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Bioaccessibility studies and human health risk assessment of potentially toxic elements in soils from Mechanic Workshops in Ogun State

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Abstract

Soils in urban areas are usually contaminated by various potentially toxic elements (PTEs) which have potential impacts on human health and the environment. Some of the major activities that contribute to the pollution of soil are automobile repair workshops since the activities are often uncontrolled. This study examined PTE contamination in soils from automobile workshops in Ogun State, aiming to assess the concentrations, contamination factor, and human health risks of manganese (Mn) and cadmium (Cd) in soils from five mechanic workshops at Ijebu Ife, Ijebu Mushin, Ijebu Ode, Mowe and Sagamu. Samples were taken at the workshops from the upper soil layer of 0 to 10 cm. The samples were subjected to physicochemical characterisation and acid digestion and the PTEs were determined using AAS. Contamination factors, bioaccessibility, and risk assessment to human health were determined. Soil pH values varied between 8.1 to 9.0, which shows that the soils were alkaline. The mean total Mn concentrations were within the range of 42.0±1.3 - 64.8±1.5mg/kg and the Cd varied between 0.3±0.05 to 1.6±0.1mg/kg. The contamination factor value revealed a low degree of contamination of Mn and Cd in the locations. The mean bioaccessibility for Mn and Cd concentrations ranged from 19.30±0.03 to 64.40±0.1 mg/kg and 0.10±0.01 to 1.20±0.02 mg/kg respectively. Hazard quotient showed no significant concern for human exposure to the Mn and Cd in the soil via oral, dermal or inhalation pathways. In conclusion, Mn and Cd contamination was generally low in all the sites. However, this study recommends continued monitoring and implementation of environmental protection measures in such areas to prevent the accumulation of PTEs beyond tolerable contamination levels.

Keywords: Soil contamination, Automobile workshops, mechanic site, heavy metal, potentially toxic element

INTRODUCTION

Soil has been contaminated seriously in some areas and the quality of agricultural soil is worse (Pan et al., 2016). This is because the potentially toxic elements can move from one ecosystem to another in different forms depending on the exchange medium of the substances, for instance in the air and water.

High concentrations of PTEs have been documented in the urban soils (Xu et al., 2018).

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The appearance of these potentially toxic elements in both rural and urban soils is a serious threat to human health and the ecosystem in general. This is because these elements might likely pose a threat to the human body through exposure routes such as oral (the mouth), inhalation (the nose) and dermal (the skin). However, it has been found that these potentially toxic elements cause irreversible harm to human beings especially children because of their higher likelihood of exposure and susceptibility. This places children at a higher disadvantage as their organs are still in development and are thereby more susceptible to the effects of potentially toxic elements than other contaminants (Egendorf et al., 2020).

Potentially toxic elements exist as naturally occurring elements in the human environment and are generally derived from the weathering of parent materials. However, in recent years potentially toxic elements have accumulated significantly in the global environment owing to various human activities such as mineral resources development, metal processing and smelting industries emissions, use of fertilizers and pesticides, sewage irrigation and atmospheric transport and hence they have become a serious threat in soil and sediment environments (Weldeslassie et al., 2018). Other human activities such as automobile repair could be a source since these activities involve different metals.

Most auto repair workshops in Nigeria include several personnels such as auto mechanics, spray painters, panel beaters, welders, battery recyclers, and radiator/air conditioning technicians who are always involved in auto-related tasks. These workshops have been considered of great concern in causing pollution to the environment mainly because of the exercises conducted by these workers. Research has shown that automobile workers are exposed to Pb toxicity in their working environment (Ishola et al., 2017). Spray painters who work in automobile sector have also been found to be exposed to toxic elements like lead, cadmium and chromium which are some of the worst toxic elements in automobile paint workshops. This is because; lead, cadmium and chromium are major toxic metals inherent in automobile paints. Welding is found to expose workers to high levels of lead and cadmium and at the same time liberate zinc fumes (Adeniyi et al., 2016). It has also been established by other researchers that automobile workers are exposed to chromium, lead, and zinc because these are elements used in spare parts industry in the construction of automobiles (Ishola et al., 2017). Likewise, during the melting process, the fumes of elements that include chromium, lead, zinc, copper, manganese, and nickel may be inhaled, ingested, or absorbed through the skin when frequently used by the panel beaters for car repairs.

Some of the extended consequences of lead exposure include central nervous system disorders, anaemia, and renal failure. Moreover, lead has been reported to reduce toxicant immunogenicity, and decrease humoral immunity. Long-term effects of cadmium include lung cancer and may be toxic to the immune, nervous, respiratory, endocrine, renal, musculoskeletal, and cardiovascular systems (Bhattacharyya et al., 2023). It has also been claimed that drinking water and food containing cadmium could result in renal tubular abnormity, disorder of calcium balance and osteoporosis in the long term. While copper and zinc are toxic metals when they are present in high concentrations. For example, at toxic levels, copper, and zinc with superoxide radical to form highly reactive hydroxylated free radicals which reduces the antioxidant capacity in an individual.

However, these auto workers do not know how much of such toxic elements they come across or the impact they have on their overall well-being they therefore do not bother to guard against the chances of inhaling or ingesting such toxic substances. The most disturbing one is that there is no awareness and limited regulations concerning exposure to environmental pollutants in the workplace in Nigeria and the level of nonchalant attitude of auto workers to the ethics of workshops and environmental protection laws is alarming. These workers also show little regard for other preventive measures like washing and wearing masks to reduce the chances of swallowing and breathing in these poisonous compounds. Several research works have also been conducted to ascertain the total concentrations of PTEs in mechanic sites (Ajeh et al., 2022; Ganiyu et al., 2023; Isah et al., 2023; Olowofila, 2021; Olugbemi, 2022). Nevertheless, there is scarce information on the bioaccessible concentration of these PTEs in soil from mechanic sites. These bioaccessible concentrations measure the amount of the PTEs which the workers can be exposed to in the soil via oral, dermal or inhalation routes. Hence, this study aimed to determine the bioaccessible concentrations of PTEs in soils from automobile workshops in five selected locations in Ogun State: Ijebu Ife, Ijebu Mushin, Ijebu Ode, Mowe and Sagamu.

MATERIALS AND METHODS

Materials

High-density polyethylene, HNO_3 (Sigma Aldrich, UK), HCl (BDH, China), distilled deionised water, plastic auger, 45um mesh sieve, desiccators, 0.45 µm PVDF filter, pH meter, hotplate, Whatman filter paper, polythene bag, beaker, watch glass, volumetric flask, glycine solution, gastric solution, syringe, cellulose acetate membrane filter, centrifuge tube, refrigerator, water bath, synthetic sweat, Teflon tubes with PTFE caps, incubator, automatic pipettes, Luer-lock syringe (60 mL), 0.45 µm PVDF filter, AAS, nitric acid, ammonium chloride, lactic acid, and sodium chloride.

Sampling

A total of thirty (30) soil samples were randomly collected using a plastic auger by digging a depth of 0-10 cm from selected five (5) different locations (Ijebu Ife, Ijebu Mushin, Ijebu Ode, Mowe, and Sagamu). The samples were stored in a polythene bag until further use and thereafter, the samples were air dried for a week at room temperature to remove moisture and passed through a 45um mesh sieve to obtain fine particles of the soil samples.

Sample Preparations for the Determination of Total Potentially Toxic Elements Concentrations

Approximately 1.0 g of soil was weighed into a 50 ml. beaker and 20 mL of aqua regia (HCI: HNO_3, 3:1 V/V) and covered with a watch glass. The beaker containing the sample mixture was left to digest on the hotplate for 2 h until the brown fumes were no longer observable and the solution was semi-solid (Rodiouchkina et al., 2023). The solution obtained was then transferred to the hot plate and the residual contents evaporated to dryness, cooled, filtered through Whatman filter paper into a 50 ml volumetric flask and diluted to the mark with deionised water. It was done in triplicates and transferred to cleaned dried plastic before proceeding with the analysis.

Physico-Chemical Analysis of The Soil Samples

1. pH

The pH was determined using BS ISO 10390:2005 (BSI, 2005: Standard, 2005) method at a soil-to-deionised water ratio of 1:5. The pH meter was calibrated with Buffer solutions of pH 4, 7, and 14. The pH meter was recalibrated after every ten determinations.

2. Determination of moisture content

Two grams of soil samples was heated at a temperature of 105℃ for 24 h in an oven then cooled in the desiccators and weighed to determine moisture content. The percentage moisture content was calculated using equation (1)

$$\% \text{ Moisture content} = \frac{A-B}{A} \times 100 \qquad (1)$$

Where A = the weight while wet and B = the weight while dry.

Oral Bio-Accessibility using the Simplified Bio-Accessibility Extraction Test (SBET) Method

This is a one phase extraction carried out by adding gastric juice containing 0.4 M glycine solution (prepared by adding 30.3 g of glycine to IL deionised water) adjusted with 12 M HCl to pH 1.5±0.2. Approximately 0.5 g sample was placed in HDPE (High- density polyethylene) screw top tubes and 50 mL gastric solution was added. The mixture was agitated in an end-over-end orbital shaker maintained at 37°C and 100 rpm for 1 h. After extraction was completed, some aliquot was removed with a disposable syringe attached to a 0.45 um cellulose acetate membrane filter. The filtrate was then transferred into a centrifuge tube and stored in a refrigerator at 4°C prior to instrumental analysis. For each sample extraction performed, the pH value of the sample solution was taken at the beginning and the end of the extraction to ensure it was within the range (pH 1.3±0.2 to 1.7± 0.1) before filtration. The extraction was also carried out in triplicates for each sample.

Inhalation Bio-Accessibility Test

Before extraction, the simulated lung fluid was brought out of the refrigerator and warmed in a water bath for 2 h at 37°C to mimic body temperature. The pH was checked to ensure it was 7.4±0.2. Triplicate sets of 0.2 g of the generated resuspended soil samples were weighed into labelled extraction tubes; 20 mL of simulated lung fluid was added to leach the samples. The sample was agitated for 10 s and pH was checked. The pH was adjusted with dropwise addition of 1 M NaOH and/or HCI where necessary. Extraction was carried out at 37°C.

Dermal Bio-Accessibility Test

This was carried out by extracting the samples with simulated sweat solutions National Institute of Health Sciences (NIHS)

96-10 at pH 4.7 and particle size of 45 µm (Leal et al., 2018). The soil samples were extracted at sweat-to-soil ratio of 1:100 and as detailed by (Anselm et al., 2022)

Inhalation Bio-Accessibility Test

Before extraction, the simulated lung fluid was brought out of the refrigerator and warmed in a water bath for 2 h at 37°C to mimic body temperature. The pH was checked to ensure it was 7.4±0.2. Triplicate sets of 0.2 g of the generated resuspended soil samples were weighed into labelled extraction tubes; 20 mL of simulated lung fluid was added to leach the samples. The sample was agitated for 10 s and pH was checked. The pH was adjusted with dropwise addition of 1 M NaOH and/or HCI where necessary. Extraction was carried out at 37°C.

Assessment of Soil Contamination

1. **Contamination factor**

The degree of contamination of the composite topsoil was determined as a summation of the individual Potentially Toxic Elements (PTE) contamination factor (CF). The CF was obtained using Equation 2

$$CF= \frac{\text{Total PTE (mgkg}-1)}{\text{Soil background value(mgkg}-1)} \quad (2)$$

Hence, C_d=ΣCF

The soil background values were obtained from the world average value while the total values were obtained from this study. Ahmad et al. (2021) suggested CF values be interpreted as follows: CF <1 indicates low contamination, 1< CF <3 moderate contamination, 3< CF <6 considerable contamination and CF >6 very high contamination.

2. **Calculation of % Bioaccessibility and Dermal Absorbed Dosage (DAD)**

The % bioaccessibility and DAD were calculated using Equation 3 and Equation 4

$$\%\text{bioaccessibility}= \frac{\text{Measured PTE concentration (mg/kg)}}{\text{Total concentration of PTE (mg/kg)}} \quad (3)$$

$$DAD=\frac{〖DA〗\_events*EF*ED*EV*SA}{BW*AT} \quad (4)$$

where SA (cm^2): skin surface area available for contact (1575 cm^2 for the industrial scenario with PPE, 2800 cm^2 for children and 5700 cm^2 for adults without PPE); EF: exposure frequency (219 d.y' for industrial scenario); ED: exposure duration (taken as 25 years for industrial workers, 6 years for children); EF: event frequency (1 event.d'); BW: average body weight (70 kg for adults, 15 kg for children); AT: averaging time (ED *365)
Co: total concentration in soil (mg.kg') (Table 1); CF: conversion factor (10^{-6}); AF adherence factor of soil to the skin (mg. cm^2-event, taken as 0.2, ABS: dermal absorption
fraction 0.03 for As and 0.001 for other PTEs).

The dermal reference values (RIDAns), which is the threshold value, were derived from oral reference values, using the equation 5

$$RfD_{ABS}=RfD_O * ABS_{GI} \quad (5)$$

RESULTS AND DISCUSSION

Results of Physiochemical Analyses of the Soil Samples

The result of pH and moisture content of the different samples were investigated. The values obtained for pH ranged from 8.1±0.2 to 9.0±0.1, indicating that the soil samples are alkaline in nature. The values of moisture content ranged (from 0.2 to 0.5) showing the amount of water present in the soil samples in the Table 1 below.

Table 1. Results of Physiochemical analyses of the soil samples

Parameters	Ijebu-Ife	Ijebu-Mushin	Ijebu-Ode	Mowe	Sagamu
pH	9.0 ± 0.1	8.5 ± 0.2	8.1± 0.2	8.4± 0.2	8.4± 0.1
Moisture Content (%)	0.5	0.2	0.5	0.4	0.2

Total Concentration of Mn and Cd.

The total concentration of Mn and Cd present in the soil samples of each location in Table 2 shows that Mn ranged from 42.0± 1.3 mg/kg to 64.8±1.5 mg/kg while Cd ranged from 0.3±0.05 mg/kg to 1.6±0.1 mg/kg. This indicated that the level of manganese present in soil samples in all the locations is greater than cadmium. This may be due to the fact that Mn is one of the abundant elements in the earth's crust and is widely distributed in soils, sediments, rocks and water unlike Cd which is distributed at average concentration of about 0.1 mg/kg. The abundance of Mn might be due to its relative abundance in soil or the anthropogenic source from the metal junkyard found in many of the auto mechanics sites.

Contamination Factor Value (CF Value) of Mn and Cd in the Mechanic Workshops.

The contamination factor values in Table 3 shows that the CF Value of Mn in all five (5) locations has low contamination (CF <1). Similarly, the contamination factors of Cd in the five locations (Ijebu Ife, Ijebu Mushin, Ijebu Ode, Mowe, and Sagamu) have low contamination (CF < 1). This means that the level of contamination for both Cd and Mn in all the sample locations cannot cause harm to human health. Duru et al. (2024) studied Spatial variability of heavy metals concentrations in the soil of auto-mechanic workshop clusters in Nsukka, Nigeria. They found moderate to considerable contamination for Cd (CF of 3.759) in most sites, which is slightly higher than the current study's findings.

Table 2. Total concentration of Mn and Cd with respect to sample locations.

Sample Location	Mn (mg/kg)	Cd (mg/kg)
ljebu-Ife	42.0±1.3	0.3±0.05
Ijebu-Mushin	64.8±1.5	0.8±0.04
Ijebu-Ode	52.8±1.6	1.6±0.1
Mowe	52.3±0.9	0.5±0.04
Sagamu	55.3±1.1	1±0.03
Average World Soil (Alloway, 2013)	418	1.1
Olayinka et al. (2017) mechanic workshops in Abeokuta, Nigeria at 0 – 5cm.	304.50±84.23	0.25±0.01
Ojekunle et al. (2014) on Heavy Metal Pollution in Mechanic Village, Ogun State.	-	0.069

Table 3. Mean contamination factor value (CF Value) of Mn and Cd.

Sample Location	Mn (mg/kg)	Cd (mg/kg)
Ijebu Ife	0.14	0.08
Ijebu-Mushin	0.22	0.20
Ijebu Ode	0.18	0.40
Mowe	0.17	0.13
Sagamu	0.18	0.25

Oral Bioaccessible concentrations of Mn and Cd in the Mechanic Workshops

The mean oral bioaccessible concentration of Mn and Cd are shown in the Table 4 shows that the level for oral ingestion in all the locations ranged from 31.30±0.02 mg/kg to 56. 80±0.04 mg/kg (Mn) and 0.3±0.01 mg/kg to 0.5±0.01 mg/kg (Cd). The dermally bioaccessible concentrations of Mn and Cd from 29.00±0.01 mg/kg to 64.40±0.1 mg/kg (Mn) and 0.08±0.01 mg/kg to 0.60±0.07 kg/mg (Cd) as shown in Table 4. Also, the bioaccessible concentrations of Mn and Cd via the inhalation route ranged from 19.30±0.03 mg/kg to 53.60±0.01 mg/kg and 0.8±0.01 mg/kg to 1.20±0.02 mg/kg respectively. Therefore, the concentrations of Cd present in all the locations are lower than the concentrations of Mn which may be because Mn is a more abundant element in the earth's crust and is widely distributed in soils, sediments, rocks and water, unlike Cd which is distributed in an average concentration of about 0.1 mg/kg in soils.

Table 4. Mean concentration of Mn and Cd in (mg/kg) through Oral, Inhalation and Dermal exposure routes.

Sample Location	Oral Bioaccessibility		Dermal		Inhalation Bioaccessibility	
	Mn (mg/kg)	Cd (mg/kg)	Mn (mg/kg)	Cd (mg/kg)	Mn (mg/kg)	Cd (mg/kg)
Ijebu-Ife	33.80±0.01	0.10±0.01	29.00±0.01	0.08±0.01	19.30±0.03	0.80±0.02
Ijebu-Mushin	44.80±0.03	0.40±0.01	64.40±0.10	0.30±0.06	45.60±0.08	0.80±0.01
Ijebu-Ode	56.80±0.04	0.40±0.01	55.84±0.02	0.30±0.03	53.60±0.01	1.20±0.02
Mowe	31.30±0.02	0.30±0.01	38.00±0.01	0.10±0.04	32.70±0.04	1.00±0.05
Sagamu	53.00±0.01	0.50±0.01	41.00±0.01	0.60±0.07	49.20±0.05	0.80±0.08

Daily Dosage of Mn and Cd in the Mechanic workshops Via Different Exposure Pathways

Figure 1 shows that human absorption of Mn and Cd in all the sample locations cannot have of hazardous effect on human health. This is because the daily dosage of human absorption through oral, dermal and inhalation processes in all the sample locations is not above the daily dosage standard which ranges from 10^{-6} to 10^{-4}.

Carcinogenic and Non-Carcinogenic Risk Assessment of Mn and Cd in the Mechanic Workshops

Adverse health effects are unlikely to occur if HQ<1, but if HQ>1, it indicates probably adverse health effects. If HQ>10, it indicates chronic risk (Ahmad et al., 2021). Figure 2 indicates that the workers and population around these locations are not prone to adverse health effects of exposure to Mn and Cd as HQ<1.

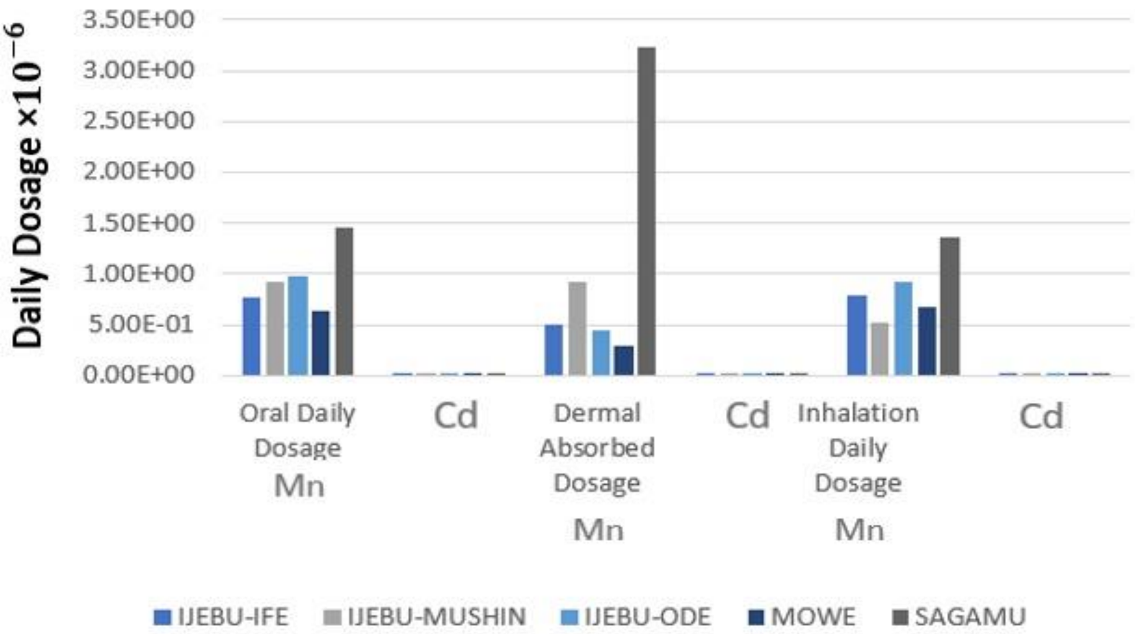

Figure 1. Mean Daily Dosage of Mn and Cd in the soil samples via different exposure pathways.

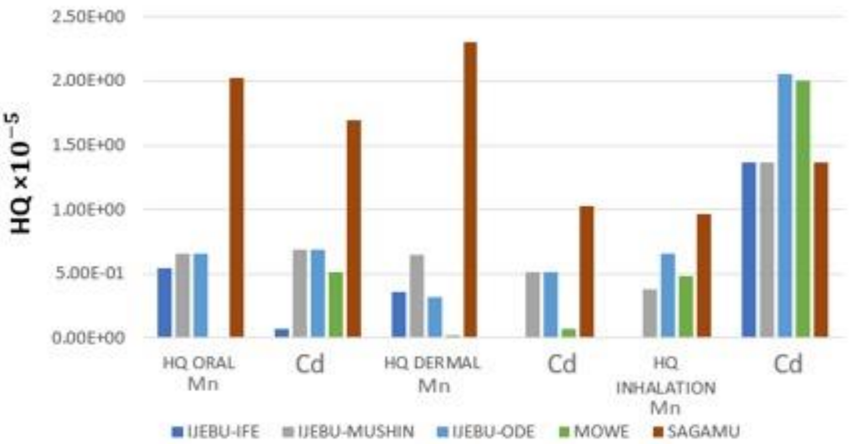

Figure 2. Hazard quotient (HQ) of Mn and Cd in soil samples.

DISCUSSION

This study's findings of low contamination factors (CF) for Mn and Cd in most locations are generally consistent with other studies on auto mechanic workshops. For instance, Iwegbue (2007) reported similar levels of Mn contamination in soils from auto mechanic waste dumps in Nigeria. However, this study's Cd contamination levels are lower than those reported by Duru et al. (2024), who found moderate to considerable contamination for Cd in Nsukka, Nigeria.

The total concentrations of Mn (42.0±1.3-64.8±1.5 mg/kg) observed in this study were lower than those reported by Olayinka et al. (2017) for mechanic workshops in Abeokuta, Nigeria (Mn: 304.50±84.23 mg/kg). Meanwhile, the total Cd concentrations (0.3±0.05 to 1.6±0.1 mg/kg) were lower than the reported Cd concentrations by Olayinka et al. (2017) (Cd: 0.25±0.01 mg/kg). These differences could be attributed to variations in local geology, workshop practices, or the age and intensity of activities at the sites.

The bioaccessibility studies across different exposure routes provides a more detailed understanding of potential risks. This study's approach aligns with recent trends in risk assessment (Pelfrêne et al., 2013; Rosende et al., 2019), emphasising on the importance of considering bioaccessibility in risk calculations (Anselm et al., 2022).

Crucially, the hazard quotient (HQ) values for all exposure routes (oral, dermal, and inhalation) were found to be less than 1 for both Mn and Cd. This indicated that adverse health effects are unlikely to occur from exposure to these PTEs at the studied sites. Meanwhile, previous studies such as Darko et al. (2017) reported higher HQ values for Cd in similar settings in Kumasi, Ghana. The lower HQ values in the current study could be due to several factors such as lower overall PTE concentrations in the soil compared to other studies, differences in soil properties that affect metal bioavailability, frequency of use of the dumpsite and variations in the area sampled or depth of sampling. However, long-term monitoring would be valuable to assess potential accumulation over time, as suggested by Al-Khashman (2012) in their study on heavy metal accumulation in urban soils.

While this study's results suggest minimal immediate health risks, continued monitoring and implementation of best practices in waste management at auto mechanic workshops remain crucial.

CONCLUSION

This study assessed the concentrations of potentially toxic elements (PTEs), specifically manganese (Mn) and cadmium (Cd), in soils from automobile workshops across five locations in Ogun state, Nigeria. The research employed a comprehensive approach, including soil sampling, physicochemical analysis, and various bioavailability tests to evaluate the potential health risks associated with these elements.

The soil samples exhibited alkaline characteristics, with pH values ranging from 8.1±0.2 to 9.0±0.1. Total concentrations revealed that Mn levels (42.0±1.3-64.8±1.5 mg/kg) were consistently higher than Cd levels (0.3±0.05-1.6±0.1 mg/kg) across all locations. Contamination factor (CF) analysis indicated low contamination for Mn (CF < 1) in all sites, and Cd also showed low contamination (CF < 1) in all locations.

Bioaccessibility studies, including oral, dermal, and inhalation pathways, provided insights into the potential exposure risks. The oral bioaccessibility of Mn ranged from 31.30±0.02 to 56.80±0.04 mg/kg, while Cd ranged from 0.3±0.01 to 0.5±0.01 mg/kg. Dermal bioaccessibility tests revealed higher potential exposure to Cd compared to oral and inhalation routes.

Health risk assessments, including daily dosage calculations and hazard quotient (HQ) evaluations, suggested that oral and inhalation exposures to both Mn and Cd pose minimal risks to human health in all locations (HQ < 1). However, dermal exposure to Cd showed potential for adverse health effects in some locations, with HQ values exceeding.

These findings highlight the importance of considering multiple exposure pathways when assessing environmental contamination risks. While the overall contamination levels of Mn and Cd in the studied automobile workshop soils were not alarmingly high, the potential for dermal exposure to Cd warrants attention. Future remediation efforts and workplace safety measures should focus on minimizing dermal contact with contaminated soils, particularly in areas with elevated Cd levels.

This study underscores the need for continued monitoring and implementation of environmental protection measures in such settings to safeguard worker health and surrounding communities.

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