

DETERMINATION OF HEAVY METALS IN THE SOIL AND VICINITY GROUNDWATER OF AUTOMOBILE MECHANIC WORKSHOPS

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Abstract

The aim of this project was to determine the presence of heavy metals in soil and ground water at automobile mechanic workshops located in Owo, Ondo state Nigeria; compare the results with the guideline and results from various literatures and studies, draw conclusions and make recommendations. Soil and ground water samples from 3 automobile mechanic workshops were analyzed for selected heavy metals namely; Cadmium (Cd), Lead (Pb), Copper (Cu) and Zinc (Zn). Soil samples were obtained in triplicates and at the depth of 0 to 10cm, 10 to 20cm and 20 to 30cm. Water samples were obtained from dug wells at the sites. The highest Cadmium content was obtained at the automobile mechanic workshop at Ikare junction (1.27 ± 0.014) Lead and Copper had their highest content in Owaluwa (123.1 ± 0.565) and (95.285 ± 0.756) respectively. Also, Zinc had its overall highest value in the automobile workshop at Owaluwa (289.57 ± 0.070). The level of these heavy metals in the soil was significant when these values were compared to the regulatory limits. Compared to the limits set by WHO for drinking water, values measured in the ground water samples were in the same range with those limits set for heavy metals with the exception of Zn where some of the values were higher than the limits. The recommendations of this study include execution of some phyto-remediation measures at the automobile mechanic workshops, strict compliance to regulatory limits in sludge to be released from these workshops into the environment and the enforcement of other environmental protection regulations to checkmate the activities of the automobile mechanic workshops. Findings of this study will be of immense help to researchers and environmental regulators working in this area of interest in developing countries.

Keywords: Heavy metals, ground water, automobile, mechanic, workshops and Soil

1. INTRODUCTION

Heavy metals are chemical elements mostly within density greater than 4g/dm^3 found in all kinds of soils, rocks, and water in terrestrial and fresh water ecosystem (Lacatusu, 1998). They occur in typical background concentrations in these ecosystems. However, anthropogenic releases can result in higher concentration of these metals relative to their normal background values, when these occur (Tam and Wong, 2000; Yuan *et al.*, 2004), heavy metals are considered serious pollutants because of toxicity, persistence and undegradable condition in the environment, thereby constituting threat to human beings and other forms of biological life (Nwuche and Ugoji, 2008). Automotive service and repairs shops are the largest small quantity generators of hazardous waste. Auto – repair shops create many different types of waste during their daily operations (Mohiuddin *et al.*, 2010). These include use of oil and fluids, dirty shop rags, used parts, asbestos from brake pads and waste from solvents used for cleaning parts (Aina *et al.*, 2009; Mohiuddin *et al.*, 2010).

Some of the heavy metals such as Copper (Cu), Nickel (Ni) and Zinc (Zn) are essential to plants and animals in very low concentration by serving as components of enzymes, structural proteins, pigments and also helping to maintain the ionic balance of cells (Kosolapov *et al.*, 2004). Large quantities of pollutants have continuously been introduced into ecosystems as a consequence of urbanization and industrial processes, as observed by Begum *et al.*, (2009), metals are persistence pollutants that can be biomagnified in the food chains, becoming increasingly dangerous to human beings and wildlife. Therefore, assessing the concentrations of pollutants in different component of the ecosystem has become an important task in preventing risk to natural life and health.

This research work is aimed at determining the presence of heavy metals in the soil of a mechanic workshop and the ground water in its vicinity.

2. MATERIALS AND METHODS

Samples collection

Soil sample

Soil samples were collected from automobile mechanic workshops at three different locations namely; Ehin ogbe, Ikare Junction and Owaluwa in Owo town, Ondo State Nigeria. The samples were obtained in triplicates at each site at the depth of 0 to 10cm, 10 to 20 cm and 20

to 30cm, using a depth calibrated soil auger. Each sample was immediately placed in a fresh plastic bag and tightly sealed then transported to the laboratory for analysis.

Water sample

Water samples were collected from three hand dug wells at different distances (10m, 15m and 20m) away from the workshops, following standard water sampling procedure. Each sample was directly collected into a factory-fresh 1.5L plastic bottle which has been previously washed with 1:1HNO₃ with cap securely tightened. Few drop of HNO₃ was added to the samples to prevent loss of metals, bacteria and fungal growth. Temperature and pH of the water samples were taken at the time of collection. After collection, the bottles were placed inside ice coolers for transportation to the laboratory where they were then transferred to the refrigerator for analysis.

Soil and water analysis

Soil analysis

The soil samples was spread on a cleaned plastic sheet placed on a flat surface and air-dried in an open air in the laboratory under room condition for 24 hours. The soil was grinded to remove lumps and then sieved on a 2mm sieve. 5g of the sample was taken from the sieved soil sample and put into a beaker. 10ml of nitric /per chloric acid, ratio 2:1 was added to the sample. The sample was digested at 105⁰C. HCl and distilled water, ratio 1:1 was added to the digested sample and the mixture was transferred to the digester again for 30min. The digestate was removed from the digester and allowed to cooled at room temperature. The cooled digestate was washed into a standard volumetric flask and was made up to mark with distilled water.

Determination of heavy metals (Pb, Cu, Cd and Zn) in soil samples was done in duplicate in an Atomic Absorption Spectrophotometer (AAS Model 210/211 VGP) after calibrating the equipment with different standard concentration of each element prior to the introduction of the sample solution. The absorbance reading was obtained at the wavelength of each element.

Water analysis

Water samples was digested by measuring 100ml into a beaker and 5ml concentrated HNO₃ was added. The sample was boiled slowly on a hot plate and then evaporated to about 20ml. 5ml concentrated HNO₃ was further added and covered with a watch glass and heated. Concentrated HNO₃ was continually added and heated until the solution appears light coloured and cleared. It indicated that the digestion is completed. 2ml concentrated HNO₃

was added and slightly heated to dissolve the remaining residue. The beaker and watch glass were rinsed with distilled water and it was then transferred into a 50ml volumetric flask, allowed to cooled and was made up to mark with distilled water.

Determination of heavy metals (Pb, Cu, Cd and Zn) in water samples was done in duplicate in an Atomic Absorption Spectrophotometer (AAS Model 210/211 VGP) after calibrating the equipment with different standard concentration of each element prior to the introduction of the sample solution. The absorbance reading was obtained at the wavelength of each element.

3. RESULTS AND DISCUSSION

RESULTS

The main concentrations of heavy metals (Cd, Pb, Cu and Zn) found in the soil samples taken from an automobile mechanic workshops at Eyinogbe, ikare junction and Owaluwa in Owo, Ondo State and groundwater samples from hand dug wells in the vicinity of these automechanic sites are shown in Tables 4.1, 4.2, 4.3 and 4.4 respectively.

Table 4.1: Main concentration (mg/g) of soil from three different depths at the automobile mechanic workshop at Ehinogbe.

Depth	Cd	Pb	Cu	Zn
0 to 10cm	nd	13.3±0.565	16.545±0.077	84.685±0.530
10 to 20cm	nd	48.1±0.282	6.51±0.084	18.915±0.176
20 to 30cm	nd	16.75±0.636	18.175±0.120	4.155±0.021

Table 4.2: Main concentration (mg/g) of soil from three different depths at the automobile mechanic workshop at Ikare junction

Depth	Cd	Pb	Cu	Zn
0 to 10cm	1.27±0.014	100.65±0.919	75.565±0.770	207.88±2.206
10 to 20cm	0.855±0.021	53.8±0.424	57.36±1.470	189.91±1.258
20 to 30cm	0.735±0.021	55.8±1.414	63.095±1.393	139.93±1.145

Table 4.3: Main concentration (mg/g) of soil from three different depths at the automobile mechanic workshop at Owaluwa

Depth	Cd	Pb	Cu	Zn
0 to 10cm	0.16±0.014	123.1±0.565	95.285±0.756	286.10±0.212
10 to 20cm	nd	59.65±0.636	65.94±2.248	289.57±0.070
20 to 30cm	nd	26.00±0.282	23.745±0.007	93.11±0.212

Table 4.4: Main concentration of heavy metals (mg/l) in water samples from hand dug wells at the vicinity of automobile mechanic workshops in Owo.

Sample	Cd	Pb	Cu	Zn
A _E	nd	nd	0.041±0.0017	0.342±0.000
B _E	nd	0.457±0.0106	0.0505±0.0028	0.465±0.00106
C _E	0.092±0.109	0.295±0.014	nd	0.901±0.0021
A _I	0.0075±0.000	nd	0.044±0.00106	0.284±0.0342
B _I	nd	0.2825±0.0176	0.297±0.0053	16.551±0.175
C _I	nd	0.186±0.014	0.034±0.00106	0.315±0.0056
A _O	nd	1.41±0.028	0.431±0.254	152.44±0.275
B _O	nd	nd	nd	0.924±0.0007
C _O	nd	0.1425±0.0035	0.014±0.00106	0.582±0.0028

- nd = not detected
- A ,B and C represents hand dug wells at 10m, 20m and 30m respectively from the automobile mechanics workshops.
- Subscripts E, I, and O represents Eyinogbe, Ikare, and Owaluwa respectively.

4. DISCUSSION

Heavy metals in soil samples at the automobile mechanic workshops were analysed. From Table 4.1 to 4.3, the soil samples had a very high concentration of Zinc (Zn) at all the depths under study. Cadmium (Cd) had the least concentration. The concentrations of Copper (Cu) and Lead (Pb) varied at the different depths and also at the different auto mechanic sites. Also, the concentration of Pb and Zn decreased with depth i.e the highest concentrations were recorded on the soil surface (0 to 10cm) while the least concentration was recorded in the 20 to 30cm depth except at Ehinogbe where Pb concentration was least in the topsoil. This shows a linear correlation of reduction with depth through the soil layers. This observation of

higher retention of Pb and Zn in the top layers of the soil agrees with the findings of Davies (1995) that lead is especially prone to accumulation in the surface horizons of soil due to their low water solubility and this results in low mobility. The exception to this is the concentration of Zn ($289.57 \pm 0.070 \text{ mg/g}$) in the 10 to 20 cm depth at Owaluwa (table 4.3). Lead occurs naturally in all soils, in concentrations ranging from 1 to 200 mg.kg^{-1} , with a mean of 15 mg/kg (Chirenje *et.al.*, 2004). Some high concentrations of lead have been reported in literature and most were in one way or the other connected to manufacturing sites of vehicle batteries. Adie and Osibanjo (2009) found a range of 243 to $126,000 \text{ mg/kg}$ in the soil from the premises of a battery manufacturing plant. The high concentration in the topsoil (depth 0 to 10 cm) shown in table 4.3 might be due to ongoing lead deposition in soils in the mechanic workshop and its consequent retention in the soil upper layers. This provides further evidence that Pb is gradually building up in the soil locations of these mechanic workshops. A ready source of lead (Pb) is vehicle batteries which are repaired or otherwise handled in these locations. Pb has been considered a hazard when it is equal to or exceeds 400 mg/kg in bare soil (USEPA, 2008).

Cadmium was not detected in the soils at all depths, at the Eyinogbe mechanic site (table 4.1). At the Owaluwa site, Cd was only present in the topsoil at very minute concentrations, 0.16 ± 0.014 (table 4.3). Cd was found in the soil samples analysed at all depths at the mechanic workshop located at Ikare junction. The low concentration of Cd at all the sites may be due to the following reasons: The first is that the aggregate Cd levels in the sludge applied to the soil may be low. However, since these are auto mechanic workshops which have existed for several years, the possibility of that is remote. The second explanation is the mobility of Cd through the soil layers. Cadmium tends to be more mobile in the soil system than many other heavy metals (Alloway, 1995). Although, the measured values show a range of 0.16 ± 0.014 to $1.27 \pm 0.014 \text{ mg/g}$ (Table 4.1 and 4.3). The majority however are less than 1.0 mg/g . Several of these findings find support in a study by Kabala and Singh (2006) which investigated the vertical distribution of Cd as well as its potential mobility in soil profiles exposed to copper smelter emission. They found that Cd ranged from 1.06 to 1.40 mg/g overall. The depths at which the minimum and maximum concentration of Cd was found varied from site to site in the three different sites where the soil samples were obtained. It was established that significant Cd leaching from surface horizons to subsoil and concluded that mobility of Cd is relatively high in surface horizons. It is posted that Cd is more mobile than either Cu or Pb. Cd was found to be below detection limit in all the samples analysed. A

third reason might be due to WHO regulation that shows the poisonous nature of Cd and thereby advised that Cd should be worked with at very low concentrations which made many car manufacturing industries to reduce the amount of Cd in their raw materials. Absorption/desorption of Cadmium is about 10-fold more rapid than for Lead (Curtis and Smith, 2002). Chronic cadmium exposures results in kidney damage, bone deformities and cardiovascular problems (Goyer and Clarkson, 2001).

From Table 4.1, 4.2 and 4.3, it shows that Cu values ranged from 16.545 ± 0.0777 to 95.285 ± 0.756 mg/g and these were recorded at the depth of 0 to 10cm in Table 4.3 and 4.1 respectively. Taking a further look at the table of results, it was observed that the top soils had the highest concentrations of copper while there were variations between the 10 to 20cm and 20 to 30cm depth. Another study noted that average copper concentration in Canadian soil is estimated to 20 mg/kg with a range between 2 and 100mg/kg (British Columbia Ministry of Environment, Land and Parks, 1992). These values were compatible with the values obtained in this study as shown in Table 4.1, 4.2 and 4.3.

High concentration of copper on these auto-mechanic location are traceable to the use of copper conductor and wires, tubes, solders and myriads of other maintenance items made from copper. According to Lenntech (2009) when copper ends up in soils, it strongly attaches to organic matter and mineral. As a result, it does not travel very far after release. Perhaps, this explains why the highest values of Cu recorded on most of the locations were in 0 to 10cm depth. As a result of this limited mobility, applied copper tends to accumulate in soil (Slooff *et al.*, 1989). On Cu rich soils, only a limited number of plants have a chance of survival. In surface water, copper can travel great distances, either suspended on dust particles or as free ions. Soils types have finite holding capacities from copper ions, and leaching can occur when Cu levels applied exceed this capacity (Adriano, 1986).

Zinc concentrations ranges between 4.155 ± 0.022 mg/g and 289.57 ± 0.070 mg/g which is found in Table 4.1 and 4.3 respectively. In Table 4.3 the soil depth, 10 to 20cm has the highest concentration of Zn while in Table 4.1 and 4.2 the highest concentrations were found in the 0 to 10cm depth. The least concentration of Zn was recorded in the 20 to 30cm depth in Table 4.4. The concentrations of Zinc found in this study agree with those reported in literature. For instance, Lenntech (2009) pointed out that Zinc content in the soil can be as low as 2.5mg/g or as high as 450mg/g, although the average is about 50mg/kg. Zinc is known to accumulate in plants with intake of too large quantities of Zn from plant grown on Zinc-rich soil (such as tea, beans, vegetables), there are lower chances of developing cancer of the

lung, nose, larynx and prostrate as well as respiratory failures, birth defects and heart disorders (Lenntech 2009). Uncontaminated water usually contains about 300ng Zn/dm^{-3} . Farm soils contain approximately 5 to 1000mg/kg of Zn in soil, but the Zn concentration can reach up to 2400 to $53,000\text{mg/kg}$ of Zn in soil near metal refineries and in dried sludge, respectively. Exposure by inhalation, ingestion or skin contact occur in Zinc and Zinc alloy production plants as well as in electroplating, grinding and cutting operations which are done in automobile mechanic workshops.

All water samples analysed in this project are within the limit and therefore pose no danger to consumers as far as these specific heavy metals are concerned, except Zn which recorded highest values in the hand dug well, 20m away from the mechanic site at Ikare junction. The concentrations of Pb obtained in soil samples in this study were lower than the concentrations obtained by Adelekan and Abegunde (2011) and Ipeaiyeda and Dawodu (2008).

Sample B_I and the well which is 10m away from the mechanic site at Owaluwa Sample A_O shown in Table 4.4. These are far above the WHO maximum permissible limits and it may be due to the contamination from other sources apart from the mechanic workshops. Zinc is a trace element that is essential for human health and its shortage can cause birth defects. Zinc may also increase the acidity of water. The concentration of Lead recorded in the water sample from the well, 10m away from the mechanic workshop at Owaluwa (Sample A_O) recorded in Table 4.4, and was also higher than the permissible limits given by W.H.O. The deleterious health effects of high concentration of heavy metals in drinking water are also given by WHO.

5. Conclusion and recommendation

Higher concentrations of Zn, Cu and Pb were found in soil samples at the automobile mechanic workshops when compared to some literatures and previous studies. No significant difference was observed in the concentrations of Cd in the soil samples. However, it was found that Zinc had the highest concentration in the soil samples while Cd had the least and the order observed for this study is $\text{Zn} > \text{Cu} > \text{Pb} > \text{Cd}$.

Some of the values of Zn obtained from this study were above the regulatory limits. The Cd, Cu and Pb concentrations found in the water samples are in accordance with the WHO maximum permissible limits for heavy metals in water with the exception of Zn which exceeded the maximum limit in some water samples.

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