<$ 1.9-3.2), As ($<$ 1.1 - 2.0), Cr ($<$ 3.0-10.0), Zn (24.5-40.9), Ni ($<$ 2.0 - 14.3), Pb ($<$ 2.0-7.2) and Cu (17.9-33.3). These levels are comparable to those found in other undisturbed environment, except for arsenic and lead, which may be attributed to mining activities in Lolgorian.There was a significant difference in metals levels among the three media sampled following ANOVA analyses. Pearson's correlation for all trace elements of interest in Sodom apple (*Solanum incanum)* and soils were very weak except for mercury. The same trend is replicated betweensoilsand water, and between water and plants, for all heavy metals of interest in this study, except for Zn and Ni, respectively. In general, Kilimapesa soils are moderately to extremely contaminated with these metals. The study therefore recommends the introduction of heavy metals bio-accumulators, like water hyacinth in the waste disposal treatment ponds and for enforcement of disposal regulations and for epidemiological studies.

Chapter 1: Introduction

1.1   Background

An unpolluted, clean, sustainable and safe environment forms a key part of Kenya's Vision 2030 - the country's economic blueprint, towards attaining socio-economic development and providing quality life to all her citizens. Achieving economic growth and development in any given country, requires that any available natural resources are responsibly exploited for profitability and benefit to society, while ensuring preservation of the environment. In the Western and South Western parts of Kenya, Gold deposits are being commercially exploited in a bid to boost the country's economy (Kenya Engineer Journal, 2017).

The Lolgorian town in Kilgoris Constituency, Narok County, has experienced steady economic and population growth following gold mining activities at the Kilimapesa area that began in 2009. According to Goldplat Company, Kilimapesa is a viable mineral resource for commercial exploitation.

Mining activities are known to cause heavy metal pollution as a result of exposure of the heavy elements to the environment. The heavy metals are transferred to different media through acid mine drainage process (Eurostat, 2010 & Fashola et al., 2016).

Heavy metals occur naturally in varying concentrations in all environments, when taken up by plants, ingested or inhaled by animals and humans, may result in poisoning upon accumulation in the tissues. They occupy sites that would ideally be occupied by essential metals leading to a malfunction of the bio-chemical processes in living tissues (Fashola et al., 2016).

Anthropogenic sources negatively affect the environmental quality due to build-up of heavy metals in toxic oxidation states. This poses a challenge to human and animal lives, with mining reported being second to agriculture, as a source of pollution by heavy metals. The heavy metals that are closely associated to mining are of interest because they are found to accumulate in sediments and soils. The probability of absorption of the metals by plants and eventually animals forms the basis for determination of pollution levels (Abdul-Wahab & Marikar, 2012).

The EPA and other agencies like UNEP and NEMA are involved in the protection of the environment, have introduced methods to identify the contaminants in environmental media.

In this study, we have determined the concentrations levels of select heavy metals in water, plants and soils around the Kilimapesa Gold Mines processing plant in Narok County, in an attempt to evaluate the possibility of potential health hazards.

Generally, gold ores are dug from the depths of the earth and then leached to separate the gold from impurities. The process uses chemicals, that, when exposed to the environment in large concentration levels or specific forms pose harmful effects. Heavy metals constitute the wastes released to the environment following gold mining processes. With an anticipated increase in gold mining activities in most western parts of Kenya, there is need to have proper methods of disposal of effluent, to protect plant, animal and human life (Kenya Engineer Journal, 2017).

When sulphide rocks react with air and water, sulphuric acid is produced. This is a process in its natural form, is known as Acid Rock Drainage (ARD). A similar process, but greater in magnitude, is Acid Mine Drainage (AMD). During excavation, rocks containing sulphide mineral react with moisture and oxygen in the atmosphere to create sulphuric acid. When acidity in water reaches a given level, naturally occurring bacteria (*Thiobacillus ferroxidans*) may accelerate the acidification and oxidation processes, leading to more trace elements being separated out of the wastes/tailings. The acid is carried by surface drainage or rainwater and deposited into water sources; groundwater, lakes, streams and rivers. Acid Mine Drainage significantly degrades the quality of water, making it virtually unusable for the aquatic life. Heavy metals that are present in the excavated ores can be leached and deposited in water sources. Chemicals agents (cyanide and/or H_2SO_4) used in the separation of gold can spill, leach or leak to adjacent water bodies. These chemicals pose a threat to nature due to their toxicity (Fashola et al, 2016).

Gold is a highly valued mineral, used in a variety of areas including; jewellery, dentistry, industry and electronics, medicine for cancer treatment, adorning buildings, artwork and furniture, food and drink. It is alsoused as a currency, and its monetary value in trading is stable and acceptable between nations. It is the reference currency acceptable for most countries (Eurostat, 2010).

Recently, incidents concerning deaths of livestock have been reported following the contamination of water sources in the Kilimapesa Gold Mines area. The cause of these deaths was attributed to contaminated water sources, possibly from the heavy metals associated with mining activities in the area (see Figure 1.1).

Figure 1.1: Livestock deaths in Kilimapesa area (Business Daily, February 2018)

Previous related studies indicate that gold bearing ores in the Migori Archean Greenstone Belts contain a level of concentration of heavy metals such as; lead, mercury and arsenic (Ngure et al., 2017; Ogola et al., 2002). Upon leaching, these metals have adverse effects to the environment. These metals are toxic and non-biodegradable and their build-up in the living tissues are known to cause diseases or even death (Mahurpawar, 2015).

1.2   Problem statement

When the concentration of heavy metals in the environmental media and living tissue exceed certain levels, it results in toxicity (Lambert et al, 2000). Despite devoted efforts to minimize contamination from heavy metals in various environmental media, they still continue to pose serious challenges worldwide, affecting 80% of mining plants. One possible cause is the laxity in enforcing regulations by respective national regulatory agencies.

The WHO has compiled a list of ten chemicals that are of great public environmental concern which include four (4) heavy metals: arsenic, lead, cadmium and mercury (WHO, 2014).

Several regional studies, have reported effects of pollution from heavy metals contamination from gold mining activities. These include; cases of deaths of birds, death of fish, skin irritation and itching, birth deformities and retarded children amongst people living in the neighbourhood of these mines along an 80 Km stretch from the vicinity of North Mara Gold Mine in Tarime District, Tanzania (Bitala et al., 2009).

1.3   Research Justification

Heavy metal pollution studies in mining areas have been conducted for a long time, in various environmental media, but more studies are needed especially in new mining sites. The levels of radioactivity in soils in Kilimapesa have been studied by Chepkwony (2018).

The stream that serves Lolgorian town, passes in close proximity to the mine and is prone to contamination from spills, effluents and tailings by various mining activities. There have been reported cases of animal deaths in the recent past, resulting in cases of out of court settlements between the gold mining company and livestock owners. A case in point is the report of livestock deaths published in the local media of 28th January 2018, where eighteen cows were allegedly reported dead following consumption of poisoned water (Daily Nation, January 28th, 2018).

In this study, we have determined the extent of heavy metals contamination around the Kilimapesa gold processing plants, in which we have assessed the levels of heavy metal contamination in the soil, water and plant vegetation samples. This study compliments the existing research in the field of environmental pollution in the country.

1.4   Description of the study area- Kilimapesa Gold mines

Kilimapesa ($1^o 24'2''$S $34^o55'29$E) is located near Lolgorian town, Narok County (Figure 1.2 and 1.3). It has a population of about 2700 people and is situated approximately 364 Km, south west of Nairobi, 1700 m above sea level, has a warm and temperate climate, temperatures average 18ºC.

Figure 1.2: Map of Kenya showing Kilimapesa location in Lolgorian, Narok (Source: https://www.google.com/maps/search/kilimapesa+mine+location+in+kenya/@-1.238491,34.6712656,11z)
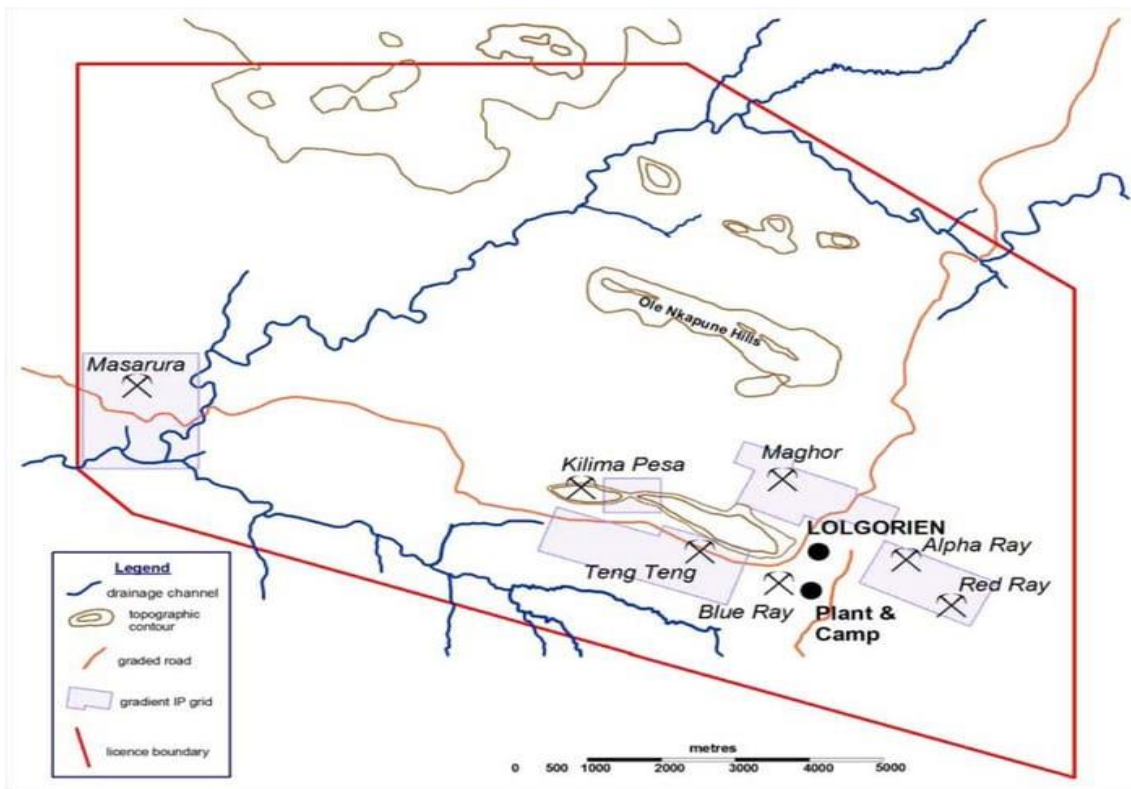
Figure 1.3: Mining blocks at Lolgorian (http://www.goldplat.com/galleries)

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The economic activities that the locals engage in and around Kilimapesa include; livestock farming and agricultural farming of wheat, barley, maize, potato, quarry, sand harvesting and gold mining; artisanal and commercial (County Integrated Development Plan, 2013). Most of these activities require substantial supply of water resources.

The commercial gold processing plants are located about 1.3 Km from Lolgorian town, within the Migori Archaean Greenstone Belt. There are two rivers around the area, Mogor and Mara to the north and south, respectively.

In general, gold mining activities at Kilimapesa follow the following protocols (Eurostat, 2010):

i. Ore extraction and transport – holes are drilled into the gold-bearing reef and filled with explosives or blocks of earth dug from the surface to extract the ore. The rock is blasted to free the gold ore from the rest of the rock. The ore is then scraped and conveyed to the surface using hoppers, conveyor belts or railway cars. The ore is then taken to a processing plant for further processing;

ii. Crushing and milling - this involves further reduction of the size of ore to powder form to ensure a greater surface area is exposed during the chemical extraction process;

iii. Leaching - particles are mixed with a sodium cyanide solution where gold forms a gold-cyanide complex. Filtration of the mixture is done to separate the complex from the ore;

iv. Carbon in pulp process – activated carbon is used to adsorb gold from the leach solution and separation is done by filtration;

v. Gold recovery- water is used to elude the gold from carbon using water. The loaded elution medium is taken through an electrochemical process, where gold is deposited on cathodes made of steel wool. Sulphuric acid is used to oxidize excess iron;

vi. Calcination- loaded cathodes are heated to about 650 ℃ to oxidize any remaining base metals. Purity of 99% is obtained;

vii. Gold smelting- the loaded cathode is melted at 1300 ℃ with silica, borax and feldspar fluxes to remove impurities. Slag is skimmed off and the gold that is melted is poured into casts (anode) and then cooled. The gold anodes are submerged together with 99.9% of pure gold cathodes in hydrochloric acid. After deposition, gold cathodes are rinsed in sodium thiosulphate, melted and cast to form bars. The gold in bar form is the final product.

1.5 Research Objectives

1.5.1 Main objective

To assess the heavy metals contaminations in water sources, vegetation and soils around the Kilimapesa Hill Gold Mines area in Lolgorian, Narok County.

1.5.2 Specific objectives

i. To determine the concentration levels of eight (8) heavy metals; lead, copper, arsenic, mercury, zinc, cadmium, chromium and nickel in soils/sediments, water and vegetation in Kilimapesa area.

ii. To evaluate the extent of contamination by heavy metals in the select environmental media by comparison with WHO standards and the correlation in concentration levels.

1.6 The Scope of study

The study focused on the levels of selected heavy metals: cadmium, lead, copper, arsenic, mercury, zinc, chromium and nickel in Sodom apple (*Solanum incanum)*, water and soils/sediments from nineteen (19) sampling points along the channel stream of Kilimapesa Gold processing plants and the settlement area. The study covered the portion of the river from (01° 13' 30.1''S, 034° 45' 02.3''E) to (01° 14' 58.2''S, 34° 48' 22.1''E), with selected sites in the settlement area. The sampled sites along the stream represent the parts that are most probably prone to heavy metal contamination from mining activities in Kilimapesa gold mines. Sodom apple (*Solanum incanum*) plant was chosen for this study since it grows wildly and is readily found in the region. Soils and sediments were taken at a depth of 0-5cm, which represents eroded media from the upstream regions.

Sampling was done around the processing plants to assess the extent of contamination of the select heavy metals in the environmental media. Sampling sites on the river downstream of the processing plants and upstream were sampled for comparison purposes. Samples from the settlement areas provided a general view of expected concentrations of metals in plants and soils. In general, the sampled media were selected due to ease in identifying them, distribution, capacity to accumulate heavy metals and longevity. Soils and plants were analysed using EDXRF technique to determine the concentration levels of heavy metals in the media. Water samples were analysed using TXRF technique. A correlation of the

concentration levels amongst the sample media and the different sample sites was done. This provided a comparison on the extent of contamination from the gold processing plants.

Chapter 2: Literature review

2.1 Introduction

In this section I have reviewed various studies that were done in line with assessment of the heavy metal contamination from gold mining areas and their effects on human health.

2.2 Sources of heavy metal pollution and their effects on human health

Naturally, heavy metals occur within the earth's crust and are present, either in elemental or in chemically combined organic and inorganic forms as minerals. They occur mainly as sulphides components, for arsenic and lead, and as oxides for aluminium and gold. The ores occur as families where metals that exist naturally in a given form occur together (Fashola et al., 2016). Heavy metal pollution is induced either from natural or anthropogenic sources. Natural causes include processes like vulcanicity, weathering and acid rain that result in the dissolution of heavy metals (Roozbahani etal.,2014). Anthropogenic sources are a significant cause of pollution and include; industrial processes, mining, combustion of fossil fuels, agricultural activities and urbanization (Roozbahani et al., 2014; Duruibe et al., 2007).

Mining operations are the major causes of heavy metals pollution in the environment for many years after mining activities cease. The impact of mining on the environment includes erosion, sinkholes formation, contamination of soil and water by the mining chemicals and loss of biodiversity. The major types of contaminations that result from mining activities and processing include; air, soil and water pollution.

In general, air pollution results from dust dispersion, for example, following mining activities and emissions from machinery used in the excavation and transport of the gold ore. The contaminated airborne particles frequently contain heavy metals like mercury and lead that are a potential hazard following exposure (Ogola et al., 2002).

Soil pollution from mining ores contains sulphides, which form sulphuric acid once exposed to moisture in the atmosphere by way of tailings in the slurry. These leach out and pollute the soil and groundwater sources that are exposed to it. The heavy metals that are left in the topsoil remain potentially toxic for many years, because of their non-biodegradable nature (Ogola et al., 2002).Water pollution results from acids finding their way to the water table or surface run-off altering the pH of streams and rivers posing a threat to the survival of plant, animal and human life. Dissolved heavy metals are deposited in river beds, have a greater potential of causing harmful effects. Tailings reservoir may burst to result in mudslides that

block water-ways and may kill living organisms that come in contact with it. Over time, the metal pollutants are concentrated in aquatic life, plankton and fish (Ogola et al., 2002).

Mining activities and geochemical processes usually result in acid mine drainage (AMD). This is a result of pyrite (FeS_2) and other minerals containing sulphide being exposed to water and air, with oxidizing bacteria present to produce ions, sulphate and acidity (Ogwuegbu and Muhanga, 2005).

The organic compounds formed adversely affect the water quality. These organic compounds are ingested, inhaled or absorbed by the skin. They accumulate within the body overtime and when in high concentrations, the heavy metals become harmful and affect normal bio-chemical processes. The metals get converted to their stable oxidation in the stomach due to the acidic environment. They convert bio- molecules in the body like enzymes and proteins to form stable chemical bonds that are strong.

A metal ion can undergo an exchange by another of a similar oxidation state, for instance, Cd^{2+} replacing Zn^{2+} leading to cadmium toxicity. The most toxic states of heavy metals are the ones that have oxidation states that are stable which make them difficult to be dissociated while extracting them from the body using medical detoxification therapy.

Living tissues require essential metals in micro quantities for normal functioning (Wang et al., 2013). When in high concentrations, they become toxic. There are non-essential metals including cadmium, arsenic, lead and antimony that are toxic to living tissue even in small concentrations (Duruibe et al., 2007).

The following is a summary of the occurrence of these heavy metals and their effects on human health.

2.2.1 Arsenic

Arsenic is found naturally at low levels in combined forms as oxides, chlorides and sulphides. It is the most common reason for acute heavy metal poisoning. When it is found in accumulated quantities, it can lead to gastrointestinal tract damage, damage to the nervous system, diabetes, cancer when consumed over a period. It inhibits energy generating processes within the body. In large doses, if absorbed, it may reduce the production of blood cell, break up of already produced red blood cells, liver enlargement, colour the skin, produce tingling and loss of sensory ability in the limbs, collapse of the cardiovascular system and even brain damage (Fashola et al., 2016).

2.2.2 Cadmium

Cadmium occurs as oxides, sulphides or chlorides in ores. It affects a number of metabolic activities especially nitrification by soil bacteria (a decrease of 14%), leads to pulmonary and bronchial irritation, failure of kidneys, nervous, lung cancer, immune system disorders and altered gene expressions leading to mutations. Bone fractures due to osteoporosis also result, hypertension and impairment in immune response (Fashola et al., 2016).

2.2.3 Chromium

Chromium is an essential metal to the body. It is co-factor in the regulation of levels of sugar in the body. In excess, it causes damage to the DNA resulting in mutations. The respiratory system is adversely affected by nasal cavity cancers resulting; damaged kidneys and livers have been reported. Skin rashes, stomach and ulcers upset complications like ulcers also result with exposure. Reproduction toxicity also results in low birth weight, birth defects and disturbed spermatogenesis. It may also result in lung cancer (Fashola et al., 2016).

2.2.4 Copper

Copper occurs in chlorides, carbonates and sulphides in nature. An essential micronutrient makes up enzymes that regulate the transportation of iron and facilitates its release from storage, melanin synthesis and functioning of the nervous system. A malfunctioning of the liver, which is associated with a genetic disorder called Wilson's disease may result and damage to kidneys (Fashola et al., 2016). It leads to gastrointestinal tract damage, DNA breakage and neuron damage.

2.2.5 Mercury

Mercury is a non-essential element for the body for any biochemical functions. It causes retardation in children. It damages the nervous system leading to memory loss when one is exposed to it. It denatures proteins, inhibits cell division altering gene expression, damages nucleic acid and inhibits enzymes. It is considered possibly carcinogenic by the International Agency for Research on cancer. High doses lead to instant death (Fashola et al., 2016).

2.2.6 Nickel

Nickel is considered a moderately toxic heavy metal. It is required by the body in trace amounts for increasing iron absorption hence preventing anaemia, and prevention of osteoporosis by assisting in calcium intake. High nickel concentrations in drinking water, results in allergies, headaches, shortness of breath, nasal and lung cancer (Fashola et al., 2016).

2.2.7 Lead

Lead is a non-essential heavy metal that affects multiple systems in the body upon accumulation. It leads to blood-related disorders like anaemia and high blood pressure, reproductive and cardiovascular systems disorders, long-lasting damage to the nervous system, gastrointestinal disorders, loss of hearing, kidney dysfunctions and brain damage (Fashola et al., 2016).

2.2.8 Zinc

Zinc makes up enzymes, hormones and binding of DNA which regulate many activities in the body. An excess of zinc within the body causes anaemia, the formation of kidney stones and reduction in the quantities of formation of bones. There are decreased immune functions of the cell rendering it susceptible to diseases. Nasal cavity and lung cancer results upon prolonged exposure together with impairment of growth and reproduction (Fashola et al., 2016).

WHO (2011) has documented allowable limits of concentration of metals in water and plants for animal and human use, and soils according to table 2.1 and table 2.2.

Table 2.1: Allowable limits of heavy metals concentration in drinking water and water supporting aquatic life (WHO, 2011)

Element	Normal conc. For Fresh water (mg/L)	Max conc. In drinking water(mg/L)
Hg	< 500	0.001
As	0.01	_
Cd	< 1000	0.003
Cr	< 2000	0.05
Zn	_	3
Ni	0.02	0.02
Pb	_	0.01
Cu	_	2

Table 2.2: Allowable levels of concentrations of metals in plants and soils (WHO, 1996; Dutch standard, 1990)

Element	Normal conc. in unpolluted soils: Dutch standard(mg/Kg)	Max conc. in plants: WHO, 1996 (mg/kg)
Hg	-	0.1
As	-	2
Cd	0.8	0.02
Cr	100	1.3
Zn	50	0.6
Ni	35	10
Pb	85	2
Cu	36	10

2.3   Analysis of *Solanum incanum* for heavy metal contamination

Most researches worldwide have used plants to determine the extent of heavy metal pollution in the environmental, specifically, in the mining areas.

Sodom apple has a variety of uses. It has an analgesic property hence its leaf, fruit and root extracts are used for body pains like headaches, toothaches and stomach-aches. It is used in the treatment of pneumonia and rheumatism, burns, wounds and sores. In some African countries, it is used to treat eye problems like ophthalmia and conjunctivitis. Snake bites are also treated using parts of the plant (Matu, 2008).

Indigenous communities have used the shrub as a pain reliever for toothaches. The stems of the plant are used as toothbrushes among the indigenous communities and the leaves are boiled and drunk to relieve stomach-aches. The other uses are to make compost from the leaves, stems, and stopping of bleeding. Mwonjoria et al. (2011) tested the pain-relieving effect in animal models and it was found to have significant effects on animals.

The plant is used in pest control in some countries. Charei et al, 2017, tested the Sodom apple fruit extract in control of root-knot nematodes. It was observed to have significant effect on the nematodes hence can be used as an environmentally friendly and effective method of

control the pests. There was an increase in nitrogen uptake hence increased in yield. The use of the extract if contaminated may result in heavy metal pollution over time.

In this study, Sodom apple was analysed for heavy metal contamination, since they have the ability to accumulate and tolerate large amounts of toxic metal, is tied to a specific place, can be collected, easily identified and handled, and it has enough tissue to be analysed (Stankovic 2014).

Taher et al., 2012, evaluated pollutant levels of uranium, radium, potassium and thorium in environmental plant samples including *Solanum incanum* and found heavy metals had accumulated in them within the allowable world averages.

Uptake of heavy metals in Lake Burullus in Egypt was investigated by Eid et al., (2012). Nickel, cobalt and silver were measured in a perennial herbaceous plant, *Typha dominngensis*. Silver was observed to be highest in concentration hence was suggested for use as bio-indicator.

Karimi et al., (2013) analysed vegetation and soils in Iran for arsenic metal. A positive correlation was observed between the soils and vegetation at the various sites that were selected. Two of the plant species showed results of hyper-accumulation when compared to the rest, and could be used for phytoextraction.

2.4 Environmental pollution studies in gold mines

In this section, we review several studies of heavy metals pollution from gold mining activities.

Ninga et al. (2011) assessed contamination of heavy metals in surface water in Linglong gold mining area in China. Zn, Cd and Hg were observed to be in the highest levels, Cr and As were moderate pollutants while Cu and Pb were in lower concentrations in the surface waters. Concentrations of the metals were observed to decrease as distance from the pollution sources increased. This clearly indicated the cause of contamination in the water was due to mining sites. The pollution was mostly attributed to the leachate and chemicals from wastewater discharge from the mining area.

In Yellowknife Bay, Pocket Lake, Canada, was found to be contaminated due to gold mining activities in Giant Mine. Accumulation of arsenic, antimony, iron and mercury has substantially increased in the background levels compared with concentrations in the pre-

mining era. The plants under study, *Cladocera* and other planktonic diatoms could not be found in the sediment since it had extinct, due to contaminations of the environmental media. There has been little success in the biological recovery of these plants, even after ceasing ore roasting activities in 1999 (Thienpoint et al., 2016).

In a study done by Teixeira et al. (2018) in Sierra Pelada mines (Brazil), elements that were potentially toxic to soil were assessed. Arsenic, cobalt, barium and mercury were in extremely high concentrations near mines posing a threat to life. An assessment of the environmental impact confirmed pollution by the mining activities in the sampled areas. These toxic elements and chemicals negatively affected the microbial activity of organisms in the soil.

Ngure et al. (2017) assessed heavy metal pollution resulting from Migori Gold Belt area (Macalder) in water, fish and human hair and nails of children between five and ten years old. Potentially harmful elements were significantly present in the nails and hair. Hg and As in water were in concentration levels above the WHO limits. Cd, Cr and Pb in water samples exceeded WHO allowable levels. Cd and Pb were also found in higher concentrations in nails in occupationally exposed residents. Pb, Cu, Cd and Cr were in high levels in the hair samples obtained from polluted areas than those found in control samples from unpolluted region. The study indicated that the children in the area were prone to high health risks of potentially harmful elements by consuming fish and contaminated water. It was recommended that the residents be educated and drastic interventions are taken to prevent multiple health risks.

Odumo et al. (2011) assessed the impact of mercury used in gold processing in soils, tailings and biota sediments in Migori- Transmara area in Kenya. They found that the concentration of mercury in the sampled media decreased with distance from the artisanal mining sites. The region was classified, as '*strongly polluted area*' since the levels of mercury was high. They advocated for alternative methods to be used in gold extraction in order to conserve the environment and minimise public exposure.

2.5   Environmental management regulatory framework in Kenya

In Kenya, there are various regulatory frameworks, spearheaded by NEMA to govern the disposal of wastes in order to minimize environmental pollution. These include the Public Health Act (1986), Environmental Management Regulations and Coordination Act, EMCA (2015) and Environmental Management Regulations Act (2006).

Public Health Act (CAP 242, Part XI, section 129 and 130) outlines the duty of the local authority to put measures to prevent pollution of water sources for the public for drinking and domestic use. The local authority is also to make measures against pollution that poses a danger to health. There is regulation in putting up of factories that would involve a risk of harmful pollution.

EMCA (CAP 387) Part VII section 72 prohibits discharging of toxic substances into the aquatic environment, and demands a restoration of the environment to its initial state. Part 91 classifies carcinogenic wastes as part of the hazardous wastes, of which heavy metals are a part of. Part 141 classifies failure to manage hazardous wastes as an offense that is punishable by law.

Environmental Management Regulation Act (2006) outlines water quality regulations to be met before issuance and reissuance of licences for industries. It focuses on the concentrations of metals in wastes from industries. Part III requires proper treatment of wastes before disposing to the environment, as per WHO guidelines. Failure to meet the specifications results in fines and/or revoking of the operation license.

2.6   Principle of EDXRF and TXRF techniques for elemental content measurements

X-ray fluorescence is a method used in characterization of materials; in liquid, solid/pellet and powder forms in terms of the element content.

In principle, an electron in the atom of the target material being analysed, is dislodged from its atomic orbital upon absorbing photons with energies that exceeds its binding energy to the nucleus, following irradiation with radioactive source. An electron from higher energy orbital, transfers to fill the vacant orbital. During this transition, a photon or fluorescent radiation is emitted; whose magnitude equals the difference in energy between the specific orbital shells of the transiting electron. This energy, which is a characteristic X-ray, is always the same for a specific element. An element can, therefore, be identified by determination of the energy of the photon that it emits (Brouwer, 2010; Ene et al, 2010).

For a fluorescent emission of a given element, the number of photons in a unit time (counts per second, cps) is related to the quantity of that element contained in the sample being analysed. The rates of photon emission are determined by measuring of the photons registered by the detector per unit time, for the various observed X-ray spectral peaks for the elements. The analysis of elements is achieved qualitatively and quantitatively by obtaining

the energy in a spectrum of X-ray lines and measurement of their respective count rates (Brouwer, 2010).

The energy of the X-ray fluorescence radiation line is unique for different elements, giving the qualitative analysis. The intensity of the radiation varies directly with the orientation of the element in the material hence giving the quantitative aspects of analysis.

In practice, EDXRF consist of an x-ray tube that generates the rays and a silicon drift detector that generates electrical pulses following absorption of X-rays emitted from a sample. In this study, analysis was done in two stages: qualitative and quantitative analyses of spectral data to determine the elements present and their respective intensities for elemental content determinations. Fundamental parameters (FP) module was used to obtain the concentrations of elements in a sample, without using a large suite of standards. The FP makes use of theoretical equations that govern how X-rays interact with matter. In the NEX CG spectrometer series used, the FP module performs a variety of functions, including background modelling, peak intensity extraction, spectral deconvolution, and X-ray absorption and enhancement correction.

The detection limits (LD) for the elements of interest were inherently calculated by the FP application of the Rigaku NEX CG spectrometer using the formula (Rousseau, 2001):

$$\text{LD} = \left(3\ \frac{C_i}{I_p - I_b}\right)\sqrt{\frac{I_b}{T_b}} \qquad (2.1)$$

Where LD- detection limit (mg/kg), C_i – concentration of the analyte, I_b- background intensity, I_p- peak intensity, T_b – background measurement

TXRF is a versatile analytical technique for determining elemental content in liquids, solids and loose powders. The main principle is that atoms, when irradiated with X-rays, radiate secondary X-rays – the fluorescence radiation. A primary beam generated by an X-ray tube is monochromatized by Bragg-reflection on a Ni/C multilayer. Monochromatized X-rays hit a polished sample carrier (quartz glass or acrylic glass) at a very shallow angle of incidence. X-rays are totally reflected by the surface of the sample carrier at a very small angle (0.3 – 0.6 °). Fluorescence radiation is emitted only by the sample deposited on the carrier surface. An energy-dispersive detector detects the characteristic fluorescence radiation emitted by the sample. Intensity is measured by means of an amplifier coupled to a multichannel analyzer.

Each element is associated with a specific wavelength and energy of the fluorescence radiation. The concentration of each element is calculated using the fluorescence intensity. TXRF analysis is based on internal standardization; an element, which is not present in the sample, must be added for quantification purposes. In practice, the method is fast and requires simple sample preparation; simultaneous multi-element trace analysis without external calibration; analysis of small sample amounts in nanogram or microgram range and is suitable for various sample types: solids, powders, liquids, suspensions.

The water samples were prepared as thin films substrates of negligible absorption matrix effects. In general, TXRF method has the advantages of; low background noise, reduced matrix effect and greater sensitivity (Klockenkamper, 1992).

For absolute quantification of samples, elemental sample intensity is directly proportional to the fraction of mass. For an element x, the mass fraction is determined by reference to all elements that have been obtained in the spectrum (Klockenkamper and Bohlen 1992).

$$C_x = \frac{\frac{I_x}{S_x}}{\left(\frac{\Sigma I_{int}}{S_{int}}\right)} \left(\frac{M_{int}}{M_{sample}}\right) \tag{2.2}$$

where C_x- mass fraction of analyte, I_x- the intensity of analyte, S_x-sensitivity of analyte, I_{int}- the intensity of internal standard, S_{int}- sensitivity of internal standard, M_{int} - mass of internal standard, M_{sample}-mass of the sample

2.7 Studies on heavy metal analyses using EDXRF & TXRF

A portable XRF machine was used in an abandoned mine site in Korea to map soil contamination for copper. The results obtained were compared with the ones obtained using inductively coupled plasma atomic emission spectrometry (ICP-AES) and were correlated with high accuracy. It was established that both techniques can be used effectively to determine copper concentrations is soils (Jangwon et al., 2016).

EDXRF and neutron activation analysis (NAA) have been used in the elemental analysis of trace, heavy and essential metals in herbaceous plants, *Corchorus tridens Linn*. The results of two methods were observed to be within the variable limits using ANOVA. The concentration of the elements that are essential in roots, stem and leaves showed that the plant could be used as a mineral supplement (Umar et al., 2017).

Selected heavy metals were analysed in samples of sediment from Pattipulam to Dhevanampattinam, found along the Eastern Coast of Tamilnadu, India, to assess the contamination and level of metal enrichment status using EDXRF. The mean values of concentration of the heavy metals were recorded as lower in the sediments that those from background values. Pollution indices like pollution load index (PLI) and contamination factor (CF) were used in assessment and both indicated low contamination (Chandramohan et al., 2016).

An analysis was done in Punjab State, India, for contamination in water sources. Zinc, chromium and uranium were observed to exceed the limits of World Health Organization. The study was done on groundwater sources in agricultural areas near a coal-fired thermal power plant, Guru Nanak Thermal Power plant in Bathinda (Bhalla et al., 2011).

Modenes et al. (2015) analysed groundwater from Serra Geral aquifer, Brazil, for eighteen elements by using TXRF and inductively coupled plasma-optical emission spectrometry (ICP-OES) for light elements, Mg and Na. Six heavy metals; As, Pb, Cu, Ni, Zn and Cr were a part of the select elements of interest. The conclusion was that levels of Cr, As, Fe, Se, Mn and Ba were above the maximum levels allowed by the Brazilian Environmental Legislation.

Espinoza-Quiñones et al. (2005) analysed the pollution of Toledo River for 15 heavy metals in Brazil over a period of one year. Monthly analyses were done by use of synchrotron TXRF and it was found that there was a small degree in increase in the concentration of all the heavy metals along the river. Copper was observed to exceed the allowable concentration limits while Zn, Ni, Cr and Mn were within the allowable limits.

Dhara & Misra (2011) analysed rainwater for trace elements including the heavy metals: Ni, Cu, Zn, Pb. The study was used in developing standards for use by the National University of Singapore. The precision was observed to be within 16%, while the concentrations of Mn, Fe, Zn, Ni, Cu, V and Pb were observed to be below 20µg/l. The variance of the determined values was seen to be within 20% of acceptable value, apart from two that were comparatively high.

Pashkova & Revenko (2015) did a review on the use of TXRF in the analysis of water samples for trace, minor and major elements. Comparison with the other methods of analysis, such as; volumetric, electrochemical, flame photometric and atomic spectrometry, it was seen to work comparatively well among popular instrumental spectrometric techniques.

An investigation by Muohi et al. (2002) on the levels of copper, cadmium, zinc and lead along the coastline of Kenyan was done using Atomic Absorption Spectrophotometer (AAS). Sediments from each of the points were analysed by EDXRF technique for comparison. The results showed a good correlation of the two methods.

The influence of heavy metals to the environment in Migori, Southwest Kenya was analysed using EDXRF. The levels of tin, titanium, arsenic and zinc were observed to exceed the allowable limit of 50mg/Kg. This was indication of pollution from mining (Odumo et al., 2011).

Githinji et al. (2015) assessed the water quality around the catchment area of Chania River using TXRF technique. Some of the sampled points were contaminated with Mn, Fe, Ni and Pbduring the dry season, above the recommended values.

Omondi (2017) analysed the levels of some heavy metals in the waters of lower Nzoia River. The concentration of metals was found to increase downstream. Fe, Cu, Ni, Cr and Mn were observed to be above the USEPA limits. Concentration of Cu was above the WHO standards indicating pollution by Cu. The lower sediments had been contaminated by Ni, Cr, Cu and Fe.

Nguyen et al (1998) compared EDXRF, ICP-MS and Graphite furnace AAS analyses of seven biological and environmental reference materials. Twenty-eight elements were determined. Coal had affected the environment with evidence in high concentrations of sulphur, nickel, zinc, cadmium, mercury, arsenic and uranium in a number of the samples. The methods indicated consistency from the results obtained. Mining activities in Ireland resulted in pollution of soils. Samples of soil were collected from the region and analysed using AAS. The samples were also analysed using a portable XRF and the results compared. The correlation between the two methods used, was excellent (Tanja et al, 2009).

A study was done to compare the use of EDXRF with inductively coupled plasma mass spectroscopy (ICP-MS) and instrumental neutron activation analysis (INAA) to determine the trace elements in lichen plants resulting from air pollution. From the assessment, EDXRF was preferred for heavy metals: nickel, copper and lead. The demerit of the technique, however, was a failure to detect many elements simultaneously. At least two of the techniques gave results of similar quality, depicting the complementary nature of the methods used (Pantelica et al., 2016).

Chapter 3: Materials and Methods

3.1 Introduction

This section outlines methods that were used in the study; procedures used in sampling, sample preservation, preparation and analysis of water, soils and plants sample media using EDXRF and TXRF methods for determination heavy metal content.

Forty-one (41) samples were collected from nineteen (19) locations; water from ten (10) sites, Sodom apple leaves (*Solanum incanum)* from fourteen (14) sites, sediments from eight (8) while soils were sampled from nine (9) points.

3.2 Description of the Sampling Sites and Media Sampling

The basis for choice of the sample sites were: existence of the sample media (soil/sediment-S, water-W and Sodom apple-P), proximity to the processing plants, ease of accessibility of the stream channel and obtaining the concentrations of the metals for comparison, for the points within the settlement area in Lolgorian town. The samples were randomly sampled from within the town centre and in the settlement areas. Water samples were sampled upstream and downstream of the river channel at the processing plants and at the confluence of the stream at spacing of 100m. The samples were collected in July 2018, which is considered a dry season, hence the unavailability of water samples at some points along the channel between the tailings deposit area and the river channel.

The sampling locations and respective sample labels are shown in Table 3.1 and Figure 3.1 and Appendix A. Samples are labelled 1-16 were collected from the town area and along the streams, while samples 31-33 were collected from the nearby settlement areas.

Table 3.1: Summary of the sampled media and labelling

Sample media	Sample site locations/labelling
Soils	S01, S02, S04, S11, S12, S18, S31, S32, S33
River sediments	S03, S05, S06, S08, S09, S10, S13, S14
Plants (Sodom apple plants leaves)	P3, P4, P5, P6, P7, P8, P 9, P10, P11, P12, P13, P14, P32, P33
River waters	W03, W05, W07, W08, W09, W10, W12, W13, W14, W15
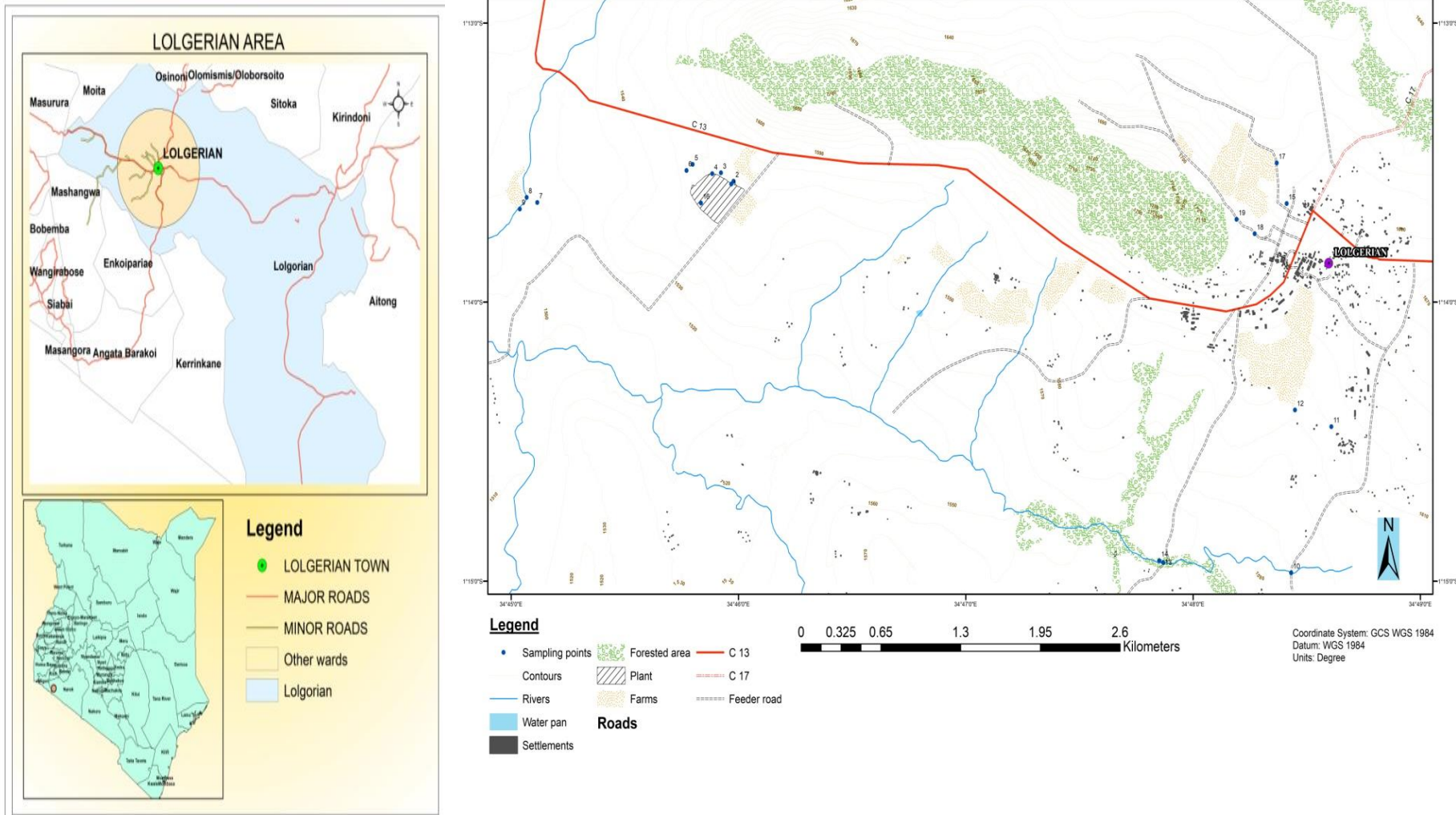
Figure 3.1: Sampling sites in Lolgorian, Kilimapesa Gold mining plant

3.2.1 Sampling and sample preservation

Prior to sampling, the equipment and containers were cleaned thoroughly to minimize contamination. The polyethylene (PE) bottles used in storage of water samples were cleaned using nitric acid and soaked for twelve hours in soapy water. They were then rinsed in tapwater and then in distilled water. The bottles were then soaked in concentrated nitric acid solution (10% v/v) for 3 days after which they were rinsed in distilled water. This was repeated and afterwards, the bottles were air dried and stored in a container (IAEA-TECDOC-950, 1997).

Half a litre of water was collected in the PE bottles from ten sample points, midway across the river by submerging them near the water surface. The water was filtered and acidified immediately with a drop of concentrated HNO_3. Nitric acid was used to achieve a pH below 2 where adsorption to the walls of the container, precipitation and degradation by microbes are minimized. HNO_3 is preferred because of its oxidizing nature by converting metal ions into their nitrate salts, which are highly soluble (IAEA-TECDOC-950, 1997; Bhalla et al., 2011).

Fourteen (14) samples of Sodom apple (*Solanum incanum)* each weighing about 0.5kg, were gathered along the stream channel, from the tailings' disposal area and from residential areas using a sharp stainless knife. The samples were put in plastic containers and labelled (figure 3.2).

Sediments and soils each weighing about 0.5kg were collected at nineteen (19) sampling points along the river stream channel, tailings disposal area and in the residential areas. They were scooped using a trowel, placed in plastic containers, then labelled. The sediment/soil samples were air dried for a week and stored before preparations for heavy metal analysis (IAEA-TECDOC-950, 1997).

The Sodom apple (*Solanum incanum)*, water and soils/sediments were labelled: P03 -P33, W03 -W15 and S01-S33, respectively. The altitude and geographical coordinates of the various sampling points were determined using a handheld GPS (model Garmin Etrex 30).

 A description of each sampling point is presented in Appendix A and in Table 3.1.

Figure 3.2: Sodom apple (Solanum incanum) plant sample

3.3   Sample preparation and analysis

3.3.1   Sodom apple (*Solanum incanum*) and soil samples for EDXRF analysis

The Sodom Apple and soil samples were initially dried in air for a week before being crushed in a motor and pestle to a fine powder, following oven drying to constant weight. The powder was mixed thoroughly to ensure homogeneity and sieved using a 75µm particle-size sieve. Three pellets, each weighing between 0.35-0.43, diameter 25mm and a maximum thickness of approximately 2 mm, were prepared from each sample after the fine powder was transferred to a die assembly then pressed at a pressure of about 8-10 x 10^3tons for a minute to ensure sufficient compression to form a pellet. Some of the soil samples had 10-20% by weight of binder material, starch added. The hydraulic press and the die assembly were disassembled to remove the pellet, as shown in Fig. 3.3. The weight of each pellet was

measured using an electric balance prior for analysis with EDXRF (IAEA-TECDOC-950, 1997).

Figure 3.3: The hydraulic press, complete with the die assembly

3.3.2   Water samples for TXRF analysis

Aliquots of water samples were shaken for a considerable time to ensure homogeneity and 20 ml of the sample was pipetted into a PTFE (polytetrafluoroethylene) vessel into which, 10 µl of gallium (internal standard) were added and mixed to achieve homogeneity. 10µl of the resultant mixture was transferred to a quartz disc, dried on a hot plate and transferred to the TXRF spectrometer for elemental analysis (IAEA-TECDOC-950, 1997).

3.4   Instrumentation for the spectrometers

3.4.1   EDXRF spectrometer

The Rigaku NEX CG EDXRF spectrometer used to analyse soils and vegetation samples is available at the Department of Physics, University of Nairobi (figure 3.4). It consists of an x-ray tube rated 50kV, 50W with a close coupled palladium anode to maximum flux stability. It has a chamber where irradiation occurs and incorporates sample analysis software, which uses fundamental parameter method for analysis.

Figure 3.4: Rigaku NEX CG EDXRF spectrometer at the Physics Department

The NEX CG analyzer has a unique 3D close-coupled Cartesian Geometry (CG) optical kernel that greatly increases the signal-to-noise ratio. It uses a monochromatic beam for secondary excitation of the target instead of the conventional direct excitation, greatly improving the sensitivity. The result is a reduced background noise and increased element peaks, resulting in better analysis of the trace element of most environmental samples. A vacuum system ensures high sensitivity of light elements in the environmental samples.

The spectrometer incorporates an RPF-SQX Pellet/Liquid Template for use with a Fundamental Parameters (FP) method. The RPF-SQX technique employs an FP program that deconvolutes the peaks of the spectrum and simulates the matrix of the sample using fundamental parameter equations. The selection of the scattering FP template allows estimation of the non-measurable components (H to F) in the sample matrix.

In practice, scattering FP makes use of the ratio of Compton and Thomson peaks to determine the average atomic number (Z) of the sample matrix, thus providing for an estimate of the elemental concentration in the sample that is impossible to measure and yielding fairly high accurate analytical results for the residual elements in the sample semi-quantitatively.

The specifications of the EDXRF spectrometer are: an X-ray tube is made of a palladium target and is air-cooled, has five secondary targets: RX9, copper, molybdenum, silicon and aluminium enables delivery of high analytical results that are precise in a very short time. A silicon drift detector (SDD) gives a high-count rate with an exceptional resolution of the spectral lines. Automated sampling is done by the 15-position sampler. The polarized monochromatic excitation of the spectrometer gives a superior peak to background signal for low detection limits. These are the reasons for preference for use in this study (Ene et al., 2010).

Each sample was irradiated for 50s using the 5 secondary targets: Al, Mo, Cu, Si and RX9. The use of five targets ensured coverage of the complete elemental range (Na-U) with optimized sensitivity (Rigaku User Manual, 2016).

3.4.2 TXRF spectrometer

Figure 3.5 shows the TXRF spectrometer, S1 Titan model available at the Ministry of Petroleum and Mining laboratories.5) was used in this study. This is a desktop system with a 40W X-ray tube Mo and a multilayer mono-chromator. The spectrometer incorporates a silicon drift detector for detection of the characteristic radiation. The x-ray spectral data was processed by system software for determination of elemental contents. In principle the elemental concentration, C_i are calculated by the software using the formula (Klockenkamper et al., 1992):

$$C_i = \frac{C_{IS} N_i S_{IS}}{N_{IS} S_i} \qquad (3.1)$$

Where C_{IS} -internal standard concentration, N_i- analyte net peak; S_{IS} - Internal standard sensitivity; N_{IS} – internal standard net peak area; S_i – analyte sensitivity
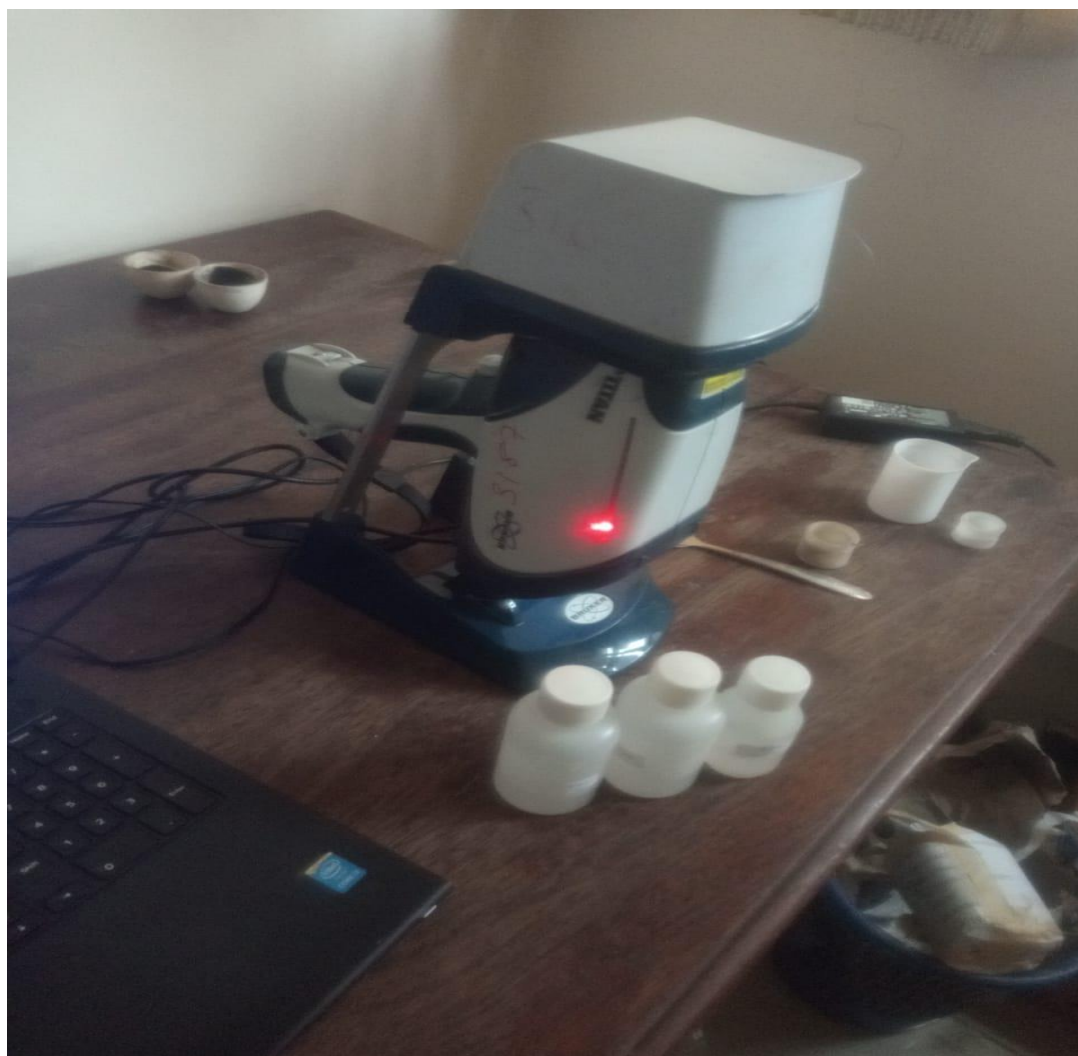
Figure 3.5: S1 Titan TXRF spectrometer (Ministry of Petroleum and Mining)

3.5   Sample analysis for heavy metal content

3.5.1   Water analyses using TXRF

The TXRF spectrometer was checked for elemental sensitivity, count rate and resolution by irradiating 1µg of: nickel sample to measure sensitivity, arsenic sample to measure count rate and manganese sample to measure resolution for 1000 seconds. KB 10 ppm reference standard was used in validation of the method used.

10µl of the water was put in a clean vial and dried at 50ºC on a hot plate to obtain a thin film substrate residue. The spectral data were automatically analysed for elemental content

by the inbuilt software and the results further analysed statistically. The detection limit (D.L) was calculated as below (Poblete & Canales, 2018):

$$D.L = 3\frac{C_i}{I_p}\sqrt{I_B} \qquad (3.2)$$

3.5.2 Soil and plant analysis using EDXRF

An MCA calibration was done prior to spectral data analysis. The weight and thickness of the sample were determined for input to the module software using fundamental parameter method. The samples were irradiated in a vacuum atmosphere to minimize scattering by molecules found in air. The metals of interest were selected in the component selection window for matching with database in the library, which had been created prior by irradiation of IAEA standard references; River Clay and Bowen Kale.

3.6 Elemental content Data analysis

3.6.1 Analysis of Variance

ANOVA was the statistical tool used to determine the distributions of heavy metal concentrations variations between the environmental media: soils/sediments, vegetation and water. The null hypothesis was that no differences existed between any two groups tested. The alternative hypothesis assumed a difference between groups existed.

Umar et al., (2017) used ANOVA to compare elemental concentrations for trace essential elements using EDRF and NAA in *Corchorus tridens* Linn. A pattern was established for some of the elements in roots, stems and leaves. Omondi (2017) compared heavy metal concentrations between sampling depths and sampling sites in the lower River Nzoia. He established a pattern of higher concentrations downstream sites and at greater depths.

3.6.2 Pearson Correlation

This analysis determined the extent of association and direction of two variables. Strength of a relationship assumes values between -1 and +1. A guide developed by Evans (1996) to describe the strengths in the correlation is as shown in table 3.1.

When the coefficient is around +1, there's a significant correlation. Towards 0, the correlation weakens and at 0 there's no correlation. The association of variables are denoted as positive (+) and negative (-) (Cohen et al, 2014).

Asiago (2018) used Pearson's correlation in analysis of heavy metals in algae and sediments along the Thika River. He observed a strong relationship in four of the five metals under study.

Table 3.2 shows the inter-element Pearson correlation coefficient classification.

Table 3.2: Pearson correlation coefficient classification

Pearson Correlation	Strength
<0.19	Very weak
0.20-0.39	Weak
0.40-0.59	Moderate
0.60-0.79	Strong
0.80-1.00	Very strong

3.6.3   Pollution indices

The extent of heavy metal contamination in sediments/soils was assessed by use of pollution factors like enrichment factors, pollution load indices, contamination factors and geo-accumulation indices. Lolgorian Hill is classified under the Nyanzian geological system of the basic volcanic group with volcanic rocks (mainly pillow lavas and metabasalts) and ironstones (Geology of Migori Gold Belt-Geological Survey of Kenya, Report No. 10).

Chandramohan et al., (2016) used pollution indices to assess the extent of pollution in sediments along the Tamil Nadu eastern coast. They observed that the sediments were not heavily polluted using both PLI and CF.

Asiago (2018) used geo-accumulation index, CF and PLI in assessing contamination in Thika River. He observed moderate contamination by all the five metals under study.

3.6.3.1 Pollution load indices (PLI)

Thomilson et al. (1980) sought to give a proper assessment of the degree of contamination using PLI. PLI is how much the content of the metal exceeds the mean natural background concentration. It gives a sum indication of overall toxicity of metal in a given sample.

$$\text{PLI} = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \ldots \ldots CF_n} \quad (3.3)$$

n- number of metals under study

PLI < 1: site is free from contamination;   PLI =1: base line level of pollution

PLI >1: deterioration of site quality

The extent of pollution according to the seven enrichment classes is in Table 3.4:

This the impact of individual trace metal on soils, CF is expressed as:

$$CF = \frac{C_n}{C_{ref}}(3.4)$$

C_n – concentration of metal in the study environment; C_{ref} - concentration of metal in the reference environment (appendix)

3.6.3.2 Geo-accumulation index

Muller (1969) gave a quantitative measure of contamination of a metal in the soils by the following:

$$I_{geo} = log_2 \frac{C_n}{1.5 B_n} \qquad (3.5)$$

C_n – average metal concentration in the soil: B_n – background concentration

The composition of elements (B_n) in the upper crust of the earth was adapted from MsLennan et al (2001) are as stated in Table 3.3, while geo-accumulation classification in Table 3.4.

Table 3.3: Composition of elements in the upper crust of the earth

Element	Concentration in the upper crust (ppm)
As	1.5
Cd	0.098
Cr	83
Cu	25
Ni	44
Pb	17
Zn	71
Hg	-

Table 3.4: Classification of degrees of pollution using geo-accumulation index

I_{geo} value	I_{geo} class	Designation of sediment quality
>5	6	Extremely contaminated
4-5	5	Strong to extremely contaminated
3-4	4	Strongly contaminated
2-3	3	Moderately to strong contaminated
1-2	2	Moderately contaminated
0-1	1	Uncontaminated to moderately contaminated
<0	0	Uncontaminated

Chapter 4: Results and Discussions

4.1 Introduction

In this chapter, the results of heavy metal measurements in environmental samples; soils/sediments, plants and water samples are discussed by cross-referencing with similar studies. The evidence of validation of analytical methods used in the study is also provided. The results of elemental content are presented using both tables, and graphs to show linear inter dependence between variables.

In summary, there was a significant difference in the concentration of the heavy metals, among the three media sampled. The soils and water samples are grossly contaminated with heavy metals. The study recommends use of heavy metals bio-accumulators for decontamination and enforcement of the existing regulations to reduce contamination of the environment.

4.2 Validation of the analytical method

To verify the accuracy of the analytical procedure used, IAEA certified reference materials: Bowen Kale, River Clay (PTXRF-IAEA09) and KB 10 ppm, were analysed for the eight metals of interest, in this study. The samples were irradiated using five targets; aluminium, molybdenum, copper, RX9 and silicon, to ensure the completely elemental range (sodium to uranium) was captured.

The typical spectra obtained from excitation using the secondary targets for the soil sample are given in appendix B.

Table 4.1, 4.2, 4.3 show the results of analysis of the IAEA standard reference materials: Bowen Kale; River Clay, PTXRF-IAEA09; and KB from Bernd Kraft GmbH; that were analysed for the eight elements of interest.

The results obtained, indicate that there was no significant difference between experimental and certified values for most elements of interest analysed in this study. The technique used was found to be reliable and accurate.

Table 4.1: Results of IAEA Bowen Kale analysed by EDXRF; n=3, $\bar{x} \pm SD$, mg/kg

Element	Detection limit	Experimental value	Certified value	Std dev (%)
Hg	1.9	<1.9	0.171 ± 0.028	-
As	1.1	< 1.1	0.131 ± 0.044	-
Cd	3.0	<3.0	0.889 ± 0.247	-
Cr	3.0	< 3.1	0.369 ± 0.101	-
Zn	1.2	35 ± 2	32.3 ± 2.8	+8
Ni	2.1	< 2.1	0.895 ± 0.14	-
Pb	2.0	2.7 ± 0.9	2.49 ± 0.57	+10
Cu	1.6	4.6 ± 1.4	4.89 ± 0.63	-7

Table 4.2: Results of River Clay, PTXRF-IAEA09 analysed by EDXRF; n=3, $\bar{x} \pm SD$, mg/kg

Element	Detection limit	Experimental value	Certified value	Std dev (%)
Hg	1.9	<1.9	0.05 ± 1.58	-
As	1.1	12.5 ± 0.8	13.4 ± 0.92	-7
Cd	3.0	< 3.0	0.50 ± 0.06	-
Cr	3.1	92.3 ± 3.3	89.6 ± 6.9	+3
Zn	1.2	95.4 ± 8.3	96.1 ± 3.8	-1
Ni	2.1	39 ± 5	37.9 ± 3.1	+3
Pb	2.0	38.4 ± 2.0	36.9 ± 3.1	+4
Cu	1.6	21.0 ± 4.0	20.1 ± 1.6	+4

Table 4.3: Results of KB 10ppm (mg/L) analysed using TXRF; n=3, $\bar{x} \pm SD$

Element	Detection limit	Experimental value	Certified value	Standard Deviation (%)
As	1.5	7.5 ± 2.4	8.00 ± 1.50	-6
Cd	4.4	8.5 ± 0.5	7.3 ± 0.90	+16
Cr	6.5	9.2 ± 0.8	10.03 ± 0.03	-8
Cu	2.0	10.0 ± 0.5	10.03 ± 0.03	0
Hg	1.0	7.7 ± 1.0	8.02 ± 1.00	-4
Ni	4.0	10.6 ± -0.8	10.03 ± 0.03	+6
Pb	3.0	10.45 ± 0.4	10.03 ± 0.03	+3
Zn	3.0	9.9 ± 0.6	10.03 ± 0.03	-1

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4.3 Concentrations of the metals in the sampled media

4.3.1 Results of water samples elemental content

Table 4.4 shows the results of analyses of the water samples analysed using TXRF.

Table 4.4: Results for TXRF analysis for water samples (mg/L), n=3, $\bar{x} \pm SD$

Sample	Hg	As	Cd	Cr	Zn	Ni	Pb	Cu
W03	< 1.0	< 1.5	<4.4	<6.5	< 3.0	< 4.0	<3.0	130 ±2.0
W05	< 1.0	< 1.5	<4.4	390 ± 7	<3.0	<4.0	<3.0	70± 2.0
W07	< 1.0	< 1.5	<4.4	<6.5	< 3.0	<4.0	<3.0	<2.0
W08	< 1.0	< 1.5	<4.4	<6.5	187 ± 3	830 ± 4	<3.0	470 ±2
W09	< 1.0	< 1.5	< 4.4	<6.5	<3.0	< 4.0	<3.0	<2.0
W10	< 1.0	< 1.5	< 4.4	<6.5	<3.0	< 4.0	<3.0	50 ±2.0
W12	< 1.0	< 1.5	<4.4	<6.5	< 3.0	<4.0	<3.0	70 ±2.0
W13	< 1.0	< 1.5	< 4.4	<6.5	< 3.0	<4.0	<3.0	<2.0
W14	< 1.0	< 1.5	<4.4	<6.5	<3.0	<4.0	< 3.0	<2.0
W15	< 1.0	< 1.5	<4.4	210 ± 7	< 3.0	<4.0	< 3.0	60 ±2.0

Mercury, cadmium, arsenic and lead were below the detection limits. The zinc concentration from site 8exceeded the WHO limits. Chromium was found at site 5 and 15, while nickel was found at site 8. Copper levels exceeded the WHO limit of 2mg/L in six out of the ten samples analysed.

Sampling site 8, which is the confluence of the stream with Paka Nyeusi stream recorded the highest concentration levels of copper, zinc and nickel. This may have resulted from creation of a vortex at the convergence point causing the eroded sediments to be deposited at this point hence an accumulation (Ali et al., 2019).

Sampling site 5, which is a portion along the stream near the dry tailings deposit area, and 15, which is at a local artisanal mine, had a high water chromium concentration. This may have been a result of accumulation over time, since chromium is highly immobile due to its insolubility in water. This may explain the high concentration in sites where it is directly deposited (Fashola et al., 2016).

Copper was observed to be above 10mg/L in six out of the ten samples analysed. It was generally observed by Fashola et al., (2016) that copper is found in high concentrations in mining areas. The low concentrations at sites 7 and 9 could be due to deposition that

already happened at the confluence. This is also observed at sites 13 and 14, which are points on the upstream side where chances of contamination due to mining are low.

4.3.2   Results of elemental content in Sodom apple (*Solanum incanum*) samples

The Sodom apple was analysed using EDXRF and the results are shown in Table 4.5.

Table 4.5: EDXRF results for Sodom apple samples (mg/kg), n=3, $\bar{x} \pm SD$

Sample	Hg	As	Cd	Cr	Zn	Ni	Pb	Cu
P03	< 1.9	< 1.1	< 3.0	3.3±1.0	35.2±1.5	5.8±1.1	4.1±0.8	24.6± 1.5
P04	<1.9	1.9± 1.1	< 3.0	7.9± 1.4	24.6±1.2	14.3±2.9	4.8±0.9	24.6± 1.7
P05	<1.9	< 1.1	< 3.0	< 3.1	30.9±1.4	6.6±1.10	<2.0	30.3± 1.7
P06	<1.9	1.6±1.1	< 3.0	< 3.1	24.6± 1.3	12.2± 1.3	4.7± 0.8	28.4±1.6
P07	3.2 ± 0.8	< 1.1	< 3.0	6.8±1.4	31.0±1.5	6.39± 1.2	<2.0	18.4±1.4
P08	<1.9	< 1.1	< 3.0	9.8± 1.7	35.2±1.6	8.2± 1.2	5.9± 0.9	21.0± 1.5
P09	2.1 ± 0.7	< 1.1	< 3.0	< 3.1	24.8±1.3	< 2.1	3.1± 0.8	17.9± 1.3
P10	<1.9	< 1.1	< 3.0	10.0±1.7	36.7±1.6	8.5±1.3	7.0±0.9	22.3±1.5
P11	<1.9	2.0 ±0.4	< 3.0	< 3.1	29.2±1.4	5.5± 1.0	4.0±0.9	21.6± 1.4
P12	<1.9	1.8 ± 0.5	< 3.0	5.7± 1.3	38.2 ±1.6	4.2±2.1	7.2±1.0	33.0±1.8
P13	<1.9	< 1.1	< 3.0	< 3.1	35.0± 1.6	4.9± 1.1	7.2±1.5	25.7±1.6
P14	<1.9	< 1.1	< 3.0	< 3.1	25.8±1.3	5.9± 1.4	<2.0	25.4 ±1.4
P32	<1.9	1.9 ±1.1	< 3.0	4.5±1.3	42.0±1.8	< 2.1	6.0± 1.0	21.2±1.6
P33	<1.9	< 1.1	< 3.0	7.4± 1.5	28.3±1.5	11.1±1.4	5.9± 0.9	33.3 ± 1.9

In general, the metals in the plants mostly occurred in the order Zn>Cu>Ni>Cr>Pb>Hg>As. Cadmium was below the detection limits (3mg/kg) in all the plant samples.

Chromium levels (mg/kg) ranged from minimum detection limits to 9.97, with a mean of 4.0 ±2.0, where measured in the samples, the levels exceeded the allowable limits. These areas were at; the bridge before the stream passed through the town and processing plants, outside plant 1, and around the confluence with Paka Nyeusi stream and in the residential areas. This could have resulted from contamination from regions outside Lolgorian town.

Mercury levels (mg/kg) ranged from detection limits to 3.2, with a mean of 0.4 ± 1.9.In all the samples that were analysed, the values were below the detection limit of 1.9mg/kg apart from sites 7 and 9. These were located downstream region after the confluence of two streams. The contamination may have resulted from accumulation from the upstream areas in the artisanal mines.

Lead levels (mg/kg) in Sodom apple samples ranged from <2.00 to 7.17, with a mean of 4.20 ± 2.00. Similarly, the areas where lead was found, had levels exceeding the WHO limits, eleven out of fourteen sites sampled. This is an indication that, the area is highly contaminated due to the mining activities (Fashola et al., 2016).

Arsenic levels (mg/kg) ranged between 1.12and 2.02, with a mean of 0.65 ± 1.12. Sampling site11 had arsenic levels that exceed the allowable limits. This site is located along the road passing through the wet tailings deposit area of processing plant 2. The high concentration could be as a result of overflow of material from the holding ponds.

Nickel levels (mg/kg) in Sodom plant ranged from <2.06 to 14.30, with a mean of 6.67, all within the within the allowable limits in most of the sampled points apart from three sites where it exceeds the 10mg/kg levels. These areas are located a distance away, from the processing plants and hence the contamination cannot be entirely attributed to the processing plants processing activities.

Copper levels (mg/kg) ranged from17.85 to 33.25, with a mean of 24.82 ± 1.63.These copper levels exceeded the allowable limit of 10mg/Kg. Sites points namely; 05, 10, 12 and 33 recorded values above 30mg/kg. This could point to a generally high zinc concentration in *Solanum incanum* (Auta et al., 2011).

Zinc was found to range (mg/kg) from24.6 to 40.9, with a mean of 31.4 ± 1.2 and exceed the WHO allowable limits in all the areas, as presented on table 2.2This could point to a generally high zinc concentration in *Solanum incanum*(Auta et al., 2011).

4.3.3 Results of elemental content in sediment/soil samples

The summary of heavy metal concentrations in soils/sediments is presented in Table 4.6. The brown colour corresponds to the results for the soil samples.

Table 4.6: Results for EDXRF analysis for sediment/ soil samples (mg/kg), n= 3, $\bar{x} \pm SD$

Sample	Hg	As	Cd	Cr	Zn	Ni	Pb	Cu
S01	11.90 ± 3.64	56.00 ± 2.31	< 3.06	186.00± 20.90	87.85± 3.68	44.50± 4.43	37.10± 2.93	63.10± 3.84
S02	< 1.90	278.50 ± 4.47	< 3.06	173.00± 9.03	119.00± 4.17	55.00± 4.38	63.05± 3.93	92.30± 4.42
S03	13.00 ± 3.07	38.10 ± 1.88	< 3.06	236.00± 9.70	115.50 ± 4.22	102.45± 5.64	26.53± 2.33	79.20 ± 4.13
S04	< 1.90	26.85 ± 1.62	< 3.06	164.50± 7.58	85.10± 3.46	54.20± 4.03	30.50± 2.20	56.75± 3.41
S05	15.45 ± 2.09	50.75 ± 2.37	< 3.06	210.50± 11.20	114.50± 4.24	69.20± 4.94	50.30± 3.27	97.75± 4.72
S06	11.50 ± 1.86	38.00 ± 2.27	< 3.06	190.00± 9.69	78.83 ± 3.30	65.25± 4.54	74.13 ± 3.54	61.53± 3.55
S08	18.50 ± 2.48	62.15 ± 2.98	< 3.06	335.50± 17.75	140.00± 5.45	138.50± 7.99	51.30± 4.97	129.50 ± 6.36
S09	23.45 ± 2.85	55.40 ± 2.75	< 3.06	350.50± 17.55	134.50± 5.48	143.50 ± 8.06	36.10± 5.18	144.00± 6.83
S10	7.70 ±2.73	17.25± 3.73	< 3.06	159.00± 9.27	61.50 ± 4.69	61.1 ± 6.70	47.55 ± 4.31	42.30± 5.44
S11	< 1.90	935.50 ± 28.20	< 3.06	111.00± 6.58	156.00± 4.70	24.35± 3.44	148.00± 4.80	174.50± 5.89
S12	17.20 ± 2.36	41.30 ± 2.31	< 3.06	406.00± 17.80	127.50± 5.24	164.00± 8.31	31.20± 4.64	150.00± 6.64
S13	11.95 ± 1.80	22.85 ± 1.67	< 3.06	192.50± 10.30	74.85± 3.33	60.50± 4.50	34.55± 2.81	52.95± 43.44
S14	14.20 ± 2.30	15.20 ± 1.40	< 3.06	151.50± 7.14	66.10± 2.87	43.90± 3.39	37.35± 2.42	44.15± 2.89
S16	13.65 ± 2.00	100.05 ± 4.03	< 3.06	144.00± 7.89	114.50± 4.00	47.45± 4.01	52.85± 2.90	75.60 ± 3.97
S31	10.30 ±2.67	14.60 ± 1.37	< 3.06	139.50± 7.46	145.50± 4.36	64.90 ± 4.26	30.00± 2.25	70.25± 3.71
S32	18.60 ± 3.02	47.75 ± 2.86	< 3.06	112.50± 6.32	148.00± 4.41	38.15± 3.44	29.25± 2.12	62.00± 3.43
S33	10.02 ± 1.70	19.30 ± 1.47	< 3.06	149.00± 8.21	116.50± 3.86	50.70± 3.99	28.20± 2.40	69.85 ± 3.70

Cadmium concentration was below 3.06 mg/kg in all the samples.

Chromium levels (mg/kg) ranged from 111 to 406, with a mean of 200 ±20 and exceeded the allowable limits of 100mg/Kg. The soils are generally contaminated with chromium. The concentration levels of chromium in soil in the area are generally high (Ichangí & MacLean, 1991).

Mercury levels (mg/kg) ranged from <1.9 to 23.5, with a mean of 11.6 ± 2.5. Fifteen out of the seventeen samples had mercury in levels above 10 ppm. This could be attributed to the widespread artisanal mining activities in the area.

Lead (mg/kg) was present in the ranges of 26.5to 148, with a mean of 47.5± 6.5. Only site 11 had a level that exceeded of the allowable concentration levels by WHO. This site was located along the road, outside processing plant 2, hence tailings could have contributed a high concentration level.

Arsenic (mg/kg) was present in the ranges of 14.6to 936, with a mean of 107± 5. All the samples had a concentration levels greater than 10ppm WHO limits. Site11 had the highest concentration levels and the contamination could be due to the tailings at the processing plant 2.

Nickel (mg/kg) was present in the ranges of 24.4 to 165, with a mean of 72.2± 6.6. All the samples had a concentration greater than the allowable limit, apart from point 11. The concentration levels of chromium in soil in the area are generally high (Ichangí, 1991).

Copper (mg/kg) was present in the ranges of 42.3 to 174.5 ± 5.9, with a mean of 86.2± 3.3. All the samples had a concentration greater than the WHO allowable limit. Site 11 had the highest concentration level which could be attributed to contamination from the tailings at plant 2. Site 8 had the second highest concentration which could be attributed to the deposition of sediments at a confluence. The soils in the region generally have a high copper content.

Zinc (mg/kg) was present in the ranges of 61.5± 4.7to 156 ± 5, with a mean of 111± 2. All the samples had a concentration greater than the WHO allowable limit. Site 11 had the highest concentration level which could be attributed to contamination by the tailings at plant 2. In general, the soils in the region have high zinc content.

4.4 Comparison between the sampled media for interrelationship

The elemental concentrations were subjected to ANOVA analysis to check whether there was a relationship in the mean concentrations of heavy metals in the media that were significant at α=0.05. The summary is shown in Table 4.7 and in Appendix C.

Table 4.7: Results of ANOVA analysis in the three media

Element	F	F critical
As	2.058	3.259
Cd	Below detection limit	
Cr	60.973	3.259
Cu	34.288	3.259
Hg	13.844	3.259
Ni	29.508	3.259
Pb	17.910	3.259
Zn	87.571	3.259

There is no significant relationship in the concentrations of Hg, Zn, Pb, Cu, Ni and Cr in the plants and soils/sediments since f >F $_{critical}$, except for the As.

Table 4.8 shows the results of Pearson correlation concentrations of heavy metals in the sampled media.

Sodom apple (*Solanum incanum)* and sediments showed a very weak relationship for all the metals, except mercury which had a strong relationship. There was no correlation between soil and water for As, Cd, Cr, Hg and Pb. A weak relation in Cu and Ni and a moderate relation were observed in Zn in analysis of sediments and Sodom apple. The inter-elemental relationship between water and plants was very weak for As, Cd, Hg and Pb, weak for Cr, Cu and Zn while a moderate relationship was observed in Ni.

Table 4.8: Pearson correlation of heavy metals in water, Sodom apple and soil

Element	Media	Water	Sodom apple	Soil/sediment
As	Water	1	-	-
	Sodom apple	0	1	-
	Soil/sediment	0	0.0774	1
Cd	Water	1	-	-
	Sodom apple	0	1	-
	Soil/sediment	0	0	1
Cr	Water	1	-	-
	Sodom apple	-0.3301	1	-
	Soil/sediment	-.01880	0.1321	1
Cu	Water	1	-	-
	Sodom apple	-0.2120	1	-
	Soil/sediment	0.3186	0.0513	1
Hg	Water	1	-	-
	Sodom apple	0	1	-
	Soil/sediment	0	0.7085	1
Ni	Water	1	-	-
	Sodom apple	0.4599	1	-
	Soil/sediment	0.3591	-.04063	1
Pb	Water	1	-	-
	Sodom apple	0	1	-
	Soil/sediment	0	-0.0719	1
Zn	Water	1	-	-
	Sodom apple	0.1990	1	-
	Soil/sediment	0.4525	0.0064	1

4.5   Evaluation of the extent of heavy metal pollution in the soils

4.5.1   Geo-accumulation index

The summary of the geo-accumulation index of the sampled points is shown in appendix D.

The variations of geo-accumulation indices for chromium, lead, arsenic, nickel, copper and zinc are shown from figures 4.1 - 4.6, respectively. The values of the geo-accumulation indices ranged from uncontaminated to extremely contaminated, in general.

Figure 4.1 shows the I_{geo} of chromium, which range between -0.17 at site 11 and 1.71 at site 12, having an average value of 0.59. Sites 11 and 32 were uncontaminated. Sites 8, 9 and12

were moderately contaminated while the rest of the sites were uncontaminated to moderately contaminated.

Figure 4.2 shows the I_{geo} of lead, which range - 0.58 and 2.54, and averages 0.65. Site 10 was uncontaminated, while site 11 was moderately to strongly contaminated. The rest of the sites were moderately contaminated.

Figure 4.3 show the I_{geo} of arsenic, which ranges between 2.70 and 8.70, having an average value of 4.40. Sites 10, 14 and 31 were moderately to strongly contaminated. Sites 4, 13 and 33 were strongly contaminated. Sites 3, 6, 8, 9, 12 and 32 were strongly to extremely contaminated, while sites 2, 11 and 16 were extremely contaminated.

Figure 4.4 shows the I_{geo} of nickel whichwas between -1.44 and 1.31, having an average value of -0.05. Twelve of sampling points were uncontaminated. Sites 3 and 5 were uncontaminated to moderately contaminated. Sites 8, 9 and 12 were moderately contaminated (see).

Figure 4.5 shows the I_{geo} of copper as between 0.17 and 2, having an average value of -1.07. Nine of sampling points were uncontaminated to moderately contaminated. Sites 2, 3, 5 and 16 were moderately contaminated, while site 11 was moderately contaminated.

Figure 4.6 shows the I_{geo} variation of zinc as between -0.79 and 0.55, having an average value of 0. Six of sampling points were uncontaminated, while the rest of the sites were uncontaminated to moderately contaminated.
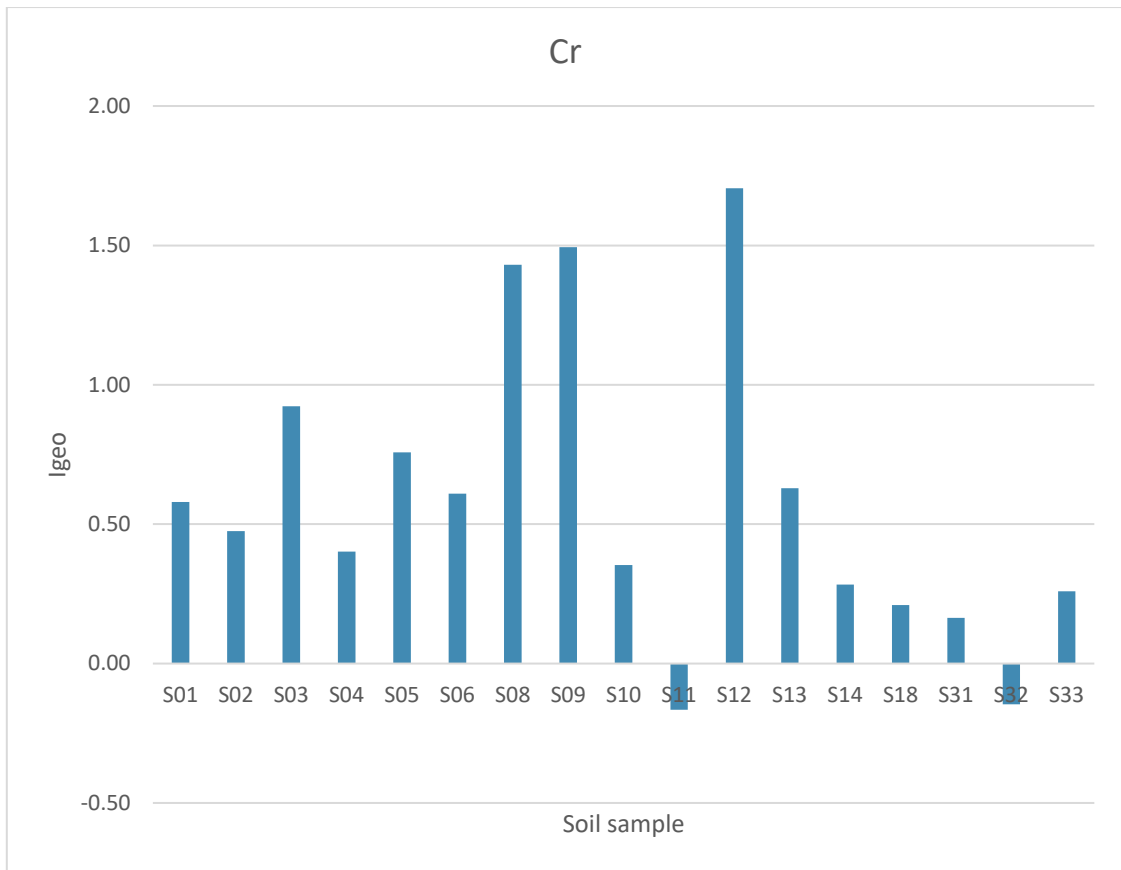
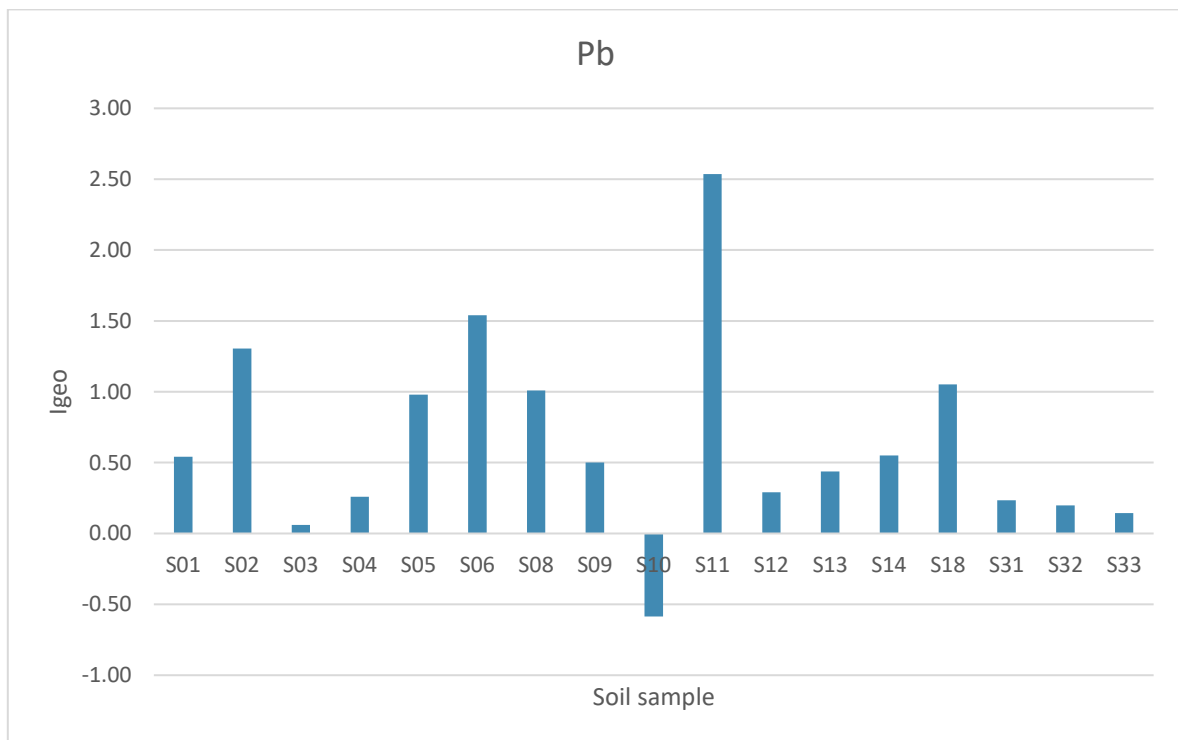*Figure 4.1: Variations of chromium in sediments/soils*

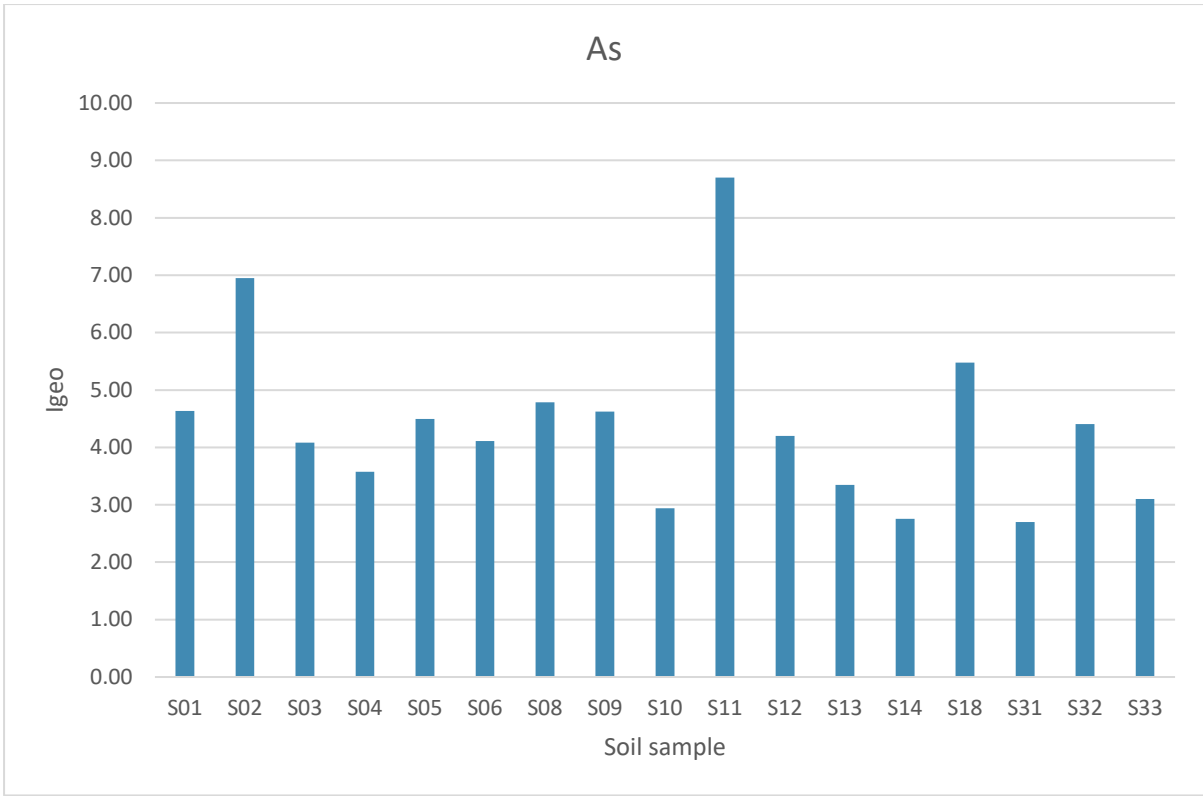*Figure 4.2: Variations of lead in sediments/soils*

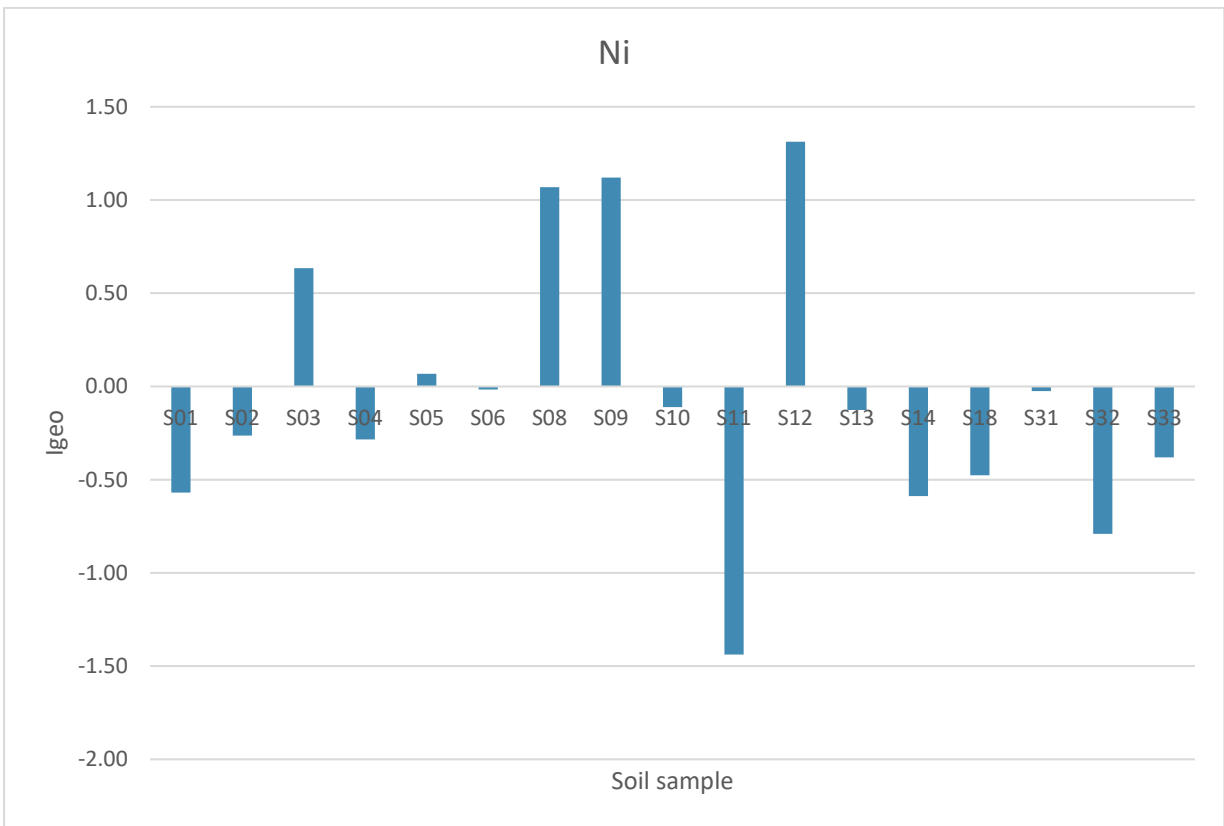*Figure 4.3: Variations of arsenic in sediments/soils*

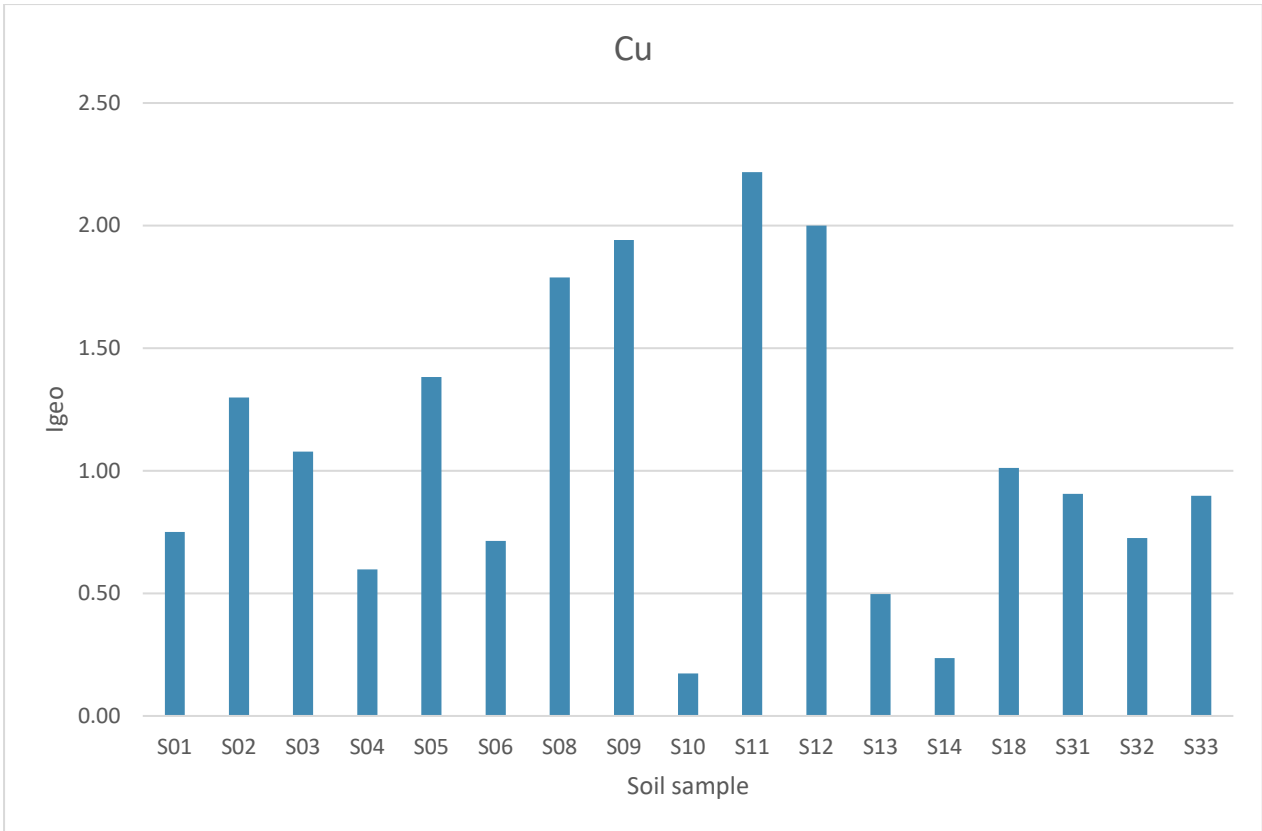*Figure 4.4: Variations of nickel in sediments/soils*

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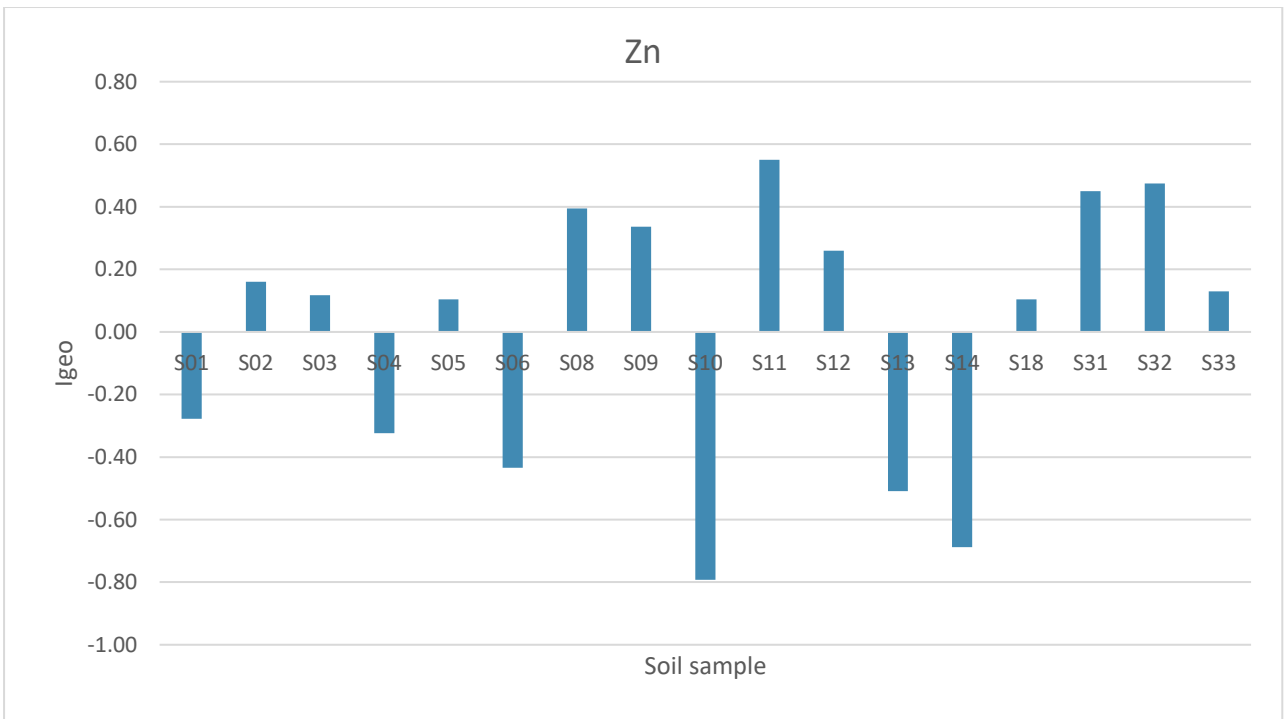*Figure 4.5: Variations of copper in sediments/soils*

Figure 4.6: Variations of zinc in sediments/soils

4.5.2   Pollution Load Index

Table 4.9 and shows a summary of the CFs and PLI values for the elements of interest determined for the soil samples analysed in this study. Appendix D and E shows the classification for the metal contamination levels in soils.

Most of the CFs and PLI values for the elements were greater than 1, implying that the metal levels exceeded the reference concentrations at the sampled sites. This is an indication that the soils are deteriorating in quality.

Table 4.9: A summary of the contamination factors and pollution load indices

Sample	Contamination factors (CF)						PLI
	Cr	Pb	As	Ni	Cu	Zn	
S01	2.24	2.18	37.33	1.01	2.52	1.24	2.89
S02	2.08	3.71	185.67	1.25	3.69	1.68	4.72
S03	2.84	1.56	25.40	2.33	3.17	1.63	3.33
S04	1.98	1.79	17.90	1.23	2.27	1.20	2.44
S05	2.54	2.96	33.83	1.57	3.91	1.61	3.69
S06	2.29	4.36	25.92	1.48	2.46	1.11	3.19
S08	4.04	3.02	41.43	3.15	5.18	1.97	5.03
S09	4.22	2.12	36.93	3.26	5.76	1.89	4.77
S10	1.92	1.00	11.50	1.39	1.69	0.87	1.89
S11	1.34	8.71	623.67	0.55	6.98	2.20	6.28
S12	4.89	1.84	27.53	3.73	6.00	1.80	4.64
S13	2.32	2.03	15.23	1.38	2.12	1.05	2.46
S14	1.83	2.20	10.13	1.00	1.77	0.93	2.01
S16	1.73	3.11	66.70	1.08	3.02	1.61	3.52
S31	1.68	1.76	9.73	1.48	2.81	2.05	2.50
S32	1.36	1.72	31.83	0.87	2.48	2.08	2.63
S33	1.80	1.66	12.87	1.15	2.79	1.64	2.42

Chapter 5: Conclusions and Recommendations

5.1   Conclusions

The study has evaluated the potential hazard as a result of the accumulation of heavy metals in plants, soils and water samples in around Kilimapesa gold processing plant in Lolgorian, following the evaluations of the concentrations of select metals: arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc.

Concentration levels of the metals in soils/sediments and Sodom apple (*Solanum incanum*) were determined using EDXRF technique while water was analysed using TXRF technique. From the comparison of certified concentrations with experimental concentrations of the standard reference materials (River Clay, Bowen Kale and KB 10ppm), the techniques were found reliable for use in analysis.

The variations of the metals in the water samples (mg/l) were: Cd (< 4.35), (Hg (< 1.00, As (< 1.50), Cr (< 6.50-390.65), Zn (< 3.00 -187.00), Ni (< 4.00-830.00), Pb (< 3.00) and Cu (< 1.14-470.00).

The variations of the metals in soil samples (mg/kg) were: Hg (< 1.90-23.45), As (14.60 - 935.5), Cr (111.00 - 406.00), Zn (61.50-156), Ni (24.35-164.00), Pb (26.60-148.00) and Cu (42.3-174.5).

The variations of the metals in Sodom apple (*Solanum incanum)* samples (mg/kg) were Hg (< 1.90-3.18), As (< 1.12 -2.02), Cr (<3.06-9.97), Zn (24.55-40.95), Ni (< 2.06 - 14.25), Pb (< 2.00-7.17) and Cu (17.85-33.25). Chromium was not detected in the plant samples (< 3.00).

There was a significant relationship in the concentrations of the heavy metals among the three media sampled following ANOVA. In general, the average concentrations of the metals in soils from the sampled points occurred as Cr > Zn > As > Cu > Ni > Pb> Hg > Cd. The average concentrations of the metals in vegetation from the sampled points occurred as Zn >Cu > Ni > Pb> Cr > Hg > As > Cd.

The levels of heavy metal concentrations in the media were soils/sediments > vegetation > water. Most of the heavy metals in the soils sampled were found to exceed the allowable limits by WHO in the soils.

Pearson's correlation in Sodom apple (*Solanum incanum)* and sediments showed a very weak relationship for all the metals except mercury which had a strong relationship. There was a weak correlation between soil and water for As, Cd, Cr, Hg and Pb, a weak relation in Cu and Ni, while a moderate relation was observed in Zn. The relationship between water and plants was very weak for As, Cd, Hg and Pb ,weak for Cr, Cu and Zn and moderate for Ni.

The geo-accumulation index showed that the soils were mostly moderately contaminated for all metals, but in extreme concentrations for lead at three of the sampled points. PLI values indicated that soils in the area were deteriorating in quality.

5.2   Recommendations

1) A comparative study of environmental and biological media should be done on the gold mining and processing plants regions in Kenya to map the extent of contamination.

2) Bioassays should be studied and incorporated in reports to obtain trends on the effects of heavy metal contamination on human population in the course of operations of the gold mining companies.

3) Use of bio-accumulators like water hyacinth to extract heavy metals from processing wastes before release to the environment to minimize concentrations of the heavy metals in the environmental media. Microorganisms like bacteria may be used to absorb the heavy metals (Wang et al, 2013)

4) Covering of the tailings at the disposal areas by the mining companies to reduce erosion by wind and channelling run-off water to a temporary storage place for analysis and treatment before it gets to water resources

5) Agricultural crops like wheat, barley, maize and potatoes should be analysed for assessment of heavy metal contamination in the area

6) NEMA should ensure the necessary steps are taken for enforcement of regulations that are currently in place about mining and environmental conservation. This may include periodic evaluation of soils and water from mining and processing areas for contaminations.

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Appendices

Appendix A: GPS locations of sampled sites

Sampling Point	Northing (S)	Easting (E)	Elevation (m)	Description	Sample medium
1	01°13'34.6''	34°45'58.1''	1566	Fence marking the boundary of wet tailings deposit area at plant 1	S01 (soils)
2	01°13'34.0''	34°45'58.7''	1565	80 m from point 1	S02 (soils)
3	01°13'32.2''	34°45'55.4''	1559	Start of stream flow from underground	S03, P03, W03(sediments/plants/water)
4	01°13'32.4''	34°45'53.1''	1563	Tailings deposit	S04, P04 (soils/plants)
5	01°13'30.4''	34°45'47.9''	1538	The portion along the stream near the tailings deposit area	S05, P05, W05 (sediments/plants/water)
6	01°13'31.7''	34°45'46.3''	1552	The portion along the stream near the tailings deposit area	S06, P06 (sediments/plants)
7	01°13'38.6''	34°45'06.9''	1500	Downstream along the stream	P07, W07 (plants/water)
8	01°13'37.5''	34°45'04.1''	1494	Downstream at the confluence with another stream (locally called Paka nyeusi)	S08, P08, W08(sediments/plants/water)
9	01°13'40.0''	34°45'02.3''	1494	Downstream after Paka nyeusi confluence	S09, P09, W09(sediments/plants/water)
10	01°14'58.2''	34°48'25.9''	1567	Upstream at a bridge, before the stream passed by processing Plant 2	S10, P10, W10(sediments/plants/water)
11	01°14'26.8''	34°48'36.5''	1612	Fence marking the boundary of wet tailings deposit area at plant 2	S11, P11 (soils/plants)
12	01°14'23.2''	34°48'26.9''	1598	Roadside outside plant 2 at a bridge	S12, P12, W12(soils/plants/water)
13	01°14'56.0''	34°47'52.1''	1554	Stream portion downstream of plant 2	S13, P13, W13(sediments/plants/water)
14	01°14'55.6''	34°47'51.1''	1560	Stream portion downstream of plant 2	S14, P14, W14(sediments/plants/water)
15	01°13'38.8''	34°48'24.7''	1647	Local artisinal mine	W15 (water)
16	01°13'38.7''	34°45'50.1''	1560	Dry tailings deposit area	S18(soils)
31	01°13'30.1''	34°48'22.1''	1633	Settlement area- road to an artisanal mine	S31 (soils)
32	01°13'45.3''	34°48'16.3''	1661	Settlement area	S32, P32 (soils/plants)
33	01°13'42.2''	34°48'11.5''	1675	Settlement area- road to an artisanal mine	S33, P33(soils/plants)

Appendix B: Soil sample spectrum using 5 targets on EDXRF

Al target

RX9 target

Si target
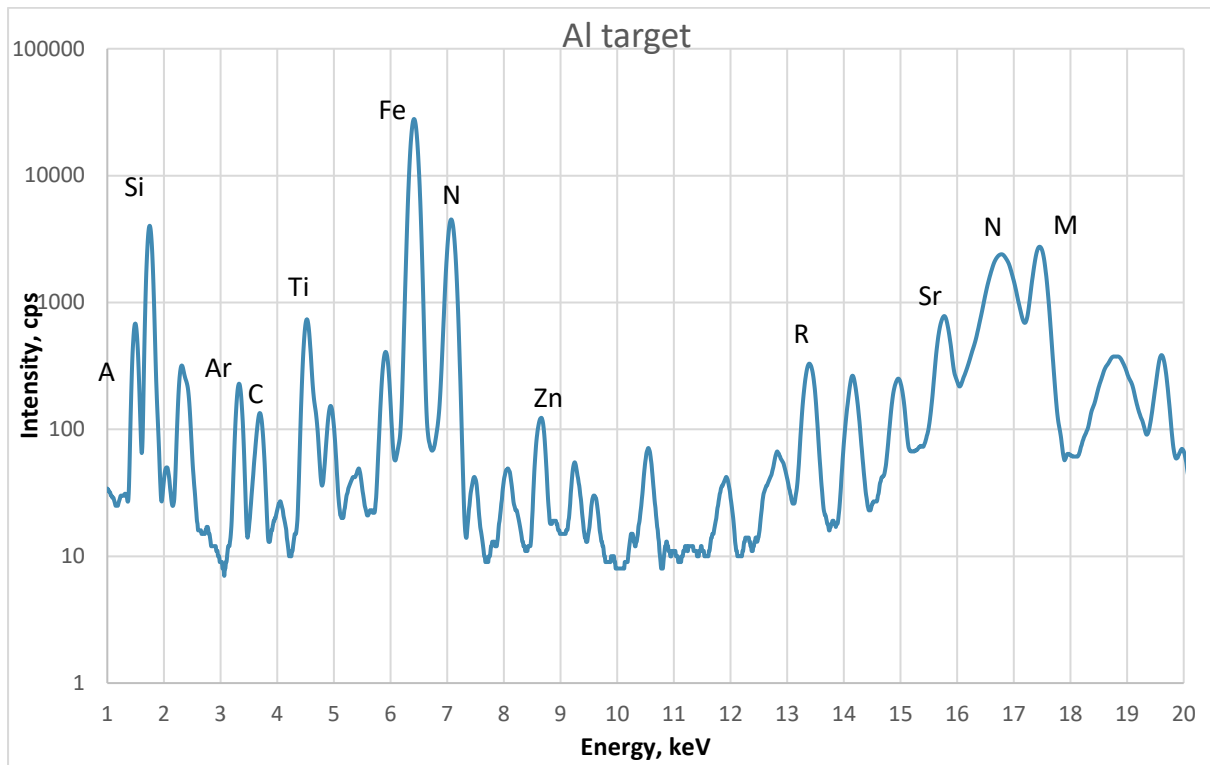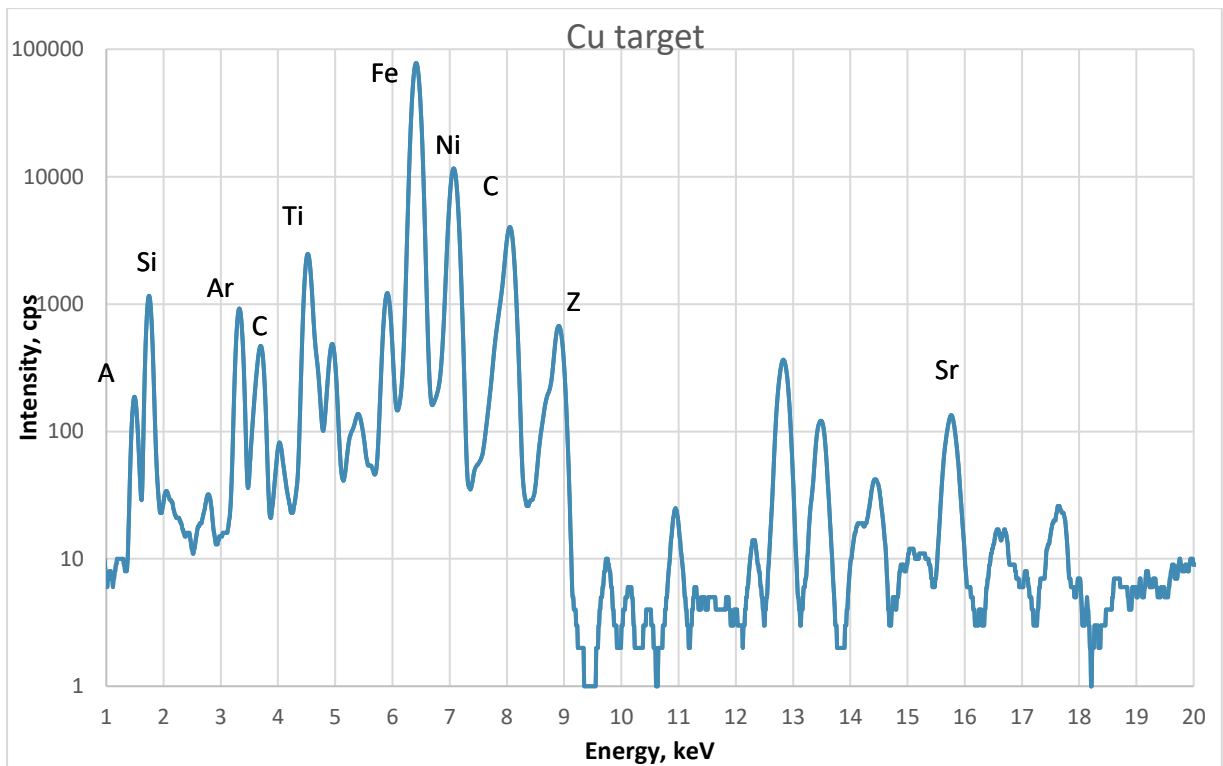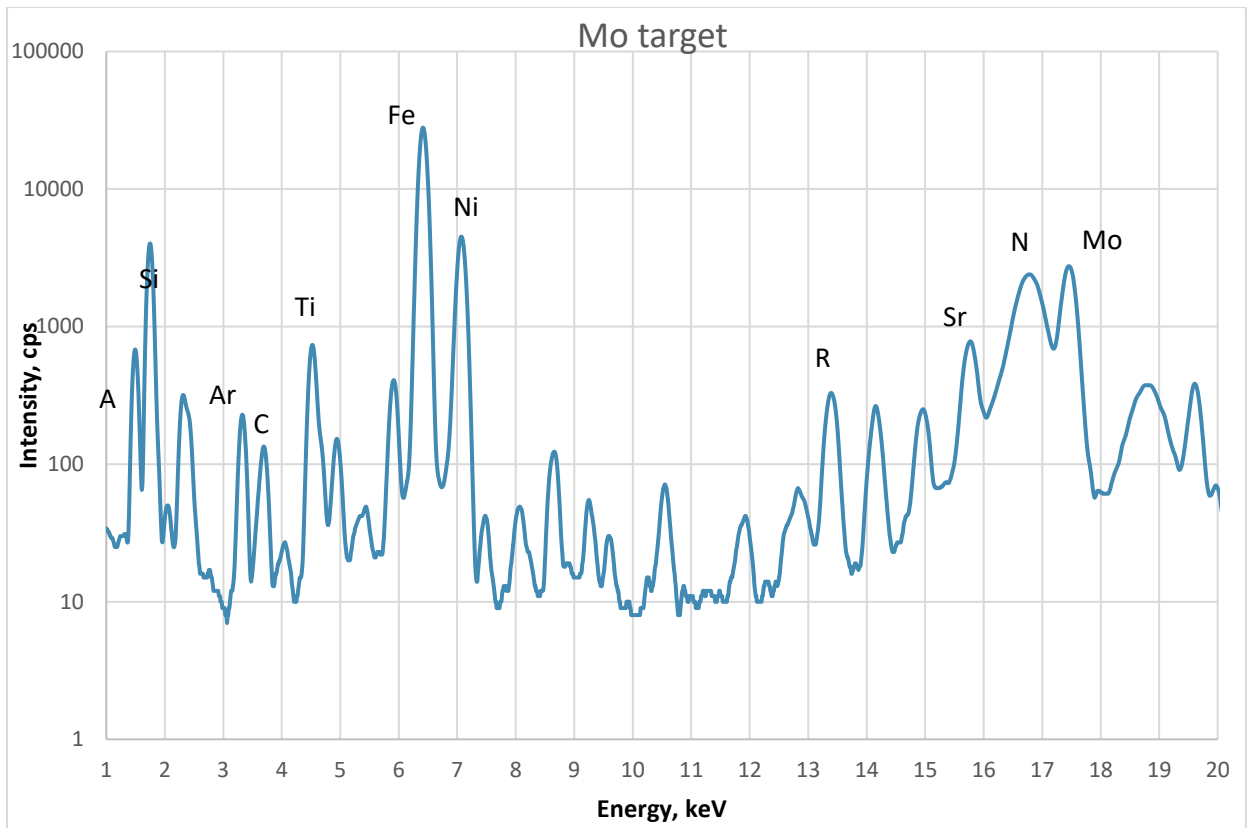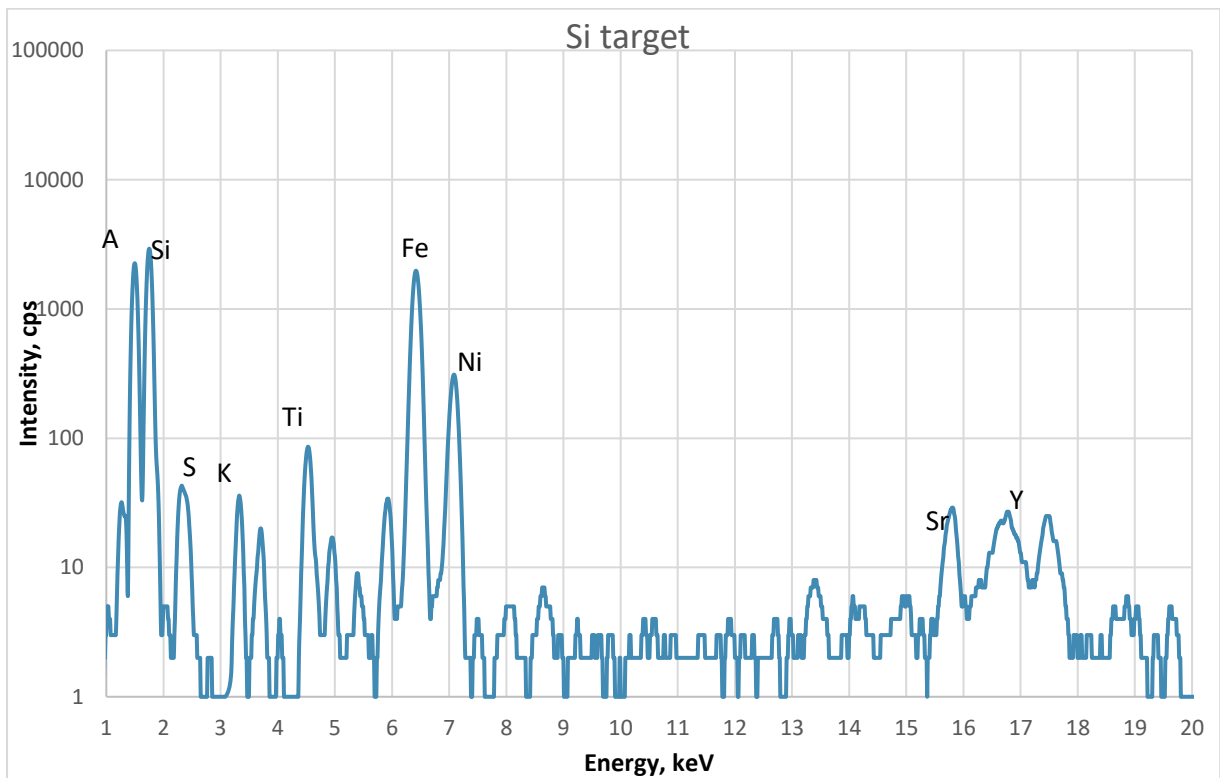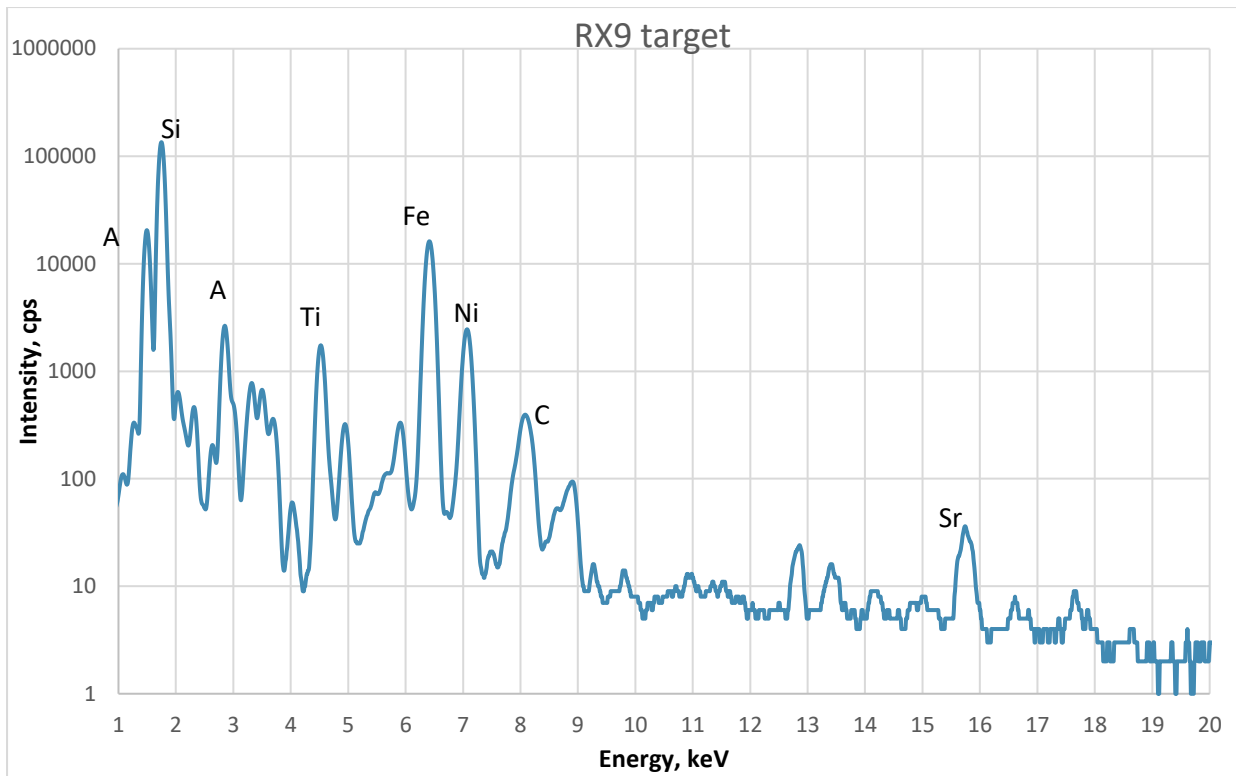
Appendix C: ANOVA analysis in the soils/sediments, vegetation and water samples

Element	Source of variation	SS	df	MS	f	P-value	F critical
As	Between Groups	85778.28	2	42889.14	2.058	0.142	3.259
	Within Groups	750229.1	36	20839.7			
	Total	836007.4	38				
Cd	Levels could not be detected (< 3.06 mg/L)						
Cr	Between Groups	364471	2	182235.5	60.973	2.76E-12	3.259
	Within Groups	107596.9	36	2988.804			
	Total	472067.9	38				
Cu	Between Groups	46815.15	2	23407.57	34.288	4.61E-09	3.259
	Within Groups	24576.05	36	682.668			
	Total	71391.2	38				
Hg	Between Groups	1291.262	2	645.631	13.844	3.47E-05	3.259
	Within Groups	1678.85	36	46.635			
	Total	2970.112	38				
Ni	Between Groups	41038.22	2	20519.11	29.508	2.59E-08	3.259
	Within Groups	25033.33	36	695.370			
	Total	66071.54	38				
Pb	Between Groups	14026.77	2	7013.385	17.910	3.99E-06	3.259
	Within Groups	14097.24	36	391.589			
	Total	28124.01	38				
Zn	Between Groups	68365.57	2	34182.78	87.571	1.48E-14	3.259
	Within Groups	14052.38	36	390.344			
	Total	82417.95	38				

SS- sum of squares   df- degrees of freedom

MS- mean squares   f- experimental result

Appendix D: A summary of the geo-accumulation indices

Sample	Cr	Pb	As	Ni	Cu	Zn
S01	0.58	0.54	4.64	-0.57	0.75	-0.28
S02	0.47	1.31	6.95	-0.26	1.30	0.16
S03	0.92	0.06	4.08	0.63	1.08	0.12
S04	0.40	0.26	3.58	-0.28	0.60	-0.32
S05	0.76	0.98	4.50	0.07	1.38	0.10
S06	0.61	1.54	4.11	-0.02	0.71	-0.43
S08	1.43	1.01	4.79	1.07	1.79	0.39
S09	1.49	0.50	4.62	1.12	1.94	0.34
S10	0.35	-0.58	2.94	-0.11	0.17	-0.79
S11	-0.17	2.54	8.70	-1.44	2.22	0.55
S12	1.71	0.29	4.20	1.31	2.00	0.26
S13	0.63	0.44	3.34	-0.13	0.50	-0.51
S14	0.28	0.55	2.76	-0.59	0.24	-0.69
S16	0.21	1.05	5.47	-0.48	1.01	0.10
S31	0.16	0.23	2.70	-0.02	0.91	0.45
S32	-0.15	0.20	4.41	-0.79	0.73	0.47
S33	0.26	0.15	3.10	-0.38	0.90	0.13

KEY

▮ (red)	extremely contaminated
▮ (yellow)	strongly to extremely contaminated
▮ (blue)	strongly contaminated
▮ (green)	moderately to strongly
▮ (brown)	moderately contaminated
▮ (light blue)	uncontaminated to moderately contaminated
▮ (white)	uncontaminated

Appendix E: A summary of the contamination factors and pollution load index (PLI)

Sample	Contamination Factor						PLI
	Cr	Pb	As	Ni	Cu	Zn	
S01	2.24 (3)	2.18 (3)	37.33 (6)	1.01 (2)	2.52 (3)	1.24 (2)	2.89
S02	2.08 (3)	3.71 (4)	185.67 (6)	1.25 (2)	3.69 (4)	1.68 (2)	4.72
S03	2.84 (3)	1.56 (2)	25.40 (6)	2.33 (3)	3.17 (4)	1.63 (2)	3.33
S04	1.98 (2)	1.79 (2)	17.90 (6)	1.23 (2)	2.27 (3)	1.20 (2)	2.44
S05	2.54 (3)	2.96 (3)	33.83 (6)	1.57 (2)	3.91 (4)	1.61 (2)	3.69
S06	2.29 (3)	4.36 (5)	25.92 (6)	1.48 (2)	2.46 (3)	1.11 (2)	3.19
S08	4.04 (5)	3.02 (4)	41.43 (6)	3.15 (4)	5.18 (6)	1.97 (2)	5.03
S09	4.22 (5)	2.12 (3)	36.93 (6)	3.26 (4)	5.76 (6)	1.89 (2)	4.77
S10	1.92 (2)	1.00 (1)	11.50 (6)	1.39 (2)	1.69 (2)	0.87 (1)	1.89
S11	1.34 (2)	8.71 (6)	623.67 (6)	0.55 (1)	6.98 (6)	2.20 (3)	6.28
S12	4.89 (5)	1.84 (2)	27.53 (6)	3.73 (4)	6.00 (6)	1.80 (2)	4.64
S13	2.32 (3)	2.03 (3)	15.23 (6)	1.38 (2)	2.12 (3)	1.05 (2)	2.46
S14	1.83 (2)	2.20 (3)	10.13 (6)	1.00 (1)	1.77 (2)	0.93 (1)	2.01
S16	1.73 (2)	3.11 (4)	66.70 (6)	1.08 (2)	3.02 (4)	1.61 (2)	3.52
S31	1.68 (2)	1.76 (2)	9.73 (6)	1.48 (2)	2.81 (3)	2.05 (3)	2.50
S32	1.36 (2)	1.72 (2)	31.83 (6)	0.87 (1)	2.48 (3)	2.08 (3)	2.63
S33	1.80 (2)	1.66 (2)	12.87 (6)	1.15 (2)	2.79 (3)	1.64 (2)	2.42

The figures in the brackets indicate the contamination classification factors

KEY: CONTAMINATION FACTOR

6	Extremely contaminated
5	Strong to extremely contaminated
4	Strongly contaminated
3	Moderately to strong contaminated
2	Moderately contaminated
1	Uncontaminated to moderately contaminated

The PLI values are greater than 1, this is indicative of deteriorating soils quality

Appendix F: Definitions

Environmental pollution- the unfavourable alteration of our surroundings, wholly or largely as a by-product of man's actions, through direct or indirect effects of the changes in the energy pattern, radiation levels, and chemical and physical constitution and abundance of organisms

Essential nutrients- elements required in micro-quantities for normal functioning of living tissues

Heavy metals– metallic and metalloid elements with a density greater than $4g/cm^3$ and are toxic even in low concentrations

Non-essential nutrients-elements that is toxic to living tissue even in small concentrations e.g cadmium, arsenic, lead and antimony