University of Nairobi

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

By

Lynda Kanguha Wamere (B. Eng- Mechanical & Production)

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

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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……………………………

This thesis has been submitted for examination with the approval of research supervisors:

1) Mr Michael J. Mangala,
   Institute of Nuclear Science and Technology,
   University of Nairobi.

   Signature……………………   Date…………………….

2) Dr Geoffrey O. Okeng'o,
   Department of Physics,
   University of Nairobi.

   Signature……………………   Date…………………….

Dedication

This work is dedicated to my family for their support and encouragement during the course of the research work. 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.

LIST OF ABBREVIATIONS AND ACRONYMS

AAS- Atomic Absorption Spectroscopy

AMD-Acid Mine Drainage

ANOVA- Analysis of Variance

ARD – Acid Rock Drainage

As- Arsenic

B- Barium

Cd- Cadmium

CF- Contamination Factor

Cr- Chromium

CRM- Certified Reference Method

Cu- Copper

DNA- Deoxyribonucleic acid

EDXRF-Energy Dispersive X-ray fluorescence

EMCA- Environmental Management Regulations and Coordination Act

Fe- Iron

FP- Fundamental Parameters

GPS- Global Positioning System

Hg- Mercury

HNO_3- Nitric acid

ICP- Inductively Coupled Plasma

MCA- Multi-channel Analyser

Mg- Magnesium

Mn- Manganese

Mo- Molybdenum

NAA- Neutron Activation Analysis

Na- Sodium

NEMA- National Environmental Management Authority

NEX CG- Cartesian Geometry software

Ni- Nickel

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Ni- Nickel

Pb- Lead

PLI- Pollution Load Index

RPF-SQX- Rigaku profile fitting analytical software

SDD- silicon drift detector

Se-Selenium

Sn- Tin

Ti- Titanium

TXRF- Total reflection X-ray fluorescence

U- Uranium

UNEP- United Nations Environmental Program

US EPA- United States Environmental Protection Agency

V- Vanadium

WHO- World Health Organization

XRF- X-ray fluorescence

Zn- Zinc

Abstract

This study determined the levels of concentrations of cadmium, arsenic, chromium, mercury, lead, copper and zinc in order to assess the extent of heavy metal pollution around Kilimapesa Gold mine processing plant in Narok County. A total of forty-one (41) samples, sampled 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 using EDXRF and TXRF techniques.

The sediments, soils and plants samples were dried, crushed, sieved and made into thin pellets. They were analysed 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 and pre-concentrated before analysis using the TXRF spectrometer at the Ministry of Petroleum and Mining Laboratories.

The results of 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 concentration was recorded at the confluence of the 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 concentrations in Sodom apple are comparable to those in other places apart from arsenic and lead, which may be attributed to mining activities in Lolgorian.

There was a significant difference in concentration of the heavy metals among the three media sampled following ANOVA analyses. Heavy metals concentrations were recorded as highest in the soils, followed by plants and water samples, had the least concentration levels.

Pearson's correlation for all trace elements of interest in Sodom apple (*Solanum incanum)* and soils was very weak except for mercury which had a strong relationship. The same trend is observed between soils and water and between water and plants, for all heavy metals of interest in this study, except for Zn and Ni, respectively.

The Kilimapesa soils are moderately to extremely contaminated with these metals, according to results from pollution indices and geo-accumulation indexes analyses, that are greater than 1. The study recommends use of heavy metals bio-accumulators like water hyacinth in the waste disposal treatment ponds and enforcement of regulations to reduce contamination of the environment. More studies on the area should be done to determine the contributors to pollution and use of bioassay data and records from the health facilities for epidemiological study over time.

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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 be 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 website, 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 has an aggregate tonnage of gold resource of 8,715,291 at 2.4g/t (http://www.goldplat.com/projects/kilimapesa-gold-kenya), hence is a viable 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 are metallic and metalloid elements with a density greater than 4g/cm^3 and are toxic even in low concentrations (Garbarino et al., 1995, Hawkes, 1997). They occur naturally in varying concentrations in all environments (Lentech, 2004). These heavy metals 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.

Environmental pollution introduces substances with harmful effects that impairs the welfare of the environment, has the effect of reducing the quality of life by causing diseases and even death.

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 from anthropogenic and natural sources by plants and eventually animals forms the basis for determination of pollution levels (Abdul-Wahab et al., 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. This research work involved determining the concentrations levels of select heavy metals in water, plants and soils around the Kilimapesa Gold Mines area in order 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 involves 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 that occurs naturally, 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, a 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 sulphuric acid) used in the separation of gold can spill, leach or leak to adjacent water bodies. These chemicals pause 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 also used 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)

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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 and Ogola et al., 2002). Upon leaching, the high concentrations have adverse effects to the environment. These heavy metals are non-biodegradable hence toxic and their build-up in the living tissues are known to cause diseases or even death (Mahurpawar, 2015).

1.2 Problem statement and Research Justification

Heavy metal pollution studies in mining areas have been conducted for a long time, in various environmental media, but more studies are ~~still~~ needed especially in less studied and new mining sites. Since heavy metals are indestructible in nature, when the concentrations in the environment exceed certain levels, if ingested, their accumulation within living tissues 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.

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 mine along an 80 Km stretch from the vicinity of North Mara Gold Mine in Tarime District, Tanzania, (Bitala et al., 2009). There is a high probability of contamination of environmental media in gold mining areas.

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, 2011), (Wikipedia retrieved June 27th, 2018).

The stream that serves Lolgorian town passes in close proximity to the activities of 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 and cases of out of court settlements between the gold mining company and the 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 reported dead following poisoned water (Daily Nation, January 28th, 2018).

This research work determined the magnitude 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 from the area. The study is relevant in adding to enrich the existing policies, in order to protect the public from the associated hazardous effects.

1.3 Description of the study area- Kilimapesa Gold mines

Kilimapesa (1^{o} 24’2’’S 34^{o}55’29E) 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 18^{o}C.

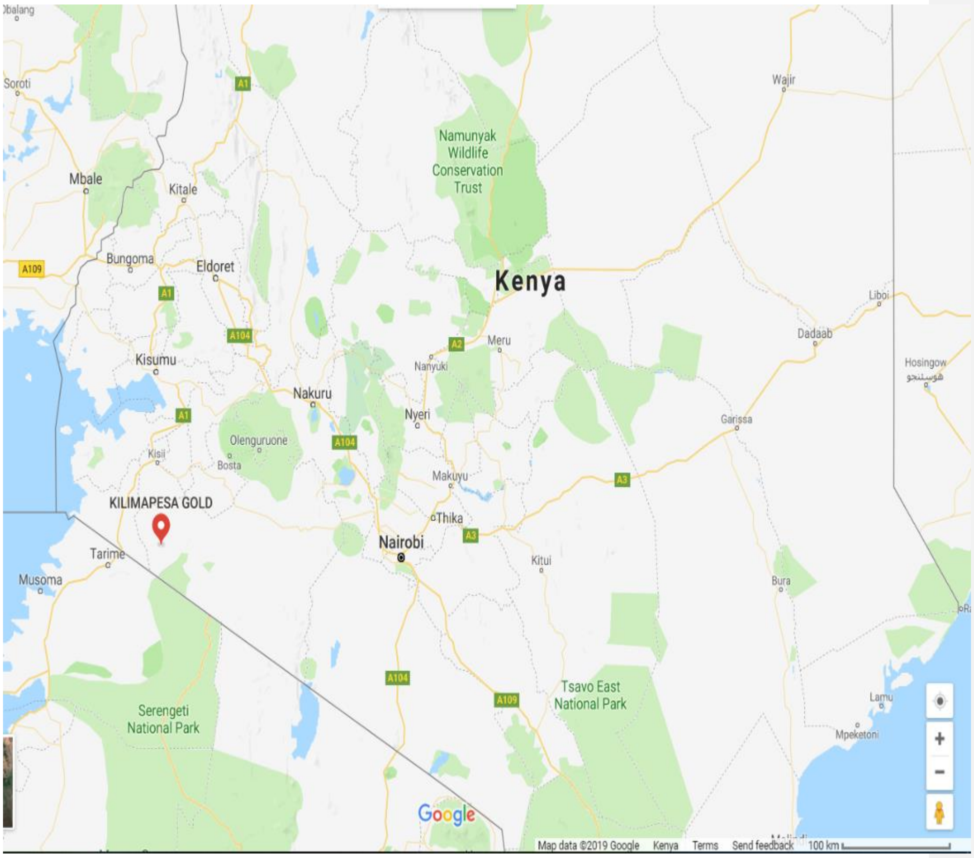

Figure 1.2: Map of Kenya showing Kilimapesa location in Lolgorian, Narok (Source: https://www.google.com/maps/search/kilimapesa+mine+location+in+kenya/@-1.238491,34.6712656,11z)

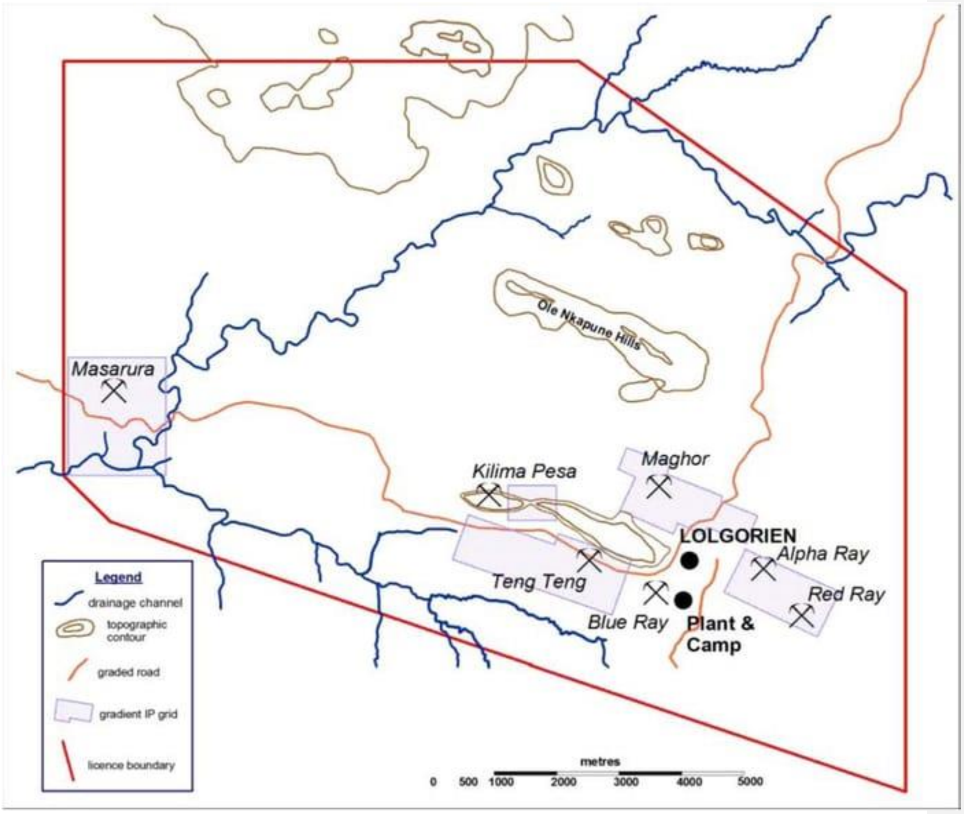

Figure 1.3: Mining blocks at Lolgorian (http://www.goldplat.com/galleries)

The economic activities that the locals engage in and around Kilimapesa Hill include livestock farming and agricultural farming of wheat, barley, maize, potato, quarry, sand harvesting and gold mining (artisanal and commercial) (County Integrated Development Plan 2013-2017). Most of these activities require quality water sources.

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 scraped into box holes 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 elute 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 at about 650 ºC to oxidize any remaining base metals. Purity of 99% is obtained;
vii. Gold smelting- the loaded cathode is melted at 1300 ºC 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.

1.4 Research Objectives

1.4.1 Main objective

To perform an analysis of the levels of heavy metals in water sources, vegetation and soils around the Kilimapesa Hill Gold Mines area in Lolgorian, Narok County.

1.4.2 Specific objectives

i. To determine the concentration levels of the heavy metals; lead, copper, arsenic, mercury, zinc, cadmium, chromium and nickel in soils/sediments, water and vegetation along the effluent channel to the river.

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

1.5 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) and selected sites in the town 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 in the area and is readily found in the region. Sediments were taken from nearby the banks of the stream at a depth of 0-5 cm, which represents eroded media from the upstream regions. Soils from the settlement areas were taken at a depth of 0-5cm.

Sampling was done around the processing plants to determine the degree of pollution of the select heavy metals in the environmental media. Sampling sites were selected along the river downstream, after the processing plants. Sites located upstream were sampled for comparison purposes. Other sites sampled 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 establish 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

This section reviews various studies done in line with heavy metal contamination from 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). The heavy metal pollution is induced either from natural and anthropogenic sources. Natural causes include processes like vulcanicity, weathering and acid rain that result in the dissolution of heavy metals (Roozbahani et al., 2015). Anthropogenic sources are a significant cause of pollution and include; industrial processes, mining, combustion of fossil fuels, agricultural activities and urbanization (Roozbahani et al., 2015), (Duruibe et al., 2007).

Mining operations are the major causes of heavy metals pollution in the environment for many years after mining activities cease. Effects of contamination have been observed to reduce as distance from mining sites and processing plants increases (Peplow, 1999).

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., 2001).

Soil pollution from mining ores contain sulphides,that 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 come in contact with 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., 2001). 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., 2001).

Mining activities and geochemical processes usually result in acid mine drainage (AMD). This results, when pyrite (FeS_2) and other minerals containing sulphide are 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 over time due to their non-biodegradable nature. 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 biomolecules in the body like enzymes and proteins to form stable chemical bonds that are strong.

A metal ion can be 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., 2009). 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 (Sinh, 2005), (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 of time. 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 (US Agency for Toxic Substances and Diseases Registry).

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. It is an essential micro-nutrient that 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 (WHO, 2011).

2.2.5 Mercury

Mercury is not an 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 (WHO, 2011).

2.2.7 Lead

Lead is the second most cause of poisoning from heavy metals poisoning (US Agency for Toxic Substances and Disease Registry). Its accumulation affects multiple systems in the body. 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; WHO, 2011).

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, plants for animal and human use, and soils according to Table 2.1 and table T2.2.

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

Metal	Normal conc. for fresh water (mg/L)	Max conc. in drinking water (WHO) (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 according to WHO (1996) and Dutch standard (1990)

Element/Metal	Max conc. in unpolluted soils (mg/Kg) (Dutch Standard)	Max conc. in plants (mg/Kg) (WHO)
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

Plants have been used in analysis to determine the extent of heavy metal pollution in mining areas around the world.

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. Skin problems like ringworms, 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 (Heine, 1963), (Matu, 2008).

The shrub has been used by indigenous communities 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 and stems and stopping of bleeding. The pain relieving effect was tested in animal models by Mwonjoria et al. (2011) 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.

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Sodom apple was analysed for contamination in this study 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 (Stanconvic 2013).

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-accummulation when compared to the rest, and could be used for phytoextraction.

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.

Hassan 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.

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2.4 Environmental pollution studies from gold mining processes globally and in Kenya

In this section, we review several studies on 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 have substantially increased in the background levels compared with concentrations in the pre-mining era. The plants under study, *Cladocera* and other planktonic diatoms, ceased to exist from the records of the sediment. There has been little success in the biological recovery of these plants, even after ceasing ore roasting activities in 1999 (Thienpoint et al., 2016).

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Las Medulas Gold mine in North-western Spain was reported to have caused contamination that spread to Europe, northern Africa and the Middle East, especially lead metal pollution. A record spanning over four thousand years of Lake Roya sediments was analysed for geochemical variations. An increase in variability of concentration levels of lead, bismuth, antimony and arsenic were recorded over the periods of mining. Peaks in concentrations of the heavy metals coincided with periods of mining in the region (Hillman et al., 2017).

In a study done by Teixeira et al. (2017) 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 acceptable levels by WHO. Cadmium, chromium and lead in water exceeded allowable levels by WHO. Cadmium and lead were in higher concentrations in nails than that which is acceptable in occupationally exposed residents. Lead, copper, cadmium and chromium were in high levels in the hair samples obtained from polluted areas than in control samples from unpolluted region. The study indicated that the children in these 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. (2014) 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 recorded were high. They advocated for alternative methods to be used in gold extraction in order to conserve the environment and minimise public exposure.

Mutono (2016) analysed the health and environmental problems caused by artisanal mining in Macalder, Migori. Water from households and soils were analysed for mercury, arsenic and lead. The metal levels were within the acceptable limits in water from the households but exceeded the WHO levels in the River Kuja waters. The soils from the river were contaminated by lead and mercury, but not arsenic.

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 (1999 & 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 in line with water quality regulations governing the issuance of licences for industries (2006), with a focus on industrial waste management. 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

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 is dislodged from its atomic orbital upon absorbing light (photon) with energy that exceeds its binding energy to the nucleus, following irradiation with radioactive source. An electron from a 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 (Goldstein, 2012). 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), (Antoaneta et al, 2015).

For a fluorescent emission line in 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 quantitatively and qualitatively 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. Fundamental parameters (FP) module was used to obtain the concentrations of elements in a sample, without 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 or 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):

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$$\mathrm{LD} = \left[3\ \mathrm{X}\ \frac{C_i}{I_p - I_b}\right] X \sqrt{\frac{I_b}{T_b}}$$

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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 technique is used where the sample is irradiated by a monochromatic radiation beam at a small angle of 0.3-0.6º and is totally reflected internally. The interactions of the beam of x-ray and atoms of the sample result in a characteristic x-ray emission whose intensity is measured from the spectral data. 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, 1997).

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).

$$C_x = \frac{\frac{I_x}{S_x}}{\left(\frac{\sum I_{int}}{S_{int}}\right)} \text{ X } \frac{M_{int}}{M_{sample}}$$

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 on mining sites

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 Suh 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 (Atul 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 ;B, 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 50 mg/Kg. This was a clear indicator of pollution that resulted 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 reported to have been contaminated with Mn, Fe, Ni and Pb during 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, ICPMS and Graphite furnace AAS analyses of seven biological and environmental reference materials. . Twenty-eight elements were determined. Coal had impacted 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 a comparison was made. 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 (Ana Pantelica et al., 2016).

Chapter 3: Materials and Methods

3.1 Introduction

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

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All the sample media were sampled from eight (8) sample points locations, water from ten (10) 1sites, Sodom apple (*Solanum incanum)* from fourteen (14), 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 of the river 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 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 (Table 3.1 and Figure 3.1).

Table 3.1: Summary of samples from different sites for the environmental media

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
2	01°13’34.0’’	34°45’58.7’’	1565	80 m from point 1	S02
3	01°13’32.2’’	34°45’55.4’’	1559	Start of stream flow from underground	S03, P03, W03
4	01°13’32.4’’	34°45’53.1’’	1563	Tailings deposit	S04, P04
5	01°13’30.4’’	34°45’47.9’’	1538	The portion along the stream near the tailings deposit area	S05, P05, W05
6	01°13’31.7’’	34°45’46.3’’	1552	The portion along the stream near the tailings deposit area	S06, P06
7	01°13’38.6’’	34°45’06.9’’	1500	Downstream along the stream	P07, W07

8	01°13’37.5’’	34°45’04.1’’	1494	Downstream at the confluence with another stream (locally called Paka nyeusi)	S08, P08, W08
9	01°13’40.0’’	34°45’02.3’’	1494	Downstream after Paka nyeusi confluence	S09, P09, W09
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
11	01°14’26.8’’	34°48’36.5’’	1612	Fence marking the boundary of wet tailings deposit area at plant 2	S11, P11
12	01°14’23.2’’	34°48’26.9’’	1598	Roadside outside plant 2 at a bridge	S12, P12, W12
13	01°14’56.0’’	34°47’52.1’’	1554	Stream portion downstream of plant 2	S13, P13, W13
14	01°14’55.6’’	34°47’51.1’’	1560	Stream portion downstream of plant 2	S14, P14, W14
15	01°13’38.8’’	34°48’24.7’’	1647	Local artisinal mine	W15
18	01°13’38.7’’	34°45’50.1’’	1560	Dry tailings deposit area	S18
31	01°13’30.1’’	34°48’22.1’’	1633	Settlement area- road to an artisanal mine	S31
32	01°13’45.3’’	34°48’16.3’’	1661	Settlement area	S32, P32
33	01°13’42.2’’	34°48’11.5’’	1675	Settlement area- road to an artisanal mine	S33, P33

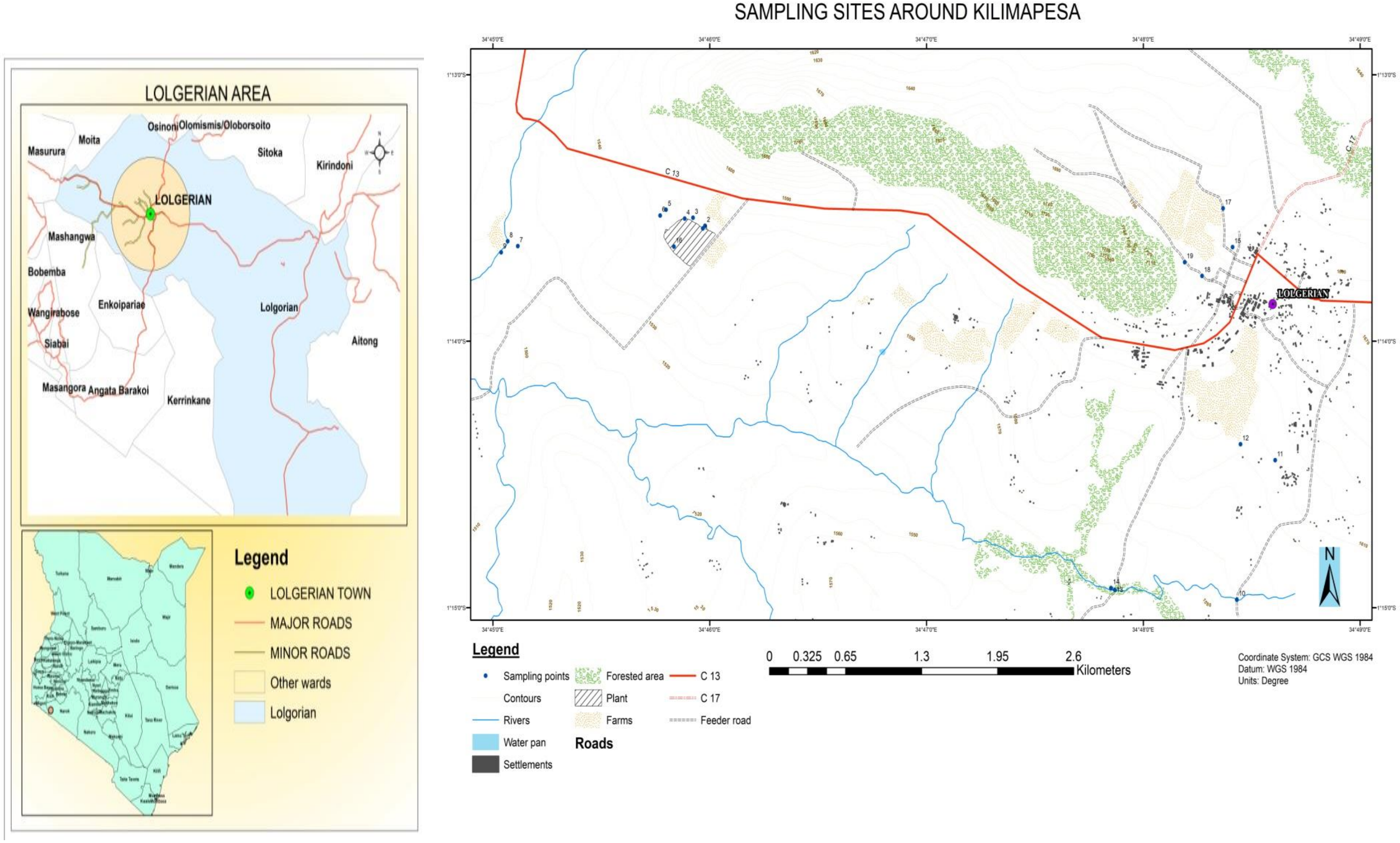

Figure 3.1: Sampling sites in Lolgorian

3.2.1 Sampling

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 piped water 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 bag (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 samples of Sodom apple (*Solanum incanum)* (figure 3.2) each weighing about 0.5 kg 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.

Sediments and soils each weighing about 0.5 kg 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 collected at the sampling points and labelled: P01-P33, W01-W33 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 brief description of each sampling point is presented in Table 3.1.

Figure 3.2: Sodom apple (Solanum incanum) plant (sampling site)

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 75 µm particle-size sieve. Three pellets, each weighing between 0.35-0.43 g, 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 10^3 tons 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 was 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).

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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. 10 µl of gallium (internal standard) were added to the water sample 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 (see 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 a sample analysis software which uses fundamental parameter method for analysis.

The NEX CG analyzer has a unique 3D close-coupled Cartesian Geometry (CG) optical kernel that greatly increases the signal-to-noise ratio. By use of a monochromatic beam for secondary excitation of the target instead of the conventional direct excitation, greatly improving the sensitivity. The result is 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 XRF equations. The selection of the scattering FP template allows estimation and better simulation 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: the X-ray tube is made of a palladium target and is air-cooled, 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 spectra. Automated sampling is done by the 15-position sampler. The polarized monochromatic excitation of the spectrometer gives a superior peak to background for low detection limits. These are the reasons for preference for use in this study (Ene et al., 2009).

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Each sample was irradiated for 50s under 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).

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3.4.2 TXRF spectrometer

The S1 Titan model of the TXRF spectrometer available at the Ministry of Petroleum and Mining laboratories (Figure 3.5) 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 ~~e~~ 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., 2015):

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$$\text{Ci} = \frac{C_{IS} \text{ X } N_i \text{ X } S_{IS}}{N_{IS} \text{ X } S_i}$$

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 3.3: The hydraulic press complete with the die assembly

Figure 3.4:Rigaku NEX CG EDXRF spectrometer (Physics Department)

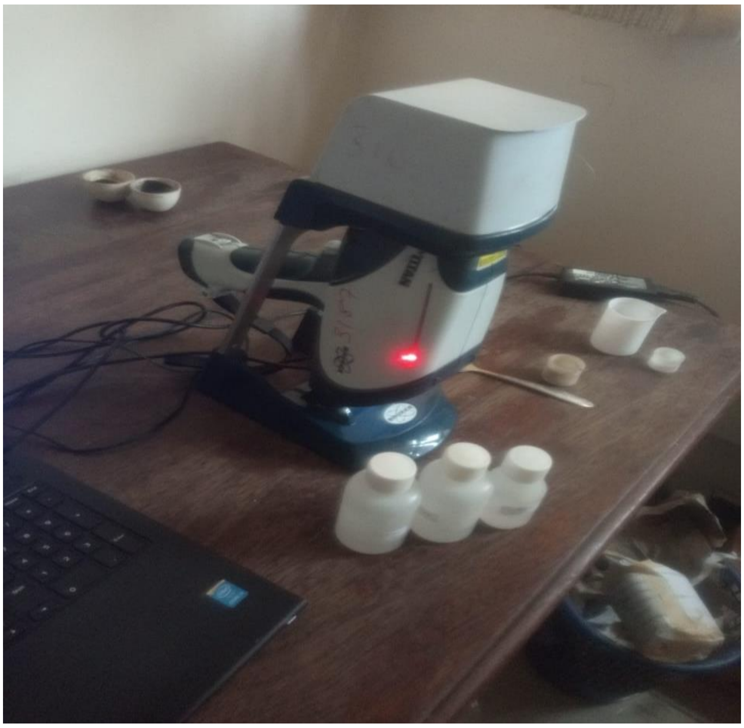

Figure 3.5: S1 Titan TXRF spectrometer (Ministry of Petroleum and Mining)

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3.5 Sample analysis

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 was the standard 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):

$$\text{D. L}= \frac{\text{Concentration}}{\text{peak area}}\, 3\sqrt{Background}$$

3.5.2 Soil and plant analysis using EDXRF

Scatter ray FP method is used with a pellet template form. The metals of interest were selected in the component selection window and a matching library was created by irradiation of a standard reference (River Clay and Bowen Kale). An MCA calibration was done prior to spectral data analysis. The weight and thickness of the sample were determined for input. The sample diameters were 25mm. The samples were irradiated in a vacuum atmosphere to minimize scattering by molecules found in air.

3.6 Data analysis

3.6.1 Analysis of Variance

ANOVA was the statistical tool used to determine the extent to which heavy metal concentrations varied 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, heavy and 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 at the 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 2.3.

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: Pearson correlation coefficients classification

Pearson Correlation Coefficient	Strength
0.00-0.19	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 contamination extent in sediments/soils were 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 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-accummulation 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 Geo-accumulation index

Muller (1969) and Parker (2008) gave a quantitative measure of contamination of a metal in the soils by the following:

$$I_{geo} = log_2 \frac{C_n}{1.5 \text{ X } B_n}$$

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.

3.6.3.2 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.

$$\text{PLI} = \sqrt[n]{CF_1 \text{ X } CF_2 \text{ X } CF_3 \text{X } \ldots\ldots\ldots \text{X } CF_n}$$

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:

$$\text{CF} = \frac{C_n}{C_{ref}}$$

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

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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

The results of the concentration levels of the metals of interest in water, vegetation and sediments/soils with their interrelationships is presented in subsequent sections.

4.2 Validation of the analytical method

To verify the accuracy of the analytical procedure used, certified reference materials: Bowen Kale, River Clay (PTXRF-IAEA09) and KB 10 ppm were analysed for the eight metals of interest in this study. For EDXRF, samples were irradiated using five targets; aluminium, molybdenum, copper, RX9 and silicon, to ensure the whole elemental range (sodium to uranium) was captured. The spectra from excitation using the secondary targets for the sample from site 32 are given in Figures 4.1 to 4.5.

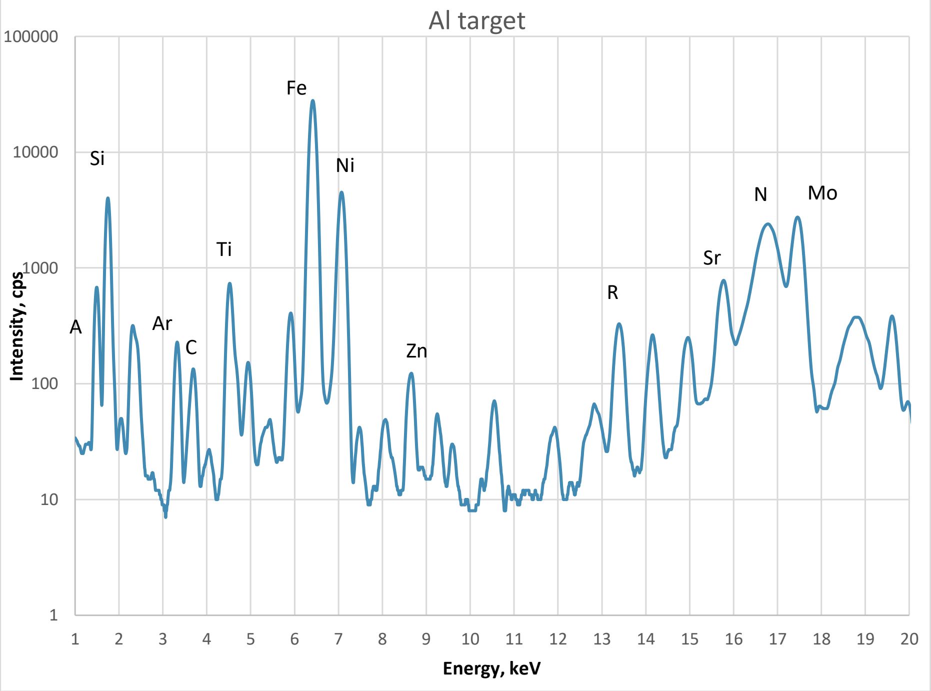

Figure 4.1: Soil sample 32 spectrum using aluminium target

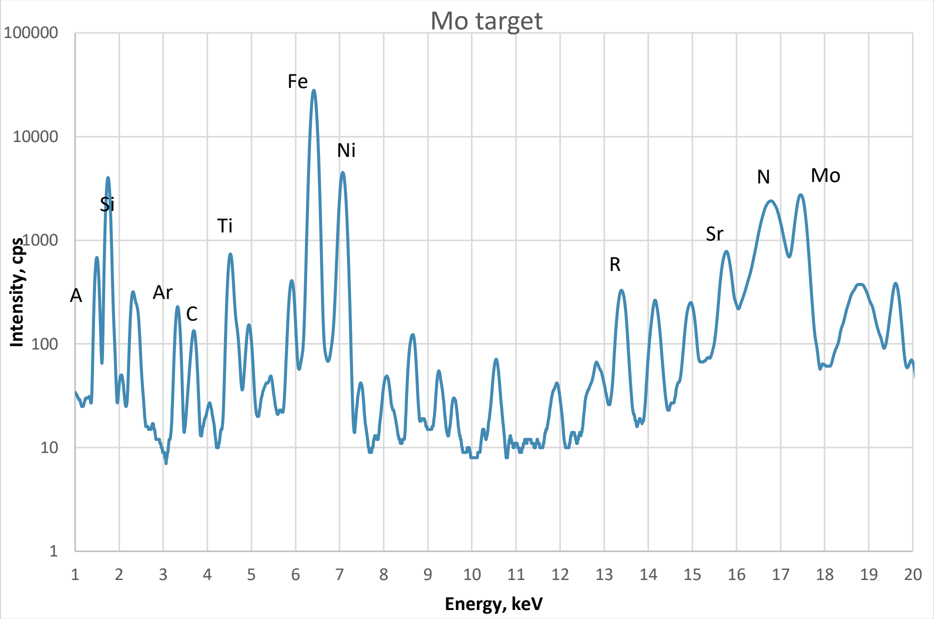

Figure 4.2: Soils sample 32 spectrum using molybdenum target

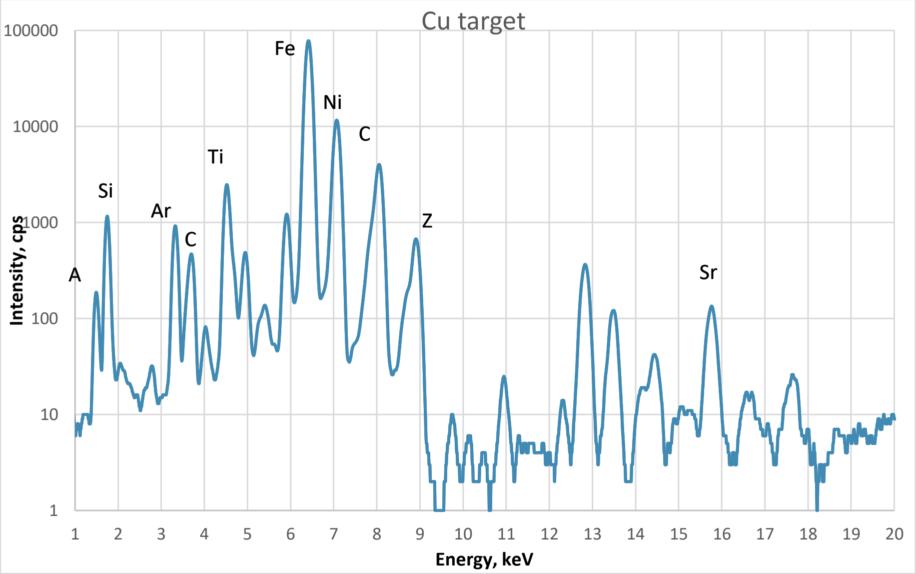

Figure 4.3: Soils sample 32 spectrum using copper target

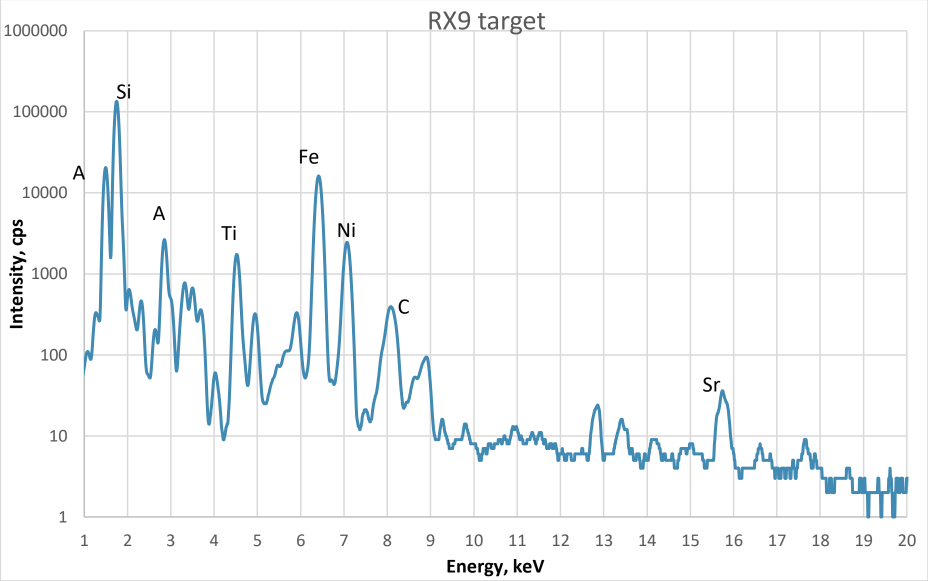

Figure 4.4: Soils sample 32 spectrum using RX9 target

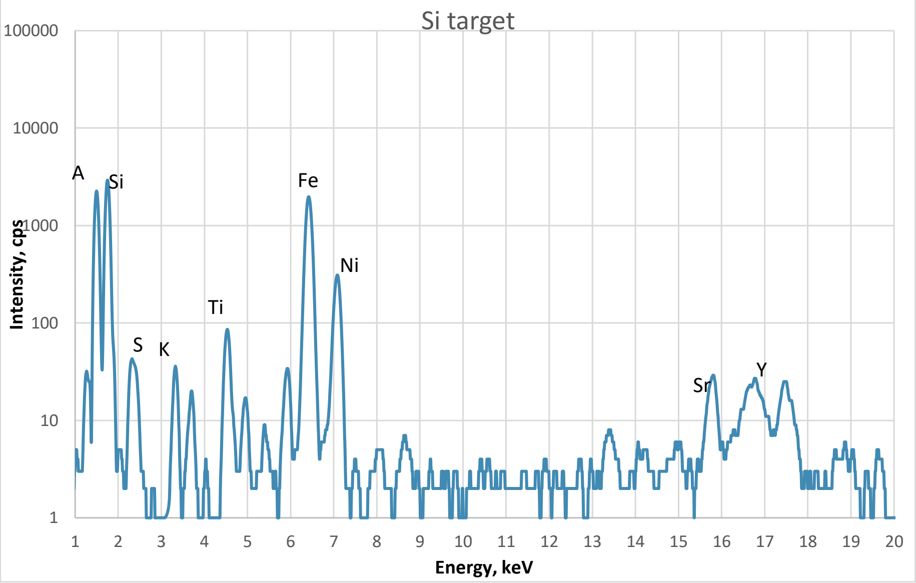

Figure 4.5: Soils sample 32 spectrum using silicon target

The peaks are combined to obtain the final result with a maximum peak to background ratio.

The obtained values were checked against the certified values as recorded in Tables 4.1 and 4.2.

Table 4.1: Results of Bowen Kale analysed by EDXRF; n=3, x̄ ± SD, mg/kg

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Element	Detection limit	Experimental value	Certified value	Std dev (%)
Hg	1.9	< 1.9	0.171 ± 0.0282	-
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	32.29 ± 2.75	+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, x̄ ± SD, mg/kg

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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	0.503 ± 0.06	-
Cr	3.1	92.3 ± 3.3	89.6 ± 6.98	+3
Zn	1.2	95.4 ± 8.3	96.1 ± 3.86	-1
Ni	2.1	39 ± 5	37.9 ± 3.06	+3
Pb	2.0	38.4 ± 2.0	36.9 ± 3.13	+4
Cu	1.6	21.0 ± 4.0	20.1 ± 1.68	+4

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 4.3 shows the results of analysis of the standard reference material (mg/L), KB 10ppm, from Bernd Kraft GmbH that analysed for the eight elements of interest. These values were comparable to the certified values for most elements.

Table 4.3: Results of KB 10ppm (mg/L) analysed using TXRF; n=3, x̄ ± 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

4.3 Concentrations of the metals in the sampled media

4.3.1 Water samples

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, x̄ ± 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

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Commented [WL27R26]: Explained in paragraph 2 of the next page

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

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Commented [WL29R28]: Limit and units included

Sampling point 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), (Ghobadan & Bajestan, 2007).

Point 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 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 Sodom apple (*Solanum incanum)* samples

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

In general, the metals in the plants mostly occurred in the order Zn>Cu>Ni>Cr>Pb>Hg>As.

Table 4.5: EDXRF results for Sodom apple samples (mg/kg), n=3, x̄ ± 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

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. The 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.

Commented [MMJM30]: Insert the appropriate units

Commented [WL31R30]: Done

Mercury levels (mg/kg) ranged from not detected to 3.2, with a mean of 0.4 ± 1.9.In all the samples analysed, the values were below the detection limit of 1.9mg/kg apart from points 7 and 9. These were located in the downstream region after the confluence of two streams. The contamination may have resulted from accumulation from the upstream areas in the artisanal mines.

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Commented [WL33R32]: Done

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 that had lead, levels exceeded 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).

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Commented [WL37R36]: Replaced

Arsenic levels (mg/kg) ranged between 1.12 and 2.02, with a mean of 0.65 ± 1.12. Sampling site 11 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.

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Commented [WL39R38]: Replaced

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 10 ppm 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.

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Commented [WL41R40]: Done

Copper levels (mg/kg) ranged from 17.85 to 33.25, with a mean of 24.82 ± 1.63. These copper levels exceeded the allowable limit of 1.63mg/L. Sites points namely; 05, 10, 12 and 33 recorded values above 30ppm. This could point to a generally high zinc concentration in *Solanum incanum* (Auta et al., 2011).

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Commented [WL43R42]: Done

Zinc was found to range (mg/kg) from 24.55 to 40.95, with a mean of 31.44 ± 1.19 and exceed the WHO allowable limits in all the areas. This could point to a generally high zinc concentration in *Solanum incanum* (Auta et al., 2011).

4.3.3 Sediment/soil samples

The summary of heavy metal concentrations in soils/sediments is presented in Table 4.6.

Cadmium concentration was below 3.06 mg/kg hence could not be measured in any of the soil samples by EDXRF.

Commented [MMJM44]: I don’t understand. Clarify

Commented [WL45R44]: Corrected- below the detection limit

Table 4.6: Results for EDXRF analysis for soil samples (mg/kg), n= 3, $\bar{x}$ ± 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
S18	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

Chromium levels (mg/kg) ranged from 111 to 406, with a mean of 200 ± 20 and exceeded the allowable limits. 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.

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Commented [WL49R48]: Done

Lead (mg/kg) was present in the ranges of 26.5 to 148, with a mean of 47.5 ± 6.5. Only point 11 had an excess levels 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 14.6 to 936, with a mean of 107 ± 5. All the samples had a concentration levels greater than 10 ppm that is acceptable. Point 11 had the highest concentration levels and the contamination could be due to the tailings at the processing plant 2.

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Commented [WL51R50]: Done

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).

Commented [MMJM52]: Units ?????
Commented [WL53R52]: Done

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 allowable limit. Point 11 had the highest concentration level which could be attributed to contamination from the tailings at plant 2. Point 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.

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Commented [WL55R54]: Done
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Zinc (mg/kg) was present in the ranges of 61.5 ± 4.7 to 156 ± 5, with a mean of 111 ± 2. All the samples had a concentrations greater than the allowable limit. Point 11 had the highest concentration level which could be attributed to contamination by the tailings at plant 2. The soils in the region generally have a high zinc content.

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Commented [WL57R56]: Done

4.4 Comparison between the sampled media

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.

Table 4.7: Summary of ANOVA analysis in the three media

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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

Commented [LK59R58]: Corrected

MS- mean squares f- experimental result

There is a no significant relationship in the mean concentration of elements in the sampled environmental. 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 $_{\text{critical}}$. For As, there is a significant relationship in the concentrations of the metals.

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

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

Sodom apple (*Solanum incanum)* and sediments showed a very weak relationship with 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 was 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, a weak for Cr, Cu and Zn and moderate for Ni.

4.5 The extent of pollution in the soils

4.5.1 Geo-accumulation index

The summary of the geo-accumulation index of the sampled points is as per table 4.9.

Table 4.9: A summary of the geo-accumulation index

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
S18	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

The variations of geo-accumulation indices for chromium, lead, arsenic, nickel, copper and lead 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 4.6 shows the I_{geo} of chromium. The range of chromium was between -0.17 at point 11 and 1.71 at point 12, having an average value of 0.59. Sites 11 and 32 were uncontaminated. Points 8, 9 and12 were moderately contaminated while the rest of the sites were uncontaminated to moderately contaminated.

Commented [MMJM60]: What kind of sites are these, are you referring to?

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Figure 4.7 show the I_{geo} of lead. The range of lead was between -0.58 and 2.54, having an average value of 0.65. Site 10 was uncontaminated, while site 11 was moderately to strongly contaminated. The rest of the sites were moderately contaminated.

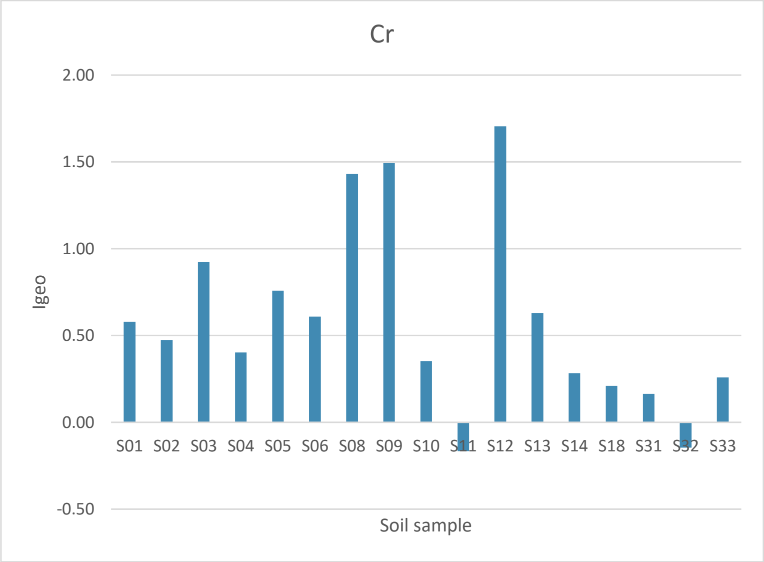

Figure 4.6: Variations of chromium in sediments/soils

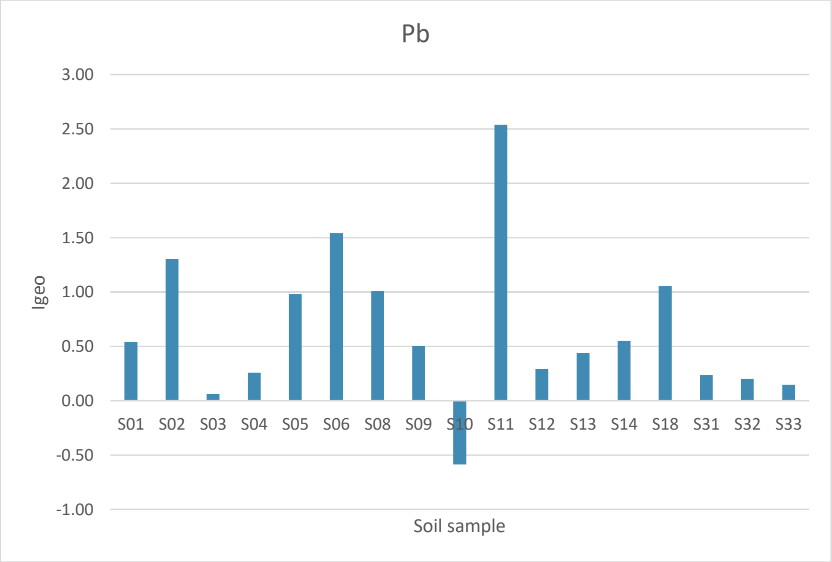

Figure 4.7: Variations of lead in sediments/soils

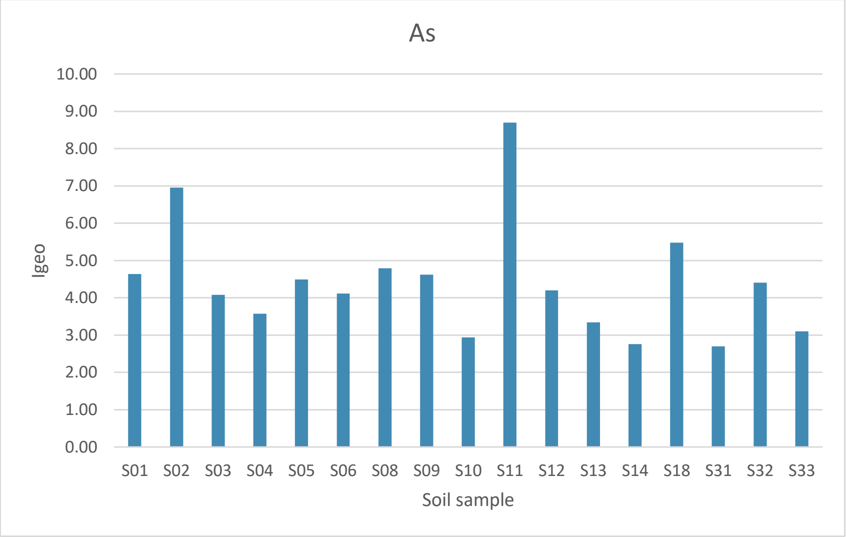

Figure 4.8: Variations of arsenic in sediments/soils

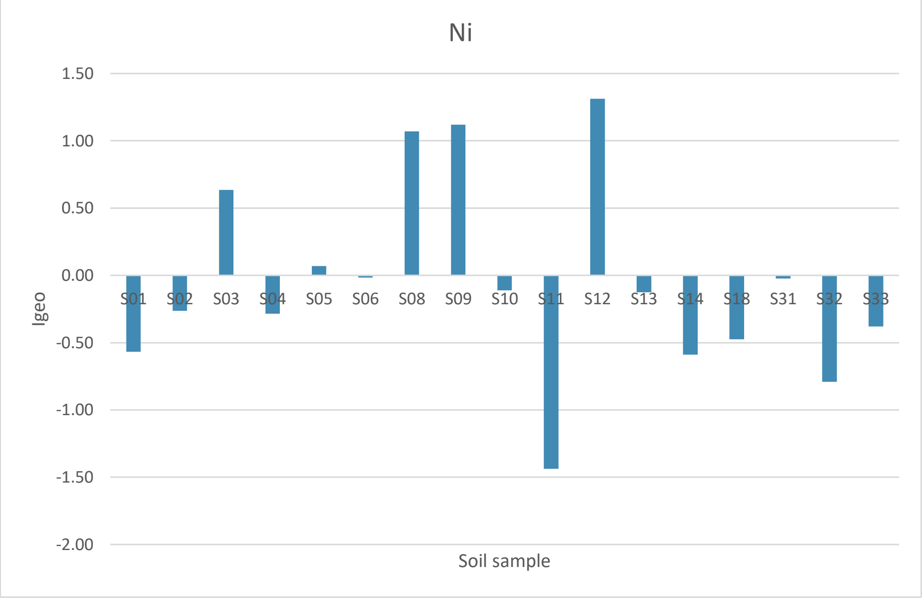

Figure 4.9: Variations of nickel in sediments/soils

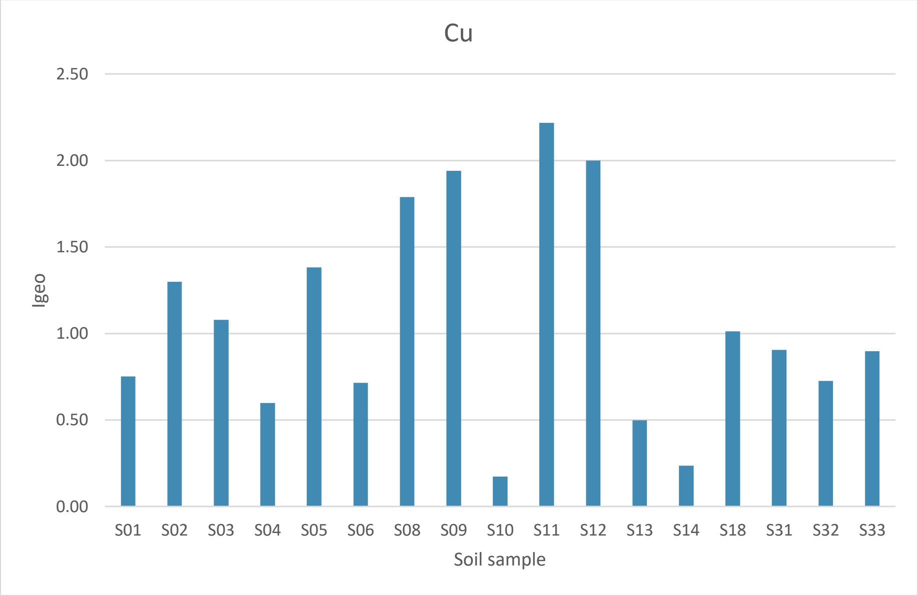

Figure 4.10: Variations of copper in sediments/soils

Figure 4.8 show the I_{geo} of arsenic. The range of arsenic was 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 18 were extremely contaminated.

The range of nickel was 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 4.9).

Figure 4.10 shows the I_{geo} of copper. The range of copper was 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 18 were moderately contaminated, while site 11 was moderately contaminated.

The range of zinc was 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 as per Figure 4.11.

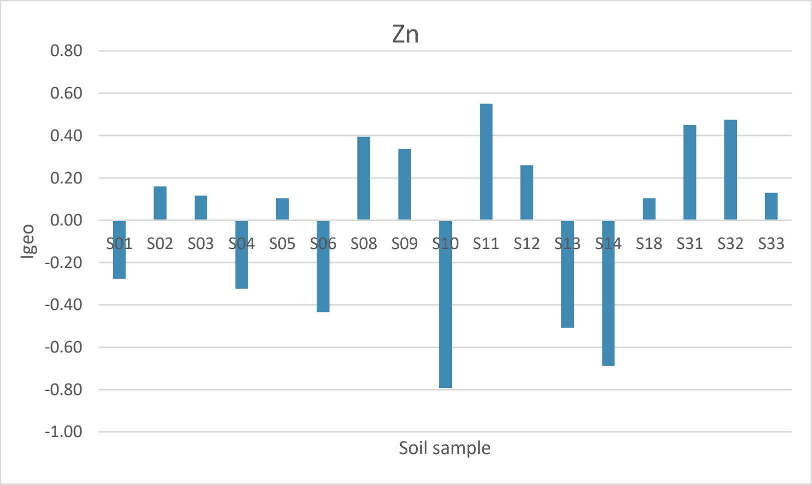

Figure 4.11: Variations of zinc in sediments/soils

4.7.2 Pollution Load Index

A summary of the CFs if as per Table 4.10.

All the CFs were greater than 1. This implies that the concentration of each of the heavy metals exceeded the reference concentrations in the sampled sites.

A summary of PLI values at each of the sampling sites is given in Table 4.11. The PLI values from all sites were all greater than one. This is an indication that the soils in Lolgorian gold processing area are deteriorating in quality.

From the three pollution indices: pollution load index, contamination factor and geo-accumulation index, the soils in Lolgorian gold processing area are contaminated.

Table 4.10: A summary of the contamination factors

Sample	Cr	Pb	As	Ni	Cu	Zn
S01	2.24	2.18	37.33	1.01	2.52	1.24
S02	2.08	3.71	185.67	1.25	3.69	1.68
S03	2.84	1.56	25.40	2.33	3.17	1.63
S04	1.98	1.79	17.90	1.23	2.27	1.20
S05	2.54	2.96	33.83	1.57	3.91	1.61
S06	2.29	4.36	25.92	1.48	2.46	1.11
S08	4.04	3.02	41.43	3.15	5.18	1.97
S09	4.22	2.12	36.93	3.26	5.76	1.89
S10	1.92	1.00	11.50	1.39	1.69	0.87
S11	1.34	8.71	623.67	0.55	6.98	2.20
S12	4.89	1.84	27.53	3.73	6.00	1.80
S13	2.32	2.03	15.23	1.38	2.12	1.05
S14	1.83	2.20	10.13	1.00	1.77	0.93
S18	1.73	3.11	66.70	1.08	3.02	1.61
S31	1.68	1.76	9.73	1.48	2.81	2.05
S32	1.36	1.72	31.83	0.87	2.48	2.08
S33	1.80	1.66	12.87	1.15	2.79	1.64

Table 4.11: A summary of PLI at each of the sampling sites

Sample point	PLI
1	2.89
2	4.72
3	3.33
4	2.44
5	3.69
6	3.19
8	5.03
9	4.77
10	1.89
11	6.28
12	4.64
13	2.46
14	2.01
18	3.52
31	2.50
32	2.63
33	2.42

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

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This study evaluated the potential hazard to the population as a result of the presence and accumulation of heavy metals in plants, soils and water around Kilimapesa gold processing plant in Lolgorian. Concentrations of select metals: arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc were determined.

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 detected 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).

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. There was a significant relationship in the concentrations of the heavy metals among the three media sampled following ANOVA.

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 with all the metals except mercury which had a strong relationship. There was a weak correlation between soil and water in As, Cd, Cr, Hg and Pb, a weak relation in Cu and Ni, while a moderate relation was observed in Zn. The relation in water and plants was very weak in As, Cd, Hg and Pb, a weak relationship in Cr, Cu and Zn while a moderate relationship existed in Ni.

The geo-accummulation index showed that the soils were mostly moderately contaminated except lead that was in extreme concentrations at three of the sampled points. PLI indicated that soils in the area were deteriorating in quality.

5.2 Recommendations

- A comparative study of environmental and biological media should be done on the gold mining and processing plants regions in Kenya should be done to map the extent of contamination in them.
- 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.
- NEMA should ensure the necessary steps are taken for enforcement of regulations that are currently in place in regard to mining and environmental conservation. This may include periodic evaluation of soils and water from mining and processing areas
- 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)
- 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

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