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The Levels of Selected Heavy Metals in Solid Wastes and Their Environmental Pollution Effects in Bungoma Town, Kenya

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Abstract: ***The levels of Pb, Cd, Cr and Zn were analysed from classified solid wastes samples from a dumpsite in Bungoma town, Kenya. Soil samples from surrounding farm lands were also analysed for pH and heavy metal levels. The soil samples were digested by wet ashing and then subjected to flame atomic absorption spectrometry (FAAS) analysis. The results showed that the municipal solid wastes comprised more than 50% of each waste sample and on average 60.90% of all the wastes from the dump site. The mean concentrations (mg kg^{-1}) of heavy metals in the dumpsite samples determined using the most reliable method of standard addition were 5.53±2.96, 6.60±2.45, 13.41±1.62 and 5.94±3.34for Pb, Cd, Zn, and Cr respectively. While the mean concentrations in farm soil samples were 4.63±0.023, 5.08±0.005, 12.57±0.011, and 3.92± 0.006 for Pb, Cd, Zn, and Cr respectively. The mean concentrations (mg kg^{-1}) for Pb, Cd, Cr and Znin the dumpsite samples obtained by less reliable but easy to perform external standard method were 1.15±0.27, 0.13±0.06, 0.097±0.09 and 11.60±2.89respectively while the mean concentrations(mg kg^{-1}) in farm soils were 0.26±0.34, 0.0063±0.0026 and 7.82±5.79for Pb, Cd and Zn respectively. The pH values range was 5.25±0.13 to 6.80±0.08 for sample D and reference sample respectively. However, there was no significant correlation between farm soil heavy metal contents and theirpH. All the heavy metal concentrations were found to be below the maximum acceptable levelsset byUnited States Environmental Protection Agency (U.S. EPA)regulations. The analysis of variance (ANOVA) F-testat $p \leq 0.05$ (95% confidence level) showed a significant difference between the two methods used in the analysis.***

Keywords: Correlation, Heavy metal, pH, FAAS, ANOVA, U.S. EPA, Farm soil

1. Introduction

Increase in solid waste menace experienced in most urban centers and beyond coupled with their potential environmental pollution hasmade environmental heavy metal contamination by solid wastes an area of interest in many previous studies (Vergara and Tchobanoglous, 2012). The contamination as shown in the past studies affects agricultural lands, water bodies such as lakes wells and rivers, recreational facilities among others due to careless disposal of the solid wastes.

In Kenya and particularly in urban centers just like in most African countries, poor solid waste management is a major concern. According to a recent survey by United Nations Environmental Programme (UNEP), Nairobi with a population of 4.0 million generates 3,200 tons of heavy metals contaminated solid wastes daily. Only 850 tons reach solid waste dumpsites with the rest unaccounted for (www.entrepreneurstoolkit.org). This has led to increase in the number of dangerously exposed dump sites along city streets and around most of the urban residential areas as evident in Bungoma town where this study was undertaken. However, the level of contamination in Bungoma is still relatively low due to its small area and also being an upcoming town with an urban population of 44,196 and a total population of 60,650(Kenya Bureau of Statistics, 1999) which is very low compared to major cities like Nairobi with high population leading to large solid waste generation. Similar previous studies revealed that solid wastes are highly contaminated with toxic pollutants among them heavy metals which could find their way into water bodies, farm lands and air thus may cause serious pollution problems (Leonard and Lynch, 1958).

Heavy metals are widely distributed throughout the environment through the wastes disposal (Madean, 1976). Industrial discharge, fertilizer, manure, pesticide, fossil fuel, municipal waste, sewage-sludge, mining waste, animal waste and contaminated water are some of the major sources of heavy metal contamination in soil and water (Alloyway *et al.,* 1988). Once an element is released into the environment, it follows some biochemical cycles being transported by air, water and gravity until they reach a geo-chemical sink. Soil is the ultimate sink for all elements where heavy metals may accumulate within a short span of time (Kabata-Pendias, 2001). Adverse effects of heavy metals on human and plants health are well documented. Levels of zinc in excess of 500 ppm in soil interfere with the ability of plants to absorb other essential metals, such as iron and manganese. Cadmium has no essential biological function and is highly toxic to plants and animals. The main target organ is kidney, which contains about 1/3 of the whole body content (Bighham, *et al.,* 1986). It's hazardous due to its tendency to accumulate in the kidney where it can cause dysfunction if the concentration in the kidney cortex exceeds 200 mg/kg^{-1} fresh weight (Fasset, 1980).Lead at certain contact degrees is a poisonous substance to animals, including humans. It damages the nervous system and causes brain disorders. Excessive lead also causes blood disorders in mammals. It is a neurotoxin that accumulates both in soft tissues and the bones (Leonard and Lynch, 1958). Exposure to high lead levels can severely damage the brain and kidneys in adults or children and ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage (Hernberg, 2000). Chromium has no verified biological role and has been classified by some as non-essential for mammals. Water insoluble chromium (III) compounds and chromium metal are not considered a health hazard, while the toxicity and carcinogenic properties of chromium (VI) have been known for a long time (Kotaś, 2000).

The present study was therefore undertaken to determine lead, cadmium, chromium and zinc contaminations in solid wastes in a dumpsite and surrounding farm lands and asses the possibility of these heavy metal contaminants finding their way into to the agricultural lands around the dump site through various possible transfer mechanisms. This would help in understanding the dangers associated with poor solid waste management which is a great challenge in the developing countries and thus emphasize the essence of the benefits of safe solid waste disposal.

2. Materials and Methods

Study area

The samples for this study were collected from a selected municipal dumpsite in Bungoma town situated in western Kenya. The town was established as a trading center in the early 20th century and is theheadquarterofBungoma County. It hosts a municipal council which is the main source of solid wastes. The municipality has an urban population of 44,196 and a total population of 60,650(Kenya Bureau of Statistics, 1999).

Sampling

The samples were collected using systematic sampling technique (www.rgs.org). The boundary surrounding the dumpsite was identified and the site divided into four equal regions A, B, C, and D. Four solid waste samples of known weight were collected at fixed points from the center of each region. The sampling was done by scooping the solid wastes up to a suitable depth togive a reasonable quantity and a well representative sample. The samples were then segregated to classify the types of solid wastes present in a given quantity of a collective waste and leaving fine solid sample which were later prepared for analysis. Another set of samples were collected on top soil at a distance of 50 meters and 100 meters to the West, East, South and North directions around the dumping site. The last sample which was treated as a reference was collected at a point approximately 2km away from the dumpsite. A total of 13 samples obtained from Bungoma dump site were prepared for analysis.Another set of three samples used for validation studies and data comparison were obtained from a small dump site in Juja town and J.K.U.A.T farm. All the analysis were done in triplicate.

Sample Pretreatment

The fine solid waste separated from the other bulky and roughwastes and soil samples were packed in clean labeled plastic polythene bags and transported to Jomo Kenyatta University of Agriculture and Technology chemistry laboratory. Care was taken to avoid contamination of the samples during transportation. The samples were then air dried separately for around 14 days in order to reduce the moisture content in the samples and also to prevent bacteria invasion before the extraction process (Pye, 1979). The samples were then ground separately using a mortar and pestle and sieved with a 2mm sieve then safely stored. The samples were subjected to wet ashing to decompose the organic matter. For analysis of cadmium, lead, zinc and chromium, the samples were subjected to wet digestion procedure described by AOAC (1970, 1975).

Instrument

Flame Atomic absorption spectrophotometer (Buck scientific model 210 VGP) was used for the determination of heavy metals levels. FAAS is preferred because of its high sensitivity, relatively free from interference, high specificity, low detection limit and easy to operate.The analytical instrument was operated under various specific conditions suitable for each metal analyzed in order to optimize the analysis (Pye, 1979).

Chemicals

All reagents were of analytical grade, nitric and hydrochloric acids, hydrogen peroxide and chromium commercial standard were purchased from Sigma (Seelze, Germany). Zinc chloride, cadmium nitrate and lead nitrate salts used to prepare the stock standards solutions were obtained from Merck, Germany.

SamplespH analysis

The pH of eachsample was determined following the standard procedure described in the working manual by Kalra, (1995) using the pH meter (JENWAY 3505 pH meter).

Method Validation Studies

Recovery studies

The study was done to validate the performance of the analytical methodsused and also to estimate proportional systematic error. This is the type of error whose magnitude increases as the concentration of analyte increases. The error is often caused by a substance in the sample matrix that reacts with the sought for analyte and therefore competes with the analytical reagent.Recovery is often expressed as a percentage because the experimental objective is to estimate proportional systematic error, which is a percentage type of error.

A recovery test was performed using method of standard addition. Standard solutions containing Zn, Cr, Cd, and Pb were prepared and used to spike digested samples and then the spiked samples diluted to 50 ml using deionized water before subjected to FAAS analysis. The formula shown below was used to accordingly calculate the recovery of each of the four heavy metals analysed using the values obtained.

$$Recovery = \frac{Xs - X}{Xadded} \times 100\%$$

Where; Xs - mean result of spiked samples
X - Mean result of unspiked samples
Xadded- Amount of known analyte (standard) added

Detection limit

The minimum detectable limit is the lowest concentration of analyte which can be quantitatively determined and is generally the concentration signal equivalent to 3-5 times the standard deviation of the blank signal. From the calibration curves of each heavy metal, the detection limit was calculated based on the standard deviation of the response (SD) and the slope of the calibration curve (S) at levels approximating the LOD according to the formula: LOD = 3.3(SD/S) (Martin and Caughtrey, 1982).

The detection limit can be used to compare two analytical techniques and brands of instruments and also to determine the limitations of the instrument or technique.

Linearity

Determination of whether the calibration curve is linear is necessary to know the suitability and reliability of the absorbance values obtained. This was defined using product moment correlation coefficient called Pearson's coefficient denoted by letter R (Miller and Miller, 1988). Graphs of absorbance versus concentration were plotted using Microsoft Excel and a linear regression equation of the form Y = a + bX obtained, where X is the explanatory variable and Y is the dependent variable. The 'correlation coefficient' r and R^2values which were used to determine linearity were obtained for each calibration curve.

3. Data Analysis

Linear regression

The concentrations of heavy metals in all the samples were first determined using method of standard addition. In this research, Method of Standard Addition (MSA) was considered as the most reliable analytical technique. A constant volume (Vunk) of each sample solution was added to each of four volumetric flasks of volume Vflask. A series of increasing volumes, (Vstd) of standard solution of each of the four heavy metals analysed were then added. Finally, each flask was made up to the mark with deionize water and mixed well. The concentration and volume of the stock solutions added were chosen so as to increase the concentration of the unknown by about 30% in each succeeding flask. The constant Csa was calculated for each of the samples using the formulae;

$$Csa = \frac{\text{Cstd x Vstd}}{\text{Vflask}}$$

Signal intensities for each of the solutions in the flasks were measured using FAAS and then plotted against Csa. The graph was extrapolated to y=0 and the negative x-intercept values obtained used to compute the concentration, Co of the unknown using the formula.

$$Co = -(x - intercept\ X\ V\text{flask}) \times \frac{Vflask}{Vunk}$$

The concentrations were also determined using external standard method. Standard solutions of each of the four heavy metals were prepared within the suitable concentration ranges by serial dilution of the stock solutions and their absorbance values obtained after aspiration into the atomic spectrometer.

Table 1: Concentration ranges of heavy metals standards

Heavy metal	*Concentration range (ppm)*	
	Lowest concentration	*Highest concentration*
Pb	0.5	4.5
Cr	0.5	4.5
Zn	2.0	16.0
Cd	0.5	4.5

Calibration curves of absorbance versus concentration were plotted using Microsoft Excel and a linear regression equation of the form Y = a + bX obtained, where X is the explanatory variable and Y is the dependent variable. The slope of the line is **b**, and **a**is the intercept (the value of y when x = 0). The concentration (x-value) corresponding to any measured absorbance (y-value) were calculated using both the determined slope and intercept of the regression line (Miller and Miller, 1988).

4. Results and Discussions

Classification of solid wastes

The solid waste samples obtained from the four sampling points within the dump site were classified according to the four main types of solid wastes. Table 2below shows the composition of each solid waste sample as per the classification.

Table 2: Composition of solid waste samples from sampling points A, B, C, D (n = 5)

Type of waste	**Mass of waste (Kg)**			
Sample codes	**Sample A**	**Sample B**	**Sample C**	**Sample D**
Municipal waste	3.20±0.20	4.36±0.25	4.90±0.43	3.46±0.32
Industrial waste	0.60±0.10	0.80±0.10	0.60±0.10	1.20±0.20
Hazardous waste	0.23±0.15	0.40±0.20	1.23±0.15	0.76±0.15
Inert waste	1.43±0.15	0.66±0.25	0.43±0.15	1.23±0.15
Sample size (kg)	5.25±0.07	5.6±0.2828	6.55±0.21	6.30±0.28

The results on the composition of solid wastes from the Bungoma dumpsite are in agreement with most previous studies done on solid wastes especially in Africa and other developing countries. Just like in this study, other research work have also reported that municipal waste in most cases forms the majority of the solid wastes, while hazardous and industrial solid wastes forms the minority. This could be attributed to large sources of municipal wastes especially in African urban centers where industrial development is still not in advance stages. Previous research by Sreeram and Ramasami, 2003reported very high percentage of municipal solid wastes in the solid waste dump sites. Below shows graphical presentation of the composition of solid wastes sampled from the dumpsite.

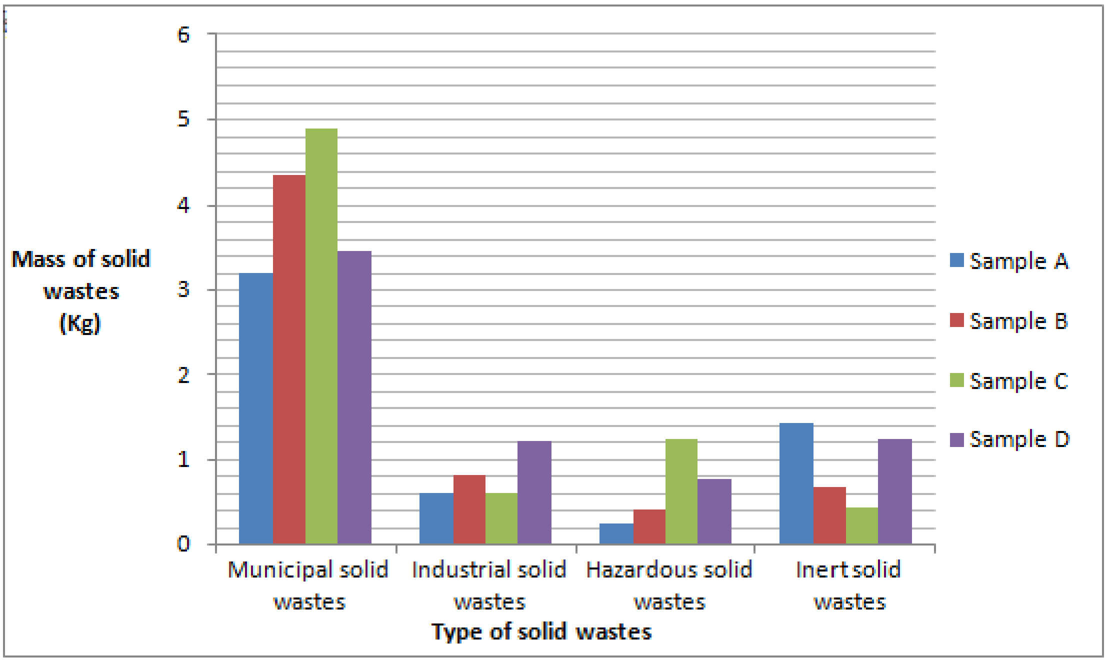

Figure 1: Solid wastes composition for Bungoma dumpsite sampling points

Samples pH measurement

Soil pH is an important parameter that can be used to assess potential availability of beneficial nutrients and toxic elements to plants. The soil and solid waste samples were measured for their pH values and the results wereas shown in table 3 below. The measurements were done by the common method using an H^+ ion – selective glass electrode which is placed in a filtrate of a mixture of soil or solid waste sample and deionized water.

Table 3: Solid wastes and soil samples pH values

Sample code	pH value (n=5)
Sample A	5.50±0.08
Sample B	5.55±0.12
Sample C	5.70±0.18
Sample D	5.25±0.13
50 meters East	5.70±0.08
50 meters West	5.75±0.13
50 meters North	5.77±0.12
50 meters South	5.90±0.08
100 meters East	6.20±0.29
100 meters West	6.03±0.03
100 meters North	5.65±0.13
100 meters South	6.33±0.22
Reference	6.80±0.08

The pH values indicate that the soil samples vary from moderately acidic (5.6–6.0) to slightly acidic (6.1–6.5) nearing neutral (6.6–7.3). Sample from location D with pH value 5.25±0.13 had the strongest acidic property while the reference sample had the least acidic property with pH value 6.80±0.01. The soil pH values obtained in the present study is in agreement with previous research work especially on agricultural lands where the soil pH value in most cases is moderately acidic asmost agronomic crops require soil-water pH values between 5.7 and 7 (Gerritse and Van Driel, 1984).However, the results on pH of solid wastes may differ depending on the sources and composition of solid waste.

Effects of pH on heavy metal concentrations in soil and solid wastes

The change in soil pH affects the mobilisation intensity of heavy metals. The mobility of metallic elements is much higher in highly acidic soils than in soils with neutral and alkaline reaction.

Other factors that affects heavy metal mobility in soil includes content and type of organic matter, granulometric composition, organic matter content, occurrence and form of cations, absorption capacity, content of macro and micronutrients, oxidation-reduction potential, activity of microorganisms among other factors (Alkorta *et al.,* 2004).

The relatively acidic pH values and heavy metal concentration values found in the dump site samples in the present study could be attributed to presence of various kinds of contaminated solid wastes which resulted in high availability of the heavy metals in the wastes.

5. Heavy Metals Concentration Analysis

Heavy metals concentration analysis by Method of Standard Addition

This method of analysis was considered as the most reliable technique. The recovery study done based on the data obtained by this method gave values that are within the acceptablerange: 95% ≤ Recovery ≤ 115% (Miller and Miller, 1988) as shown in recovery table 4 below. The validation studies done in this research shows that the analytical technique used is an acceptable method and can be applied for this purpose in conventional conditions (Foy *et al.,* 1978).

Table 4: Recovery studies for heavy metals

Metal	Volume of known analyte (standard) added (ml)	Mean concentration of unspiked sample (ppm) (n=6)	Mean concentration of spiked sample (ppm) (n=6)	Concentration of known analyte (standard) added (ppm)	Recovery (%)
Pb	10	0.71±0.55	5.53±2.96	10	96.46
Cd	6	0.09±0.08	6.60±2.46	10	108.57
Zn	3	10.34±3.94	13.41±1.62	10	102.00
Cr	6	0.09±0.09	5.94±3.34	10	97.45

The linearity was verified using product moment correlation coefficient called Pearson's coefficient denoted by letter R. The R^2 values for each metal calibration graph was determined giving values $R^2 \geq 0.965$ for all the metals analyzed showing a perfect positive linear correlation with chromium having the best R^2 value of 0.999, cadmium $R^2 = 0.996$, lead $R^2 = 0.988$ and zinc $R^2 = 0.965$.

Heavy metal concentrations (mg kg^{-1}) by Method of Standard Addition

The method of standard addition gave higher concentration for lead as compared to external standard method. The highest concentration of 10.50 mg kg^{-1} was recorded from sample location A and the lowest value of 1.50 mg kg^{-1} from the reference sample. The dumpsite samples concentrations were in the range of 6.25 mg kg^{-1} - 10.50 mg kg^{-1} while the farm soil concentration varied from 2.25 mg kg^{-1} to 9.51 mg kg^{-1} for lead metal.

Cadmium concentration from both within the dumpsite and farm soil samples were between 0.06 mg kg^{-1} and 0.21 mg kg^{-1} while farm soil samples gave 0.01 mg kg^{-1} for sampling locations 50 meters West and 100 meters south with the rest of sampling sites for farm soil recording concentrations which were below detectable limits.

For chromium, dumpsite samples showed concentrations in the range of 4.55 mg kg^{-1} to 10.21 mg kg^{-1} while the farm soil concentrations ranged between 7.96 mg kg^{-1} to 0.40 mg kg^{-1} with six samples within the farm soil region giving concentration below detectable limits.

Zinc concentration results from dumpsite samples gave 14.60 mg kg^{-1} to 15.38 mg kg^{-1} while the farm soil samples concentrations ranges from 10.43 mg kg^{-1} to 15.38 mg kg^{-1}.

The high levels of heavy metals concentration in dumpsite samples as compared to farm soil samples could be attributed to contribution by the solid wastes particularly the industrial solid wastes in the dumpsite while the heavy metals levels detected on the surrounding farm soils could be as a result of dispersion of the toxic contents from the dumpsite to the farms though leaching, surface run offs or other means (Papp and Lipin 2006).

The results on the levels of heavy metals levels detected in this study reflects similar discoveries in what had been reported in previous research works where heavy metals contamination have been noted in solid wastes and farm soils but the level of contamination for most heavy metals is still below the maximum permissible levels for various relevant regulatory authorities (TZS, 2003). The contaminations can thus be contained if early precautionary measures are taken but could be lethal if the pollution continues unabated.

Table 5: Concentrations (mg kg $^{-1}$) of heavy metals in solid wastes and soil samples

Sample Code	**Concentration (mg kg^{-1})**							
	Method of standard addition				*External standard method*			
Heavy metal	**Pb**	**Cd**	**Zn**	**Cr**	**Pb**	**Cd**	**Zn**	**Cr**
Sample A	10.50	9.50	14.89	4.55	0.96	0.14	9.49	0.24
Sample B	6.25	9.52	15.38	7.14	0.95	0.06	11.78	0.07
Sample C	7.60	6.65	14.60	7.96	1.53	0.21	9.49	0.01
Sample D	9.01	6.82	14.75	10.21	1.15	0.12	15.63	0.07
50 meters East	3.50	BDL	12.96	BDL	BDL	BDL	BDL	BDL
50 meters West	5.95	8.50	15.38	0.40	0.05	0.01	3.73	BDL
50 meters North	9.51	BDL	13.69	BDL	0.77	BDL	11.92	BDL
50 meters South	2.38	3.57	10.43	BDL	0.05	BDL	BDL	BDL
100 meters East	3.50	3.76	12.27	7.96	BDL	BDL	BDL	BDL
100 meters West	5.95	BDL	12.96	3.41	BDL	BDL	BDL	BDL
100 meters North	4.01	BDL	11.82	BDL	BDL	BDL	BDL	BDL
100 meters South	2.25	4.50	11.08	BDL	BDL	0.01	BDL	BDL
Reference	1.50	BDL	BDL	BDL	0.18	BDL	BDL	BDL
Variance	**2.96**	**2.29**	**1.55**	**3.09**	**0.52**	**0.07**	**3.59**	**0.09**

NB: BDL – Below detectable limit

The heavy metals levels found in all the samples studied were below the maximum permissible levels for farm soil and wastes according to United States environmental protection agency (U.S. EPA, 1993) regulations.

Table 6: Regulatory limits on heavy metals applied to soils (Adapted from U.S. EPA, 1993)

Heavy metal	Maximum concentration in sludge (mg kg^{-1})	Annual pollutants loading rates			
		Kg/ha/yr	Lb/A/yr	Kg/ha	Lb/A
Cadmium	75	2	1.8	41	36.6
Chromium	3000	150	134	3000	2,679
Lead	420	21	14	420	375
Zinc	7500	140	125	2800	2500
Arsenic	75	2	1.8	41	36.6
Mercury	840	15	13.4	300	268
Molybdenum	57	0.85	0.80	18	16
Nickel	75	0.90	0.80	18	16
Selenium	100	5	4	100	89

Heavy metals concentration analysis by external standard method

The heavy metal concentrations in solid waste and farm soil samples were also determined using external standard method. The detection limits for each heavy metal weredetermined as a validation procedure for analysis. Table 7 below shows the FAAS detection limit values as given in the equipment manual and the instrumental determined method detection limit. The discrepancies between the two detection limit values may be attributed to systematic and mathematical errors during analysis procedures. However, the method detection limits obtained are reliable as smaller values of detection limit indicate that the presence of trace amounts of metals of interest in the sample can be detected by the method (Pye, 1979).

Table 7: Detection limits for heavy metals analyzed

Heavy metal	Method detection limit (mg kg^{-1})	Equipment manual detection limit values (mg kg^{-1})
Pb	0.15	0.08
Cd	0.04	0.01
Cr	0.05	0.04
Zn	0.008	0.005

The determined method detection limits in this research compares well with a previous similar study according to Mekebo and Chandravanshi (2014). In their study, the detection limit for Zn was determined to be 0.001 mg kg^{-1} as found in this study while the values for Pb, Cr and Cd were 0.005, 0.002 and 0.001 respectively. The inconsistencies in the DL values could be due to differences in the degree of accuracy and precision of the two researchers and the instrumental conditions of the two equipment used (Markowski and Markowski, 1990).

Heavy metals concentrations (mg kg^{-1})by external standard method

All the data obtained for the concentrations of heavy metals for samples from both the dump site and the neighboring farm lands are below the maximum permissible levels for farm soils and dump sites. This could be due to low scale of pollution given that Bungoma town is still a small growing urban center with not so much environmental management challenges. However, higher heavy metal concentrations could have been recorded were this study done in a major city like Kisumu or Mombasa, Kenya where poor solid waste disposal is a major environmental challenge.

The highest lead concentration obtained was 1.53 mg kg^{-1} from location C while the minimum concentration was 0.05 mg kg^{-1} obtained from sampling location 50 meters south and 50meters west of the dumpsite. Farm soil sample from 50meters north of the dumpsite gave 0.77 mg kg^{-1}. The mean concentration (mg kg^{-1}) of lead in the dumpsite was 1.14±0.26 while in the farm soil the value obtained was 0.26±0.34.Slope and human activities which affect leaching and other transport mechanism of heavy metals in soil could be the cause of high heavy metal concentration in some parts of the dump site and around the site as compared to other parts. Sampling point C which had high concentrations for Pb and Cd could have been experiencing more leaching effect due to its down slope positioning resulting in high heavy metal concentration.

Cadmium concentration from sampling location C with 0.21 mg kg^{-1} was the highest and 0.01 mg kg^{-1} at from locations 100 meters south and 50 meters West of the dumpsite being lowest. On average the concentrations of cadmium in the samples from the dumpsite was 0.13±0.06 mg kg^{-1} while for farm soil sample the average concentration was 0.01±0.003 mg kg^{-1}.

Chromium concentrations were below detectable levels in all sampling areas around the dumpsite. However, samples obtained within the dumpsite had the highest concentration of 0.24 mg kg^{-1} from sample location A and the lowest concentration being 0.01 mg kg^{-1} obtained from sample location C, sample locations B and D recorded similar values of 0.07 mg kg^{-1} each..

The results obtained for zinc analysis gave the highest concentration values of all the four heavy metals analyzed. The maximum concentration was obtained at sampling location D with the value 15.63 mg kg^{-1} and minimum concentration 3.73 mg kg^{-1} at sampling location 50 meters west of the dumpsite.On average the concentrations of zinc in the samples from the dumpsite was 11.60 ± 2.89 mg kg^{-1} while for farm soil samples, the average concentration was 7.82±5.79 mg kg^{-}1 with seven sampling sites within the farm soil giving concentrations below detectable limits.

Table 8: Concentrations (mg kg^{-1}) of heavy metals in solid wastes and soil samples from Juja area

These values were initially obtained for validation studies and data comparison purposes.

Sample code	Zn	Cd	Cr	Pb
Juja dumpsite	3.68	0.04	0.09	3.77
JKUAT farm	BDL	BDL	BDL	2.64
50 meters	BDL	BDL	BDL	2.79

NB: BDL – Below detectable limit

Statistical comparison

The F-test one way analysis of variance (ANOVA) at P≤0.05 (95% confidence level)showed a significance difference between the two methods used for analysis for each of the four metals.

Table 9: F test ANOVA values and comparisons

Heavy metal	*Variance (σ) values*		*F calculated*	*F tabulated*
	Method of Standard Addition	*Method of external standard*		
Pb	2.96	0.52	32.40	2.77
Cd	2.29	0.07	1070.22	3.58
Cr	3.09	0.09	1178.78	3.69
Zn	1.55	3.59	5.36	3.00

The method of standard addition gave relatively high concentrations for all the four heavy metals as compared to results obtained by external standard method. This is due to the assumption that in the former method the matrix effect is eliminated and the standards used to spike the samples also contribute to the high absorbance signal obtained. Based on this study, it can be recommended that the standard addition method should be prioritized in future analysisover external standard method as it gives better and reliable results.

Correlation among heavy metal concentrationsin samples from Bungoma dumpsite

The below Pearson's correlation coefficient curves shows positive **r** values for the correlations between different heavy metals concentrations from Bungoma dump site samples.

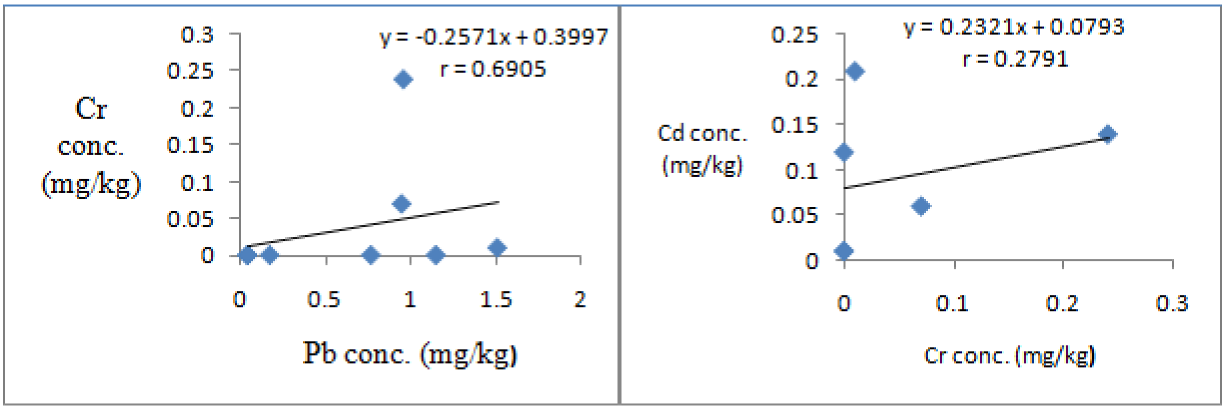

Figure 2: Spearman's correlation coefficients curves between Cr and Pb, Cd and Cr concentrations respectively from Bungoma dumpsite samples

There was no negative r value for correlation coefficient in all the cases as shown in table 10 below.

Table 10: Spearman's correlation coefficients between Bungoma dumpsite samples heavy metals concentrations

Heavy metal	Pb	Zn	Cd	Cr
Pb	_	0.98	0.56	0.69
Zn	0.98	_	0.34	0.21
Cd	0.56	0.34	_	0.28
Cr	0.69	0.21	0.28	_

Correlation among heavy metal concentrations in sample from Bungoma and Juja dumpsites

Positive **r** values were obtained for the correlation between the concentrations of heavy metals in samples from Bungoma and Juja dump sites as shown in table 11 below. The values were obtained by plotting a graph of Juja samples concentration values against Bungoma samples concentration values.

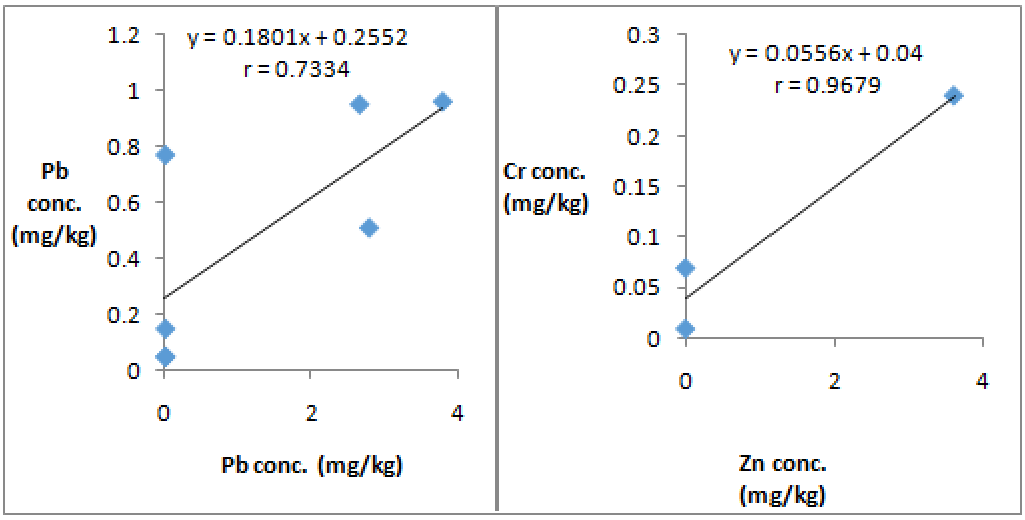

Figure 3: Spearman's correlation coefficient curves between Pb and Pb, Cr and Zn concentrations respectively from Bungoma and Juja dumpsites samples

Table 11: Spearman's correlation coefficients between Bungoma and Juja dumpsites samples heavy metals concentrations

Heavy metal	Pb	Zn	Cd	Cr
Pb	0.73	0.98	0.82	0.36
Zn	0.98	0.68	0.71	0.97
Cd	0.82	0.71	0.64	0.46
Cr	0.36	0.97	0.46	0.66

By looking at the correlation between the heavy metals concentrations from Bungoma and Juja dumpsites, it can be observed that the same trend of positive correlation as found in the case of correlation of heavy metals concentrations in solid wastes from the Bungoma dumpsite is also depicted here. A positive correlation occurs when the combined physiological effect of two or more elements is greater than the sum of their independent effects while negative correlation occurs when the combined physiological effect of two or more elements is less than the sum of their independent effects (Foy *et al.,* 1978).

6. Conclusions

The solid waste and farm soil samples analysed in this research contain heavy metal whose concentration levels are below the maximum permissible levels according to United States Environmental Protection Agency for agricultural farm lands and sewage sludge. Although the level of contamination of surrounding farm soil as a result of heavy metals from solid wastes in the dump site as shown in this study is still low, however; solid wastes is evidently a potential lethal environmental pollutant and thus urgent good solid waste management policy should be adopted to avoid any further pollution. The high heavy metal concentrations found in samples within the dumpsite and regions around the dump site as compared to concentrations in samples from farm soils far away from the dump site is an indication of pollution effect by the solid wastes present in the dump site which contributed to such high heavy metal concentrations. It's also noted that wet digestion method is a good technique for heavy metal analysis and gave reliable concentrations values for the samples while F.A.A.S should also be preferred because of its high sensitivity, relatively free from interference, high specificity, low detection limit and easy operation.

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