

**ANALYSIS OF THE LEVELS OF SELECTED HEAVY METALS IN  
THE VICINITY OF A LEAD BATTERIES RECYCLER PLANT IN  
ATHI-RIVER, KENYA**

**BY**

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## DECLARATION

### Declaration by the student

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**DEDICATION**

To my loving dad Nemwel Omanwa, mum Agnes Kemunto and wife Bethsheba Mainya.  
You will always be my most treasured angels.

## ABSTRACT

The levels of heavy metals in the environment have been increasing in the recent past as a result of human activities. Since toxicity of heavy metals is widely known, their speciation is increasingly attracting attention. There is therefore need to determine the extent of contamination, in particular those of toxic heavy metals. This study thus aimed to ascertain the levels of heavy metals in soils around a lead battery smelting plant in Athi River, Kenya. A total of thirty-six (36) soil samples were collected randomly from six sampling sites around the plant. Sampling was conducted three times both in dry and wet seasons. The concentrations heavy metals (Zn, Cd, Cr, Ni, Pb and Cu) were determined using the Atomic Absorption Spectrophotometer machine (AAS). The results showed that the average concentration of Pb for the dry season was 3918.5 ppm and wet season was 3706 ppm. For Zn, the mean concentration was 111.83 ppm for dry and 90.83 ppm for wet season. For Cd, the average concentration for the dry season was 13.52 ppm and wet season was 9.63 ppm. For Cr, the mean concentration was 186.67 ppm for dry and 147.17 ppm for wet season. For Cu, the mean concentration was 0.9 ppm for dry and 0.4 ppm for wet season. Finally, the mean concentration of Ni was 23.25 ppm for dry and 22.15 ppm for wet season. The concentrations of Pb, Cr and Cd which were higher than the set limits by USEPA while those of Zn, Cu and Ni were below the set limits. The t-test results showed that the concentrations of all the metals were significantly different for the dry and wet seasons. Additionally, the results showed that the soils were acidic with pH values ranging from 3.85 – 5.00. In order to safeguard the health of the residents of this area, the study recommends that the government through the National Environmental Management Authority (NEMA) should deal with solid waste disposal at the smelting plant by imposing strict measures.

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**LIST OF ABBREVIATIONS**

AAS	-	Atomic Absorption Spectrophotometer
ABM	-	Associated Battery Manufacturers
ARBP	-	Athi River Basin Program
ATSDR	-	Agency for Toxic Substances and Disease Registry
BAJ	-	Battery Association of Japan
BOC	-	British Oxygen Company
BOD	-	Biological Oxygen Demand
CDC	-	US centre for disease control
CEKL	-	Chloride Exide Kenya Limited
COD	-	Chemical Oxygen Demand
EC	-	Electrical Conductance
EEA	-	European Environment Agency
EHT	-	Extra Heat Tension
EPA	-	Environmental Protection Agency
EU	-	European Union
FAO	-	Food and Agriculture Organization
HPI	-	Heavy metal pollution index
HTMR	-	High-Temperature Metal Reclamation
ISO	-	International Standardization Organization
IQ	-	Intelligence Quotient
IUDs	-	Intra Uterine Devices
LIBs	-	Lithium-ion Batteries

NEMA	-	National Environmental Management Agency
RBRC	-	Rechargeable Battery Recovery Co-operation
SPSS	-	Statistical Package Social Sciences
SSLA	-	Small Sealed Lead Acid
TDS	-	Total Dissolved Solid
TOC	-	Total Organic Carbon
UNEP	-	United Nations Environmental Program
WHO	-	World Health Organization

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## CHAPTER ONE

### INTRODUCTION

#### 1.1 Background of the Study

Pollution is one of the most important problems around the world today in which thousands of millions of world inhabitants suffer health problems related to industry and atmospheric pollutants (Martinez *et al.*, 2001). Recent years have witnessed significant attention being paid to the problems of environmental contamination by wide variety of chemical pollutants including heavy metals (El-Demerdash & Elagamy, 1999).

Heavy metals enter into the environment from both natural and anthropogenic sources (Kabata-Pendias and Pendias, 1986). They contaminate food sources and accumulate in both agricultural products and seafood through water, air and soil pollution (Lin *et al.*, 2004a). All heavy metals are toxic at soil concentration above normal level. Addition of heavy metals to soil may affect microbial proliferation and enzymatic activities, possibly leading to a decrease in the rates of the biochemical process in the soil environment. Worldwide increasing level of industrialization and urbanization has lead to environmental pollution (Filazi *et al.*, 2003).

Industries have largely been reported to be responsible for discharging pollutants containing heavy metals such as zinc, copper, manganese, cadmium, nickel, mercury, lead, chromium, iron and cobalt into our environments (Chen & Chen, 2001). Metal distribution between soil and vegetation is a key issue in assessing environmental effect of metals in the environment (Abulude & Adesoje, 2006). Heavy metal toxicity has an inhibitory effect on plants growth, enzymatic activity, photosynthetic activity and

accumulation of other nutrient elements, and also damages the root system (Gune *et al.*, 2004).

Nadal *et al.* (2004) and Onder *et al.* (2007) have observed that the most economical and reasonable method for monitoring heavy metals in the atmosphere is using soil and vegetation samples which have been widely used as cumulative matrices of long and short term exposure .

Metals are natural elements that have been extracted from the earth and harnessed for human industry and products used for a long time (John, 2002). Metals are notable for their wide environmental dispersion from mining and smelting; their tendency to accumulate in selected tissues of the human body; and their overall potential to be toxic even at relatively minor levels of exposure (Yu, 2005). There are both environmental and health risks associated with metals. Not all metals are toxic, some are either “xenobiotics” that is they have no useful role in human and plant physiology an example is tin, and some metals are useful especially in life processes for example copper and iron are important in metabolism in human body. Metals such as aluminum, lead and cadmium are the other toxic metals and have no known function in the body (Duruibe *et al.*, 2007).

Metal poisoning occurs through inhaling the fumes and through ingestion of food contaminated with toxic metals. The heavy metals in soils can be absorbed by plants up to certain levels which are toxic and through ingestion by herbivores or omnivores metal poisoning takes place. Children are also highly vulnerable to metal poisoning since they eat soils and also play around with toys contaminated with toxic metals (Yu, 2005).



According to Agency for Toxic Substances and Disease Registry (ATSDR) the top four most toxic metals in the environment are lead, mercury, arsenic, and cadmium. Other toxic heavy metals at elevated levels are copper, nickel, zinc, antimony, and selenium (ATSDR, 2004).

## **1.2 Statement of the Problem**

The area around the Associated Batteries Manufacturers (ABM) Co. Ltd in Athi River is increasingly choking with uncollected garbage, industrial waste and other wastes. The wastes contain heavy metals especially lead which is well known to cause harmful health effects. Children are particularly susceptible to increased levels of Pb in their blood, because their enteral Pb absorption is higher than that of adults (10% vs.50%) besides children relative to adults eat, drink, and inhale more on a body-weight basis. Furthermore, their behavioural characteristics (outdoor activity, hand-to-mouth-activity) place them at a higher risk of exposure and the developing brain is more vulnerable to the effects of many chemicals than the adult brain (Grandjean & Landrigan, 2006). These considerations have led to defining a lower blood-Pb-concentration as being critical for neurobehavioural effects in children than for adults, namely 100 vs. 400 µg/l. There is evidence today that, even at blood-Pb levels below 100 µg/l, neurobehavioural effects of Pb are likely to occur in children, although such effects are typically minor and of doubtful clinical relevance (Nicolescu *et al.*, 2008).

Associated Battery Manufacturers (ABM) is a smelter plant in Athi-River Town (Mavoko Town) which specializes in secondary smelting of Pb from dead batteries. Of major concern is the level of heavy metals which supposedly emanates from this smelter thereby polluting the area around the smelter. Heavy metals enter the environment when

industrial and consumer waste, or even from the water run – off from the neighboring mining sites drain directly to the environment. These heavy metals have bio-accumulated in the soils to dangerous levels which pose negative effects to human health and the environment generally (Ofosu-Asiedu *et al.*, 1999). The common polluting heavy metals are Pb, Cd, Cu, Cr, Se and Hg. Diffuse pollution of the environment by heavy metals is a major environmental problem world-wide. An important input pathway is the atmospheric deposition of industrial, traffic, and household emissions (Schulin *et al.* 2007). The risk of heavy metal contamination is pronounced in the environment adjacent to large industrial complexes. Many cases of particularly severe metal pollution by atmospheric deposition have been reported from areas surrounding nonferrous metal smelters in many countries (Steinnes *et al.*, 2000; Kabala & Singh 2001; McMartin *et al.* 2002; Martley *et al.*, 2004).

The effects of these heavy metals on the inhabitants of the area have been done. Ascertaining of possible sources of the heavy metal pollutants deposited in this area has to be established. This research was therefore targeted to determine the quantity of heavy metals (Cd, Cr, Zn, Pb, Cu and Ni) around ABM.

### **1.3 Justification of the Study**

Heavy metals such as Pb, Zn and Cd are toxic heavy metals both to man and living things at elevated concentrations (Apostoli & Catalani, 2010). Soils act as a major avenue for heavy metal exposure and this is so because high concentrations are especially found in top layer of soils. In addition, plants are another avenue for exposure of these heavy metals (Tijani *et al.*, 2004). At the site of research there is a Pb smelter acting as the main source of pollution. The neighborhoods of the smelter are residential, commercial houses

and learning institutions. In addition there exists idle land which may be used for other uses in future.

No prior study on soil in the vicinity of the smelter has been carried out while schools and residential houses are located near the plant without caution. The raw materials of smelting Pb are dead batteries and scrap Pb bought from as far as Zambia. Apart from Pb being the main toxic metal deposited on soil other expected metal deposits are Cd, Ni, Zn, Fe, As and Sb which are the metals found in the recovered plates of dead Pb acid accumulator batteries. Due to the high potential risk of heavy metal pollution imposed by the smelter there is therefore need to determine the extent of pollution and to alert people of risks posed by the metals.

#### **1.4 Objectives of the Study**

##### **1.4.1 General objective**

The major goal of the study was to assess the levels of heavy metals (Cd, Cr, Ni, Zn, Pb and Cu) in the soil samples collected around ABM using AAS.

##### **1.4.2 Specific objectives**

1. To determine the levels of Cd, Cr, Ni, Zn, Pb and Cu in soils around ABM.
2. To compare the levels of the selected heavy metals with the set limits of the heavy metals in the environment by various environmental agencies.

#### **1.5 Hypothesis**

1. The levels of all heavy metals around the smelting plant are not significantly high.

2. There is no significant difference in the levels of heavy metals around ABM or the dry season and the wet season.
3. The levels of the various metals under study would be within the set limits by NEMA and USEPA.

## **CHAPTER TWO**

### **LITERATURE REVIEW**

#### **2.1 Introduction**

Recycling Pb is relatively simple and cost effective and in most of the applications where Pb is used, especially Pb-based batteries, it is possible to recover it for use over and over again without any loss in quality. The Pb-battery recycling process can be repeated indefinitely, meaning that new Pb batteries are made with materials that have been recycled many times over. Furthermore, as all Pb-based batteries have the same basic chemistry, this means that all types of Pb battery can be processed easily by lead smelters. This is not the case with all automotive battery technologies which are used for hybrid and electric vehicles and, owing to a range of factors such as the high recycling yield of Pb batteries, the well-developed collection and recycling infrastructure and the intrinsic economic value of lead, it is believed it is reasonable to assume that all batteries collected are recycled (EU Report, 2012).

The scrap battery business is now an established market, and knowing where to go with the batteries is as important as ever. The emergence of battery recycling companies has now spread worldwide. In Kenya there are over ten battery manufacturing and recycling companies (Kioko, 2013).

#### **2.2 Battery Recycling Processes**

##### **2.2.1 Recycling**

Recycling by definition is the reuse of materials, either pre-consumer or post-consumer, that would ordinarily be considered waste (Thormark, 2002). Recycling helps lessen the

amount of waste that goes into landfills, helps reduce the amount of toxic chemicals absorbed into the earth and, in some cases, significantly reduces manufacturing costs and energy consumption.

### **2.2.2 Battery Recycling**

Battery recycling is a recycling activity that aims to reduce the number of batteries being disposed of as municipal solid waste. Batteries contain a number of heavy metals and toxic chemicals; their dumping has raised concern over risks of soil contamination and water pollution (Bernardes *et al.*, 2003).

Battery recycling is good for the earth and good for future generations. Battery recycling is the act of processing used or abandoned batteries, which would otherwise be considered waste and harmful to our environment (Apostoli & Catalani, 2010). Many communities have curbside battery recycling services to help out and there are battery recycling centres all across the country where spent battery can be brought. Often times battery recycling centres pay for dropping spent battery off, so it's a win-win situation (Technical Workshop Group, 2001).

There are many misconceptions about what materials can and cannot be recycled. These misconceptions hinder the success and cost-efficiency of recycling programs worldwide. However, with a little consumer education, recycling can be a very important and environmentally sound solution to waste management (Bernardes *et al.*, 2003).

Battery recycling plants require that the batteries be sorted according to chemistries. Some sorting must be done prior to the battery arriving at the recycling plant. Nickel-cadmium, nickel-metal-hydride, lithium-ion and lead acid are placed in designated boxes

at the collection point. Battery recyclers claim that if a steady stream of batteries, sorted by chemistry, were available at no charge, recycling would be profitable. But preparation and transportation add to the cost (Pistoia *et al.*, 2001; Bernardes *et al.*, 2003).

### **2.2.3 The Recycling Process**

Most types of batteries can be recycled. However, some batteries are recycled more readily than others, such as lead-acid automotive batteries (nearly 90% are recycled) and button cells (because of the value and toxicity of their chemicals). Other types, such as alkaline and rechargeable, for instance, nickel–cadmium (Ni-Cd), nickel metal hydride (Ni-MH), lithium-ion (Li-ion) and nickel–zinc (Ni-Zn), can also be recycled (Balkrishena *et al.*, 1999).

The recycling process starts by removing the combustible material, such as plastics and insulation, with a gas fired thermal oxidizer. Gases from the thermal oxidizer are sent to the plant's scrubber where they are neutralized to remove pollutants. The process leaves the clean, naked cells, which contain valuable metal content (Miller *et al.*, 2001).

The cells are then chopped into small pieces, which are heated until the metal liquefies. Non-metallic substances are burned off; leaving a black slag on top that is removed with a slag arm. The different alloys settle according to their weights and are skimmed off like cream from raw milk (Balkrishena *et al.*, 1999).

Cadmium is relatively light and vaporizes at high temperatures. In a process that appears like a pan boiling over, a fan blows the cadmium vapour into a large tube, which is

cooled with water mist. This causes the vapours to condense and produces cadmium that is 99.95 percent pure (Cotton, 1999).

Current Battery recycling methods requires a high amount of energy. It takes six to ten times the amount of energy to reclaim metals from recycled batteries than it would through other means (Bernardes *et al.*, 2003).

Batteries contain a range of metals which can be reused as a secondary raw material. There are well-established methods for the recycling of most batteries containing Pb, Ni-Cd, nickel hydride and mercury. For some, such as newer nickel-hydride and Li systems, recycling is still in the early stages (Cotton, 1999).

There are a number of different battery recycling processes, which are aimed at recovering a variety of materials: Pb can be recovered by either separating the different materials that make up the battery (Pb, plastics, acid, among the many prior to metallurgical processing (Tijani *et al.*, 2004). Alternatively, batteries can be processed as a whole through heat treatment in a particular type of furnace with metals being recovered at the end of the process.

Ni-Cd batteries can be reprocessed through a similar thermal technique, which recovers cadmium and iron-nickel for steel production (Espinosa *et al.*, 2004).

Batteries containing mercury are most commonly processed using a vacuum-thermal treatment, in which the mercury vaporizes (Boening, 2000). It condenses and eventually solidifies when temperatures are reduced and can then be reintroduced into the material cycle. NiMH batteries are reprocessed by mechanically separating the individual



materials within a vacuum chamber to prevent the escape of hydrogen. The output of this process is a product with high nickel content which can be used in the manufacture of stainless steel (Xu, 2004).

Li-ion batteries are currently reprocessed through pyrolysis (heat treatment) with the primary recovery of the metal content. Zinc-carbon/air and alkaline-manganese batteries can be reprocessed using a number of different methods, which include smelting and other thermal-metallurgical processes to recover the metal content (Denis *et al.*, 2002).

Table 2.1 shows various different types of batteries with their percentage composition by type in terms of metals and solutions.

Table 2.1: Battery composition by % type

Type[4]	Fe	Mn	Ni	Zn	H g	L i	A g	C d	C o	A l	Pb	Othe r	KO H	Pape r	Plasti c	Alkal i	C	Acid s	Wate r	Other s
<b>Alkaline</b>	24. 8	22. 3	0. 5	14. 9	-	-	-	-	-	-	-	1.3	-	1	2.2	5.4	3. 7	-	10.1	14
<b>Zinc- carbon</b>	16. 8	15		19. 4	-	-	-	-	-	-	0.	0.8	-	0.7	4	6	9. 2	-	12.3	15.2
<b>Lithium</b>	50	19	1	-	-	2	-	-	-	-	-	-	-	-	7	-	2	-	-	19
<b>Mercury -oxide</b>	37	1	1	14	31								2		3		1		3	7
<b>Zinc-air</b>	42	-	-	35	1	-	-	-	-	-	-	-	-	-	4	4	1	-	10	3
<b>Lithium</b>	60	18	1			3									3		2			13
<b>Alkaline</b>	37	23	1	11	0. 6	-	-	-	-	-	-	-	-	-	6	2	2	-	6	14
<b>Silver oxide</b>	42	2	2	9	0. 4		31	-	-	-	-	4	-	-	2	1	0. 5	-	2	4
<b>Nickel- cadmiu m</b>	35	-	22	-	-	-		15	-	-	-	-	-	-	10	2	-	-	5	11
<b>NiMH</b>	20	1	35	1	-	-	-	-	4	-	-	10	-	-	9	4	-	-	8	8
<b>Li-ion</b>	22	-	-	-	-	3	-	-	18	5	-	11	-	-	-	-	13	-	-	28
<b>Lead- acid</b>	-	-	-	-	-	-	-	-	-	-	65	4	-	-	10	-	-	16	-	-

Source: Dutt, 2013

## **2.3 Battery Recycling by Type**

### **2.3.1 Lead Acid Battery Recycling**

These batteries include but are not limited to: car batteries, golf cart batteries, UPS batteries, industrial fork-lift batteries, motorcycle batteries, and commercial batteries. These can be regular Pb acid, sealed Pb acid, gel type, or absorbent glass mat (AGM) batteries (Denis *et al.*, 2002). These are recycled by grinding, neutralizing the acid, and separating the polymers from the Pb. The recovered materials are used in a variety of applications, including new batteries (Chang *et al.*, 2009).

The Pb of Pb-acid battery can be recycled. Elemental Pb is toxic and should therefore be kept out of the waste stream. Lead-acid batteries are collected by an auto parts retailer for recycling. Many cities offer battery recycling services for lead-acid batteries. In some jurisdictions, including USA and Canadian Provinces, a refundable deposit is paid on batteries. This encourages recycling of old batteries instead of abandonment or disposal with household waste. In the United States, about 97% of lead from used batteries is reclaimed for recycling (WHO, 1995).

Businesses which sell new car batteries may also collect used batteries (and may be required to do so by law) for recycling. Some businesses will accept old batteries on a "walk-in" basis (not in exchange for a new battery). Most battery shops and recycling centres will pay for scrap batteries. This can be a lucrative business, enticing especially to risk-takers because of the wild fluctuations in the value of scrap lead that can occur overnight. When lead prices go up, scrap batteries can become targets for thieves (EEA, 1998).

The battery is broken apart in a hammer mill; a machine that hammers the battery into pieces. The broken battery pieces are then placed into a vat, where the lead and heavy materials fall to the bottom and the plastic floats (Banks *et al.*, 1997). At this point, the polypropylene pieces are scooped away and the liquids are drawn off, leaving the lead and heavy metals. Each of the materials goes into a different recycling “stream”.

### **2.3.2 Alkaline/Zinc Carbon/Zinc Air Batteries**

These batteries are recycled in a specialized “room temperature,” mechanical separation process where the battery components are separated into 3 end products. These items are a) zinc & manganese concentrate, b) steel, c) paper and plastic. All of these products are put back into the market place for reuse in new products. These batteries are 100% recycled (Winter & Brodd, 2004).

### **2.3.3 Lithium ion Batteries**

Prior to the smelting process, plastics are separated from the metal components. The metals are then recycled via a High-Temperature Metal Reclamation (HTMR) process during which all of the high temperature metals contained within the battery feedstock that is, nickel, iron, manganese, and chromium are deposited to the molten-metal bath within the furnace, amalgamate, then solidify during the casting operation (Balbuena & Wang, 2004). The low-melt metal that is, zinc and cadmium separate during the melting, the metals and plastic are then returned to be reused in new products. These batteries are 100% recycled (Yoshio *et al.*, 2009).

### **2.3.4 Nickel-Cadmium, Nickel Metal Hydride Batteries**

Prior to the smelting process, plastics are separated from the metal components. The metals are then recycled via a high-temperature metal reclamation (HTMR) process during which all of the high temperature metals contained within the battery feedstock that is: - nickel, iron, manganese, and chromium are deposited to the molten-metal bath within the furnace, amalgamate, then solidify during the casting operation (Rodrigues & Mansur, 2010). The low-melt metals that are zinc and cadmium) separate during the melting; the metals and plastic are then returned to be reused in new products. These batteries are 100% recycled.

### **2.3.5 Lithium Batteries**

The contents of the batteries are exposed using a shredder or a high-speed hammer depending on battery size. The contents are then submerged in caustic (basic not acidic) water. This caustic solution neutralizes the electrolytes, and ferrous and non-ferrous metals are recovered. The clean scrap metal is then sold to metal recyclers. The solution is then filtered. The carbon is recovered and pressed into moist sheets of carbon cake. Some of the carbon is recycled with cobalt. The lithium in the solution (lithium hydroxide) is converted to lithium carbonate, a fine white powder. What results is technical grade lithium carbonate, which is used to make lithium ingot metal and foil for batteries. It also provides lithium metal for resale and for the manufacture of sulfur dioxide batteries (Balbuena & Wang, 2004).

### **2.3.6 Mercury Batteries**

The batteries and heavy metals are recovered through a controlled-temperature process. It is important to note: the percentage of mercuric oxide batteries is decreasing since the

passage of the Mercury-Containing Rechargeable Battery Management Act (The Battery Act) of 1996. This act prohibits, or otherwise conditions, the sale of certain types of mercury-containing batteries that is alkaline-manganese, zinc-carbon, button-cell mercuric-oxide and other mercuric-oxide batteries) in the United States (Lin *et al.*, 2004b).

### **2.3.7 Environmental Effects of Battery Recycling**

The recycling process has the potential for significant environmental impacts and risks to human health and safety. Generally the more notable environmental impacts include particulate (including lead and other heavy metals) and acidic (sulfur dioxide – SO<sub>2</sub> and possibly some hydrochloric acid in the gaseous form, HCl) discharges into the atmosphere during the smelting and refining processes. The growing recognition of such impacts within communities, and by regulatory authorities, has been paralleled by the tightening of environmental protection standards and by higher environmental protection costs for recycling plant operators (Crocce *et al.*, 2004).

### **2.3.8 Battery recycling by location**

The European Union (EU) has been stringent on battery recycling. In 2006 the EU passed the Battery Directive of which one of the aims is a higher rate of battery recycling. The EU directive states that at least 25% of the entire EU's used batteries must be collected by 2012, and rising to no less than 45% by 2016, of which, that at least 50% of them must be recycled. To achieve this goal, it must be possible to remove batteries readily and safely. It is for member states in EU to ensure that manufacturers design their appliances accordingly. Also, member states in EU have to ensure that, from 26 September 2009;

batteries that have been collected are treated and recycled using the best available techniques. Recycling must exclude energy recovery (Amarasinghe & Williams, 2007).

In USA and Canada, the rechargeable battery industry has formed the Rechargeable Battery Recycling Corporation (RBRC) which operates a free battery recycling program. The program will provide businesses with prepaid shipping containers for rechargeable batteries of all types while consumers can drop off batteries at numerous participating collection centres. The organization claims that no component of any recycled battery eventually reaches a landfill. A study estimated battery recycling rates in Canada based on RBRC data. In 2002, it wrote, the collection rate was 3.2%. This implies that 3.2% of rechargeable batteries were recycled, and the rest were thrown in the trash. By 2005, it concluded, the collection rate had risen to 5.6%. A November 2011 report claims that batteries collected in the United States are increasingly being transported to Mexico for recycling as a result of a widening gap between the strictness of environmental and labour regulations between the two countries (Smith & Gray., 2010).

In Japan, there is no single national battery recycling law so the advice given is to follow local and regional statutes and codes in disposal of battery waste. The Battery association of Japan (BAJ) recommends that alkaline, zinc-carbon and lithium primary batteries can be disposed of as normal household waste. The BAJ's stance on button cell and secondary batteries is toward recycling and of increasing national standardization of procedures for dealing with these types of batteries (Pistoia *et al.*, 2001).

In April 2004 the Japan Portable Rechargeable Battery Recycling Center (JBRC) was created to handle and promote battery recycling throughout Japan. They provide battery recycling containers to shops and other collection points (Fujimoto, 2001).

#### **2.4 Heavy Metals**

Heavy metals can be released into the environment by both natural and anthropogenic causes (Alloway, 1995). The major causes of emission are the anthropogenic sources specifically mining and industrial operations. Heavy metals form persistent environmental contaminants since they cannot be degraded or destroyed (Yu, 2005). To a certain degree, they enter the body system through food, air, and water and bio-accumulate over a period of time.

Numerous studies have been conducted in this area aimed at determining the heavy metal concentrations in soils around major smelters in the world and thus developing an efficient and economical way to remediate the soil contaminated with heavy metals.

Globally, properly disposed of batteries are sent to a licensed recycler where, under strict environmental regulations, the Pb and plastic are reclaimed and then sent to a battery manufacturer to be used to produce a new battery. In China, batteries disposed of as regular trash pose a danger to refuse collectors, who can come into contact with Pb and corrosive sulfuric acid. Improperly disposed of Pb-acid batteries can leak and contaminate soil, groundwater and surface water supplies. A single used battery, if disposed of improperly, could lead to the contamination of 12 cubic meters of water or one cubic meter of soil (Lee and Jing, 2008).



Despite the risks associated with Pb poisoning, there are families in rural communities whose main source of income is from small-scale recycling plants that process e-waste, some of which inevitably contains Pb-based batteries. Moreover, scrap collectors can make a considerable income rummaging through mounds of waste. China's underdeveloped battery recycling infrastructure and weak enforcement of e-waste imports from industrialized countries has resulted in a low-tech, citizen-based recycling network that puts many of its participants at serious risk of ill health, both from Pb and a host of other toxic materials (Lee and Jing, 2008).

Contamination of soil with Cu has health hazards implication as the excessive concentration of Cu could bring anaemia, infections, thinning of bones, thyroid gland dysfunction, heart diseases and nervous systems problems (IPCS, 1998).

The study by Adegoke *et al.* (2009) hereby concluded that the dumpsite had been heavily contaminated with Pb and Cu owing to the anthropogenic activities by an automobile lead battery producer. This therefore has made the study area unsafe for humans and agricultural activities.

#### **2.4.1 Lead**

It is the most toxic metal and the main pollutant around a Pb smelter. Pb is strongly precipitated by soil yet many plants take up as much as 30 ppm in the roots. Most plants retain the Pb entirely in the roots except for sulfur deficient plants (Amarasinghe & Williams, 2007).

Pb is a soft pale grey metal occurring naturally. It is the heaviest metal known. The global production of Pb from both smelter and mining operations has been relatively high

throughout this century and will continue slowly in the future. Pb is one of the metals widely spread in the environment, largely because of human activities (Alloway, 1995).

When released into the environment, Pb has long residence time compared to other pollutants. As a result, Pb and its compounds tend to accumulate in the soils and sediment. Due to the high degree of solubility and relative freedom from microbial degradation they remain accessible to the food chain and human metabolism far into the future (Yu, 2005). Other sources of Pb including smelting and burning petroleum containing tetraethyl Pb and trimethyl Pb. Trialkyl lead compounds are formed in the environment due to the breakdown of tetraalkyl Pb. Trialkyl leads are less volatile and more readily soluble in water. This species may also be lost to environment as emissions and remain available to organisms (WHO, 2004).

Leafy and root vegetables tend to accumulate mostly Pb. Toxicity of Pb in plants is related to its chemical form, availability for and mechanisms for uptake, translocation and detoxification and physiochemical characteristics of the plants directly into the environment (Lavecchia *et al.*, 2010). Many plants appear to have mechanisms for storing lead in an insoluble form or for limiting its translocation within the plant. Toxic effects of lead in plants are most likely to occur near point sources of lead emission where environmental concentrations are very high or when the availability of phosphorous for uptake by plants is high (Yu, 2005).

In adults exposure to Pb results in reproductive problems in both female and male, high blood pressure and hypertension, nerve disorders, memory and concentration problems, muscle and joint pain. In adults the maximum allowable Pb level is 40 micro grams per

deciliter. The symptoms of acute lead poisoning in children include brain and nervous system damage among other organs. A child with severe Pb poisoning complains of stomach-ache and headache. The child feels tired and generally over reactive, eats less, sleeps more and may vomit (WHO, 2004).

#### **2.4.2 Cadmium**

Cadmium is a toxic metal in the environment and follows Pb and Hg in toxicity order (ATSDR 2002). It is a relatively volatile element not essential to plants, animals, and humans. Its presence in living organisms is unwanted and harmful. An increased level of Cd in air, water, and soil increases its uptake by living organisms. It is taken up by plants and animals and through them also by humans. This results in the cadmium cycle; "soil-plant-animal-man". The cycle shows that up to 90% Cd taken up by plants originates from soil and only 10% from atmosphere (Yu, 2005).

High concentrations of cadmium in soil represent a potential threat to human health because it is incorporated in the food chain mainly by plant uptake. The behaviour of Cd in soils depends on several factors related to both soil and plant characteristics. Species such as oats, soya beans, corn and tomato accumulate more Cd in roots than in aerial parts of the plant. Conversely, lettuce, carrot and potato accumulate more in the leaves. Soya bean plant accumulates more in the seeds than in leaves (Sharp, 1990).

Cadmium is a major hazard to human health where chronic accumulation in the kidney can cause dysfunction. The FAO (2001) recommends a maximum tolerable intake of 70 micro grams per day. According to MIT press journal of 2002 on "human health and heavy metal exposure" "the health implications of Cd are exacerbated by the relative

inability of human beings to excrete cadmium (it is excreted but then reabsorbed by the kidney). Acute high dose can cause severe respiratory irritation. Occupational levels of cadmium exposure are a risk factor for chronic lung disease (through airborne exposure) and testicular degeneration and still under investigation as a risk factor for prostate cancer. Low levels are mainly of concern with respect to toxicity to kidney. Apart from kidney damage, Cd causes loss of calcium leading to “itaitai” disease, an epidemic of bone fractures. Initially found in Japan from gross cadmium contamination of rice stocks (ATSDR, 2004).

Cadmium is harmful not only to humans and animals but also the most adverse effects are on microbial biomass and its activity which plays an important role in biological cycles of almost all the major plant nutrients cycling and maintaining soil fertility. Cadmium can also cause changes in the size, composition, and activity of soil microbial community. Maximum cadmium levels in soils for residential and gardening purposes should be 47mg/kg (Sharp, 1990).

Cadmium is used extensively in electroplating and alloys. Common alloys include copper for frame way wires, aluminum for casting with tin, bismuth in fusible alloys. Other uses include manufacture of batteries, atomic reactors, pigments (Cadmium compounds), plasticizers and phosphorous in colour TV tubes (Sharp, 1990).

### **2.4.3 Zinc**

Zinc occurs naturally in air, water and soil but zinc concentrations are rising unnaturally due to addition of zinc through human activities. Most zinc is added during industrial activities such as mining, smelting, and steel processing. Zinc is the 23<sup>rd</sup> most abundant

element in the earth crust. Dominant ore is zinc blend also known as sphalerite. It is a trace element essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc shortages can even cause birth defects (ATSDR 2004).

Although humans can handle proportionally large concentrations of Zn, too much Zn can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of Zn can damage the pancreas and disturb protein metabolism and cause arteriosclerosis. In the work place environment high zinc concentration can lead to flu like condition known as metal fever. This condition will pass after two days (ATSDR 2004).

Zn primarily enters the body through the mouth in food, water or by small soil or dust particles. Zn can also be inhaled (from smelting or welding operations) and is less commonly absorbed through the skin. Zn intoxication is an infrequent occurrence. Many of the toxic effects attributed to Zn may have been due to other metals present, namely Cd, Pb, Sb, and As. Metal fumes, brass chills, Zn shakes and galvo-shelter shakes have been attributed to Zn oxide fumes and dusts, which are hazardous. Inhalation of Zn fumes causes fever, depression, vomiting, excess salivation and headache. Zn unlike Pb, Cd, As and Sb does not accumulate in the biosystems including man. This therefore minimizes the chances of its toxic effects (Yu, 2005).

Zn ranks fourth among metals in animal consumption being surpassed only by Fe, Al and Cu. The principal source of Zn in municipal sewage and waste water is the waste generated in plants that manufacture consumer and industrial product that utilize Zn.

Background levels of Zn in natural inland surface water way vary from 0.001 to 0.2 mg/l or higher. Wastewater containing Zn is often acidic and may also have high content of Cu, Fe and Cd (Jasonof, 1986).

#### **2.4.4 Copper**

Cu may occur in drinking water either by contamination of the source water used by the water system, or by corrosion of Cu plumbing. Corrosion of plumbing is by far the greatest cause for concern (Alkarahi *et al.*, 2009). Cu is rarely found in source water, but Cu mining and smelting operations and municipal incineration may be sources of contamination. Other sources include birth control pills, congenital intoxication, Cu cookware, Cu IUDs, Cu pipes, dental alloys, fungicides, ice makers, industrial emissions, insecticides, swimming pools, water (city / well), welding, avocado, beer, bluefish, bone meal, chocolate, corn oil, crabs, gelatin, grains, lamb, liver, lobster, margarine, milk, mushrooms, nuts, organ meats, oysters, perch, seeds, shellfish, soybeans, tofu, wheat germ and yeast (WHO, 2004).

Natural sources of copper include wind blown dust, forest fires and decaying vegetation. This metal is widely distributed in free state in sulphides, arsenides, chlorides and carbonates. It is also commonly present in natural surface water in trace amounts. Soil solutions and river water contain copper at a level of about 0.01mg/mL. Copper may be released to water as a result of natural weathering of soil and discharges from industries and sewage treatment plants (Jasonof, 1986).

### **2.4.5 Chromium**

The two largest sources of Cr emission in the atmosphere are from the chemical manufacturing industry and combustion of natural gas, oil, and coal (Brodnjak-Vončina *et al.*, 2002). Other sources of Cr exposure are as follows: cement-producing plants, since cement contains Cr; the wearing down of asbestos brake linings from automobiles or similar sources of wind-carried asbestos, since asbestos contains Cr; incineration of municipal refuse and sewage sludge; exhaust emission from catalytic converters in automobiles; emissions from air conditioning cooling towers that use Cr compounds as rust inhibitors; wastewaters from electroplating, leather tanning, and textile industries when discharged into lakes and rivers; and solid wastes from the manufacture of Cr compounds, or ashes from municipal incineration, when disposed of improperly in landfill sites (Kotti *et al.*, 2005). Some consumer products that contain small amounts of Cr are: some inks, paints, and paper; some rubber and composition floor coverings; some leather materials; magnetic tapes; stainless steel and a few other metal alloys; and some toner powders used in copying machines (Lester & Birkett, 1999).

### **2.4.6 Nickel**

It is a silvery-white lustrous metal with a slight golden tinge, hard and ductile. Pure Ni shows a significant chemical activity that can be observed when Ni is powdered to maximize the exposed surface area on which reactions can occur, but larger pieces of the metal are slow to react with air at ambient conditions due to the formation of a protective oxide surface. Even then, Ni is reactive enough with oxygen that native Ni is rarely found on Earth's surface, being mostly confined to the interiors of larger Ni-Fe meteorites that were protected from oxidation during their time in space (McNeil & Ian, 1990).

In the US, the tolerable upper limit of dietary Ni is 1000 µg/day, while estimated average ingestion is 69-162 µg/day, large amounts of Ni and Cr – comparable to the estimated average ingestion above – leach into food cooked in stainless steel. For example, the amount of Ni leached after 10 cooking cycles into one serving of tomato sauce averages 88 µg. Sensitized individuals may show an allergy to Ni, affecting their skin, known as dermatitis. Sensitivity to Ni may also be present in patients with pompholyx. Ni is an important cause of contact allergy, partly due to its use in jewelry intended for pierced ears. Ni allergies affecting pierced ears are often marked by itchy, red skin. Many earrings are now made Ni-free due to this problem. The amount of Ni allowed in products that come into contact with human skin is regulated by the European Union and set at 50 ppm (FAO, 2001). In 2002, researchers found amounts of Ni being emitted by 1 and 2 Euro coins far in excess of those standards. This is believed to be due to a galvanic reaction. Ni was voted allergen of the year in 2008 by the American Contact Dermatitis Society (Kuck & Peter, 2012).

Ni is one of the most widely used metals on the planet. According to the Ni Institute, the metal is used in over 300,000 different products. Most often it is found in steels and metal alloys, but it is also used in the production of batteries and permanent magnets. The Mond (or Carbonyl) Process is the most common and efficient method to treat Ni sulphide. In this process, the sulphide is treated with hydrogen and fed into a volatilization kiln. Here it meets carbon monoxide at about 60° C to form Ni carbonyl gas. The Ni carbonyl gas decomposes on the surface of pre-heated nickel pellets that flow through a heat chamber until they reach the desired size. At higher temperatures, this process can be used to form Ni powder (Street *et al.*, 1998).



## 2.5 Related Studies

In a research done by Duruibe *et al.* (2007) around a battery smelter in Imo State, Nigeria, the results showed heavy metals of Fe, Pb and Cr to exhibit concentrations that are more than 20 times the recommended international limits. The pollution was attributed to the improper disposal of recycler waste by the company around the smelter. The outcome revealed that 100% of the children around the area had blood-lead levels exceeding 10  $\mu\text{g}/\text{dL}$  (the international standard for the maximum safe levels of lead in blood), 96% exceeded 45  $\mu\text{g}/\text{dL}$ , and 84% exceeded 70  $\mu\text{g}/\text{dL}$ . In many areas in all villages sampled, including family homes and compounds, the soil lead concentration exceeded 100,000 ppm, far above the recommended maximum of 400 ppm considered acceptable for residential areas. Ingestion of contaminated soil and air inhalation has been the primary pathway of Pb exposure.

In another study heavy metals pollution of soil by slag from a battery manufacturing recycler plant in Nigeria was done to ascertain the potential danger they pose on the environment. Soil samples were randomly collected at 0 - 15 cm and 15 - 30 cm depths from the premises of the plant and an uncontaminated site as control for both dry and wet seasons. Samples were analyzed for Pb, Cd, Cr and Ni using standard analytical methods. The premises showed Pb level ranging from 243 – 129,000 mg/kg for both seasons and depths with about 97 and 94% samples higher than the maximum permissible level of 400 mg/kg of Pb in soil (Chen *et al.*, 2003) and 1000 mg/kg of Pb in soil, respectively defined by USEPA as level that correlates with the critical blood Pb level of  $7\mu\text{g}/\text{dL}^{-1}$  (USEPA, 2011) in children. Most soil samples also exceeded the lead soil quality criteria of other countries (Adie & Osibanjo, 2009).

Cadmium, Chromium and Nickel levels on average were comparable with background concentrations for both seasons and depths. This generally suggests that the sources of these metals may not have been anthropogenic, but rather associated with the natural weathering of the metalliferous parent rock that formed the soil. However, there were anomalously high levels of Cadmium in samples for 0 – 15 cm depth during the dry season and during the wet season. Also for samples 15 – 30 cm depth during wet season showed high concentrations of cadmium. The corresponding levels of Pb in these samples were also very high. The source is associated with galena (PbS) alloy as Cd often is an impurity in the alloy. Chromium showed concentrations in the soil samples that fluctuated between 50 - 309 mg/kg and they were comparable with the background levels implying that Chromium was from the parent material that formed the soil not from the slag. Nickel was not detected in about 95% of all soil samples (Adie & Osibanjo, 2009).

Most metals in the pH range of 6.0 - 9.0 are not always in the free form. The pH range of all the soil samples in the present study is slightly acidic to neutral implying that some metal ions may exist in the free form and hence could be leached into subsoil and subsequently into groundwater (Adie & Osibanjo, 2009).

In another study Pb and Cd concentrations were determined in the Pb recycling smelter in Chi Dao, Vietnam. The concentration of Pb was found to be in the range of 7,000 – 15,000 mg/kg and Cd 1.8 – 3.6 mg/kg. The concentrations of Pb in paddy soil areas within 300 m radius from the Pb smelter were from 3.6 to 100 fold higher than the safe limit. The sediment from the ditch near the Pb smelters contained extremely high levels of Pb and Cd (Dang *et al.*, 2008).

The toxic effect of Pb is mainly based on its ability to react with functional groups such as sulfhydryl, carboxyl and amine, leading to a decrease or loss of activity of many enzymes that are important for cell functions (Peng *et al.*, 2005).

In Chi Dao, Pb- recycling activities have been operated for Pb and Cd. Pb contents in soils were found to decrease with the distance from centralized smelter area in the paddy field near the road. Belgium is an important Cd producer, but certain areas of the country are polluted mainly by Cd due to past emissions from non-ferrous industries (Dang *et al.*, 2008).

In the Chi Dao study the Pb contents in almost of all the soil samples at the investigated sites exceeded the safe level. For Cd, the soils collected from sites (garden soils of Pb recycling household and soil area less than 20 m far from smelters) had the concentrations of Cd higher than the safe level (Dang *et al.*, 2008).

Martley *et al.* (2004) conducted a study on the heavy metal concentrations in soils around the copper smelter and surrounding industrial complex in Australia. Soil samples collected were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) to determine the concentrations of different heavy metals in the soils. Their findings showed high levels of Cu, Pb and Zn above the set limits by EPA. From their investigation, they discovered that the extent of the contamination emanating from the Port Kembla industrial complex is limited to 1–13 km, depending on the element; the contamination at the greater distance may not originate from the industrial complex.

In another study done by Chaoyang *et al.* (2008) on the characterizing spatial distribution and sources of heavy metals in the soils in Shuikoushan, China, soil samples were collected in an area of about 100 km<sup>2</sup>. Concentrations of total As, Cd, Pb, Zn, Cu and Cr were measured using inductively coupled plasma mass spectrometry (ICP-MS). As and Pb were found to have a common source, indicating the same sources and spreading processes. Airborne sources from smelting chimneys contributed greatly to Cd in the area, which demonstrated the same dispersion pattern as As and Pb. However, two hot spots of Cd around smelters were possibly enlarged by wastewaters, demonstrating another important source of Cd in Shuikouhsan, China. Geo-statistic interpolated mapping demonstrated that hotspots of Zn were only found proximal to the large smelters, suggesting that Zn primarily came from the chimneys of larger smelters.

In another research done by Aucott (2006) on levels of heavy metals in a landfill nearby a battery smelter in New Jersey, the results indicated that the leachate concentrations generally exceeded, except for Ba, drinking water standards and groundwater maximum contaminant levels (MCLs). As and Cd stood out by exceeding the MCLs by wide margins; both having mean concentrations more than 40 times higher than drinking water MCLs. Some states, for example New Jersey, have imposed an As MCL of 0.005 mg/l (Zaw & Emett, 2002); the mean As leachate concentration was more than 80 times higher than the standard. Pb also stood out by exceeding the MCLs by wide margins. The origin of these heavy metals was surmised to be the battery smelter since they disposed of their wastes in the landfill.

In the Adegoke study of levels of heavy metals of an old Pb-battery dumpsite in Nigeria. Analysis of Cu, Cr, Pb, Zn, Cd, and Ni and As was done using AAS. The results showed

that all sample collection points were contaminated with Pb. The study location was polluted with Pb due to anthropogenic effect and this posed hazardous effects to human health as high concentration of Pb exceeded the threshold levels (Adegoke *et al.*, 2009).

In Kenya, a study done by Okeyo & Wangila (2012) found severe evidence of lead poisoning in Owino Uhuru, a slum area in Mombasa city adjacent to a lead battery recycling factory. The lead content within the Owino Uhuru slum study area, adjacent to the lead-acid battery recycling factory, ranged from 7.933 mg/L to 25.024 mg/L as compared to those in the Maweni area, ten kilometers away from the factory, which averaged at 2.695 mg/L. There was also more lead content within the dust in Owino Uhuru slums mostly ranging from 45.586mg/L to 207.840 mg/L.

## CHAPTER THREE

### MATERIALS AND METHODS

#### 3.1 Study Area

The smelter is Associated Battery Manufacturers (ABM) in Athi-River Town (Mavoko Town) which specializes in secondary smelting of Pb from dead batteries. Its parent company is Chloride Exide Kenya Limited (CEKL) which is ISO certified (ISO 9001). Athi-River Town is outside Nairobi in Machakos County and covers an area of approximately 693 km<sup>2</sup> (figure 3.1). The headquarters of the county is Machakos Town; according to the 2009 population census Athi River has an estimated 546,098 people mostly young under the age of 30 years (KNBS, 2013). The local climate is semi-arid; the terrain is hilly, altitude of 1000-1600 metres above sea level. It is also a growing residential area due to proximity of the capital hence a very high risk to heavy metal poisoning to the residents.

The study focused on six (6) sampling sites (for the case of soil); three is at the front of the smelter (S1, S2 and S3) and the other three at the back of the smelter (S4, S5 and S6). Site in front of the smelter is small and has a tarmac road; beyond the tarmac road is Makadara Shopping Centre. At the back of the smelter is a plant chimney, while land is normally used by herders to graze their animals and also used by local people to grow food crops such as Kales. Land at the back of smelter is bigger and is likely to be occupied in the future for residential purposes hence large samples were collected.

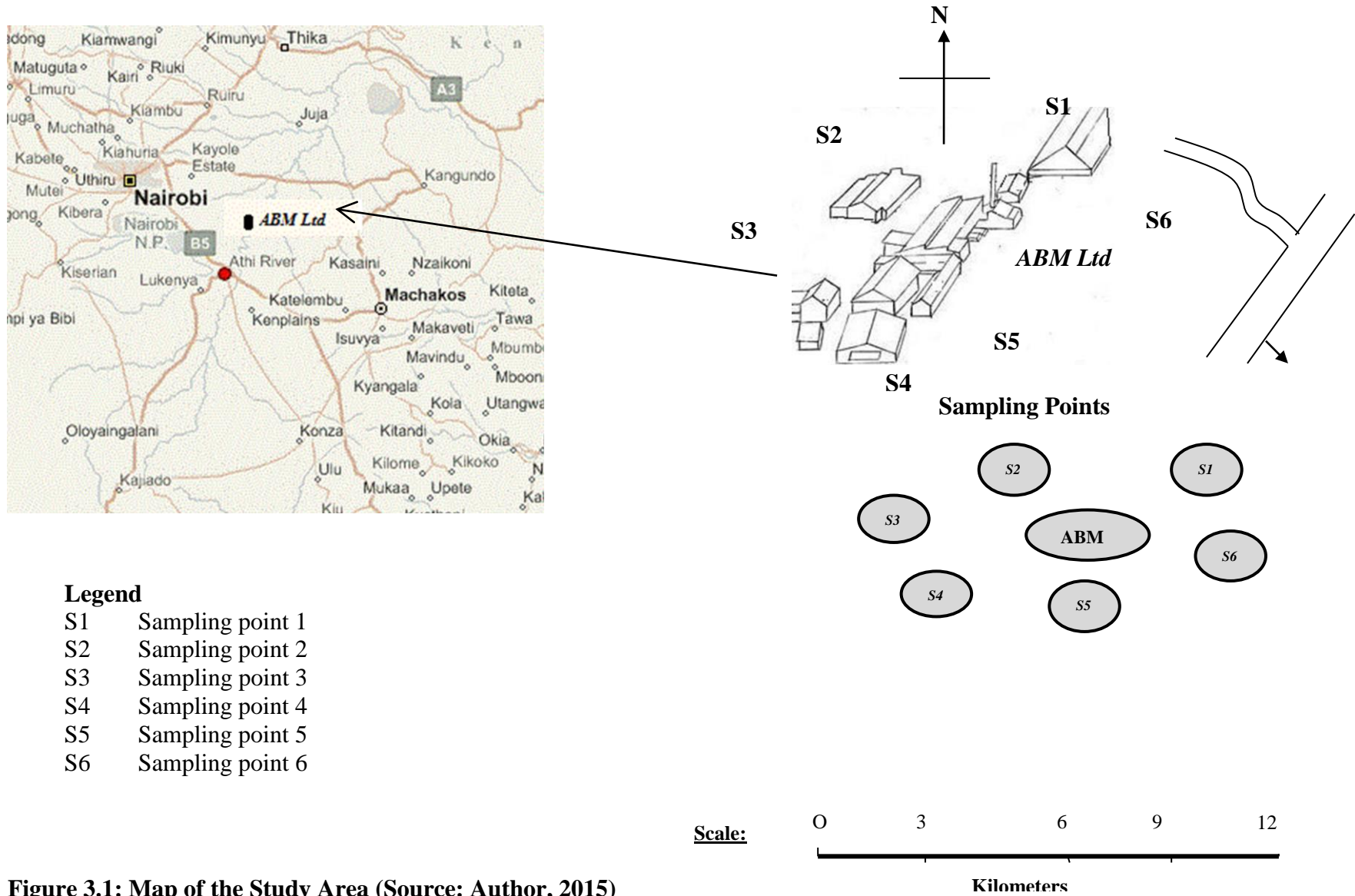


Figure 3.1: Map of the Study Area (Source: Author, 2015)

### 3.2 Sample Collection

Six bulk and intact-core soil samples were collected from six different sites around the smelter. Sampling was done six times (3 times in the dry season and 3 times in the wet season). Systematic sampling was employed since it is more representative and efficient than random sampling and easier when using statistics for analysis. Soil samples were taken from a depth of 20 cm using soil auger. A total of six deep-soil grab samples were collected from each site.

### 3.3 Reagents and Apparatus

1. Conc.  $\text{HNO}_3$  (Analytical grade, 98% Purity)
2. Conc.  $\text{HCl}$  (Analytical grade, 99% Purity)
3. Pestle and Mortar
4. Whatman filter paper
5. Conical flasks
6. Weighing scale (Model 7329B)
7. Drying oven
8. Distilled deionized water

### 3.4 Digestion of Perchloric Acid

Suitable volume of the water in evaporating dishes taken and acidified to methyl orange with conc.  $\text{HNO}_3$ . Further, 5mL conc.  $\text{HNO}_3$  acid was added and evaporated to 10mL. Then it was transferred to a 125mL conical flask. 5mL of conc.  $\text{HNO}_3$  acid and 10mL of perchloric acid (70%) were added. Then heated gently, till white dense fumes of  $\text{HClO}_4$  appear. The digested samples were cooled at room temperature, filtered through Whatman No. 41 or sintered glass crucible and finally the volume was made upto 100mL.

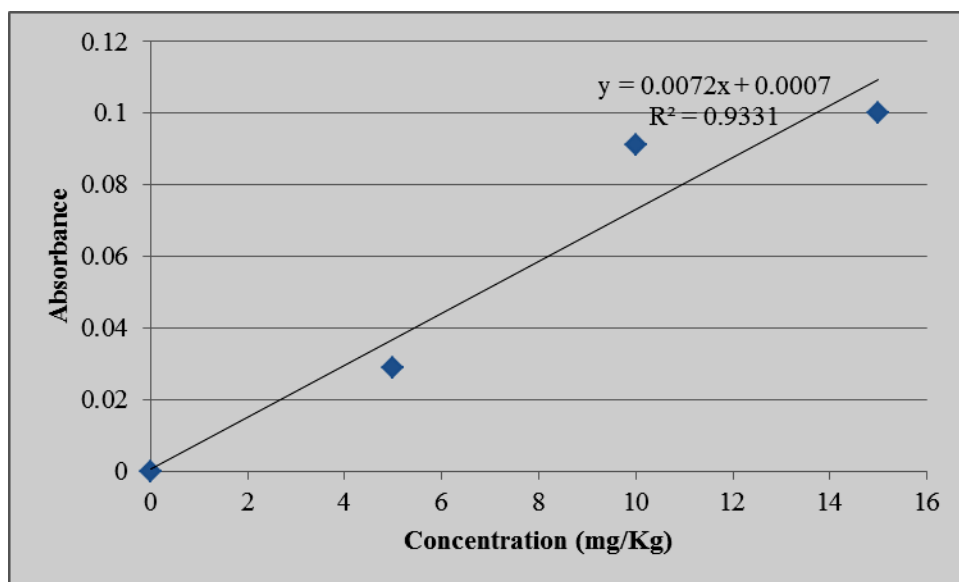


with distilled water. Then this solution was boiled to expel oxides of nitrogen and chlorine. This solution contained 0.8M in  $\text{HClO}_4$ . The solution was used for the use of determination of heavy metals.

### 3.5 Preparation of Stock Solutions

#### 3.5.1 Preparation of Stock and Working Solution of Lead

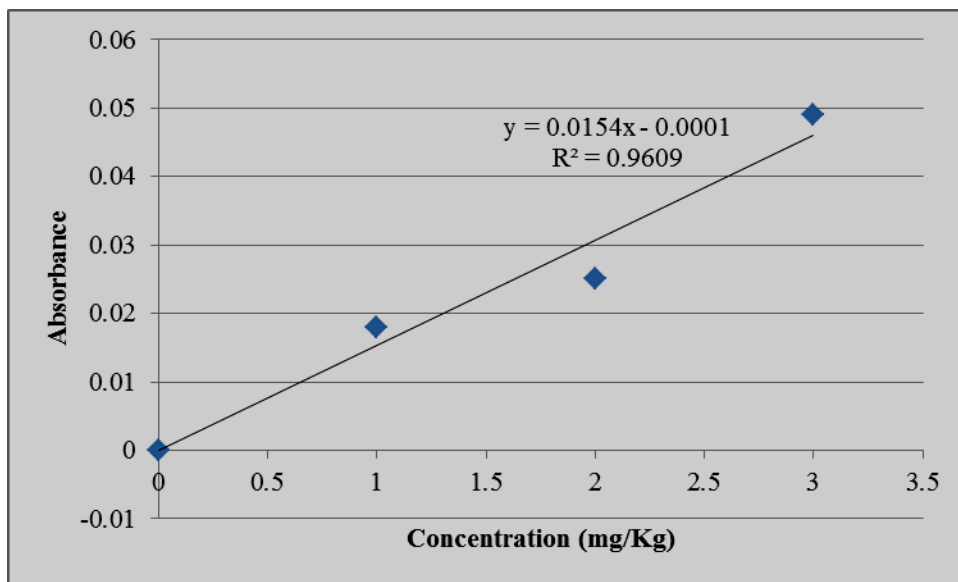
Stock solution of lead was prepared by dissolving 1.0 g of lead in 20 mL of 1:1 nitric acid then diluted to 1 L to give 1000 ppm of lead. A working solution of 100 ppm was prepared by pipetting 10 mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water. Standard solutions of 5 ppm, 10 ppm and 15 ppm were prepared by pipetting 5 mL, 10 mL and 15 mL respectively of the working solution into 100 mL volumetric flask then made to the mark using distilled water. Using the standards, a calibration curve shown below was produced and concentration of lead in each sample was determined directly using AAS. Analysis was done in triplicate to enhance the accuracy of the results.



**Figure 3.2: Calibration Curve of Lead**

### 3.5.2 Preparation of Stock and Working Solution of Cadmium

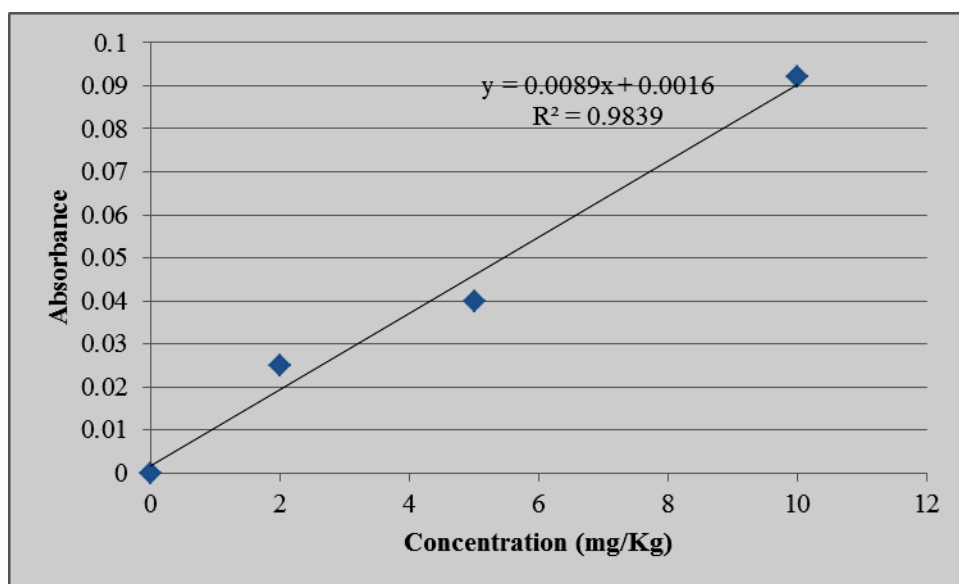
Stock solution of cadmium was prepared by dissolving 1.0 g of cadmium in 10 mL of 1:1 nitric acid: water ratio then diluted to 1 L to give 1000 ppm of cadmium. A working solution of 100 ppm was prepared by pipetting 10 mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water. Standard solutions of 1 ppm, 2 ppm and 3 ppm were prepared by pipetting 1 mL, 2 mL and 3 mL respectively of the working solution into 100 mL volumetric flask then made to the mark using distilled water. Using the standards, a calibration curve shown below was produced after which concentration of cadmium in each sample was determined directly using AAS. Analysis was done in triplicate to enhance the accuracy of the results.



**Figure 3.3: Calibration curve of cadmium**

### 3.5.3 Preparation of Stock and Working Solution of Copper

Stock solution of copper was prepared by dissolving 1.0 g of copper in 10 mL of 1:1 nitric acid: water ratio then diluted to 1 L to give 1000 ppm of copper. A working solution of 100 ppm was prepared by pipetting 10 mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water. Standard solutions of 2 ppm, 5 ppm and 10 ppm were prepared by pipetting 2 mL, 5 mL and 10 mL respectively of the working solution into 100 mL volumetric flask then made to the mark using distilled water. Using the standards, a calibration curve shown below was produced then concentration of copper in each sample was determined directly using AAS. Analysis was done in triplicate to enhance the accuracy of the results.

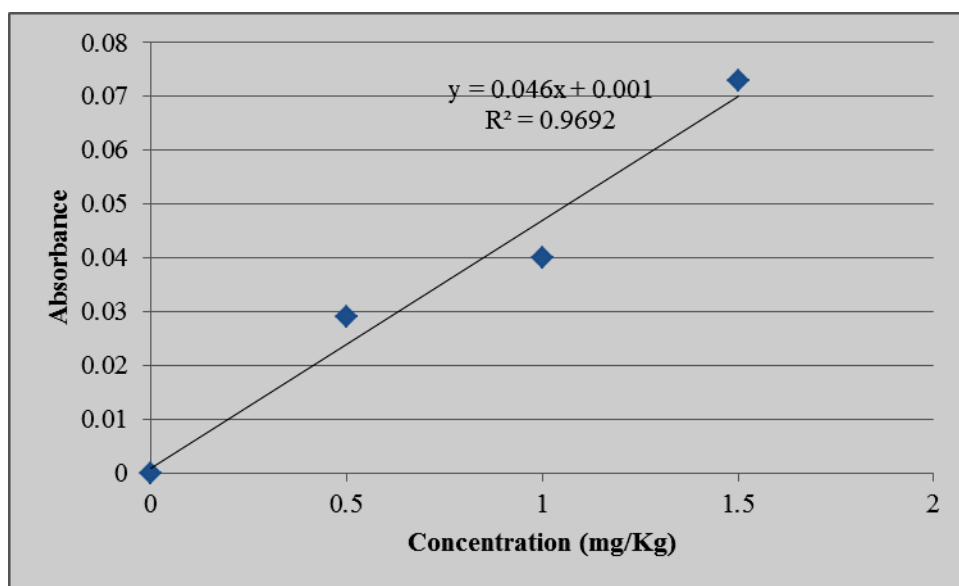


**Figure 3.4: Calibration Curve of Copper**

### 3.5.4 Preparation of Stock and Working Solution of Zinc

Stock solution of zinc was prepared by dissolving 1.0 g of zinc in 40 mL of 1:1 hydrochloric acid: water ratio then diluted to 1 L to give 1000 ppm of zinc. A working

solution of 100 ppm was prepared by pipetting 10 mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water. Standard solutions of 0.5 ppm, 1.0 ppm and 1.5 ppm were prepared by pipetting 0.5 mL, 1.0 mL and 1.5 mL respectively of the working solution into 100 mL volumetric flask then made to the mark using distilled water. Using the standards, a calibration curve shown below was produced and concentration of zinc in each sample was determined directly using AAS. Analysis was done in triplicate to enhance the accuracy of the results.

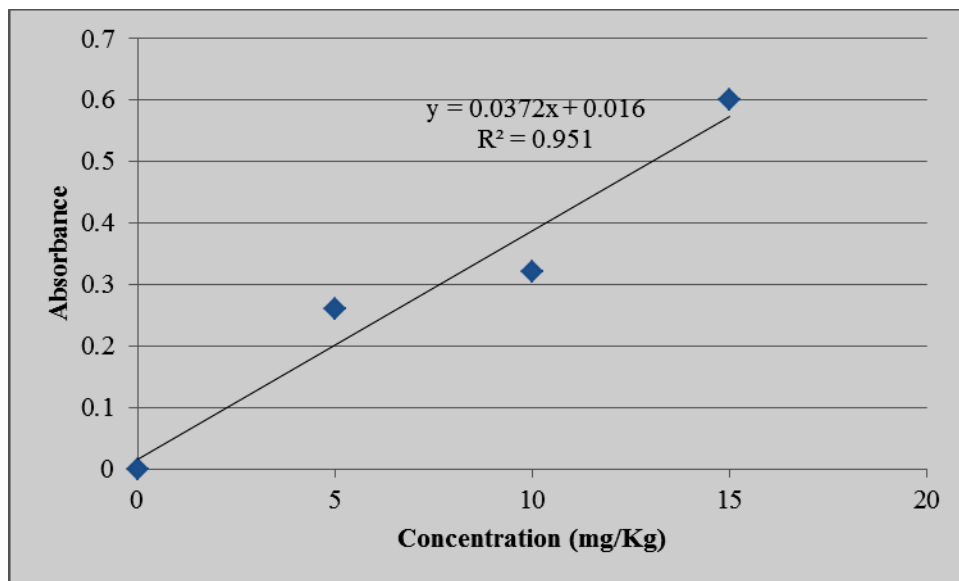


**Figure 3.5: Calibration curve of zinc**

### **3.5.5 Preparation of Stock and Working Solution of Chromium**

Stock solution of chromium was prepared by dissolving 1.0 g of chromium in 10 mL of 1:1 nitric acid then diluted to 1 L to give 1000 ppm of chromium. A working solution of 100 ppm was prepared by pipetting 10 mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water. Standard solutions of 5 ppm, 10 ppm and 15 ppm were prepared by pipetting 5 mL, 10 mL and 15 mL

respectively of the working solution into 100 mL volumetric flask then made to the mark using distilled water. Using the standards, a calibration curve shown below was produced and concentration of chromium in each sample was determined directly using AAS. Analysis was done in triplicate to enhance the accuracy of the results.

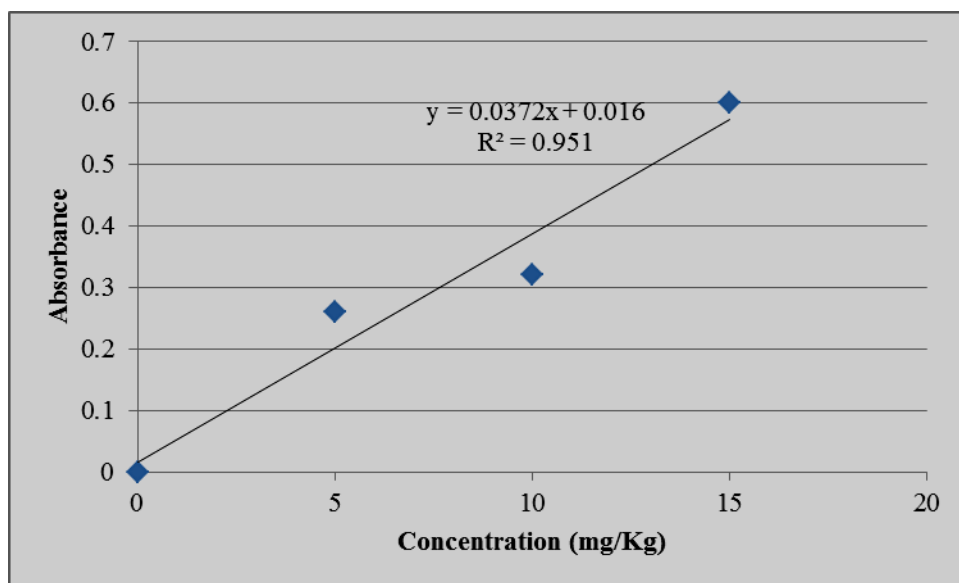


**Figure 3.6: Calibration Curve of Chromium**

### 3.5.6 Preparation of Stock and Working Solution of Nickel

Stock solution of Nickel was prepared by dissolving 1.0 g of chromium in 10 mL of 1:1 nitric acid then diluted to 1 L to give 1000 ppm of nickel. A working solution of 100 ppm was prepared by pipetting 10 mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water. Standard solutions of 5 ppm, 10 ppm and 15 ppm were prepared by pipetting 5 mL, 10 mL and 15 mL respectively of the working solution into 100 mL volumetric flask then made to the mark using distilled water. Using the standards, a calibration curve shown below was produced and

concentration of nickel in each sample was determined directly using AAS. Analysis was done in triplicate to enhance the accuracy of the results.



**Figure 3.7: Calibration Curve of Nickel**

### **3.6 Processing the samples in the laboratory**

The soil samples were dried in the oven at 30<sup>0</sup>C for 24 hours. The dried soil samples were then ground using pestle and mortar till the desired fineness was achieved; this was mainly to increase the surface area for extraction of the heavy metals from the soil samples. The ground soil samples were sieved using a sieve of mesh-size 72. A 100 grams of each dry sample was weighed and placed in a clean Kjeldahl flask to which 10 mL of aqua – regia solution was added that is, a mixture of concentrated HNO<sub>3</sub> with concentrated HCl in the ration 1:3. The samples were then digested by electric digester with glass fume exhaust for a stretch of 2 – 3 hours. The solution was filtered using Whatman’s No.1 filter paper. Each of the resulting clear solutions was diluted to 100 mL

using distilled deionized water in acid cleaned volumetric flasks. These solutions were now ready for analysis of heavy metals.

### **3.7 Determination of pH of the soil samples**

pH was determined using a pH meter (PHS-3C). A sample of 20 gram of soil was weighed and transferred into a 100 mL of beaker and 40 mL of distilled water added. The mixture was stirred with a glass rod and allowed to stand for 30 minutes with stirring, and the temperature was adjusted and recorded. The meter readings of pH values corresponding to the soil samples were then recorded, the procedure was repeated for all the six samples.

### **3.8 Laboratory-based heavy metal analysis**

The metals were analyzed with Perkin Elmer Analyst 200 Flame Atomic Absorption Spectrophotometer (2003 model).

#### **3.8.1 Optimizing operating conditions**

The instrument's operating conditions were optimized before the actual analysis. The fixed parameters were automatically set upon selection of the element to be analyzed. These parameters included; wavelength, lamp current, slit width and extra heat tension (EHT). The other parameters were set according to the manufacturers specifications in the manual. The acetylene and oxygen flow rate was set to attain maximum transparency of the flame. The optimized conditions for the AAS instrument during analysis are shown in Table 3.1 below.

**Table 3.1: Optimized Conditions for AAS**

Element	Wavelength $\lambda$ (nm)	Lamp Current (mA)	Slit Width (nm)	Acetylene flow rate (L/min)	Oxidant flow rate (L/min)	BH (mm)	EH T (v)	Detection Limit
Zn	213.9	5	1	2	13.5	13.5	800	(ppm)
Cu	324.8	4	0.5	2	13.5	13.5	494	0.0 – 1.6
Pb	217	10	1	2	13.5	13.5	485	0.0 – 8.8
Cd	228.8	4	0.5	2	13.5	13.5	562	0.0 – 3.3
Cr	357.9	7	0.2	2.9	13.5	13.5	594	0.0 – 6.5

Key: BH - Burner height

EHT - Extra Heat Tension

### 3.8.2 Calibration Curves

Sensitivity and detection limit checks were carried out to ensure that they were in agreement with the operating parameters by running the stock solution before the actual analysis. Calibration curve for each element were prepared using the standard working solutions. The curves had absorbance in the y – axis and concentrations in the x – axis.

### 3.8.3 Heavy Metal Analysis

A reagent blank sample was taken through the method, analyzed and subtracted from the samples to correct for reagent impurities and other sources of errors from the environment. The concentrations of the heavy metals were determined in triplicates. The accuracy and precision of the analytical procedure were determined. Series of standards were prepared for instrumental calibration by serial dilution of working solutions (100 mg/L) prepared from analytical grade stock solutions (100 mg/L).



### **3.9 Data Analysis**

Uni-variate and multivariate statistical methods of analysis were used in the study. The software SPSS was used for statistical analysis. The correlation matrix which was based on the Pearson's correlation coefficient was utilized for displaying relationships between variables. The obtained matrix of data was subjected to multivariate analytical technique. Factor analysis which aims to explain an observed relationship between numerous variables in terms of simple relations was applied. Data was also represented in graphs and charts using MS-Excel.

## CHAPTER FOUR

### RESULTS AND DISCUSSION

#### 4.1 Introduction

A statistical summary of the concentrations of the heavy metals for the six analyzed samples in the two seasons is presented in in this chapter. Table 4.1 presents the soil quality criteria in some countries and a consequent comparison to the results of this study.

**Table 4.1: Soil quality criteria in some countries and a consequent comparison to the results of this study**

<b>Country</b>	<b>Pb</b>	<b>Cd</b>	<b>Cr</b>	<b>Ni</b>	<b>References</b>
Norway (action level)	50	1	100	30	Reimann <i>et al.</i> , 1997
Netherlands (action level)	530	12	380	210	Reimann <i>et al.</i> , 1997
Canada (residential)	140	10	64	50	CCME, 1999
Canada (agricultural)	70	1.4	64	50	CCME, 1999
Canada (commercial)	260	22	87	50	CCME, 1999
Canada (industrial))	600	22	87	50	CCME, 1999

#### 4.2 Concentration of heavy metals in soil samples

The concentrations of lead, cadmium and zinc levels on average were high above the permissible limits by USEPA (2011). This generally suggests that the sources of these metals may have been dominant from the smelter since their raw material has high concentrations of these metals and thus high concentrations are expected from the wastes.

#### 4.2.1 Concentration of Pb in Soil Samples

The concentration of Pb in the six sampling points for the two seasons is presented in Table 4.2.

**Table 4.2: Concentration of Pb in the six sampling points**

Sample	Pb (ppm)		
	Dry Season	Wet Season	Mean
S1	5426±30.12	5402±30.11	5414±30.12
S2	4505±26.54	4457±25.25	4481±25.90
S3	5210±29.02	5023±28.06	5117±28.54
S4	2610±15.09	2140±12.45	2375±13.77
S5	3006±17.41	2700±17.07	2853±17.24
S6	2754±17.34	2514±16.09	2634±16.72

Soil samples from the sampling point showed very high levels of Pb ranging from 2375 - 5414 ppm. The concentration of Pb was higher in the dry season than wet season.

These values were far higher than the maximum permissible limits outlined by USEPA of 400 mg/kg of Pb in soil defined by USEPA as the level that correlates with the critical blood Pb level of 7  $\mu\text{gdl}^{-1}$  (USEPA, 2011). Most soil samples from the sampling sites also exceeded the Pb soil quality criteria of other countries like Norway, Netherlands, Switzerland and Canada as shown in Table 4.1.

The mean concentration of Pb in the soil samples from sampling points S1 – S3 (table 4.2) was higher than for sampling points S4, S5 and S6. This implies that the lead concentrations were higher at the upper side of the industry compared to the lower side.

Soil from sampling points S4 – S6 (table 4.2) also showed high levels of Pb but lower than those of S1 – S3. This could be attributed to the fact that these samples were collected from an undeveloped portion of land within the premises of the recycler plant

which probably had served in the past as a dumpsite for the slag waste as pieces of weathered slag were found scattered everywhere within this site. The source of Pb in other portions of the premises could be due to leaching, run off or aerial depositions of particulate of Pb from smelting activities. An effective pollution control system is a necessity to prevent Pb emission. Continuous improvement in battery recycling plants and furnace designs is required to keep pace with emission standards for lead smelters.

To ascertain whether the concentration of Pb in the dry season was significantly different from the wet season, a paired sample t-test was done. The results are presented in Table 4.3 below:

**Table 4.3: t - test for the concentrations of lead in the soil samples for both seasons**

Paired Differences					t	df	Sig. (2-tailed)
Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
			Lower	Upper			
212.500	166.762	68.080	37.494	387.506	3.121	5	.026

Based on the results, the p value attained was 0.026 implying there was a statistically significant difference of concentration of Pb in the soil sample for the dry and wet seasons at 95% confidence level.

The above results correlate to the findings of Sloan (2011) who conducted a study on levels of arsenic and lead in the Tacoma smelter plume footprint and Hanford site old orchards in USA. Their results showed that the highest Pb concentration in the soil was 6043 mg/kg and the lowest was 806 mg/kg. These levels were far beyond the set limits

by USEPA. The concentrations were attributed to the poor disposal methods of the smelting waste by the industry.

The study also correlates with the study by Adegoke in Nigeria, in which the results showed all the sampling points had an excess of Pb by more than 10 fold the recommended USEPA levels (Adegoke *et al.*, 2009).

#### 4.2.2 Concentration of Zn in Soil Samples

The concentration of Zn in the six sampling points for the two seasons is presented in Table 4.2.

**Table 4.4: Concentration of Zn in the 6 sampling points for the two seasons**

Sample	Zn (ppm)		
	Dry Season	Wet Season	Mean
<b>S1</b>	100±3.11	98±2.98	99±3.05
<b>S2</b>	150±4.03	127±3.07	139±3.55
<b>S3</b>	138±3.76	112±3.00	125±3.38
<b>S4</b>	95±2.87	71±1.92	83±2.40
<b>S5</b>	98±2.98	77±1.99	88±2.49
<b>S6</b>	90±2.43	60±1.24	75±1.84

The mean Zn levels in all the effluents studied varied between 75 to 139 mg/kg within six points studied. The concentrations in the dry season were higher in the dry season compared to the wet season.

To ascertain whether there existed statistically significant differences between the Zn concentrations in the dry and wet seasons, a paired sample t-test was used to determine.

The results are shown in Table 4.5.

**Table 4.5: t - test for the concentrations of zinc in the soil samples for both seasons**

Paired Differences					t	df	Sig. (2-tailed)
Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
			Lower	Upper			
21.000	9.798	4.000	10.718	31.282	5.250	5	.003

Based on the results, the p value attained was 0.003 implying that there was a statistically significant difference in concentration of Zn in the soil sample for the dry and wet seasons at 95% confidence level.

The samples from the smelter were below the set limits of 2,200 ppm of Zn in soils (USEPA, 2011). These levels of Zn could be as a result of several effluents resulting from the recycling of Zn batteries. Zinc is widely used in the smelter for manufacture of a variety of batteries but primary zinc-carbon batteries conveniently manufactured, and disposed of, a single Zn-carbon dry cell has low environmental impact on disposal, compared with some other battery types. The Zn levels only become environmentally unfriendly over a long period due to bioaccumulation of the heavy metal.

#### **4.2.3 Concentration of Cd in soil samples**

The concentration of cadmium in the six sampling points for the two seasons is presented in Table 4.6.

**Table 4.6: Concentration of Cd in the 6 sampling points for the two seasons**

Sample	Cd (ppm)		
	Dry Season	Wet Season	Mean
<b>S1</b>	15.50±0.35	12.41±0.21	13.96±0.28
<b>S2</b>	18.56±0.42	14.35±0.19	16.46±0.31
<b>S3</b>	17.86±0.40	12.54±0.24	15.20±0.32
<b>S4</b>	9.34±0.12	5.23±0.04	7.29±0.08
<b>S5</b>	9.23±0.10	5.01±0.07	7.12±0.09
<b>S6</b>	10.65±0.18	8.24±0.08	9.45±0.13

The corresponding levels of Cd in these samples were also very high. The concentrations ranged from 7.12 (S5) to 16.46 ppm (S2). The concentrations in the dry season were higher compared to the wet season. Additionally, S1, S2 and S3 had higher concentrations compared to S3, S4 and S5. The average concentrations of Cd in the six sampling sites were higher than the set limits of 0.86 ppm (USEPA, 2011).

To ascertain whether there existed statistically significant differences between the Cd concentrations in the dry and wet seasons, a paired sample t-test was used to determine.

The results are shown in Table 4.7.

**Table 4.7: t - test for the concentrations of cadmium in the soil samples for both seasons**

Paired Differences					t	Df	Sig. (2-tailed)
Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
			Lower	Upper			
3.893	1.013	.414	2.830	4.957	9.411	5	.000

Based on the results, the p value attained was 0.000 implying there was a statistically significant difference in concentration of Cd in the soil sample for the dry and wet seasons at 95% confidence level.

The source of Cd could probably be associated with the recycling of Ni–Cd battery since Cd is often an impurity in the Ni-Cd alloy (Markus & McBratney, 2000). Ni–Cd batteries contain between 6% (for industrial batteries) and 18% (for consumer batteries) cadmium, which is a toxic heavy metal and therefore requires special care during battery disposal.

These results closely correlate to those of a study conducted by Staniland *et al.* (2010) on concentration and toxicity levels of heavy metal pollutants in soils and vegetation in Kitwe (Copperbelt), Zambia. Their results showed that the levels of Cd ranged between 2202 to 7005 mg Cd/kg. Their results also indicated the levels of Cd were very high (1212 mg/kg). Their conclusion was that the Cd in the study site was mainly anthropogenic and not directly from the smelter.

#### 4.2.4 Concentration of Cr in soil samples

The concentration of chromium in the six sampling points for the two seasons is presented in Table 4.8.

**Table 4.8: Concentration of Cr in the 6 sampling points for the two seasons**

Sample	Cr (ppm)		
	Dry Season	Wet Season	Mean
<b>S1</b>	315±3.10	284±2.26	299.50±2.68
<b>S2</b>	275±2.11	207±2.08	241.00±2.09
<b>S3</b>	280±2.27	211±2.12	245.50±2.19
<b>S4</b>	120±1.37	83±1.07	101.50±1.22
<b>S5</b>	50±0.76	37±0.62	43.50±0.69
<b>S6</b>	80±1.01	61±0.98	70.50±0.99

The mean concentrations ranged from 43.50 (S5) to 299.50 ppm (S1). The average values of Cr in these soil samples from the six sampling sites were higher than the set limits of 22 – 36 ppm (USEPA, 2011). The concentrations in the dry season were higher compared



to the wet season. Additionally, S1, S2 and S3 had higher concentrations compared to S3, S4 and S5.

The source of the high concentrations of Cr might have been the parent material that formed the soil and not from the slag. Cr in the samples was purely anthropogenic and not from the battery recycling process. This is because Cr is only used in the manufacture of Fe-Cr reduction-oxidation flow batteries which are extremely rare and used in high-tech industries (Chaoyang *et al.*, 2008).

To ascertain whether there existed statistically significant differences between the Cr concentrations in the dry and wet seasons, a paired sample t-test was used to determine. The results are shown in Table 4.9.

**Table 4.9: t - test for the concentrations of chromium in the soil samples for both seasons**

Paired Differences					t	df	Sig. (2-tailed)
Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
			Lower	Upper			
39.500	24.015	9.804	14.298	64.702	4.029	5	.010

Based on the results, the p value attained was 0.01 implying there was a statistically significant difference in concentration of Cd in the soil sample for the dry and wet seasons at 95% confidence level ( $p < 0.05$ ).

The results are supported by those reported by (Chaoyang *et al.* 2008) on the characterizing, spatial distribution and sources of heavy metals in the soils from mining-smelting activities in Shuikoushan, China. Their results indicated that the levels of Cr

were very low (10 ppm) implying that the smelting process didn't produce Cr byproducts and thus the wastes had extremely low levels of Cr.

#### 4.2.5 Concentration of Ni in soil samples

The concentration of nickel in the six sampling points for the two seasons is presented in Table 4.10.

**Table 4.10: Concentration of Ni in the 6 sampling points for the two seasons**

Sample	Ni (ppm)		
	Dry Season	Wet Season	Mean
<b>S1</b>	-	-	-
<b>S2</b>	-	-	-
<b>S3</b>	-	-	-
<b>S4</b>	0.80±0.02	0.30±0.01	0.55±0.01
<b>S5</b>	1.30±0.07	0.91±0.04	1.11±0.06
<b>S6</b>	0.60±0.01	-	0.60±0.01

Nickel was not detected in S4, S5 and S6 in the dry season and in S1, S2, S3 and S5 in the wet season. The concentration in S4 – S6 was extremely low compared to the set limits of 72 – 140 ppm (USEPA, 2011).

It was concluded that the sources of Ni in S4, S5 and S6 are non-point and could be associated with the slag because these points were close to the slag waste deposit. Ni is used in low volumes in the manufacture of Ni–Cd batteries which are also rare and this explains why the levels of Ni were very low around the smelter.

The findings are in agreement with those of Aucott (2006) who carried out a study on levels of heavy metals in a landfill nearby a battery smelter in New Jersey which showed that Ni was very low and undetectable.

#### 4.2.6 Concentration of Cu in soil samples

The concentration of copper in the six sampling points for the two seasons is presented in Table 4.11.

**Table 4.11: Concentration of Cu in the 6 sampling points for the two seasons**

Sample	Cu (ppm)		
	Dry Season	Wet Season	Mean
<b>S1</b>	20.36±0.85	19.21±0.94	19.79±0.90
<b>S2</b>	31.25±1.11	25.25±0.99	28.25±1.05
<b>S3</b>	42.00±1.69	40.00±1.37	41.00±1.53
<b>S4</b>	15.38±0.72	17.01±0.88	16.20±0.80
<b>S5</b>	14.20±0.68	15.02±0.71	14.61±0.70
<b>S6</b>	16.30±0.87	16.42±0.89	16.36±0.88

The mean concentrations ranged from 14.61 (S5) to 41.00 ppm (S3). The corresponding levels of Cu in these samples were low compared to the set limits of 270 ppm (USEPA, 2011). This generally suggests that the sources may not have been anthropogenic, but rather associated with the natural weathering of the metalliferous parent rock that formed the soil. This is because this recycler plant does not recycle lithium-ion batteries (Jasonof, 1986).

To ascertain whether there existed statistically significant differences between the Cu concentrations in the dry and wet seasons, a paired sample t-test was used to determine and the results are shown in Table 4.12.

**Table 4.12: t - test for the concentrations of copper in the soil samples for both seasons**

Paired Differences					t	Df	Sig. (2-tailed)
Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
			Lower	Upper			
1.097	2.737	1.117	-1.775	3.969	.982	5	.371

Based on the results, the p value attained was 0.371 implying the difference in concentration of Cu in the soil sample for the dry and wet seasons was statistically insignificant at 95% confidence level ( $p < 0.05$ ).

These findings are in line with those of Bakirdere & Yaman (2008) who reported that concentrations of copper in soil samples were found in the range of 11.1–27.9 ppm. However, Kabala and Singh (2001) reported higher concentrations of 45 – 60 ppm near a copper smelter in Poland.

#### 4.3 pH levels of the soil samples

The pH of the soil samples from the six sampling points for the two seasons is presented in Table 4.13.

**Table 4.13: Concentration of pH in the 6 sampling points for the two seasons**

Sample	Cr (ppm)		
	Dry Season	Wet Season	Mean
<b>S1</b>	4.3	5.7	5.00
<b>S2</b>	3.2	4.9	4.05
<b>S3</b>	4.6	5.3	4.95
<b>S4</b>	3.7	4.0	3.85
<b>S5</b>	4.3	5.1	4.70
<b>S6</b>	3.6	4.6	4.10

The average pH levels ranged from 3.85 (S4) to 5.00 (S1) which imply that the soils are slightly acidic. The pH of the soil samples was lower in the dry season compared to the wet season. The low soil pH can be attributed to the fact that some metal ions specifically cations exist in the soil in free form thus making the soils acidic. In addition, the process of battery manufacture uses sulfuric acid and disposal of the acid in the waste causes the pH of the surroundings to be quite acidic.

S1, S2 and S3 sampling points showed higher pH values compared to S4, S5 and S6. This is because the first three sampling points are close to the company's dumping site where there was a high level concentration of heavy metals and the toxic effluents had not dissolved at high degree underneath the ground. This can be supported by the fact that the pH is seen to be increasing as the corresponding heavy metal concentrations increase, because it is basically the levels of the free  $H^+$  ions in the soil.

To ascertain whether there existed statistically significant differences between the pH of the soil samples in the dry and wet seasons, a paired sample t-test was used to determine. The results are shown in Table 4.14.

**Table 4.14: t - test for the pH of soil samples for both seasons**

Paired Differences					t	df	Sig. (2-tailed)
Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
			Lower	Upper			
-.983	.504	.206	-1.512	-.455	-4.782	5	.005

Based on the results, the p value attained was 0.005 implying the difference in pH of the soil sample for the dry and wet seasons was statistically significant at 95% confidence level ( $p < 0.05$ ).

The findings of this study agree with those reported by Scokart *et al.* (1983) who showed that pH values of soils samples from a Zn smelter ranged from 4 - 5. However, the findings were different from those of Ullrich *et al.* (1999) who reported pH range 7 – 8 in smelting in Upper Silesia, Poland.

## CHAPTER FIVE

### CONCLUSION AND RECOMMENDATIONS

#### 5.1 Conclusion

Based on the findings, it was concluded that the slag from the smelting plant in Athi-River contained concentrations of Pb, Cr and Cd which were higher than the set limits by USEPA (2011). These metals pollute the soil around its dumpsite to over several times the beyond the permissible limit.

Other toxic metals (Zn, Cu and Ni) were at the background levels compared to the set limits by USEPA (2011). Therefore, they were within the recommend safe levels of the heavy metals regulations of disposal.

#### 5.2 Recommendations

In order to safeguard the health of the residents of this area, intervention measures need to be undertaken. Firstly, the ministry of Health should come up with health education programs to clean – up these polluted soils so that the heavy metals will not be transferred to the food surface and underground water sources.

Secondly, the government through the National Environmental Management Authority (NEMA) should deal with solid waste disposal at the smelting plant by imposing strict measures.

Further research on the following aspects is recommended: -

1. More research should be done on the physico-chemical properties of soil around the recycling plant such as Biological Oxygen Demand (BOD), Chemical Oxygen

Demand (COD), Total Dissolved Solids (TDS) and such other tests that were never covered in this thesis for instance elements.

2. Further work should be carried out on the adverse effects of the heavy metals in the recycler plant effluent on both flora and fauna around the study site.
3. Research can also be conducted in other battery recycler plants in the country to establish whether the same volume of pollutants exist in the environs.



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## APPENDICES

### Appendix I: Acceptable standards of heavy metals in soil (ppm)

	US EPA		
	Soil screening level	Unrestricted use	Residential use
As	0.4	0.11	0.21
Cd	70	0.43	0.86
Cr (hexavalent)	230	11	22
Cr (trivalent)	120,000	18	36
Cu		270	270
Pb	400	200	400
Ni	1600	72	140
Zn	23,600	1100	2200

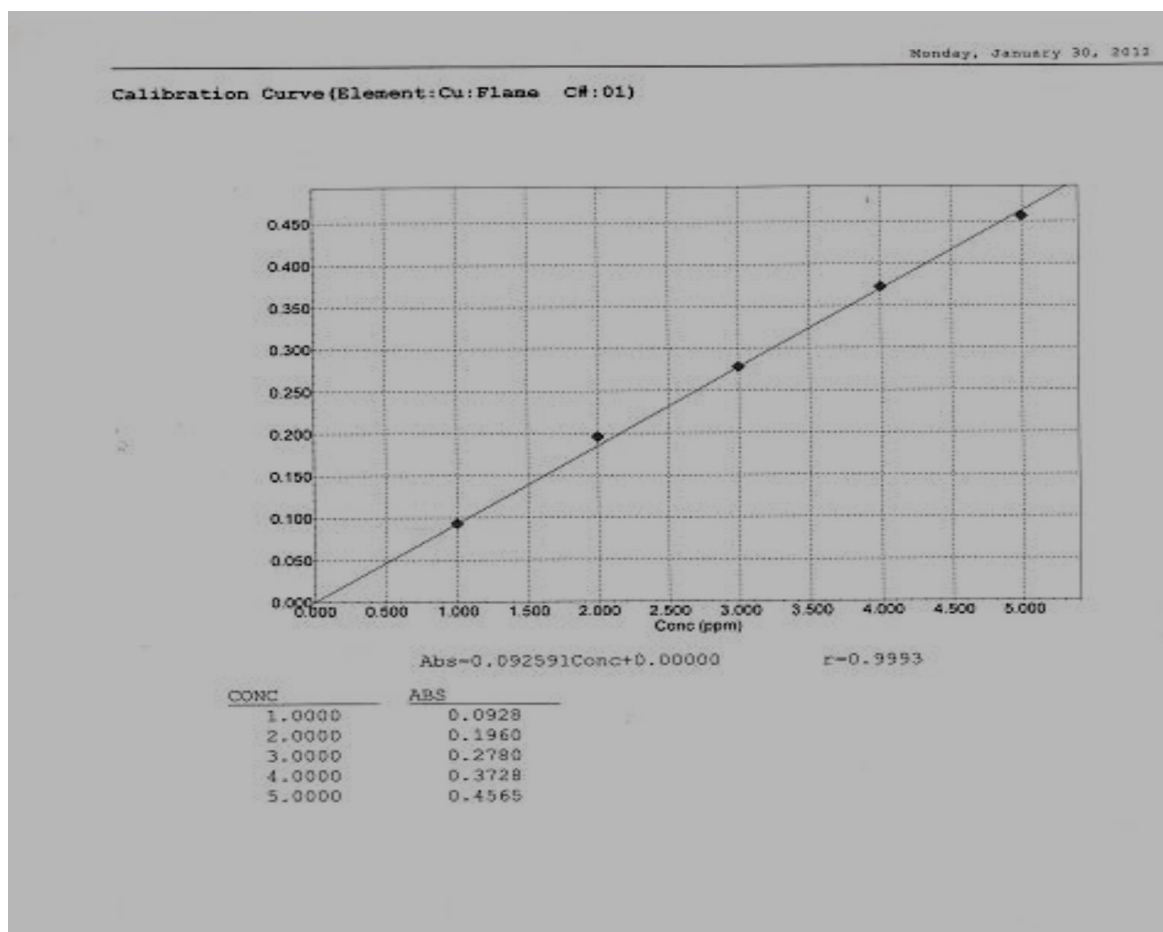
**Appendix II: Physical properties of elements to be analyzed**

<b>ELEMEN T</b>	<b>ATOMIC NUMBER</b>	<b>MASS NUMBER</b>	<b>M.P. °C</b>	<b>B.P. °C</b>	<b>DENSITY (g/cm<sup>3</sup>)</b>
Pb	82	207.19	327.4	1740	11.34
Cd	48	112.4	321	765	8.65
Cr	24	51.995	1930	2480	7.2
Cu	29	64	1083	2595	8.96

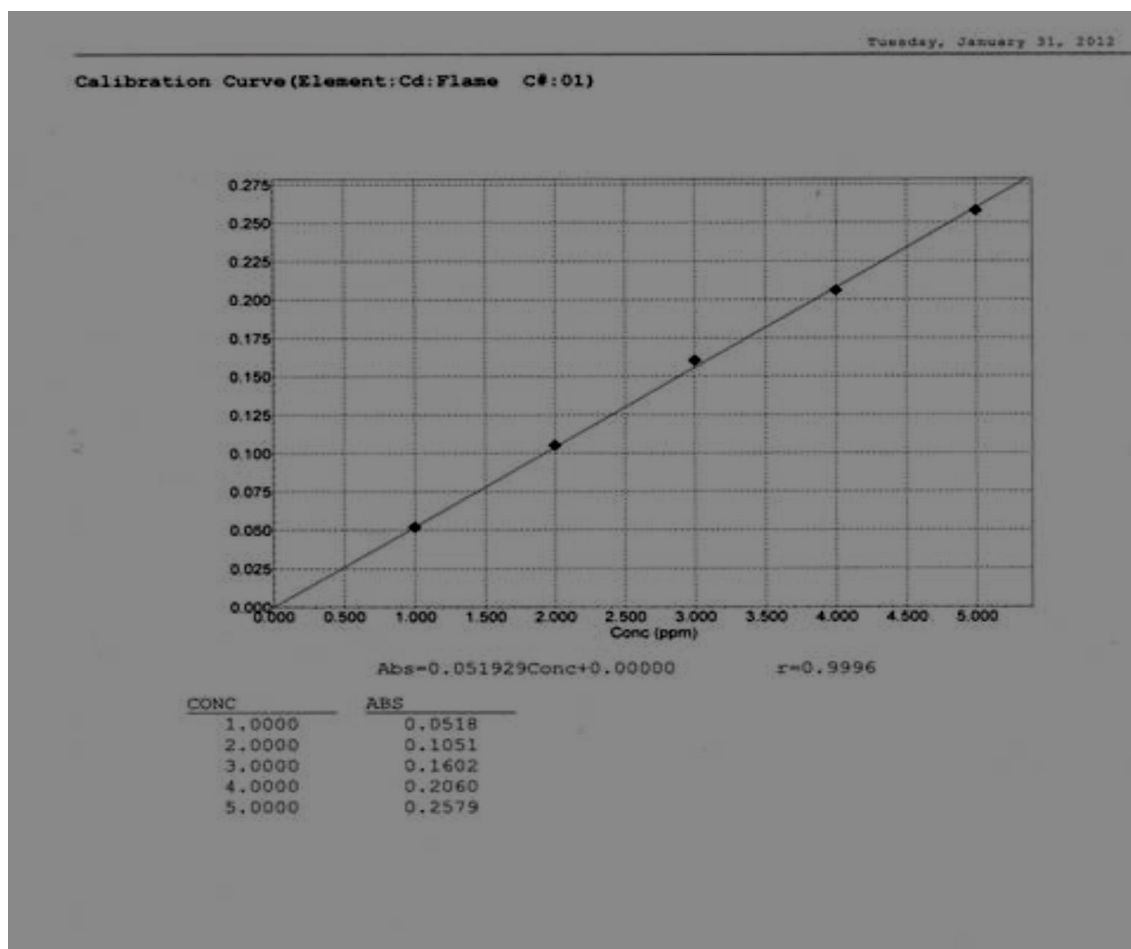
**Appendix III: Disassembling Used Lead Batteries in the Smelting Plant**

Source: Steinnes *et al.*, 2000

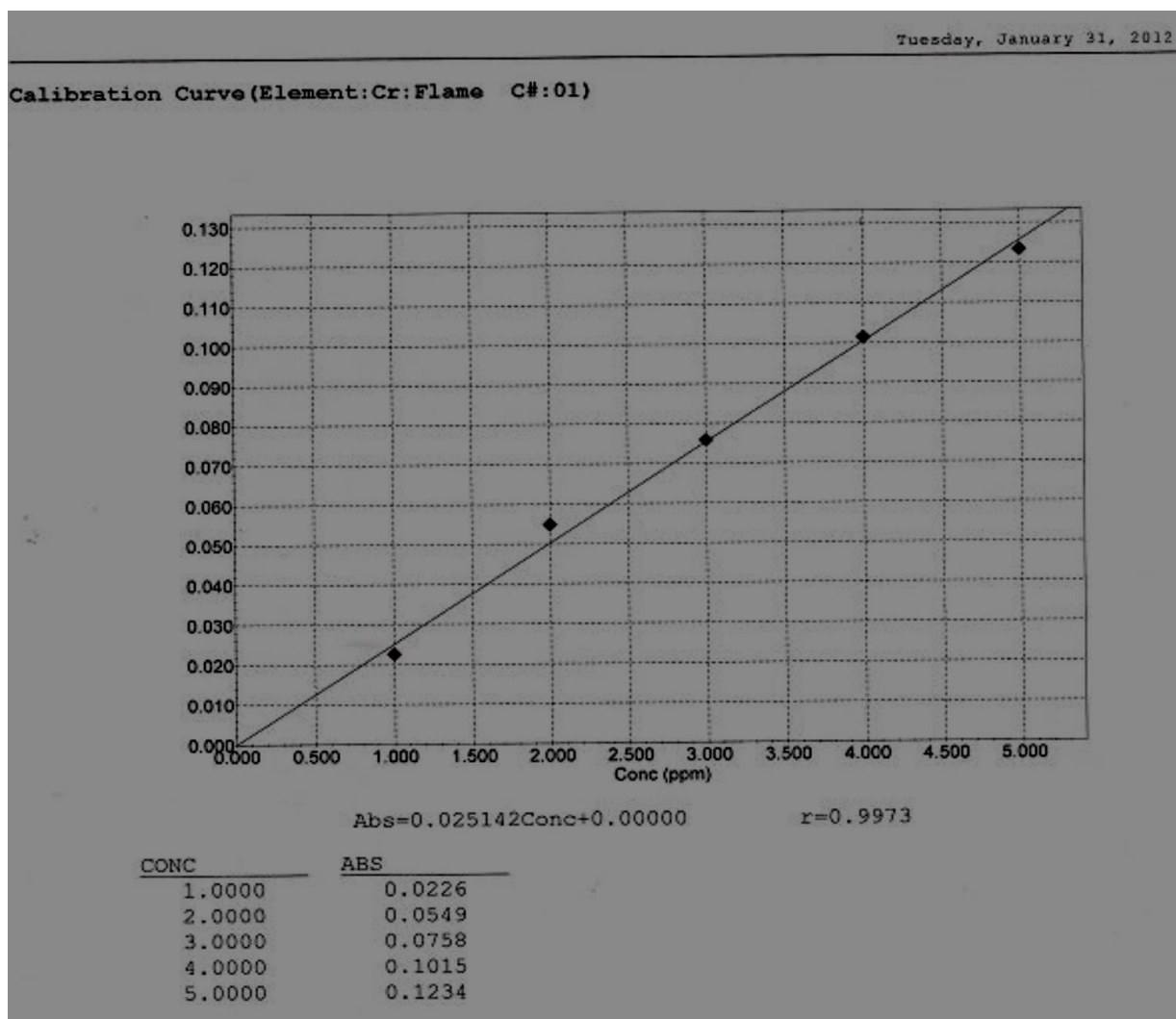
## Appendix IV: Cu calibration curve



## Appendix V: Cd calibration curve

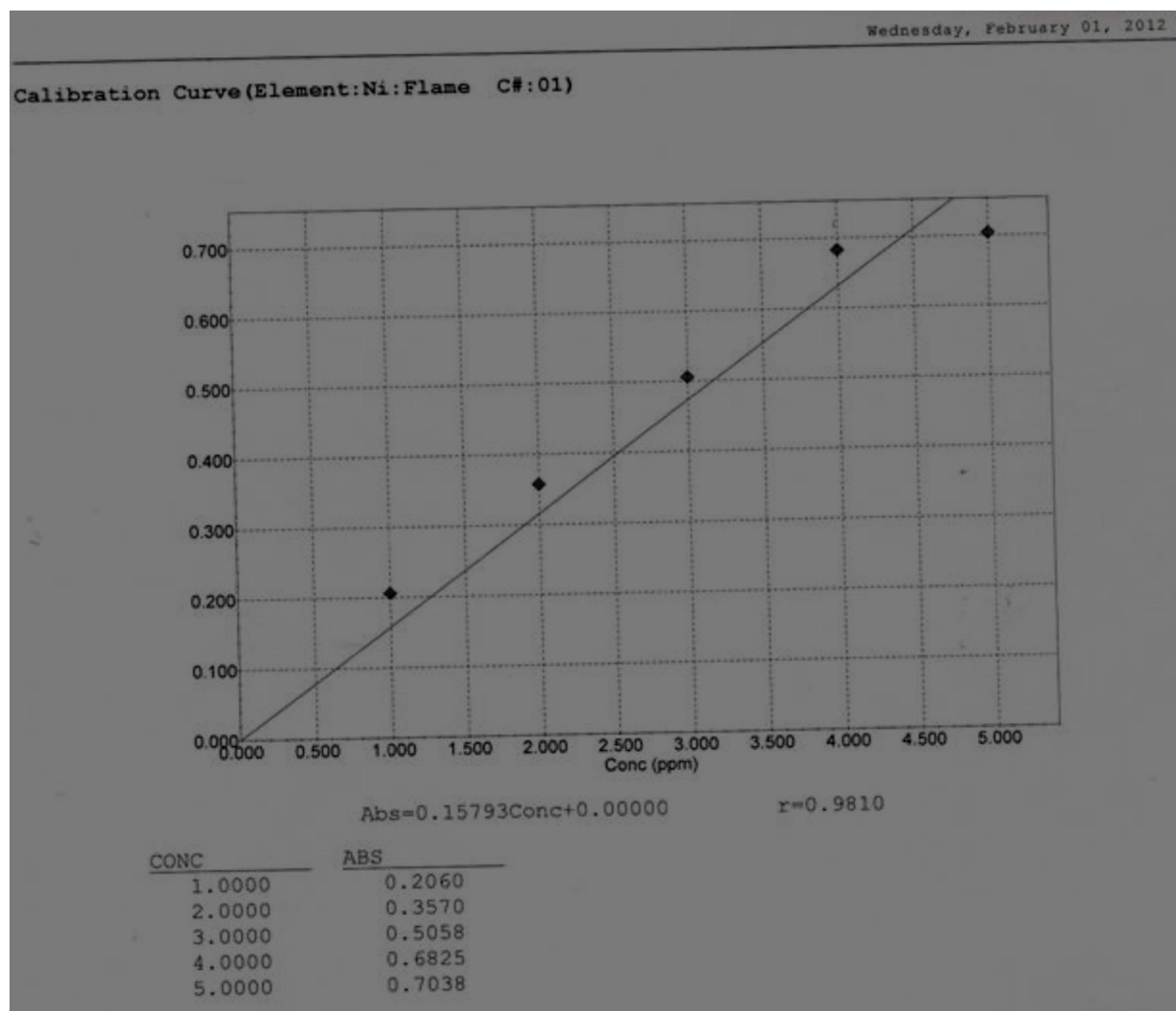


## Appendix VI: Cr calibration curve





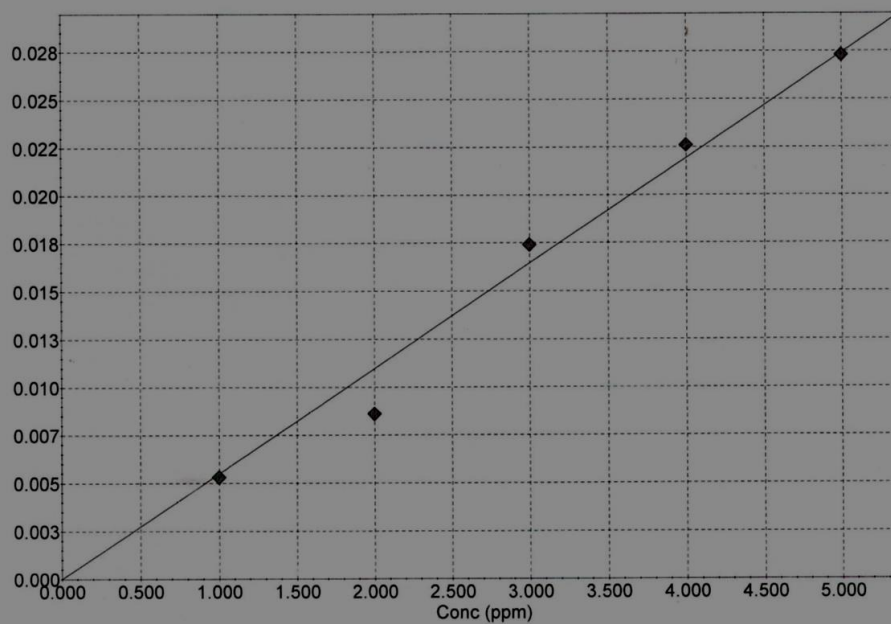
## Appendix VII: Ni calibration curve



## Appendix VIII: Pb calibration curve

Friday, November 18, 2011

Calibration Curve (Element: Pb: Flame C#: 01)



$$\text{Abs} = 0.0054836 \text{Conc} + 0.00000$$

$$r = 0.9915$$

<u>CONC</u>	<u>ABS</u>
1.0000	0.0053
2.0000	0.0086
3.0000	0.0174
4.0000	0.0226
5.0000	0.0273