

LEVELS OF SELECTED HEAVY METALS IN SOIL SAMPLES AT AUTOMOBILE MECHANIC WORKSHOPS IN LOKOJA, NIGERIA

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ABSTRACT

The present study provided the level of heavy metal levels in two distinct soil depths, namely 0-15 cm and 15-30 cm, at automobile mechanic workshops in Zawangi, Lokongoma Phase I and Lokongoma Phase II of Lokoja metropolis, Nigeria. The study was also subjected to sequential extraction using a modified Tessier's procedure on soil samples to determine the mobility of metals in the soils. The results showed that the soil sample fractions from the study area exhibited very high levels of contamination with Zn, Pb, Cd, Fe and Ni across the three sites in relation to their depths. However, in residual, water soluble and exchangeable fractions, high contamination levels of Ni, Cd and Fe were not recorded in all locations across the two depth profiles of the soil samples. Overall, all fractions were found to be bonded with heavy metals which indicated that heavy metal contamination increases as soil depth increases in all locations. The total heavy metal concentrations exceeded WHO 2011, regulatory limits for safe agricultural soil, which poses a health risk.

Keyword: Bioavailability, heavy metals, sequential extraction, soil.

INTRODUCTION

The escalation in automotive maintenance and repair establishments and their operations in Nigeria are in part as a result of the rise in demand for private vehicles, a large portion of which are of foreign origin. This has led to the issue of soil contamination in several urban areas. Automobile waste consists of waste oil, oxidation byproducts and metallic fragments that result from the wear and tear of machinery, organic and inorganic chemicals found in oil additives, used batteries and metals [1]. The existence of trace elements in soil is rapidly becoming a global concern, particularly since soil is a vital component of both rural and urban environments [2]. The non-degradable heavy metals like cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb),

manganese (Mn), nickel (Ni), and zinc (Zn) often used as additives in some lubricants and gasoline can pose a threat to groundwater due to soil percolation of leachates from these substances [3, 4]. The co-occurrence of toxic heavy metals and hydrocarbons (HCs) at numerous contaminated mechanics sites in Nigeria and other developing nations poses a severe and worrisome threat to the environment [5].

There have been studies conducted in the Southern region of Nigeria regarding soil and vegetation pollution from spent oil [1]. Also, studies have shown that automobile workshop may increase heavy metal concentration in soil [1, 5]. This may have effects on the soils, crops and human health [4]. Therefore, the environmental impacts of waste from automobile workshop are greatly influenced by their heavy metal contents. As a result, this study aimed to investigate the soil pollution resulting from heavy metals in spent lubricating oil in the vicinity of selected mechanic workshops within the Lokoja Metropolis of North Central Nigeria.

MATERIALS AND METHOD

Description of Study Area

The geographical location of the study area, as depicted in Figure 1, is situated within the latitudinal coordinates of 70461 and 70521N and longitudinal coordinates of 60381 and 60461E. Lokoja, the focal point of this study is the capital of Kogi State and confluence town within Nigeria. The town experiences a distinctive wet and dry seasons, with an annual rainfall range of 804.5-1767.1 mm [6]. The average annual temperature is estimated to be around 27.7 ^oC, with a relative humidity of 30% in dry seasons and 70% in wet seasons. Furthermore, the town average daily wind speed measures 89.9 km/hr [6], while the average daily vapour pressure is approximately 26 Hpa. The most noteworthy hydro-geological characteristic of this area is the confluence Rivers, River Niger and River Benue. The region is also situated in Guinea Savanna, with the presence of gallery forests along watercourses [6]. The land rises from about 300 m along the Niger valley to between 300-900 m above sea level in the uplands. In terms of population, Lokoja has a population of 82,483 in 1991 [7].

Sample Collection

Soil samples were procured from three automobile mechanic workshops situated in Zawangi (ZW), Lokongoma Phase 1 (LP1) and Lokongoma Phase 2 (LP2) sections of Lokoja town. For the collection of samples, the soil surface was cleared employing a hand trowel and subsequently

gathered with the aid of a stainless steel spoon. In order to maintain the integrity of the samples, the hand trowel and spoon were rinsed with distilled water after each collection.



Figure 1: Map of Lokoja showing Soil Sampling Points (Source: Modified from the Administrative Map of Lokoja L.G.A.

The number of sampling points was dependent on the size of the mechanic sites and consequently, each of the three mechanics was partitioned into four (4) quadrants. Samples were obtained from two distinct depths of 0-15 cm, and 15-30 cm. Additionally, within a location; samples were collected from three different points at depths of 0-15 cm and 15-30 cm, referred to as topsoil and sub-soil, respectively [4, 8]. The soil samples that were gathered were ground using a porcelain mortar with pestle and subsequently subjected to air-drying for a week to eliminate any traces of moisture. Furthermore, they were sifted through a 2 mm stainless steel sieve [9]. These soil samples were then properly labeled and stored in polythene bags for further analysis [10].

Heavy Metal Analysis

The collected specimens were subjected to heavy metal analysis, as documented in prior research [11]. Specifically, a precise quantity of 5 grams of air-dried soil sample was measured and placed into a 25 ml polypropylene centrifuge tube. Sequential extractions were conducted, whereby 5 grams of air-dried soil sample, sieved to a diameter of 2 mm, was weighed and added to a pre-weighed centrifuge tube. Next, 25 ml of distilled water was introduced and the resultant suspension was vigorously agitated for 120 minutes. Subsequently, centrifugation was performed at a rate of 3500 rpm for 10 minutes, followed by filtration through Whatman No. 42 filter paper

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under vacuum into a 100 ml vial. This fraction was denoted as SOL, which served as water extraction F1. The residue from F1 was extracted by adding 25 ml of 0.25 M K₂SO4. The suspension was shaken for duration of 16 hours, centrifuged for 10 minutes at 3500 rpm, and filtered through Whatman No. 42 filter paper into a 100 ml vial. The resulting fraction was labeled as EXCH (F2). The extraction of the residue from F2 was carried out through the addition of 25 ml of 0.05 M Na₂EDTA. Following this, the suspension underwent a period of shaking for duration of 8 hours, followed by centrifugation for 10 minutes at 3500 rpm. The resulting solution was then filtered through Whatman No. 42 filter paper and collected in a 100 ml vial. This fraction was given the designation of CARBON (F3). Subsequently, 25 ml of 0.5 M NaOH solution was added to the residue from F3, after which it was shaken for a period of 16 hours. The mixture was then centrifuged at 3500 rpm for 10 minutes and the supernatant was filtered through Whatman No. 42 filter paper into a 100 ml vial. This fraction was given the designation of ORG (F4). Determination of the residual fractions of the respective metals was carried out through the computation of the sum of fraction F1-F4, which was then subtracted from the respective total metal concentration [12]. Determined through HClO₄-HNO₃-H₂SO₄ digestion F5 [13]. At the conclusion of the extraction period, the individual metals present in the filtrates were determined through the use of varian model AA240FS atomic absorption spectrophotometer (AAS).

Quality assurance validation

Validation of the technique for the metal determination was conducted on digested soil samples. This was done by spiking the pre-digested samples with multi-element standard solution (0.5 mg/l of Cd, Fe, Ni, Pb and Zn) as reported by Awofolu [8].

RESULT AND DISCUSSION

Quality Assurance

The reports on the validation of a technique utilized for the determination of metals in soil samples that have been subjected to digestion. Table 1 illustrates the percentage recovery of the metals under investigation in the soil samples.

Heavy Metal Analysis

The concentration levels of metals across various depth levels and locations are presented in Tables 2-5 for the water soluble F1, Exchangeable fraction F2, Organic fraction F3, carbonate fractions, and residual fractions, respectively.

Table 1: Results of validations experiment				
Metal	Percentage (%) Recovery			
Cd	89.00			
NI	97.00			
Zn	85.00			
Fe	99.00			
Pb	94.00			

The Tables illustrate a decrease in the concentration of metals (Cd, Ni, Pb, Zn, and Fe) between the depths of 0-15 cm and 15-30 cm. It is worth noting that the residual fraction constitutes the most mobile and potentially bio-available heavy metal species [13]. The chemical fractionation results of Zinc in mechanic workshop soils at the two different depths are presented in Tables 3 to 5. In both cases, the chemical associations of Zinc were dominated by the residual fraction, which ranged from BDL to 36.5 g/mg across the depth levels.

The majority of automobile mechanic sites examined in Tables 3-5 exhibited levels of extractable zinc (F1+F2+F3+F4+F5) that exceeded the permissible limit of 300 mg/kg, with only a small number of exceptions. The residual fraction (F5) contained the highest concentrations of zinc at both depths for all soils studied, indicating that under severe conditions, this element could be released into the environment. However, the residual fraction is not generally considered to be an environmental hazard, as it is a stable compound in which metals are tightly bound within a mineral lattice, reducing the bioavailability of this metal [15]

Through comparison of zinc levels in residual and water-soluble fractions at varying depths across multiple sites, it is evident that the residual fractions contain the highest concentration of this element, measuring 36.10 mg/kg. Such a notable quantity of zinc associated with the residual fractions suggests that it would be highly accessible for uptake by plants.

The discoveries made in this investigation are consistent with the observations made by previous researchers [16, 17], who reported comparable levels of zinc concentration in soils from tanneries located in Uttar Pradesh, India and mechanics workshops in Okigwe, Nigeria, respectively [15]. Additionally, it was noted that the total metal contents of the mechanic workshop soil were lower at the depth of 0-15 cm than at the depth of 15-30 cm, which can be attributed to metal leaching. This observation is indicative of the deposition of zinc in soils resulting from the activities of mechanic workshops, specifically from lubricants and metal scrap

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originating from automobiles. Generally, the affinity of zinc with the soil fraction increases in the following order: F5 < F4 < F3 < F4 > F1 for both respective depths.

Tables 2-5 exhibit the outcomes of the chemical fractionation of lead (Pb) in soil from

Table 2: Heavy Metal concentration (mg/kg) in the Exchangeable fraction in all locations and across all depths

Location	Depth	Zn	Pb	Cd	Fe	Ni
/Metals						
ZN	0-15 cm	1.74	5.26	0.67	3.96	1.65
LP I		1.03	4.75	1.28	1.52	ND
LP 2		1.23	5.36	0.77	1.61	2.17
ZN	15-30 cm	0.89	3.97	1.70	2.00	1.59
LPI		1.53	8.44	1.55	2.94	ND
LP 2		1.22	3.31	0.65	2.66	2.25

mechanical workshop, at depths of 0-15 cm and 15-30 cm. The water-soluble fraction ranged from 1.72 to 3.23 kg/mg, the exchangeable fraction ranged from 3.97 to 8.44 g/mg, the organic fraction ranged from 4.24 mg/kg, the carbonate fraction ranged from 6.77 to 26.46 g/mg, while that of residual fraction varied from 5.78 to 9.80 g/mg for both depths, across all sites. At 0-15 cm depth, the highest value of the extractable fractions of Pb was 26.46 mg/kg at the carbonate fraction, and the lowest was 1.72 mg/kg at the water-soluble fraction, while at the 15-30 cm depths, the highest level was 9.80 mg/kg and the lowest was 2.73 mg/kg. The Pb values in the investigated soil surpassed the maximum permissible limit of 3.0 mg/kg, as set at FEPA 1991 and EU 2008. Concentrations of lead were high in both depths, with F4 carbonate fraction being the dominant contributor across the site. Through comparison of residual (F4) and water soluble fraction concentrations of lead across the mechanic workshop for both depths, it was demonstrated that high percentages of extractable fractions were present in the dumpsite soils at both respective depths. This suggests that Pb may be released into the environment, leading to contamination throughout the two depths. The high association of Pb in the carbonate fraction

Location /Metals	Depth	Zn	Pb	Cd	Fe	Ni
ZN	0-15 cm	4.48	4.75	0.47	42.63	1.78
LP I		25.58	5.26	0.47	21.18	1.78
LP 2		8.83	4.75	0.47	21.00	1.78
ZN	15-30 cm	1.25	4.75	0.40	9.62	1.65
LPI		2.64	4.24	0.47	35.58	2.04
LP 2		3.00	4.24	0.47	5.47	1.25

Table 3: Heavy Metal concentration (mg/kg) in the Organic fraction in all locations and across all depths

 Table 4: Heavy Metal concentration (mg/kg)in the Carbonate fraction in all locations and across all depths

Location	Depth	Zn	Pb	Cd	Fe	Ni
/Metals						
ZN	0-15 cm	27.82	12.33	0.28	32.63	0.73
LP I		37.21	14.35	0.28	33.72	0.20
LP 2		4.04	26.46	0.28	18.65	1.12
ZN	15-30 cm	23.68	9.30	0.28	36.47	2.83
LPI		11.46	7.78	0.18	64.22	0.07
LP 2		2.84	6.77	0.23	26.60	0.33

(F4) of the mechanic workshop soils may be attributed to the alkaline stabilization process of the soils [4]. Such results have been corroborated by previous studies [20]. The findings suggest that Pb is highly bioavailable to the environment and can cause environmental toxicity during mobility, particularly at depths of 0-15 cm [18, 4].

Table 2-5 illustrates the chemical association of cadmium at all phases in the soil sequential extraction process. Notably, the water-soluble

fractions (44.55 g/kg) and residual fractions (1.65 mg/kg) at depths of 15-30cm and 0-15cm, respectively, contained the highest concentrations of Cd. Furthermore, the water-soluble fraction (F1) of the entire mechanic workshop exhibited the highest concentrations of Cd, indicating a potential for easy release of Cd into the environment. The association of Cd in the water-soluble

Location	Depth	Zn	Pb	Cd	Fe	Ni
/Metals						
ZN	0-15 cm	27.89	9.30	1.65	65.45	9.67
LP I		36.51	7.78	1.06	55.19	8.09
LP 2		2.14	6.27	0.57	34.10	0.57
ZN	15-30 cm	20.17	9.80	1.36	60.83	11.91
LPI		9.65	7.28	0.57	42.83	ND

Table 5: Heavy Metal concentration (mg/kg) in the Residual fraction in all locations and across all depths

fraction poses a significant environmental risk due to the unstable nature of the compound and the strong binding of metals within a mineral lattice, which limits its bioavailability [21]. The findings in these investigations are in agreement with the observations which reported similar Cd concentration from Ado Ekiti metropolis southern western Nigeria) [22, 23].

The chemical association of iron was dominant in the residual fraction (F5) at depths of 0-15 and 15-30 cm, respectively, across all the study sites. The concentration of iron in the residual fraction ranged from 34.10 to 65.45 mg/kg for both depths, while the water-soluble fraction exhibited a range of 3.07 to 44.70 mg/kg. Similarly, the organic fraction displayed a range of 5.47 to 42.63 mg/kg for both depths. The carbonate fraction, on the other hand, exhibited a range of 18.65 to 64.22 mg/kg across all depths and study sites. It is noteworthy that the residual fraction exhibited the highest concentration of Fe in all five fractions for both depths (65.45 mg/kg and 24.83 mg/kg). The results indicate that at a depth of 15-30 cm, the residual fractions exhibit the highest percentage of iron. This finding suggests that the release of Fe metal into the environment, causing contamination, is unlikely. However, the water-soluble fraction at the depth of 0-15cm contains a notable amount of Fe (33.75 mg/kg), indicating that Fe may be

easily transferred to the food chain through water reservoirs. The uptake of Fe by plants growing in these soils may have a potentially negative impact on the environment and human health. Additionally, the total extractable concentrations of Fe in all soils exceeded the toxic limit of 140 mg/kg set by Oluyemi *et al* [16] for both respective depths.

Moreover, the Exchangeable fraction of nickel in all locations at 0-15 and 15-30 cm increased from BDL to 5.01 mg/kg. In this fraction, all the metals were found in all the locations but not such significantly higher concentrations than they were in the depth of 15-30 cm compared to other fractions. The concentration of nickel in the organic carbon fraction, observed across various locations at depths of 0-15 cm and 15-30 cm, indicates that this metal exhibits potential for mobility and can lead to environmental pollution. The data presented in Tables 3-5 demonstrate an increase in the amount of nickel with depth in the carbonate fraction across all locations at depths of 0-15 cm and 15-30 cm. The highest concentration of nickel, amounting to 11.91 mg/kg, was found in F5, which was consistent across the site and depth. Moreover, the exchangeable fraction at depths of 0-15 cm and 15-30 cm exhibited an average of 2.17-2.25 mg/kg of nickel, indicating the highest level of contamination across the sites and depth profile. Additionally, the organic fraction at a depth of 15-30 cm displayed a nickel concentration of 2.83 mg/kg, which was higher than other fractions. This result is in consistent with finding of Ogunfowokan et al [11].

CONCLUSIONS

The limited number of investigations was conducted on soil depth ranging from the top 0 - 15 cm. With the exception of Pb (24.00 to 45.22 mg/kg), falling within the range (23.04 to 47.11 mg/kg) reported by Nnachi *et al* [4], the average concentrations of all other metals exceeded levels (09.15 to 11.04 mg/kg) previously documented in literature. The elevated concentrations of certain metals may be attributed to the presence of additives (comprising metals in varying proportions) found in lubricants utilized by automobile mechanics. Slight variations are evident in the levels of individual metals across all sampling locations, although no significant mean differences were observed ($\alpha \ge 0.95$). The causes of such variation may be attributed to factors such as the age of mechanic workshops, the volume of work undertaken at each site, the types of automobile services or repairs provided, the type of lubricant commonly utilized, the mode of waste disposal, and the type of soil. Conversely, significant variation and mean differences were noted between the levels of individual metals (p < 0.05). The comparison of metal concentrations

with the permissible levels of heavy metals in the soil, as outlined by DPR [26], shows that the cadmium value (2.89 mg/kg) in the study areas exceeded the Cd value (0.8 mg/kg) of DPR [26]. Given that metals like cadmium have no biological function, this calls for public concern [12]. The concentrations of these metallic elements in the soil profiles pose a grave peril to both the surface and underground water bodies. A few of these metals displayed a noteworthy correlation with the percentage of organic carbon, which decreased with the soil's depth. In the present study, the overall metal concentrations were juxtaposed with other studies, primarily conducted in Nigeria.

Recommendations

This study has undertaken an assessment of the degree of heavy metal contamination in soils present within a select number of mechanic workshops. Based on the research findings, it is highly recommended that the government should allocate appropriate areas that can serve as automobile villages where auto repairs can be performed at a safe distance from residential areas. Furthermore, it is advised that education and legislation on waste management in places like auto-mechanic workshops should be intensified to avert the consequences of heavy metal related wastes on the environment, particularly on groundwater. Additionally, it is essential that metals speciation be conducted so that the form and the extent of metal bioavailability can be further assessed.

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