Journal Homepage: - www.journalijar.com
INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)
ISSN NO. 2320-5407
Article DOI: 10.21474/IJAR01/1463
DOI URL: http://dx.doi.org/10.21474/IJAR01/1463

RESEARCH ARTICLE

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

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Manuscript Info

Manuscript History

Received: 12 July 2016
Final Accepted: 13 August 2016
Published: September 2016

Key words:-
Toxicity, contamination, concentration, speciation, smelting

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 eighteen (18) 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 and Pb) 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. The concentrations of Pb and Cd which were higher than the set limits by USEPA while that of Zn which was 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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Introduction:-

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).

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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 led 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).

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 neuro behavioural effects in children than for adults, namely 100 vs. 400 µg/l. There is evidence today that, evenat blood-Pb levels below 100 µg/l, neuro behavioural effects of Pb are likely to occur in children, although such effects are typically minor and of doubtful clinical relevance(Nicolescu *et al*.,2008).

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

Objectives:-

1. To determine the levels of Cd, Zn and Pb 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.

Literature review:-

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).

Battery Recycling Processes:-

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.

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).

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).

Battery Recycling by Type:-

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).

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).

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 chromiumare 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).

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).

Lead:-

It is the most toxic metal and the main pollutant around a Pbs melter. 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)

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 result 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).

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 23rd 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 pancrease 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).

Materials and methods:-

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 693km^2 (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.

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.

Digestion of Perchloric Acid:-

Suitable volume of the water in evaporating dishes taken and acidified to methyl orange with conc. HNO_3. Further, 5mL conc. HNO_3acid was added and evaporated to 10mL. Then it was transferred to a 125mL conical flask. 5mL of conc. HNO_3 acid and 10mL of perchloricacid (70%) were added. Then heated gently, till white dense fumes of $HClO_4$ 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 100mLwith distilled water. Then this solution was boiled to expel oxides of nitrogen and chlorine. This solution contained 0.8M in $HClO_4$. The solution was used for the use of determination of heavy metals.

Preparation of Stock Solutions:-

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.

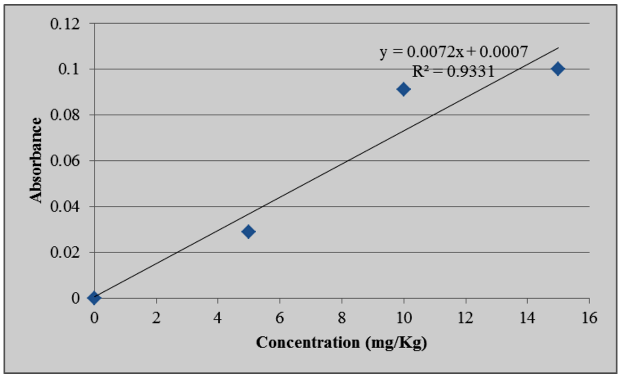

Figure 3.1:- Calibration Curve of Lead.

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.

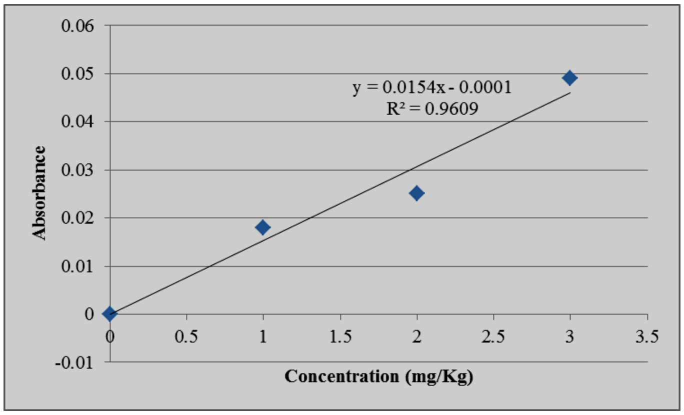

Figure 3.2:- Calibration curve of cadmium.

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.

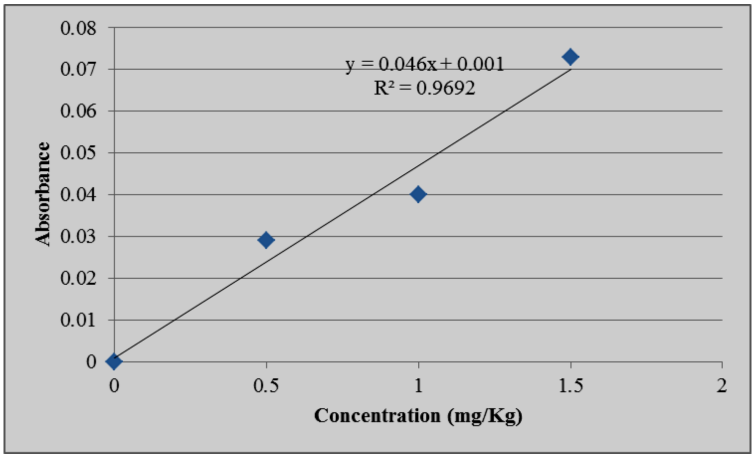

Figure 3.3:- Calibration curve of zinc.

Processing the samples in the laboratory:-

The soil samples were dried in the oven at 30^0C 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 Kjedahl flask to which 10 mL of aqua – regia solution was added that is, a mixture of concentrated $HN0_3$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 m Lusing distilled deionized water in acid cleaned volumetric flasks. These solutions were now ready for analysis of heavy metals.

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 100mL of beaker and 40mL of distilled water added. The mixture was stirred witha 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.

Laboratory-based heavy metal analysis:-

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

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 λ (nm)	Lamp Current (mA)	Slit Width (nm)	Acetylene flow rate (L/min)	Oxidant flow rate (L/min)	BH (mm)	EHT (v)	Detection Limit
Zn	213.9	5	1	2	13.5	13.5	800	(ppm)
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

Key: BH - Burner height EHT - Extra Heat Tension

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.

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 (100mg/L) prepared from analytical grade stock solutions (100mg/L).

DataAnalysis:-

Uni-variate and multivariate statistical methods of analysis wereused 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.

Results and discussion:-

Introduction:-

A statistical summary of the concentrations of the heavy metals for the six analyzed samples in the two seasons is presented 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.

Country	Pb	Cd	Cr	Ni	References
Norway (action level)	50	1	100	30	Reimann*et al.*,1997
Netherlands (action level)	530	12	380	210	Reimann*et al.*,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

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.

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 $7\mu gdL^{-1}$ (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 (table4.2) 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 the 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 foot print 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).

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**
S1	100±3.11	98±2.98	99±3.05
S2	150±4.03	127±3.07	139±3.55
S3	138±3.76	112±3.00	125±3.38
S4	95±2.87	71±1.92	83±2.40
S5	98±2.98	77±1.99	88±2.49
S6	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.

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**
S1	15.50±0.35	12.41±0.21	13.96±0.28
S2	18.56±0.42	14.35±0.19	16.460.31
S3	17.86±0.40	12.54±0.24	15.20±0.32
S4	9.34±0.12	5.23±0.04	7.29±0.08
S5	9.23±0.10	5.01±0.07	7.12±0.09
S6	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 & Mc Bratney, 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 (Copper belt), 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.

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 4.8:- Concentration of pH in the 6 sampling points for the two seasons.

Sample	**Cr (ppm)**		
	Dry Season	**Wet Season**	**Mean**
S1	4.3	5.7	5.00
S2	3.2	4.9	4.05
S3	4.6	5.3	4.95
S4	3.7	4.0	3.85
S5	4.3	5.1	4.70
S6	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 S3sampling 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 damping 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 4.9:- 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.

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.

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.

References:-

1. Abulude, F. O. and Adesoje, H. (2006). Characterization of heavy metal pollution around processingfactory using Atomic Absorption Spectrophotometer. *Research J. Appli. SC.*, *1*(1-4):16-18. Apostoli, P., andCatalani, S. (2010). Metal ions affecting reproduction and development. *Metal ions in life sciences*, *8*, 263-303.
2. Adegoke, J. A., Owoyokun, T. O., and Amore, I. O. (2009).Open Land Dumping: "An Analysis of Heavy Metals Concentration of an Old Lead-Battery Dumpsite”. *Pacific Journal of Science AndTechnology.10* (2):592-595.
3. Alloway, B. J. (1995). *Heavy metals in soils*, 2nd Ed. Chapman and Hall, India: Australia. Amarasinghe, B. M., and Willliams, R. A., (2007).Tea waste as a low cost adsorbent for the Removal of Cu and Pb from wastewater. *Chemical Engineering Journal*, *132*(1), 299-309.
4. Balbuena, P. B., and Wang, Y. (2004). Lithium-ion batteries. *Solid–Electrolyte Interphase*.
5. Balkrishena, K., Randhir, S., Sandhu, C., and Franklin, R. (1999). Follow-Up Screening of Lead Poisoned Children Near an Auto Battery Recycling Plant, Haina, Dominican Republic. *Environ. Health Perspect. 107*(11) 12-14.
6. Bernardes, A. M., Espinosa, J. A., Tenorio, S. (2003). "Recycling of batteries: a review of current processes and technologies". *Journal of Power Sources 130* (1–2): 291–298.
7. Chang, Y., Mao, X., Zhao, Y., Feng, S., Chen, H. and Finlow, D.(2009). Lead-acid battery use in the development of renewable energy systems in China. *Journal of Power Sources 191* (1):176-183.
8. Chen, Y. and Chen, M. (2001). Heavy metal concentrations in nine species of fishes caught in coastal waters of Ann-ping SW Taiwan. *J. Food Drug Anal.*, 9: 107-114.
9. Denis, S., Archambault, P., Gautier, E., Simon, A., and Beck, G. (2002). Prediction of residual stress and distortion of ferrous and non-ferrous metals: current status and future developments. *Journal of materials engineering and performance*, *11*(1), 92-102.
10. Duruibe, J. O., Ogwuegbu, M. C., and Egwurugwu, J. N. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*, *2*(5), 112-118.
11. El-Demerdash, F. M. and Elgamy, E. J. (1999). Biological effects in *Tilapia nitotica*Fish as indicator of pollution by cadmium and mercury. *Int. J. Environ. Health Res.*, 9: 173.
12. EU Report (2012).The availability of automotive lead-based batteries for recycling in the EU Over the period 2010-2012.
13. Filazi, A., Baskaya, R., Kum, C., and Hismiogullari, S . E. (2003). Metal concentrationin tissues of the Black sea fish Mugilauratus from Sinop-Iclimari, Turkey. *Hum., Exp. Toxicol.*, 22:85-87.
14. Grandjean, P., &Landrigan, P. J. (2006). Developmental neurotoxicity of industrial chemicals. *The Lancet*, *368*(9553), 2167-2178.
15. Gune, A., Alpasalan, M., and Inal, A. (2004). *Plant growth and fertilizer. Ankara University of Agriculture publication.* No: 1539, Ankara, Turkey.
16. John, H. D. (2002). "Heavy metals" a meaningless term? (IUPAC Technical Report)" *Pure and Applied Chemistry*, *Vol. 74*, pp. 793–807.
17. Kenya National Bureau of Statistics, KNBS. (2013, April). *Kenya - 1999 Kenya Population and Housing Census.* Retrieved February 11, 2015.
18. Kioko, T. (2013). *Reusing and recycling poo and pee to produce, biogas, battery power, fertilizer and water for irrigation.*
19. Lee, D.Y., and Jing, C. (2008). "*Growing Up In A Leaded Environment: Lead Pollution and Children in China.*" China Environment Forum.
20. Markus, J., and McBratney, A. B. (2000). A review of the contamination of soil with lead. I. Origin, occurrence and chemical form of soil lead. *Progress in Environmental Science*,
21. Martinez, T., Lartigue, J., Avilaperez, P., Navarrete, M., Zarazua, G., Lopez, C., Cabrera, L. and Ramirez, A. (2001). Metallic pollutants in Mexico valley. *Presented in 16th International Conference on Application of Accelerators in Research and Industry, at American Institute of Physics*, 512- 515.
22. Miller, D. G., McLaughlin, B., Pistoia, G., Wiaux, P., Wolsky, S. P. (2001). *Used Battery Collection and Recycling*, 1st ed., Elsevier Science, ISBN 0-444- 50562-8.

23. Nadal, M., Schuhmacher, M., and Domingo, J. L. (2004). Metal pollution of soils and vegetation in a petrochemical industry. *Science of Total Environment*, 321: 59-69.
24. Nicolescu, R., Petcu, C., Cordeanu, A., Fabritius, K., Schlumpf, M., Krebs, R., Krämer, U.,Winneke, G. (2008).*Environmental exposure to lead, but not mercury,aluminium,or arsenic, is related to aspects of the attention deficit hyperactivity disorder (ADHD) in) Romanian children*: Performance measures and questionnairedata. Environ Health Persp.
25. Onder, S., Dursun, S., Gezgin, S. and Demirbas, A. (2007). Determination of heavy metal pollution in grass and soil of city centre Green areas (Konya, Turkey). *Polish J.Environmental Studies,16* (1): 145 -154.
26. Scokart, P. O., Meeus-Verdinne, K., & De Borger, R. (1983). Mobility of heavy metals in polluted soils near zinc smelters. *Water, Air, and Soil Pollution*, *20*(4), 451-463.
27. Staniland, S., Coppock, M., Tuffin, M., Zyl, L. V., Roychoudhury, A. N., and Cowan, D. (2010). Cobalt Uptake and Resistance to Trace Metals in Comamonastestosteroni Isolated From a Heavy-Metal Contaminated Site in the Zambian Copperbelt. *Geomicrobiology Journal*, *11*(2), 20 - 35. doi:10.1080/01490450903527994.
28. Technical Workshop Group (2001). *Draft of Technical Guidelines on environmentally sound management of Lead-Acid Battery Wastes*, Eighteenth session, April 2001.
29. Thormark, C. (2002). A low energy building in a life cycle—its embodied energy, energy need for operation and recycling potential. *Building and environment*, *37*(4), 429-435.
30. Ullrich, S. M., Ramsey, M. H., & Helios-Rybicka, E. (1999). Total and exchangeable concentrations of heavy metals in soils near Bytom, an area of Pb/Zn mining and smelting in Upper Silesia, Poland. *Applied Geochemistry*, *14*(2), 187-196.
31. USEPA (2011). *USEPA regulations "Lead; Identification of Dangerous Levels of Lead;*Final Rule" Federal Register Friday January 5 2001, Part III Environmental ProtectionAgency "Clearance Standards for Dust".
32. Winter, M., and Brodd, R. J. (2004). What are batteries, fuel cells, and supercapacitors?. *Chemical reviews*, *104*(10), 4245-4270.
33. Yoshio, M., Brodd, R. J., &Kozawa, A. (2009). *Lithium-Ion Batteries*. Springer.
34. Yu, M. H. (2005). *Environmental Toxicology – Biological and Health. Effects of Pollutants*. 2nd Ed. CRC Press, Boca Raton, Florida.