

**Full Length Research****DETERMINATION OF THE PHYSICOCHEMICAL AND HEAVY METALS CONTENT OF SOIL AROUND SELECTED METALURGICAL WORKSHOPS IN MINNA*****AJAI A. I., INOBEME A., JACOB J. O., BANKOLE M. T. and OLAMOJU K. M.***Department of Chemistry, Federal University of Technology, Minna Niger State Nigeria***ABSTRACT**

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This study investigated the physicochemical properties and heavy metals content around some metallurgical workshops in Minna metropolis Nigeria, using standard analytical methods. The pH, electrical conductivity and texture of the sampled soils and the concentrations of heavy metals which include Cu, Cr, Cd, Pb, Ni, Fe, and Zn were determined. The pH of the soils in all the sampling sites ranged from 6.83 ± 0.14 to 8.93 ± 0.18 , which implied that the soil were neutral to slightly alkaline. The soil electrical conductivity ranged from 25.00 ± 13.23 to $78.33 \pm 2.89 \mu\text{s}/\text{cm}$ and the textural characteristics of the soil samples collected were sandy-loamy for all the sampling sites. The results obtained for heavy metals analysed were Cu (4.83 ± 2.75 to $12.50 \pm 3.50 \mu\text{g}/\text{g}$); Cr (7.83 ± 2.25 to $22.00 \pm 5.77 \mu\text{g}/\text{g}$), Ni (14.33 ± 12.43 to $27.33 \pm 3.51 \mu\text{g}/\text{g}$), Fe (58.17 ± 12.07 to $77.50 \pm 2.50 \mu\text{g}/\text{g}$), Zn (9.00 ± 2.78 to $16.50 \pm 3.77 \mu\text{g}/\text{g}$) while Cd and Pb were below detection limit in all the sampling sites. The concentrations of all the metals in the entire sampling sites were below the NYSDEC standard of heavy metals in soil. The concentration of heavy metals obtained in this study does not pose harm to human health but constant monitoring is recommended.

Key words: Heavy metals, metallic workshop, analytical, concentration.

INTRODUCTION

Heavy metals make up a vague group of inorganic chemical substance that constitutes one of the major classes of environmental contaminants. The most common at contaminated sites include lead, chromium, arsenic, zinc, cadmium, copper, mercury, and nickel (GWRTAC, 1997). The term 'heavy metal' does not avail itself to a single definition. Different definitions exist, however a common convergence is that these metals have a relatively high density and are poisonous or toxic even at low concentration (Lenntech, 2004). The presence and toxicity of heavy metals in different parts of the environment has been documented by various researchers (Shrivastava and Mishra, 2011).

When some heavy metals are present in low concentrations, they do not have any toxic effect on

plants or animals but, lead, cadmium and mercury are toxic even in very low concentrations (Devries and Schutze, 2007). Soil is so prone to environmental contaminants. Basically the sources of soil contamination include domestic, agricultural and industrial activities. Presumably, it is accepted that elemental composition of soils could only be explained on the basis of local geology. It is also estimated that the contributions of metals from anthropogenic sources in soil is higher than the contribution from natural ones. Soils may become contaminated by the accumulation of heavy metals metalloids through emissions from the rapidly expanding industrial areas, disposal of metallic wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage

sludge, pesticides, and waste water irrigation (Zhang *et al.*, 2010).

Soil the thin uppermost layer of the earth surface acts as a natural reservoir for various environmental contaminants. Among the various contaminants known, heavy metals make up one of the most poisonous group, most especially due to their ability to bioaccumulate within vital tissues and organs in the bodies of organisms (Cottenie, 2005). Anthropogenic influence has continually increased the contamination of the environment. Prolonged exposure to heavy metals can cause damage and, in some cases, can be life threatening, but moderate exposures over time should also be monitored. Low concentration of heavy metals in the body can be release, but moderate to large quantities can accumulate in the kidneys, liver, bones and brain. Some of these metals are considered carcinogenic (Aloysius *et al.*, 2013a).

Though there are various work on heavy metal concentration in soil around metallic workshop in different parts of the world, there is need to continually monitor the heavy metal contents in different localities considering the health implications of the accumulation of these metals. There is also scarcity of information on the impact of metallic works on heavy metal content of soil, from this part of the country. This research is therefore aimed at assessing the heavy metals distribution in soil around some selected metallurgy workshop within Minna metropolis in order to establish their safety level for domestic and agricultural activities.

MATERIALS AND METHODS

Materials

The following materials; Conductivity meter (Kent Eil 5007) AAS (Buck Scientific Model 210 VGP) and reagents; concentrated HNO₃, H₂SO₄, and Perchloric acid (HClO₄) were used in this present study.

Study area

The metallurgy workshops used in this study are located in Minna metropolis of Niger state Nigeria. Minna is the capital of Niger state, Nigeria. It covers an area of about 88 km². It is located approximately on 9° 36' 50" and 6° 33' 25" in Sudan savannah. The area has a tropical climate, with an average annual temperature of 30°C. It is also known for its sparse rainfall and drought as such, its soil is characterised by dryness most often and the presence of spares shrubs. The

economy of the study area supports cattle trading, Shea nut processing and gold mining. Traditional industries and craft works such as leather work and metal casting are also prominent (Britannica encyclopaedia, 2007).

Method of sampling

The soil samples were collected from the following sampling areas: Shiroro Road (SR), Dutsen Kura Road (DKR), Bosso Secondary School Road (BSR), David Mark Road (DMR), and Western Bypass Minna (WBP).

The samples were collected using a soil auger at a depth of 20 cm below the soil surface. This is because heavy metals usually contaminate the upper layer of the soil at a depth of 0 - 40 cm (Krishna and Govil, 2007). This implies that high concentration of these pollutants could be present at this depth.

From each of the metallurgy workshop, four samples were collected from the four cardinal points. From each sampling position, samples were collected from, three points 10 m away from each other and the samples were neatly packaged in a polythene bags. The samples in the labeled polythene bags were carefully conveyed to the laboratory.

Sample treatment

The soil samples were air - dried at room temperature for a period of 5 days, after which they were ground into fine particles using laboratory mortar and pestle. Each sample was initially sieved with a 2 mm mesh sieve, then further pulverized and sieved with a 0.5 mm mesh sieve.

Determination of physicochemical properties of soil

The concentration of heavy metals in soil is influenced by various physicochemical characteristics of soil such as pH, particle size distribution, organic matter (OM), cation exchange capacity (CEC), and moisture content of the soil (Aloysius *et al.*, 2013a).

Soil pH

Twenty (20 g) of the soil samples was weighed into a 250 cm³ beaker and 100 cm³ of distilled water was added. The mixture was stirred at regular interval for 1 hour to ensure effective dispersal and dissolution of all soluble compounds. The pH metre was calibrated with a buffer solution (the neutral range). The pH was then recorded using a pH metre. The electrodes were rinsed with distilled water after each use.

Electrical conductivity

Twenty (20 g) of soil sample was weighed into 250 cm³ beaker and 100 cm³ of distilled water was added. The mixture was stirred at regular interval for 1 hour to ensure effective dispersal and dissolution of all soluble compounds. The conductivity meter (Kent Eil 5007) was used to record the conductivity of each sample. After each test, the electrode of the conductivity meter was thoroughly rinsed with distilled water

Soil particle size determination

The soil particle size determination was done using hydrometer method (IITA, 1979).

Digestion of samples and total heavy metal analysis

Digestion of soil sample was carried out using a mixture of concentrated nitric and perchloric acid solution in the ratio of 20:1 and in line with AOAC (2002) standard method.

One gram of the soil sample was placed in a 250 cm³ digestion flask and 100 cm³ of concentrated HNO₃ was added. The mixture was boiled gently for 30-45

minutes in a fume hood to oxidize all easily oxidizable matter. After cooling, 5 cm³ of 70% HClO₄ was added and the mixture was boiled gently until dense white fumes appeared. After cooling, 20 cm³ of distilled water was added and the mixture was boiled further to release any fumes. The solution was cooled and further filtered through Whatman No. 42 filter paper and then transferred to a 100 cm³ volumetric flask and made up to the mark with distilled water.

A reagent blank was run for the digestion procedure to correct for reagent impurities and other environmental contaminants during analysis. The analysis was duplicated in order to ensure precision in the digestion procedure and analytical instrument. The digested samples were analyzed for Pb, Cr, Zn, Fe, Cd, and Cu using atomic absorption spectrometer (AA240FS). Analysis of reagent blank was also done.

RESULTS AND DISCUSSION

The results of analyses of the physicochemical characteristics of the soil samples from the metallic workshops are depicted in Table 1.

Table 1: Physicochemical properties of soil samples within some metallic workshops in Minna Metropolis

Sampling site	pH	EC(μS/cm)	Sand%	Silt%	Clay%	Textural Class
WBP	8.93±0.18 ^c	61.67±17.56 ^b	82.80±10.00	8.00±10.00 ^a	9.20±0.00 ^a	SL
SR	7.71±0.36 ^b	33.33±11.55 ^a	81.47±5.77	8.33±11.54 ^{ab}	10.20±0.00 ^a	SL
BSS	6.83±0.14 ^a	25.00±13.23 ^a	80.13±11.55 ^{ab}	9.67±11.55 ^{ab}	10.20±0.00 ^a	SL
DMR	8.06±0.22 ^b	58.33±7.64 ^b	80.80±0.00 ^{ab}	9.67±11.55 ^{ab}	9.53±0.00 ^a	SL
DKR	8.90±0.10 ^c	78.33±2.89 ^b	79.80±26.46 ^a	10.33±5.77 ^a	9.53±15.28 ^b	SL

Key: SL = Sandy- loamy; WBP = Western Bye passes; DKR = Dutsen Kura Road; BSS = Bosso Secondary School; DMR = David Mark Road; SR = Shiroro Road
Results expressed as mean ± standard deviation. Values within the same column with different superscripts are significantly different at P = 0.05, while those with same superscripts are not significantly different at P = 0.05

pH

The pH in all the sampling points ranges from 6.3±0.14 to 8.93±0.18 which indicate that the soils were neutral to strongly alkaline. The ranges of values obtained in this study are within the ranges of 6.80 to 8.20 and 6.50 to 8.30 reported by Aruleba and Ajayi (2012) and Inobeme *et al.* (2014) respectively. It is however higher than 3.60 to 6.73 reported by Osakwe (2014). The presence and mobility of heavy metals in the soil is affected by the pH of the soil. Soil pH is a major determinant of metal mobility in the soil. The solubility of metal cation generally increases with a decrease pH.

Electrical Conductivity

The electrical conductivity ranges from 25.00±13.23 to 78.00±2.89 μS/cm. These results were lower when compared to 140±28.30 to 530± 28.20 as reported by

Inobeme *et al.* (2014), in soils around paint industries in Kaduna. The discrepancy in the electrical conductivity values could be as a result of the differences in the soluble salts content of the soil.

Particle size distribution

The result for particle size distribution of the soil shows that the sand fraction was higher than silt and clay in all the sampling sites. The result were 82.80, 10.33±5.77 and 10.20±10.00 percent for sand, silts, and clay respectively. This result for particle size from this study is compare favourably with 80.76±6.01 sand, 8.02±2.15 silt, 3.19±0.67 clay reported by Aloysius *et al.* (2013) and 82.00±2.08 sand, 5.67±0.47 silt, and 13.00±2.17 clay reported by Okoron *et al.* (2013) respectively. This shows that the sandy components of the soil are within same range.

The textural characteristics of the soil sample collected were sandy-loamy for all the sampling sites. This is expected as soil texture is maximally inherited from the soil forming materials (Tukura *et al.*, 2013). The proportion of sand, silt and clay suggest that the soil were coarse. Coarse-texture sandy soils usually have a

low supply of nutrients and moisture but provide physical support to plants. Fine textured soils on the other hand, have sufficient water holding capacity, good aeration and often a high supply of nutrients (Wilde *et al.*, 1972).

Table 2: Heavy Metal Concentrations in Different Soil ($\mu\text{g/g}$)

Sampling site	Cu	Cr	Cd	Pb	Ni	Fe	Zn
WBP	5.17±1.15 ^{ab}	9.33±2.47 ^{ab}	BDL	BDL	14.33±12.43 ^b	77.50±2.50 ^c	9.83±3.18 ^b
SR	9.17±4.65 ^{ab}	8.50±1.33 ^{ab}	BDL	BDL	14.33±13.20 ^b	60.00±4.04 ^c	10.50±2.18 ^{ab}
BSS	4.83±2.75 ^a	7.83±2.25 ^a	BDL	BDL	22.00±3.61 ^b	71.83±15.05 ^c	9.00±2.78 ^a
DMR	10.17±3.18 ^b	11.33±2.89 ^b	BDL	BDL	22.67±3.51 ^c	60.67±12.41 ^d	12.50±4.44 ^b
DKR	12.50±3.50 ^b	22.00±5.77 ^{bc}	BDL	BDL	27.33±3.51 ^c	58.17±12.07 ^d	16.50±3.77 ^b

Key: BDL = Below detection limit; results expressed as mean \pm standard deviation. Values within the same column with different superscripts are significantly different at $P = 0.05$, while those with same superscripts are not significantly different at $P = 0.05$

Copper

From Table 2, comparing the mean concentration of copper in all the sampling sites, it can be observed that it ranges from 4.83±2.75 $\mu\text{g/g}$ to 12.50±3.50 $\mu\text{g/g}$. Sampling site DKR, has the highest concentrations of 12.50±3.50 $\mu\text{g/g}$, and sampling site BSS, the lowest concentration of 4.83±2.75 $\mu\text{g/g}$. The values of Cu obtained in this study is lower than 54.04±0.23 $\mu\text{g/g}$ to 253.30±1.30 $\mu\text{g/g}$ reported by Adekeye *et al.* (2011), but higher than 0.25 to 1.20 $\mu\text{g/g}$ reported by Osakwe (2014), in soil from other areas. The concentration of copper in all the sampling sites was below the permissible limit of 270 $\mu\text{g/g}$ recommended by NYSDEC (2006) for unrestricted soils. This shows that the soil in this area is not highly contaminated by copper and is therefore safe for human activities.

Chromium

The concentration of chromium (Cr) varies in the entire sampling site. The mean concentration of Cr ranges from 7.83±2.25 to 22.00±5.77 $\mu\text{g/g}$. The highest concentration of Cr (22.00±5.77 $\mu\text{g/g}$) was at DKR. The high concentration of chromium in site DKR could be attributed to the discharge of waste products from the metallic workshop directly into the environment. The lowest concentration of Cr (7.83±2.25 $\mu\text{g/g}$) was obtained at BSS. The mean concentration of Cr obtained in this study is lower than 15.40 to 86.40 $\mu\text{g/g}$ obtained by Aruleba and Ajayi (2012), in a similar study, but higher than 1.095±0.00 to 39.975±0.129 $\mu\text{g/g}$ reported by Zauro *et al.* (2013). The concentration of Cr in sampling site DKR of 22.00 $\mu\text{g/g}$ is above the permissible level of 11 $\mu\text{g/g}$ as recommended by NYSDEC.

Nickel

The lowest mean concentration of Ni in the entire sampling site of 14.33±12.43 $\mu\text{g/g}$ was obtained from sampling sites WBP and SR. The relatively higher concentration of nickel at DKR (27.33±3.51) could be attributed to the higher pH of the soil in this area, which favours the accumulation of the metal. As pH decreases, the solubility of the metal cation increases due to desorption from soil minerals such as carbonates, metal oxides and hydroxides (Bozkurt *et al.*, 2002). The results obtained from present study are above 0.96±0.00 $\mu\text{g/g}$ reported by Adu (2012) and 5.88±3.72 to 0.49±1.20 $\mu\text{g/g}$ reported by Adeniyi and Afolabi (2002), in a similar study. This high concentration of nickel can be attributed to the fact that it is used in this type of workshop for the design of their industrial machines and electronic equipment (Adu, 2012). This high concentration could pose some negative health effect to the residence of these areas and need to be constantly monitored.

Cadmium

Cadmium and lead were below detection limit in the entire sampling site, which could be attributed to the fact that the release of the two metals (Cd and Pb) was very low or not at all the released during the metallurgical activities in the entire sampling sites. The absence of these metals in the entire sampling sites could be attributed to the fact that the usage of it could be very low in all the sampling sites. The values obtained in this study deviates from 123.00±90.50 $\mu\text{g/g}$ reported by Aloysius *et al.* (2013b) for Pb and 0.60±0.13 $\mu\text{g/g}$ for Cd respectively.

Iron

Iron has the highest concentration in all the sampling areas, but as you move farther away from the site, its concentration decreases. The high concentration of Fe in the entire sampling area may be attributed to the continual usage of iron in the electroplating and galvanizing process during their welding and construction. Also iron is a key component of most parent rocks from which the soils are formed. It has a concentration ranging from 58.17 ± 12.07 to 77.50 ± 2.50 $\mu\text{g/g}$. The highest concentration of 77.50 ± 2.50 $\mu\text{g/g}$ was obtained from sampling site WBP, and the lowest concentration of Fe (58.17 $\mu\text{g/g} \pm 12.07$) was obtained from sampling site DKR. The values reported in this study were higher than 14.50 to 8.90 $\mu\text{g/g}$ reported by Aruleba and Ajayi (2012) but lower than the 1760.00 ± 2.23 to 505.00 ± 2.07 $\mu\text{g/g}$ reported by Adekeye (2001). The concentration of Fe obtained in this study is within the acceptable limits of Fe in soil based on international standard.

Zinc

The concentration of Zn varies in all the sampling sites; this may be as a result of different types of activities going on in various sampling sites. Zn has a concentration ranging from 9.00 ± 2.78 to 16.50 ± 3.77 $\mu\text{g/g}$. The source of zinc in the sample area could be from the various metallic materials used in the areas. Also, percolation of leachates from these materials poses threats to groundwater water. The result obtained is less than 295.5 ± 50.3 $\mu\text{g/g}$ reported by Aloyius *et al.* (2013b).

CONCLUSION

The results obtained in this study showed that the pH was neutral to slightly alkaline. The soil electrical

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conductivity varied from the various sampling areas which imply that the soluble salt content of the areas differ. The textural classification was sandy – loamy for all the sampling sites. The concentration of heavy metal in the study area were in the order $\text{Fe} > \text{Ni} > \text{Cr} > \text{Zn} > \text{Cu} > \text{Cd} > \text{Pb}$. Iron had the highest concentration among the various metals investigated the mean value obtain was however within the permissible limit based on international standard. Cd and pb were not detected in the entire sampling sites. The concentrations of all the metals in the entire sampling sites were within the permissible limit as recommended by NYSDEC for soils, with the exception of Cr and Nickel which were higher in sampling site DKR.

Based on the obtained results, it is recommended that more studies should be carried out during the dried and rainy seasons in order to ascertain the effects of seasonal variation on the concentration of heavy metals in soils around metallic workshops areas. Continual monitoring of soil in such areas is also necessary in order to prevent excessive built up of these metals. Also, due to contaminants rising from these types of activities, such workshop should be located away from residential areas.

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CONFLICT OF INTEREST

None declared.

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