MOBILITY AND BIOAVAILABILITY OF HEAVY METALS IN SOILS OBTAINED FROM OPEN-AIR AUTOMOBILE REPAIR SHOP IN JOS NORTH LGA, PLATEAU STATE, NIGERIA

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ABSTRACT

In this work, the forms of Cadmium (Cd), Lead (Pb), Zinc (Zn), Copper (Cu) and Nickel (Ni) were determined in soil samples from four automobile maintenance and repair shops (garages) within Jos North LGA of Plateau State. Samples were collected from four different garages namely; Army Engineer (site A), Angwan Rukuba (site B), Farin Gada (site C) and Tudun Wada (site D). The samples collected were prepared and analyzed for the various forms (exchangeable, reducible, oxidizable and residual) of the heavy metals using the Community Bureau of Reference (BCR) sequential extraction techniques and detected using an Atomic Absorption Spectrophotometer (AAS). The result showed Zn concentration as highest in all the sites with an average of 37.62 ± 0.03 mg/kg, followed by Pb with average concentration of 3.38 ± 0.01 mg/kg, Cu and Ni with average values of 2.03 ± 0.01 mg/kg and 0.18 ± 0.00 mg/kg respectively. Cd was only found to be in the exchangeable form at site D and below the detectable limit in sites A, B, and C. However, Cu was more associated to the exchangeable forms in sites C and D while in sites A and B it was associated with the oxidizable and residual forms, respectively. The residual form of Ni was highest in all the sites while the reducible form showed highest for Pb. Zn was more associated with the exchangeable fraction in all the sites except site A which has more of the residual form. Zn and Cu were found to be mobile and bioavailable in all the sites while Ni was not. However, Pb was mobile and bioavailable in sites B and D, while Cd was only bioavailable in site D. The individual contamination factor (ICF) was highest for Cu, followed by Zn and Pb. This suggests higher risk of Zn, Cu and Pb pollution in garage soils. The work recommends in the immediate run that both in-situ and ex-situ remediation techniques be used to rectify the heavy metal contamination in this sites.

Keywords: Heavy metals; Pollution index; Garage soil; Mobility; Bioavailable; Contamination factor.

INTRODUCTION

The high influx of fairly used vehicles popularly called ‘Tokumbo’ cars from abroad into Nigeria has resulted in indiscriminate proliferation of open air automobile repair shops (garages) in the country, and
consequently an increased in automobile waste resulting in heavy metal contamination of the soil, surrounding rivers and plants. Garage wastes that could probably contribute to heavy metal contamination are; waste oils, lubricants, discarded oil filters, tyres, acid batteries, paints, gas filters, brake pads, corroded galvanized parts, bearings and nuts (FCV, 2005). Heavy Metals have severe effects on living organisms (plants, animals, humans) and ultimately on the environment. In humans, they enter into body through various ways like ingestion, skin absorption and inhalation. Bioavailability of heavy metals is the fraction of the total amount of the heavy metal in a specific environmental compartment that, within a given time span, is either available or can be made available for uptake by organisms from the direct surrounding of the organism (Olaniran et al., 2013). This indicates that, total metal concentrations do not necessarily correspond with metal bioavailability (Levanthal and John, 2013). The mobility and bioavailability of heavy metals depend on their form (chemical specie) in the soil (Kabala and Singh, 2001). The process of identifying and quantifying these different chemical species of metals in a sample is referred to as speciation (Prokop et al., 2001). Since the heavy metals exist in different forms in the soil, their determination is usually performed using sequential extraction, a method first introduced by Campbell and Tessier (1979). This consists of a series of chemical extractants, each being more drastic in action and of different nature than the previous one (Abdul-Raheem and Isiaka, 2015). The use of sequential extraction procedure, although more time consuming, gives detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of heavy metals (Tessier et al., 1979). In this study, the modified Community Bureau of Reference (BCR) sequential extraction procedure by Rauret et al. (1999) was used. This method analyses different fractions of metals in the soil: acid-extractable (water soluble, exchangeable and bound to carbonates), reducible (bound to Fe and Mn oxides), oxidizable (bound to sulphides and organic matter), and residual (Saracoglu et al., 2009; Ražić and Dogo, 2010).

**MATERIALS AND METHODS**

**Materials**

All reagent used were of analytical grade and sourced from chemical vendors within Jos City. Atomic absorption spectrophotometer (AAS) model 210VGP (Buck Scientific) was used for metal analysis.

**Study area**

Jos North Local Government Area is the capital city of Plateau State and is located on latitude 9°56’21.7’’North and longitude 8° 54’8’’ East of Greenwich meridian (GM). Samples for analysis were collected from four different automobile garages situated in different locations of Jos North LGA indicated in Figure 1. The four locations are; Army Engineer, Angwan Rukuba, Farin Gada Market and Tudun Wada. All these automobile garages have hosted these activities for more than fifteen (15) years.

![Map of Jos North Showing Sampling Areas. Source: Mafuyai et al. (2014)](image)

**Sampling and sample Preparation**

Samples were collected into new polyethylene bags within depths range of 1-10 cm from all automobile garages using the stratified random sampling design. The samples collected were air-dried for three days and those collected at the same garage site were combined and homogenized to form a representative sample for that site. This was done to avoid bias and give a good representation of each garage site. All representative samples were pulverized to powder using an agate mortar and pestle to particle sizes of nanometers range then collected into polyethylene
bags labeled A, B, C, and D, to represent samples from the automobile garages of Army Engineer, Angwan Rukuba, Farin Gada, and Tudun Wada respectively.

**Determination of physicochemical characteristics of soil samples**

The physicochemical parameters of interest were; pH and soil organic matter (SOM).

Soil pH was determined (1:1 w/v) using digital pH meter. The soil organic matter was determined according to the method reported by Osuji and Adesiyan (2005).

**Sequential extraction procedure**

The modified Community Bureau of Reference (BCR) three-step sequential extraction procedure described by Nemati et al. (2011) was used to extract the various forms of heavy metals in the soil samples. The sequential extraction was done altering the acidic and basic conditions of the media to aid in the separation based on the form of heavy metals. The atomic absorption spectrophotometer (AAS) was used to determine the concentration of individual heavy metals; cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn), in each of the fractions. While, percentage recovery of the sequential extraction was calculated using the formula according to Wali et al. (2014).

\[
\text{Recovery (\%) = \frac{\text{Step1} + \text{Step2} + \text{Step3} + \text{Step4} \times 100}{\text{Step5}}}
\]

**Determination of Individual Contamination Factor, Global Contamination Factor and Pollution Index**

Individual contamination factors (ICFs) and the global contamination factor (GCF) evaluates the degree of toxicity or risk to the environment and the bioavailability of trace metals in the soil relative to its retention time. ICFs were calculated for the five metals at all sites as the sum of the concentrations of trace metals extracted in the first three steps (exchangeable/soluble, reducible, and oxidizable fractions) divided by the concentration in the residual fraction (Nemati et al., 2011). The GCF was calculated by summing the ICFs of all the heavy metals which includes; Cd, Cu, Ni, Pb and Zn (Aiju et al., 2012). Similarly, the Pollution Index is calculated using the expression below, reported by Ubuoh et al. (2019).

\[
\text{C} = \frac{\text{Concentration of metal in soil}}{\text{Target value for reference table}}
\]

**RESULTS AND DISCUSSION**

**Soil Characteristics**

The results obtained for selected physicochemical properties of soil samples are summarized in Figure 2. The pH in the soil samples were in slightly alkaline condition and ranged from 8.15 ± 0.02. The values were higher than those reported (Samkwar, 2015 and Tukura et al., 2007). This type of alkalinity is common in anaerobic soils as a result of oxygen deficiency in the soil caused by spilled engine oils (Osakwe and Egharevba, 2008). Heavy metals are mostly insoluble and hence unavailable at high pH (Munoz-Melendez et al., 2000). Soil alkalinity also increases the adsorption capacity of oxides, including manganese and iron hydroxides, which are strong natural adsorbents (Bozkurt et al., 2000). Values for soil organic matter (SOM) ranged from 2.023% to 9.177% as seen in Figure 2. SOM plays an important role in metal binding (Pam et al., 2013). From the results, site C has the highest SOM (9.177%) while site D had the least (2.023%). SOM immobilizes heavy metals at strongly acidic conditions by forming insoluble organo-metallic complexes and mobilizes metals at weakly acidic to alkaline conditions by forming soluble organic metal complexes (Pam et al., 2013). The distribution of pH and SOM among the garage sites showed a reasonable impact of anthropogenic pollution by spilled engine oil and other vehicular waste materials.

**Total Metal Concentration and Pollution Index**

The total metal concentration and pollution/contamination index of Cd, Cu, Ni, Pb and Zn were as
given in Table 1. The pollution/contamination index expresses the potential threat posed by the heavy metals (Chokor and Ekanem, 2016). The work of Lacatusu (2000), established that the contamination/pollution index value is directly proportional to their level of contamination and pollution of specific metal species. Traditionally, the data obtained from calculation of the contamination/pollution index is grouped into different grades ranging from very slight contamination to excessive pollution (Table 1 and 2).

Table 1: Total Metal Concentration (mg/kg) and their corresponding Pollution Indexes (%) and global contamination factor (GCF) of the Sample Sites.

| Sample Site | Cadmium (Cd) | Copper (Cu) | Nickel (Ni) | Lead (Pb) | Zinc (Zn) |
|-------------|--------------|-------------|-------------|-----------|-----------|
|             | TMC          | Pi          | TMC         | Pi        | TMC       | Pi        | TMC       | Pi        | GCF       |
| A           | BDL          | 1.23±0.01   | 0.82        | 0.11±0.03 | 0.54      | 0.31±0.00 | 6.26      | 25.54±0.05 | 5.10      | 5.66      |
| B           | 0.58±0.01    | 0.39        | 0.29±0.02   | 1.45      | 11.42±0.02 | 228.48   | 41.49±0.01 | 8.30      | 5.63      |
| C           | BDL          | 5.46±0.02   | 3.64        | 0.21±0.06 | 1.06      | 1.21±0.02 | 24.20     | 37.80±0.04 | 7.56      | 10.58     |
| D           | 0.01±0.02    | 0.60        | 0.84±0.01   | 0.56      | 0.10±0.05 | 0.51      | 0.58±0.01 | 11.64     | 45.66±0.03 | 9.13      | 17.18     |
| *FEPA       | 0.003        | 1.00        | 0.02        | 0.01      | 3.00      |

TMC = Total metal concentration; Pi = Pollution index; BDL = Below detectable limit; *FEPA (1991) MAL Standards in Sediments (mg/kg)

The total concentration of Cd in the four sample sites were most likely below the detection limit of the AAS, except for site D with a TMC of 0.01 mg/kg which is slightly above the maximum allowed limit (MAL) of 0.003 mg/kg in soils. Cd is widely reported to be released from wear and tear of rubber in small quantities and also from the waste engine oil in the small amounts (Aikpokpodion et al., 2012). It is very soluble and easily leached away or swept by rain water, which explains why it was not detected in most of the samples.

Apart from the low detection limit of the instrument used, it might have been low due to its occurrence in forms that may be not detectable by the instrument. Cd concentrations were therefore very low and did not yield enough data for studying its mobility and bioavailability.

Table 2: Pollution Index (Pi) for heavy metals

| Range of Pollution Index | Significance         |
|-------------------------|----------------------|
| <0.1                    | Very slight contamination |
| 0.1-0.25                | Slight contamination  |
| 0.26-0.50               | Moderate contamination|
| 0.51-0.75               | Severe contamination  |
| 0.76-1.0                | Very severe contamination |
| 1.1-2.0                 | Slight pollution      |
| 2.1-4.0                 | Moderate pollution    |
| 4.1-8.0                 | Severe pollution      |
| 8.1-16.0                | Very severe pollution |
| >16.0                   | Excessive pollution   |

Source: Lacatusu (2000)

The total concentration of copper in the four sample sites ranges between 0.58±0.00 and 5.46±0.02 mg/kg. The concentrations in sites A, B and D were found to be below the maximum allowed limit of copper in soil which is 1.00 mg/kg (FEPA, 1991), while only that of site C was slightly higher than the MAL set by FEPA. This result is in agreement with works done by Katana et al. (2013) who reported Cu concentration to be highest in the residual and oxidizable fraction. This high concentration of Cu in the residual and oxidizable (organic bound) fractions indicates its strong ability to form complexes with organic matter thereby reducing its mobility and phytotoxicity (Kashem et al., 2007). The contamination / pollution index values showed that; sites A, B, C, and D were very severely contaminated, moderately contaminated, moderately polluted, and severely contaminated, respectively (Table 2). For Ni, the total concentration ranges from 0.10±0.05 to 0.29±0.02 mg/kg. With site A and D having concentrations below the MAL of 0.02mg/kg set by FEPA while site B and C had concentration levels slightly higher than the FEPA limit. The contamination/pollution index values showed that site A and D was severely contaminated while site B and C was slightly polluted. The concentration of Pb in the four sites ranged from 0.03±0.00 to 11.42±0.02 mg/kg with the highest concentration found in Angwan Rukuba garage site while the lowest was at Tudun Wada garage. All the sites had Pb concentrations above the MAL (0.01 mg/kg) set by FEPA. The contamination/pollution index values showed that Army Engineer garage was severely polluted while the other garage sites were excessively polluted, with the Angwan Rukuba garage being the most excessively polluted. For Zn, the total metal concentration ranges between 25.54±0.05 in
Army engineer garage to 45.66±0.03 mg/kg in Tudunwada garage. This level is however low as compared to other studies by Pam et al. (2013) and Yahaya et al. (2010). The contamination pollution index value showed that site A and C were severely polluted while sites B and D were very severely polluted. The relatively high concentration of these heavy metals in the study area have provide a useful hint to fact that the soil are polluted and provides a potentials threat to public health, as majority of people working or residing in these places rely on ground water obtained from these places as source of their drinking water.

CONCLUSION

The impact of the activities within the study area is indicated on the increase in the concentration of the heavy metals detected. This is seen from concentration of Ni, Pb and Zn investigated in this study, which was found to be above the MAL set by major regulatory authorities (FEPA). Only Cd in all the sites was found to be below the concentration set by FEPA in sediment. It is obvious that the workers within these areas are at health risk arising from exposure to these chemical substances. Being heavy metal pollution in soil contaminated with oil and greasy waste, the work recommends in the immediate run, both in-situ and ex-situ remediation techniques to rectify the heavy metal contamination in this sites. In a long run auto mobile garages should be re-located from densely populated locations to secluded places designed with facilities for collection and discharge of greasy, oily and other automobile related waste.

ACKNOWLEDGEMENT

The authors would like to thank the Management and Staff of University of Jos, Nigeria for allowing free access to Laboratory facilities needed for this work.

CONFLICT OF INTEREST

None declared.

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**Article’s citation**

Gushit JS, Omadefu KO and Egila JN (2019). Mobility and bioavailability of heavy metals in soils obtained from open-air automobile repair shop in Jos North LGA, Plateau State, Nigeria- *Ew J Anal & Environ Chem* 5(1): 198 – 203.

**Authors’ contributions**

GJS and OKO conceived and designed the study. GJS and OKO carried out all field, laboratory work and conducted literature search and review. GJS and EJN interpreted data. GJS drafted the manuscript. All authors reviewed and approved the final manuscript.