

**ASSESSMENT OF HEAVY METAL POLLUTION IN SOILS AND WATER OF
SAMBURU COUNTY, KENYA**

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**A Thesis Submitted in Partial Fulfillment of the Requirements for the Award of the Degree
of Master of Science in Applied Analytical Chemistry in the School of Pure and Applied
Sciences of Kenyatta University**

July, 2013

DECLARATION

I declare that this thesis is my original work and has not been presented to any other University for the award of a degree

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DEDICATION

This work is dedicated to my late mother Sera Musimbi who taught me the value of education.

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ABSTRACT

Heavy metal pollution in soil and water arising from anthropogenic sources continue to pose a great challenge to human and animal population. In Samburu County conflicts arising from cattle rustling, military trainings in the county which have led to heavy use and disposal of arms, a growing population without proper sewerage facilities, increase in the number of aging automobiles and fertilizers from the wheat and barley farms in the highlands of Lorroki are the biggest contributors of heavy metals in the soil and water. Since heavy metals in the environment have continued to increase there is need to determine their levels in the environment for efficient environment management, hence the need to determine the levels of heavy metals in the soil and water in Samburu County. The heavy metals that were analyzed included Zn, Pb, Cr, Mn and Cd. 136 water samples and 176 soil samples were collected from the agricultural, residential and commercial areas of Kirisia and Lorroki Divisions of Samburu County. The soil samples were digested using aqua regia while the water samples were digested using nitric acid and hydrochloric acid. The soil and water digested samples were analyzed for heavy metals using atomic absorption spectroscopy. The data was analyzed using ANOVA. From the results, means of Cd, chromium, manganese, lead and zinc in wells in Kirisia in mg/l were 0.010 ± 0.000 , 0.050 ± 0.010 , 0.080 ± 0.010 , 0.130 ± 0.080 and 0.050 ± 0.010 mg/l respectively. While the mean levels in dams were 0.020 ± 0.010 , 0.050 ± 0.010 , 0.050 ± 0.010 , 0.060 ± 0.030 and 0.050 ± 0.010 mg/l. Similarly the mean of the same metals in boreholes in Kirisia were BDL, 0.030 ± 0.010 , 0.090 ± 0.020 , 0.320 ± 0.110 and 0.020 ± 0.010 mg/l respectively. The mean levels of Cd, Cr, Mn, Pb and Zn in Lorroki in wells were 0.003 ± 0.001 , 0.030 ± 0.010 , 0.040 ± 0.010 , 0.052 ± 0.010 and 0.030 ± 0.010 mg/l while the mean in dams were 0.004 ± 0.001 , 0.040 ± 0.010 , 0.050 ± 0.010 , 0.230 ± 0.050 and 0.040 ± 0.010 mg/l respectively. The mean levels of the same metals in soils in the Kirisia and Lorroki divisions in mg/kg were 0.60 ± 0.14 , 2.65 ± 0.30 , 17.44 ± 1.02 , 55.33 ± 5.93 and 376.35 ± 46.64 mg/kg while the mean levels of the respective metals in the soils in Lorroki in mg/kg were 0.570 ± 0.13 , 3.690 ± 0.390 , 21.91 ± 1.82 , 51.80 ± 4.16 and 265.95 ± 59.75 mg/kg. The mean levels of the Pb in all the water sources were found to be above the WHO maximum contamination level. With the exception of the level of lead in dams and wells in Kirisia and Lorroki Divisions, there was no significant different between the levels of all the other analyzed heavy metals in dams and wells in Kirisia and Lorroki Divisions. This study provides an opportunity for frequent monitoring of heavy metals in this environment and hence providing an opportunity to the stakeholders to help in curbing heavy metal pollution in Samburu County. Though most levels of the heavy metals were within the WHO (2003) maximum recommended contamination level, the level of lead in water was above this recommended level hence the need to put mechanisms in place to reduce the contamination due this heavy metal.

CHAPTER ONE

INTRODUCTION

1.1 Background information

Pollution is a worldwide problem and its potential in influencing health of the human population is great (Khan and Ghouri, 2011). The impact of pollution in the vicinity of overcrowded cities and from industrial effluents and automobiles has reached a disturbing magnitude and is arousing public awareness (Begum *et al.*, 2009). Excessive levels of pollution are causing a lot of damage to human and animal health, plants including tropical rain forests as well as the wider environment (Khan and Ghouri, 2011). Pollution is the cause of many diseases, which affect not only the old but also the young and the energetic and all animals and plants (Kanmony, 2009). The WHO report points out that twenty million children worldwide suffer from pollution which has become critical because of overpopulation (Kanmony, 2009; Pain, 2008). An estimated 1.2 billion people drink unclean water which is the source of water related diseases that kill between five-ten million people mostly children around the world (Ahuja, 2009).

The natural substances which cause water pollution include, gases, soils, minerals, humus materials, waste created by animals and other living organisms present in water. Water resources continue to be scarce and insufficient in most areas to meet the growing demands of a rapidly increasing population and because of this scarcity, the resources have continued to be overexploited leading to its salinity, increased pollution and eutrophication due to intensive agricultural practices (Al-Weher, 2008). Estimation indicates that more than fifty countries of the

world with an area of twenty million hectares area are treated with polluted or partially polluted water including parts of all continents and this poor quality water causes health hazards and death of human beings, aquatic life and also disturbs the production of different crops (Khan and Ghouri, 2011).

The most common environmental pollutants in the world are heavy metals (Papatilippaki *et al.*, 2008). The presence of heavy metals at trace level and essential elements at elevated concentration causes toxic effects if exposed to human population (Fong *et al.*, 2008). The knowledge of heavy metal accumulation in soils, the origin of these metals and their possible interactions with soil properties are a priority in many environmental monitoring (Qishlaqi and Moore, 2007). The accumulation of heavy metals in agricultural soils is of increasing concern due to food safety issues and potential health risks as well as its detrimental effects on soil ecosystems (Qishlaqi and Moore, 2007).

Food chain contamination by heavy metals has become a burning issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air (Begum *et al.*, 2009). Heavy metals can accumulate in the soils to toxic levels as a result of long term application of untreated waste waters and fertilizers. Soil irrigated by waste water accumulate heavy metals in surface soils and when the capacity to retain heavy metals is reduced due to repeated application of waste water, heavy metals leach into ground water or soil solution available for plant uptake (Papatilippaki *et al.*, 2008). Research findings indicate that application

of heavy doses of fertilizer, pollute ground water by nitrates and heavy metals through leaching and this affects the quality of water (Mico *et al.*, 2006).

Metal poisoning arise from heavy metals that have toxic properties leading to adverse effects on human and ecosystem health (Voet *et al.*, 2008). Although acute poisoning from heavy metal poisoning is rare through ingestion or dermal contact chronic exposure to even small doses can be disastrous (Sherameti and Varma, 2010). Chronic exposure to heavy metals leads to accumulation in the food chain which leads to an increased stock in biota, therefore magnifying the human dose (Voet *et al.*, 2008). The chronic problems associated with long term heavy metals exposure include; Serious hematological and brain damage, anaemia and kidney malfunctioning (Sonayei *et al.*, 2009). Heavy metals such as Pb and Cd are lethal even in very small doses. Lead has a negative influence on the somatic development, decreases the visual acuity and auditive thresholds (Simeonov *et al.*, 2010). Acute exposure to lead causes brain damage, neurological symptoms, brain damage and could lead to death (Simeonov *et al.*, 2010). Cd exposure on the other hand, causes renal dysfunction, calcium metabolism disorders and also increased incidence of some forms of cancer possibly due to the inhibition by Cd of DNA mismatch remediation (Kumar, 2009). Malignant neoplasia and skin ulcers have been reported due to various occupations with exposure to chromium compounds. Chromium (VI) inhalation is responsible for bronchial asthma (Sakar, 2005). Manganese toxicity affects the central nervous system, visual reaction time, hand steadiness and eye-hand coordination (Calkins, 2009). A syndrome named manganism characterized by feelings of weakness and lethargy, tremors, a masklike face and psychological disturbance. Respiratory effects have also been noted in workers chronically exposed by inhalation. Impotence and loss of libido have also been noted in

male workers afflicted with manganism (Calkins, 2009). Zinc toxicity is rare, but at concentrations in water up to 40 mg/l, may induce toxicity characterized by symptoms of irritability, muscular stiffness and pain (Al-Weher, 2008).

In Samburu County, chemicals and agro-based wastes are the major source of pollution and this arises from agro-chemicals and fertilizers used in the highlands of Lorroki and Kirisia Divisions where wheat and barley is grown on large scale. Close to 6000 hectares are utilized for wheat and barley growing in the divisions (NEMA, 2009). Pollution from small arms used in cattle rustling and military training in the area is also evident.

1.2 Problem statement and justification

The environment has continued to suffer from pollution due to increased population and industrialization (Goel, 2009). On the other hand resources like land have remained constant leading to overcrowding of population around towns and main cities. The biggest challenge resulting from this overcrowding is waste disposal. The overcrowding has led to domestic and industrial wastes being disposed of in water bodies like rivers and dams and this has led to the contamination of soil and the water bodies, especially from heavy metals (Lesamana, 2009).

In Samburu County, conflicts arising from cattle rustling have led to frequent use and disposal of small fire arms. The military training in the area and the heavy use of fertilizers for wheat and barley farming could be a source of heavy metal contamination in the soil and the waters (Bhandari *et al.*, 2007; NEMA, 2009). Lack of planning in Maralal town especially, has resulted

in overcrowding with no proper sewerage disposal system for waste and this could contribute to heavy metal contamination of soil and water (Lesamana, 2009).

People in Samburu County rely on water from bore holes and the dams for domestic use and farming. The absence of permanent rivers in Samburu County could have accumulative effect on the heavy metals as rivers help carry some of the metals downstream hence reducing their concentration. Some of the signs of heavy metal contamination among the population like mental retardation and cancer are evident among the population (Lesamana, 2009). Samburu County is riddled with poverty and therefore this community cannot afford to live with the effects of these pollutants as this will be too costly for them to seek treatment. Preventive measures if taken could be the best way to avert such expenses. Despite this, no work has been reported on the level of heavy metals in water and soils of Samburu County. This study therefore proposes to determine the levels of Cd, chromium, lead, zinc and manganese in soils and water from Samburu County.

1.3 Hypothesis

The levels of heavy metals in soils and water in Kirisia and Lorroki divisions of Samburu County are not significantly different and are below the recommended toxic levels.

1.4 Objectives

1.4.1 General Objective

To determine the levels of heavy metals in the soils and water in Lorroki and Kirisia Divisions of Samburu County.

1.4.2 Specific Objectives

- i. To determine the levels of lead, chromium, Cd, zinc and manganese in wells, boreholes and dam waters of Lorroki division and Kirisia divisions of Samburu County
- ii. To determine levels of lead, chromium, Cd, zinc and manganese in agricultural soils and roadside soils in Lorroki and Kirisia divisions of Samburu County

1.5 Significance of the study

The determination of levels of manganese, zinc, lead, chromium and Cd in soils and water of Samburu County will be used to sensitize the general population of Samburu County on the importance of environmental conservation. The study will also inform the authorities in environment management on the level of heavy metal pollution in Samburu County hence providing a reference for future studies on the same. The results from the study will also be used to determine the remedial action to be taken including treatment of the water to remove the heavy metals where the levels are too high.

1.6 Scope and limitations

There are many heavy metals but this study considered only five metals which from literature are prevalent in soils and water in Samburu County. The study also covered only two divisions of Samburu County because of its expansiveness, inaccessibility and resource availability. Some metals could be present in the underlying rocks and this could be reflected in the levels and assumed to be from anthropogenic sources.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Pollution includes natural as well as manmade substances or energy that may have an adverse impact on human health or well being or on the natural or cultural heritage. Environmental degradation due to pollution in poor countries is pervasive, accelerating and unabated (Farmer, 2002). In developed countries, a lot of resources have been used to ensure that there is cleaner air, drinking water, sewage treatment, safe food laws and food refrigeration (Hill, 2010). It is usually easy to see the effects of pollution on the earth and in plants and animals, but it is more difficult to reduce the amount of pollution put into the environment (Shafi, 2005). For example it is estimated that at least 1.6 million lives are lost each year through lack of access to sanitation and drinking water (Farmer, 2002) and more millions of people are left chronically ill from the water they must drink (Hill, 2010). It is important to note however that even a very small concentration of persistent pollutants may cause irreparable damage to the ecosystem. Organisms susceptible even to low concentration may get eliminated (Shafi, 2005). Scientific analysis is important for those pollutants with threshold for impacts to determine the nature of the threshold and for those without thresholds, to determine the significance at a level of “acceptable” impact (Farmer, 2002).

The major sources of pollution include; burning fossil fuel in engines, waste disposal, accidental spills of chemicals from factories and use of agricultural chemicals on farms (Greenaway *et al.*,

2002). There are several types of pollution including air pollution, water pollution and soil pollution.

2.2 Soil pollution

Soil is a very important natural resource to man as it is a source of his life on this planet. Without soil the earth would be as barren as the moon hence lifeless (Misra and Mani, 2009). Despite its importance, soil is often contaminated by human activities and this is reflected in the high horizontal and vertical variability brought about by the anthropogenic influence on soil formation and development (Fong et al., 2008). A variety of human activities including municipal waste disposal, industrial emissions, military testing and agricultural practices have left their impacts on soils in the form of elevated and high level of toxicants (Van and Krivolutsky, 1996).

Materials that find their entry into the soil system persist and accumulate in toxic concentrations becoming sources of pollution in the soil (Misra and Mani, 2009). The concentration of heavy metals in soil and their impact on ecosystems can be influenced by many factors such as the parent rock, climate and anthropogenic activities (Jia *et al.*, 2010). Among the pollutants that persist and accumulate in the soils include; inorganic toxic compounds for example fertilizers, organic wastes, organic pesticides and radio nucleides (Misra and Mani, 2009; Jia *et al.*, 2010). The soil is thus becoming increasingly polluted with chemicals and other pollutants which can reach the food chain, surface water or ground water and ultimately be ingested by man (Misra and Mani, 2009).

2.3 Water pollution

Pollution of water still remains one of the most significant environmental problems of recent times. Water can be regarded polluted when it gets changed in its quality or composition either naturally or as a result of human activities so as to become less suitable for drinking, domestic, agricultural, industrial, recreational, wildlife and other uses for which it would have been otherwise suitable in its natural or unmodified state (Goel, 2009).

Gross pollution of water has its origin mainly in urbanization, industrialization, agriculture and increase in human population being observed (Calhoun, 2005; Goel, 2009). In addition to toxic chemicals, water pollutants occur in many other forms, including pathogenic microbes, excess fertilizers and trash floating on streams, lakes and beaches. Water pollution can also take the form of sediment eroded from stream banks, large booms of algae, low levels of dissolved oxygen or abnormally high temperatures (Calhoun, 2005). Water pollution threatens our health and environment and therefore we need to implement an expanding array of techniques for its assessment, prevention and remediation (Calhoun, 2005).

2.4 Heavy metal and environmental pollution

2.4.1 Introduction

There are different types of pollution among which pollution caused by toxic level of heavy metal pollutants is called heavy metal pollution (Bose and Hemantaranjan, 2005). Heavy metals are elements having a density greater than 5 g/cm^3 in their elemental form (Bose and

Hemantaranjan, 2005; Misra and Misra and Mani, 2009). Heavy metal pollution has received the attention of researchers all over the world, mainly due to their harmful effects on living beings (Misra and Misra and Mani, 2009).

Human biology is full of instances where heavy metal toxicity has led to mass deaths (Shrivastav, 2001). All heavy metals are toxic to living organisms at excessive concentrations, but some are essential for normal healthy growth and reproduction by plants at low but critical concentrations (Bose and Hemantaranjan, 2005). The heavy metals essential in trace elements to plants include Co, Cu, Fe, Mo and Zn and for animals are Cr, Ni and Sn. The heavy metals Cd, Hg and Pb have not been shown to be essential for either plants or animals (Misra and Misra and Mani, 2009).

It is important to note however that the concentrations of individual metals in living tissues must be kept very low and should be maintained within narrow limits to permit the optimum biological performance of most organisms (Misra and Mani, 2009). Heavy metals are non-biodegradable and once they enter into an environment, they will stay there for a longtime (Voet et al., 2008). Heavy metals are considered serious pollutants because of their toxicity, persistence and nonbiodegradable conditions in the environment, thereby constituting a threat to human beings and other forms of biological life (Adeleken and Abegunde, 2011). Heavy metals occur in atmosphere basically in particulate form. Hence, the transfer of airborne particles to land or water surfaces by dry, wet and occult deposition constitutes the first stage of atmospheric heavy metals (Shrivastav, 2001).

Adeleken and Abegumde (2011) note that heavy metals have low environmental mobility as a result of this, a single contamination could set a stage for a long term exposure of human, microbial, fauna, flora and other edaphic communities to heavy metals. The problem of atmospheric heavy metal pollution is not going to disappear overnight. On the contrary it will remain a legacy of mass industrial activity for many generations and is likely to escalate further in future. In this regard, the compilation of past and present catalogues of atmospheric heavy metal concentration is an activity of great importance (Shrivastav, 2001).

2.4.2 Soil pollution from heavy metals

Heavy metal pollution in soils refers to cases where the quantities of the elements in soils are higher than maximum allowable concentrations and this is potentially harmful to biological life at such locations (Adeleken and Abegunde, 2011). Heavy metals occur at typical background in all ecosystems, however, anthropogenic releases can result in higher concentrations of these metals relative to their normal background values hence the pollution (Adeleken and Abegunde, 2011). Heavy metals released from vehicular emission can accumulate in surface soils and their deposition over time can lead to abnormal enrichment, thus causing metal contamination of the surface soils (Fong *et al.*, 2008).

High concentrations usually occur in soils below or near landfills and agricultural lands that have been irrigated with contaminated water (Mamtaz and Chowdhury, 2006). Studies have shown that both long term and short term contamination of soils have effects on microbial

activity and enzyme activities of the soil (Adeleken and Abegunde, 2011). The toxicity and mobility of heavy metals in soils depend not only on the total concentration but also on their specific chemical form, bonding state, metal properties, environmental factors, soil properties and organic matter content (Osu and Okoro, 2011). Exposure of children, generally accepted as the highest risk group who have a higher adsorption rate of heavy metals because of their active digestion system and sensitivity of haemoglobin, to heavy metals, can greatly increase ingestion of metal laden soil particles via hand –to-mouth activities. In addition, adults may be exposed to threat since inhalation is easier pathway for toxic metals to enter their body (Fong *et al.*, 2008).

2.4.3 Heavy metals in water

The contamination of fresh waters with a wide range of pollutants has become a matter of great concern over the last few decades (Al-Weher, 2008). The aquatic systems receive a large amount of heavy metals from natural occurring deposits and natural processes and anthropogenic activities (Wogu and Okaka, 2011). Anthropogenic sources arising from human activities such as industrial, municipal effluents, as well as non-point source run off are the main sources of metals in rivers (Sonayei *et al.*, 2009).

Discharge of heavy metals into rivers or any other aquatic environment can change both aquatic species diversity and ecosystems due to their toxicity and accumulative behaviour (Al-Weher, 2008). Heavy metals dissolved in water also endanger the lives of the public who use it for drinking and also irrigation. When used for irrigation heavy metals have the danger of being

incorporated in food chain and therefore ingested by the public (Wogu and Okaka, 2011). Heavy metals accumulate in the soils at toxic levels as a result of long term application of untreated waste water and therefore soils irrigated by wastewater accumulate heavy metals in their soil surface (Sonayei *et al.*, 2009). When the capacity of the soil to retain heavy metals is reduced due to repeated application of waste water, the metals leach into ground water or soil solution available for uptake (Sonayei *et al.*, 2009). Table 2.1 shows metal limits in water set by national and international organizations.

Table 2.1 Heavy metal limits ($\mu\text{g/l}$) in water set by different national and international organizations

	Cd	Cr	Mn	Pb	Zn
USEPA	5	100	50	10	5000
EU	5	50	50	10	Nm
WHO	3	50	400	10	NGL
Iranian	10	50	500	50	Nm
Australian	2	50	500	10	3000
Indian	10	50	100	100	5000
New Zealand	4	50	400	10	1500

Nm- not mentioned

NGL – No guideline, because it occurs in drinking water at concentrations well below those at which toxic effects may occur

Source; Mebrahtu and Zerabruk (2011)

2.5 Heavy metals and their effects

2.5.1 Lead

Lead has a negative influence on both children and adults. For children, Pb reduces the physical growth and mental growth (Simeonov *et al.*, 2010). The intelligent quotient of children is diminished and symptoms of irritability and fatigue could be observed. Pregnant women exposed to Pb have higher rates of infertility, miscarriage and still births (Ediin *et al.*, 2000). Chronic exposure to Pb can affect physical growth and can cause anaemia, kidney damage, headache, hearing problems, speaking problems, fatigue or irritable mood (Simeonov *et al.*, 2010). The toxicity of Pb is multiple biochemical effects. It has the ability to inactivate enzymes, compete with calcium for incorporation into bones and interfere with nerve transmission and brain development (Ediin *et al.*, 2000).

The WHO maximum allowed contaminant level in the water is 0.01 mg/l (Monudu and Anyakora, 2010). The main sources of Pb in the environment include, dust from leaded paints from older houses, leaded gasoline and tap water from soldered pipes (Ediin *et al.*, 2000). Indoor chemicals and indoor smoking is also a source (Simeonov *et al.*, 2010). Mebrahtu and Zerabruk (2011) in their study of concentration of heavy metals in drinking water from urban areas of the Tigray Region, Northern Ethiopia using atomic absorption spectroscopy method of analysis detected levels of Pb of 1.347 mg/l at Indasilase and a minimum of below detection limit in drinking water samples from Alamata, Korem, Hagereselam, Zelambessa, Firewoini, Axum, Adwa and Enticho. More than 70.15 % of the water samples analyzed contained lead concentration within the WHO (2008) maximum allowable limit of lead in drinking water. In a

similar research carried out by Kaplan and Yildrimi (2011) at Tunceli in Turkey, Pb was only detected in drinking water from one station, out of the sampled. The highest value of Pb detected was 0.31 µg/l and this was below the maximum permissible limit for lead in water. Similar results were obtained by Wogu and Okaka (2011) in a study on heavy metals in Warri river in Nigeria. They recorded a variation of Pb levels in water ranging from 0.0 to 0.001 mg/l which were below the maximum WHO (2003) permissible limits of lead in drinking water of 0.01 mg/l. A similar study by Raji *et al.* (2010) recorded the following Pb levels in water in the following stations; station T1, 0.720 mg/l, station T2, 0.390 mg/l, station T3, 0.310 mg/l, station WB(R), 0.340 mg/l and station WB(T), 0.350 mg/l.

In the soils, the maximum allowable limits of lead in UK and USA are 100 mg/kg and 200 mg/kg (Mamtaz and Chowdhury, 2006). A study carried out by Mico *et al.* (2006) on heavy metal content of agricultural soils in a Mediterranean Semiarid Segura River Valley in Spain recorded 19.6 mg/kg of Pb in the soil and a lead level range of 8.9 mg/kg-34.5 mg/kg. The soil samples were analyzed by flame atomic absorption spectroscopy. A study by Ijeoma *et al.* (2011), on heavy metal content in high traffic area soils of Pakistan, recorded a minimum lead concentration of 10.06 mg/kg and a maximum Pb concentration of 29.71 mg/kg. A study by Atiemo *et al.* (2010) recorded levels of Pb in road soils ranging from 33.640 mg/kg to 117.45 mg/kg. Similarly Jaradat and Momani (1999) recorded levels of Pb in roadside soils at different distances from the road ranging from 3.700 mg/kg to 272.200 mg/kg.

2.5.2 Cd

Cd is a heavy metal characterized by high mobility in biological systems. It is emitted to the atmosphere in combustion processes, mainly in the form of oxides (Wieczorek *et al.*, 2004). Cd uptake by plants is partly limited by presence of calcium, phosphorus and chelating compounds in the soil (Wieczorek *et al.*, 2004). The exposure of Cd and especially chronic exposure can cause renal dysfunction, calcium metabolism disorders and also increased incidence of some forms of cancer (Selinus and Alloway, 2005).

In plants, Cd induces oxidative stress in plant cells and inactivates some enzymes (Wieczorek *et al.*, 2004). Cd taken up by plants from the soil accumulates first of all in the roots, and then transported in smaller quantities to stems and seeds (Wieczorek *et al.*, 2004). Among the sources of Cd in the environment include; mining and smelting of metal ores, fossil fuel combustion and also phosphate fertilizers (Challa and kumar, 2009). Cd is also used in the production of nickel-Cd rechargeable batteries that become deposited in sewage sludge, thus raising environmental levels of Cd (Challa and kumar, 2009). Farming practices such as tobacco growing also increases the level of Cd in the environment as tobacco is known to accumulate in its tissues (Selinus and Alloway, 2005). The sources of Cd in the urban areas are much less well defined than those of Pb, but metal plating and tire rubber were considered the likely sources of Cd within Kirisia Commercial area which houses Maralal town (Jaradat and Momani, 1999). Cd is also found in lubricating oils as part of many additives and car tyres as a result of the vulcanization process. In the absence of any major industry in the sampling sites, the levels of Cd could be due to

lubricating oils and/or old tires, that are frequently used, and the rough surfaces of the roads which increase the wearing of tires (Jaradat and Momani, 1999).

At higher concentrations, it is known to have a toxic potential. The other sources of Cd are industrial activities; the metal is widely used in electroplating, pigments, plastics, stabilizers and battery industries (Mehbrahtu and Zerabruk, 2011). Cd is highly toxic and responsible for several cases of poisoning through food. Small quantities of Cd cause adverse changes in the arteries of human kidney. It replaces zinc biochemically and causes high blood pressures and kidney damage (Mehbrahtu and Zerabruk, 2011).

The maximum contaminant level of Cd allowed in water by WHO is 0.003 mg/l (Monudu and Anyakora, 2010). The recommended concentration in the soils is 3 mg/l (Adeleken and Abegunde, 2011). A study by Wogu and Okaka (2011) on Warri river water in the Delta region of Nigeria, recorded a Cd mean level of 0.0072 mg/l in the water and a range of 0.0 to 0.04 mg/l of Cd the water. The maximum value of Cd that was detected in the water was above the maximum permissible level of Cd in drinking water. A similar study carried out by Singh and Chandel (2006) on heavy metals of industrial effluents at Jaipur, Rejasthan in India, Cd was undetected in all the samples that were tested.

A study by Kisamo (2003) on the environment hazards associated with heavy metals in Lake Victoria Basin reported levels of Cd in soils ranging from 0.16 mg/l to 0.55 mg/l. The range

recorded in the above study was below the WHO maximum permissible limit of Cd set at 3 mg/l. A similar study by Mwegoha and Kihampa (2010) on heavy metal contamination in agricultural soils in Dar es Salaam city recorded values below detection limit in all the water samples analyzed. Kaplan *et al.* (2011) recorded the following levels of Cd in the following stations; station I 1.27 µg/l, station II <0.05 µg/l, station III <0.05 µg/l and station IV 1.67µg/l. A similar study by Mebrahtu and Zebrabruk (2011) recorded levels of Cd in water ranging from 14 µg/l to 21 µg/l in Makelle area with a mean of 17 µg/l.

A study by Delbari and Kulkarni (2011) recorded Cd values in agricultural soils ranging from 0.000 to 0.004 mg/l with a mean value of 0.002 mg/kg in summer season and 0,001 to 0.004 mg/kg with the mean value of 0.002 mg/kg in winter season. Similarly, Jaradat and Momani (1999) recorded Cd levels in roadside soils ranging from 0.21 mg/kg to 0.75 mg/kg.

2.5.3 Chromium

Chromium is one of those heavy metals in the environment whose concentration is steadily increasing due to industrial growth, especially the development of metals, chemicals and tanning industries (Adeleken and Abegunde, 2011). The most common forms of chromium are chromium VI and chromium III (Hilgenkamp, 2006). Chromium III is an important component of a balanced human and animal diet and its deficiency causes disturbance to the glucose and lipid metabolism in humans while chromium VI is carcinogenic (Chernoff, 2005). Although chromium toxicity in the environment is rare, it still presents some risks to human health since

chromium can be accumulated on skin, lungs, muscle fat, in liver, dorsal spin, hair, nails and placenta where it is traceable to various health conditions (Adeleken and Abegunde, 2011).

Among the health effects brought about by the exposure to chromium VI include lung cancer, malignant neoplasia, chromium dermatitis and skin ulcers (Sarkar, 2005). Perforations and ulcerations of the nasal septum and bronchial asthma have also been reported. In one of the studies, a fourfold increase in childhood leukemia was attributed to possible consumption of water with chromium VI levels above standard recommended value (Sarkar, 2005). The prevalence of chromium in drinking water above 5 mg/l results in bleeding of the gastrointestinal tract, cancer of the respiratory tract, ulcers of the skin and mucus membrane (Adeleken and Abegunde, 2011).

The sources of chromium in the environment include, cement, leather, plastics, dyes, textiles, paints, printing ink, cutting oils, photographic materials, detergents, wood preservatives among others (Hilgenkamp, 2006). Other sources of chromium are water erosion of rocks, power plants, liquid fuels, brown and hard coal and industrial and municipal wastes. Non biodegradability of chromium is responsible for its persistence in the environment and once mixed with soil, it undergoes transformation into various mobile forms before ending into environmental sink (Adeleken and Abegunde, 2011).

The Environmental protection Agency (EPA) has set the limit for chromium in drinking water at 100 $\mu\text{g/l}$ (Hilgenkamp, 2006) while maximum allowable limit of chromium in the soil set by united kingdom is 300 mg/kg. In a study by Mebrahtu and Zerabruk (2011) in the Tigray region of Ethiopia on heavy metals in drinking water, chromium was detected in 12 out of 16 of the sampling areas. The mean levels of chromium detected in the 12 sampling areas ranged from 97 $\mu\text{g/l}$ to 146 $\mu\text{g/l}$. The mean range was much higher than the WHO maximum admissible limit of chromium in drinking water of 50 $\mu\text{g/l}$. Of all the analyzed samples, 64.18% contained chromium above the WHO maximum admissible limit with the highest level of chromium recorded in water samples from Makelle (mean concentration, 146 $\mu\text{g/l}$). In a similar study by Pandey *et al.* (2010), in river Ganja in India, chromium detected ranged from 1.2 to 29.6 $\mu\text{g/l}$ and this was well below the 50 $\mu\text{g/l}$ WHO maximum admissible limit. In a similar study by Wogu and Okaka (2010) chromium levels ranging from 0.000-0.060 mg/l was recorded. Raji *et al.* (2010) recorded values in drinking water ranging from 0.510-0.800 mg/l. The values were above the WHO acceptable limit set in 2003.

A study by Adeleken and Abegunde (2011) on the levels of heavy metals contamination at automobile mechanic villages in Ibadan, Nigeria reported levels of chromium in soil ranging from 2.0 to 29.75 mg/l and this reported values were within the maximum allowable limit of chromium in the soils set by United Kingdom. Similarly, a study by Delbari and Kulkarni (2011), recorded chromium in the agricultural soils around Tehran ranging from 0.234 to 1.577 mg/kg with a mean value of 0.58 mg/kg.

2.5.4 Manganese

Manganese is essential for normal physiological functioning of humans and animals and exposure to low levels of manganese in the diet is considered nutritionally essential in humans. However chronic exposure to higher doses is detrimental to human health (Calkins, 2009). In higher doses manganese is toxic and its toxicity varies with route of exposure, chemical species, age, sex and animal species (EPA, 2004; Kohl and Medlar, 2007). The nervous system has been determined to be the primary target organ with neurological effects generally observed (EPA, 2004). Syndrome called manganism may result from chronic exposure to higher levels of manganese (EPA, 2004; Calkins, 2009). Manganism is characterized among other symptoms, weakness, tremors, a masklike face and psychological disturbance (Calkins, 2009).

Manganese is naturally occurring in many surface and ground water sources and in soils that erode into these waters. Human activities are also responsible for much of this manganese contamination in water in some areas (EPA, 2004). Sources of manganese due to human activities in the environment include; combustion of coal, residential combustion of wood, iron and steel production plants and power plants (Calkins, 2009). The primary sources of manganese for surface and ground water releases are industrial facility effluent discharge, landfill and soil leaching and underground injection (EPA, 2004). Manganese in the form of potassium permanganate may also be used in drinking water treatment to oxidize and remove iron, manganese and other contaminants (EPA, 2004).

The WHO has put the maximum limit for manganese in drinking water at 0.4 mg/l (Calkins, 2009). In a study done by Mebrahtu and Zebrabruk (2011) on heavy metals in drinking water in Tigray region of Northern Ethiopia, manganese levels varied from below detection in various samples to 215 µg/l. None of the drinking water samples analysed, contained manganese above WHO maximum admissible limit of 400 µg/l. Raji *et al.* (2010) recorded the following levels of manganese in drinking water in Sokoto, Nigeria; station T₁ 0.670 mg/l, station T₂ 0.800 mg/l, station T₃ 0.550mg/l, station WB(R) 0.550 mg/l and WB(T) 0.510 mg/l. A similar study done by Oyugi (2000) on heavy metals in sea water along the Mombasa Coastline reported the following levels of manganese in these stations; Nyali Bridge (166.74 mg/l), KMC Mombasa (219.99), Vanga (1100.02 mg/l), Marine Park (648.21 mg/l).

2.5.5 Zinc

Zinc is an essential trace element for plants, animals and humans found in virtually all food and potable water in the form of salts or organic complexes (Swaminathan *et al.*, 2011). Although drinking water seldom contains zinc above 0.1 mg/l, levels in tap water can be considerably higher because of the zinc used in plumbing material (Swaminathan *et al.*, 2011). The average adult body contains between 2-3 g of zinc (Miculescu *et al.*, 2011). Zinc is used to form connective tissues like ligaments and tendons (Miculescu *et al.*, 2011).

Zinc toxicity is rare but at concentrations of up to 40 mg/l, it may induce toxicity characterized by symptoms of irritability, muscular stiffness and pain (Al-Weher, 2008). Some of the

anthropogenic sources of zinc in soil and water include, discharges of smelter slag and wastes and the use of commercial products such as fertilizers, paints and wood preservatives containing zinc (Lew, 2008). There is no guideline for zinc in drinking water; however, drinking water containing zinc levels above 3 mg/l may not be acceptable to consumers. A guideline value of 3 mg/l was suggested by WHO for zinc content in drinking water (Swaminathan *et al.*, 2011).

A study carried by Raji *et al.* (2010), recorded the following zinc level range in tap, well and pure water in Sokoto, Metropolis values within the maximum acceptable WHO limit. A similar study carried out by Reza and Singh (2010) in India on heavy metal contamination and its indexing approach for river water, found relatively higher values of zinc of 80.1 µg/l and 75 µg/l and was attributed to the unused remains of zinc sulphate fertilizer, however this level did not exceed the highest permitted value for zinc in water tentatively set at 300 mg/l by WHO (Swaminathan *et al.*, 2011). In a similar study by Jia *et al.* (2010) on levels of heavy metals in soils of Yucheng city in China, recorded levels of zinc ranging from 48.49-124.30 mg/l with a mean level of 71.94 mg/l. A similar study by Kar *et al.* (2008) recorded zinc values in surface water ranging from 0.012 to 0.370 mg/l. Similarly, a study by Papafilippaki *et al.* (2008) recorded levels of zinc in river water ranging from 16 µg/l to 142 µg/l during warm season and 0.000 to 11.000 µg/l during wet season. Kisamo (2003) recorded values of zinc ranging from 0.040 to 0.080 mg/l. Okonola *et al.* (2007) recorded values of zinc in soils ranging from 41.66 mg/kg to 237.96 mg/kg. Similarly, a study by Yahoya *et al.* (2010) recorded zinc values in roadside soils ranging from 30.2 mg/kg to 131.06 mg/kg during wet season and 73.3 mg/kg to 202.4 mg/kg during dry season.

2.6 Samburu County

Samburu County is situated in the northern half of Rift Valley province of Kenya. The County lies between latitudes $0^{\circ} 40'$ north and $2^{\circ}50'$ north of equator and longitudes $36^{\circ}20'$ east and $38^{\circ}10'$ east of prime meridian (Nanyingi *et al.*, 2008). It lies within the semi arid areas of the country and has a total population of approximately 21,120.5 km² (Nanyingi *et al.*, 2008). The county has four divisions and of the four divisions, Kirisia Division has the highest population due to its good climate, fertile soils and many trading centres. Maralal town is the main urban centre in this division (Lesamana, 2009). The highlands of Lorroki Divisions have a much favourable climate sand soils and have thousands of hectares under wheat and barley farming (Nema, 2009).The major types of wastes in Samburu is solid wastes and is more profound in urban centres. Major sources of water pollution in the county are farm herbicides, wild life and livestock wastes, soil erosion and human wastes (NEMA, 2009).

Maralal town, for example has no sufficient wastes disposal management. There are no dumpsites in this town and even the villages. The increase on the consumer activity of the population of Maralal also entails more wastes and further pressure on sanitary facilities. This, therefore leads to environmental degradation through pollution of soil and water (Lesamana, 2009). According to NEMA (2009) the main sources of water in Samburu County are boreholes, springs, wells, sand dams, dams, rivers. In addition to other pollutants, small arms used in cattle rustling and other illegal activities are also known to pollute these water sources and soils in this

county Ruto *et al.*, 2010). Charcoal being the main source of energy has also contributed to the environmental degradation and pollution of the water in this county.

2.7 Methods for heavy metal analysis

Several techniques for the determination of heavy metal elements are currently in use. These include flame atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Sonayei *et al.*, 2009), inductively coupled plasma –mass spectroscopy (ICP-MS) (Nassef *et al.*, 2006), X-ray fluorescence and neutron activation analysis (Magdaleno *et al.*, 2011). The AAS was used in this study because of its simplicity, reliability and sensitivity (Sarkar, 2005). A lot of studies on heavy metals in water, soil plants and animals have used atomic absorption spectroscopy as the method of analysis for the heavy metals. A study by Begum *et al.* (2009) in the analysis of lead, iron, zinc, nickel and copper in soil and plants employed the method for analysis. Similarly, Fong *et al.* (2008) in the analysis of copper, Cd, manganese, lead and zinc in urban roadside soils used atomic absorption spectroscopy in their analysis. Other researchers who have employed atomic absorption spectroscopy in their analysis of heavy metals include, Mantaz and Chowdhury (2006) who studied iron, copper, manganese and zinc levels in urban solid waste, Awokunmi *et al.* (2010) in their study of Cd, cobalt, chromium, copper, lead, manganese, nickel and zinc levels in soils from a dumpsite, Mico *et al.*, (2006) employed atomic absorption spectroscopy method in analysis of Cd, cobalt, chromium, copper, iron, manganese, nickel, lead and zinc in the agricultural soils of Segura River Valley in Spain. Al weher (2008), analysed levels of Cd, copper and zinc in three species of fish using atomic absorption spectroscopy method. Similarly Wieczorek *et al.* (2005) employed the same

method of analysis in determining the levels of lead in cereal grains and soils adjacent to roadways.

2.8 Atomic spectroscopy

This technique is applicable to most gas phase elements over a wide range of concentrations and involves detecting, measuring and analyzing radiation that is either absorbed or emitted from the atoms or ions of the element of interest (McMahon, 2007). It involves three techniques: Absorption, emission and fluorescence. In all the above, the sample is decomposed by intense heat into hot gases consisting of free atoms and ions of the element of interest (McMahon, 2007). As atoms are the simplest and purest form of matter and cannot rotate or vibrate as a molecule does when subjected to high energy radiation, electrons within the atom undergo transitions. The high energy radiation is commonly produced by

- a. Flame in flame atomic absorption spectroscopy (FAAS)
- b. Electrothermal furnace in flameless graphite furnace atomic absorption spectroscopy (GFAAS)
- c. Plasma in inductively coupled plasma-optical emission spectroscopy (ICP-OES)
- d. X-ray in X-ray fluorescence spectroscopy (XRF) ((Lajunen and Paavo, 2007))

The above four belong to one of three major types of atomic spectroscopy namely absorption, emission and fluorescence ((Lajunen and Paavo, 2007)).

2.9 Atomic absorption spectroscopy

2.9.1 Principle of AAS

An atom is made up of positively charged nucleus surrounded by a number of negatively charged particles necessary to provide neutrality. These atoms occupy discrete energy levels but it is possible for an electron to be moved from one level to another by introduction of energy. Such transitions will only occur if the available energy is equal to the difference between the two levels. Energy levels and the energies associated with electron transitions are unique for each element. When light (energy) of a characteristic wavelength enters an analytical system, outer shell electrons of corresponding atoms within the light path will be excited as energy is absorbed. The amount of light transmitted through the system from a source to the detector will be less. The loss of light is proportional to the number of atoms. The measurement of the radiation transmitted (using Beer-Lambert's law) in such a transition form the basis of AAS. Beer-Lambert's law relates absorbance, a to the concentration of metallic atoms in the atom cell, c as follows

$$\text{Log}T^{-1} = a b c$$

Where

a is the absorptivity in grams per litre-centimetre

b is the atom width in centimeters

c is the concentration of atoms

The AAS involves the measurement of the drop in light intensity of initial radiation I_0 to final radiation I depending on the concentration of the metal. Modern instruments automatically

convert logarithmic values into absorbance (Nollet, 2011). Figure 2.1 below illustrates AAS instrumentation.

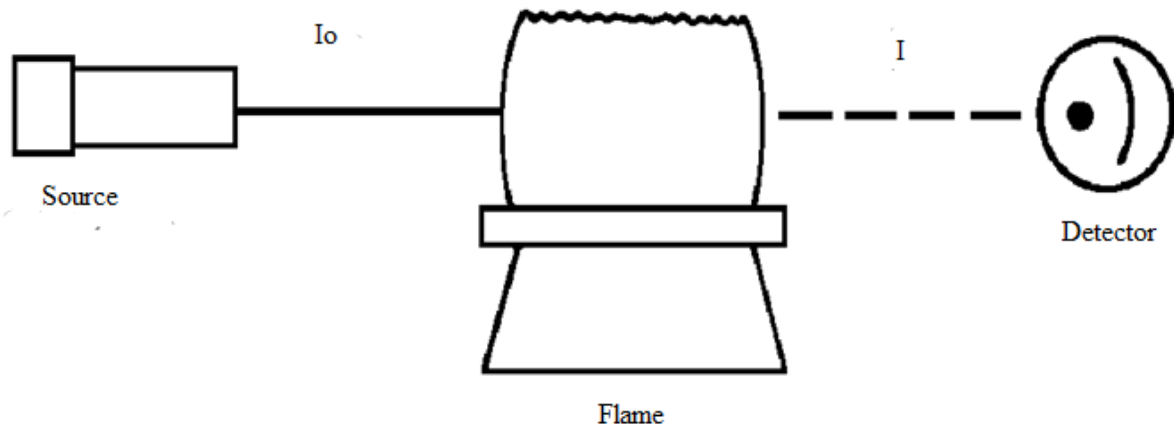


Figure 2.1: Diagram to illustrate instrumentation of AAS

2.9.2 Instrumentation of AAS

Any atomic absorption spectrometer consists basically of a light source which emits the sharp line spectrum of elements to be determined, a method to produce atomic vapour of the sample to be analyzed, a monochromator for the spectral dispersion of the source radiation, a detector connected to an amplified read out system and a computer

2.9.2.1 Light source

A continuous source of radiation is required. A series of sources which can give sharp emission lines for a specific element are used. A hollow cathode glow discharge lamp is used. A hollow cathode lamp has two electrodes; one is cup shaped and made of a specific element. The metal used for the cathode is the same as the metal to be analyzed. The lamp is filled with noble gas at low pressure. It will produce a glow discharge from the hollow cathode. Metal atoms are evaporated by sputtering. The atoms accept energy of excitation and emit radiation with the lines of the metal. Hollow cathode lamps made out of several elements are available (Khopkar, 1998). The figure 2.3 below shows one of the light source used by AAS machine; a hollow cathode lamp

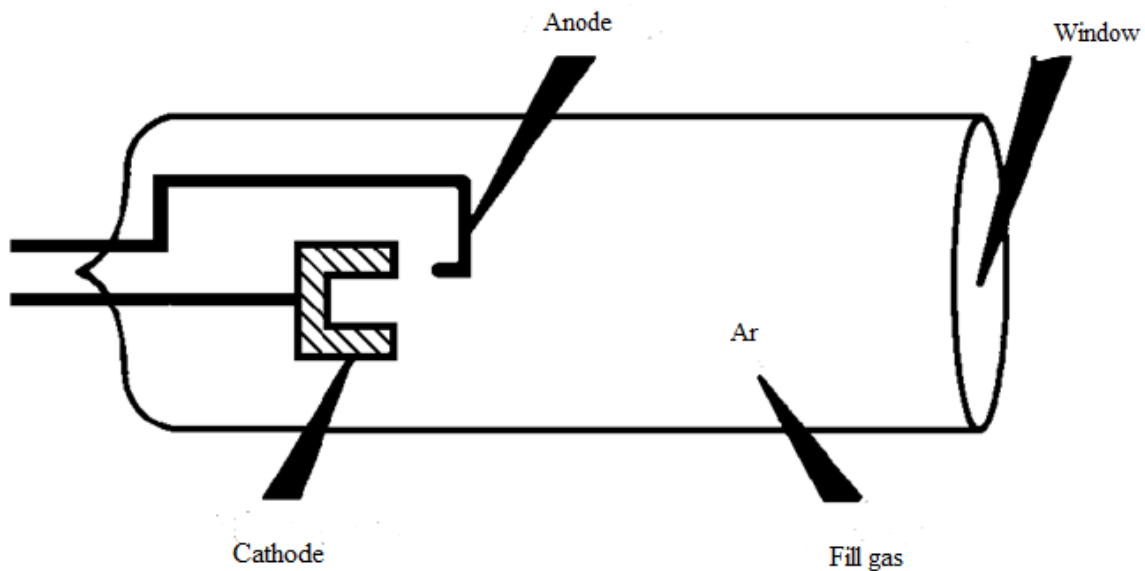


Figure 2.2: A hollow cathode lamp

2.9.2.2 Atomization

Several types of atomizers are used for atomization. These include flame, electrothermal, cold vapour technique for mercury and hydride generation (Nielsen, 2010). The flame atomizers consist of a nebulizer and a burner. The nebulizer is designed to convert the solution into a fine mist or aerosol. In flame atomization, atomization is carried out by flame. Heat energy is utilized to convert the metallic element to atomic dissociated vapour. The temperature should be controlled very carefully to convert it to atomic vapour. At too high or too low temperatures, atoms will be ionized and they will not be absorbed.

In atomization, fuel and oxidant gases are fed into a mixing chamber which passes through baffles to the burner head. A flame is produced and the sample is aspirated through the air into the mixing chamber. Only droplets of a small size pass through the baffles to the burner head. A narrow burner is therefore preferred and careful readjustment of the gas (Khopkar, 1998; Nielsen, 2010).

In electrothermal atomization, electrothermal atomizers are used. Electrothermal atomizers are typically cylindrical graphite tubes connected to an electric power supply. The sample is introduced into the tube through a small hole using a microlitre syringe. The system is flushed with an inert gas to prevent the tube from burning and exclude air from the sample compartment. The tube is heated electrically to evaporate the solvent, the sample is then ashed and further heated to quickly vapourized and atomize the sample (Nielsen, 2010). Cold vapour technique of

atomization works for mercury only. In this technique, mercury compounds in a sample are reduced to elemental mercury by the action of stannous chloride, a strong reducing agent. The elemental mercury is then carried in a stream of air or argon into an absorption cell where absorption takes place (Nielsen, 2010). In hydride generation technique of atomization, volatile hydrides of elements are formed by reacting samples with sodium borohydride. The hydrides are carried into an absorption cell and heated to decompose them into free atoms. The atomic absorption measurements are then carried out (Nielsen, 2010).

2.9.2.3 A monochromator

A monochromator produces monochromatic light by removing unwanted wavelengths from the source light beam. It isolates a single atomic resonance line from the spectrum of lines emitted by hollow cathode lamp. Essentially it is an adjustable filter that selects a specific, narrow region of spectrum for transmission to the detector and excludes all wavelengths outside this region.

A monochromator comprises an entrance slit, a dispersion device and an exit slit.

- i. The entrance slit selects a defined beam of light from the source
- ii. The dispersion device causes the different wavelength of light in the source beam to be dispersed at different angles
- iii. The exit slit enables selection of a particular wavelength to produce the required monochromatic light

Figure 2.3 below shows a model of a monochromator used by an AAS machine

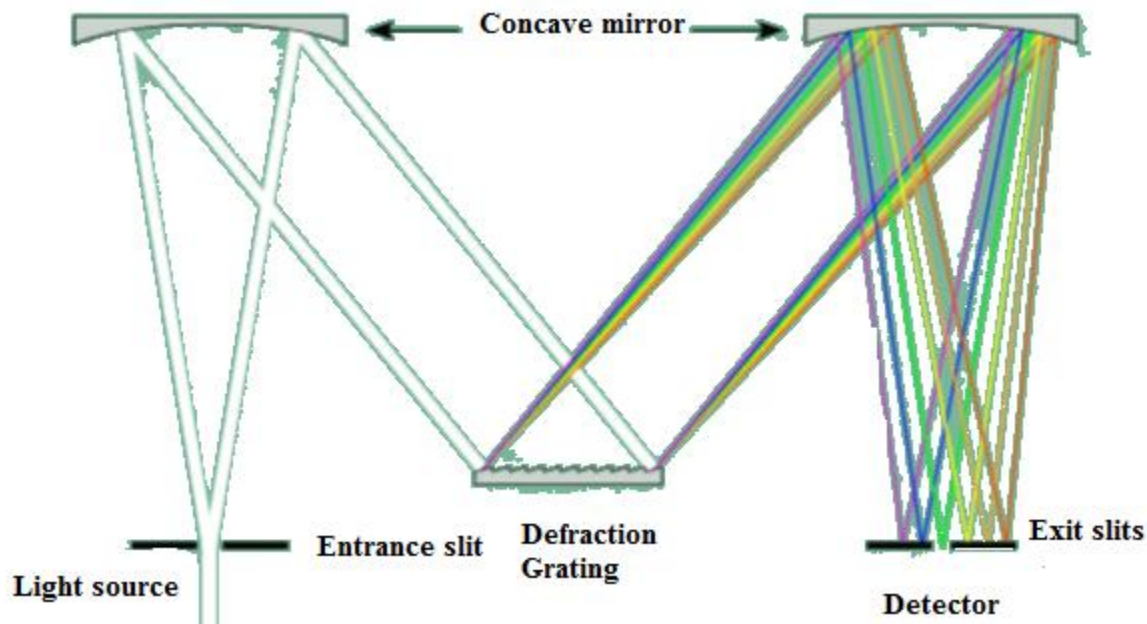


Figure 2.3: A model of a monochromator

There are two types of monochromators; prism and grating systems. Prisms and grating systems separate various wavelengths of light in different fashions. Prisms refract light at the interface of two surfaces with differing refraction indexes creating angular dispersion. Prisms have limitations, their resolution is significantly lower than a grating system and their separation technique is non-linear which creates mechanical problems with focusing a specific wavelength on the exit slit.

Diffraction gratings are materials with a large number of parallel and closely spaced slits or ridges. Diffraction causes constructive interference at unique points for each wavelength. The separated wavelengths are collimated with a concave mirror towards the exit slit. The tilt angle

of the grating device determines the band of wavelength exiting the monochromator and reaching the detector.

2.9.2.4 The detector

Two detectors are used in atomic absorption spectrometers; photomultiplier tubes and solid state detectors (Nielsen, 2010). Detectors convert the radiant energy reaching it into an electrical signal. The signal is processed to produce either an analogue or digital read out. Modern instruments are interfaced with computers for data collection, manipulation and storage. The photomultiplier tubes are the most common types of detectors used.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Research design

Purposive nonprobability sampling design was used in this study where the cases best contributing to the information needs of the study were selected. Two divisions of Samburu County were selected, Lorroki division representing large scale wheat and barley farming and Kirisia division representing heavy human activities such as construction, wrong disposal of sewerage and locomotives.

3.2 Study Area

The Figure 3.1 shows a map of Samburu County showing the areas of study, Kirisia and Lorroki divisions of the county. Samburu County, falls within latitudes $0^{\circ} 40''$ and $2^{\circ} 50''$ north and $36^{\circ} 20''$ and latitudes $38^{\circ} 10''$ East of Prime Meridian (Nanyingi *et al.*, 2008). Kirisia division has a relatively higher population since it houses Maralal town which is the County headquarter. Lorroki division on the other hand is a very rich agricultural area with more than 6,000 hectares under wheat and barley plantations (NEMA, 2009). Livestock farming is also practised in the two divisions. Heavy use of fertilizers and acaricides is therefore evident in the two divisions. The two divisions also have the highest number of aging auto mobiles plying its roads which contribute greatly to the sources of heavy metals in the environment. Kirisia division hosts Maralal town which is the county headquarters and the key source of contamination in Kirisia Division. Maralal town is poorly planned with very poor sewerage system and sewerage facilities

especially around the slum areas of Loikas and this contributes to heavy metal pollution especially in water (Lesamana, 2009).

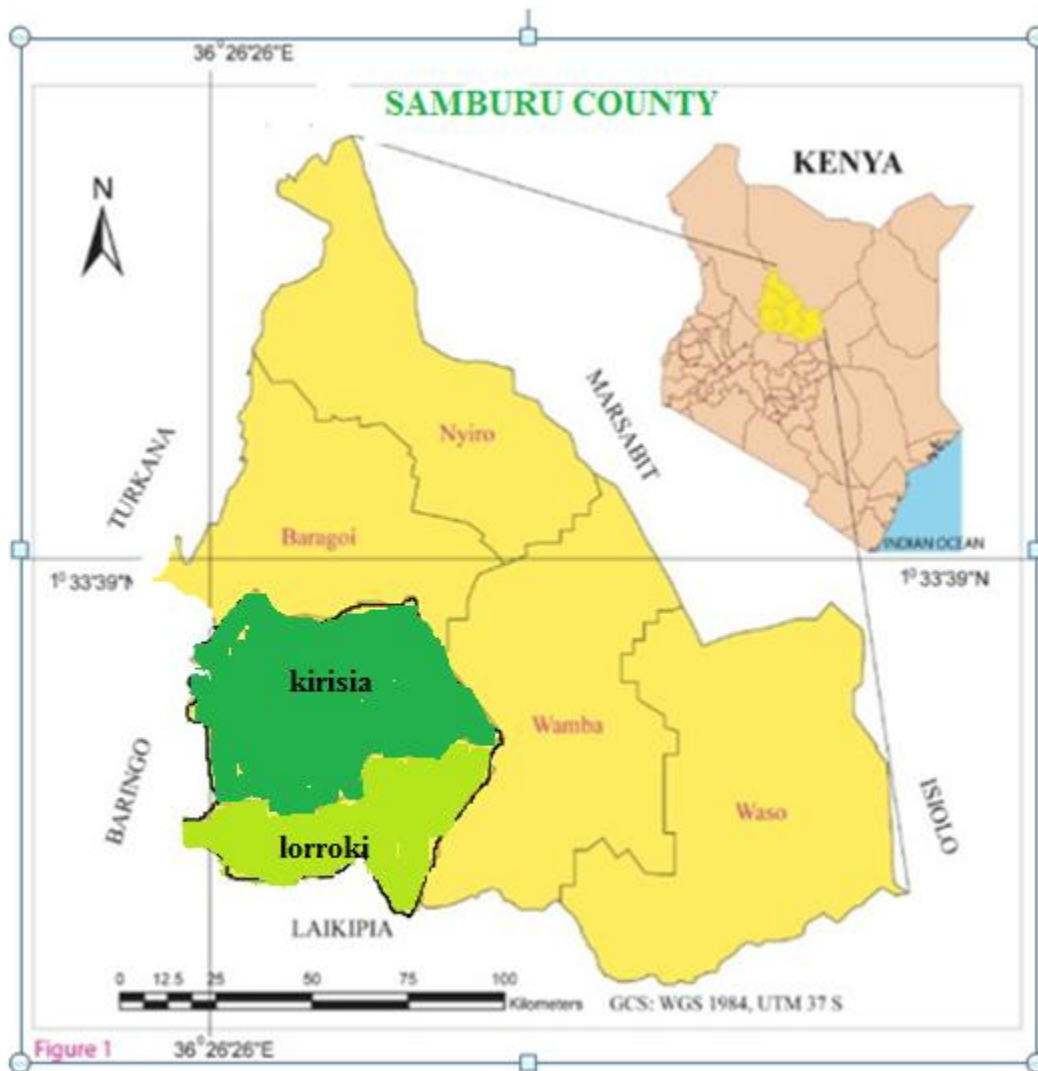


Figure 3.1: Map of Samburu County

Source: Nanyingi *et al.* (2008)

3.3 Chemicals reagents

Chemicals and reagents used were of analytical grade. They included; nitric acid, hydrochloric acid, distilled water, hydrogen peroxide, lead nitrate, zinc nitrate, Chromium oxide, manganese powder, ammonium chloride and Cd nitrate. The chemicals were purchased from Lemah Laboratories in Nairobi which buys its chemicals from Sigma Laboratories in the United States of America.

3.4 Cleaning of glassware

All apparatus were initially washed with detergents then soaked in 2 M nitric acid for 24 hours then washed thoroughly. They were rinsed with aqua regia, followed by tap water and then rinsed in distilled water. The glassware was then dried in a hot oven at 105⁰C.

3.5 Sampling

3.5.1 Soil sampling

Sampling sites were chosen in line with anthropogenic sources of heavy metals. At each sampling point, approximately 0.5 kg of soil was collected 0-10 cm in depth using a stainless steel sampler. Soil samples along the roads were collected at a distance of one metre away from the road and within an area of one square metre. Three samples were collected from each point, thoroughly mixed in a clean plastic container to obtain a representative sample dried, crushed and sieved with 2 mm mesh before being stored in labeled polythene bags prior to the analysis.

The soil samples were labeled according to the regions from which they were obtained. Plate 3.1 and 3.2 show some of soil sampling sites



Plate 3.1: Soil sampling site from a maize farm in Lorroki



Plate 3.2: Soil sampling from wheat farm in Lorroki

3.5.2 Water sampling and pre-treatment

Water from bore holes was pumped for 2 minutes before obtaining a 500 ml sample for analysis. Water from the dams was sampled 10-15 cm below the water surface using labeled acid washed plastic containers to avoid unpredictable changes in characteristic as per standard procedures (Reza and Singh, 2010). The water was labeled according to the source from which it was obtained and also the region from which it was obtained. The water was acidified with 2 ml of analytical grade nitric acid in order to preserve metals and avoid precipitation (Kar *et al.*, 2008). The water samples were stored at a 5°C temperature awaiting the transportation to the laboratory for analysis. The pictures in the plates 3.3 and 3.4 show some of the water sampling sites.



Plate 3.3: Water sampling site, Porro dam



Plate 3.4: Water sampling site, ragae

3.6 Sample digestion

3.6.1 Water digestion

The water sample bottles were shaken thoroughly in their plastic containers by use of hand. A volume of 100 ml of the sample was measured using a 100 ml volumetric flask and put in a conical flask and 5 ml of concentrated nitric acid was then added. The mixture was heated slowly on a hot plate and evaporated to about 20 ml ensuring that the water did not boil. A further 5 ml of concentrated nitric acid was added and the beaker was covered with a watch glass while heating continued. Nitric acid continued to be added until the solution appeared light coloured and clear. Lastly, 2 ml of concentrated hydrochloric acid was added and heated slightly to dissolve any remaining residue. Few drops of hydrogen peroxide were then added to ensure complete digestion had take place. The solution was filtered and the filtrate was transferred to a 100 ml volumetric flask to cool and the filtrate was made up to the mark with distilled water (Radojovenic and Bashkin, 2006).

3.6.2 Soil digestion

Well mixed samples of 1 g each were weighed using a scientech Zeta series electronic balance manufactured in the year 2000. The samples were put into 250 ml glass beaker and digested with 24 ml of aqua regia and then evaporated to near dryness. The soil samples were then dissolved in 10 ml of 2% nitric acid, filtered and then diluted to 100 ml with distilled water (Begum *et al.*, 2009).

3.7 Preparation of stock solutions and standards

3.7.1 Lead stock solution and standards

Lead stock solution (1000 mg/l) was prepared by dissolving 1.59 g of lead (ii) nitrate in 500 ml of distilled water and then made up to 1 litre of solution using distilled water. Through serial dilutions, standard working solutions of lead of 1, 2, 3, 4 and 5 mg/l were made which were used to generate a calibration curve for lead.

3.7.2 Zinc stock solution and standards

Zinc stock solution (100 mg/l) was prepared by dissolving 0.289 g of zinc nitrate salt in 300 ml of distilled water and then made up to 1 litre of solution using distilled water. A working zinc standard solution (20 mg/l) was made by diluting 20 ml of the stock solution to 100 ml of solution. The calibration graph was made using solutions with the following concentrations; 0.5, 1, 1.5, 2, and 2.5 mg/l of zinc.

3.7.3 Manganese stock solution and standards

Manganese stock solution (100 mg/l) was prepared by dissolving 0.10 g of manganese metal powder in 10 ml of concentrated hydrochloric acid mixed with 1 ml of concentrated nitric acid. A 10 ml of nitric acid was then added and the solution finally diluted to 1000 ml with distilled water. A working manganese standard solution (20 mg/l) was made by diluting 20 ml of the

stock solution to 100 ml of solution using distilled water. The calibration graph was made using solutions with the following concentrations; 0.5, 1, 1.5, 2 and 2.5 mg/l of manganese.

3.7.4 Cd stock solution and standards

Cd stock solution (1000 mg/l) was prepared by dissolving 0.275 g of Cd nitrate salt in 500 ml of distilled water and made up to 1 litre of solution using distilled water. A working Cd standard solution (10 mg/l) was made by diluting 10 ml of the stock solution to 100 ml of solution with distilled water. The calibration graph was made using solutions with the following concentrations; 0.2, 0.4, 0.6, 0.8, and 1.0 mg/l of Cd.

3.7.5 Chromium stock solution and standards

Chromium stock solution (1000 mg/l) was prepared by dissolving 0.38 g of CrO_3 in a solution of 20 ml water and 4 ml of concentrated nitric acid and diluted to 200 ml using distilled water. Through serial dilution, standard working solutions of chromium were made. The calibration graph was made using solutions with concentrations of 1, 2, 3, 4 and 5 mg/l.

3.8 Method Validation

The digestion method and atomic absorption spectroscopy analysis were validated by recovery method. One gram of randomly selected soil powder was spiked with three different concentrations of heavy metals one at a time (1.0, 1.5, 2.0 ppm) each run in with the AAS

machine. This was followed by the digestion of the spiked samples and determination of metal concentration using AAS. Blank or unspiked samples were digested through the same process and analyzed by same AAS. The amount that was recovered after digestion of the spiked samples was used to calculate % recovery (Al-weher, 2008). A mean recovery of the matrix was evaluated at 95% confidence level (Borosova *et al.*, 2002).

3.9 Sample analysis

Buck scientific (210 VGF) flame atomic absorption spectrophotometer machine was used in this analysis. Its parameters were set according to the specifications given in the manufactures manual including lamp current and fuel system of air/acetylene flame. The AAS machine had a picking meter that indicated when the optimum conditions had been realized. Its optimization was automatic. The Table 3.1 below shows elements and their wavelength of analysis in air acetylene flame.

Table 3.1: Elements and their conditions of analysis.

Element analyzed	Wavelength of analysis (nm)
Zinc	213.8
Chromium	357.9
Manganese	278.5
Lead	283.3
Cd	228.8

3.10 Data analysis

The data derived from various determinations was subjected to statistical analysis including mean, Pearson Correlation, t-test and ANOVA. The means for the levels in water and soil in the two divisions were determined. Using ANOVA and t-test, the means were compared to determine whether they were significantly different. Pearson correlation was used to relate the levels of heavy metals in water and soil.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

In this chapter the levels of heavy metals in water and soil from two divisions of Samburu County are reported and discussed. The results of the analysis are presented and discussed in the following subsections

4.2 Method validation

The analytical performance of the method of analysis was done using recovery test on some samples to be analyzed. In all the calculations of percentage recovery cases, the method produced a percentage recovery of between 95%-102% as shown in Table 4.1 hence making the method reliable for this analysis (Magdaleno *et al.*, 2011). The detection limits were also calculated. Ten blank samples were run in the machine for each element that was being analyzed. Their absorbancies were read. The mean of each ten blanks was calculated and hence the detection limits determined for each element

Table 4.1: Calibration curves correlations, detection limits and %recovery

Element	Detection limit (mg/l)	Detection limits (mg/l)	Correlation variance	% Recovery
	(Current study)	(Theoretical)		
Pb	0.011	0.010	0.999	98.000-99.300%
Mn	0.028	0.003	0.999	97.600-98.000%
Zn	0.003	0.0026	0.999	96.600-99.100%
Cr	0.031	0.003	0.996	96.700-101.000%
Cd	0.003	0.003	0.993	97.300-102.000%

The standards were also run in the machine before real analysis of each element and after the analysis of the same element. Calibration curves were then drawn for all the elements to be analyzed. Regression equations were then determined for every calibration curve. In all the cases regression was found to be above 0.99. The regression and regression equations are shown in the Table 4.1.

The detection limit was calculated by calculating the mean of the results of ten blank samples inclusive of the outliers plus three times the standard deviation of the blanks (Reeuwijk, 1998). The theoretical detection limits compare well with the detection limit of the machine used for this analysis (Cantle, 1998). The calibration curves were drawn from standards prepared within the linear range of the machine for each particular element. From the correlation variance, the graphs were within the accepted linear range of above 0.99.

4.3 Heavy metals in surface and ground water

4.3.1 Kirisia and Lorroki Divisions

Table 4.2 presents the mean levels of Zn, Cd, Mn, Pb and Cr in wells, dams, and bore holes water from Kirisia and Lorroki Divisions analyzed using the AAS

Table 4.2: Levels of heavy metals in wells, dams and boreholes in Kirisia and Lorroki Divisions

Parameter	Wells n=24 mean±SE (mg/l) (Kirisia)	Wells (n=24) mean±SD (mg/l) (Lorroki)	Dams n=15 mean±SE (mg/l) (Kirisia)	Dams (n=48) (mean±SD) (mg/l) (Lorroki)	Boreholes n=15 mean±SE(m g/l) (Kirisia)	MAL (WHO 2003) mg/l
Cd	0.010±0.000	0.003±0.001	0.02±0.010	0.004±0.001	BDL	0.003
Cr	0.050±0.010	0.030±0.010	0.050±0.010	0.040±0.010	0.030±0.010	0.050
Mn	0.080±0.010	0.040±0.010	0.050±0.010	0.050±0.010	0.090±0.020	0.400
Pb	0.130±0.080	0.052±0.010	0.060±0.030	0.230±0.050	0.320±0.110	0.010
Zn	0.050±0.010	0.030±0.010	0.050±0.010	0.040±0.010	0.020±0.010	3.000

Mean± Standard error

The mean concentration of Cd in wells in Kirisia was 0.010±0.000 mg/l while in dams was 0.020±0.010 mg/l. Cd was not detected in borehole water in Kirisia. The levels of Cd was highest in dams followed by wells in the same region. The level of Cd detected in the water samples from wells and dams was above the maximum allowed limit of WHO in Table 4.2. One way ANOVA (p=0.05) revealed no significant difference between the mean level of Cd in

borehole water, well water and dam water withi Kirisia Division ($p=0.077$). The levels of Cd obtained in well and dam water in Kirisia were similar to levels obtained in studies from other regions. Kaplan *et al.* (2011) recorded values in drinking water ranging from 0.050 to 1.670 $\mu\text{g/l}$. A similar study by Mebrahtu and Zerabruk. (2011) recorded values of Cd in drinking water ranging from 2.000 to 10.000 $\mu\text{g/l}$ in the Tigray region of Northern Ethiopia. Samuding *et al.* (2009) recorded the highest value of Cd in ground water as 13.100 $\mu\text{g/l}$. Cd occurs mostly in association with zinc and gets into water from corrosion of zinc coated (“galvanized”) pipes and fittings (Mehbrahtu and Zerabruk, 2011).The levels of Cd recorded in the studies by Mebrahtu and Zerabruk., (2011) and Samuding *et al.* (2009) were similar to the levels of Cd recorded in this study.

The mean of Cd in wells in Lorroki was 0.003 ± 0.001 mg/l and that in dams was 0.004 ± 0.001 mg/l. These values were on the limit of the maximum allowed limit of WHO (2003) of 0.003 mg/l. Statistical analysis using ANOVA at 95% confidence level, revealed no significant difference in the levels of Cd in the wells and dams in Lorroki Division ($p=0.801$). Comparison in the levels of heavy metals in dams and wells in Kirisia and Lorroki is as revealed in the Tables 4.3.

Table 4.3 Levels of heavy metals in dams and wells in Lorroki and Kirisia Divisions

Parameter	Source	Kirisia (mg/l)	Lorroki (mg/l)	P-value
Cd	Wells	0.010±0.000	0.003±0.001	0.189
	Dams	0.020±0.010	0.004±0.001	0.151
Cr	Wells	0.050±0.010	0.030±0.010	0.323
	Dams	0.050±0.010	0.040±0.010	0.619
Mn	Wells	0.080±0.010	0.040±0.010	0.051
	Dams	0.050±0.010	0.050±0.010	0.999
Pb	Wells	0.130±0.080	0.052±0.010	0.391
	Dams	0.060±0.030	0.230±0.050	0.038
Zn	Wells	0.050±0.010	0.030±0.010	0.323
	Dams	0.050±0.010	0.040±0.010	0.618

Figure 4.1 compares the levels of Cd in the wells and dams in Lorroki and Kirisia divisions

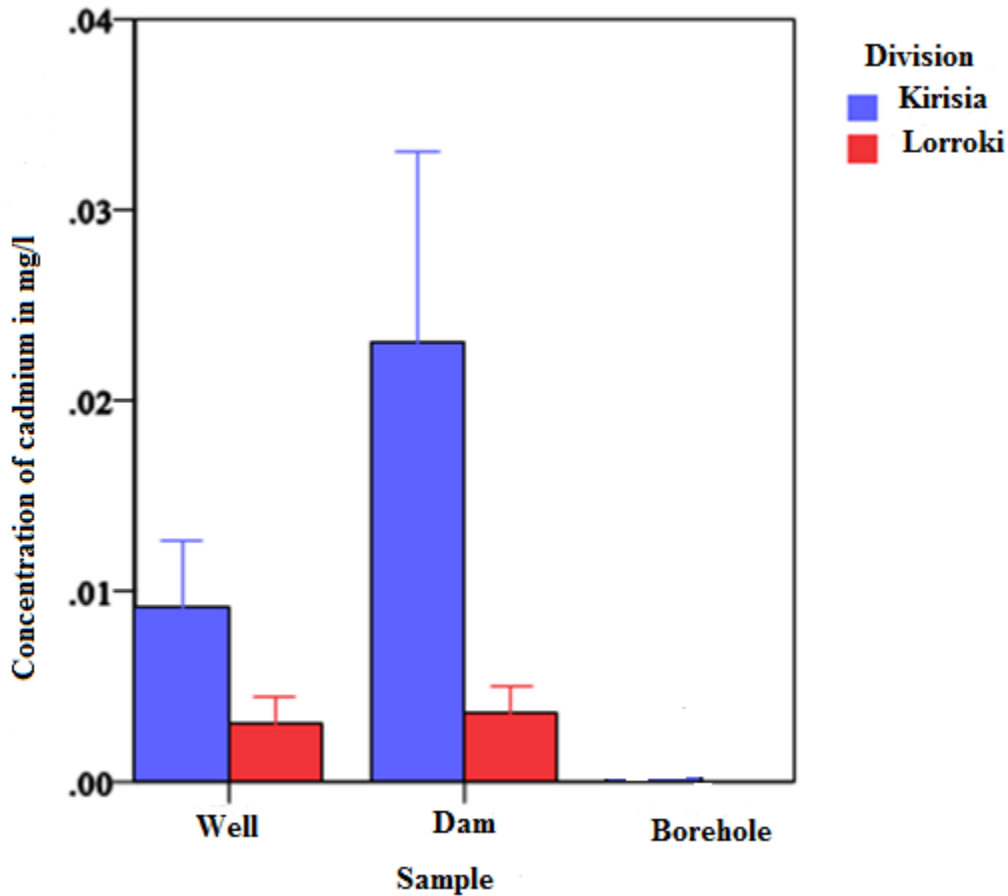


Figure 4.1: Levels of Cd in water in Kirisia and Lorroki Divisions.

The mean levels of Cd in water in Kirisia Division were higher than the levels in Lorroki Division. The dams in Kirisia had the highest levels of Cd followed by the wells from the same division. Wells in Kirisia Division had higher levels of Cd than wells in Lorroki though the levels were not significantly different ($P=0.189$). The mean level of Cd in borehole water in Kirisia Division was the Lowest. The high levels of Cd in water from Kirisia division compared

to Lorroki results from sewage sludge from various sources including human excretion, domestic produce and storm water containing particles of rubber tyres (Selinus and alloway, (2005) produced within Maralal town. This area also has poor sanitary facilities and very few public toilets coupled with an underdeveloped sewerage system (Lesamana, 2009). The surface runoff when it rains propels these wastes into the water bodies hence elevating the levels of this heavy metal in the water.

The mean level of Cr in Kirisia Division in wells was 0.050 ± 0.010 mg/l in dams 0.050 ± 0.010 mg/l and in boreholes 0.030 ± 0.010 mg/l against the maximum allowed limit of 0.050 mg/l. Comparably these values were lower than the WHO (2003) maximum allowed limits of Cr in water. The levels of Cr were high in wells and dams compared to the levels in boreholes. There was no significant difference between the levels of Cr in boreholes, wells and dams in Kirisia Division ($P=0.238$) meaning that the levels of Cr in water in Kirisia Division was independent of its source. However, the levels of Cr obtained in water from the division was lower than those obtained in other regions with similar climatic conditions (Abulude *et al.*, 2007; Raji *et al.*, 2010). A study done to determine the levels of heavy metals in the Tigris region of Northern Ethiopia recorded the following mean levels; Alamata 0.11 mg/l, Mekelle 0.146 mg/l, Wekro 0.116 mg/l (Mebrahtu and Zebrabruk, 2011). These levels were higher than the levels recorded in this study.

The mean levels of Cr in Lorroki division in wells and dams were 0.003 ± 0.01 mg/l and 0.004 ± 0.01 mg/l respectively. The levels differed slightly with the mean level of dams being

slightly more. These values were lower than the WHO maximum allowed limit of 0.05 mg/l for Cr. ANOVA revealed that there was no significant difference between the mean levels of Cr in well water and dam water within Lorroki Division ($P=0.674$). Lower levels of Cr were obtained in a study by Wogu and Okaka (2011) in a study on surface water of Warri River, Nigeria where Cr levels ranging from 0.0 mg/l-0.06 mg/l recorded. The levels of Cr in water in Lorroki and Kirisia Divisions revealed the pattern shown in the Figure 4.2.

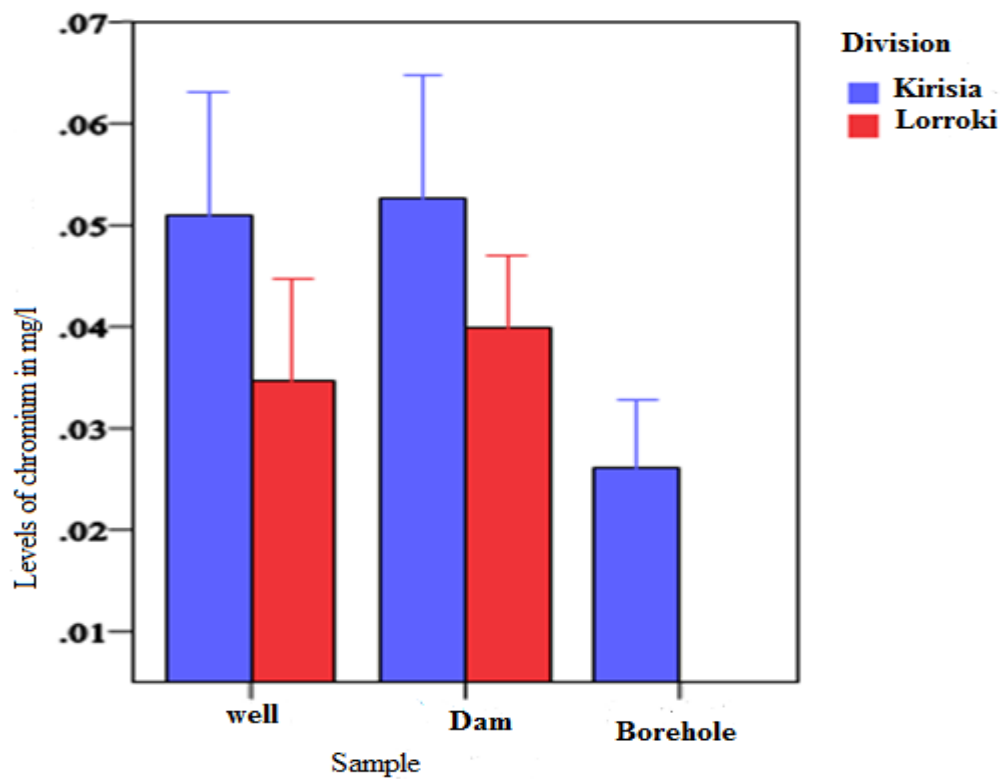


Figure 4.2: Levels of Cr in water in Kirisia and Lorroki Division

The levels of Cr in water in Kirisia were non significantly higher than the levels in Lorroki Division. There was also a non significant variation in the levels of Cr in dam and borehole water in Kirisia and Lorroki Division. The level of Cr in the borehole water was the lowest as compared to the other sources of water. The levels of Cr in wells in Kirisia was nonsignificantly

higher than the levels in wells in Lorroki Division ($P=0.323$). Similarly the levels of Cr in dams was nonsignificantly higher than the levels of Cr in dams in Lorroki ($P=0.619$). Sources of Cr in water include; cement, dyes, paints, printing ink, cutting oils, detergents, wood preservatives among others (Hilgenkamp, 2006). These sources are more common in Kirisia division which generally has a high population and houses Maralal town hence the high levels of Cr in water sources from Kirisia division. Excess of pesticides and fertilizers which are not used by plants will percolate into the soil with the irrigation water. Consequently, they can reach the groundwater wherever the permeability of the soil permits. Wrong farming activities such as uses of large amounts of phosphate fertilizers in agriculture and many types of pesticides may also led to the relatively high concentrations of Cr in water (Mandour and Azab, 2011). Other sources include plastics and batteries use and disposal may also be considered additional reason for high concentrations of Cr in water (Mandour and Azab, 2011).

Manganese mean levels in wells in Kirisia Division was 0.08 ± 0.01 mg/l, 0.05 ± 0.01 mg/l in dams and 0.09 ± 0.02 mg/l in boreholes. Borehole water had the highest level of manganese while the dams had the lowest level within the division. ANOVA revealed no significant difference between the mean levels of manganese in well water, dam water and borehole water in Kirisia division ($P=0.130$). The levels of manganese in dams, boreholes and wells were therefore independent of the source. The levels of manganese in this study were lower than levels obtained by Raji *et al.* (2010) and Wogu and Okaka (2011) but similar to a study done by Mebrahtu and Zerabruk, 2011. Raji *et al.* (2010) in their study recorded a manganese range of 0.510-0.800 mg/l in tap water, 0.510-1.200 mg/l in well water and 0.510-0.720 mg/l in pure sachet water. The values of manganese obtained in this study were greater than the maximum recommended

contamination level of 0.400 mg/l. Similarly in their study, Wogu and Okaka (2011) recorded values of manganese in river water ranging from 0.020-0.680 mg/l.

Mn mean levels in wells and dams in Lorroki Division were the second highest after lead levels. Mn mean levels in wells were 0.040 ± 0.010 mg/l while those of dams were 0.050 ± 0.010 mg/l. Dams recorded a higher mean of Mn than wells within Lorroki division. Statistical analysis using ANOVA revealed that there was no significant difference between the mean levels of Mn in the wells and dams within the Division ($P=0.478$). A study done by Mebrahtu and Zebrabruk, 2011 on concentration of heavy metals in drinking water from urban areas of the Tigray Region, Northern Ethiopia using atomic absorption spectrophotometry revealed levels ranging from BDL-0.2 mg/l which were similar to the levels in this study. Figure 4.3 compares the levels of Mn in the water in Lorroki and Kirisia division

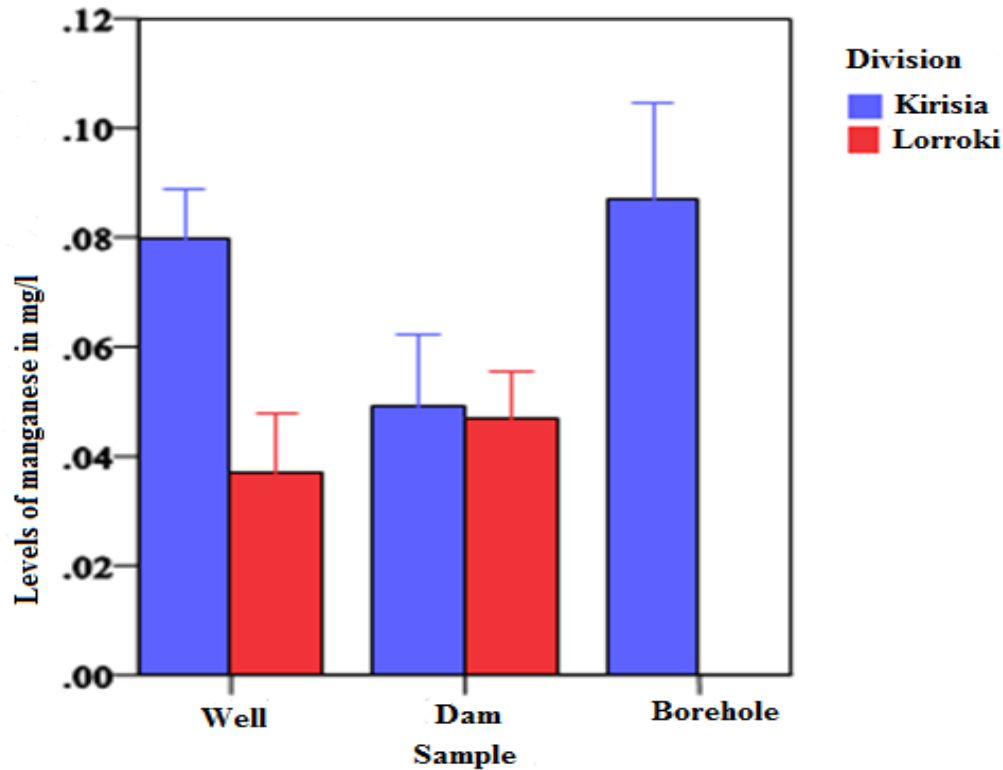


Figure 4.3: Levels of Mn in Different sources of water in Lorroki and Kirisia

The mean level of Mn in borehole water in Kirisia division was the highest followed by the well water and the dam water. The level of Mn in well water in this division was higher than that in wells in Lorroki though the difference was not significant ($P=0.051$). Similarly the levels of this element in dams in Kirisia were nonsignificantly higher than those in dam water in Lorroki ($P=0.999$). In general the levels of Mn were higher in Kirisia Division than Lorroki Division. The levels of Mn were also higher in ground water than in surface water because ground waters contain Mn naturally derived from rock water interaction. Mn is also likely to be present in ground water because ground water contains low dissolved oxygen. The reduced forms of Mn which are promoted by low oxygen present in ground water are more soluble than oxidized

forms (Nath and Langdon, 2010). In addition Mn is consequently associated with slow moving water a characteristic of ground water (Nath and Langdon, 2010).

The high mean levels of Mn in water sources in Kirisia division could be attributed to the presence of Maralal Town within the division. The urban population heavily relies on charcoal as the major source of fuel. There is no sufficient waste disposal management in Maralal town and no dumpsites. Plastic bags and batteries are found everywhere within the town (Lesamana, 2009). Charcoal burning and wastes especially from batteries are known to be a major source of Mn.

The mean of level of Pb in Kirisia division in wells was 0.13 ± 0.08 mg/l, in dams 0.06 ± 0.03 mg/l and in boreholes 0.32 ± 0.11 mg/l. These values were however, above the maximum allowed limits of WHO of 0.01 mg/l of Pb levels in water. Borehole water had the highest levels of Pb in Kirisia Division while dam water had the lowest. One way ANOVA revealed no significant difference in the level of Pb in the dam, borehole and well water in Kirisia Division ($P=0.151$). The levels of Pb in water in Kirisia division was therefore independent of its source. The levels of Pb in water in Kirisia Division is particularly high due to the many sources of Pb within the division. The sources of Pb in this division include; sewage, old houses which were painted with Pb-pigmented paints, old automobiles and fertilizers. During rainy seasons the surface runoffs due to poor vegetation in this region carries residues from the above mentioned source hence the to dams, wells and sometimes boreholes hence the elevated levels.

Pb is the most significant of all the heavy metals because it is toxic, very common and harmful even in small amounts (Mebrahtu and Zerabruk, 2011). Pb enters the human body in many ways. It can be inhaled in dust from Pb paints, or waste gases from Pb gasoline. It is found in trace amounts in various foods, notably in fish, which are heavily subjected to industrial pollution. Some old homes may have Pb water pipes, which can then contaminate drinking water. Most of the Pb we take is removed from our bodies in urine; however, as exposure to Pb is cumulative over time, there is still risk of buildup, particularly in children. Studies on Pb are numerous because of its hazardous effects. High concentration of Pb in the body can cause death or permanent damage to the central nervous system, the brain, and kidneys (Mebrahtu and Zerabruk, 2011).

Lorroki division in the region sampled for analysis did not have boreholes. This region receives enough rainfall and therefore the population relies on dams and wells for their water needs. The mean of Pb in wells was 0.052 ± 0.1 mg/l and in dams was 0.050 ± 0.01 mg/l. The mean level of lead in dam water in Lorroki division was significantly higher than the mean level in well water. Statistical analysis using ANOVA revealed a significant difference between the mean levels of lead in dams and wells in Lorroki Division ($P=0.023$). A study done by Raji *et al.* (2010) recorded mean values of lead in drinking water ranging from 0.30-0.39 mg/l and 0.3-0.54 mg/l in wells water. Figure 4.4 shows how the mean levels of lead in wells, dams and boreholes compare in Lorroki and Kirisia Divisions

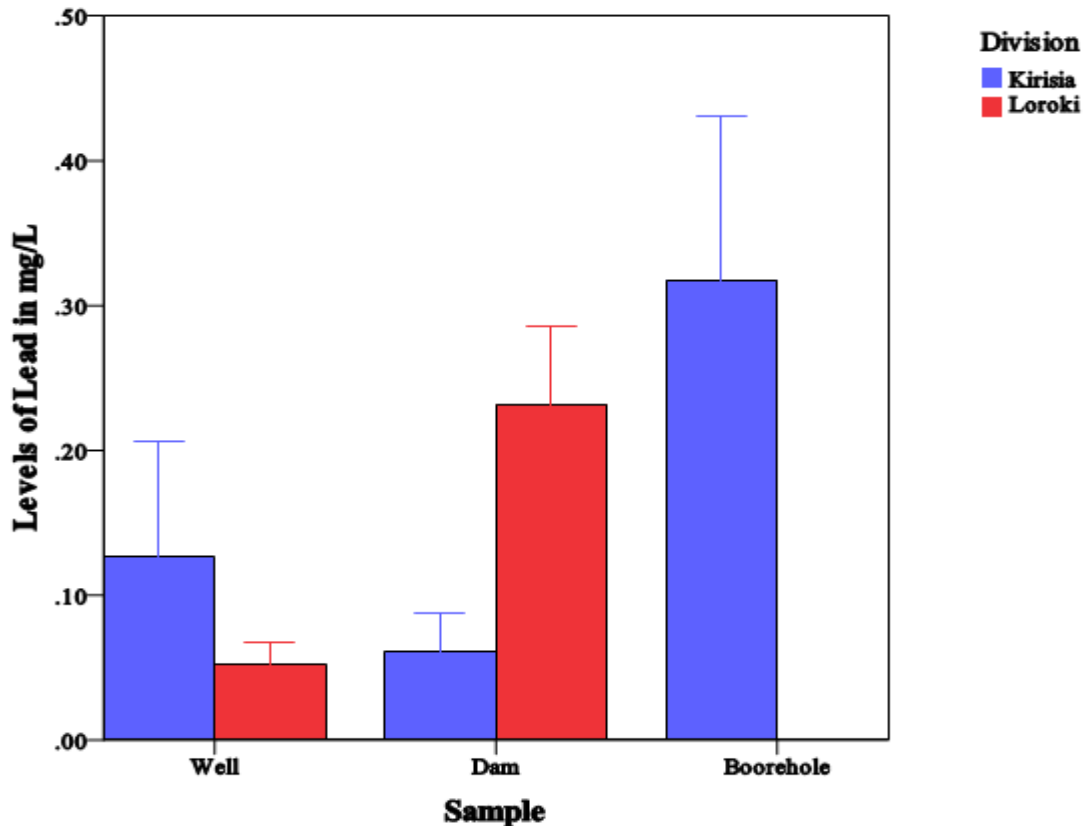


Figure 4.4: levels of Lead in three water sources in Kirisia and Lorroki Divisions

The mean level of Pb in boreholes in Kirisia division was the highest in comparison to the dams and wells in both Kirisia and Lorroki. The wells from Kirisia division had the lowest mean levels of Pb. The wells in Kirisia had nonsignificantly higher levels of Pb than the wells in Lorroki ($P=0.391$). On the contrary, the dams in Lorroki had significantly higher levels of Pb than the wells in Kirisia ($P=0.038$). High levels of Pb in wells and dams in Lorroki division could be attributed to heavy use of fertilizers, fungicides and pesticides on large scale barley and wheat farms within the division. Lorroki division has over 6000 hectares of land under wheat and barley (NEMA, 2009). During heavy down pour, Pb which dissolves in water is washed down into the wells and dams and since most of them don't have outlets, the levels accumulate leading to increased levels. Conflict resulting from cattle rustling and land leads to the use of small arms

in this division as a common practice. This has also been found to be the biggest contributor of Pb in soils and water (Pkalya *et al.*, 2003; Bhandari *et al.*, 2007). Kirisia division equally has high levels of Pb in borehole water and dam water. This division is generally drier compared to Lorroki division hence few agricultural activities take place. However, Kirisia division houses Maralal town which is the county headquarters of Samburu County. It, therefore, has a higher population compared to Lorroki Division, intensive housing facilities and more automobiles compared to Lorroki Division. Due to this high population, Maralal town has a problem of waste disposal. The town has a poor sewerage system and during rainy season most of this sewage ends up in water sources (Lesamana, 2009). This also contributes to the levels of Pb in water in Kirisia Division

The mean levels of Zn in Kirisia division in well, dam and borehole water were 0.05 ± 0.01 mg/l, 0.05 ± 0.01 mg/l and 0.02 ± 0.01 mg/l respectively. Statistical analysis using ANOVA at 95% confidence level revealed no significant difference between the mean of zinc in dam, borehole and dam water in Kirisia division ($P=0.207$). The levels of zinc obtained in this study were similar to the levels obtained in studies in other regions (Kar *et al.*, 2008; Papafilippaki *et al.*, 2008).

The mean levels of zinc in wells and dams in Lorroki Division were 0.03 ± 0.01 mg/l and 0.04 ± 0.01 mg/l respectively. ANOVA analysis revealed nonsignificant difference between the Zn levels in wells and dams in Lorroki Division ($P=0.688$). Kisamo (2003) in his study on environmental hazards associated with heavy metals in Lake Victoria Basin (East Africa),

Tanzania recorded similar levels of zinc in water. Kisamo recorded values of Zn ranging from 0.04-0.08 mg/l. Figure 4.5 shows how the mean values of Zn compare in different water sources from Lorroki and Kirisia Divisions.

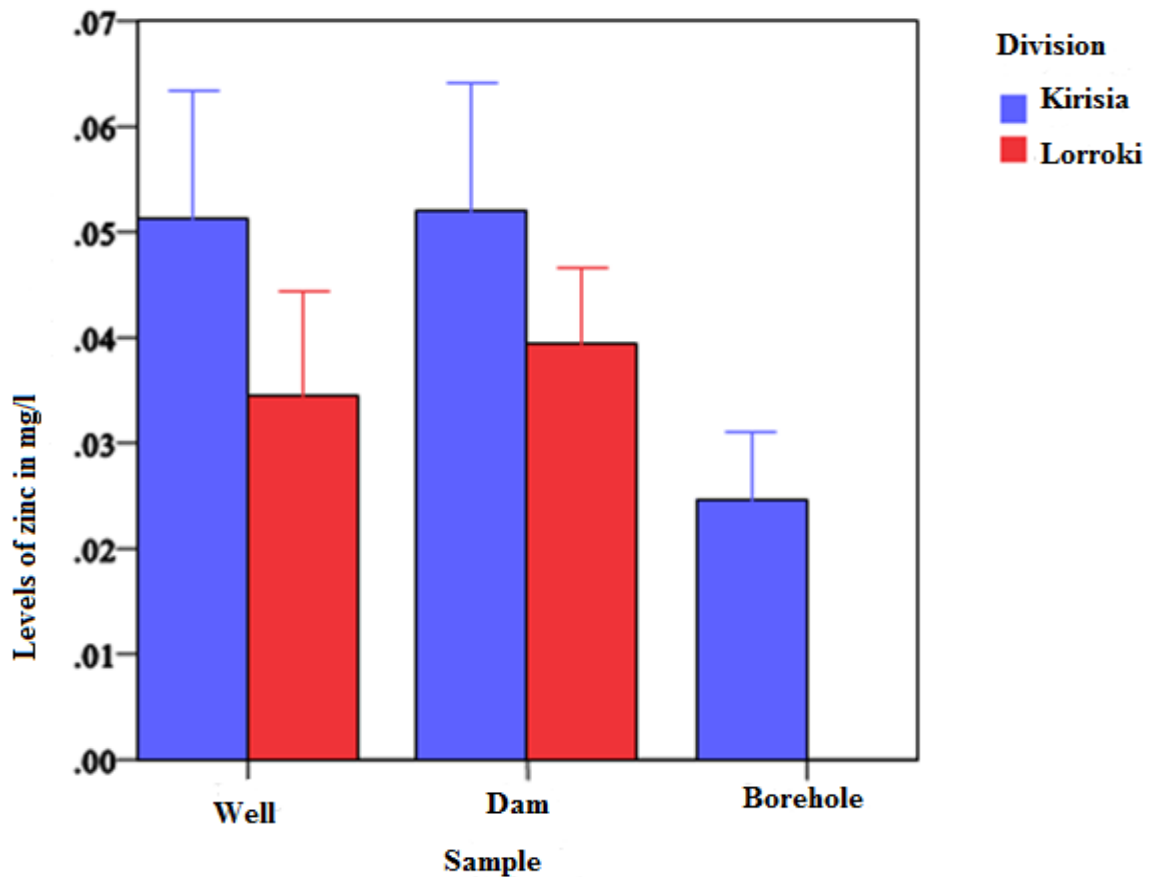


Figure 4.5: Levels of zinc in different water sources in Kirisia and Lorroki Divisions.

The mean levels of Zn in water in Kirisia Division were non significantly higher than the levels observed in Lorroki Division. The wells and dams in Kirisia had higher levels of Zn than the

wells and dams in Lorroki Division. The higher values of Zn in wells and dams in Kirisia were however not significantly different (wells $P=0.323$ and dams $P=0.618$). The high levels of Zn observed in wells and dams in Kirisia division could be attributed to the high number of anthropogenic sources of Zn within Kirisia division including paints from old houses within Maralal town, wood preservatives, soaps and shampoos used by high population within Maralal town (Lew, 2008). The levels in Lorroki are attributed to the fertilizers used in wheat and barley farms in Porro Area of Lorroki Division. The Table 4.4 shows how the levels of the heavy metals in this study compare with some standard guideline values of drinking water.

Table 4.4: Heavy metal concentration (mg/l), mean and range values, compared with some standard guideline values of drinking water

Guidelines	Cd	Cr	Pb	Mn	Zn
Mean of current study	0.01	0.04	0.17	0.06	0.04
Standard Organization of Nigeria (2007)	0.005	0.05	0.01	0.20	-
WHO (2003)	0.003	0.05	0.01	0.04	3
EPA (2002)	0.003	0.05	0.05	0.02	-

Nd- not detected

Source: Wogu and Okaka (2011)

The concentration values of some of the heavy metals compared with standard guideline values for drinking water are shown in Table 4.4. The result obtained in this study showed that lead and Mn levels were greater than recommended values by the Environmental Protection Agency (EPA) (2002), World Health Organization and Standard Organization of Nigeria (SON) (2007). The concentration levels of these metals would markedly impair the portability of the water.

4.4 Heavy metals in agricultural and roadside soil

4.4.1 Levels in individual regions

The Table 4.5 below shows the mean levels of the elements obtained in the four regions of Kirisia and Lorroki divisions.

Table 4.5: Heavy metals in different sub regions of Lorroki and Kirisia divisions of Samburu County in mg/kg

Parameter	Maralal Town(n=60) Mean±SE	Loikas Village Areas(n=30) Mean± SE	Lorroki crop growing area(n=60) Mean± SE	Lorroki Livestock Area(n=24) Mean± SE	p- value
Cd	0.530±0.150	0.760±0.280	0.620±0.170	0.450±0.160	0.792
Cr	3.250±0.41 ^b	1.460±0.270 ^a	3.480±0.480 ^b	4.210±0.640 ^b	0.008
Mn	19.480±1.220 ^a	13.370±1.620 ^a	19.950±2.140 ^a	26.830±3.290 ^b	0.004
Pb	67.500±7.760 ^b	31.000±6.930 ^a	54.660±4.410 ^{ab}	44.650±9.530 ^{ab}	0.005
Zn	403.300±44.340	322.440±108.990	305.990±83.030	165.990±16.820	0.260

Mean ±SE values followed by same letters within the same row are not significantly different (p-value 0.05, SNK test)

The mean level of Cd in the soil within the four selected sub regions, ranged from 0.450-0.760 mg/kg. Loikas village area had the highest Cd mean of 0.760 mg/kg in the soil followed by Lorroki crop growing area with a mean of 0.620 mg/kg. Lorroki livestock area had the lowest mean of 0.450 ± 0.160 mg/kg. Cd exhibited lower levels of contamination than those of other metals in this study.

ANOVA indicated no significant difference between levels of Cd in soils from Maralal Town, Loikas villaage, Lorroki crop growing area and Lorroki livestock area ($P=0.792$). A study by Mico *et al.* (2006) on heavy metal content of agricultural soils recorded similar levels of Cd in the soil ranging from 0.150-0.880 mg/kg. The recommended range of Cd in the soil is 0.070 – 1.100 mg/kg (Mico *et al.*, 2006). Concentration above 0.500 mg/kg reflects the influence of human activity (Mico *et al.*, 2006). Figure 4.6 shows how the percentage levels of Cd from the four sub regions within the two divisions compare.

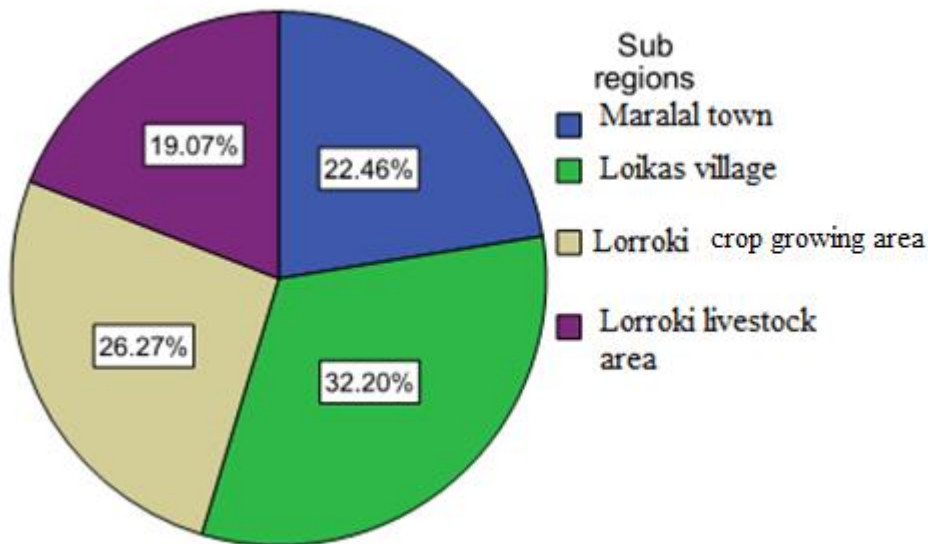


Figure 4.6: Percentage Mean Cd levels in soils

Human activity can contribute to increased Cd levels as a result of urban-industrial activity and/or agricultural practices (Mico *et al.*, 2006). In Lorroki Division, fertilizers used to increase productivity could be the Cd source. Mico *et al.* (2006) reported that Cd content was increased due to the use of phosphatic fertilizers and other agrochemicals used on vegetable crops. Wastewater insufficiently treated for soil irrigation is also a source of Cd contamination (Mico *et al.*, 2006).

The mean level of Cr in the soil within the four sub regions ranged from 1.460 ± 0.270 to 4.210 ± 0.604 mg/kg. Lorroki livestock area had the highest mean of 4.210 ± 0.660 mg/kg followed by Lorroki crop growing area with a mean of 3.480 ± 0.480 mg/kg . The levels of Cr in the soil in the four sub regions were much less compared to other regions in the world. ANOVA at 95% revealed that the mean level of Cr in Loikas village was significantly different from the mean in the other three sub regions. However the mean levels of Cr in Lorroki crop growing area, Lorroki livestock area and Maralal town areas were not significantly different from each other at 95% confidence level.

Figure 4.7 shows comparison of the mean levels of Cr compared in the four regions of Lorroki and Kirisia divisions

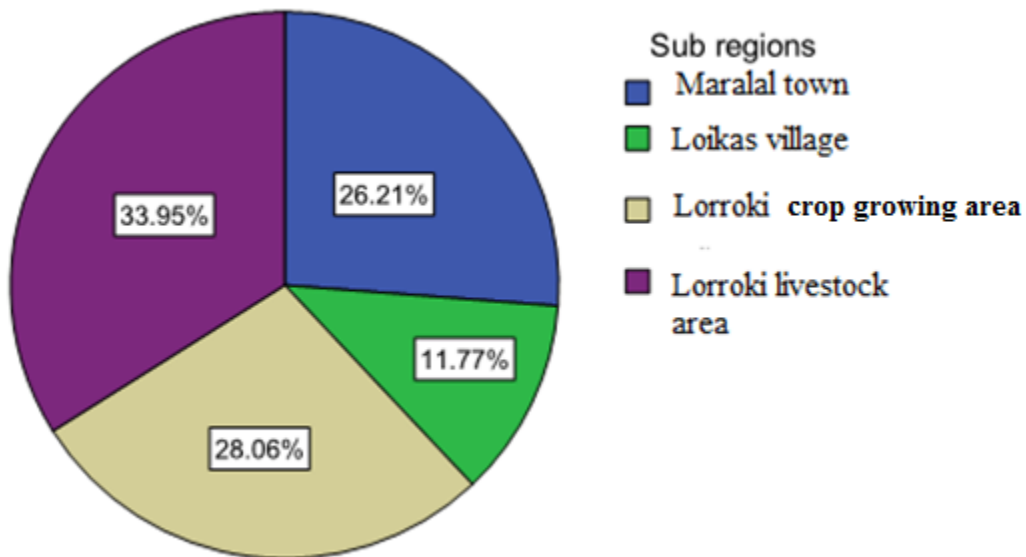


Figure 4.7: Percentage Cr levels in soil from the four selected sub regions.

Cr is one of those heavy metals whose concentration is steadily increasing due to industrial growth, especially the development of metal, chemical and tanning industries (Adelekan and Abegunde, 2011). Other sources of Cr permeating the environment are air and water erosion of rocks, power plants, liquid fuels, brown and hard coal, and industrial and municipal waste. Although there is no risk of Cr contamination on a global scale, local permeation of the metal to soil, water or the atmosphere might result in excessive amounts of this pollutant in biogeochemical circulation (Adelekan and Abegunde, 2011). Nonbiodegradability of Cr is responsible for its persistence in the environment; once mixed in soil, it undergoes transformation into various mobile forms before ending into the environmental sink (Adelekan

and Abegunde, 2011). The above sources of Cr are rare in Samburu County and perhaps that is why the levels of Cr in this regions are generally lower than that the other regions of the world.

The mean levels of Mn in the soil in the four sub regions ranged from 13.370 ± 1.620 to 26.830 ± 3.290 mg/kg. Lorroki livestock area recorded the highest mean of 26.830 ± 3.290 mg/kg and Maralal Town area recorded a mean of 13.370 ± 1.620 mg/kg. Maralal town area and Lorroki crop growing area recorded similar mean levels of Mn in the soil. These levels of Mn recorded in this sturdy were similar to those recorded by Al Yemen and Hashem (2006) in their study on heavy metals and microbial analysis of soil samples. ANOVA at 95% confidence level revealed a significant difference between the mean level of Mn in livestock area and the other three sub regions ($P=0.004$). Fig 4.8 below compares the mean of Mn in soil in the four sub regions.

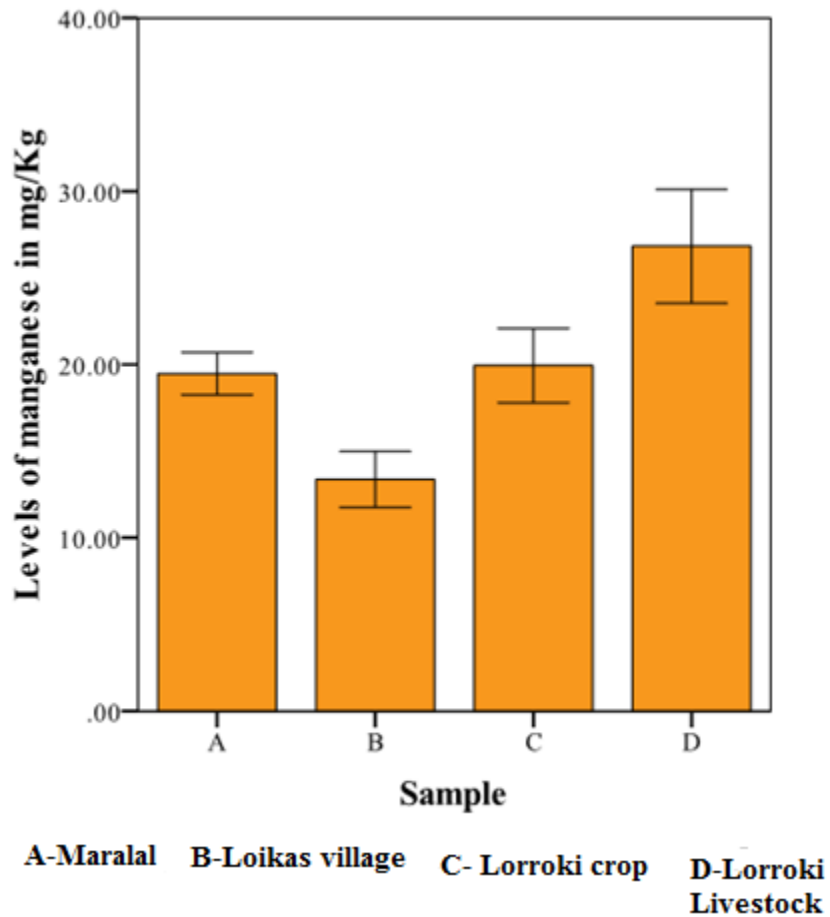


Figure 4.8: Mean Mn levels in soil from the four selected sub regions.

Soil generally contains 200 – 3000 mg/kg of Mn with an average value of 600 mg/kg (Okunola *et al.*, 2007). In the present study, amount of Mn ranged from 13.37 –26.83 mg/kg. The levels of Mn in soils were relatively low, implying mild contamination of the metal in the soil.

The mean levels of lead in Maralal Town, Loikas village, Lorroki crop growing area and Lorroki Livestock area are 67.50 ± 7.76 , 31.00 ± 6.93 , 54.66 ± 4.41 and 44.65 ± 9.53 mg/kg respectively. Loikas village had the highest mean of lead in the soil of the four sub regions. This could be attributed to the surface runoff during rainy season why this carried to the dams and wells as

high levels are reflected in this water sources. The mean lead value in the soil in the four sub regions were lower than those reported in most studies of soil heavy metals around the world (Jaradat *et al.*, 1999; Atiemo *et al.*, 2011). The higher value of lead in agricultural area could be due to high soil organic matter content. This soil component could possibly be responsible for higher soil lead retention (Mico *et al.*, 2006). Lead could also be from the application of agrochemical and fertilizers in the agricultural area (Mico *et al.*, 2006) eg urea and superphosphate. Statistical analysis of the mean levels of lead in the soil in the four sub regions using ANOVA revealed a significant difference between the level of lead in soils in Maralal Town and Loikas villaage. There was no significant difference however in the mean level of lead between Lorroki crop growing area and Lorroki livestock area. Figure 4.9 shows how the mean levels of lead compared in the four sub regions of Kirisia and Lorroki divisions.

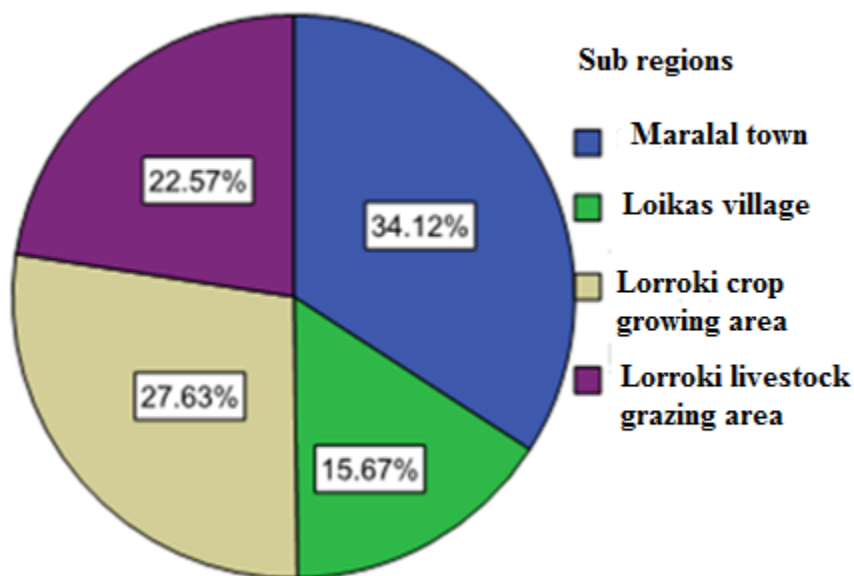


Figure 4.9: Percentage lead levels in soil

Maralal Town and Lorroki crop growing area had the highest mean level of lead in the soils. The high level of lead in Maralal Town particularly was due to lead particulate matter emitted from gasoline and wastes emitted from garages.

The mean levels of zinc in the soil within the four selected sub regions ranged from 165.99-403.30 mg/kg. Maralal Town had the highest mean of 403.30 ± 44.34 mg/kg while Lorroki livestock area had the lowest mean of 165.99 ± 16.82 mg/kg. Zinc exhibited higher levels of contamination in the soil than those of other metals in this study. ANOVA revealed no significant difference between the levels of zinc in the soil from Loikas village, Maralal Town, Lorroki crop growing area and Lorroki livestock area ($P=0.260$). The mean values exhibited in this study are higher than values exhibited in other studies (Jaradat *et al.*, 1999; Okonola *et al.*, 2007; Yahaya *et al.*, 2010). However, Awokunmi *et al.* (2010) recorded higher values of zinc in soils than the values in this study. Awokunmi *et al.* (2010) recorded zinc values in soils ranging from 261.700 to 8100 mg/kg. Since no major industries exists in the study area such as metal smelting, primary sources of zinc may assume are probably the attrition of motor vehicle tyre rubber exacerbated by poor road surfaces and the lubricating oil in which zinc is found as part of many additives (Okonola *et al.*, 2007). A comparison between the levels of zinc in the four sub regions is as shown in the Figure 4.10.

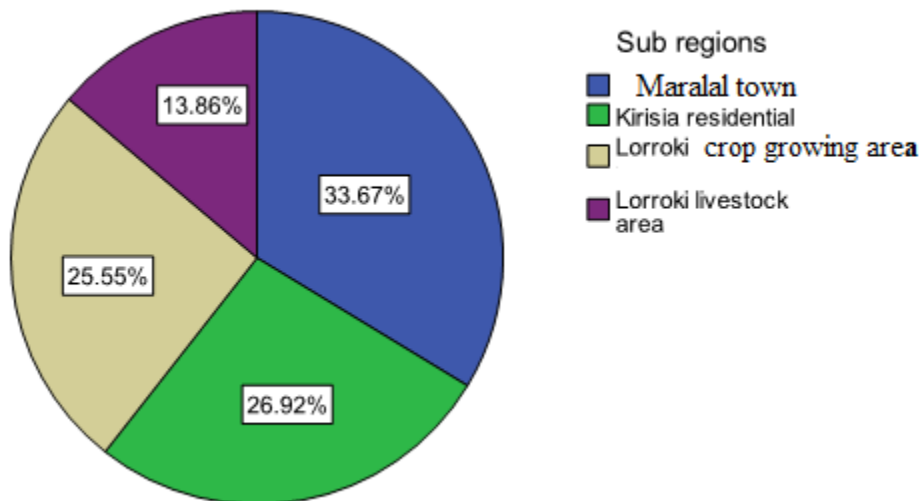


Figure 4.10: Percentage zinc levels in soil from the four selected sub regions in Kirisia and Lorroki divisions.

It can be seen from the chart that Maralal town area had the highest mean of zinc followed by Lorroki area. Lorroki area is basically an agricultural area and the levels of zinc in this area could be attributed to excessive use of fertilizers in Wheat and Barley farms within the area (Nema, 2009; Reza and Singh, 2010). Table 4.6 shows summary of means levels of heavy metals in Kirisia and Lorroki divisions

4.4.2 Levels in Kirisia and Lorroki region

The Table 4.6 below shows the levels of the elements obtained in Kirisia and Lorroki divisions

Table 4.6: Levels of heavy metals in combined region

Parameter	Kirisia Mean± SE(mg/kg)	Lorroki Mean± SE (mg/kg)	P value
Cd	0.60±0.14	0.57±0.13	0.859
Cr	2.65±0.30	3.69±0.39	0.033
Mn	17.44±1.02	21.91±1.82	0.033
Pb	55.33±5.93	51.80±4.16	0.626
Zn	376.35±46.64	265.99±59.75	0.144

SE- standard error

The mean levels of pollution of the selected heavy metals in Kirisia division were higher than those in Lorroki division. The mean levels of Cd, lead and zinc were non significantly higher in Kirisia division than Lorroki division. However, Mn and Cr levels were significantly higher in soils of Lorroki Division than Kirisia division. The mean levels of Cd, lead and zinc in the soil therefore were independent of the region of sampling but the mean levels of Mn and Cr were dependent on the region of analysis.

Zinc had a mean of 376.35±46.64 mg/kg in Kirisia division. The means obtained in similar studies around the world, indicate the mean of this study was generally higher (Jaradat *et al.*, 1998; Okunola *et al.*, 2007; Yahaya *et al.*, 2010). The mean of Pb was the second highest with a mean range of 51.80-55.33 mg/kg. This mean was in line with other studies done in other countries (Okunola *et al.*, 2007; Yahaya *et al.*, 2010). The highest mean concentration of Cd was obtained in Kirisia Division. The value was 0.60±0.14 mg/kg and this value was not significantly ($p>0.05$) higher than mean value obtained from Lorroki Division. The source of Cd in soil may be attributed to vehicular emissions. Cd is released as a combustion product in the accumulators

of motor vehicles or in carburetors (Ijeoma, 2011). Contamination of soil poses a serious threat to the environment and there is a risk of transfer of toxic and available metals to biota (Ijeoma, 2011). Table 4.7 shows the overall mean of the heavy metals of the region studied, the range of the levels of the metals and the WHO maximum recommended values in the soil.

Table 4.7: Mean and range of current study in comparison with WHO maximum allowed limits

parameters	Mean±SE (Range) of present study in mg/kg	WHO values (mg/kg)
Cd	0.59±0.09 (0.00-5.91)	3.00
Cr	3.15±0.24 (0.00-18.59)	100.00
Mn	19.60±1.03 (0.00-86.72)	1000.00
Pb	53.63±3.66 (0.00-257.86)	100.00
Zn	323.07±37.73 (19.47-3121.92)	300.00

Source: Mamtaz and Chowdhury (2006); Atieno *et al.*, 2011

Zinc had the highest mean and range in the study with a mean of 323.07±37.73 mg/kg which was higher than the maximum permissible limit of 300 mg/kg recommended by the WHO. The range of zinc in the present study was 19.47-3121.92 mg/kg. This clearly shows that not all the soils in the two divisions in the county were polluted. However, the above range shows extreme pollution in some areas of the county. The higher limit of the range of 312.92 mg/kg was above WHO permissible limit of zinc in the soil raising concern as this could cause a lot of health problems associated with excess zinc levels in soils for example, dust from these contaminated

sites could also pose great health problems especially on those people that live close to these contaminated sites (Atiemo *et al.*, 2011).

The range of Pb in this study was BDL-257.86 mg/kg and the mean value was 53.63 mg/kg. The WHO maximum permissible limit of this element in the soil is 100 mg/kg. The mean is almost half the value of the WHO permissible value of Pb in the soil. From the range it is clear that lead was absent in some of the sites, but in some, it was present almost three times the WHO maximum permitted value. Mn levels in the soil in this region ranged from BDL -86.72 mg/kg and the mean was 19.60 mg/kg. The WHO maximum permissible level of Mn in the soil is 1000 mg/kg (Mamtaz and Chowdhury, 2006). All the soil sampled in this region was found to contain Mn below the WHO maximum permissible level of 1000 mg/kg.

Cr had a mean of 3.15 mg/kg in the soils of this study and the range was BDL-18.59 mg/kg. The WHO permissible value of Cr in the soil is 100 mg/kg. The mean value of Cr in the soils from these study area was below the WHO maximum permissible contamination level. All the soils sampled from this area were found to contain Cr below the WHO maximum permissible value. Generally as regards to Cr in the soil in this study area, the soils are not polluted. The mean level of Cd in the soils of Kirisia and Lorroki was 0.59 mg/kg and range of Cd in the soils from this region was BDL-5.91 mg/kg. The WHO maximum permissible level of Cd in the soil is 3 mg/kg. The mean value of Cd in the soil was found to below the WHO maximum permissible contamination level. However, from the range, the levels in some areas exceeded the WHO maximum permissible level of 3 mg/kg.

Different countries have different maximum allowed values for the heavy metals in the soils.

Table 4.8 shows the MAL for different countries in comparison to the levels obtained in the study.

Table 4.8: Mean values obtained in this study in comparison with the maximum allowed levels for different countries in mg/kg.

Element	Australia	Canada	Poland	Uk	Germany	USA	Mean Obtained In current study
Cd	5.000	8.000	3.000	3.000	-	0.7.000	0.590
Cr	100.000	75.000	100.000	50.000	200.000	1000.000	3.150
Pb	100.000	200.000	100.000	100.000	500.000	200.000	53.630
Zn	300.000	400,000	300.000	300.000	300.000	300.000	323.070
Mn	-	-	-	-	-	-	19.600

Source: Mamtaz and Chowdhury (2006).

The mean values of Cd, Cr and lead were below the MAL for all the countries listed above. The levels of Zn, however, exceeded the MAL for all the countries with the exception of Canada. When the mean levels of heavy metals in the soil and water in the Kirisia and Lorroki were correlated the results were as tabulated in the Table 4.9.

Table 4.9: Relationship between individual heavy metals in water and in soils

Water \ Soil		Cd	Cr	Mn	Pb	Zn
Cd	Pearson Correlation	-0.0684	-0.1916	0.0019	-0.1830	0.0533
	P value	0.4466	0.0317	0.9833	0.0403	0.5530
Cr	Pearson Correlation	-0.1048	0.0491	-0.0981	-0.1693	-0.1146
	P value	0.2427	0.5850	0.2747	0.0581	0.2011
Mn	Pearson Correlation	0.0809	0.1281	-0.0439	0.0554	0.0634
	P value	0.3679	0.1529	0.6254	0.5375	0.4807
Pb	Pearson Correlation	0.1315	-0.1077	0.1207	0.0174	-0.0873
	P value	0.1422	0.2298	0.1784	0.8466	0.3310
Zn	Pearson Correlation	-0.1501	-0.0606	-0.2084	-0.1590	-0.0824
	P value	0.0935	0.5000	0.0192	0.0753	0.3589

From the Table 4.9, there was a positive correlation between the levels of lead and Cr in water and in soils, however, the correlation was not significant. There was a negative correlation between the levels of zinc, Cd and Mn in soils and water; **but** this correlation was not significant ($P < 0.05$).

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The study has shown that there was considerable amount of heavy metals in ground and surface water, though the levels were below WHO maximum permissible levels for Mn, zinc and Cr. In few cases the levels of Cd exceeded the WHO maximum permissible limit. The mean of lead was above the WHO maximum permissible limits in ground and surface water from Kirisia and Lorroki divisions.

The wells in Kirisia Division were more polluted than the dams and boreholes. This could be attributed to the surface runoff of water during heavy down pour which led to heavy metals depositing into the wells. In Lorroki Division, the dams had higher levels of the heavy metals than the wells in the same region. There was no significant difference between levels of heavy metals in dams, wells and boreholes in Kirisia Division ($P < 0.05$). However, in Lorroki Division, there was a significant difference between the levels of Pb in wells and dams. However for the Zn, Mn, Cr and Zn there was no significant difference.

Kirisia had higher levels of heavy metals in surface and ground water than Lorroki Division. This could be attributed to the many sources of anthropogenic origin being more in Kirisia division than Lorroki division because the former houses the county headquarters and is therefore more populated than Lorroki division. Kirisia division also lies at a lower altitude than

Lorroki Division and therefore likely to act as a collection point for surface runoff water during heavy downpour hence the contamination.

The mean of the four analyzed heavy metals, Cd, Cr, Mn and lead in the soils in Kirisia and Lorroki Divisions was below the WHO maximum permissible limits. However, the level of zinc was above the world health organization permissible limit for Kirisia Division. The soil in Lorroki was therefore not heavily polluted compared to the soil in Kirisia division. The mean levels of Cd, lead and zinc in Kirisia Division, exceeded those of Lorroki Division by a considerable margin. There was a positive correlation between the levels of lead and Cr in water and in soils, however, the correlation was not significant. There was a negative correlation between the levels of zinc, Cd and Mn in soils and water.

5.2 Recommendations

5.2.1 Recommendations from this study

The following may be recommended from this research and should be taken to the researchers in this area

- i. The levels of lead and Cd in the water should be continuously monitored to check on their levels. Lead levels in both the surface and ground water is already beyond the WHO recommended maximum limit. The two heavy metals are very poisonous even in their smallest quantities.
- ii. Sources of heavy metals in soils like inorganic fertilizers, pesticides and acaricides need to be controlled. Fertilizers, pesticides and acaricides are known to be the sources of some of the heavy metals like lead, zinc and Cd which have been detected both in soils and water at high levels.
- iii. Kirisia Division had the highest contamination levels of lead in water and soils. Since most of the water and soil sampling was done around Maralal town, there is need to institute mechanisms to reduce the level of contamination including fixing the sewerage system, building of toilets and checking on the conditions of automobiles that ply the town routes.

5.2.2 Recommendations for further studies

- i. Further research similar to this one be carried out in other areas of the Samburu County, especially the remotest parts that are riddled with conflicts arising from cattle rustling.
- ii. Since there was a considerable level of the heavy metals studied in water and soil, a research should be carried out in food crops to determine whether similar levels are reflected in the food stuffs especially in Kirisia where the contamination of poisonous metals like lead and Cd in water is high.
- iii. A further study should be done to include metals like copper, arsenic and mercury to determine their contamination. This is because their anthropogenic origins like acaricides, and lack of recommended dumpsites within the two districts exists.

REFERENCES

- Abulude, F.; Obidiran, G. and Orungbemi, F. (2007). Determination of physic-chemical parameter and trace metal content of drinking water samples in Akure, Nigeria. *Electronic Journal of Environmental, Agricultural and Food Chemistry*; **6**: 2297-2303.
- Adeleken, B. and Abegunde, K. (2011). Heavy metal contamination of soil and ground water at automobile mechanic village in Ibadan, Nigeria. *International Journal of the Physical Sciences*; **6**: 1045-1058.
- Agbaire, P. and Oyibo, P. (2009). Seasonal variation of some physic-chemical properties of bore hole water in Abraka. Nigeria. *African Journal of Pure and Applied Chemistry*; **3**: 116-118.
- Ahuja, S. (2009). Handbook of water purity and quality. New York, USA: Academic press. Pp 1-3.
- Akbar, k.; Hale, G.; Headley, A. and Athar, M. (2006). Heavy metal contamination of roadside soils of Northern England. *Soil and Water Research Journal*; **4**: 158-163.
- Al Yemen, N. and Hashem. (2006). Heavy metals and microbial analysis of soil samples from Aramco Gulf Operating Company Al-Khatji, (AGOC) Saudi Arabia. *Saudi Journal of Biological Sciences*; **13**: 129-133.
- Al-Weher, M. (2008). Levels of heavy metal Cd, Cu and Zn in three fish species collected from the Northern Jordan Valley. *Jordan Journal of Biological Sciences*; **1**: 41-46.
- Atiemo, S.; Ofuso, F.; Mensah, K.; Tutu, O.; Palm, L. and Blackson, A. (2011). Contamination assessment of heavy metals in road dust from selected roads in Accra Ghana. *Research Journal of Environmental and Earth sciences*; **3**: 473-480.
- Awokunmi, E.; Asaolu, S. and Ipinmoroti, K. (2010). Effect of leaching on heavy metals concentration of soil in some dumpsites. *African Journal of Environmental Science and Technology* ;**4**: 495-499
- Bashkin, V. (2003). Environmental chemistry: Asian lessons. Dordrecht, Netherlands: Kluwer Academic Publishers. Pp 150-170.
- Beckhoff, B.; Kanngieber, B.; Langhoff, N.; Wedell, R. and Woiff, H. (2010). Handbook of practical X-ray Fluorescence analysis. New York, USA: Springer. Pp 20-200.
- Begum, A.; Ramaiah, M.; Harikrishna,; Khan, I. and Veena, K. (2009). Heavy metal pollution and chemical profile of Cauvery River water. *E-Journal of Chemistry*; **6**: 47-52.
- Bevre, P. and Gunzler, H. (2002). Traceability in chemical measurements. Berlin, Germany: Springer. Pp 210.

- Bhandari, A.; Surampalli, R.; Champagne, P.; Saykee, O.; Tyagi, R. and Irene, M. (2007). Remediation Technologies for Soils and Ground Water. Virginia, USA: American Society of Civil Engineers. Pp 355.
- Borosova, D.; Mocak, J.; Beinrohr, E. and Miskovic, P. (2002). Validation and quality assurance of arsenic determination in urine by GFAAS after toluene extraction. *Polish Journal of Environmental Studies*; **11**: 617-623.
- Bose, B. and Hemantaranjan, A. (2005). Developments in physiology, biochemistry and molecular biology of plants. New Delhi, India: New India Publishing Agency. Pp 105.
- Calhoun, Y. (2005). Water pollution. New York, USA: Chelsea House Publishers. Pp 1-7
- Calkins, M. (2009). Materials for sustainable sites: A complete guide to the evaluation. Hoboken, New Jersey: John Wiley and Sons. Pp 451.
- Cantle, E. (1998). Atomic absorption spectrometry. Amsterdam, Netherlands. Elsevier Science Publishing Company. Pp 48.
- Challa, S. and Kumar, R. (2009). Nanostructured oxides. Weinheim, Germany: Wiley. Pp 29.
- Chernoff, R. (2005). Geriatric nutrition: the health professional's handbook. Ontario, Canada: Jones and Bartlett Publishers. Pp102.
- Daniel, W. (1999). Biostatistics: A foundation for analysis in health sciences. New York, USA: Wiley. Pp180-186, 268-270.
- Delbari, S. and Kulkarni, D. (2011). Seasonal variations in heavy metal concentration in agricultural soils in Tehran, Iran. *Bioscience Discovery Journal*; **2**: 333-340.
- Ediin, G.; Golantu, E. and Brown, M. (2000). Essentials for health and wellness. Toronto, Canada: Bartlett Publishers. Pp 368.
- EPA. (2004). Drinking water health advisory for Mn. Accessed from <http://www.epa.gov/safewater/>.
- Farmer, A. (2002). Managing environmental pollution. New York, USA: Taylor and e-Library. Pp 3-18.
- Fong, F.; Seng, C.; Azan, A. and Tahir, M. (2008). Possible source and pattern distribution of heavy metals content in urban soil at Kuala Terengganu Town Centre. *The Malaysian Journal of Analytical Sciences*; **12**: 458-467.
- Fritioff, A.; Kautsky, L. and Greger, M. (2004). Influence of temperature and salinity on heavy metals uptake by submersed plants. *Environmental Pollution Journal*; **133**: 265-274.
- Goel, P. (2009). Water pollution. New Delhi, India: New Age International. Pp 1-2.

- Greeley, A. (2003). Pollution in our world. New York, USA: Rosen Publishing Group. Pp 4-6.
- Greenaway, T.; Bailey, J.; Chiney, M.; Ponny, M.; Steele, P.; Oxlade, C.; Preston, K.; Preston, R.; Oliver, C. and Birchfield, D. (2002). Rain forests of the world. New York, USA: Marshal Carvendish Corporation. Pp 463-465.
- Harrison, R. (2001). Pollution causes, effects and control. Cambridge, UK: Royal Society of Chemistry. Pp 1-3.
- Hilgenkamp, K. (2006). Environmental health: ecological perspective. Toronto, Canada: Jones and Bartlett Publishers. Pp 83.
- Hill, M. (2010). Understanding environmental pollution. Cambridge, UK: Cambridge University Press. Pp 9-22.
- Hillstrom, K. and Callier, H. (2003). Africa and the Middle East: A continental overview of environmental issues. California, USA: Library of Congress. Pp 8.
- Hook, G. and Ulcer, G. (2000). Reviews in environmental health 1998: Toxicological defense mechanisms. Diane publisher Pp 205-208.
- Ijeoma, L.; Ogbonna, P. and Ogbonna, C. (2011). Heavy Metal content in soil and Medicinal plants in high traffic urban area; **10**: 618-624.
- Jaradat, M. and Momani, A. (1999). Contamination of roadside soil, plants and air with heavy metals in Jordan, a comparison study. *Turk journal of Chemistry*; **23**: 209-220.
- Jia, L.; Yonghua, L. and Yang, L. (2010). Heavy metals in soil and crops of an intensively farmed area: Case study in Yucheng City, Shandong province, China. *International Journal of Environmental Research and Public Health*; **7**: 395-412.
- Kanmony, C. (2009). Human rights and health care. New Delhi, India: Mittal Publication. Pp 73-76.
- Kaplan, O.; Yildirim, N. and Tayhan, N. (2011). Assesment of some heavy metals in drinking water of Tunceli. *Turkey. E Journal of Chemistry*; **8**: 276-280.
- Kar, D.; Sur, P.; Mandal, S.; Saha, T. and Kole, R. (2008). Assessment of heavy metal pollution in surface water. *International Journal of Science and Technology*; **5**: 119-124.
- Kaur, K. (2007). Hand book of water and waste water analysis. New Delhi, India: Atlantic Publishers and Distributors (p) Ltd. Pp 89-92.
- Khan, A. and Ghouri, A. (2011). Environmental pollution: its effects on life and its remedies. *Journal of Arts, Science and Commerce*; **2**: 276-285.
- Khopkar, S. (1998). Basic Concepts of analytical chemistry. New Delhi, India: New Age International. Pp 267-280.

- Kisamo, H. (2003). Environmental hazards associated with heavy metals in Lake Victoria Basin (East Africa). *African Newsletter on Occupational Health and Safety*; **13**: 67-69.
- Kohl, P. and Medlar, S. (2007). Occurrence of Mn in drinking water and Mn control. New York, USA: IWA Publishing. Pp 16-18.
- Kumar, R. (2009). Nanostructured oxides. Weinheim, Germany: Wiley VCH. Pp166.
- Lajunen, J. and Paavo P. (2008). Spectrochemical analysis by atomic absorption and emission. Burlington, UK: Royal society of Chemists. Pp 78-82.
- Lemasana, M. (2009). Transition from subsistence to monetary economy – A counter discourse to mainstream development strategies. Case study from Samburu District Kenya. (unpublished masters dissertation). University of Agder, Kristiansand. Norway. Pp 67-69.
- Leo, M. and Nollet. (2011). Analysis of endocrine disrupting compounds in food. New York, USA: Blackwell Publishing Ltd. Pp 291-300.
- Lew, K. (2008). Understanding the elements of the periodic table: zinc. New York, USA: Rosen Publishing Group. Pp 3-14.
- Magdaleno, F.; Villa, O.; Saenz, E; Bolanos, O. and Olivas, A. (2011). Heavy metals in agricultural soils and irrigation wastewater of Mixquiahuala, Hidalgo, Mexico. *African Journal of Agricultural Research*; **6**: 5505-5511.
- Mamtaz, R. and Chowdhury, H. (2006). Leaching characteristics of solid waste at an urban solid waste dumping site. *Journal of Civil Engineering*; **34**: 71-79.
- Mandour, R. and Azab, Y. (2011). Toxic levels of some metals in drinking ground water in Dakahlyia Governorate, Egypt in the year 2010. *Monsouria University Journal*; **2(2)**: 112-117.
- McMahon, G. (2007). Analytical instrument: A guide to laboratory, portable and miniaturized instruments. West Sussex, England: John Willey and Sons Limited. Pp 52-54.
- Mebrahtu, G. and zebrabruk, S. (2011). Concentration of heavy metals in drinking water from urban areas of the Tigray Region, Northern Ethiopia. *Maejo international Journal of Science and Technology*; **3**: 105-121.
- Mico, C.; Peris, M.; Sanchez. and Recatala, L. (2006). Heavy metal content of agricultural soils in a Mediterranean Semiarid area: the Segura River Valley (Alicante, Spain). *Spanish Journal of Agricultural Research*; **4**: 363-372.
- Miculescu, F.; Miculescu, M.; Ciocan, L.; Ernuteanu, A.; Antoniac, I.; Pencea, I. and Matei, E. (2011). Comparative studies regarding heavy elements concentration in human cortical bone. *Digest Journal of Nanomaterials and Biostructures*; **6**:1117-1127.
- Misra, S. and Mani, D. (2009). Soil pollution. New Delhi, India: S. B Nangia APH publishing corporation. Pp 29-59.

Monudu, M. and Anyakora, C. (2010). Heavy metal contamination of ground water. *The Serulere Case Study Journal*; **2**:39-40.

Murray, R. (2009). Nuclear energy: An introduction to the concepts, systems and applications of nuclear processes. Burlington, USA: Butterworth-Heinemann. Pp 253.

Mwegoha, W. and Kihampa, C. (2010). Heavy metal contamination in agricultural soils and water in Dar es Salaam City, Tanzania. *African Journal of Environmental Science and Technology*; **4**: 763-769.

Nanyingi, M.; Mbaria, J.; Lanyasanya, A.; Wagate, C.; Koros B.; Kaburia, H.; Munenje, W. and William, O. (2008). Ethnopharmacological survey of Samburu District Kenya. *Journal of Ethnobiology and Ethnomedicine*; **4**:1-12.

Nassef, M.; Hannigan, R. and Elsayed, K. (2006). Determination of some heavy metals in the environment of Sadat Industrial City. *Proceedings of the 2nd Environmental Physics Conference in Egypt*, 145-152.

Nath, H. and Langdon, A. (2010). Electrochemical determination of iron and Mn from ground water. Accessed from <http://www.groundwater2010.com>.

NEMA. (2009). Samburu District environment action plan 2009-2013. Retrieved from www.nema.go.ke.

Nielsen, S. (2010). Food analysis laboratory manual. New York, USA: Springer.

Nollet M. (2011). Hand book on analysis of edible animal by product. New York, USA: Taylor and Francis. Pp193-197.

Okunola, O.; Uzairu, A. and Ndukwe, G. (2007). Levels of Trace metals in soil and Vegetation along major and minor roads in Metropolitan City of Kaduna, Nigeria. *African journal of Biotechnology*; **6**: 1703-1709.

Opong, R. and Opong, D. (2004). Kenya. New York, USA: Chelsea House Publishers. Pp 23.

Osu, C. and Okoro, J. (2011). Comparative evaluation of physical and chemical parameter of sewage water from selected areas in Port Harcourt Metropolis, Rivers state, Nigeria. *Continental Journal of Water, Air and Soil pollution*; **2**:1-14.

Oyugi, M. (2000). Heavy metals and pesticides in marine, sea water and sea plants along the Mombasa coastline. (Unpublished masters dissertation). Kenyatta University, Nairobi. Kenya. Pp 57.

Pain, A. (2008). A brief look at lie: One man's view predicament. Leicester, UK. Troubador Publi limited. Pp 81-84.

Pandey, J.; Shubhashish, K. and Pandey, R. (2010). Heavy metal contamination of Ganga at Varanasi in relation to atmospheric deposition. *Tropical Ecology Journal*; **51**: 365-373.

Papafilippaki, A.; Kotti, M. and Stavroulakis, G. (2008). Seasonal variations in dissolved heavy metals in the Keritis River Chania, Greece. *Global Nest Journal*; **3**:320-325.

Pkalya, R.; Adan, M. and Masinde, I. (2003). Conflict in Northern Kenya, a focus on the internally displaced victims in Northern Kenya. Accessed from [http://practicalaction.org/docs/region east Africa/ conflict in Northern Kenya](http://practicalaction.org/docs/region%20east%20Africa/conflict%20in%20Northern%20Kenya).

Qishlaqi, A. and Moore, F. (2007). Statistical analysis of accumulation and sources of heavy metals occurrence in agricultural soils of Khoshk River Banks, Shiraz, Iran. *American –Eurasian Journal of Agriculture and Environment Science*; **2**:565-573.

Radojovenic, M. and Bashkin, V. (2006). Practical environmental analysis. Cambridge, UK: The Royal Society of Chemistry. Pp 254.

Raji, M.; Ibrahim, Y. and Ehinmidu, J. (2010). Physiochemical characteristics and heavy metal levels in drinking water resources in Sokoto Metropolis in North-western Nigeria. *Journal of Applied Science Environment and Management*; **14**: 81-85.

Reeuwijk, V. (1998). Guidelines for quality management in soil and plant laboratories. Wageningen, Netherlands: Wageningen Agricultural University.

Reza, R. and Singh, G. (2010). Heavy metal contamination and its indexing approach for river water. *International Journal of Environmental Science and Technology*; **7**:785-792.

Ruto, D.; Musoi, K.; Tule, I. and Kirui, B.(2010). Conflict dynamics in Isiolo, Samburu East and Marsabit South Districts of Kenya. *Amani Papers*; **1**: 1-19.

Sarkar, B. (2005). Heavy metals in the environment. New York, USA: Taylor and Francis. Pp 33-41.

Samuding, K.; Abustan, I.; Rahaman, A. and Isa, M. (2009). Distribution of heavy metal profile in ground water system at solid waste disposal site. *European Journal of Scientific research*; **37**: 58-66.

Schmoll, O.; Howard, G.; Chilton, J. and Chorus, I. (2006). Protecting groundwater for health: managing the quality of drinking water resources. London, UK: IWA Publishing. Pp 328.

Schroder, K. (2006). Semiconductor materials and device characterization. Hoboken, New Jersey: John Wiley and Sons. Pp 694-696.

Selinus, O. and Alloway, B. (2005). Essentials of medical geology: impact of the natural environment. London, UK: Blackie Academic and Professional Publishers. Pp 187.

Shafi, S. (2005). Environmental pollution. New Delhi, India: Atlantic Publishers and Distributors. Pp 9-15.

Sharma, B. (2002). Environmental pollution. New Delhi, India: Anmol Publication PVT LTD. Pp 9-12.

Sherameti, I. and Varma, A. (2010). Soil heavy metals. Berlin, Germany: Springer. Pp 15-18, 241-243.

Shrivastav, R. (2001). Atmospheric heavy metal pollution, development of chronological records and geological monitoring. Accessed from www.ias.ac.in.

Simeonov, L.; Kolhubovski, M. and Simeonov, B. (2010). Environmental heavy metal pollution and effects on child mental development. Dordrecht, Netherlands: Springer. Pp 114-115.

Singanen, M.; Wondimu, L. and Tesso, M. (2008). Water quality of Wench Crater Lake in Ethiopia. *Maejo International Journal of Science and Technology*; **2**: 361-373.

Singh, V. and Chandel, S. (2006). Analytical study of heavy metals of industrial Effluents at Jaipur, Rajasthan (India). *Journal of Environment science and Engineering*; **48**: 103-108.

Sokhi, R. (2008). World atlas of atmospheric pollution. London, UK: British Library. Pp6.

Sonayei, Y.; Ismail, N. and Talebi, S. (2009). Determination of heavy metals in Zayandeh Road River, Isfahan-Iran. *World Applied Sciences Journal*; **6**: 1204-1214.

Swaminathan, S.; Seshadri, M. and Karagasapathy. (2011). Effect of tannery effluent on the zinc content of ground water. *Journal of Pharmaceutical and Biomedical Services*; **11**: 1-3.

Tayyeb, Z. A.; Farid, S. M. and Otaibi, K. (2004). Trace elements concentration of commercially available drinking water in Makkah and Jeddah. *JKAU Engineering Science Journal*; **15**:149-154.

Van, N.; Krivolutsky. (1996). Bioindicator systems for soil pollution. Dordrecht, Netherlands: Kluwer Academic Publishers. Pp 1-8.

Voet, E.; Guinee, B. and Udode, H. (2008). Heavy metals: A problem solved?. Dordrecht, Netherlands: Kluwer Academic. Pp 4.

Wieczorek, J.; Wieczorek, T. and Bieniaszewski, T. (2004). Cd and lead content in cereal grains and soil from cropland adjacent to roadways. *Polish Journal of Environmental Studies*; **14**: 535-540.

Wogu, D. and Okaka, E. (2011). Pollution studies on Nigerian rivers: Heavy metals in surface water of warri River, Delta state. *Journal of Biodiversity and Environmental Sciences*; **1**: 7-12.

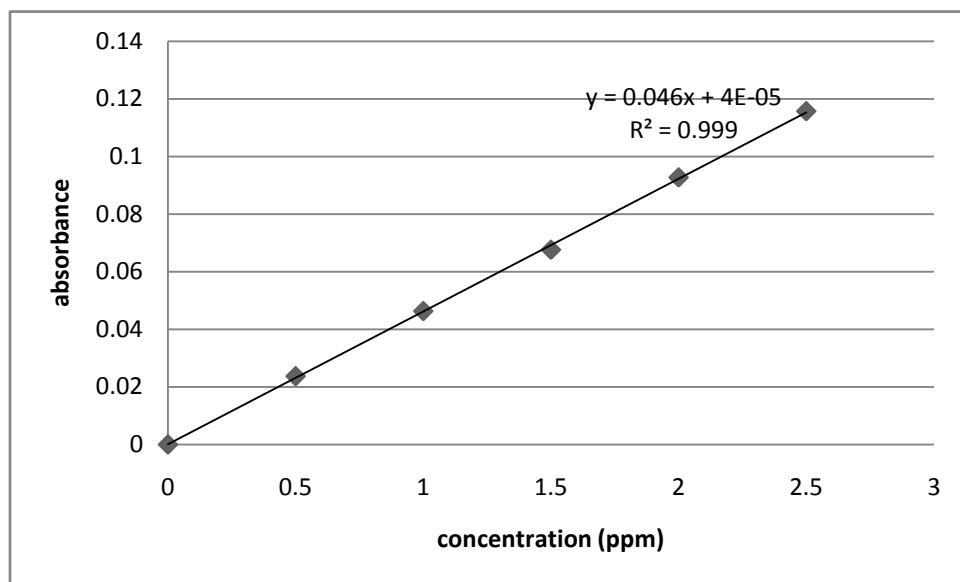
Wokunmi, A.; Asaolu, S. and Ipinmoroti, K. (2011). Effect of leaching on heavy metals concentration in some dumpsites. *African Journal of Environmental Science and Technology*; **4**: 495-499.

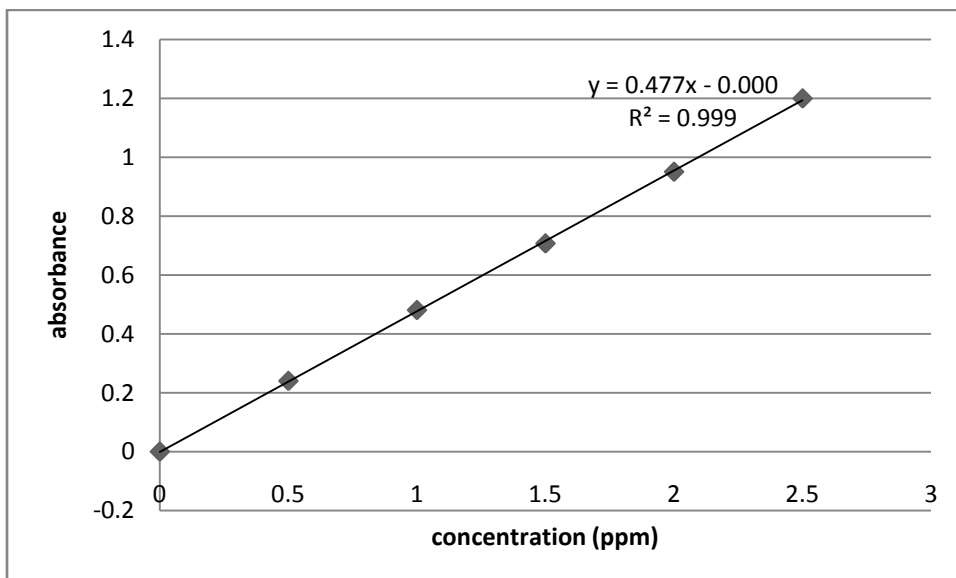
Yahoya, M.; Ezeh, G.; Musa, F. and Mohammad, Y. (2010). Analysis of heavy metals concentration in roadside soils of Yauri, Nigeria. *African Journal of Pure and Applied Chemistry*; **4**: 22-30.

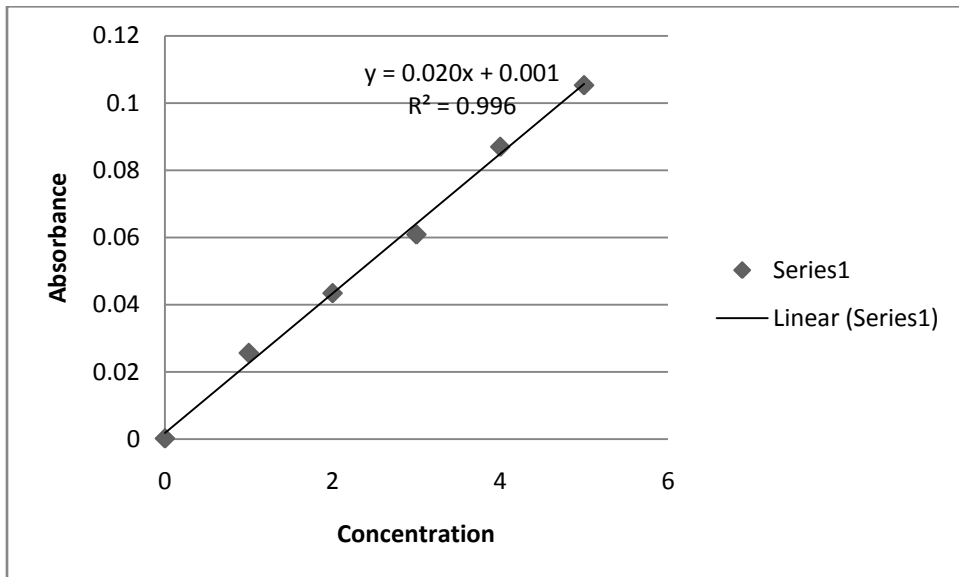
Yisa, J.; Jacob, J. and Onoyima, C. (2011). Identification of sources of heavy metal pollution in road deposited sediments using multivariate statistical analysis. *Journal of Emerging Trends in Engineering and Applied Sciences*; **2**: 658-663.

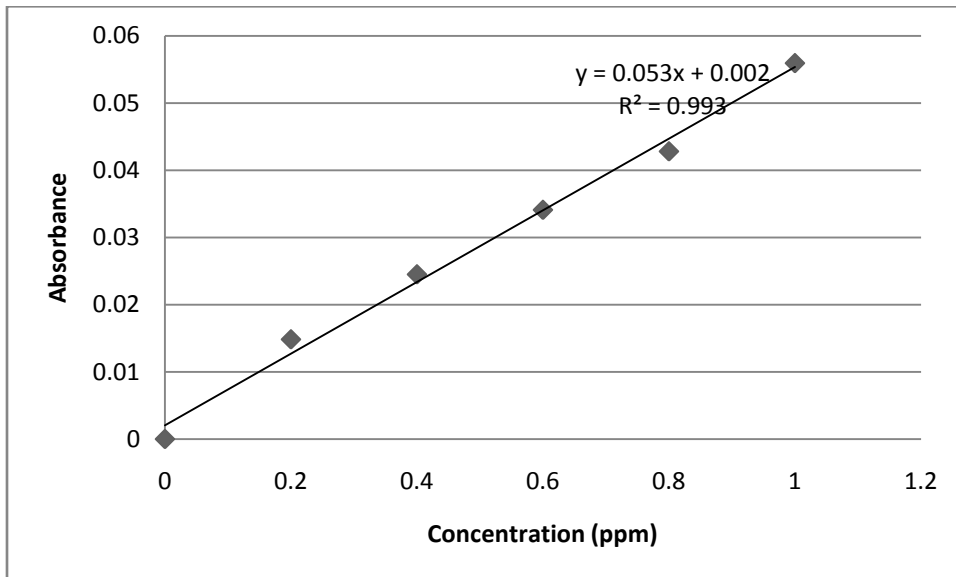
APPENDICES

Appendix I: Calibration curve for Mn



Appendix II: Calibration curve for zinc

Appendix III: Calibration curve for Cr

Appendix IV: Calibration curve for Cd

Appendix V: Calibration curve for lead