CANCER RISKS ASSOCIATED WITH ARSENIC, CADMIUM, CHROMIUM AND LEAD EXPOSURE IN FLUORSPAR MINING BELT ELGEYO-MARAKWET COUNTY, KENYA

BY

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DECLARATION

Declaration by the Candidate

This thesis is my original work and has not been presented for a degree in any other University. No part of this thesis may be reproduced without the prior written permission of the author and/or University of Eldoret.

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DEDICATION

I dedicate this work to my late Dad Mr. Jonathan Kiboss and Mum, MrsLinahSokome Kipkemoi, for their diligent efforts in molding, instructing and bringing me up in an upright way which has enabled me excel to this high level of academics.

ABSTRACT

The elevated levels of heavy metals due to the mining activities in Fluorspar mining belt are a cause of environmental and health concern. The study was aimed at determining the concentrations of Arsenic (As), Cadmium (Cd), Chromium (Cr) and Lead (Pb) in soils, water and food (milk, maize, millet and beans) in the study area. The study area covered Fluorspar mining belt in Kimwarer sub-catchment zoned into upper, middle and lower Kimwarer.Samples were prepared and digested then analyzed for Cd, Cr and Pb using Atomic Absorption Spectrophotometer (AAS). Arsenic was analyzed using AAS coupled with hydride vapour generator. The exposure of the selected metals was determined by daily Estimated Daily Intake (EDI) of heavy metals in water, food and also by determining the concentrations of the metals in human hair. Cancer risks were determined from Incremental Lifetime Cancer Risk (ILCR) while target hazard quotient (THQ) estimated non-carcinogenic risks using USEPA probabilistic models. Cancer prevalence was obtained from a cross sectional survey. The results showed metal mean concentration of water were all above the WHO recommended levels of (<0.05mg/l) in dry and wet season. All the soil samples were above the levels of what is considered as unpolluted soils.Themetal mean concentrations in food were above the CODEX Alimentarium Commission recommended levels of As (0.14ppm), Cd (0.1mg/l), Cr (1ppm) and Pb (6ppm). The EDI results of selected metals within acute, intermediate and chronic Minimal Risk Levels (MRL) as recommended by Agency for Toxic Substances and Disease Registry were 20%, 9.17% and 5.83% respectively. The female had a higher percentage (98.7%) of EDI above recommended MRLs compared to their male counterparts who had 95% of EDI results. The concentration of As and Pb in hair had a positive significant ($P>0.01$) correlation to cancer while Cr had a negative significant difference with cancer prevalence in the study area. The values of THQ for the individual heavy metals and the hazard indices (HI) due to the combined non-cancer effects of all the metals considered in the study were $HI>1$. The sum totals of ILCR were all above WHO acceptable levels of 1×10^{-6} to 1×10^{-4} for all the metals. The prevalence of cancer cases in the study area was 39 cases in a sample population of about 355 people.In conclusion, the study established that there was a significant spatial and temporal variation in the selected metal concentration in the study area between the wet and dry seasons. The THQ and ILCR showed potential health riskfor humans due to the intake of water, milk, maize, beans and millet especially in the villages closest to the mine (MK and LK)due to As Cd Cr and Pb. The study recommended a concerted effort from the stakeholders to create awareness of the dangers of the heavy metals and find ways of mitigating the effects and enforcing the safe environmental practices, regulations and laws.

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LIST OF ACRONYMS AND ABBREVIATIONS

ATSDR:	Agency for Toxic Substance and Disease Registry
AAS:	Atomic Absorption Spectrophotometer
ANOVA:	One-way analysis of variance
BAT:	Best Available Techniques
BLL:	Blood Lead Levels
CV:	Cardiovascular
CNS:	Central Nervous System
EU:	European Commission
FAO:	Food Organization of the United Nations
FDA:	Food and Drug Administration
GIT:	Gastro Intestinal Tract
HBM:	Human Bio-monitoring
IARC:	International Agency for Research on Cancer
IREC:	Institute of Research and Ethical Committee
JECFA:	Joint Expert Committee of Food Additives and Contaminants
KNA:	Kenya News Agency
KCRG:	Kimwarer-Sugutek Community Rights Group
KCM:	Kenya Chamber of Mines
KFC:	Kenya Fluorspar Company Ltd
LPO:	Lipid Per Oxidation
MRL:	Minimal Risk Level
OSHA:	The Occupational Health and Safety Management
PNS:	Peripheral Nervous System
PTDI:	Provisional Tolerable Daily Intake
PTWI:	Provisional Tolerable Weekly Intake
PTMI:	Provisional Tolerable Monthly Intake
RTI:	Respiratory Tract Infection
SNK:	Students Newman Kaules
TCR-mf:	T-Cell Receptor Mutation Frequency

TCR:	T-Cell Receptor
UTI:	Urinary Tract Infection
WHO:	World Health Organization
UK:	Upper Kimwarer
MK:	Middle Kimwarer
LK:	Lower Kimwarer

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CHAPTER ONE

INTRODUCTION

1.1 Background Information

Heavy metals are naturally occurring and widely distributed in air, soil, water and food (Khan 2012; Hussain*et al.*, 2012). All countries across the globe are now conscious of the dangerous effects the heavy metal pose to animals, plants and humans, due to their distribution patterns, non-biodegradability and persistence in the environment (Singh *et al.*, 2011).Heavy metals can be useful and others are harmful to the human body beyond certain levels. The useful heavy metals include Iron (Fe), Copper (Cu), Manganese (Mn), and Zinc (Zn) which are useful at trace levels. They are cofactors of many enzymes that facilitate metabolic processes(Jamp, 2003).

Essential heavy metals become toxic in human body after accumulation to a certain high concentration levels. However, Arsenic (As), Lead (Pb) and Cadmium (Cd) are harmful at low concentration levels (Adriano, 2001). The main sources of heavy metals in the environment include mining activities which are well known for their deleterious effects on the environment, due to the deposition of large volumes of wastes on the soil (Goyal *et al.*, 2008). The contamination of agricultural soils is often a direct or indirect consequence of anthropogenic activities. Industrial effluents and emissions is a common source that directly deposits the pollutants into water in case of effluent and in air for atmospheric emissions. The effluents flow into water sources and sometimes on the earth surface that finally gets washed into water bodies affecting not only human but also the entire ecosystem (Otitoju& Otitoju, 2013). Industrial emissions and vehicle exhaust have been found to be of great concern because of the quantity pollutants emitted and the speed of dispersion to wide geographical zones from the sources and the invisible potential of exposure (Ammune- Matthews& Kakulu, 2012).

Heavy metals are used for various purposes industrially. Arsenic is used in a wide variety of industrial applications, namely as wood preservatives, making weapons, pigments and as an ingredient in medicine (Jones, 2007).Cadmium is highly used in phosphate fertilizers and making rechargeable nickel-Cadmium batteries (Harmanescu*et al.*, 2011; Jamp, 2003). Chromium is used in the manufacture of chemicals; stainless steel, chrome plated metals, treatment of wood, and chrome tanning of leather (Kotaś & Stasicka, 2000).Lead is used as additives in motor fuels, manufacturing of Lead-based paints and glazing food containers (Jarup, 2003). It is the accumulation of the heavy metals in the environment and human body that makes them become toxic and of concern to environmental and public health.

World Health Organization (WHO) and Food Agriculture Organization (FAO) have developed international standards for the allowable heavy metals concentration in food, water and air that form the basis of countries taking measures to control environmental pollution from these heavy metals (WHO, 2011). However, the environmental pollution from heavy metals is increasing by day in developing countries as compared to developed countries. Increased anthropogenic and industrial activities that are not adequately regulated such as mining, use of fertilizers in farming and use of Lead rich gasoline have been reported to contribute to high concentrations of heavy metals in air, soil and water in developing countries(Ladwani *et al*., 2012).Some of these economic activities such as mining are lucrative businesses and have political connection such that they avoid meeting the required standards. They continue to pollute the environment and are abetted by the government authorities at the expense of human life (Harmanescu *etal*., 2011).

All heavy metals become toxic to humans at high concentrations in the body. Unfortunately, their accumulation to high levels takes a long period without any physical detection. Soil is known to be reservoir of heavy metals which eventually lead to accumulation in water and foods (Liu, 2013;Oyoo-Okoth et al., 2010). When heavy metals get into the body, they accumulate in the soft tissue such as the heart, liver, bones, kidney and reproductive organs causing health problems such as cancer, retarded cognitive development, immunological disorders, cardiovascular diseases, infertility and sometimes death (Khan *et al,* 2011;Singh *et al.*, 2011). Human exposure is through common pathways that include ingestion of contaminated food and soil, inhaling polluted air, drinking contaminated water and skin contact with heavy metals either through the palm, feet, arms and facial surfaces (Jamp, 2003;Nikolaidis*et al.*, 2012). The bioavailability of the heavy metals and levels of concentrations in common pathways have direct effects that are harmful onthe human body(Ikenaka *et al.*, 2010; Jagrati*et al.*, 2012;Kim *et al.*, 2005).

Environmental exposures to hazardous heavy metals is significant toxicological concerns due to their acute toxicity at higher concentrations and also the ability to mediate development of additional pathologic conditions in individuals exposed chronically to low levels (Oskarrson*et al.*, 2004).Health effects of the heavy metals to humans range from acute to chronic poisoning. Acute poisoning results from exposure to large amount of heavy metals but rarely occurs. Most of the health effects are attributed to chronic poisoning that occur due to long term exposure to lower levels until the toxic levels are reached (Khan *et al*., 2009).Among the most important elements in this regard are As, Cd, and Cr whose adverse toxic effects are now well recognized including their carcinogenicity and/or mutagenicity (Fishbain, 2007). Arsenic and Pb are considered potent human hazards because of their neoplastic outcomes and the increasing epidemiologic evidence that indicates a link between the heavy metal exposure and health risk (Dong-soon 2001).

International Agency for Research on Cancer (IARC)has classified heavy metals basedon theircharacteristicsas carcinogens to humans. As, Cd and Cr(VI)have been classified inGroup 1 as carcinogen to humansand Pb and its compoundsin Group 2A (probable carcinogen to human)in Group 2B (possibly carcinogen to human) and in Group 3 (not yet classified as to its carcinogenicity to human) as stated in Appendix 3.Past studies show that Ascauses cancers of the lungs, skin, lung, bladder and kidney(WHO, 2001).Cadmium has been associated withtestis, prostate, bladder andlung cancer (Fasinu & Orisakwe, 2013), and further analytical researches are needed to confirm breast cancer and human pancreatic cancers (Reiss *et al*; 2000). Chromium causes lung cancer (Gibb*et al*; 2000). Lead has been classified as a “possible human carcinogen” based on the sufficient animal data and limited human data in 1987 with its most likely candidates being lung cancer, stomach cancer and gliomas (Steenland & Boffetta, 2000).

Kenya like most of the African countriesis endowed with mineral resources which are being mined or are yet to be mined (Xinhai, 2016). There has been an increase in industrialization and urbanization within its borders which comes with pollution of the environment, particularly the watersources and food by heavy metals. With a weak legal regime, the country has experienced pollution of major water sources and serious air pollution (Maina, 2004; Kamau, 2010).Physico-chemical analyses from the Water Resources Management Authority (WRMA) indicated traces of Pb in the water samples collected in Kimwarer River(WRSR, 2007). The presence of the Pollutants in the water was an indication that the ore that contain Fluorspar could be having Pbas one of its impurities. Previous studies inIllinois in a Fluorspar mining belt showed presence of Cd and, Pb in water samples from Rivers within the belt (González *et al.*, 2008).

1.2 Statement of the problem

The Fluorspar Company of Kenya is one of the largest mining companies in Kenya.It is located at the Lower area of Kimwarersub-catchment. Since the start of the mining processes in 1970s, the community within the fluorspar belt has been exposed to various forms of pollution through the mining processes.Investigations by the Kenya News Agency (KNA) revealed that over 1,400 families still lived within the mining environs although they were to be relocated when the land was earmarked for mining in the 1970s.

In 2005, the Kimwarer-Sugutek Community Rights Group (KCRG) accused the Fluorspar mining company of disregarding environmental laws by discharging harmful effluent into the Kimwarer-Kerio River among other pollutants. They blamed the company's processing operations for the observed contamination of soils, water, plant and high levels of mineral content in animal tissue. The community complained that Kenya Fluorspar Company had continued to expose them to constant health hazards through its mining activities. They estimated that about 30% of the health issues experienced within the community could be related to the mining activities carried out by the FluorsparCompany. The community group appealed to the National Environment Management Authority (NEMA) to protect their right to a clean, healthy and sustainable environment(KNA, 2005).

Human exposure to pollutants released to the ambient environment from the mining activities in the study area are likely to result from contact with contaminated air, water, soils, and food. Physio-chemical analyses done by Water Resources Management Authority (WRMA) from Kimwarer River indicated traces of Lead in the water samples (WQPCO, 2007).This indicates that the rural community living and drawing water from Kimwarer River are exposed to Pb poisoning that could be as a result of the mining activities within the mining belt or the geological formations within the sub-catchment. Since Lead is a cumulative toxin in the mammalian body (Papritz A and P.U. Reichard,2009; Wu *et al,* 2016) and also a"probably or possibly carcinogenic to humans" by IARC it was important to confirm its presnce in the environment.The public health and clinical officers within Soy division reported that they have observed increased cases of cancer which could be an indication of the adverse effects of pollution of the drinking water, food and the air (Author report, 2010).

This study was aimed at investigating the presence of As, Cd, Cr and Pb in air, water, soil,food and human hair of adult residents in the study area.The study also determined the prevalence of cancer, estimated daily intake of metals and cancer risks associated the selected metals.

1.3 Justification

The study area is inhabited by a population of 936 households (PHCK, 2009) and some of them were exposed to emission from fluorspar mining. The prevalence of cancer within the mining belt could have been due to chronic exposure to toxic heavy metals. The study documented exposure and health risks associated with the heavy metals in water, soils and food stuff. Theseresults have information that the public health and concerned stakeholders can use for decision making on preventive measures to heavy metals exposure.

The selected heavy metals for the study are highly relevant for consideration to human exposure. As, Cd, Cr, and Pb, are the top fourheavy metals in site frequency count by the ATSDR Completed Exposure Pathway Site Count Report (ATSDR, 2005); three of these, As, Pb, and Cd are among the Superfund Top 10 Priority Hazardous Substances (Wuana & Okieimen, 2011). These heavy metals are considered to pose the greatest hazard to human health. In addition, as confirmed by ATSDR using the HazDat database, thesemetals most often occur together; they are present in 8 of 10and 5 of 10 of the top 10binary combinations of contaminants in soil and water respectively (Bae *et al.*, 2001).

1.4 Research Objectives

1.4.1 General Objective

The general objective of the study was to assess the health risks associated with exposure to Arsenic, Cadmium, Chromium and Lead to people living within Fluorspar mining belt in Kimwarer sub-catchment, Elgeyo -Marakwet County, Kenya.

1.4.2 Specific Objectives

In order to achieve the above overall objective the following four specific objectives guided the study:

i. To determine the concentrations of Arsenic, Cadmium, Chromium and Lead in water, soil and food (maize, millet, beans and milk) inFluorspar mining beltin Kimwarer sub-catchmentin KeiyoSub County.

ii. To determine the exposure to concentrations of Arsenic, Cadmium, Chromium and Lead in hair among the people living in Fluorspar mining belt in Keiyo Sub County;

iii. To determine cancer risks among the people living in Fluorspar mining belt in Kimwarer sub-catchment in Keiyo Sub County; and

iv. To determine the prevalence of cancer in the Fluorspar mining beltinKimwarer sub-catchmentin Keiyo Sub County;

1.4 Hypotheses

The following sets of null hypothesesformed the basis of the study.

H_o: Arsenic, Cadmium, Chromium and Lead in soil, waterand food arenot significantly above recommended levels for uncontaminated media in Fluorspar mining belt in Kimwarersub-catchment, Keiyo sub-county.

H_o: There is no significant seasonal variation in Arsenic, Cadmium, Chromium and Lead in water, milk and cereals in Fluorspar mining belt in Kimwarer Sub-catchment, Keiyo sub-county.

H_o: There is no significant variation in Arsenic, Cadmium, Chromium and Lead in soil, water, milkand cereals between different zones in Fluorspar mining belt in Kimwarer Sub-catchment, Keiyo sub-county.

H_o: Arsenic, Cadmium, Chromium and Lead arenotin hair among the people living in Fluorspar mining belt in Kimwarer Sub-catchment, Keiyo sub-county

H_o: Cancer risks in Fluorspar mining belt inKimwarer sub-catchment is not caused by Arsenic, Cadmium, Chromium andLead

H_o: The people living inFluorspar mining belt in Kimwarer sub-catchment in Keiyo sub-county are not at risk of cancer diseases.

1.5 Scope of the Study

The study covered the Upper, Middle and the Lower areas of Kimwarer sub-catchment. The main focus was in the mining belt which is the LowerKimwarer but the study also considered the two zones in the Kimwarer sub-catchment for comparison purposes. The study focused on three selected heavy metals Cd, Cr andPband one metalloidAs in soil, water, cereals (millet, maize and beans), milk and hair. An epidemiological study to determine the prevalence of cancer was conducted among adult residents. Carcinogenic and non-carcinogenic health risks were determined using United States Environment Protection Agency (US EPA) human health risk assessment models.

1.6 Limitation of the Study

The study area was large and could not be covered wholly in the sampling and therefore only randomly selected homesteads were sampled. The study was limited by the inaccessibility to the whole sub- catchment due to the bad terrain. The conservative nature of the community raised challenges in the collection of the hairsamples but participants were assured ofconfidentiality of the samples and the resultsafter analysis.

1.7 Assumptions of the Study

The studyassumed that those whose scalp hair were sampled had been residing in the study area for over five years and had been drinking the water and eating food from the locally grown crops. It was also assumed that cows whose milk was sampled grazed and were watered in the study area. The cereals sampled were grown in the study area and not imported from other cereal growing areas. The amounts of food consumed per household were based on the 5 number average family size without visitors and other dependents. It was assumed that the ingested dose is equal to the adsorbed contaminant dose and that cooking has no effect on the toxicity of selected heavy metal in sample.

1.8 Ethical Considerations

Entry to the community was done through the provincial administration, spending quality time to explain clearly the purpose of the study. All participants in this study wereinformed about the content and objectives of this study andwere requested for consent of participation. The permission to carry out the epidemiological study and sampling of hair were obtained from the Institute of Research and Ethical Committee (IREC), registration number(PAN 1648)(Appendix:4)of Moi University, School of Medicine and all the conditions were followed to the letter. No invasive technique was used for obtaining specimen or surgical procedures.

CHAPTER TWO

LITERATURE REVIEW

2.1 Arsenic, Cadmium, Chromium and Lead Occurrence, Monitoring and Safety Standards

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water. Their multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment; raising concerns over their potential effects on human health and the environment (Tchounwoou*et al.*, 2014). Heavy metal poisoning can be acute or chronic and may be caused by the following: Lead, Mercury, Iron, Cadmium, Thallium, Bismuth andmetalloids such as Arsenic(Jackson, 2012).

2.1.1 Sources of Arsenic, Cadmium, Chromium and Lead

General Sources

The sources of the heavy metal pollutants have been also widely documented(Wei. B *et al* 2010). Industrial effluents and emissions is a common source that directly deposits the pollutants into water (Holt, 2002). Industrial effluents and solid waste from the urban areas are the leading sources of heavy metals to water and land(Singh &Ghosh, 2005; Jamp, 2003; Harmanescu*et al*., 2011).Cadmium and Pb are heavy metals mostly found in industrial waste at high concentration (Jagrati *et al*., 2012).A previous study by (Oyoo-Okoth et al., 2010) revealed that there was high level of Pb from Kisumu city effluent.

Heavy metal contamination on agricultural soil comes from mining activities through mineral excavation, ore transportation and disposal of tailings (Ashraf *et al.*, 2011; Ladwani *et al*., 2012).Soil is a reservoir of heavy metals and medium of transmission to common pathways. Diet dominated exposure to heavy metals is attributed to soil contamination that lead heavy metals getting into food chains (Liu *et al*., 2013).(Otitoju & Otitoju, 2013;Hussain *et al*., 2012; Khan *et al*., 2009) confirmed thatLead and Cadmium are most abundant in the plants though their concentration was lower in plant than mother soil. The accumulation of metals in food chains is the major source of exposure to humans.

Related to industrial waste is the industrial activities that lead to waste as by products. These activities include mining which contribute to heavy metals pollution.The mine workers are usually exposed to dust of various potentially toxic substances. Common toxicants present in the mining environment are Lead, Cadmium, Arsenic, etc. Inhalation and absorption through the skin are common routes of exposure (Li R. K., 2018). These metals may be transported through soils to reach groundwater or may be taken up by plants, including agricultural crops (Atafar *et al*., 2008). The existence of trace metals in aquatic environments has led to serious concerns about their influence on plant and animal life (Zvinowanda*et al*, 2009; Sheikh, 2007).

Burning of the fossil fuel has also been found to have significant contribution to heavy metal pollution. This is the main source of Lead as the gasoline gets burnt by the motor vehicles. Fuel combustion is also found in industries. Other metals that arise from combustion are As, Cd, andCr.In most cases, the burnt fuel releases the pollutants into the atmosphere in gas form. This gas is inhaled into the human body (Khan, 2012; Maina, 2004; Ikenaka, 2010).Industrial emissions from industrial activities and vehicle exhaust have been found to be of great concern because of the quantity emitted and the speed of dispersion to wide geographical zones from the sources and the invisible potential of exposure (Ammune-Mathew, 2012).These emissions are in form of dusts, fumes and smokes which are air borne and of low density.

Mining

Metal mining is the second largest source of heavy metal contamination in soil after sewage sludge (Nouri, 2009). Mining activities are well known for their deleterious effects on the environment, due to the deposition of large volumes of wastes on the soil (Nouri *et al*., 2009).Mining activities pollute soil, water and air in equal measure. From the mining tailings, liquid effluent is released into water and soil. The heavy metals in the mining tailings are taken up by crops that later get into human body as food stuff. Accumulation of Lead and Cadmium in plants was found to be high (Jagarati *et al*., 2012).Studies by (Lee, 2005)observed that Singapore and Korean minesstreams and ground water sources were found be highly contaminated with Arsenic, Cadmium and Lead from abandoned mines.Heavy metals get into water and bio accumulates in sea foods that finally get into the human body (Sadovska, 2012).

Over 30% of the world's global mineral reserves are found in Africa (Robert , 2014), indicating that the impacts on the environment associated with mining should be of equal measure to the mining activities. Compared to more industrialized regions and with the exception of some hot-spot sites, the concentrations of heavy metals in African aquatic systems were low and close to natural background levels (Kishe & Machiwa, 2003).

Mining in Kenya is primarily for production of non-metallic mineralsencompassing industrial minerals such as soda ash (trona), fluorspar, diatomite, kaolin, gemstone and limestone (Xinhai, 2016). Fluorspar is a halide mineral composed of calcium fluoride with a global annual consumption of approximately 5.6 million tones.It is used in aluminum production, fire-retardant protective clothing, Teflon for non-stick frying pans, refrigerants and air conditioning, lithium batteries and as a component of environmental technologies. Fluorite deposits occur in the Musgut-Kimwarer area, Kerio Valley, in the Republic of Kenya. They are mined by Fluorspar Company of Kenya Limited. The fluorite bodies occur in isolated areas within the basement system of the Mozambique belt and lie in the Rift Valley system. Previous studies on the concentrations of heavy metals Cd, Cr andPb, were analyzed and found in water and surface sediments of five Rift Valley lakes Nakuru, Elementaita, Naivasha, Bogoria and Baringo(Ochieng *et al*., 2007).

2.1.2 Arsenic, Cadmium, Chromium and Lead Monitoring

Exposure to heavy metals may result in adverse health effects, and national and international health agencies have methodologies to set health-based guidance values with the aim to protect the human population(Dorne *et al.*, 2011).Different countries have put in place systems and agencies that have sets regulatory limits for the amounts of certain contaminants in water and food to protect public health. These include Environmental Protection Agency (EPA), Food Agricultural Organization (FAO) and

Kenya Bureau Statistics(KEBS) in Kenya.The law in Kenya provides that the set water quality standards should not place the health of the public customers at risk(GOK, 2012) hence the need for compliance to these set provisions.

Bio-monitoring

The human bio-monitoring (HBM) technique of measuring the concentration of natural and synthetic compounds in tissues (hair) can provide valuable information on environmental exposures and, in some cases, help, identifying potential health risks (COPHES, 2015;Guyton, 2000).For heavy metal toxicity monitoring and environmental risk assessment, the identification of heavy metals from biological samples such as blood, urine or hair is useful for identifying exposure. Hair sample can be a useful assessment tool in characterizing long-term exposure of the measured contaminant, whereas blood and urine often reflect most recent exposures (Qu *et al*., 2012).

The stringent environmental laws in industrialized countries, contamination levels of public concern are often too low to cause an increase in the incidence of disease that is large enough to be detected by epidemiological studies. Thus, the determination of biomarkers of exposure is a more appropriate method of assessment than to take the respective diseases as an endpoint. Hair samples have been widely used to assess human exposure to different contaminants because of its many advantages ((Rodrigues*et al.*, 2008).

USEPA Probabilistic risk assessment (PRA), in its simplest form, is a group of techniques that incorporatevariability and uncertainty into risk assessments. Variability refers to the inherent naturalvariation, diversity and heterogeneity across time, space or individuals within a population orlifestage, while uncertainty refers to imperfect knowledge or a lack of precise knowledge of thephysical world, either for specific values of interest or in the description of the system (USEPA).

The International Agency for Research on Cancer documented estimates of the worldwide incidence and mortality from 27 major cancers which were 14.1 million new cases and 8.2 million deaths in 2012. The mostcommonly diagnosed cancers were lung (1.82 million), breast (1.67 million), and colorectal (1.36 million) and he most commoncauses of cancer death were lung cancer (1.6 million deaths), liver cancer (745,000 deaths), and stomach cancer (723,000deaths) (Ferlay*et al.*, 2018).

2.1.3 Arsenic, Cadmium, Chromium and Lead Safety Standards

World Health Organization (WHO) and FAO has developed international standards for the allowable heavy metals concentration in food, water and air that form the basis of countries taking measures to control environmental pollution from these metals (WHO, 2011) (Table 2.1). However,environmental pollution from heavy metals is increasing by day in developing countries as compared to developed countries.

Increased anthropogenic and industrial activities that are not adequately regulated such as mining, use of fertilizers in farming and use of Lead rich gasoline have been reported to contribute to high concentrations of heavy metals in air, soil and water in developing countries (Ladwani, 2012). Some of these economic activities such as mining are lucrative businesses and have political connections such that they avoid meeting the required standards.They continue to carry out environmental pollution and abetted by the government authorities at the expense of human life (Harmanescu *et al*., 2011).

Table 2- 1: Recommended threshholds by different authorities.

Heavy Metal	**CODEX Alimentarius Commission (CODEX) Maximum Levels**	**US Food and Drug Administration (FDA) Maximum allowable Mg/l**	**European Commission (EU)**
Arsenic	Cereals: 0.01 0.1mg/kg	Water: 0.010 mg/l	Water: 10µ
Cadmium		Bottled drinking water:<0.005 mg/l	Water: 5µ
	Cereals: 0.1mg/kg Pulses: 0.1 mg/kg	Lifetime exposure to 0.005 mg/L Cd is not expected to cause any adverse effects.	
Chromium	Not available	Water: 0.1	Water: 50µ
Lead	Cereals: 0.2 mg/kg Pulses: 0.1	Drinking water: 0.005	Water: 10µ

Source: WHO & FAO, 1995

The World Health Organization has established a provisional tolerable weekly intake (PTWI) for Cadmium at 7 µg/kg of body weight. This PTWI weekly value corresponds to a daily tolerable intake level of 70 µg of Cd for the average 70-kg man and 60 µg of Cd per day for the average 60-kg woman(European Commission, 2004).A PTWI for inorganic arsenic in drinking water was established to be 0.015 mg kg^{-1} bodyweight (European Commission, 2004).

The Food and Agriculture Organization of the United Nations (FAO) and Joint Expert Committee of Food Additives and Contaminants (JECFA) of the World Health Organization (WHO) established a provisional tolerable monthly intake (PTMI) of 25 μg/kg body weight/month at the 73rd meeting of the JECFA (FAO, 2010). The Codex Alimentarius Commission is a joint intergovernmental body of the Food and Agriculture Organization of the United Nations and WHO with 180 Member States and one Member Organization (EU). Codex creates a harmonized international food standards to protect the health of consumers.

The Agency for toxic Subatance and Disease Registry have determined the minimal risk levels for heavy metals which acts as a refernce point when determining the estimated daily intake of the metal contaminant in food or water consumed.

Table 2- 2: ATDSR Minimal Risk Levels (MRLs)

Agency for Toxic Substances and Disease Registry MINIMAL RISK LEVELS (MRLs) October 2015					
Metal	Route	Duration	MRLs	Uncertainty Factor	End point
Arsenic	Oral	Acute	0.005mg/kg/day	10	Gastro
		Chronic	0.0003mg/kg/day	3	Dermal
Cadmium	Oral	Int.	0.0005 mg/kg/day	100	Musculo
		Chr.	0.0001 mg/kg/day	3	Renal
Chromium(III) insol. Particulates	Inh.	Int.	0.005 mg/m3	90	Resp.
Chromium(VI)	Oral	Int.	0.005 mg/kg/day	100	Hemato.
		Chr.	0.0009 mg/kg/day	100	Gastro.
Lead			Not available		

Source: (CDC, 2015)

For Duration; Acute = 1 to 14 days, Intermediate = 15 to 364 days, and Chronic = 1 year or longer.

The minimal risk levels (MRL) being an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse, non-cancer health effects over a specified duration of exposure. The information in this MRL serves as a screening tool to help public health professionals decide where to look more closely to evaluate possible risk of adverse health effects from human exposure(ATSDR, 2015).

2.2 Concentration of Arsenic, Cadmium, Chromium and Lead in the Environment

Contamination of heavy metals in soil and water is becoming a major health concern for public and health care professionals.These heavy metals include Arsenic, Cadmium, Chromium and Lead, whose concentrations beyond a recommended level is hazardous to the environment and the people exposed to them.

2.2.1 Arsenic Concentration in the Environment

Arsenic is a natural component of the earth's crust and is widely distributed throughout the environment in the air, water and land. It ranks 20th in abundance in the earth's crust, 14thin seawater and 12thin the human body (Mondal, 2002).It is highly toxic in its inorganic form (WHO, 2012). The source of Arsenic is mainly geological, but anthropological activities like mining, burning of fossil fuels, metal refining, wood preservation and uses of pesticides also cause Arsenic contamination (Harmanescu, 2011).

Arsenic is a toxic element at low concentration. The recommended level of Arsenic in water and air is 0.01mg/l. More than one hundred million people worldwide are at risk of elevated Arsenic exposure(Vahter M1, 2002). The common pathway into the human body is through drinking water and eating food (ingestion), inhalation and skin contacts (Bissen*et al.*, 2003;Nikolaidis *et al.*, 2012).

Arsenic is a potent endocrine disruptor and can alter hormone-mediated cell signaling processes in living organisms at extremely low concentration (Kaltreider et al., 2001). Exposure to As has been associated with certain forms of cancers (Bhuiyan*et al.*, 2010). Chronic exposure of high concentrations of As causes keratosis, hyperpigmentation, and depigmentation which are the most common cutaneous lesions (Ahmad*et al.*, 2010.) that are often viewed as useful precursors of severe diseases such as skin cancer (WHO, 2000).Arsenic is excreted through urine for both acute and chronic poisoning. Hair and nails are used as bio markers of long exposure to Arsenic and its compounds (IACR, 2012).

Arsenic was determined in water samples from Lake Victoria, River Nyamasaria, and tap water as well as in the soil samples. The results showed that Arsenic content in the water and soil ranged from 0.00 to 8.30 ng/100 ml and 12.39 to 24.36 ng/100 g, respectively, and the mean Arsenic levels in all water and soil samples were within the safe WHO limits for Arsenic(Makokha *et al.*, 2012)

2.2.2 Cadmium Concentration in the Environment

Cadmium is a natural element in the earth's crust. It is usually found as a mineral combined with other elements such as oxygen (Cadmium oxide), chlorine (Cadmiumchloride), or Sulfur (Cadmium sulfate, Cadmium sulfide). It occurs naturally especially in ores that contains zinc, Lead and copper. Cadmium does not corrode easily and has many uses, including batteries, pigments, metal coatings, and plastics(ATSDR, 2008).

Cadmium is a toxic heavy metal that exhibits various adverse effects in human and animal organisms. Its resemblance to essential heavy metals such as calcium, iron, and zinc leads to an unintended uptake in cells after intake through inhalation and ingestion (Riemschneider*et al.*, 2015).It is widely distributed in water, soils, food products and medicinal plants. It is also toxic at low concentration. The allowable concentration in water is 11.2mg/l. Its main source is industrial emissions, phosphate fertilizers,smoking and rechargeable nickel Cadmiumbatteries. Inhalation and ingestion are common pathways for Cadmium (Jamp, 2003).In the body, Cdsubstitutes Zinc in formation of DNA and RNA and other proteins. It also inhibits apoptosis and DNA repair and therefore leading to cancer. It has been known to cause kidney and bone damage and other cancers such as bladder, prostrate and lungs. Due to its tendency to get excreted and reabsorbed, urine becomes the best bio marker of Cdexposure (Fasinu & Orisakwe, 2013).

2.2.3 Chromium Concentration in the Environment

Chromium is widely used in metal plating, stainless steel production, wood preservation and textile manufacturing (Cone, 2009).Chromium poisoning in most cases results from occupational exposure, burning of fossils fuel and mining. It has a tendency of accumulating in soft tissues such as liver and bones. It has been associated with liver cancer, kidney damage and bones (Sadovska, 2012).

2.2.4 Lead Concentration in the Environment

Lead is used in the production of batteries, Lead alloys, ammunition, soldering materials, medical equipment, in ceramic glazes, and in the manufacture of corrosion and acid-resistant materials used in the building industry(ATSDR, 2005); (Levin, 2008).The common anthropogenic sources for Lead include vehicular emissions that contribute to 50% of the human exposure, old paints and battery manufacturing.It persists in the environment and accumulates in soils and sediments through deposition from air sources, direct discharge of waste streams to water bodies, mining, and erosion (Mulaku, 2001).Acute exposure to high amounts of Lead produces abdominal pain, cramps, and vomiting. Chronic exposures to Pb causeencephalopathy delirium, convulsions, brain damage, paralysis, anaemia, coma, and death (ATSDR, 2005). Children and workers are vulnerable groups for lead(Hussain *et al*., 2012; Fasinu and Orisakwe, 2013).

2.3 Concentration of Arsenic, Cadmium, Chromium and Lead in Food

The single most important factor in the etiology of chronic diseases is the perpetual over-consumption of food energy (Bennick, 2015). Excess body fat increases the risk of developing some types of cancer (WHO, 2002).Human exposure to heavy metalsthrough food items account for at least 90% of overall human exposure (Llobet , 2008).The contamination of living environment with potentially toxic heavy metals is considered as a very important health concern, which may result in accumulation of the elements in many food items (Arianejad, Alizadeh, Bahrami, & Arefhoseini, 2015).In Niger Delta, where there are industrial activities from crude oil exploration, industrial pollutants and contamination of sea foods is high(Otitoju & Otitoju, 2013).

2.3.1 Arsenic Concentration in the Food

The greatest threat to public health from Arsenic originates from contaminated groundwater. Drinking-water, crops irrigated with contaminated water and food prepared with contaminated water are the sources of exposure. Fish, shellfish, meat, poultry, dairy products and cereals can also be dietary sources of Arsenic, although exposure from these foods is generally much lower compared to exposure through contaminated groundwater (WHO, 2012).A study done in Turkey to determine the contents of some heavy metals in milk samples collected from three different regionshad average As concentration of 0.05, 0.009, 0.0002 mg/kg in the samples of milk in an industrial, ruraland traffic intensive regionrespectively.The highest heavy metal content was found in the milk samples collected from industrial region followed by traffic intensive region and rural region (Simsek *et al*, 2000).

A household survey on dietary habits in Bangladesh revealed that on an average, the women consumed 3.1 liters of water, 1.1 kg of cooked rice and 42gm of dry weight of curry per day. The total ingestion of Arsenic rates ranged from 31.1 to129.3 microgram per day with a mean of 63.5 microgram per day. It was indicated that the major route of Arsenic is rice followed by curry and water (Islam, 2012).

A study in West Bengal found out that As in ground water which was used by the villagers for drinking, cooking and other household purposes was above the maximum permissible limit of 0.05 mg l^{-1} which is recommended by the WHO. Arsenic was determined in staple a food samples from Lake Victoria, River Nyamasariaand the Arsenic content in the maize and bean samples ranged from 5.21 to 7.03 µg/100 g. respectively which was within the safe WHO Arsenic limits(Makokha*et al.,* 2012)

2.3.2 Cadmium Concentration in Food

Cadmium is an ubiquitous environmental pollutant of increasing worldwide concern. Food crops grown on Cadmium-containing soils or on soils naturally rich in this heavy metal constitutes a major source of non-workplace exposure to Cd other than exposure from cigarette smoking (Satarug *et al.*, 2010).Previous studies on cereal and beans sampled from an open market in north-eastern China were analyzed for Cr andCadmium was found to have substantially higher concentrations in beans (55.7 ng Cd/g) than in cereals (maize and millet) (9.2 ng Cd/g).

Studies by(He*et al.*, 2013) on an exposure assessment of dietary Cd among Shanghainese forover 40 showed an average daily environmental Cd exposure of the participants was 16.7 μg/day and approached 33.8% of the provisional tolerable daily intake (PTDI). Dietary and tobaccoCdexposureapproached 25.8% and 7.9% of the PTDI, respectively.The dietary intakes of Cd in adults living in Jinhua area in China were 1.49 μg $(kg_{bw})^{-1}$ $week^{-1}$ (Liua*et al.*, 2010).

2.3.3 Chromium Concentration in Food

Chromium (VI) can be ingested with drinking water, other beverages and food. Chromium is reduced into Chromium (V) and Chromium (IV) which are suspected to play a role in Chromium genotoxicity and carcinogenicitythrough reaction with other cellular components (Jefferson, 2016).

2.3.4 Lead Concentration in the Food

The study by(Simsek et al, 2000) found Pb in milk samples collected from three different regions: an industrial region, rural region and traffic intensive region had the average amounts in the samples from these regions as: Pb 0.032, 0.049, 0.018 mg/kg respectively. The highest Pb content was found in the milk samples collected from the industrial region followed by the traffic intensive region and rural region (Simsek, 2000).

Cereals and beans samples were collected from open markets in north-eastern China, and analyzed for Pb. The average Pblevels were 25.7ng/g, 54.3ng/g and 35.4 ng /g for foxtail millet and maize respectively.

2.4 Exposure of Arsenic, Cadmium, Chromium and Lead in Hair

2.4.1 Arsenic Concentration the Hair

Arsenic is a widely occurring environmental contaminant. To assess human exposures to As, public health officials and researchers often conduct biomonitoring. Biomonitoring for As in hair and nails has been used in many studies and is particularly useful in evaluating chronic exposures to As.Interpreting the health implications of As concentrations in biological samples is limited by the small number of studies that provide information on the correlation and dose-response relationship between biomonitoring test results and adverse health effects (Kenneth Orloffa, 2009).

(Hassanien & Mohmoud, 2001)in a study on As level of hair samples of apparently healthy Egyptians found levelsrangingfrom 0.04 to 1.04 mg As/kg hair of which about 55% of the analyzed hair samples were within the range of allowable values (0.08–0.25 mg As/kg hair). The study concluded that As levels in water at concentrations of 100 μg/liter or less seem not to produce an undue body burden.

2.4.2 Cadmium Concentration in Hair

Bioavailability of ingested Cd has been confirmed in studies of persons with elevated dietary exposure, and the findings have been strengthened by the substantial amounts of Cd accumulated in kidneys, eyes, and other tissues and organs of environmentally exposed individuals(Saturget, 2010).Most persons are in an approximate Cd balance and tend to excrete Cd until approximately age 50, after which a negative balance ensues.

The correlation of heavy metal concentrations in hair with those in the critical organs was investigated by tracer studies using ^{51}Crand^{109}Cd in mice. Hair was found to be a poor indicator of Cadmium contamination, as the concentration of Cd in hair was not parallel to that in the critical organs of the experimental animal, the mouse.

2.4.3 Chromium Concentration in Hair

A study in Turkey showed asignificant positive correlation between hair chromium concentrations and urinary chromium/creatinine ratios in workers working in a tannery indicating that urinary chromium excretion can be used as an indicator of chromium exposure.

2.4.4 Lead Concentration in the Hair

An evaluation of the use of human hair for bio-monitoring the deficiency of essential andexposure to toxic elements indicated that there was a weak correlation ($r=0.22$, $p<0.001$) between Pb levels in hair and blood (Rodrigues JL, 2008). The findings also suggested that while the idea of measuring trace elements in hair is attractive, hair is not an appropriate biomarker for evaluating Pb exposure.

2.5 Effects ofArsenic, Cadmium, Chromium and Lead Exposure to Humans

The most dangerous and pernicious forms of pollution arises from the potential mobilization of a spectrum of toxic trace heavy metals and metalloids in our environment(Fishbein, 1984). The toxic effects of heavy metals depend on the forms and routes of exposure, interruptions of intracellular homeostasis which include damage to lipids, proteins, enzymes and DNA via the production of free radicals. Following exposure to heavy metals, their metabolism and subsequent excretion from the body depends on the presence of antioxidants associated with the quenching of free radicals by suspending the activity of enzymes (Jan *et al*., 2015).

2.5.1 Potential for Human Exposure to Heavy Metals

Human exposure to heavy metals is through common pathways that include ingestion of contaminated food, inhaling polluted air, drinking contaminated water and skin contact either through the palm, feet, arms and facial surfaces (Jamp, 2003;Nikolaids, 2012).The heavy metal toxicity depends on several factors including the dosage, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals(Tchounwou, 2014).The bioavailability of the heavy metals and their levels of concentrations in common pathways have direct effects on level of exposure to human body. High human exposures have been documented in areas where there is high concentration of heavy metals(Qu, Ma, Yang, Liu, Bi, & Huang, 2012).

Mining tailings, streams sediments, agricultural soils, ground water sources, food chains and atmospheric emissions from industries cause direct contamination of human environment leading to exposure (Kim, 2005;Jigrati, 2012; Ikenaka *et al*., 2010).Both occupational and environmental exposure to hazardous metals, such as As, Cd, Cr, and Pb, are of significant toxicological concerns. Not only do these heavy metals lead to acute toxicity at higher concentrations, but they may also mediate development of additional pathologic conditions in individuals exposed chronically to low levels (Bae *et al.*, 2001).

Humans are exposed to a number of "heavy metals" such as cadmium, lead, and other metals as well as metalloids, such as arsenic, in the environment, workplace, food, and water supply(Dorne*et al.*, 2011).

Harmful health effects from heavy metals to human, ranges from acute to chronic poisoning. Acute poisoning results from exposure to large amounts of heavy metals but rarely occurs. Most of the health effects are attributed to chronic poisoning that occur due to long term exposure to lower levels until the toxic levels are reached (Khan *et al*., 2009).When heavy metals get into the body, they accumulate in the soft tissue such as the heart, liver, bones, kidney and reproductive organs causing health problems such as cancer, retarded cognitive development, immunological disorders, cardiovascular diseases, infertility and sometimes death (Khan, 2009)

Heavy metals are known to be persistent in the human body, with excretion half-lives that last for decades. Heavy metals can lead to a wide range of toxic effects, such as carcinogenicity, mutagenicity and teratogenicity(Qu, 2012). As, Cd, Cr, Hgand Pbhave been scientifically proven to cause several cancers(Liu *et al*., 2013). Heavy metals are known to affect different groups in a population. However, they affect children more than adults because their gastrointestinal tract is developing and therefore absorption of metals is very high (Nikolaidis *et al*, 2012).

Arsenic is a significant health risk to millions of people worldwide when it is there in food and drink. It is highly poisonous at higher doses but chronic exposure to Lower levels increases the risk of cancer of skin, bladder, lungs, kidney, liver, colon, prostrate; cardiac disease, pulmonary disease, cardiovascular disease, diabetes; diseases of arteries and capillaries; increased sensitivity to Hepatitis B infection, infertility, and other ailments (WHO, 2000).

2.5.2 Mechanisms of Toxicity and Carcinogenicity

Arsenic, Cadmium, Chromium and Lead Toxicity

When toxins enter the body by way of food, drinking water, and air, these heavy metals produce toxicity by forming complexes with cellular compounds containing Sulfur, Oxygen, or Nitrogen that activate enzyme systems or modify critical protein structures leading to cellular dysfunction and death (Ibrahim *et al.*, 2006). Body cells reduce their burden of heavy metals or metalloids to provide a basis for acquired tolerance by active extrusion (Xie, 2004).

Arsenic, Cadmium, Chromium and Lead Carcinogens

Chemical carcinogens induce cancer in humans after excessive or prolonged period of exposure to natural and/or synthetic industrial, agricultural or commercial substances. They exert carcinogenic effects via distortion of the conformation of DNA during replication and transcription; mutational activation of proto-oncogenes and/or inactivation of tumor suppression genes; non mutational processes such as the clonal expansion of pre-malignant cells. All toxic heavy metals are toxic at high concentration because of disrupting enzyme functions, replacing essential metals in pigments or producing reactive oxygen species (Babula *et al.*, 2009).Among the most important elements in this regard are As,Cdand Cr whose adverse toxic effects are now well recognized including their carcinogenicity and/or mutagenicity (Fishbein, 1984).

Heavy metals can lead to a wide range of toxic effects, such as carcinogenicity, mutagenicity and teratogenicity(Tong *et al*., 2000).Cancersare malignant tumors and neoplasms with one defining feature of rapid creation of abnormal cells that grow beyond their usual boundaries, and which can then metastases to adjoining parts of the body and spread to other organs. Metastases are the major cause of death from cancer (WHO, 2015; Langtree, 2008).

Cancer arises from one single cell. The transformation from a normal cell into a tumor cell is a multistage process, typically a progression from a pre-cancerous lesion to malignant tumors. These changes are the result of the interaction between a person's genetic factors and three categories of external agents, including: physical carcinogens, such as ultraviolet and ionizing radiation; chemical carcinogens, such as asbestos, components of tobacco smoke, aflatoxin (a food contaminant) and Arsenic (a drinking water contaminant); and biological carcinogens, such as infections from certain viruses, bacteria or parasites. WHO, through its cancer research agency, International Agency for Research on Cancer (IARC), maintains a classification of cancer causing agentsas shown in Appendix 3(WHO, 2015).

Arsenic and inorganic Arsenic compounds, Cadmium and Cadmium compounds, and Chromium IV compounds have been classified by IARC (IARC, 2012) to be in Group 1. The Group 1 chemicals are those that are carcinogenic to humans, implying that there is availability of sufficient evidence (epidemiological, occupational exposure and animal studies) of carcinogenicity to humans with a clear understanding of the relevant mechanism of human carcinogenicity. The inorganic Lead compounds are in Group 2A.

Group 2A are probably carcinogenic to humans, implying the availability of limited evidence of carcinogenicity to humans, sufficient evidence of carcinogenicity in experimental animals with strong evidence that the method of carcinogenesis is operable in humans.

Lead metal falls in Group 2B. Group 2B is possibly carcinogenic to humans; implying the availability of limited evidence of carcinogenesis to humans, less than sufficient evidence in experimental animals and inadequate evidence in humans but sufficient or limited in experimental animals**.** The metallic Chromium, Chromium III compounds and organic Lead compounds are in Group 3. The Group 3 metals are not yet classifiable as to their carcinogenicity to humans. The availability of inadequate evidence in humans, inadequate or insufficient evidence in experimental animals and the mechanism of carcinogenesis does not operate in humans.

Arsenic Toxicity and Carcinogenicity

Analyzing the toxic effects of arsenic is complicated because its toxicity is highly influenced by its oxidation state and solubility, as well as many other intrinsic and extrinsic factors (Hughes, 2002). Inorganic Arsenic is well known as an environmental carcinogen. Reports from several countries show that an elevated exposure to Arsenic is associated with several diseases, especially neoplasia(Thomas W Gebel, 1998). The inorganic trivalent arsenite (As III) is two to ten times more toxic than pentavalent arsenate (As V) (Goyer R. , 2001). By binding to thiol or sulfhydryl groups on proteins, As (III) can inactivate over 200 enzymes. This is the likely mechanism responsible for arsenic's widespread effects on different organ systems. As (V) can replace phosphate, which is involved in many biochemical pathways(Hughes, 2002;Goyer R, 2001).

Several studies have indicated that the toxicity of arsenic depends on the exposure dose, frequency and duration, the biological species, age, and gender, as well as on individual susceptibilities, genetic and nutritional factors (Kapaj et al., 2006). One of the mechanisms by which arsenic exerts its toxic effect is through impairment ofcellular respiration by the inhibition of various mitochondrial enzymes, and the uncouplingof oxidative phosphorylation. Most toxicity of arsenic results from its ability to interact withsulfhydryl groups of proteins and enzymes, and to substitute phosphorous in a variety ofbiochemical reactions(Wang Z Rossman, 1996). The pathway analysis of Arsenic toxicity showing the potentials of genomic interaction, cellular processes, and diseases induced by exposure of Arsenic is shown in Figure 2-1.

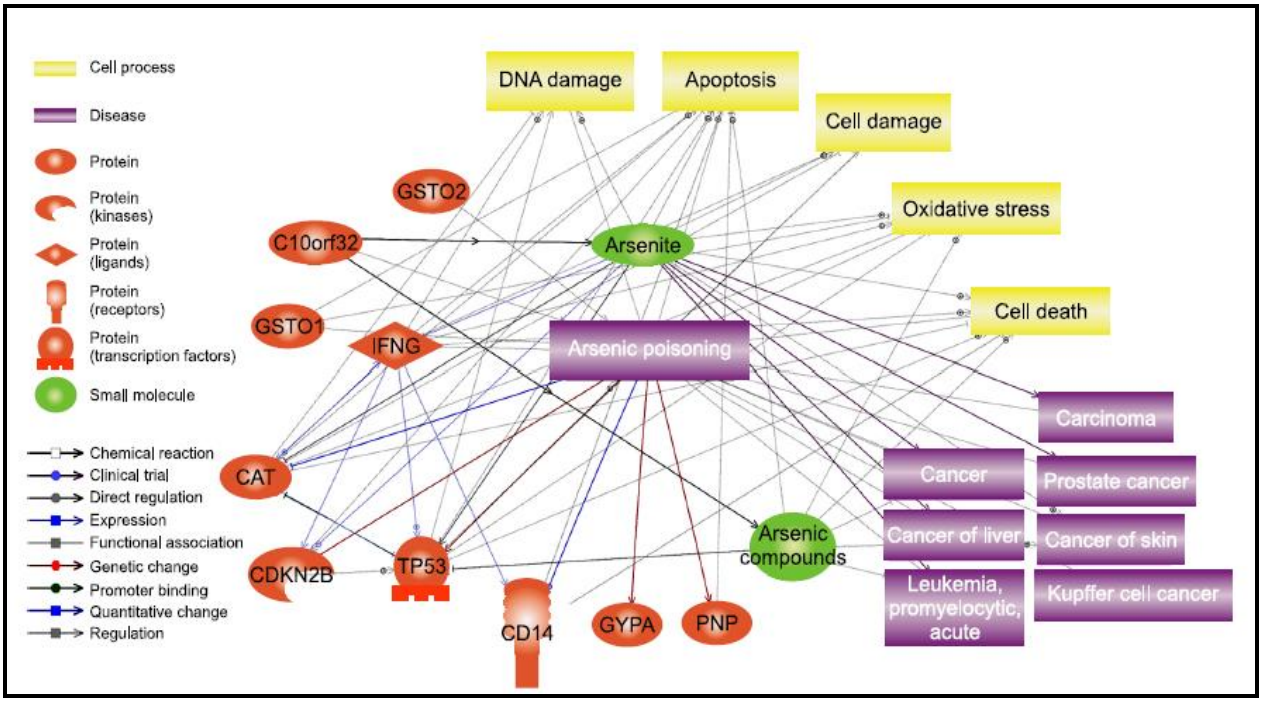


Figure 2- 1: Pathway analysis of arsenic (Source: Jan et al, 2015)

A toxicokinetic and genomic analysis of chronic exposure to Arsenic in mice showed highexpression of cyclin D1, PCNA and c-myc, all of which havethe potential to contribute to Arsenic carcinogenesis (Yaxiong Xie, 2004).

Cadmium Toxicity and Carcinogenicity

Cadmium is a heavy metal that has been suggested to be a carcinogen by evidence. A number of published studies have investigated the association between Cd levels and prostate cancer, but the results were inconsistent. The data suggested that Cd exposure might exert an influence on the tumorigenesis of prostate tissues (Zhang *et al*., 2015). The pathway analysis of Cadmium toxicity showing the potentials of genomic interaction, cellular processes, and diseases induced by exposure of Cadmium is shown in Figure 2-2.

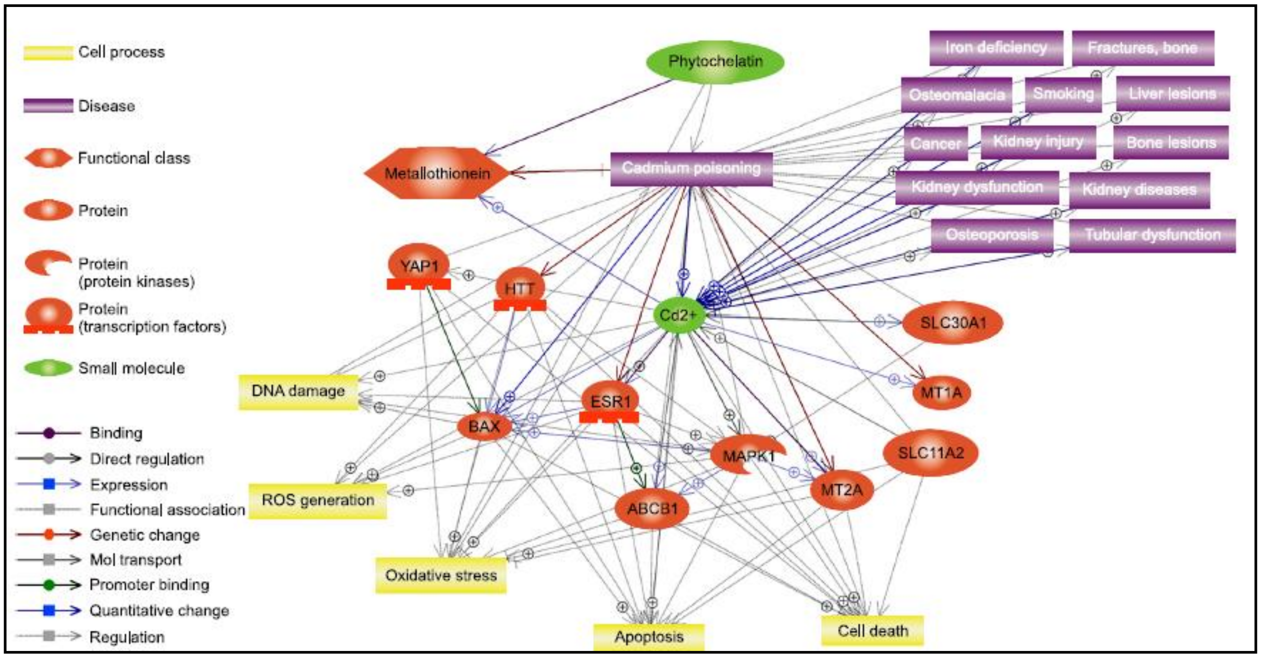
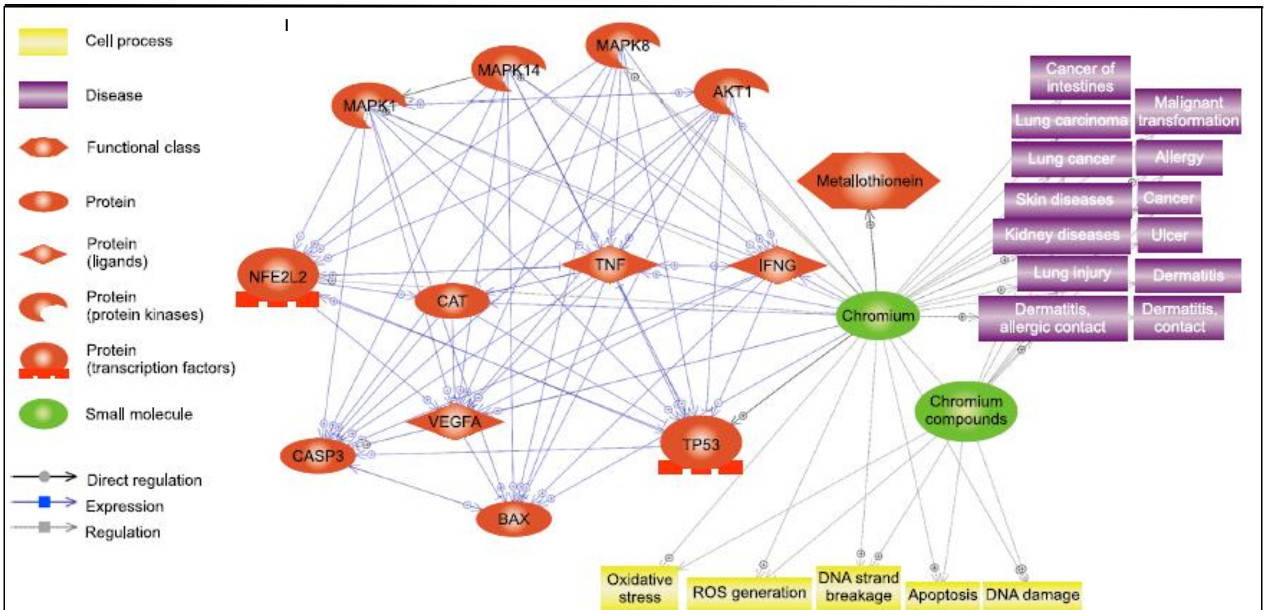


Figure 2- 2: Pathway analysis for Cadmium toxicity (Source: Jan et al, 2015)

Chromium Toxicity and Carcinogenicity

Chromium, like many transitionalheavy metal elements, is essential to life at low concentrations yet toxic to many systems at higher concentrations. In addition to the overt symptoms of acute chromium toxicity, delayed manifestations of chromium exposure become apparent by subsequent increases in the incidence of various human cancers (Costa & Klein, 2006).Experimental studies clearly demonstrated the malignant potential of Chromium (VI) compounds, with solubility being an important determining factor.

The toxicokinetics of Chromium are of two different oxidation states, Cr(III) and Cr(VI), linked by reduction processes that are ubiquitous in body fluids and tissues. The kinetic behaviors of these two major oxidation states of Cr are very different. Reduction of Cr(VI) to Cr(III) in the body, is relative to the carcinogenicity of Cr(VI) in the lungs. Therefore, a comprehensive understanding of the toxicokinetics of Cr must include the disposition of both Cr(III) and Cr(VI). The Figure 2-3 below shows the pathway analysis of Chromium toxicity showing the potentials of genomic interaction, cellular processes, and diseases induced by exposure of chromium.



Pathway analysis of chromium toxicity showing the potentials of genomic interaction, cellular processes, and diseases induced by exposure of chromium. Source: (Jan et al., 2013)

Figure 2- 3: Pathway analysis for Chromium toxicity (Source: Jan et al, 2015)

Various hypotheses have been proposed to explain the carcinogenicity of chromium and its salts, however some inherent difficulties exist when discussing metal carcinogenesis. A heavy metal cannot be classified as carcinogenic per se since its different compounds may have different potencies. Because of the multiple chemical exposure in industrial establishments, it is difficult from an epidemiological standpoint to relate the carcinogenic effect to a single compound. Thus, the carcinogenic risk must often be related to a process or to a group of metal compounds rather than to a single substance (Tchounwou *et al*., 2014).

Lead Toxicity and Carcinogenicity

An important determinant of body Pb burden and Pb toxicity in exposed humansismetabolism, or Pbtoxicokinetics.A previous study was done by (Garcia-Lestona *et al*., 2012)on the genotoxic effects of occupational exposure to Lead and influence of polymorphisms in genes involved in Leadtoxicokinetics and in DNA repair. The results also showed genotoxic effects related to occupational Lead exposure to levels under the Portuguese regulation limit of 70µg/dl.

2.6. Cancer Prevalence

Epidemiology is the study of the distribution and determinants of health-related states or events in specified populations and the application of such studies to control health problems.Muller (2011 was used in the current study to determine the prevalence of cancer within the study area. Previous studies reviewed epidemiologic evidence on the relation between exposure to metals and cancer. The carcinogenicity of As and Cr, has been established.

In 2012, the worldwide burden of cancer rose to an estimated 14 million new cases per year, a figure expected to rise to 22 million annually within the next two decades. Over the same period, cancer deaths were predicted to rise from an estimated 8.2 million annually to 13 million per year. Globally, in 2012 the most common cancers diagnosed were those of the lung (1.8 million cases, 13.0% of the total), breast (1.7 million, 11.9%), and large bowel (1.4 million, 9. 7%). The most common causes of cancer death were cancers of the lung (1.6 million, 19.4% of the total), liver (0.8 million, 9.1%), and stomach (0.7 million, 8.8%) (IARC, 2014).

Cancer statistics in Kenya shows that cancer is the 3rd highest cause of morbidity in Kenya (7% of deaths per year), after infectious diseases and cardiovascular diseases. It is difficult to get accurate national data because most data is coming from Nairobi and other urbanized settings. It is estimated that 39,000 new cancer cases are recorded each year with more than 27,000 deaths per year. 60% of Kenyans affected by cancer are younger than 70 years old. Leading cancers in Kenya for women arebreast (34 per 100,000) and cervical (25 per 100,000), andmen for prostate (17 per 100,000) andesophageal (9 per 100,000). I70-80% of cancer cases. These are diagnosed in late stages due to lack of awareness, inadequate diagnostic facilities, lack of treatment facilities, high cost of treatment and high poverty index(KNCO, 2016).

Nearly 18% of the global cancer burden is attributable to infectious agents, with a higher percentage (26.3%) in developing countries than in developed countries (7.7%) (Parkin, 2006;).Cancer is the leading cause of death in developing countries (Jemal et al., 2011; Malvezzi*et al*., 2013).Cancer is an emerging public health problem throughout the African region. Women in the region commonly suffer breast and cervical cancers whereas men have higher rates of liver, stomach, bladder, prostate, lung and esophageal cancers.It is estimated that about 100 million Africans will develop cancer before 75 years of age (WHO, 2015).

A study was done to address the increasing concern over the health effects of Chromium (Cr) exposure stemming from various activities in tanneries in Kenya. Chromium in its hexavalent form is a toxic heavy metal which is widely used in the tanning process (Were *et al*., 2014). Though Cr is a carcinogen the study just looked at respiratory and dermatological conditions on the adverse human health effects among the workers.

2.7 Control Measures of Exposure to Arsenic, Cadmium, Chromium and Lead

Many of the impacts of extractive industries, including: social displacement, community marginalization/re-location, vegetation clearance, dust, disturbance, erosion, overuse or degradation of water resources, chemical and fuel spills, waste and pollution and limits on land access and traditional practice.These effects become apparent in terms of a degraded environment contaminated drinking water, and loss of agricultural citation.

The Kenya Chamber of Mines (KCM) was formed in 2000 to represent the interests of Kenyan miners, exploration companies and mineral traders. KCM also seeks to associate these interests with national and local community interests, and to involve other stakeholders in order to ensure that these interests do not cause harm to the environment and the communities (KCM, 2014).

Mining should be conducted in such a manner that the environment is not damaged to the extent that large areas of land are permanently removed from future beneficial use. Therefore it is very important to conduct an assessment of the environment to assess the potential impacts of a mining operation (Environmental Impact Assessment) and the development process has to be undertaken to keep environmental degradation as low as reasonably achievable (Mwinyi, 2014).

Best Available Techniques (BAT)which consists of the use of the latest stage of development (state of the art)processes, facilities and methods of operation which are suited to reduce discharges, missions and waste. Governmental regulatory bodies must begin to contemplate how to safeguard the population when such mixtures of contaminants are found in foods(Larke*et al*., 2015).

Concerted efforts have been made by developed countries by reducing the introduction of lead into theambient environment in recent years, reflecting a decline in the commercial use of lead, particularly inpetrol (WHO, 2000). Sustainable Development Goals No 3; stresses the need of ensuring healthy lives and promoting the well-being for all at all ages is essential to sustainable development. Efforts are needed to fully eradicate a wide range of diseases and address many different persistent and emerging health issues.WHO and the International Agency for Research on Cancer (IARC), the specialized cancer research agency of WHO, collaborates with other United Nations organizations and partners to:Conduct high-level advocacy to increase political commitment for cancer prevention and control, Develop strategies for cancer prevention and control and disseminate existing knowledge to facilitate the delivery of evidence-based approaches to cancer control(WHO, 2013).

2.8 Knowledge gaps identified

Heavy metal levels have been determined by many researchers. Tchounwou et al., 2015 reviewed and analysed heavy and provided an analysis of their environmental occurrence, production and use, potential for human exposure, and molecular mechanisms of toxicity, genotoxicity, and carcinogenicity. Xio et al., 2017looked at soil heavy metal contamination and health risks associated with artisanal gold mining in Tongguan, Shaanxi, China. Xio found out that the local residents had high chronic risks due to the intake of Pb, while their carcinogenic risk associated with Cd through inhalation was low.

Thousands of people in a poor urban district outside Mombasa face serious health consequences from toxic lead from a battery recycling plant. At least 90% of the villagers who stay in Owino Uhuru village have tested positive despite closure of the lead factory (Maundu, 2018). Studies by (Etiang, et al., 2018) confirmed that children in Owino Uhuru had significantly higher blood lead levels compared with children in Bangladesh settlement. Arstisinal mining of gold is carried ou in Migori, Kenya. Studie by (Ngure et al., 2017) showed that children in the study area are exposed to high health risks associated with ingestion of potentially harmful elements through contaminated drinking water from the rivers flowing through the gold mining area.

Since health risks associated with heavy metals are in the rise, several researches are being done to establish the levels of risks the people are facing in an area with high levels of pollution. Studies by Tchounwou et al., 2018; have assessed health risks associated with heavy metal metals. Bamuwamye et al. 2015 studied cancer and non-cancer risks associated with heavy metal (As, Cd, Cr and Pb) exposures from street foods in Uganda found out that evaluation of roasted meats in an urban setting. The results showed that the people consuming the contaminated meats are at arisk of non-carvcinogenic and carcinogenic diseases. The sum of the Incremental lifetime cancer risks for pork, goat and chiken were higher than acceptable risk levels (ILCR > 10-4).

Some of the gaps identified in the literature review of previous researches included the fact that the toxicity of heavy metals and their non-carcinogenic and cancer risks in a mining set up needed to be carried out to establish the rsiks the people in Kimwarer Sub-catchment were facing. The community members living within the catchment had low levels of understanding on the human adverse effects due to heavy metals which the study will use the results to create awareness and recommend further reaseches to unearth ythe solution s required.

CHAPTER THREE

METHODS AND MATERIALS

3.1 Introduction

This chapter highlights the location of the study area, the materials and methodology used to collect and analyze water, soils, food cereals, milk and human hair for the selected heavy metals studied. The procedure for estimating cancer risk and non-cancer risks caused by the selected heavy metals were determined.

3.2 Study Area

3.2.1 Location

The study was carried out in Flourspar mining belt located inKimwarer sub-catchment area which is administratively in part of Soy and Metkei division in Elgeyo-Marakwet County. The county is divided into three topographic zones; the Highlands, the Kerio Valley and the Escarpment. The study areacovered two divisions whichincluded part of Soy, Chemoibon, Turesia, and Tumeiyo sub-locations. Figure3-1 shows the study area that was subdivided into three zones namely;LowerKimwarer (LK),MiddleKimwarer (MK) and UpperKimwarer (UK) zones.UpperKimwarer is located in the highland which is the source of KimwarerRiver, MiddleKimwareris located along the slopes of Elgeyoescarpment while LK is at the Lower region where the mining sites andthemining factoryare located.

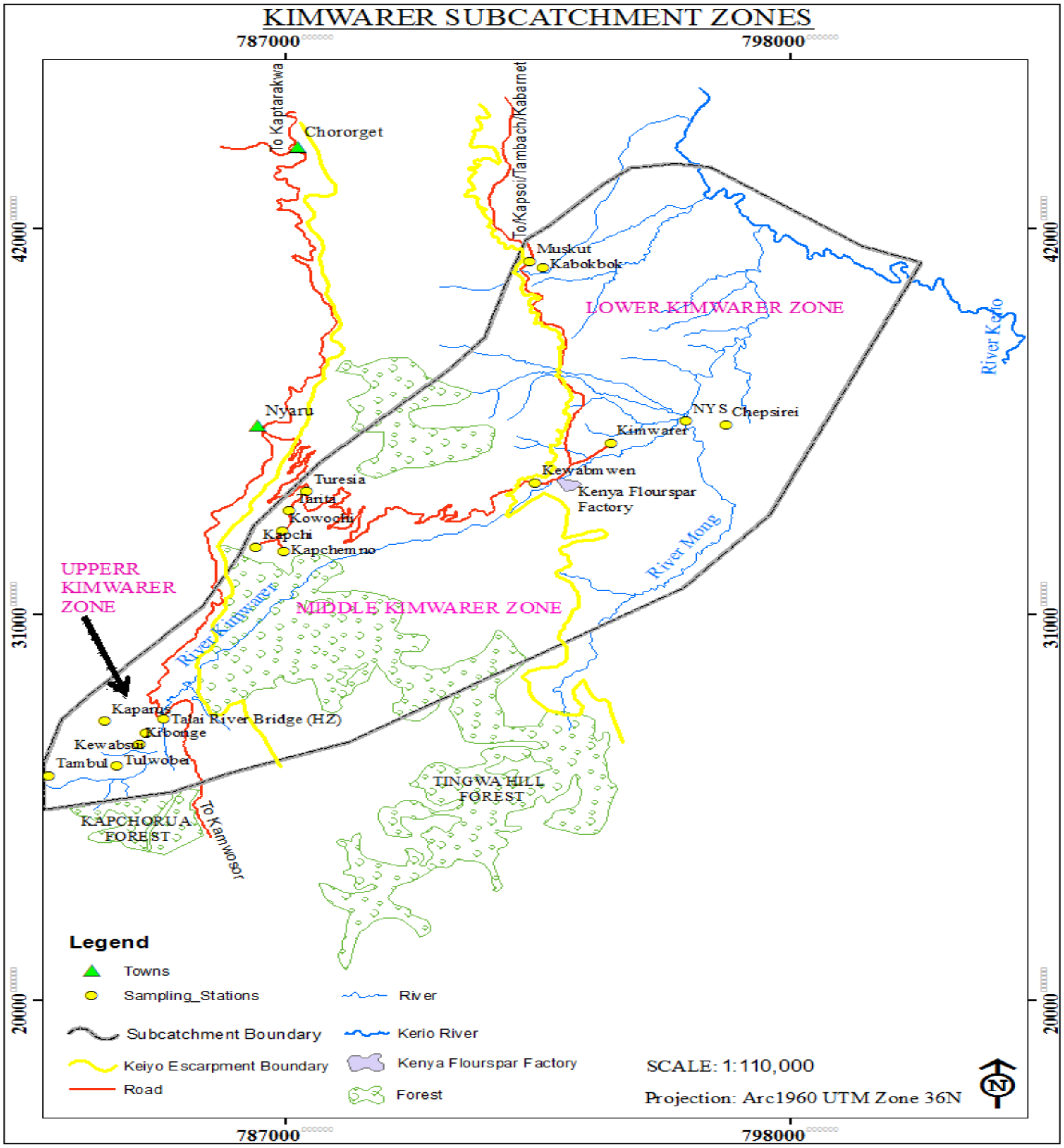


Figure 3- 1: Map showing the zones and sampling areas in Kimwarer sub-catchment

(Source: UOE GIS LAB, 2017)

3.2.2 Population

The provincial boundaries of the sub-locations where the Kimwarer sub-catchment is located has a population of 369, 998 people, 77,555 households and population density of 122 people /Km^2according to the 2009 National Population andHousing Census(Kenya Census, 2009; USAID, 2012).

3.2.3 Climatic Condition

The altitude varies from 900 m at the Kerio Valley to 2700 m above sea level in the highlands giving rise to considerable differences in climatic conditions. The temperatures ranges from 15° C to 23° C in the Highlands and 17° C to 30°C in the, Escarpment and Kerio Valley in cold and hot seasons respectively(EMC, 2013).

The Highlands receive between 1200mm and 1500mm per annum while the Escarpment gets rainfall ranging between 1000mm to 1400mm per annum. The Kerio Valley, on the other hand, receives between 850mm to 1000mm of rainfall per annum. Long rains usually fall between the months of March and July every year while the short rains fall between August and November(EMC. 2013).

3.2.4 Socio-economic activities

The majority of the population within the sub-catchment area practice mixed farming that includes crop farming and rearing of livestock. These practices form the major source oflivelihood. The main crops produced vary with ecological zones. In the highlands, food crops such as maize, wheat, Irish potatoes, beans and millet at small scale are produced. Further, cash crops here include tea, pyrethrum and coffee. In the Kerio Valley, mangoes, pawpaw, watermelon, oranges and bananas are produced together with high value cassava, millet and sorghum(EMC, 2013).The escarpment forms a transition where both the crops at the highlands (Upper Kimwarer) and the Kerio Valley (Lower Kimwarer) are found.

3.2.5 Geology of the area

Geologically, the area forms a section of the Mozambique belt which is part of the Precambrian basement complex of the rift valley overlain by Miocene, phonolites and trachytes. Fluorite mineralization was emplaced either pre- or early to mid- Tertiary times (Miocene and Pleistocene), possibly at the onset of rifting during the development of the East African Rift system.

3.2.6 Hydrology of the area

The Kerio escarpment isthe main water divide between the east and west drainage systems.

Kimwarer River and Mong River joins to form the Kerio River that drains into LakeTurkana. Kimwarer River has smaller tributaries that include Turesia, Simit and Kapchemno streams(EMC, 2013).

3.3 Materials

Apparatus

The following are the apparatus or equipment which were used during the analysis of the samples, Filtration apparatus with Coarse (40 to 60µm) fritted disk as filter support, a suction flask, of sufficient size for sample size selected; drying oven; Analytic balance capable of weighing to 0.1mg; Whatman filter paper No. 1; Graduated cylinder; Volumetric flasks of 100mL; Volumetric flasks of 50mL; Aluminum dish; Crucibles; Series Atomic Absorption Spectrophotometer (AAS, Model Spectra AA 10/20); High purity (99.55 %) Acetylene gas; High purity (99.55 %) Argon gas and a Hydride Vapour Generator System.

3.4 Research Design

3.4.1 Mixed methods approaches

The research design used in the study was of the mixed methods approacheswhere bothquantitative and qualitative designs were used. The quantitative design used correlational and causal comparative designs. The correlational design explored the relationship between variables through a correlational analysis to determine the relationship and the strength or the degree the variables were related without implying that one causes the other. The causal comparative design compared two groups with the intent of understanding the reasons or causes for the two groups being different. Thedescriptive design was used for observations, surveys and interviews, case studies and historical designsinvolving collecting historical data to understand and learn from the past. The data also used to demonstrate causal effect relationship between the concentrations and cancer prevalence in the study area.

This study used the multistage sampling method using the stratified and the simple random sampling methods in stages (Qeadan, 2015). The population was partitioned into two groups basing on their geographical set up of the Kimwarer sub-catchment and the probable impacts from the mining activities.Upper Kimwarer being at the farthest area from the mining belt and also located at the highlands formed the unexposed group which was the control group.Middle Kimwarer andLower Kimwarer formed one group of the exposed population. The exposed group lives within and close to the mining belt and their locality falls in the Great Rift Valley.

Simple random sampling was used to get 59 peoplein UpperKimwarer, 118 from Middle Kimwarer and 178 from Lower Kimwarer out of the a total population of 369, 998.The sample size in each zone was selected proportionate to the area coverage and the population in the study area. The data on household interviews were collected using the administration of structured questionnaire that was conducted in the sampled households.

The Cross sectional study was carried out to estimate a population parameter of cancer prevalence in the population. The prevalence of cancer which is qualitative variable to know the proportion of adults who were sick in a population within Kimwarer sub-catchment. The sample size for this epidemiological survey was calculated using the stated formula to estimate proportion of the target population(Charan and Biswa, 2013).The study descriptive cross-sectional was chosen in view of the fact that, it is a small-scale study of relatively short duration and it involves a systematic collection and presentation of data to give a clear picture of cancer situation.According to the annual reports from five health facilities within Kimwarer sub-catchment found out that about 30% of the sick in the health facilities have conditions similar to those caused by heavy metals and pollution from mining industries(PHO, 2010).

$$\mathbf{n = \frac{Z^2pq}{d^2}} \text{..} \textbf{Equation 1}$$

Where:

n= the desired sample size

Z= the standard normal deviate at 95% confidence interval which is 1.96.

p=the proportion of population with ill effects related to heavy metals. According to the Sugutek-Kimwarer Community Group (KNA, 2005) approximately 30% of the sick have conditions similar to those caused by heavy metals and pollution from the mining industries.

q= 1- p

d = acceptable sampling error (5%)

Using Equation 1the total sample size was 355people inclusive of the 10%non-response rate. Information on the health cases records were abstracted from existing records in the health facilities in the study areas. These included Nyaru health centre in the Upper zone, Turesia dispensary in the Middle zone and Muskut, Kimwarer health centers and ChebireiNYS dispensary at the Lower zone.

3.4.2 Selection of Sampling Stations

Kimwarersub-catchment was divided into three zones; the Lower (LK), the Middle (MK) and the UpperKimwarer (UK) zonesas shown inFigure 3-1. These zones were selected on the basis of the distances or the proximity to the mining belt, on the altitudes and topography of the sub-catchment.The UpperKimwarer zone is located in the highlands which is the source of Kimwarer River. It is the furthest zone, about 20-25km on the windward direction from the mining site. The Elgeyo escarpment separates the UpperKimwarer from the MiddleKimwarer zone. The villages which were sampledin Upper Kimwarer included: Kibonge, Kewabsui, Hz Company, Tambul, and Kiparus.MiddleKimwarer zone is located in between the Upper on the western side and the LowerKimwarer in the Eastern side. It has a range of 10-15km from the mining site.

The villages inMiddleKimwarerwhere sampling was done included: Turesia, Kowochi, Kapchi, Tarita and Kapchepno. LowerKimwarer zone is where the mining site, factory and most of the residential areas for the company workers are located. Both the Middle and the LowerKimwarer zone are located within the Great Rift Valley; the Middle part is on the slopes and the LowerKimwarer is located on the base of the valley. Villages in LowerKimwarer where sampling was done included; Muskut, Kabokbok, Kimwarer, Kewabmwen and Chepsirei.

The sampling design used was the multistage sampling namely the stratified and simple random sampling methods combined in stages**.** Stratified sampling method was used in selecting the three zones Upper Kimwarer, Middle Kimwarer and Lower Kimwarerzones. A total of 15 sampling siteswere purposely selected for sampling in the study area where each zone had5households.A total of 90duplicate samples of soils, drinking water, cereals (maize, millet, beans) and milk werecollected from each selected households within the selected villages each season.The sample collection was done during the drywet seasons to bring out the seasonality variations for the 24 months from December 2012 to December 2014. The human hair was collected from ten(10) people at the barber shops one in each zone totaling to 30 duplicate hair samples. The hair was collected from the people who had been residing in the study area for the last 5 years and above. The collection of the hair samples were done from July 2016 to November 2016 due to the delay in acquiring the permit from Moi Teaching and Refereal Hospital, Institute of Reaearch Ethics Committee

3.5 Sample and Data Collection

In preparation for the field work, all the required equipment were prepared, cleaned and packed. The plastic bottles for water samples were soaked in nitric acid and sulphuric acid solution of 1:1 volume ratio, washed in about 2 litres of tap water and rinsed three times in distilled water then dried prior to fieldwork.

3.5.1 Sampling of Water

Water samples were collected in pre-cleaned 0.5L polyethylene bottles. Water samples were collected in duplicates from each of the five sampling stations. In total 60 water samples werecollected from rivers, springs, taps and wells using a bucket close to the homesteads where the soil and cereals were taken. . The water was then poured into the sampling bottles.The water samples destined for determination of heavy metals were acidified tolower pH to 1.5-2 by adding 2 drops of concentratednitric acidaccording to

(Davis 1996), to prevent absorption of dissolved heavy metals to interior walls of the storage bottles precipitation and minimizing post microbial activity. After treatment, water samples were placed into an icebox at 4°C and transported to the University of Eldoret School of Environmental Studies Biochemical Laboratory for temporary storage and analysis.

3.5.2 Sampling of Soil

A total of 60 soil samples were collected during the study. Two samples were collected in each sampling station (village) in each zone in dry and wet season. Two composite near surface (10-30cm) soil samples were collected from each sampling site. Using the assembled sectional auger soil samples were collected from the corners of the $2m^2$grid in accordance with (Fordyce *et al*., 2000), from whence soil was scooped and homogenized on a plastic sheet. A 1 kg set sample was collected from the composite using a quartering method and put into a tight plastic container to retain the moisture content (Fordyce*et al*., 2000) and then transported to the laboratory for storage, preparation and then for analyses of the selected heavy metals.

3.5.3 Sampling of Cereals

A total of 60 food samples were collected from the farms within the homesteads close to where the soil samples were collected and stored in polythene bags. Duplicate samples of each cereal namely maize, millet and beans were collected during the study period.

3.5.4 Sampling of Milk

Milk samples were collected from homesteads close to where the soil samples were collected and stored in 100ml plastic bottles. A total of 60 milk samples were collected during the study period and the milk collected were from the cows within the area of study.Freshly drawn milk which contains air and gaseswas allowed to cool for one hour as per procedures (Barbano & Lynch, 2006).

3.5.5 Sampling of Human Hair

Hair samples were obtained from the people at the barber salons. The hair samples collected were for men above 18 years old. A total of30 hair samples of approximately125 milligrams or one full teaspoon of hair each were collected during the study period with 10 hair samples from each of the three zones.The hair samples were put in envelopesafter collecting sufficient weight of dry hair and stored in the laboratory awaiting analysis.

3.5.6 Epidemiological Survey

Prevalence of cancer and non-carcinogenic diseases

A cross sectional survey was conducted within the three zones in the study area and the requisite research ethics followed. Confidentiality of the information obtained was respected and the data recorded under a coded system and the names of individuals were avoided. The responses were confined to the set of questions in the questionnaire (Appendix I).

Amount of water, milk and cereals consumed

The questionnaire with structured questions (Appendix 1) was used to determine the amounts of water, milk and cereals that were consumed per household during wet and dry seasons in the study area. The amount of water drunk by respondents, the amount of milk consumed by the household per day and the amount of cereals consumed per household per week was determined.

3.6 Sample Preparation, Digestion and Analysis

3.6.1 Preparation of soil, water, milk and cereal samples

The soil samples were divided in 4 portions (quartering) by volume and grinding 50g of dry soil into fine powder by using mortar and pestle. The ground sample was then dried in an oven maintained at 70^oC for 4hrs. The sample was then removed from the oven and placed in a desiccator to cool to constant weight.

3.6.2 Preparation of the Digestion Mixture

The analytical reagent grade ('AR') chemicals were used in preparing the digestion mixture for digestion of soil and cereal samples as stated in (Okalebo et al., 2002 laboratory manual. The chemicalsused to prepare the digestion mixture were Selenium powder (Se), Lithium Sulphate ($Li_2SO_4.H_2O$), Hydrogen peroxide (H_2O_2) and Concentrated Sulphuric Acid (H_2SO_4**).** The digestion mixture was made from adding 0.42g of Selenium powder and 14g of Lithium Sulphate to 350ml 30% Hydrogen Peroxide and mixed well. Then 420ml concentrated $H_2SO_4$was added slowly with care while cooling in an ice bath. The mixture was stored at 2^0C for the analysis.

3.6.3 Soil and Cereal Sample Digestion and Analysis

Digestion of soil and cereals for total metals determination was done using a block Digester (Digestion System 20 1015 Digester. SNO. 3846, Sweden) following the stated procedure by (Okalebo et al., 2002). 0.3±0.001g of finely ground homogenousoven dried (70^{0}C), ground cereal or soil (<0.25mm, 60mesh) were put into a labeled, dry and clean digestion tube. Digestion mixture 4.4 ml digestion mixture was added to each tube and also to 2 reagent blanks for each batch of samples. The mixture and sample was heated at 120^{o}C for 2 hours till the solution turned tocolorless and any remaining sand turned to white. The solution was further heated for 1 hour to ensure all the colored had turned colorless.The contents were allowed to cool and 25ml of deionised water was added and mixed well until no more sediment dissolved. Then allowed to cool and topped up with distilled water to 50ml in a volumetric flask. The digests was allowed to settle, then sieved using a 0.45µmwhiteman filter paper into sample bottles for analysis. Analysis followed by aspirating the samples and standards into AAS.

3.6.4 Milk, water and blank samples preparations

The pre-measured amount of milk and water sample was transferred into a 250ml conical flask. The amount of milk and water taken for digestion was 50ml. 5 ml of concentrated Nitric acid was added to the conical flask and two silicon carbide boiling chips. The solution was heated for 2 hrs but care was taken not to heat the sample to dryness by adding drop of nitric acid. The final volume at the end of digestion was 5ml. The digest was allowed to cool and the sieved using 45um whatman filter paper into a 50ml volumetric flask and the top up to the mark with deionized water. Then transferred into a 50ml polyethylene bottles ready for AAS analysis.

3.6.5 Hair Samples Preparations

Samples (30 pieces) of human hair weighing 20 mg were washed twice with a mixture of ethyl ether/Acetone and then de-ionised water and dried on a clean paper. Once dry the hair was cut into 2-4 cm lengths and 0.5gm were weighed and put into a digestion block test tubes and 2ml of nitric acid and 1ml of H_2O_2 were added. It was then heated at 160^oC for 4hrs following the procedure in (Gang liang et al 2017). The digest was transferred into a 25 ml volumetric flask and was filled to 25 ml mark by adding with de-ionized water and analyzed using the AAS analysis for As, Cd, Cr and Pb.

3.7 LaboratoryAnalysis using AAS

The determination of the concentrations of As, Cd, Cr and Pb in the laboratory was done using air/ acelylene AAS for Cd,Cr andPb and Gas Vapour Generation (GVP) AAS for Arsenic. Varian-Spectra100 AAS Single-Element Calibration Standards for Atomic Spectroscopy were used for the analysis of the metals. The calibration standards of As, Cd, Cr and Pb metals that were used to calibrate the AAS instrument was prepared from 1000 ppm standard stock solution. A working solution of 100ppm of each metal standard was prepared from the sock solution. For each metal analyzed, calibration standards were prepared from the working solution based on their linear range as provided in instrument manual

Arsenic Analysis

Arsenic calibration standard solution was prepared by diluting the 100mg/l earlier prepared working solution to give 1.5mg/l, 2.0mg/l and 2.5mg/l of arsenic. All calibration standard solutions were freshly prepared the day of analysis from the working standard solution. The carrier solution for As determination was a 10% (v/v) hydrochloric acid (HCl) solution. The hydride generation reducing agent was an aqueous solution of 0.5% weight/volume (w/v) NaBH4in a 0.05% (w/v) NaOH solution, which were freshly prepared each day.

The samples and standards for arsenic analysis were pre-reduced prior to analysis. This was achieved by adding a reducing solution containing 5% (w/v) KI and 5% (w/v) ascorbic acid. 10ml of standard or sample was placed in a 50 mL polypropylene tube. To this, 1 mL of the reducing solution and 5 mL of concentrated HCl was added. The treated samples or standards were set to stand at room temperature for 30-60 minutes prior to analysis. The tube was brought to the 50 mL mark with deionized water and the peristaltic pump was used to sucks in the borohydride solution, the 10% hydrochloric acid solution and the sample solution.

Cadmium Analysis

Cadmium calibration standards solution was prepared by diluting the 100mg/l working solution to give 0.5mg/l, 1.0mg/l, 2.0mg/l and 2.5mg/l. of Cadium.

Chromium Analysis

Chromium calibration Standard solution was prepared by diluting the 100mg/l working solution to give 0.5mg/l, 1.0mg/l, 2.0mg/l and 2.5mg/l of Chromium

Lead Analysis

Lead calibration Standard solution was prepared by diluting the prepared 100mg/l working solution to give 1mg/l, 2mg/l, 4mg/l and 8mg/l.of lead.

3.8 Quality Control

All the procedures were strictly followed in order to produce quality results. These included the use of high purity analytical grade acids in cleaning and preparation of samples. Calibration of the equipment was done after every batch of the analysis. The contamination of the analysis using AAS was checked using the analysis of blank samples. The readings obtained from the blanks were subtracted from all the concentrations obtained from the analyses.

3.8.1 Daily Dietary Intake

The daily average consumption of water milk maize beans and millet was obtained throughquestionnaires with structured questions on the amount of water consumed per individual per day, the amount of milk the family consumes per day and the amount of maize, beans and millet the family consumed per week. The survey also established that the average number of people per household were five people.

3.8.2The Estimated Daily Intake of Arsenic, Cadmium, Chromium and Lead

The estimated daily intake (EDI) of heavy metals (As, Cd and Pb) depended on both the heavy metal concentration in crops and the amount of consumption of the respective food crop. The EDI of metals was determined by the following equation:

$$\mathbf{Estimated Daily Intake (EDI)} = \frac{C_{metal} x W_{food/water}}{B_w} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{Equation 2}$$

Where: $C_{metal}$is the concentration of heavy metal in the contaminated cereal, milk or water (mg/kg) or (mg/L); $W_{food/\ water}$ represent the daily average consumption of food or water in the study area and $B_w$is the bodyweight considered was 60 kg and 70Kg respectively.

The health risk posed to consumers was determined by the specific dietary intake of each contaminant and compared with toxicologically acceptable levels.Agency for Toxic Substance and Disease Registry recommended Minimal Risk Levels for Arsenic; acute 0.005mg/Kg/day and chronic 0.003mg/Kg/day, Cadmium; intermediate 0.0005mg/Kg/day and chronic 0.0001, Chromium; 0.005mg/Kg/day and 0.009mg/kg/day(CDC, 2015).

3.8.3 Chronic Daily Intake of Chemicals

Chronic Daily Intake of chemical, $mgkg^{-1}BWday^{-1}$ (CDI)is also referred to as Lifetime average daily dose (mg/kg-day) (LADD) which represents the lifetime average daily dose of exposure to the chemical was calculated on the basis of the estimated daily intakeconsumed over a lifetime period as shown in equation 4

$$\mathbf{CDI} = \frac{\mathbf{EDI\ xEFrxEDtot}}{\mathbf{AT}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \mathbf{Equation\ 3}$$

Where: EDI is estimated daily intake of heavy metal through consumption; EFr is exposure frequency (365 days/year); EDtot is the exposure duration 63.3 years and 61.1 for female and male respectively for Kenya; AT is the period of exposure for non-carcinogenic effects (equal to EFr x EDtot), and 70 year life time for carcinogenic effects (i.e., 70 years x 365 days/year).

3.9Arsenic, Cadmium, Chromium and Lead Risk Assessment

3.9.1 Non-carcinogenic Risk Assessment

Non-cancer risks are assumed to exhibit a threshold below which no adverse effects are expected to be observed (Pepper *et al.*, 2012). The non-carcinogenic health hazards were evaluated by the target hazard quotient (THQ) to get a ratio of the chronic dietary intake and the oral reference dose of the contaminant as depicted in Equation 5. The oral reference dose (mg/kg/day) is an estimation of the maximum permissible risk on human population through daily exposure.

$$\mathbf{THQ} = \frac{\mathbf{CDI}}{\mathbf{RfD}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \mathbf{Equation\ 4}$$

Where: CDI is the exposure dose obtained from Eqn (4) and RfD is the oral reference dose of the contaminant. The RfD values for Arsenic, Cadmium, Chromium and Lead are $3.0x10^{-4}$, $1.0x10^{-3}$, $1.5x10^{0}$, $4.0x10^{-3}$ respectively (Harmanescu*et al*., 2011 and Ogwok *et al*., 2014).

Exposure to multiple contaminants results in additive and or interactive effects. Therefore, to evaluate the potential risk to human health through more than one heavy metal, the chronic hazard index (HI) is obtained as the sum of all hazard ratios (THQ) calculated for individual contaminants for a particular exposure pathway (Liu *et al* 2013). The calculated HI is compared to a benchmark; the population is assumed to be safe when HI < 1 and in a level of concern when 1< HI < 5 (Ogwok *et al* 2013).

3.9.2 Cancer Risk Assessment

Potential cancer risks associated with exposure to a measured dose of chemical contaminant was estimated using the incremental lifetime cancer risk (ILCR). This is the incremental probability of an individual developing any type of cancer over a lifetime due to a 24 hour/day carcinogenic exposure to a given daily dose of a chemical for 70 years (Li and Zhang, 2010).

$$\mathbf{ILCR} = \frac{\mathbf{CDI}}{\mathbf{CSF}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \mathbf{Equation\ 5}$$

The ILCR for the selected heavy metal was worked out using respective slope factors of As (1.5),Cd (6.3) and Pb (0.0085) (mgkg-1day-1) in equation 6,where the CDI (chronic daily intake of chemical(mgkg^{-1}BWday^{-1}) represented the lifetime average daily dose of exposure to the chemical.

The US EPA cancer risk considered *de minimus* or acceptable for regulatory purposes is within the range of 1 X 10^{-6} to 1 x 10^{-4}. A value of ILCR of one in a million (1 x 10^{-6}) means that if a million people are exposed, one additional cancer case would be expected

(Pepper *et al*., 2012).The total cancer risk as a result of exposure to multiple contaminants due to consumption of a particular type of food and water was assumed to be the sum of the individual heavy metal incremental risks(Σ ILCR, n=1 to n).

3.9.3 Odds Ratio

Kimwarer sub-catchment was divided into two regions consisting of the exposed region which consisted of the Middle and the Lower Kimwarer where the factor existed. The Unexposed zone consisted of the Upper zone where the factor is absent. The factor and the disease were estimated using the data odds ratio from epidemiological data.

Table 3- 1: Factor and Disease Ratio.

	Disease present	**Disease Absent**
Factor Present	A	B
Factor absent	C	D

Where,

$$\mathbf{Odds\ Ratio} = \frac{\mathbf{cb}}{\mathbf{ad}}\ \mathbf{or}\ \frac{\mathbf{ad}}{\mathbf{cb}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{Equation\ 7}$$

3.10 Data Analysis

3.10.1 Analysis of data on Arsenic, Cadmium, Chromium and Lead concentrations

The data collected were entered, organized, managed and analyzed by MS EXCEL spreadsheet.

Statistical analysis of the data such as mean, standard deviation, odds ratio, one-way analysis of variance (ANOVA) and t-test were performed by SPSS software version 21.The data on the concentrations of heavy metals Arsenic, Cadmium, Chromium and Lead in water, soils, crops and human hair were calculated as mean (±S.D) for each site on each sampling site. One way ANOVA was used to determine whether there was any significant difference between the means of three independent variables (zones).

The significant difference between zones was determined by a post hoc test –Students Newman Kaules (SNK) Test. The difference between dry and wet seasons wasanalyzed using student t-test. Spatial temporal variations in heavy metals concentrations were examined by one-Way ANOVA (Michael &Douglas, 2004).The independent interrelationships between heavy metals in water, soil, crops, hair and cancer were examined using Pearson's Correlation (Zar, 2001), where coefficient of variations was established from multiple R-square statistics. Significance was declared at $p \leq 0.05$ for all analysis.

3.10.2 Epidemiological Data Analysis

The data was analyzed using descriptive statistics.The mean and standard deviations were used for analyzing continuous variables such as number of cancer cases, distance from the mining belt and years of exposure.

CHAPTER FOUR

RESULTS

4.1 Introduction

This chapter presents the results obtained from the study. The data obtained is summarized, interpreted and presented in tables and figures.

4.2 Concentration of the Arsenic, Cadmium, Chromium and Lead

The concentration of the selected heavy metals As, Cd, Cr and Pb in soils, water, maize, millet, beans and milk in the three zones of the Upper, Middle and LowerKimwarer sub-catchment during the entire period of the study are presented in the sub sequent subsections.

4.3 Spatial and temporal metal concentration in the environment

4.3.1 Concentration of Arsenic, Cadmium, Chromium and Lead in soils

Concentration of Arsenic in soil

The results showed that there was significant difference in the level of Arsenic between seasons in Lower and MiddleKimwarer ($P<0.05$, T-test at 95% CL).In Upper Kimwarer region the levels of Arsenic in the soil was not significantly different during the dry season as compared to the wet season ($p = 0.083$, T-test at 95% CL).During the dry season the levels of Arsenic was significantly higher in LowerKimwarer as compared to Upper and MiddleKimwarer ($p = 0.014$,One way ANOVA,SNK, t-test). The wet season had a significantly higher levels of Arsenic inLowerKimwarer as compared to Upper and

MiddleKimwarer ($p<0.001$,one-way ANOVA,SNK, t-test). The results of Arsenic concentration is shown in Table 4-1.

Table 4- 1: Concentration of Arsenic in the soil.

	UK (µg/g)	MK (µg/g)	LK (µg/g)	p-value	Standard (mg/kg dry weight)
Dry	3.19±1.47[a]	5.44±0.79[a]	27.31±7.71[b]	0.014	3.0
Wet	0.22±0.04[a]	1.49±0.51[a]	5.71±0.91[b]	<0.001	
p-value	0.083	0.002	0.016		

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA,SNK, t-test,$\alpha=0.05$)

The concentrations of Arsenic in soil were all above ecological screening levels of 3.0mg/Kg dry weight (USEPA, 2005) except for Arsenic levels in Upper and Middle Kimwarer during wet season. The lowest level of Arsenic in soil was 0.22±0.04mg/l in Upper Kimwarer during the wet season and the highest level was 27.31±7.71[b] mg/l in Lower Kimwarer in dry season.

Concentration of Cadmium in soil

The levels of Cadmium in the soil during the dry seasons were 4.92±0.22 µg/g, 5.26±0.19 µg/g and 73.39±14.87 µg/g in Upper,Middle and LowerKimwarer respectively.In the wet season the concentration of Cadmium in the soil were 6.39±0.20 µg/g, 6.18±0.17 µg/g and 5.56±0.22 µg/g in Upper,Middle and LowerKimwarer respectively.T-test showed that the concentration of Cadmium differed significantly between the wet and dry season ($p<0.05$ at 95%CL) in all zones. The results of Cadmium levels are shown in Table 4-2.

Table 4- 2: Concentration of Cadmium in soil.

Season	U.K (µg/g)	M.K (µg/g)	L.K (µg/g)	p-value	Standard
Dry	4.92±0.22[a]	5.26±0.19[a]	73.39±14.87[b]	<0.001	0.1
Wet	6.39±0.20[a]	6.18±0.17[ab]	5.56±0.22[b]	0.032	mg/Kg dry weight
p-value	<0.001	0.004	0.001		

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA,SNK, T-test,α=0.05). The concentrations of Cadmium in soil were all above ecological screening levels of 0.1 mg/Kg dry weight (USEPA, 2005). The lowest level of Cadmium in soil was4.92±0.22mg/Kg in Upper Kimwarer during the wet season and the highest level was73.39±14.87 mg/l in Lower Kimwarer in dry season.

Concentration of Chromium in soil

The concentration of Chromium during the dry season in LowerKimwarer was 18.74±7.02 µg/g while in the wet season it was 4.54±0.29 µg/g however the variation between the two season were not statistically significant ($p = 0.068$,T-test,$\alpha=0.05$).The levels in the Upper and MiddleKimwarer were 4.09±0.08µg/gand 4.66±0.48µg/g during the dry season while the levels in wet season were 3.73±0.06µg/gand 3.14±0.05µg/g for Upper and MiddleKimwarer respectively. T-test showed that the levels of Chromium differed significantly between the seasons in Upper and MiddleKimwarer ($p<0.05$). Chromium conentations are shown in Table 4-3.

Table 4- 3: Concentration of chromium in Soil.

Season	UK (µg/g)	MK (µg/g)	L.K (µg/g)	p-value	Standard
Dry	4.09±0.08	4.66±0.48	18.74±7.02	0.091	13.4 mg/kg dry weight
Wet	3.73±0.06^{ab}	3.14±0.05^{a}	4.54±0.29^{b}	<0.001	
p-value	0.005	0.031	0.068		

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, SNK, t-test,α=0.05).

The concentrations of Chromium in soil were all within the ecological screening levels of 13.4 mg/kg dry weight (USEPA, 2005) except for Chromium levels in Lower Kimwarer in dry season. The lowest level of Chromium in soil was 3.14±0.05 mg/kg in

Upper Kimwarer during the wet season and the highest level 18.74±7.02mg/l in Lower Kimwarer in dry season.

Concentration of Lead in soil

The concentration of Lead in the soil in the Upper,Middle and LowerKimwarer were 5.12±1.09 µg/g, 8.26±0.67 µg/g and 16.20±4.08 µg/g respectively in the dry season while in the wet season the levels were 4.10±0.94 µg/g, 9.74±1.35 µg/g and 10.13±1.07 µg/g for Upper, Middle and Lower respectively.There was no significant variation between the season in all the sites (p>0.05,T-test at 95% CL).The results of Lead levels are shown on Table 4-4.

Table 4- 4: Concentration of Lead in soil.

Season	U.K (µg/g)	M.K(µg/g)	L.K (µg/g)	p-value	Standard mg/Kg
Dry	5.12±1.09	8.26±0.67	16.20±4.08	0.052	5.0 dry weight
Wet	4.10±0.94^{a}	9.74±1.35^{b}	10.13±1.07^{c}	0.010	
p-value	0.499	0.294	0.241		

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, Student Newman Kaules, T-test,α=0.05)

The concentrations of Lead in soil were all above the ecological screening levels of 5.0 mg/kg dry weight (USEPA, 2005) except for Lead concentrations in Upper Kimwarer in wet season. The lowest level of Lead in soil was 4.10±0.94 mg/Kg in Upper Kimwarer during the wet season and the highest level was 16.20±4.08 mg/l in Lower Kimwarer in dry season.

The trend in Arsenic, Cadmium, Chromium and Lead in the study area showed a trend of higher concentrations in dry season than in the wet season Similar results were obtained in previous studies by (Osobamiro & Adewuyi, 2015) which established that seasons, agronomic practise, and soil geological make-up do affect the level of heavy metals soils.

4.3.2 Concentration of Arsenic, Cadmium, Chromium and Leadin water

The concentration of Arsenic, Cadmium,Chromium and Lead in water in Upper Middle and LowerKimwarer are presented in the subsequent subsection.

Concentration of Arsenic in water

The levels of Arsenic in water in the Upper, Middle and LowerKimwarer were3.67±0.77mg/L,5.39±1.01mg/L and 15.59±1.37mg/L respectively during the dry season while the levels were 2.36±1.29mg/L,3.50±0.57mg/L and 7.39±2.07mg/L in Upper,Middle and LowerKimwarer respectively during the wet season. There was no significant variation in the level during the wet and dry season in Upper and MiddleKimwarer ($p>0.05$,T-test,$\alpha=0.05$).However, the levels of Arsenic differed significantly between the dry and wet season in LowerKimwarer($p=0.003$,T-test,$\alpha=0.05$). The levels of Arsenic in water is shown in Table 4-5

Table 4- 5: Concentration of arsenic in water.

Season	U.K (mg/L)	M.K(mg/L)	L.K(mg/L)	p-value	Max. allowable levels- mg/l
Dry	3.67±0.77[a]	5.39±1.01[a]	15.59±1.37[b]	<0.001	WHO-0.001
Wet	2.36±1.29	3.50±0.57	7.39±2.07	0.102	
p-value	0.408	0.097	0.003		

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, SNK, T-test,α=0.05)

The concentrations of Arsenic in water were all above US Food and Drug Administration Maximum Allowable levels of 0.01mg/l in all the Zones. The lowest level was 2.36±1.29mg/l in Upper Kimwarer during the wet season and the highest level (15.59±1.37mg/l) in Lower Kimwarer in dry season.

Concentration of Cadmium in water

The results for concentration of Cadmium in water showed the levels did not vary significantly between dry and wet season in Upper ,Middle and LowerKimwarer (p>0.05,T-test,95%CL).T-test showed that the concentration of Cadmium in water differed significantly between the wet and dry season (p<0.05 at 95%CL).

Table 4- 6: Concentratio of cadmium in water.

Season	UK (mg/L)	MK(mg/L)	LK(mg/L)	p-value	Max. allowable level
Dry	3.24±0.51[a]	4.18±0.53[a]	9.62±1.65[b]	0.005	WHO- 0.001 mg/l
Wet	2.20±0.49[a]	2.90±0.62[ab]	11.64±1.50[b]	<0.001	
p-value	0.163	0.128	0.460		

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, SNK-test,α=0.05)

The concentrations of Cadmium in water in all were all above US Food and Drug Administration Maximum Allowable levels of 0.005mg/l in all the Zones. The lowest level was 2.20±0.49mg/l in Upper Kimwarer during wet season and highest level (11.64±1.50 mg/l) in Lower Kimwarer in dry season.

Concentration of Chromium in water

The levels of Chromium in water in Upper,Middle and LowerKimwarer were 3.16±0.98mg/L 4.35.±0.75mg/L and 7.27±1.18 mg/L respectively during the dry season while during the wet season the levels were 1.31±0.45mg/L, 4.39±0.44mg/L and 10.47±1.62mg/L in Upper,Middle and LowerKimwarer respectively.The variation of season did differ significantly ($p<0.05$,T-test,α=0.05).

Table 4- 7: Concentration of Chromium in water

Season	UK (mg/L)	MK (mg/L)	LK (mg/L)	p-value	Max allowable level
Dry	3.16±0.98[a]	4.35.±0.75[a]	7.27±1.18[b]	0.005	WHO 0.005mg/l
Wet	1.31±0.45[a]	4.39±0.44[ab]	10.47±1.62[b]	<0.001	
p-value	0.090	0.955	0.137		

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, SNK, T-test,α=0.05)

Chromium levels in water were all above US Food and Drug Administration Maximum Allowable levels of 0.005mg/l in all the Zones. The lowest concentration was 1.31±0.45mg/l in Upper Kimwarer during wet season and highest levelwas 10.47±1.62mg/l in Lower Kimwarer in wet season.

Concentration of Lead in water

The levels of Lead in water in Upper, Middle and LowerKimwarer were 3.84±0.61 mg/L 5.56±1.00 mg/L and 18.18±0.95 mg/L respectively during the dry season while during the wet season the levels were 3.68±0.90mg/L , 3.73±0.67 mg/L and 14.12±1.97 mg/L in Upper, Middle and LowerKimwarer respectively. The variation of season did differ significantly ($p>0.05$,T-test,$\alpha=0.05$). The results on the levels of Lead in water is shown in Table 4-8.

Table 4- 8: Concentration of Lead in water.

Season	UK (mg/L)	MK (mg/L)	LK (mg/L)	p-value	Standard
Dry	3.84±0.61[a]	5.56±1.00[a]	18.18±0.95[b]	<0.001	FDA
Wet	3.68±0.90[a]	3.73±0.67[a]	14.12±1.97[b]	<0.0001	0.005mg/l
p-value	0.880	0.127	0.046		

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, SNK, T-test, α=0.05)

The concentrations of Lead in water were all above US Food and Drug Administration Maximum Allowable levels of 0.005mg/l in all the Zones. The lowest level (2.20±0.49mg/l) was in Upper Kimwarer during wet season and highest level of Lead were (11.64±1.50 mg/l) in Lower Kimwarer in dry season.

The trend in Arsenic, Cadmium, Chromium and Lead in the study area showed a trend of higher concentrations in dry season than in the wet season. Previous studies (Mondol et al., 2010) concurred with the results that heavy metal concentration at different sampling points varied in different seasons and the maximum amount was observed in the dry. (Koulousaris *et al*., 2009) found out that concentrations of heavy metals in rain water depends on different factors such as vicinity of sources, the amount of precipitation and direction of air masses. Mondol et al., 2010 eplained why the concentration of the heavy metals in the water was low. The study concluded that in the rainy season the pollution was lower because of heavy rainfall.

4.4 Arsenic, Cadmium, Chromium and Lead levels in milk and cereals

4.4.1 Concentration of Arsenic, Cadmium, Chromium and Lead in milk

The levels of Arsenic,Cadmium,Chromium and Lead in milk in the three zones in Kimwarer sub-catchment are shown in the subsequent sections

4.4.2 Concentration of Arsenic in milk

The results showed that the levels of Arsenic in the milk had no significant differences during the dry season as compared to the wet season in the Upper Kimwarer ($p = 0.1129$, T-test at 95% CL). The Middle Kimwarer($p = 0.151$,T-test at 95% CL), and LowerKimwarer($p =0.218$,T-test at 95% CL) had also similar results or no significant difference.There was a significant difference in the level of Arsenic between seasons in Lower and MiddleKimwarer ($P<0.05$, T-testat 95% CL. During the dry season the levels of Arsenic were significantly higher in Lower Kimwarer as compared to Upper and Middle Kimwarer ($p = <0.001$, One way ANOVA, SNK, T-test). The results on the concentration of Arsenic in milk is shown in Table 4-9.

Table 4- 9: Concentration of Arsenic in milk.

Season	UK (mg/L)	MK (mg/L)	LK (mg/L)	p-value	Standards
Dry	0.27±0.10[a]	2.20±0.39[a]	0.10±0.20[b]	<0.001	(0.02mg/L)
Wet	0.53±0.13	1.44±0.34	2.65±0.78	0.087	
p-value	0.129	0.151	0.218		

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, SNK, T-test,α=0.05)

The results of mean concentrations of milk in Upper, Middle and Lower Kimwarer Arsenic levels in milk were all above the levels recommended 0.02mg/Kg by CODEX Alimentarius International Food Standards (FAO and WHO, 2015). The lowest concentration 0.27±0.10mg/l in Upper Kimwarer during dry season and highest concentration was 2.65±0.78mg/l in Lower Kimwarer in dry season.

4.4.3 Concentration of Cadmium in milk

The mean concentration of Cadmiumin milk in the Upper, Middle and LowerKimwarer were 2.97±1.01 µg/g, 2.78±0.22 µg/g and 16.98±11.44 µg/g respectively in the dry season while in the wet season the levels were 2.50±1.03 µg/g, 3.23±0.63 µg/g and 0.65 ±0.45 µg/g for Upper, Middle and Lower respectively. There was a significant variation between the wet seasonbetween Upper KimwarerandLower Kimwarer (p>0.05, T-test at 95% CL). The results on the concentration of Cadmium in milk is shown in Table 4-10.

Table 4- 10: Concentration of Cadmium in milk.

Season	UK (mg/L)	MK (mg/L)	LK (mg/L)	p-value	Standards
Dry	2.97±1.01	2.78±0.22	16.98±11.44	0.378	0.02mg/Kg (0.02mg/L)
Wet	2.50±1.03[a]	3.23±0.63[a]	0.65±0.45[b]	0.026	
p-value	0.748	0.513	0.116		

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, SNK, T-test,α=0.05)

The mean concentrations of milk in Upper, Middle and Lower Kimwarer Cadmium levels in milk were all above the levels recommended 0.02mg/Kg by CODEX Alimentarius International Food Standards (FAO and WHO, 2015). The lowest Cadmium concentration 0.65±0.45mg/l in Lower Kimwarer during dry season and highest concentration was 16.98±11.44mg/l in Lower Kimwarer in dry season.

4.4.4 Concentration of Chromium in milk

The results showed that there was no significant difference between the wet and dry season in the Upper, Middle and Lower Kimwarer zones. The p-values for Upper, Middle and Lower Kimwarerwere p=0.261. p=0.439 and p=0.927 respectively. The results of Chromium levels in milk is shown in Table 4-11

Table 4- 11: Concentration of Chromium in milk.

Season	UK(mg/L)	MK(mg/L)	LK(mg/L)	p-value	Standards
Dry	1.24±0.30	1.06±0.26	2.44±0.72	0.172	0.02mg/Kg (0.02mg/L)
Wet	0.78±0.26	0.79±0..23	2.54±0.76	0.674	
p-value	0.261	0.439	0.927		

Mean values followed by the same small letter within the same row do not differ significantlyfrom one another (one-way ANOVA, SNK, T-test,α=0.05)

Results showed that the Chromium levels in milk were all above the levels recommended 0.02mg/kg by CODEX Alimentarius International Food Standards (FAO and WHO, 2015)in Upper, Middle and Lower Kimwarer. The lowest Chromium concentration was 0.78±0.26mg/l in Upper Kimwarer during wet season and highest concentration was 2.54±0.76mg/l in Lower Kimwarer in wet season.

4.4.5 Concentration of Lead in milk

The levels of Lead in milk in Upper, Middle and LowerKimwarer were 3.90±0.68 mg/L 5.49±0.44 mg/L and 4.84±032 mg/L respectively during the dry season while during the wet season the levels were 2.22±0.42mg/L , 3.23±0.46 mg/L and 2.51±52 mg/L in Upper, Middle and LowerKimwarer respectively. The variation of season did differ significantly (p>0.05,T-test, α=0.05) in the Middle and Lower zones. The results Lead levels in milk is shown in Table 4-12.

Table 4- 12: Concentration of Lead in milk.

Season	UK (mg/L)	MK (mg/L)	LK(mg/L)	p-value	Standards
Dry	3.90±0.68	5.49±0.44	4.84±0.32	0.101	0.02mg/Kg (0.02mg/L)
Wet	2.22±0.42	3.23±0.46	2.51±0.52	0.389	
p-value	0.046	0.002	0.006		

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, SNK, t-test,α=0.05)

Results showed that the Lead levels in milk were all above the levels recommended 0.02mg/Kg by CODEX Alimentarius International Food Standards (FAO and WHO, 2015)in Upper, Middle and Lower Kimwarer. The lowest Lead levels were2.22±0.42mg/l in Upper Kimwarer during wet season and the highest concentration was 5.49±0.44mg/l in Lower Kimwarer in the dry season.

Toxicity of heavy metal in animal products is a result of long term exposure to pollution.

The current study showed that the concentration of heavy metals were higher in dry season for all the heavy metals in milk except in Cadmium. (Ziarati et al,, 2019)Stude shows that the heavy metal contamination in milk is a result of cows feeding on heavy metal contaminated animal feed or drinking contaminate d water. hese heavy metals ultimately lead to agricultural land

4.5 Concentration of Arsenic, Cadmium, Chromium and Lead in cereals

4.5.1 Concentration of Selected heavy metals in maize

Maize (Zea mays L.) is an edible flowering plant in the gramineae family and is a warm-season crop that serves as the main food source for humans and animals around the world (Lu et al., 2015). Arsenicresults showed no significant variation between the Upper, Middle Kimwarer zones and Lower Kimwarer zone ($p<0.001$, 95%CL).Cadmium, Chromium and Lead concentrations in maize differed significantly between the Upper and Lower Kimwarerand also between Upper Kimwarer with Lower Kimwarer zone ($p<0.001$, 95%CL). The significant difference in Cd, Cr and Pb concentration in the different zones is a reflection of the concentration of the soils where the plants are drawing their nutrients.

Heavy metal levels in maize showed that the lowest heavy metal concentration was Chromium 0.95 ±0.50µg/g in Upper Kimwarer and highest was Cadmium19.17±2.82µg/g both in Lower Kimwarer. Upper Kimwarer had the lowest levels in all the heavy metals except for Lead levels whose lowest concentration was in the Middle Kimwarer zone. Lower Kimwarer had the highest levels of the heavy metal except Arsenic which had highest levels in Middle Kimwarer. Hence the heavy metal concentration in descending order as per the zones was Lower Kimwarer>Middle Kimwarer>Upper Kimwarer. The order of concentrations from the highest in Upper Kimwarer was Pb>Cd>As>Cr, Middle Kimwarer was Cd>As>Cr>Pb and Lower Kimwarer was Cd>Cr>Pb>As.

The overall order of heavy metal concentrations from the highest in all the zones was Cd>Cr>Pb>As. The order of heavy metal concentrations from the highest in Upper Kimwarer was Pb>Cd>As>Cr, Middle Kimwarer was Cd>As>Cr>Pb and Lower Kimwarer was Cd>Cr>Pb>As. Concentration of selected heavy metals in maize is shown in Table 13

Table 4- 13: Concentration of Selected Heavy Metals in Maize.

	UK (μg/g)	MK (μg/g)	LK (μg/g)	p-value	Reference (mg/kg)
As	2.31 ±1.12	4.36±0.96	2.13±0.12	0.107	0.1
Cd	3.41 ±0.81[a]	4.57±0.38[a]	19.17±2.82[b]	<0.001	0.1
Cr	0.95 ±0.50[a]	3.81±0.78 [a]	15.23±1.63[b]	<0.001	Not available
Pb	3.71±0.88[a]	2.31±0.82[a]	10.83±0.79[b]	<0.001	0.2

Mean values followed by the same small letter within the same row do not differ Significantly from one another (one-way ANOVA, SNK, α=0.05)

The mean concentrations of As, Cd and Pb in maize in Upper, Middle and Lower Kimwarer were above recommended level of As and Cd by CODEX Alimentarius Commission. The CODEX Alimentarius International Food Standards levels for maize are 0.1mg/kg, 0.1mg/kg and 0.2 mg/kg for As, Cd and Pb respectively (FAO and WHO, 2015). Previous studies in China showed concentration of Cr and Pb in maize with mean values of 0.23 and 0.49 mg/kg respectively. However, Cr and Pb concentrations were generally higher in the current study. The same study showed that maize is a potential accumulator plant, which can be used to decrease the pollution level by harvesting, disposing of, and recovering the plant material. A similar study done by (Akenga et a., 2017) on heavy metals uptake in maize grains in Uasin Gishu County indicated elevated levels of Cd in maize grains which were above the WHO standard.

4.5.2 Concentration of selected heavy metals in beans

Beans are one of the common foods that are being consumed by residents in the study area. The results showed no significant variation in Arsenic, Cadmium and Lead concentrations in beans between Upper and Lower Kimwarer and also between Middle and Lower Kimwarer ($p > 0.05$, One way ANOVA, SNK). However, Chromium concentrations in beans varied significantly between Upper and Lower Kimwarer and also between Middle and Lower Kimwarer ($p = 0.033$, One way ANOVA, SNK).

Heavy metal levels in beans showed that the lowest heavy metal concentration was Chromium 1.28±0.64 µg/g in Middle Kimwarer and highest was Lead 17.24±2.30 µg/g both in Lower Kimwarer. Upper Kimwarer had the lowest levels in all the heavy metals except for Cadmium levels whose lowest concentration was in the Middle Kimwarer zone. Lower Kimwarer had the highest levels in all heavy metals in the study area. Therefore, Lower Kimwarer had the highest level of heavy metals followed by Middle Kimwarer then Upper Kimwarer with the least levels. The order of heavy metal concentrations from the highest in Upper Kimwarer was Pb>Cd>As>Cr, Middle Kimwarer was Cd>As>Pb>Cr and Lower Kimwarer was Pb>Cr>Cd>As. The overall order of heavy metal concentrations from the highest in all the zones was Pb>Cd>Cr>As. Concentration of selected heavy metals in beans is shown in Table 4-14

Table 4- 14: Concentratio of Selected Heavy Metals in Beans.

	UK (µg/g)	MK (µg/g)	LK (µg/g)	p-value	Reference (mg/kg)
As	2.56±1.23	4.39±0.70	9.09±2.78	0.122	0.1
Cd	2.98±1.07	5.66±1.52	12.33±8.45	0.561	0.1
Cr	2.44±1.37[ab]	1.28±0.64[a]	14.10±4.81[b]	0.033	Not available
Pb	3.33±1.07	4.34±0.76	17.24±2.30	0.205	0.1

Mean values followed by the same small letter within the same row do not differ Significantly from one another (one-way ANOVA, SNK, α=0.05)

The lowest level of heavy metal concentration in beans was Chromium (1.28±0.64µg/g) in Upper Kimwarer and highest level was Lead (17.24±2.30 µg/g) in Lower Kimwarer. The concentrations of As, Cd and Pb in beans in the Upper, Middle and Lower Kimwarer were above the recommended levels by CODEX Alimentarius International Food Standards levels (FAO and WHO, 2003). This implies that the beans are contaminated with Arsenic, Cadmium, Chromium and Lead in Upper, Middle and Lower Kimwarer. Therefore, consumption of beans in the study area is a health risk to the people.

4.5.3 Concentration ofselected heavy metals in millet

The results showed that the levels of Arsenic, Cadmium, Chromium and Lead were significantly higher in millet between Upper and Lower Kimwarer and also between Middle and Lower Kimwarer ($p<0.05$, One way ANOVA, SNK). The lowest heavy metal level in millet was Chromium 1.74±0.16 µg/g in Upper Kimwarer and highest was Cadmium 17.19±2.48 µg/g in Lower Kimwarer. Upper Kimwarer had the lowest levels in all the heavy metals except for Arsenic levels whose lowest concentration was in the Middle Kimwarer zone. Lower Kimwarer had the highest levels in all heavy metals in the study area. Hence the order of concentration in an ascending order per zones was; Upper Kimwarer followed by Middle Kimwarer the Lower Kimwarer. The order of heavy metal concentrations from the highest in Upper Kimwarer was

Pb>As>Cd>Cr, Middle Kimwarer was Pb>Cr>Cd>As and Lower Kimwarer was Cd>As>Pb>Cr overall order of concentrations from the highest in all the zones was Cd>Pb>Cr>As. Concentration of selected heavy metals in millet is shown in Table 3

Table 4- 15: Concentration of selected heavy metals in millet.

	UK (µg/g)	MK (µg/g)	LK (µg/g)	p-value	Reference (mg/kg)
As	3.75±0.47[a]	1.99±0.45[a]	10.26±2.30[b]	0.007	0.1
Cd	3.51±0.83[a]	3.21±0.67[a]	17.19±2.48[b]	<0.001	0.1
Cr	1.74±0.16[a]	4.63±0.67[ab]	10.20±2.77[b]	0.035	Not available
Pb	5.58±1.51[a]	5.02±0.58[a]	10.21±0.42[b]	<0.001	0.2

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, SNK, T-test, α=0.05)

Results on heavy metal concentrations in millet were lowest in Chromium 1.74±0.16µg/g in Upper Kimwarer (1.92±0.44µg/g) and highest in Cadmium (17.19±2.48µg/g) in Lower Kimwarer. The mean concentrations of As, Cd and Pb were above the recommended CODEX Alimentarius International Food Standards of 0.1 mg/kg/g, 0.1mg/kg 0.2 mg/kg respectively in millet of Upper, Middle, and Lower Kimwarer. The CODEX Alimentarius

International Food Standards levels for maize are 0.1mg/Kg, 0.1mg/Kg and 0.2 mg/Kg for As, Cd and Pb respectively (FAO and WHO, 2015). The people within the study area are at risk of cancers and non-carcinogenic diseases caused by Arsenic, Cadmium, Chromium and Lead as they ingest contaminated millet.

In summary, cereals in the current study had the lowest concentration in Chromium (0.34±0.095µg/g) in Upper Kimwarer and highest was 19.17 µg/g) in Lower Kimwarer during both in maize. The highest levels for As, Cd, Cr and Pb in maize were, 4.36±0.96µg/g, 19.17±2.82µg/g, 15.23±1.63µg/g and 10.83±0.79 respectively. In beans the concentrations of As, Cd, Cr and Pb were 9.09±2.78µg/g, 12.33±8.45µg/g, 14.10±4.81µg/g and 17.24±2.30µg/g respectively. For millet, the levels of As, Cd, Cr and Pb were 10.26±2.30 µg/g, 17.19±2.48, 10.20±2.77 and 10.21±0.42 respectively. The order of concentrations from the highest for As was Millet>maize>beans, Cd: maize>millet>beans, Cr: maize>beans>millet and the overall order for all the metals was millet>maize >beans. The observed variation in metal concentrations for analyzed cereals might be due to variable capabilities of absorption and accumulation of metals by the cereal crops (Pandey & Pandey, 2009).

Maize, beans and millet results showed a spatial significant difference in As, Cd, Cr and Pb levels between the zones in the study area ($P<0.05$, 95%CL).All the levels in maize, beans and millet were above the CODEX Alimentarius International Standards of food. This shows that the people consuming these ccontaminated cereals are at risk of suffering from diseases which are associated with the selected heavy metals. Previous studies on Cadmium showed concentrations above the recommended CODEX level in cereals hence a potential hazard to the consumers (Sadovska, 2012).In Poland, Krelowska (1991) found lead levels of 0.07 µg/g in cereals, this result was lower than the results found in the study area. A study done by (Makokha et al., 2012) in Kisumu revealed that Arsenic content in the maize and beans samples ranged between 5.21 to 7.03 µg/100 g. These values are lower than the results obtained in the current study.

4.6 Concentration of Arsenic, Cadmium, Chromium and Lead in human hair

The results showed a significant difference in Arsenic concentration Upper and Lower Kimwarer and also in Middle and Lower Kimwarer($p>0.05$, t-test, $\alpha=0.05$). Cadmium and Chromium levels in all the sites had no significant difference with $p=0.133$ and $p=0.290$ respectively. Lead had a significant difference of $p<0.001$ between the Upper and the Lower and also with the Upper Kimwarer and Lower Kimwarer zones. Concentration of Arsenic, Cadmium, Chromium and Lead in human hair is shown in Table 4-16.

Table 4- 16: Concentration of Arsenic, Cadmium, Chromium and Lead in Human Hair

Mean concentration /Zones	As(μg/g)	Cd (μg/g)	Cr (μg/g)	Pb (μg/g)
UK	0.04 ±0.01[a]	0.55±0.21	1.25±0.37	0.16±0.07[a]
MK	0.18±0.03[a]	1.26±0.33	2.07±0.42	0.53±0.30[a]
LK	2.83±0.50[b]	1.53±0.28	2.81±0.62	2.83±0.50[b]
P-value	<0.001	0.133	0.290	<0.001

Mean values followed by the same small letter within the same row do not differ significantly from one another (one-way ANOVA, SNK, T-test,α=0.05)

The results showed a significant difference in Arsenic concentration Upper and Lower Kimwarer and also in Middle and Lower Kimwarer(p>0.05, T-test,α=0.05). Cadmium and Chromium levels in all the sites had no significant difference with p=0.133 and p=0.290 respectively. Lead had a significant difference of p<0.001 between the Upper and the Lower and also with the Upper Kimwarer and Lower Kimwarer zones.

4.7 Correlation ofArsenic, Cadmium, Chromium Lead, soil, water, cereals, milk, hair and cancer

Table 4- 17: Correlation of Arsenic levels in soil, water, food hair and cancer prevalence.

	Soil	Water	Milk	Maize	Beans	Millet	Hair	Cancer
Soil	1	.500**	0.229	-0.028	0.235	0.198	0.272	-0.081
Water		1	0.081	0.117	.497**	.449**	-0.006	0
Milk			1	0.079	0.057	.351**	0.07	0.19
Maize				1	-0.006	0.042	0.083	0.122
Beans					1	0.147	0.009	-0.065
Millet						1	-0.265	-0.032
Hair							1	0.14
Cancer								1

**** Correlation is significant at the 0.01 level (2-tailed)**

*** Correlation is significant at the 0.05 level (2-tailed).**

The relationship of the concentrations of Arsenic in soil, water, food and hair, and the prevalence of cancer is shown below. In Kimwarer sub-catchment As in soil had a significant ($P < 0.01$) positive correlation with water sample. The concentration of Asin hair had an insignificant positive correlation to milk, maize and beans and a negative insignificant correlation to water and millet. The concentration of As in hair had a positive insignificant correlation to cancer prevalence in the study area.

4.7.1 Correlations of Cadmium in soil, water, cereals, milk, hair and cancer

The relationship of the concentrations of Cd in soil, water, food and hair, and the prevalence of cancer in Kimwarer sub-catchment is shown in Table 4-19.

Table 4- 18: Correlation of Cadmium in soil, water, food, hair and cancer Prevalence

	Soil	Water	Milk	Maize	Beans	Millet	Hair	Cancer
Soil	1	0.075	0.043	.725**	0.17	.333*	-0.174	-0.048
Water		1	.439**	0.138	-0.028	.631**	0.078	-0.097
Milk			1	.583**	-0.137	0.242	0.216	-0.051
Maize				1	.367**	0.127	-0.018	-0.018
Beans					1	.315*	-0.047	0.011
Millet						1	-0.186	-0.013
Hair							1	-0.009
Cancer								1

**** Correlation is significant at the 0.01 level (2-tailed)**

*** Correlation is significant at the 0.05 level (2-tailed).**

In the study area Cd in soil had a significant ($P < 0.01$) positive correlation with maize and a significant ($P < 0.05$) positive correlation to millet. Water had a significant ($P < 0.01$) positive correlation to milk. The concentration of Cd in hair had an insignificant negative correlation to maize, beans and millet. The concentration of Cd in hair had an insignificant negative correlation to maize, beans and millet. The concentration of Cd in hair had an insignificant negative correlation (P<0.01) to cancer prevalence.

4.7.2 Correlations ofChromium insoil, cereals, milk, hair and cancer

The relationship of the concentrations of Cr in soil, water, food and hair, and the prevalence of cancer is shown in Table 4:20.

Table 4- 19: Correlation of Chromium in soil, water, food, hair and cancer prevalence.

	Soil	Water	Milk	Maize	Millet	Hair	Beans	Cancer
Soil	1	0.25	.326*	0.189	.353*	-0.188	0.032	-0.043
Water		1	.594**	.457**	.645**	-0.098	0.026	-0.037
Milk			1	0.077	.643**	-0.085	.310*	-0.042
Maize				1	0.032	0.026	.360**	-0.142
Millet					1	-0.233	0.051	-0.032
Hair						1	-0.137	-0.029
Beans							1	-0.085
Cancer								1

**** Correlation is significant at the 0.01 level (2-tailed)* Correlation is significant at the 0.05 level (2-tailed).**

In the study area Cr in soil had a significant (P < 0.01) positive correlation with milk and a significant (P < 0.05) positive correlation to millet. Chromium in water had a significant (P < 0.01) positive correlation to millet, milk and maize. Chromium in hair had an insignificant positive correlation to maize and a negative insignificant correlation to water, milk and millet. Chromium in hair had a significant negative correlation (P> 0.01) (2-tailed) to cancer prevalence.

4.7.3 Correlations ofLead insoil, water, cereals, milk, hair and cancer

The relationship of the concentrations of Pb in soil, water, cereals, milk and hair, and the prevalence of cancer is shown in Table 4-21.

Table 4- 20: Correlation of Lead in soil, water, food, hair and cancer prevalence.

	Soil	Water	Milk	Maize	Beans	Hair	Millet	Cancer
Soil	1	.327*	0.192	.379**	.399**	-0.023	.441**	0.064
Water		1	0.103	.348**	.727**	-0.053	.643**	-0.105
Milk			1	0.166	0.123	.403**	0.173	-0.143
Maize				1	0.183	-0.024	.548**	-0.138
Beans					1	-0.059	.616**	-0.093
Hair						1	-0.11	0.206
Millet							1	0.048
Cancer								1

**** Correlation is significant at the 0.01 level (2-tailed)**

*** Correlation is significant at the 0.05 level (2-tailed).**

In the study area Pb in soil had a significant (P < 0.01) positive correlation with maize, beans and millet. Water had a significant (P < 0.01) positive correlation to millet, maize and beans.Lead in hair had a significant positive correlation to milk and a negative insignificant correlation to water, maize and beans. The concentration of Pbin hair had a positive significant correlation (P>0.01)to cancer prevalence.

The results showed that in overall, there was no correlation of heavy metal concentration in water, food, hair and cancer that had a significant relationship between the concentrations of the metal to cancer except for concentration of Lead in milk between hair and cancer which had a weak relationship of r=0.0403.

4.8 Exposure ofArsenic, Cadmium, Chromium and Lead consumed in water and cereals

4.8.1 Amount of Food consumed

The daily average consumption of water milk maize beans and millet is the amount of water and milk consumed per individual per day, and amount of maize, beans and millet the family consumes per week. The amount of food and water consumed in the study area is shown in Table 4-21

Table 4- 21: Amount of food and water consumed.

Food type	UK Mean±SE	MK Mean±SE	LK Mean±SE	p-value
Water (L/day/person)	0.246±0.014	0.269±0.010	0.269±0.006	0.432
Milk (L/day/person)	0.417±0.0.08	0.362±0.028	0.311±0.016	0.118
Maize (Kg/person/day)	0.1007±0.038[a]	0.219±0.124[b]	0.1945±0.076[b]	0.011
Beans (Kg/person/day)	0.0643±0.068	0.077±0.05	0.0643±0.028	0.249
Millet (Kg/person/day)	0.268±0.066	0.230±0.036	0.232±0.022	0.586

The results on the amount of food showed a significant difference in maize between Upper and Middle and between Upper and Lower. There was no significant difference between the Middle and Lower Kimwarer. There was no significant difference between dry and wet seasons in the Upper, Middle and Lower Zones.

4.8.2 Estimated Daily Intake of Arsenic, Cadmium, Chromium and Lead in water, milk and cereals

The results showed that the people exposed to As had23.4% of all As resultsbelow the Agency for Toxic Substances and Disease Registry (ATSDR) (CDC, 2015)Minimal Risk Levels (MRL)of acute-0.005mg/Kg/dayand all the results were above the chronic levels. These was Arsenic in milk, maize and beans in Upper Kimwarer, beans in Middle for both male and female except in Lower Kimwarer which was only below for the men.The EDI for Cadmium had 10% of Cd resultsbelow intermediate (0.0005mg/Kg/day)for

ATSDR (CDC, 2015)Minimal Risk Levels inbeans for both female and male in Upper Kimwarer and maize in male also in the Upper zone. For the chronic levels all the Cd results were above the ATSDR recommended MRL levels of 0.0001mg/Kg/day. Estimated Daily Intake of metals in drinking water, milk and cereals is shown in Table 4-22

Table 4- 22: Estimted Daily Intake of metals in drinking water, milk and cereals.

Site	Food type	Amount of food/person/ day	Sex	As mg/L/day mg/Kg/day	Cd mg/L/day mg/Kg/day	Cr mg/L/day mg/Kg/day	Pb mg/L/day mg/Kg/day
UK	Water	0.246 L	M	0.0105	0.0095	0.0079	0.0131
			F	0.0123	0.0111	0.0092	0.0153
	Milk	0.417 L	M	0.0025*	0.0160	0.0060	0.0042***
			F	0.0030*	0.0190	0.0060	0.0180
	Maize	0.1007 Kg	M	0.0039*	0.0045	0.0009***	0.0028***
			F	0.0045*	0.0052	0.0055**	0.0032***
	Bean	0.0643 Kg	M	0.0026*	0.0024	0.0021**	0.0019*
			F	0.0030*	0.0028	0.0024**	0.0022***
	Millet	0.268 Kg	M	0.0118	0.0130	0.0078	0.0192
			F	0.0138	0.0151	0.0091	0.0224
MK	Water	0.269 L	M	0.0170	0.0135	0.0168	0.0177
			F	0.0198	0.0158	0.0196	0.0207
	Milk	0.362 L	M	0.0095	0.0155	0.0050**	0.0225
			F	0.0110	0.0180	0.0055	0.0260
	Maize	0.2185 Kg	M	0.0133	0.0128	0.0107	0.0043***
			F	0.0155	0.0149	0.0125	0.0051
	Bean	0.0773 Kg	M	0.0045*	0.0055	0.0018**	0.0043***
			F	0.0052	0.0064	0.0021**	0.0050***
	Millet	0.230 Kg	M	0.0064	0.0104	0.0091	0.0118
			F	0.0074	0.0122	0.0106	0.0138
LK	Water	0.259L	M	0.0423	0.0391	0.0328	0.0594
			F	0.0493	0.0456	0.0383	0.0693
	Milk	0.311 L	M	0.0090	0.0390	0.0110	0.0160
			F	0.0105	0.0445	0.0130	0.0190
	Maize	0.1945 Kg	M	0.0109	0.0328	0.0272	0.0210
			F	0.0127	0.0383	0.0318	0.0245
	Bean	0.0643 Kg	M	0.0063	0.0102	0.0078	0.0106
			F	0.0074	0.0120	0.0090	0.0124
	Millet	0.232 Kg	M	0.0350	0.0419	0.0293	0.0213
			F	0.0408	0.0489	0.0342	0.0249

As: Acute-0.005/ Chronic- 0.0003;Cd: int.-0.0005,Chronic-0.0001;

Cr: int.-0.005Chronic 0.0009; Pb-Acute-0.002 and Pb-Chronic- 0.005

***below acute MRL level (0-14 days)**

****below intermediate MRL level (15-364 days)**

***** Below chronic MRL level (1 year)**

The results showed that the 23.3% of results on estimated daily intake of As were within the acute (0.005mg/Kg/day) MRLs levels. The foods which had the safer levels were milk, maize and beans in Upper Kimwarer for both female and male and bean in Middle Kimwarer for the male. The results on EDI levelsfor Cd were all above the intermediate and chronic levels of 0.0005 mg/Kg/day and 0.0001mg/Kg/day respectively in Cr in all the zones.The EDI results for Cr had 23.3% within the intermediate 0.005mg/Kg/day and 0.33% within the chronic level of 0.0009mg/Kg/day. Lead also had 26.7% of EDI results below the acute levels (0.002mg/Kg/day and 20% within the chronic levels of 0.005mg/Kg/day.

Lead had safer levels followed by Arsenic and Chromium. All the EDIs results for Cd were above the minimal risk levels. The results for all the selected metals had 20% of the total results within the acute minimal risk levels. The EDI results for the intermediate were 9.17% of the total EDI results for the selected metals. For the EDIs within the chronic minimal risk was5.83 % of the total EDI results from all the selected metals.

The summary results on EDI showed that As, Cd and Pb in water and Cd in millet had the highest levels of estimated daily intake in Lower Kimwarer compared to other cereals and milk in Upper and Middle Kimwarer. The concentrations of As, Cd and Pb in beans had the lowest levels of EDIof metals in all the zones in the study area. The EDI of metals in the foods and water results showed that; water: Pb>As>Cd>Cr, milk: Cr>Pb>Cr>As, Maize: Cd> Cr>Pb>As, Beans: Cr>As>Pb>Cd and millet Cd>As>Pb>Cr. The results also showed that the highest concentrations of As, Cd,Cr and Pb in water and food consumed in descending order was water>millet>maize>beans>milk in the study area.

4.9 Risk Assessment

4.9.1 Hazards in Estimated Daily Intake of Arsenic, Cadmium, Chromium and Lead

The summary results showed on Estimated Daily Intake of metal that are above the minimal risk levels as recommended by the Agency for Toxic Substance and Disease Registry (CDC, 2015). showed that the 100 % in water and millet. The EDIs results for all the female had98.5% above the recommended MRLs while the male had a lower value of 97.7% of the EDI results with levels above MRLs in all the zones. The EDI results showed that acute, intermediate and chronic levels were 96.5%, 97.8% and 98.9% above the minimal risk levels of all results studied. The summary of the results for hazards in estimated daily intake of metal for a lifetime period is shown in Table 4-23.

Table 4- 23: Hazards in Estimated Daily Intake of metal.

Water/ Food	EDI results above MRLs (%)					Minimal Risk Levels mg/Kg/day(ATSDR)
	Acute	**Int.**	**Chronic**	**Sex**		
				M	**F**	
Water	100	100	100	100	100	**As-**Acute-0.005
Milk	97.5	98.3	99.2	96.7	99.2	**As-**Chronic-0.0003
Maize	94.2	96.7	96.7	96.7.	97.5	**Cd-**Int.-0.0005
Beans	90.8	94.2	97.5	95	95.8	**Cd**-Chronic-0.0001
Millet	100	100	100	100	100	**Cr-**Int.-0.005
Totals	**96.5**	**97.84**	**98.9**	**97.7**	**98.5**	**Cr**- chronic-0.0009
						Pb-Acute-0.002
						Pb-Chronic- 0.005

The minimal risk levels(MRL) being an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse, non-cancer health effects over a specified duration of exposure. The information in this MRL serves as a screening tool to help public health professionals decide where to look more closely on evaluating possible risk of adverse health effects from human exposure(ATSDR, 2015).

4.9.2 Non-carcinogenic Hazard

The non-carcinogenic health hazards were evaluated using the target hazard quotient (THQ) which is a ratio of the chronic daily intake of metal and the oral reference dose (RfD) of the contaminant as stated in Equation 3. The potential risk to human health through Arsenic, Cadmium, Chromium and Lead was evaluated through the sum of all individual target hazard quotient which results to chronic hazard index (HI). Target Harzads quotients by metal and milk, water amd cereals concumed in Kimwarer is shown in Table 4-24

Table 4- 24: Target Hazard Quotient by metals and milk, water and cereals consumed in Kimwarer.

Heavy Metal	Maize	Milk	Millet	Beans	Water
As	34	25	64	16	84
Cd	36	50	47	13	45
Pb	25	50	47	15	81
HI	95	125	158	44	210

HI = Hazard Index; THQ = Target Hazard Quotient

The results for sum of Target Hazard Quotient showed that all the Hazard Index was above the recommended range of 1<HI which is the benchmark indicating that the

population is safe. The HI levels are also above the level 1<HI<5 where it is considered as a level of concern.

4.9.3 Incremental lifetime cancer risks of adult population through ingestion

The results showed that the incremental lifetime cancer risk (ILCR) were within the US EPA deminimusor acceptable levels for regulatory purposes for Lead in maize in Upper and Middle zone with 2.54 x 10^{-4} and 3.99 x 10^{-4} respectively. Lead in beans was within the levels for regulatory purposed in all the zones. The sum of the ILCR for Arsenic, Cadmium and Lead in water, milk, maize, beans and millet were above acceptable levels of 1 x 10^{-6} to 1 x 10^{-4} in the Upper, Middle and Lower zones which implies a potential cancer risks to the people exposed to these metals. The practical safety was expressed with an ILCR of 10^{-6} or less and a potential high risk was evaluated by an ILCR of higher than 10^{-4} (Wang et al., 2011). Risk management decisions are recommended by U.S. EPA Risk Assessment Guidance for Superfund Program when cancer risk level is at ILCR level of 1x10^{-6}. Incremental lifetime cancer risks of adult population through ingestion is shown in Table 4-25

Table 4- 25: Incremental lifetime cancer risks of adult population through ingestion.

Item	Heavy metal	UK	MK	LK
Maize	As	6.33 x 10^{-3}	2.17 x 10^{-2}	1.76 x 10^{-2}
	Cd	3.04 x 10^{-2}	8.71 x 10^{-2}	2.24 x 10^{-1}
	Pb	2.54 x 10^{-4*}	3.99 x 10^{-4*}	1.94 x 10^{-3}
	∑ILCR	3.70 x 10^{-2}	1.09 x 10^{-1}	2.44 x 10^{-1}
Millet	As	1.92 x 10^{-2}	1.04 x 10^{-2}	5.69 x 10^{-2}
	Cd	8.84 x 10^{-2}	7.11 x 10^{-2}	2.86 x $10^{-}1$
	Pb	1.77 x 10^{-3}	1.09 x 10^{-3}	1.96 x 10^{-3}
	∑ILCR	1.09 x 10^{-1}	8.26 x 10^{-2}	3.45 x 10^{-1}
Beans	As	4.16 x 10^{-3}	7.30 x 10^{-3}	1.02 x 10^{-2}
	Cd	1.61 x 10^{-2}	3.74 x 10^{-2}	7.00 x 10^{-2}
	Pb	1.77 x $10^{-}4$*	3.94 x 10^{-4*}	9.79 x 10^{-4*}
	∑ILCR	2.05 x 10^{-2}	4.51 x 10^{-2}	8.12 x 10^{-2}
Milk	As	3.85 x 10^{-3}	1.52 x 10^{-2}	1.46x 10^{-2}
	Cd	1.11 x 10^{-1}	1.06 x 10^{-1}	2.66 x 10^{-1}
	Pb	1.67 x 10^{-3}	2.07x 10^{-3}	1.50x 10^{-3}
	∑ILCR	1.156x 10^{-1}	1.233 x 10^{-1}	2.721 x 10^{-1}
Water	As	1.71 x 10^{-2}	2.76 x 10^{-2}	6.87 x 10^{-2}
	Cd	6.49 x 10^{-2}	9.23 x 10^{-2}	2.67 x 10^{-1}
	Pb	1.21 x 10^{-3}	1.63 x 10^{-3}	5.47 x 10^{-3}
	∑ILCR	8.32 x 10^{-2}	1.22 x 10^{-1}	3.41 x 10^{-1}

***ILCR Acceptable Levels: 1x10^{-6} to 1 x 10^{-4}**

Basing on ILCR results of Arsenic, Cadmium and Lead in maize, millet, beans, milk and water, and the projected population of approximately 10,000 people in each zone, the numbers of cancer cases were determined. The consumption of maize with Arsenic, Cadmium and Lead contaminants in Upper, Middle and Lower were cases within each zone cancer risk assessment results showed that in a population of 10,000 people each in the Upper Kimwarer, Middle and Lower Kimwarer zones, there people who will develop cancer would be as stated in table 4-26

Table 4- 26: Cancer cases per 10,000 per zone.

Food	UK	MK	LK
Maize	370	1092	2437
Milk	1156	1233	2721
Millet	1094	826	3447
Beans	205	451	812
Water	832	1215	3410

The projections show that the highest number of cancer cases would be from drinking water and consumption of milk, maize and millet. This shows that consumption of beans would result into lower exposure to Arsenic, Cadmium and Lead in the study area. The projections show that the Lower Kimwarer and relatively the Middle part will have the greatest burden compared to Upper Kimwarer. The high numbers in milk is due to the quantities and the frequency of the milk being consumed.

4.10 Disease prevalence

4.10.1 Non-carcinogenic diseases

The results of the study showed the prevalence of the diseases associated with metal poisoning among the local residents sampled during the epidemiological survey carried out were skin conditions, diabetes, cardiovascular and mental conditions. Out of 346 people interviewed there the people suffering from skin, diabetes, cardiovascular and mental were 44, 32, 23, and 7 respectively. Disease ranking of 10 top most prevalent diseases from five health centers Muskut, Kimwarer, Chepsirei, Turesia and Nyaru were skin>Respiratory tract infection> malaria> cardiovascular> diarrhea> arthritis> intestinal worms> eye infections>pneumonia> urinary tract infection. The sresults of total male and female cancer cases is shown in Table 4-25.

4.10.2 Cancer prevalence

Table 4- 27: Total male and female cancer cases

Sampling Zones	**No. of cancer cases**	**Male**	**Female**
UpperKimwarer	4(10.2)	2(9.5)	2(11.1)
MiddleKimwarer	9(23.1)	5(23.1)	4(22.2)
LowerKimwarer	26(66.7)	14(66.7)	12(66.7)
Totals	**39(100)**	**21(100)**	**18(100)**

Values in parenthesis are percentages of respondent

The cross-sectional study results recorded 39No. of cancer cases of which 4 were in the Upper Kimwarer, 9 in the Middle Kimwarer and 26 in Lower Kimwarer. The results showed the number of cancer cases in Lower Kimwarer, Middle Kimwarer and Upper Kimwareras having 66.7%, 23.1% and 10.3% respectively. The 53.8% of cancer cases were male and 46.2% were female. The females had the highest number of cancer cases in Lower Kimwarer Middle Kimwarer and Upper Kimwarer with 12, 4, and 2 cases respectively. Age bracket, total respondents and cancer cases in the study area is shown in Table 4-28

Table 4- 28: Age bracket, total respondents and cancer cases.

Age bracket (years)	Total Respondents	Cancer Cases
20-29	116 (38)	13(33.3)
30-39	88(28.9)	10(25.6)
40-49	60(19.7)	7(17.9)
>50	41(13.4)	9(23.1)
Total	305(100)	39(100)

Values in parenthesis are percentages of respondent

The results showed that 33.3% of the cancer cases were between 20-29years of age. The other cancer cases had 25.6%, 17.9% and 23.1% for ages between 30-39, 40-49, and more than 50 years respectively.

4.10.3 Cancer types

Cancer types in Flourspar mining belt results are shown in Table 4-29

Table 4- 29: Cancer types in Flourspar mining belt.

Cancer type	Skin	Bone	Lungs	Prostate	Throat	Cervical	Other
Frequency	12	3	3	7	3	4	7

The results on cancer cases showed 6No. major categories with skin cancer being the highest with 30.8 % followed by prostate 17.9% , cervical 10.3% bone,lungs and throat cancer were 7.7% and others which included breast, blood and were 17.9% of the total cancer cases reported.

Alcohol consumption

The number of respondents consuming alcohol in the study ares are shown in Tble 4-30

Table 4- 30: Alcohol Consumption.

Period (years)	Alcohol	U.K	M.K	L.K
<1	7(10.8)	1(7.1)	2(10)	4(12.1)
1-5	19(29.2)	4(28.6)	6(30)	11(33.3)
5-10	15(23.1)	3(21.4)	5(25)	7(21.2)
> 10	24(36.9)	6(42.9)	7(35)	11(33.3)
Total	66(100)	14(100)	20(100)	32(100)

***Values in parenthesis are percentages of respondents**

The results showed 66 respondents consume alcohol and 36.39% of the total alcohol consumers have been taking over 10 years. The people who consume alcohol were highest at Lower >Middle > Upper Kimwarer with 32, 20 and 14 respectively.

Age and period of respondent smoking.

Age and period of respondent smoking in the study area ares shown in Table 4-31

Table 4- 31: Age and period of respondent smoking

Age of respondent	**Period of respondents smoking**				**Total**
	<1 year	1-5years	5-10 years	>10years	
20-29 years	1	4	1	0	6
30-39 years	0	2	3	1	6
40-49 years	1	2	2	6	11
> 50 years	0	0	1	5	6
Total	2	8	7	12	29

The study recorded 12 No. of the total 29 respondents who have smocked for more than 10 years and 6No. of the smokers are between 40-49 years old. The people who are more than 50 years of age have been smoking for more than 5 years. The smokers who are between 20-29 years old have been smocking for a period of between 1-10 years.

CHAPTER FIVE

DISCUSSIONS

5.1 Introduction

This chapter discusses the interpretations and explanations of the results obtained from the sample analysis of soils, water, food cereals (maize, millet and beans) and milk, and human hair from samples obtained from in Fluorspar mining belt in Kimwarer sub-catchment area. The differences in distribution of the selected heavy metals As, Cd, CrandPb analyzed in the three zones (spatial) and in the two seasons (temporal) are discussed. The exposure risk of these selected metals and the prevalence of cancer is discussed.

5.2 Arsenic, Cadmium, Chromium and Lead in Environment

5.2.1Arsenic, Cadmium, Chromium and Lead in Soil

In the present study, the ATSDR (2006), CDC, (2015) and various published reports were used as guideline values to give an insight on the safety of the soils, water and food crops planted in the study area and the level of exposure to the selected metals in Kimwarer sub-catchment. The concentrations of the selected heavy metals compared to the standards were used to determine the risks of their exposure to the people and the health implications brought in by the elevated concentrations to the consumers within the study area.

The results on the concentration of metal in soil showed a spatial variation ($P<0.05$) in As and Cd in both wet and dry seasons but showed significant variation in Cr and Pb during wet season. There was a temporal variation $P<0.05$ in As, Cd and Cr for all the zones except for Pb ($P>0.05$) in the Lower Kimwarer zone. Arsenic, Cd, Cr and Pb were above ecological screening levels (USEPA, 2005 except As in Upper and Middle Kimwarer Cr in Lower Kimwarer and Pb in Upper Kimwarer.

The concentrations of Arsenic and Cadmium in soil were all above ecological screening levels of 3.0mg/Kg dry weight and 0.1mg/Kg dry weight (USEPA, 2005) respectively except for Arsenic levels in Upper and Middle Kimwarer during wet season. The lowest level of Arsenic in soil was 0.22±0.04mg/l in Upper Kimwarer during the wet season and the highest level was 27.31±7.71^{b}mg/l in Lower Kimwarer in dry season. The lowest level of Cadmium in soil was 4.92±0.22 mg/Kg in Upper Kimwarer during the wet season and the highest level was 73.39±14.87 mg/l in Lower Kimwarer in dry season.

The concentrations of Chromium in soil were all within the ecological screening levels of 13.4 mg/Kg dry weight (USEPA, 2005) except for Chromium levels in Lower Kimwarer in dry season. The lowest level of Chromium in soil was 4.92±0.22 mg/Kg in Upper Kimwarer during the wet season and the highest level was 73.39±14.87 mg/l in Lower Kimwarer in dry season.

Lead levels in soil were all above the ecological screening levels of 5.0 mg/Kg dry weight (USEPA, 2005) except for Lead concentrations in Upper Kimwarer in wet season. The lowest level of Lead in soil was 4.10±0.94 mg/Kg in Upper Kimwarer during the wet season and the highest level was 16.20±4.08 mg/l in Lower Kimwarer in dry season.

The levels of As, Cd, Cr and Pb in soil in the study area shows that soils are contaminated hence a potential hazard to ecosystem and humans. The Maize, beans and millet grown in contaminated soils takes up nutrient from the soils and ended up being contaminated with the same chemicals that were in the soils. The plants which are edible or have seeds which are edible end up as foods with contaminants of the same chemicals which were in the soils. This is the soil-plant-food contamination explained in (Zhuanga *et al*., 2009; (Liu et al., 2005).

In general the heavy metal concentrations in soil within the study area had both spatial and temporal variations. The temporal variation could be due to activities within the zone like the Lower Kimwarer had more of the mining impacts than the other zones of Upper Kimwarer and Middle Kimwarer. The Upper Kimwarer zone location had the least levels of heavy metal concentrations which could be attributed to the distant location in relation to the mining activities. Upper Kimwarer is approximately 5kilometres in radius from the mining belt though there results indicated the presence of As, Cd, Cr and Pb. Theseheavy metal levels could be due to depositions of particles caused from air pollution from the mining activities. The geological variations between Upper and Middle and Lower Kimwarer could be contributing to the heavy metal concentration in the different zones.

The level of pollution in the soil could have contributed to the level of heavy metal pollution in the water, crops and the people that depend on the foods obtained from farming within the Kimwarer sub-catchment.

5.2.2 Arsenic, Cadmium, Chromium and Lead in Water

The local communities in Kimwarer sub-catchment uses water from the rivers, springs, wells and the piped water from taps for domestic purposes which include drinking, cooking, bathing, washing of utensils and clothes. The assessment of the selected heavy metals in drinking water among thesampled zones was therefore important to determine the safety levels of these heavy metals in the water as it's compared to the set standards.

There was spatial and temporal variations in the amounts of water consumed per day in the three zones during the wet and dry season. The lowest amounts were observed at the Upper zone where the temperatures is low due to the high altitude compared to the Middle zone and Lower zone which falls in the escarpment and lowlands respectively. The Middle zone had the highest amounts of water consumed compared to the Upper zone.

The results showed that there was a spatial and temporal variation concentration of heavy metals in water during wet and dry seasons in the zones. The spatial variation had a significant difference ($P<0.05$) in As during dry season and in Cd, Cr and Pb in all the zones. The concentrations of As, Cd, Cr and Pb in water were all above US Food and Drug Administration maximum allowable levels of 0.01mg/l, 0.005mg/l, 0.005mg/l and 0.005mg/l respectively in all the Zones. The highest levels for As, Cd, Cr and Pb were 15.59±1.37mg/l, 11.64±1.50 mg/l 10.47±1.62 mg/l and 11.64±1.50 mg/l respectively and all were from Lower Kimwarer.

The high levels of As, Cd, Cr and Pb is an indication that water in the study is contaminated with respective heavy metals and water in the study area is a potential hazard both for the ecosystem and humans who are using the water for domestic purposes. (Ngure, 2017) found out that the concentration of Cd, Cr and Pb were above the recommended in a gold mining area in Migori Kenya. This indicates that there are high chances of having heavymetals in water with concentrations above the recommended levels in a mining area. The total mean heavy metal burden in Kimwarer sub-catchment had the highest in the Lower zone followed by the Middle zone and the Upper zone having the least in terms of concentration distribution. The total mean heavy metal burden in the three sampled zones in all the assessed media; soil, water, food and hair were as follows: Cd>As>Pb>Cr. The higher Cd and As concentrations could be attributed to their ubiquitous nature in the environment. The Lower zone had this order Cd>As>Pb>Cr of the metal concentration which was similar to the overall for the sub-catchment. The mean heavy metal concentration order in the MiddleKimwarer was Pb>Cd>As>Cr and in the UpperKimwarer was Cd>Pb>As>Cr.

5.3 Arsenic, Cadmium, Chromium and Lead in Food

5.3.1 Arsenic, Cadmium, Chromium and Lead in Milk

Results showed that the Lead levels in milk were all above the levels recommended 0.02mg/L by CODEX Alimentarius International Food Standards (FAO and WHO, 2015)in Upper, Middle and Lower Kimwarer. The lowest Lead levels were 2.22±0.42mg/l in Upper Kimwarer during wet season and the highest concentration was 5.49±0.44mg/l in Lower Kimwarer in dry season. Milk is one of the major foods that the community consumes it most. The amount of milk consumed per person per day was 0.417litres, 0.362litres and 0.311litres in Upper, Middle and Lower respectively. The Upper part of Kimwarer is located in the highlands where dairy farming is more established than the middle and Lower Kimwarer the availability of more milk and increased intake than the other regions. Though the levels of metal concentration in milk is low compared to Middle and Lower zones, and since the estimated daily intake (EDI)is determined by the amounts of milk and concentration of the heavy metal then it makes EDI to be above the recommended levels.

5.3.2 Arsenic, Cadmium, Chromium and Lead in Cereals

Maize, beans, millet and milk are the most common stable foods consumed by the people living in Kimwarer sub-catchment.The selected heavy metal concentrations in the cereals grown within the sub-catchment are similar to the crops that have been grown in contaminated soils. These results confirm that there is relative uptake of the selected heavy metals that occur in various crops in the various zones.

The results on cereals showed a spatial significant difference in As, Cd, Cr and Pb levels between the zones in the study area. There was also a significant seasonal variation on the heavy metal concentration in Upper, Middle and Lower Kimwarer zone. The highest levels for As, Cd, Cr and Pb in maize were, 5.73±1.93, 19.17±2.82µg/g, 15.23±1.63µg/g and 10.83±0.79 respectively. In beans the concentrations of As, Cd, Cr and Pb were 9.09±2.78, 12.33±8.45, 14.10±4.81 and 17.24±2.30 respectively. For millet, the levels of As, Cd, Cr and Pb were 11.03±2.90 µg/g, 17.19±2.48, 10.20±2.77 and 10.21±0.42

respectively. As per the concentrations of the metals order from the highest was As: Millet>maize>beans, Cd: maize>millet>beans, Cr: maize>beans>millet and the overall order for all the heavy metals was Millet>maize >beans.

The results on As Cd, Cr and Pb were checked against the CODEX Alimentation Commission standards (FAO & WHO, 2015) recommended levels which showed that the concentrations in cereals were above the maximum allowable limits except for beans in both dry and wet season and Maize and millet in dry season in Lower Kimwarer. Humans are exposed to heavy metals as well as metalloids, such as arsenic, in the environment, workplace, food, and water supply (Dorne et al., 2011; Jarup, 2003). Previous studuies on Cadmiumshowed levels above CODEX levels in cereals and also Chromium high levels are a potential hazard like Chromium as stated by (Sadovska, 2012).

5.4 Arsenic, Cadmium, Chromium and Lead Exposure

5.4.1 Arsenic, Cadmium, Chromium and Lead through food

The concentration of the selected heavy metals in the soil, and the presence of these heavy metals in the cereals (maize, millet and beans) and in milk showed that crops within the sampling areas are not safe for consumption. The animals also graze on the grass growing on the polluted soils and drink water from polluted sources resulting into traces of these selected heavy metals in animal products like milk. The water sources within the study area are polluted with contaminated soils that contain heavy metals from the mining sites either getting to the water sources by water run offs during rainy seasons or by point pollution sources from the effluents from the mining factory.

The Agency for Toxic Substance and Disease Registry developed thresholds (Minimal Risk Levels) for safety to exposureto hazardous chemicals that can cause human adverse effects. These thresholds were developed and grouped basing on the mode of exposure, whether oral, inhalation or dermal and the period of exposure. The duration of exposure was categorized into acute which takes1 to 14 days followed by intermediate which takes 15 to 364 days, and finally chronic which takes a period of over one year.

The estimated daily intake of selected heavy metals was above acute, intermediate and chronic minimal risk levels recommended by Agency for Toxic Substances and Disease Registry acceptable levels 80%, 90.8% and 94.8% .in water, milk and cereals in all the zones in Kimwarer. This implies that the people visiting the study area for two weeks are 20% within the safe MRLs exposure levels of Arsenic, Cadmium, Chromium and Lead and the people who intend to stay for a period of one year are 9.2% within the minimal risk levels. For longer periods of over one year the safe exposure levels reduces to 5.2% of metals studied in Kimwarer.

The highest to the lowest estimated daily intake of metals in water milk and cereals were in the following order water>millet>maize>milk>beans. Arsenic, Cadmium, Chromium and Lead concentrations in water and food in Upper Kimwarer were lowest compared to the Middle and Lower Kimwarer. The people within Kimwarer could consume more of the beans which have the lowest concentrations, reduce the consumption of millet and maize and reduce the quantities and the frequencies of consumption. The estimated daily intake in Upper zone was 12.5% of EDI within the acceptable limits while the Middle and Lower zone were 5.8% and 0% of EDIs within the minimal risk levels in water, milk and cereals. This indicates that people in Upper zone are relatively safer from the heavy metal exposure compared to Middle and Lower Kimwarer.

The elevated concentrations of heavy metals in ingested into the body end up being deposited in organs and some smaller percentage get eliminated through excretion. Some of these toxic substances are excreted through urine sweat and feaces especially for acute exposures and some are deposited in the nails, hair and the various organs of the body. The end points of deposition of the selected heavy metals in As are deposited in the gastrointestinal system and the dermis. The Cd is deposited in the respiratory, the renal and musculoskeletal and the Cr is deposited in the respiratory, the hematopoietic and gastrointestinal systems (ATSDR, 2002).

The Estimated Daily Intake of heavy metal for male and female indicated variations caused by the different body weights of average weights of 60Kg and 70Kgs for females and males respectively. The male in the study had 97.7% of the estimated daily intake of heavy metal above minimal risk levels while the female were 98.5% of EDI results in all the zones. Smaller body weights have higher adverse effects from heavy metal exposure as confirmed by (Ngure, 2017).Previous studies shown as data indicated gender differences in the biotransformation by methylation, possibly also in susceptibility to certain arsenic-related cancers. It has been concluded by (Vahter *et al*., 2002) that gender-related differences in exposure and health effects caused by heavy metals are highly neglected research areas, which need considerable focus in the future.

5.4.2 Exposed Arsenic, Cadmium, Chromium and Lead in hair

The study established that there were traces of As, Cd, Cr and Pb in the sampled human hair in UK, MK and LK zones. Arsenic, Cadmium, Chromium and Lead were present in water, milk, maize, beans and millet in all the zones. There was no significant variation in As and Pb in hair between the zones unlike Cd and Cr which had a significant difference between the zones. The heavy metal concentrations in the human hair were higher in the exposed zone compared to the unexposed zone.The presence of heavy metals in hair indicates that exposure to the corresponding metal took place either through inhalation, ingestion or dermal routes.

Previous studies showed that hair sample are useful assessment tool in characterizing long-term exposure of the measured contaminant (Qu *et al*, 2012), though with some challenges. Interpreting the health implications of As concentrations in biological samples is limited by the small number of studies that provide information on the correlation and dose-response relationship between bio-monitoring test results and adverse health effects (Orloffa *et al*, 2009). Hair also was found to be a poor indicator of Cd contamination, as the concentration of Cd in hair was not parallel to that in the critical organs of the experimental animal, the mouse.

5.5 Risk assessment

5.5.1 Carcinogenic risks.

The risks associated with heavy metals are non-carcinogenic diseasess and cancers. The cross sectional survey results showed that the non-carcinogenic diseases that people suffer from within the study area reported are cardiovascular diseases, diabetes, cancers, mental disorders and skin conditions. These conditions are also similar to the diseases that have been documented to be associated with selected heavy metals.

Cancer is one of the chronic diseases that are associated with exposure to Arsenic, Cadmium, Chromium and Lead (Fishbain, 2007). The US EPA risk assessment probabilistic model assesses cancer risks basing on exposure to a carcinogen for a lifetime period of seventy years. Incremental lifetime cancer risk is one of the ways of determining cancer occurrence during one's lifetime period basing on the chronic daily intake of the heavy metal and its cancer risk factor which varies from one metal to another.

EPA considers excess cancer risks that are below about 1 chance in 1,000,000 (1×10^{-6} or 1E-06) to be so small as to be negligible, and risks above 1 in 10,000 (1×10^{-4}) to be sufficiently large that some sort of remediation is desirable. An ILCR greater than one in ten thousand (ILCR $>10^{-4}$) is benchmark for gathering additional information whereas 1/1000 or greater (ILCR $> 10^{-3}$) is moderate increased risk and should be given high priority as a public health concern (Li, 2010).

The results (Table 4-34) showed that 11.1% ILCR of the selected heavy metals were within the acceptable levels of (ILCR $> 10^{-4}$) and the remaining 88.9% ILCR were above 10^{-3} where some remediation is required. The remaining ILCR (82.2%) were above greater than (ILCR $> 10^{-3}$) is considered as a moderate increased risk and should be given high priority as a public health concern. In the case of more contaminants, the risk is greater due to the individual heavy metal contribution of risk. This results into a total sum of all the contaminants that an individual is exposed. From the results the levels of ILCR (Table 4-34), the range of the sum total of all the hazards in water, milk, maize, beans and millet was 2.05 x 10^{-2} to 3.45 x 10^{-1} which is greater than (ILCR > 10^{-3}) in water, milk and cereals foods in the study area, which is an indication of cancer risks in the study area that requires high priority as a public health concern.

EPA considers excess cancer risks that are below about 1 chance in 1,000,000 (1×10^{-6} or 1E-06) to be so small as to be negligible, and risks above 1 in 10,000 (1×10^{-4}) to be sufficiently large that some sort of remediation is desirable. An ILCR greater than one in ten thousand (ILCR >10^{-4}) is benchmark for gathering additional information whereas 1/1000 or greater (ILCR > 10^{-3}) is moderate increased risk and should be given high priority as a public health concern (Li, 2010).

The projected percentage of number of people who will be suffering from cancer due to the exposure of Arsenic, Chromium and Lead in milk in the next seventy year in Upper, Middle and Lower Kimwarer are 11.6%, 12.3% and 27.2% in a population of 10,000 people. Results from present and previous studies (Liu *et al*., 2005) demonstrated that the food crops grown on contaminated soil in the vicinity of mine and threatened health for the local inhabitants

The epidemiological results showed that there are risks at different zones which are attributed to the exposure of the selected heavy metals. The zones were grouped into unexposed region-Upper Kimwarer and exposed region which consisted of Middle and Lower Kimwarer. Odds Ratio (OR) or Relative Risk (RR) was determined in the unexposed to the exposed groups to determine the cancer risks associated to the selected metals as a result of mining activities in on the people living within the sub-catchment. The odds ratio for the exposed to unexposed zone was 2.56. This implies that there is a likelihood of getting cancer disease in the exposed group by 2.56 times compared to the unexposed group. It also indicates that there is a percentage relative risk of 156% of getting cancer in the exposed region than the unexposed region. Hence the disease cancer is associated with the exposure. The percent relative ratio also shows that the exposed group is 156% increased risk of getting cancer than the unexposed group.

5.5.2 Non-carcinogenic

Several non-communicable diseases worldwide have been reported to have very strong relationship with the environmental heavy metal status. Both occupational and environmental exposures to hazardous metals can lead to acute toxicity at higher concentrations and can also mediate development of additional pathologic conditions in individuals exposed chronically to low levels (Bae *et al*, 2001).

The results shown in Table 4-34 on the values of THQ for the individual heavy metals showed potential health risk for humans due to the intake of water, milk, maize, beans and millet in all the zones. The levels of HI in the study are high showing a potential risk to the local inhabitants through consumption of food stuff, milk and water. The Hazard Index levels were higher than the level of concern HI>5 level. Furthermore, hazard indices due to the combined non-cancer effects of all the heavy metals considered in the study were HI>1 which shows that the population is not safe from the exposure to Arsenic, Cadmium, Chromium and Lead.

Previous and present studies showed that estimated daily intake (EDI) of heavy metals and THQs for Cd and Pb of in water, milk and cereals were above the FAO/WHO permissible limit (Zhang et al., 2016).Previous studies stated the fact that regular consumption of food that have high levels of the hazard is a health risk with respect to levels of Cd, Cr and Pb (Tchouwou *et al*., 2004).

5.6 Cancer prevalence

There are three major causes of cancer; physical carcinogens, such as ultraviolet and ionizing radiation; chemical carcinogens, components of tobacco smoke, aflatoxin and arsenic and biological carcinogens such as infections from certain viruses, bacteria, or parasites (WHO, 2013). Cancer risk factors are tobacco use, alcohol use, unhealthy diet and physical inactivity are the main cancer risk factors worldwide. Chronic infections from hepatitis B virus (HBV), hepatitis C virus (HCV) and some types of Human Papilloma Virus (HPV) are leading risk factors for cancer in low- and middle-income countries(WHO, 2013).

WHO studies show that nine environmental and behavioral risks, together with seven infectious causes, are responsible for 45% of cancer deaths worldwide. The predisposing factors like tobacco smoking alone cause 71% of lung cancer deaths worldwide. Tobacco accounted for 18% of deaths in high-income countries (WHO, 2009).The consumption of alcohol appeared to have a role to play in the aetiology of esophageal cancer among the local residents with an Odds Ratio of 2.64 in Rift Valley. (Korir *et al*., 2013)study showed evidence of H. pylori in gastric cancer cases to be in 25% of patients.

Korir et al (2013) studied esophageal cancer and its potential risk factors that include; low socioeconomic, smoking, snuff use, alcohol, tooth loss, cooking with charcoal and firewood, hot beverage, and use of *mursik* were independently associated with esophageal cancer ($P< 0.05$). It also revealed that the consumption of alcohol appeared to have a role to play in the aetiology of esophageal cancer among the local residents with an odds ratio of 2.64. This showed that the chance of getting cancer is 2.64 higher risk for people who take alcohol than the people who do not consume.

Poisoning by exposure to heavy metal is well known to affect central nervous function, damage blood composition, lungs, kidneys, liver and other vital organs (Dinis and Fiuza, 2011). The epidemiological results were skin, lung, prostate, throat, cervical and others that included blood, stomach, liver, limbs, head, bones. The cancer group with the highest cases was skin> prostate>cervical>throat and lungs in that order. The prevalence of the different types of cancers shows some similarities to the ones the selected metals have been confirmed to cause. The cancers caused by Arsenic are lung, skin, bladder, kidney, liver, colon and prostrate. Cadmium causes bladder, prostate and lung cancers. Chromium causes liver cancers while Lead causeslung, stomach, and gliomas cancers (Steenland & Boffetta, 2000). CDC documented that gastro intestinal system and dermal are the end points for Arsenic, renal and muscular for Cadmium and blood and gastro intestinal system for chromium (CDC, 2015).

Studies by Tenge et al. (2009) results showed that the top ten male cancer in Uasin Gishu Hospital in 2004 to 2008were oesophageal, skin>NHL> prostate> leukemia>stomach>nasopharynx>colon-rectum>eye and liver while the top ten female cancer were cervix> breast >esophagus> skin> NHL> leukemia>stomach>ovary, nasopharynx > colon-rectum. All the cancer types reported by the current study were among the top ten diseases reported by the (Tenge *et al*, 2009).

5.7 Worst Case scenario

The worst case scenario was on females who have been consuming mostly milk, cereals and drinking water and living in Lower Kimwarer zone. The females were at a possible higher risks than their male counterparts due to their smaller body weights and highest levels of metal concentrations, highest levels of estimated daily intake of metal and Hazard Index were all greater that HI>5Lower Kimwarer zone.

The case can worsen still for those women who smoke and take alcohol. The women who are not employed formally spent most of their time working in their farms hence get more exposed to the sun which can be a predisposing factor due to the ultraviolet radiations more than the men.

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

This section summarizes the findings of the study which ought to establish if there was any significant variation in selected heavy metal concentration in Fluorspar mining belt and between the wet and dry seasons. The exposure to the selected metals As, Cd, Cr and Pb and the health risks of chronic cancer disease among the unexposed (UpperKimwarer and the exposed (Middle and LowerKimwarer) groups in the sub-catchment.

The study established that there was a spatial variation in As, Cd, Cr and Pb concentrations in soil, water, maize, millet, beans, milk and hair in UK, MK and LK zones in Kimwarer sub-catchment. There was also a significant temporal variation in concentration of heavy metals in the sampled media in all the zones.

The study also established that there the heavy metal concentrations in water and foods were higher that the recommended values, putting people at risk in consuming cereals, water and milk in the study area. The heavy metal concentrations per body weight were higher than the minimum risk levels recommended by Agency for Toxic Substance and Disease Registry(ATSDR) (CDC, 2017). There was spacio-temporal variation on risks was established in the study area.The study determined that there was a higher cancer cases in the exposed group (LK and MK) compared to the unexposed group in the UK zone. This indicated that the cancer determinants were within the exposed region. The study indicated higher cancer prevalence in the exposed regions than in the unexposed regions.

The study showed that the Minimal Risk Levels (MRL) of selected heavy metals was all aboveintermediate MRLs in water, milk and cereals except for Arsenicand Chromium which formed 1% and 1.5% of the total results studied respectively. The risks from the heavy metal concentrations exposure were higher in dry seasons than in the wet seasons and women had a higher risk values than men. Arsenic, Cadmium, Chromium and Lead contributed to higher values of Incremental Lifetime Cancer Risks probability of getting cancer over a lifetime period. Further Hazard Index values were above the safe levels of H<1 and also above level of concern HI>5. The values of Target Hazard Quotient for the individual heavy metals and the hazard indices due to the combined non-cancer effects of all the metals considered in the study were >1.

An epidemiological survey using the cross-sectional design conducted showed the prevalence of cancer cases in the study area as 39 cases in a population of about 4,680 people. The common type of cancer cases reported were: skin (12), prostate (7), cervical (4), lungs (3), throat (3), bone (3) and others (7) in number. The concentration of As and Pb in hair had a positive significant (P>0.01) correlation to cancer while Cr had a negative significant difference with cancer prevalence in the study area. The concentration of Cd in hair had an insignificant negative (P>0.01) correlation to cancer prevalence. The study reported possible sources of heavy metals which are mainly anthropogenic and geologic as depicted through the significant difference on the temporal heavy metal concentrations. Consumption of water, milk, maize, millet, beans in

Flourspar mining belt and its environs is a health risk with respect to Arsenic, Cadmium, Chromium and Lead especially for women should be given higher priority as a public health concern.

6.2 Recommendations

1. The people living within the mining belt should be sensitized on the adverse health effects in living within a polluted area like the Fluorspar mining belt.
2. The findings of this report should be used to develop and give a policy direction towards the prevention measures in an extractive industry.
3. The community should be sensitized to reduce the consumption of water and milk and maize especially within the exposed zones.

6.3 Further Research Areas

1. The development and implementation of the mining health risk management Model to mitigate the impacts of exposure to heavy and hazardous materials within the mining belt
2. Investigate combined synergies the metals could have on the exposure risks to humans living in the study area.
3. Investigation ofthe cause for elevated heavy metal concentration in UpperKimwarer which is the furthest point from the mining belt but had quite an amount of heavy metals.

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APPENDICES

Appendix I: Household Questionnaire

Introduction

I am a PhD student from University of Eldoret. For research purposes, I am interested to know about the general health of the people within the Kimwarer sub-catchment area. I need your assistance to complete this questionnaire regarding your perception on how the environment, the food and water have affected your health. Most of the questions asked are about your past and present occupations, some personal habits, and general illnesses and health effects especially in relation to environmental activities. You have the right to rescind your participation in this interview any time. Your answers will be kept confidential and used for research purposes only. Thank you for your co-operation.

PART A. Demographic Data

Household No………………………..Date of visit………………………

A1. Respondent Profile

Respondent No.	**District**		**Division**	**Location**	**Village**		
Sex	Male		Female				
Age	<1yr	1-9	10-19	20-29	30-39	40-49	>50

A2. What is your occupation?Activitiesinvolved, hours of exposure, physical health effects and remarks……………………………………..

A3. How far is your home/residential place from the mining site?

< 2Km	2<5km	5<10Km	>10Km

A4. How long have you lived here?

<1yr	1-9 yrs	10-19yrs	20-29yrs	30-39yrs	40-49yrs	>50yrs

A5. Are you a member of the Kimwarer-Mong Water Resource Users association? Y/N..............

Part B: Exposure measurement

B1. Which is the **<u>MAI N</u>** source of your water for general household use/drinking

Well	Stream	Spring	Tap	Rain	Other Source (Specify)

B2.How many litres of water to you take per day?

Half a litre	1 litre	1.5 litres	2litres	Other (specify)….

Which of the following problems do you have with this source of water?

Colour	Smell	Taste	Particles	Other Source (Specify)

B3. Do you smoke or drink alcohol, never, yes, If stopped, was this for medication reasons (specify)

B4. Which of the following food crops do you plant in this area?

(i) Maize (ii) Beans (iii) Sorghum (v) Finger mill

B5. How many days in a week do you consume the following foods? Maize, beans, millet and milk. State if the food stuff where from your farm or where bought.

B6. How much maize flour do you use for cooking (ugali) for your family per week?..........and what’s is the size of your family?..

B7. How much beans do you need per week? …………………….

B8. How much finger millet do you need per week? …………………….

B9. How many litres of milk do you need per day?

PART C: Health related illness

C1. Has any of your family members suffered from the following diseases?

Cancer, diabetes cardiovascular disorders, skin conditions, mental disorders and kidney problem.

C2. If yes state the part of the body is/was the cancer patient is/was suffering from?: part of the body, Sex and age

C3. What are some of the common cancer cases within your area? Lungs, liver, prostrate, skin, bone and others

5. What do you associate the illness with? Mining, witchcraft, curse, family lineage; hereditary

PART D: Control measures

D1: What has the company done to prevent pollution in the area?

D2: What can the community and the Kimwarer-Mong Water Resource Users Association (WRUA) do to manage pollution at the sub-catchment area?

D3. What do you suggest should be done?

……………………………………………………………………………………………

Thank you so much

Appendix II: Questionnaire to the Health Officers

Introduction

I am a student/representing a student from the University of Eldoret. For research purposes, I am interested to know about the prevalence of cancer cases within the Kimwarer sub-catchment area. I need your assistance to complete this table regarding the cancer patients who came for treatment in the health facility in the past years. The information will be kept confidential and used for research purposes only. Thank you for your co-operation.

Name of the health facility ………………………………………………..

Date of data collection ………………………………………………….

Year………………………………………

Top 10 diseases:

Reg. No of patient	Date of diagnosis	Gender	Age	Marital status	Disease	Dead/Alive

Appendix III: Classification of Heavy Metal Human Carcinogens

IARC Classification of Heavy Metal Human Carcinogens, Updated in 2012

Metal	**Class**	**IARC monograph reference**
Arsenic and inorganic arsenic compounds	1	23, supp 7, 100C
Cadmium and cadmium compounds	1	58, 100C
Chromium, metallic	3	49
Chromium III compounds	3	49
Chromium IV compounds	1	49, 100C
Lead	2B	23, supp 7
Lead compounds, inorganic	2A	87
Lead compounds, organic	3	23, supp 7

Source: (IARC, 2012)

Group 1: Carcinogenic to humans: implying the availability of sufficient evidence (epidemiological, occupational exposure and animal studies) of carcinogenicity to humans with a clear understanding of the relevant mechanism of human carcinogenicity. **Group 2A**: Probably carcinogenic to humans: implying the availability of limited evidence of carcinogenicity to humans, sufficient evidence of carcinogenicity in experimental animals with strong evidence that the method of carcinogenesis is operableinhumans.

Group 2B: Possibly carcinogenic to humans: implying the availability of limited evidence of carcinogenesis to humans, less than sufficient evidence in experimental animals; inadequate evidence in humans but sufficient or limited in experimental animals.

Group 3: Not yet classifiable as to its carcinogenicity to humans: availability of inadequate evidence in humans, inadequate or insufficient evidence in experimental animals, and mechanism of carcinogenesis does not operate in humans.

Group 4: Probably not carcinogenic to humans: Negative evidence in humans despite suggestions from no-human studies

Appendix IV:Institute of Research and Ethics Committee Approval Letter

INSTITUTIONAL RESEARCH AND ETHICS COMMITTEE (IREC)

MOI TEACHING AND REFERRAL HOSPITAL
P.O. BOX 3
ELDORET
Tel: 33471//2/3

MOI UNIVERSITY
SCHOOL OF MEDICINE
P.O. BOX 4606
ELDORET

Reference: IREC/2015/196
Approval Number: 0001649

2nd June, 2016

Ms. Naomy Jebet Kemboi Olero,
University of Eldoret,
School of Environmental Studies,
P.O. Box 1125-30100,
ELDORET-KENYA.

INSTITUTIONAL RESEARCH & ETHICS COMMITTEE
02 JUN 2016
APPROVED
P. O. Box 4606-30100 ELDORET

Dear Ms. Olero,

RE: FORMAL APPROVAL

The Institutional Research and Ethics Committee has reviewed your research proposal titled:-

"Assessment of Exposure and Human Health Risk Associated with Arsenic, Cadmium, Chromium and Lead within Fluorspar Mining Belt in Kimwarer-Mong Sub-Catchment Area in Keiyo District, Elgeyo/Marakwet County, Kenya".

Your proposal has been granted a Formal Approval Number: ***FAN: IREC 1649*** on 2nd June, 2016. You are therefore permitted to begin your investigations.

Note that this approval is for 1 year; it will thus expire on 1st June, 2017. If it is necessary to continue with this research beyond the expiry date, a request for continuation should be made in writing to IREC Secretariat two months prior to the expiry date.

You are required to submit progress report(s) regularly as dictated by your proposal. Furthermore, you must notify the Committee of any proposal change (s) or amendment (s), serious or unexpected outcomes related to the conduct of the study, or study termination for any reason. The Committee expects to receive a final report at the end of the study.

Sincerely,

For

PROF. E. WERE
CHAIRMAN
INSTITUTIONAL RESEARCH AND ETHICS COMMITTEE

cc	CEO	-	MTRH	Dean	-	SOP	Dean	-	SOM
	Principal	-	CHS	Dean	-	SON	Dean	-	SOD