# Speciation Study of Cadmium and Zinc in Water and Soil Samples Obtained at the Vicinity of Abbatoir, Bukuru and Busa-Buji Dumpsites in Jos Metropolis

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Abstract:-Sequential extraction was used to fractionate heavy metals (Cd and Zn) from the Abattoir, Bukuru and Busa Buji dumpsites. Water samples were collected from 6 wells located near the dumpsites at different proximities for the assessment of concentration of metals leached from the various sites and analyzed for pH, color, turbidity, total hardness, alkalinity, cadmium and zinc heavy metals. From the results, pH of the water was slightly acidic (6.20-7.20) whereas the total hardness, turbidity, color and alkalinity values were all found to be within WHO limits. The Heavy metals were determined by Atomic Absorption Spectrophotometry (AAS). Among the metals examined, zinc has the mean concentration of 5.489mg/L, 8.282mg/L and 1.186mg/L for Abattoir, Bukuru and Busa-Buji dumpsites respectively, while cadmium has the mean concentration of 1.036mg/L, 0.183mg/L and 0.301mg/L for Abattoir, Bukuru and Busa-Buji respectively. The concentration of metals in the well water also varied based on their proximities to the dumpsites. Zinc has the mean concentration of 1.353mg/L, 0.453mg/L for Abattoir downhill and uphill respectively while Busa Buji has the mean concentration of 1.041mg/L, 0.529mg/L for downhill and uphill respectively whereas bukuru has the mean concentration of 1.098mg/L, 0.970mg/L for downhill and uphill respectively. Cadmium has the mean concentration of 0.558mg/L, 0.338mg/L for Abattoir downhill and uphill respectively while Busa Buji has the mean concentration of 0.136mg/L for downhill and not detected for uphill. Analysis of the extracts was carried out by atomic absorption spectrometry (AAS). All the metals analyzed were above the maximum acceptable limits by WHO Zn (5.0 mg/L) and Cd(0.01 mg/L) respectively. The study concludes that the hand dug well water around the refuse dumps sites are not safe for human consumption.

*Keywords:* Speciation, Dumpsite, Waste disposal, Heavy metals, Physicochemical, Consumption, Sequential extraction.

# I. INTRODUCTION

Open dumping of solid waste remains the prevailing form of waste disposal in developing countries like Nigeria. Contamination of water bodies has become an issue of serious environmental concern (Akpoveta et al; 2010).

Municipal solid waste management gets the lowest priority, mainly because disruptions and deficiencies in it do not directly and immediately affect public life and cause public reaction (Rao et al; 2003. Cited by mohammed, 2011). Lack of proper municipal bodies to manage the solid waste generated from residential, commercial and institutional activities, therefore the populace decided to dump their solid waste in any available space within the community, by so doing it get accumulated with time.

Dumpsite generally refers to a place for disposal of waste materials and is the oldest form of waste treatment (Abdul-salam et al; 2011). Historically, dumpsites have been the most method of un-organized waste disposal and remain so in many places around the world. Most dumpsites are located within the vicinity of living communities and wetland (Abdul-Salam et al; 2011). The dumpsites are not lived or basement prepared for selective adsorption or toxic substances. Therefore, it is prone to the release of pollutants to nearby water and to the air through leachates and dumpsites gases respectively

Water is an elixir of life. It governs the evolution and function of the universe on the earth hence water 'mother of all living world'. Majority of water available on the earth is saline in nature; only small quantity is fresh water. Freshwater has become a scare commodity due to over exploitation and pollution. (Muhibbu-Din et al; 2014).

Waste and wastes are terms for unwanted materials; Waste is anything, which is no longer of use to the disposer. It can also be defined as any unavoidable material resulting from an activity, which has no immediate economic demand and which must be disposed of (Ugwu et al; 2009) The poor collection of waste in Jos metropolis leads to indiscriminate refuse dumping close to resident. In the peri-urban areas, domestic waste collection is not done at all. Thus, disposing of wastes can give rise to serious pollution of ground and surface water resources especially where there is uncontrolled tipping of waste. It normally takes many years and takes place within a particular distance from the refuse dump site.

Waste is commonly classified into three. These are solid, liquid and gaseous wastes. Solid wastes are residual from homes, businesses and institutions and referred to as trash, garbage, rubbish, refuse, discards and throwaways that are no longer of any relevance to the disposer. For example, broken bricks, broken glass and bottles, can, plastics, paper, battery casings, plantain skin, and nylon (Adedibu, 1982).

One of the major sources of heavy metal input into the aquatic environment is through landfill sites of municipal solid wastes. Contamination of soils by heavy metals from refuse dump has been a major concern because of their toxicity and threat to human life and the environment. Heavy metals are potentially toxic to human life and the environment. Hence, determining the chemical form of a metal in soils is important to evaluate its mobility and bio availability. This study intends to explore the effect of these metals (Cd and Zn) on ground water from three different dumpsites. The total heavy metal content in soils provide a convenient means of expressing a measure of pollution, numerous reports have highlighted that such measures are deficient in predicting toxicity of metal pollutants (Yusuf, 2006).

#### Aim:

To determine heavy metal bioavailability in soil and underground water sources obtained at the vicinity of some selected dumpsites in Jos metropolis.

#### Objectives:

- To present a competent and practical baseline of the concentrations of some heavy metals (Zn, and Cd,) in the underground water.
- To make the results available and give reference data to groundwater impacts assessment,
- To suggest any further studies that could be carried out on the same or similar topics in this area.
- To carry out a chemical speciation to determine the distribution of heavy metals in the dumpsite and well water.

#### **II. MATERIALS AND METHODS**

#### Study Area

Jos is the capital city of Plateau State, is located in Nigeria's middle belt, it is made up of three local governments, Jos north, Jos south and Jos east. The state shares common boundaries with Benue, Kaduna, Taraba, Bauchi and Gombe States, with an area of 26,899 square kilometers, the State has an estimated population of about three million people (2006 Census). (http://en.wikipedia.org/wiki/Plateau\_State).

# Location

It is located between latitude 80°24'N and longitude 80°32' and 100°38' east. The state is named after the picturesque Jos Plateau, a mountainous area in the north of the state with captivating rock formations. Bare rocks are scattered across the grasslands, which cover the plateau. The altitude ranges from around 1,200 meters (about 4000 feet) to a peak of 1,829 metres above sea level in the Shere Hills range near Jos. Years

of tin mining have also left the area strewn with deep gorges and lakes. (http://en.wikipedia.org/wiki/Plateau\_State)

Bukuru Dumpsite is located between latitude  $09^{0}47$ 'N and longitude  $008^{0}57$ 'E, the altitude is about 4170 feet with an area of about415.30 square meters.

Abattoir Dumpsite is located between latitude  $09^{0}52$ 'N and longitude  $008^{0}53$ 'E, the altitude is about 4143 feet with an area of about374.70 square meters.

Busa-Buji Dumpsite is located between latitude  $09^{0}56$ 'N and longitude  $008^{0}52$ 'E, the altitude is about 3807 feet with an area of about 784.92 square meters.

JOS PLATEAU STATE



Fig. 1 Map Showing Jos metropolis.

#### Sampling

Top soil (0-15cm) samples were collected from four different points in a quadrant from each of the 3 dumpsites (Abattoir, Bukuru and Busa-Buji). Samples were scooped with plastic spoon and transferred into polythene bags, after which they were transported to the laboratory for analysis. The four samples were mixed together to form a composite sample. Soil samples were spread in Petri dishes and dried. The dried soil was grinded and passed through a sieve with 0.2mm mesh, soil samples were later stored in polythene bags prior to analysis. Water samples were collected from 6 hand dug wells, 2 samples from each dumpsite at different proximities (uphill and downhill) to the dumpsites. The wells sampled were functional, active, located away from toilets, have not undergone any chemical treatment and were continuously used for drinking and domestic purposes. Samples were obtained using same material normally used by the householders to draw water from each well. Water samples were collected in 1L plastic bottles and stored in the refrigerator prior to analysis using the standard procedure (APHA, 2005).

Fig. 2 Busa Buji Dumsite



Fig.3 Abattoir Dumpsite



Fig. 4 Bukuru Dumpsite



# **Digestion Procedures**

#### Water Digestion

A 100ml of water samples was measured into a beaker, 2mL of concentrated HNO<sub>3</sub> and 6mL of concentrated HCl were added respectively. The samples were covered with a ribbed watch glass and heated on a hot plate at 90 to 95 C until the volume has been reduced to 15-20 mL. The beakers were removed and allow to cooled. The beaker were washed down with deionised water and filtered. The final volume was adjust to 100 ml with deionised water and stored in a refrigerator for analysis. (Amadi et al; 2012).

#### Soil digestion

A 1.00g of the soil samples was accurately weighed out into 100ml beakers. A small amount of water (2-3mL) was added to generate a slurry and then 7.0ml concentrated HNO<sub>3</sub> and 21ml concentrated HCl (3:1 ratio, 3 parts con. HCL and 1 part HNO<sub>3</sub>)) was added in several portions of the 3 dumpsite samples. The mixture was manually shaken. The beakers were covered with a watch glass and the solution gently heated under reflux for 2 h on an Electric hot plate adjustable and capable of maintaining a temperature of 90-95 C. After the samples had cooled down, the condenser was rinsed with deionised water the rinses were collected in the roundbottomed flask. The condenser was removed and the sample filtered through Whatman No. 542 filter papers to remove any undigested solid material. The filtrate was collected in a 100mL volumetric flask and the solution was then made up to 100mL with deionised water and stored in a 100ml sample bottle for analysis.

# Speciation

# Summary of the sequential extraction procedure (SEP)

According to the Tessier's procedure, the SEP operationally groups heavy metals into the following five fractions: (Tessier et al, 1979)

# F.1. Soluble and exchangeable Fractions

The soluble and exchangeable metals from soil were extracted with 20 mL of a 1.0

M MgCl<sub>2</sub> solution adjusted to a pH of 7.0 by shaking with electrical vibrator for 1 h at  $20^{\circ}$ C.

# F.2. Carbonates fractions

The carbonates in the residue from F.1 were extracted with 20 mL of a 1.0 M  $CH_3COONa$  solution adjusted to a pH of 5.0 with  $CH_3COOH$  by shaking with electrical vibrator for 4 h at room temperature.

#### F.3. Iron and Manganese oxides

The Metals bound to iron and manganese oxides were extracted from the residue of the F.2 by shaking with 50 mL of a 0.04 M NH<sub>2</sub>OH·HCl, 25 % CH<sub>3</sub>COOH Solution using an

electrical vibrator. The extraction was performed at  $96^{\circ}$ C for 5.5 h.

#### F.4. Bound to organic matter

Metals bound to organic matter were extracted by pouring 7.5 mL of a 0.02 M HNO<sub>3</sub> solution and 12.5 mL of a 30 %  $H_2O_2$  solution adjusted to a pH of 2.0 unto the residue from F3, then providing continuous agitation for 2 h at the temperature of 85°C. An additional volume of 7.5 mL of the 30 %  $H_2O_2$  solution adjusted to a pH of 2.0 is then added, while maintaining continuous agitation and a temperature of 85°C for another 3 h. This solution was then cooled to room temperature and filtered.

#### F.5. Residual fraction

The residue from F4 was quantitatively transferred into a digestion vessel and metals were dissolved in aqua regia using 6mL of 10 M HCl and 2 mL of 15.8 M HNO<sub>3</sub>. The temperature of the reaction mixture was slowly risen until reflux conditions and maintained for 2 h.

All the filtrates were stored in a refrigerator for analysis.

# *Physicochemical Parameters in Groundwater Located Close to the Three Dumpsites*

# Determination of pH

The pH disk was mounted onto the comparator, 10ml of the water sample measure was measured into a test tube, seven drops of bromothymol blue was added to the measured sample as indicator and the solution was whirled thoroughly to ensure a homogenous mixture. The mixture was then inserted into the comparator and rotated to observe the color that match with the standard. (APHA, 1992)

# Determination of Total Hardness

About 50.0 mL of the sample was measured into a 250 mL conical flask, 2 mL of the buffer solution and few drops of the erichrome black-T was added and titrated with the EDTA solution (0.1M) to a distinct blue endpoint. (APHA, 1992)

# Calculation

Total hardness as 
$$CaCO_3(ml) = vol of EDTA X 1000$$

Vol. of the sample

Total hardness as  $CaCO_3(ml) = Xmg/L$  as  $CaCO_3$ 

# Determination of Alkalinity

About 50.0 mL of the sample was measured into a 250 mL conical flask, 2 drops of methyl orange were added and titrated with the  $H_2SO_4$  solution to a distinct orange endpoint. (APHA, 1992)

Calculation

Total Alkalinity (ml) = 
$$\underline{\text{vol. of H}_2\text{SO}_4 \text{ X 1000}}$$

Vol. of the sample

Total Alkalinity(ml) = Xmg/L

# Determination of Turbidity

A 20ml of the sample into a sample cell, the sample is inserted into the chamber of the Nephelometer, the sample 'Read' button was pressed. The result was displayed in NTU.(APHA, 1992)

#### Determination of Color

The color disc was mounted onto the comparator, 10ml of the water sample was measure into a test tube, the measured sample was inserted into the comparator and the disc rotated to see the color that matched with the standard, the color of the water was read from the color disc and recorded. (APHA, 1992)

#### Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state.

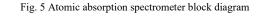
#### Principles

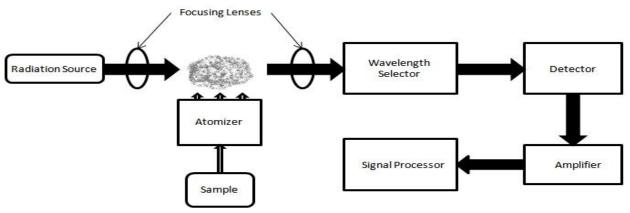
The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on the Beer-Lambert Law.

In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This amount of energy, i.e., wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm), which gives the technique its elemental selectivity. The radiation flux without a sample and with a sample in the atomizer is measured using a detector, and the ratio between the two values (the absorbance) is converted to analyte concentration or mass using the Beer-Lambert Law. For each wavelength of light passing through the spectrometer, the intensity of the light passing through the reference cell is measured. This is usually referred to as *Io* - that's *I* for Intensity.

The intensity of the light passing through the sample cell is also measured for that wavelength - given the symbol, *I*. If *I* is less than *Io*, then obviously the sample has absorbed some of the light.

Instrumentation





In order to analyze a sample for its atomic constituents, it has to be atomized. The atomizers most commonly used nowadays are flames and electrothermal (graphite tube) atomizers. The atoms should then be irradiated by optical radiation, and the radiation source could be an element-specific line radiation source or a continuum radiation source. The radiation then passes through a monochromator in order to separate the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by a detector. (http://en.wikipedia.org/wiki/AAS)

#### Evaluation

Scale of Operation Atomic absorption spectroscopy is ideally suited for the analysis of trace and ultratrace analytes, particularly when using electrothermal atomization. By diluting samples, atomic absorption also can be applied to minor and major analytes. Most analyses use macro or meso samples. The small volume requirement for electrothermal atomization or flame microsampling, however, allows the use of micro, or even ultramicro samples. (Harvey, 2000).

#### Accuracy

When spectral and chemical interferences are minimized, accuracies of 0.5–5% are routinely possible. With nonlinear calibration curves, higher accuracy is obtained by using a pair of standards whose absorbances closely bracket the sample's absorbance and assuming that the change in absorbance is linear over the limited concentration range. Determinate errors for electrothermal atomization are frequently greater than that obtained with flame atomization due to more serious matrix interferences. (Harvey, 2000).

#### Precision

For absorbances greater than 0.1-0.2, the relative standard deviation for atomic absorption is 0.3-1% for flame atomization, and 1-5% for electrothermal atomization. The principal limitation is the variation in the concentration of free-analyte atoms resulting from a non-uniform rate of aspiration, nebulization, and atomization in flame atomizers,

and the consistency with which the sample is heated during electrothermal atomization. (Harvey, 2000).

#### Sensitivity

The sensitivity of an atomic absorption analysis with flame atomization is defined as the characteristics concentration of an element required to produce a signal of 1% absorbance (0.0044 absorbance units). The sensitivity of an atomic absorption analysis with flame atomization is influenced strongly by the flame's composition and the position in the flame from which absorption is monitored. Normally the sensitivity for an analysis is optimized by aspirating a standard and adjusting operating conditions, such as the fuelto-oxidant ratio, the nebulizer flow rate, and the height of the burner, to give the greatest absorbance. With electrothermal atomization, sensitivity is influenced by the drying and ashing stages that precede atomization. The temperature and time used for each stage must be worked out for each type of sample. (Harvey, 2000).

#### **III. RESULTS AND DISCUSSION**

The results of analysis of soil samples obtained from the various dumpsites located at Abbatoir, Busa-Buji and Bukuru are shown in Tables 1 to 5.

Table 1:Results of the physicochemical parameters in groundwater located

close to the three dumpsites

LOCATIO N	pН	TOTAL ALKALINI TY mg/L	TOTAL HARDNES S mg/L	TURBIDIT Y NTU	COLO R Hazen
Abattoir A	6.20	50	52	3	2
Abattoir B	7.20	52	46	2	1
Bukuru A	6.40	44	38	3	3
Bukuru B	7.00	46	30	1	2
Busa-Buji A	6.50	45	40	4	2
Busa-Buji B	6.80	48	40	2	2
WHO LIMIT	6.50- 8.50	500	300	0-5	0-5

Note: A= downhill, B= up hill, WHO=World Health Organization

Sample	Zn (mg/L)	Cd (mg/L)
Abattoir dumpsite soil	5.49±0.10	1.04±0.03
Busa Buji dumpsite soil	1.19±0.10	0.30±0.10
Bukuru dumpsite soil	8.28±0.40	0.18±0.01
WHO Limit	5.0	0.01

Table 2:Results of total metal concentration (mg/L) of soil

Table 3:Results of total metal concentration (mg/L) of water

Sample	Zn (mg/L)	Cd (mg/L)
Abattoir water sample (Down hill)	1.35±0.20	0.56±0.20
Abattoir water sample (Up hill)	0.45±0.10	0.34±0.02
Busa Buji water sample (Down hill)	1.04±0.01	0.14±0.01
Busa Buji water sample (Up hill)	0.53±0.30	ND
Bukuru water sample (Down hill)	1.10±0.10	ND
Bukuru water sample (Up hill)	0.97±0.01	ND
WHO Limit	5.0	0.01

Table 4: Concentration (mg/L) of sequential fractionation of metals in Abattoir Dumpsite

Sample site	Abattoir Dumpsite				
Metal	Zn		Cd		
wietal	Mean(mg/L)	%	Mean(mg/L)	%	
Exchangeable	$1.04{\pm}0.06$	8.01	$0.03{\pm}0.01$	14.84	
Fe-Mn Oxide	$3.25 {\pm} 0.05$	24.94	0.05±0.02	24.73	
Organic	$5.57{\pm}0.01$	42.74	0.05±0.02	25.27	
Carbonate	$0.82{\pm}0.02$	6.28	0.02±0.01	13.19	
Residual	2.35±0.01	18.04	0.04±0.01	21.98	
WHO Limit	5.0		0.01		

Table 5: Concentration (mg/L) of sequential fractionation of metals in Bukuru Dumpsite

Sample site	Bukuru Dumpsite					
Metal	Zn Mean(mg/L) %		Metal		Co Mean(mg/L	-
Exchangeable	1.01±0.03	7.88	0.04±0.02	16.90		
Fe-Mn Oxide	3.55±0.02	27.71	0.05±0.01	23.47		
Organic	4.70±0.01	36.68	0.05±0.02	24.41		
Carbonate	0.97±0.02	7.60	0.03±0.01	14.09		
Residual	2.58±0.010	20.13	0.05±0.01	21.13		
WHO Limit	5.0		0.01			

Table 6: Concentration (mg/L) of sequential fractionation of metals in Busa-Buji Dumpsite

Sample site	Busa-Buji Dumpsite			
Metal	Zn Mean(mg/L)	%	Cd Mean(mg/L)	%
Exchangeable	1.01±0.06	7.22	0.05±0.02	20.26
Fe-Mn Oxide	1.76±0.05	12.57	0.05±0.01	22.41
Organic	6.86±0.01	49.11	$0.05 \pm 0.02$	19.83
Carbonate	1.70±0.02	12.18	0.04±0.01	16.38
Residual	2.64±0.01	18.91	$0.05 {\pm} 0.02$	21.12
WHO Limit	5.0		0.01	

#### Discussion of Results

#### pH

The pH values of the six wells, two each from the three dumpsites at different proximities to the well water where the samples were collected was found to range between 6.20 and 7.2. When these results are compared with the WHO standard (6.5-8.5), they were observed to be within the range. The highest value of pH was recorded at the Abattoir up hill (7.2). This lessens the ability of the water to contain metal ions (this is because metals tend to be less soluble at higher pH and vise versa) and therefore does not pose any health risk to the consumers. However samples from Abattoir downhill and Bukuru downhill rather showed lower pH values of 6.20 and 6.40, respectively, when compared with the WHO standard for drinking water (6.50-8.50). Most of the values however fell within 6.50 - 6.80, few were slightly below 6.0. This result is in conformity with the work of Bozkurt, 2008.

# Turbidity

Turbidity is the degree to which water loses its transparency due to the presence of suspended particulates. From the result obtained, it can be observed that the turbidity of the various water samples collected were not uniform. The results showed that the downhill wells had values ranging between 1 and 4 NTU while that of the uphill wells ranged between 1 and 2 NTU. The samples were observed to have clear natural color during the study period which is in conformity with the work of Palamuleni, 2002. The results also show that the values obtained were within the WHO standards.

The turbidity values recorded in the downhill wells almost doubled that in the uphill wells. Because this analysis was carried out during raining season increased infiltration (peculation) into the aquifers could have been responsible to increased turbidity of the water source. Turbidity in water could affect water purification processes such as flocculation and filtration which normally increases the cost of water treatment. High turbidity values may also increase the possibility of microbiological contamination (DWAF, 1998).

#### Color

Color standard is set for reasons of appearance and requires that water be virtually colorless. According to WHO standards for drinking water, the color limit should be 5 Hazen. All the water samples were within the WHO limit and ranged between 1-3 Hazen (Table 1). Color in natural water usually results from the leaching of organic materials and is primarily the result of dissolved and colloidal humic substances. Color is also strongly influenced by the presence of iron and other metals. However the overall color content of the samples analyzed do not pose any health threat to those that use the water

# Hardness

Hardness of water may not have any health implications but may affect the taste of water as well as influence its lathering ability when used for washing. Agbalagba, (2011), stated that the World Health Organization (WHO) International Standard for Drinking Water in 1998 classified water with a total hardness of CaCO3 < 50 mg/L as soft water, 50 to 150 mg/L as moderately hard water and water hardness above. Based on these classifications, all the water samples analyzed were within the WHO limits as the values were found to be below the recommended value 300 mg/L and thus can be classified as soft water. Except for abattoir downhill that is moderately high, the water is suitable for domestic use in terms of hardness. This is because moderately hard water is preferred to soft water for drinking purposes as hard water is associated with low death rate from heart diseases. (Benjamin, 2010). Values above 200 mg/l for total hardness do not have any associated adverse healthrelated effects on humans but is an indication of deposits of Ca and/or Mg ions. Their presence will disallow water from forming lather with soap thereby preventing economic management of water resources (Akinbile et al; 2011).

# Alkalinity

The total alkalinity concentration of the samples ranged between 40 and 216 mg/L. Alkalinity values of 0 - 100mg/L often results in corrosive water if the pH is also low (less than 7). Alkalinity values of 100 - 200 mg/L are ideal. Alkalinity values greater than 200 mg/L can lead to deposits or scaling in the plumbing, therefore the result gotten in all the analysis is within rage hence safe for human consumption except for Abattoir downhill which is 216mg/L which may cause deposits or scaling in the plumbing. The WHO standard for alkalinity is 0-500mg/L.

A summary showing the result of analysis of soil and ground water at different distances (uphill and downhill) from the three dumpsites is shown in Table 2. From results the water samples were found to be slightly acidic with the pH values for the water samples at Abattoir ranging from 6.2-6.8, Bukuru in the range 6.4 -7.0 while that of Busa-Buji in the range 6.5-6.8. In the three sites, the farther the well away from the dumpsite the higher the pH. This is an indication of the influence of the dumpsites on the pollution of the ground water samples.

Among the examined variables, zinc has the mean concentration of 5.489 mg/L, 8.282mg/L and 1.186mg/L for Abattoir, Bukuru and Busa-Buji dumpsites respectively, while cadmium has the mean concentration of 1.036mg/L, 0.183mg/L and 0.301mg/L for Abattoir, Bukuru and Busa-Buji respectively. Furthermore, zinc also remains the most absolutely varied parameter among the examined water quality parameters within the study area. The concentration of metals in the wells also varied based on their proximities to the dumpsites as shown in Table 2. Zinc has the mean concentration of 1.353mg/L, 0.453mg/L for Abattoir downhill and uphill respectively; while Busa Buji has the mean concentration of 1.041mg/L, 0.529mg/L for downhill and uphill respectively, whereas Bukuru has the mean concentrartion of 1.098mg/L, 0.970mg/L for downhill and uphill respectively. Cadmium has the mean concentration of 0.558mg/L, 0.338mg/L for Abattoir downhill and uphill respectively, while Busa Buji has the mean concentration of 0.136mg/L for downhill and not detected for uphill. However, cadmium was not detected at Bukuru uphill and downhill. Of the three dumpsites the concentration of zinc is higher than that of Cadmium, with the highest concentration (8.282mg/L) at the Bukuru dumpsite which exceeded the WHO permissible limit (5.0mg/L). This probably might be due to the presence of a specific waste material possibly rich in zinc. (Nubi and Ajuonu, 2011).

The WHO permissible level of cadmium (0.01mg/L) is exceeded in all the three dumpsite with Abattoir dumpsite having the highest concentration (1.036mg/L). There is growing concern about the dangers of cadmium in the environment. The presence of cadmium in these dumpsites could be as a result of; rechargeable batteries are made with cadmium and nickel. Cadmium can escape from landfills (where trash is buried) and get into the ground and groundwater. From there, it can become part of the food and water that humans and animals ingest. This is in agreement with the work of other researchers (Mor et al; 2006). Therefore consumption of this water will be risky. The effects of extensive cadmium exposure is not known, but are thought to include heart and kidney disease, high blood pressure, and cancer. A cadmium poisoning disease called itai-itai, Japanese for "ouch-ouch," causes aches and pains in the bones and (http://www.chemistryexplained.com/elements/Ajoints. C/Cadmium.html)

Similarly, the WHO permissible level of zinc (5.0 mg/L) was found to be lower than stipulated limit at Abattoir, Bukuru and Busa-Buji downhill and uphill in all the sample wells of the study area (Table 2). Their presence may be attributed to the gradual leaching or water-wash of the metals from the dumpsite soil to the well water (underground water). Even though the heavy metal concentration fell below the WHO permissible limit for drinking water, it seems that their persistence in the soil of dumpsite may lead to increase uptake of this heavy metals by plants. Plants can also accumulate relatively large amounts of these elements by foliar absorption. (Mohammed, 2011).

Summarily, the downhill wells to the dumpsite had the highest concentration of metals compared to the uphill wells.

# Speciation

Metal concentration within the individual metals fractions of the sequential extraction analysis are presented in Tables 3-5 for zinc and cadmium in the three dumpsites. A summary of the percentage range of elements in samples in different phases of sequential fractionation are displayed in Table 3-5. The mean and standard deviation of results of three tests and the percentage of elements in the extracts are given for the study sites. The results are described in terms of the distribution within each fraction. The speciation patterns show broad agreement between the samples collected from the wide range of the dumpsites. (Maina et al; 2012)

Irrespective of sampling point, the distribution of metals in waste site soil samples generally followed the order below for the various metals studied in the three dumpsites.

Zn: organic > Fe-Mn oxide > residual > exchangeable > carbonate

Cd: organic > Fe-Mn oxide > residual > exchangeable > carbonate

#### Zinc

The highest concentration of zinc is associated with organic fraction in the Busa-Buji dumpsite with the value of 6.855mg/L, this could be as a result of waste containing zinc materials deposited in this dumpsite and also due to bioaccumulation or complexation process being the primary source in which trace metal get associated with organic material such as living organisms. Similar results are shown in Abattoir and Bukuru dumpsite with organic fraction having 5.565mg/L and 4.699mg/L respectively. The high concentration of zinc in both dumpsites could be as a result of discharge of waste from the city which agreed with the work of others (costal et al, 1991). Fe-Mn fraction followed organic fraction in concentration. Fe-Mn oxides are excellent scavengers of trace metals and sorption by these oxides tend to control Zn solubility in soils (Pickering, 1986). Chlopecka et al, 1996 found Zn to be strongly bound in the Fe-Mn oxide fraction. Zinc oxide has stability constants high enough to be concentrated in this fraction. In agreement with these results, several other workers have also reported the dominance of the Fe-Mn oxides bound in Zn (Ahumada et al., 1999; Narwal et al., 1999; Karczewska et al., 1996; Ramos et al., 1994)

Zinc is an important element to both plants and animals. Its bioavailability defined by the exchangeable fraction is low because of the low results for the exchangeable fraction. Zinc has the least value in the carbonate fraction in all the three dumpsites with Abattoir dumpsite having the least value of 0.819mg/L.

# Cadmium

In all the three dumpsites studied, cadmium has the lowest concentration compared to zinc. This may be as a result of low industrialization around the studied area which means most of the waste that contain higher percentage of cadmium are low in the dumpsites, this is in agreement with the work of others (Egila et al, 2013).

Cadmium is distributed more as organic, Fe/Mn oxides and as residual. Cadmium seemed to be the most mobile element. These characteristic plus hazards of cadmium to human health, suggest that frequent examination of the

levels of this element in soil samples may determine potential health hazards to residents living near the contaminated area. Such high percentage of specifically adsorbed cadmium in soil samples agrees with the findings of Harrison et al. (1981) and Baron et al. (1990). Since cadmium is a cumulative poison for mammals, its main ways of entering the environment as a waste product are especially from metal refining and electroplating and also from the chemical and paint industries. The major role for the organic fraction in the speciation of cadmium noted in the present study is consistent with the high adsorption constant of cadmium to organic matter. cadmium levels in the operationally defined extraction sequence followed the order: Cd: organic > Fe-Mn oxide > residual > exchangeable > carbonate

The high content of cadmium in the residual and Fe-Mn oxide fractions was probably due to the high association or retention ability of the mineral's crystal structure, such as with detrital silicates and resistant sulfides.

# Mobility and Availability

In the sequential extraction scheme used in the present study it is reasonable to envasage the mobility and bioavailability decreasing approximately in the order of the extraction procedure from readily available to unavailable as described by Harison and Laxen, (1981). The portion of the metals extracted with MgCl<sub>2</sub> is the one that is presumed to be readily available and decreases down the extraction process. In this work almost all the metals do not have significant fractions to consider them bioavailable (table 3-5) at almost all the locations. Hence their occurrence largely in the organic and residual phases is of very limited availability. (Maina et al; 2012).

Overall, results of the present study suggest that the mobility and bioavaibility of the two metals decline in the following order: Zn > Cd.

Results obtained in this study reveal that the quality of the groundwater resource underlying the three dumpsites has been moderately impacted.

# IV. CONCLUSION AND RECOMMENDATION

# Conclusion

This work was carried out to determine the influence of waste dumps on some underground water sources.

The outcome of the investigation carried out in this study has been very revealing in terms of the chemical and physical hazards associated with the waste from dumpsite. The characteristic nature of the waste in the dumpsite showed that the solid waste have high proportion of biodegradable organic materials that ontain polluting heavy metals. It reveals that the Well water was acidic as a result leaching from the dumpsite.

#### Recommendation

Based on the outcome of the study, the following are recommended;

- 1. Solid waste handling, controlling and monitoring techniques in Jos metropolis must be geared towards achieving quality environmental condition for man to live in.
- 2. Solid waste should be recycled instead of taking them to dump sites unless if otherwise, waste collection and management authority that is Ministry of Environment and Waste Management Board should be properly reorganized.
- 3. The communities should be educated on the need to keep their surroundings clean most especially around the wells.
- 4. The communities should be educated on the dangers associated with sighting wells close to dumpsites especially downhill.
- 5. In view of the limitation in research and screening facilities, more work is needed to establish the levels of some of the most toxic elements; Hg, Cd, Cr, Tl, Ni and As. It would also be necessary to study the speciation of soil profiles in the area to ascertain the validity of the results obtained in this study.

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