

ORAL INGESTION RISKS OF HEAVY METAL ACCUMULATION AT TOP SOILS OF AUTOMOBILE WORKSHOPS IN OWERRI CAPITAL CITY OF IMO STATE, NIGERIA

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Abstract: This investigation was carried out to assess the heavy metal concentrations and health risks associated with automobile workshops in Owerri Metropolis. Using an Atomic Absorption Spectrophotometer, soil samples from Orji Mechanic Village (OMV), Naze Mechanic Village (NMV), New Market Automobile Workshops (NMAV), Matrix Mechanic Yard (MMY) and Alvan Mechanic Yard (AMY) were assayed for Silver (Ag), Cobalt (Co), Nickel (Ni), Mercury (Hg), Lead (Pb), Arsenic (As), Chromium (Cr) and Cadmium (Cd) concentrations. The result showed that at majority of the sites, the Ag, Pb, As, and Cd levels exceeded their baseline values, whereas the Ni and Co levels were equivalent to those of their baselines, at some sites. Soil samples at MMY were the most acidic while that of NMAV was the most alkaline. The pollution models indicated very high Ag contamination at OMV, NMV, and NMAV while all the sites showed very high contamination of Pb and Cd, and no Co, Ni, Hg, and Cr pollution was recorded for all the sites as shown by their Igeo values. The result for the enrichment factor showed anthropogenic sources of deposition of these heavy metals at all the sites. From the risk assessment models applied, none of the contaminated sites showed an estimated daily intake, hazard quotient, and total hazard index beyond the reference values, with Pb found to possess the greatest potentials of toxicity. This study has shown the necessity to

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periodically monitor and apply measures that can halt the environmental decay, occurring at the automobile workshops.

Keywords: Heavy metals; Geoaccumulation index; Risk assessment; Contamination; Pollution

Introduction

Soil pollution with heavy metals is becoming one of the most severe environmental and human health hazards.¹ Heavy metal pollution refers to cases where the contents of these elements in soils are higher than the maximum concentration, which has potential harmful effects on vegetation.² Some heavy metals are essential to maintain human metabolism although many, at higher concentrations, may be poisonous as they tend to bioaccumulate in human bodies making them dangerous, and posing massive health and environmental risks.² Gazso³ reported that heavy metals come from diverse sources and some in very minute concentrations serve as components of enzymes, pigments as well as help to maintain the ionic balance of cells.⁴ These and other trace elements are essential for the proper functioning of biological systems and a number of disorders could emerge when they become deficient or in excess. However, environmental contamination by heavy metals has become a course for concern in recent years because of their potential accumulation in biosystems through contaminated air, soil and water.⁴ As observed by Begun et al.,⁵ large quantities of pollutants have continuously been introduced into ecosystems as a consequence of urbanization and industrial processes which could come in form of a low solubility compound, like pyrite,⁶ or sorbed on surface-reactive phases like those of iron and manganese oxides.^{7,8} The largest small quantity generators of hazardous wastes are automotive service and repair shops. During their daily operations, they generate different kinds of wastes.

Some of these wastes include waste from solvents used for cleaning metallic parts, dirty shop rags, asbestos from brake pads, used motor parts and used oil and fluids. Solvents used to clean parts are the most dangerous wastes commonly generated in autorepair shops. The chemical components of these solvents are extremely toxic to humans and the environment⁹ and if these chemicals are not properly handled, they could contaminate the soil, water for domestic uses, lakes and streams and even the atmosphere.¹⁰

In Owerri Metropolis with antecedents of huge environmental decay, automobile workshops lack waste management practices. There, wastes are discarded indiscriminately on the vicinity, and as envisaged, eventually the soil becomes a repository for metals released from activities performed in these auto-repair workshops, thus leading to pollution.¹¹ Hence, it became a matter of essence to assess the present heavy metal contamination status of these activity laden workshops in the heart of the city, and to determine the health risks resulting from the deposition of these heavy metals. Therefore this study was carried out to determine the heavy metal concentrations of five popular automobile workshops in Owerri Capital City of Imo State Nigeria, and the health risks posed to the populace, considering the diverse activities performed in these automobile workshops.

Results and Discussion

Table 1 reveals the heavy metal concentrations of top soils of some automobile workshops in Owerri Metropolis. The silver contents of all the automobile workshops soils were above their baseline values except for AMY that was below detection level. After absorption into the circulatory system, high concentrations of silver can be deposited in the tissues of the body and this could result to a condition known as argyria.¹²

Table 1. Heavy metal contents (mg/kg) of top soils of automobile workshops in Owerri Metropolis.

Metals	Sites	OMV	NMV	NMAV	MMY	AMY
Ag	Test	0.26±0.01 ^a	0.31±0.01 ^a	0.39±0.02 ^a	0.08±0.00 ^a	BDL
	Control	0.05±0.01 ^b	0.03±0.01 ^b	0.09±0.01 ^b	BDL	BDL
	Baseline	0.04±0.02 ^b	0.04±0.02 ^b	0.04±0.02 ^b	0.04±0.02 ^b	0.040±0.03
Co	Test	2.68±0.01 ^a	1.04±0.05 ^a	4.50±0.07 ^a	2.11±0.04 ^a	2.88±0.05 ^a
	Control	0.37±0.09 ^b	0.35±0.03 ^b	0.55±0.02 ^b	BDL	0.31±0.01 ^b
	Baseline	6.30±4.15 ^c	6.30±4.15 ^c	6.30±4.15 ^a	6.30±4.15 ^b	6.30±4.15 ^c
Ni	Test	22.08±0.73 ^a	14.77±1.13 ^a	28.60±2.04 ^a	19.07±0.85 ^a	25.51±3.33 ^a
	Control	2.81±0.14 ^b	1.01±0.06 ^b	3.72±0.1 ^b	4.47±0.21 ^b	1.96±0.07 ^b
	Baseline	23.66±3.21 ^a	23.66±3.21 ^c	23.66±3.21 ^a	23.66±3.21 ^a	23.66±3.21 ^a
Hg	Test	0.16±0.01 ^a	0.17±0.01 ^a	0.25±0.03 ^a	0.07±0.00 ^a	0.06±0.05 ^a
	Control	0.12±0.00 ^b	0.18±0.0 ^a	0.09±0.0 ^b	BDL	0.04±0.00 ^a
	Baseline	0.13±0.17 ^{ab}	0.13±0.17 ^a	0.13±0.17 ^{ab}	0.13±0.17 ^c	0.13±0.17 ^b
Pb	Test	418.94±11.25 ^a	364.61±9.84 ^a	484.57±15.71 ^a	210.30±5.78 ^a	339.02±3.44 ^a
	Control	2.40±0.07 ^b	11.71±2.06 ^b	17.83±2.29 ^b	6.82±0.71 ^b	7.73±1.19 ^b
	Baseline	20.00±5.2 ^c	20.00±5.2 ^b	20.00±5.2 ^b	20.00±5.29 ^c	20.00±5.29 ^c
As	Test	5.60±0.66 ^a	0.79±0.31 ^a	4.01±1.21 ^a	BDL	0.64±0.11 ^a
	Control	BDL	0.09±0.01 ^b	BDL	0.05±0.00 ^a	0.57±0.20 ^a
	Baseline	0.60±1.03 ^b	0.60±1.03 ^a	0.60±1.03 ^b	0.60±1.03 ^b	0.60±1.03 ^a
Cr	Test	18.23±1.52 ^a	6.77±0.42 ^a	46.90±3.05 ^a	11.58±2.15 ^a	40.61±7.48 ^a
	Control	1.34±0.07 ^b	2.03±0.07 ^b	4.81±0.59 ^b	0.92±0.23 ^b	11.05±0.40 ^b
	Baseline	81.33±21.3 ^c	81.33±21.3 ^c	81.33±21.3 ^c	81.33±21.38 ^c	81.33±21.3 ^c
Cd	Test	22.06±3.36 ^a	28.93±2.57 ^a	11.70±2.23 ^a	9.11±1.03 ^a	20.52±1.66 ^a
	Control	0.14±0.01 ^b	1.22±0.82 ^b	0.85±0.08 ^b	0.36±0.02 ^b	0.23±0.05 ^b
	Baseline	0.20±0.11 ^b	0.20±0.11 ^c	0.20±0.11 ^c	0.20±0.11 ^b	0.20±0.11 ^b

Values are means and standard deviations of triplicate determinations.

For each metal, values bearing different superscript letter(s) (a, b, c) down the column denote that the mean difference is significant at $p < 0.05$. BDL means Below Detection Level.

This is a rare disfiguring condition with characteristic blue-grayish pigmentation of the skin, eyes and mucuous membranes. Cyanosis is often times mistaken for less severe forms of argyria. This infers that automobile workshop workers and their customers are environmentally predisposed to contracting argyria. The cobalt concentrations in the automobile workshop soils were significantly higher than their control values except in NMAV that their baseline values. A similar study by Olayiwola,¹⁶ revealed high cobalt content of the soil in the different automobile units; autowelding unit 12.75 ± 6.20 mg/kg next to the automechanic unit. The range of cobalt concentration was 13.75 ± 3.00 - 9.50 ± 0.90 mg/kg. The study explained that the high concentration in some units might have been due to the presence of cobalt in the materials being used by the automechanics. As these materials are used, some of it get leached into the soil and contaminate it. The auto-electrician unit had some cobalt in its soil (9.50 ± 0.90 mg/kg) and the least cobalt level. Runoff water during rain or wind can wash or disperse soil particles from one place to the other and contaminate the soil¹⁶. The nickel contents of OMV, NMV and MMY were below the baseline value whereas NMAV and AMY exceeded the baseline. From natural and anthropogenic sources, global input of nickel to the human environment is approximately 150,000 and 180,000 metric tonnes respectively per year. These include emissions from fossil fuel consumption, and the industrial production, use, and disposal of nickel compounds and alloys. The automobile workshops soils in this present study do not contain abnormal concentrations of nickel when compared to other studies. For rural UK soils, with a mean value of 21.1 mg/kg^{-1} , the UK Soil and Herbage Survey found total nickel concentrations in the range 1.16 to 216 mg/kg^{-1} . With a mean value of 28.5 mg/kg^{-1} , urban UK soils were found to contain nickel concentrations in

the range 7.07 to 102 mg/kg⁻¹.¹⁷ Berrow and Reaves,¹⁸ reported from a survey of soils in Scotland a geometric mean concentration of nickel in soil of 27 mg/kg⁻¹. A study by Adelekani and Abegunde,¹⁹ showed that nickel manifested a range of 2.0 to 25.0 mg/kg-1 found on the study locations in the automobile mechanic villages while it was below detection limit in the control soil. Nickel content in soil can be as low as 0.2 mg/kg-1 or as high as 450 mg/kg⁻¹ although the average is about 20 mg/kg⁻¹.² Exposures by inhalation, ingestion or skin contact occur in nickel and nickel alloy production plants as well as in welding, electroplating, grinding and cutting operations which are done in auto-mechanic workshops.²⁰ Further, the mercury concentrations were below their baseline values in MMY and AMY but were above the baseline values in OMV, NMV and NMAV. Its concentrations were comparable to the control sites in all the workshops except in MMY that was below detection level. Olarenwaju et al.,²¹ revealed that the levels of mercury in the soil were within tolerable limits, however, with all the automobiles workshops around residential and commercial areas where access is not restricted, there was a risk that prolonged exposure as predicated by that scenario could have a considerable human health impact (for tradesmen and local communities). The study further showed that mercury was relatively lower across the site, and this could be attributed to its limited use compared to cadmium and lead. However, mercury sources in automobiles include relays (with mercury switches) to control airbags, relays to control power to pumps and heaters, some seat belt and suspension systems, anti-lock brakes and safety switches and relays in trunk/hood light switches. The lead contents in the soils of this present work exceeded their baseline values in all the workshops and there were significant differences when compared to their control values in NMV and NMAV. This present

finding is similar to a study by Olayiwole,¹⁵ where the soil lead level was highest in the auto-electrician unit (325 ± 10 mg/kg) of the automobile workshop. The levels of lead obtained were higher than the values obtained by Ano and Nwoko²² and Egunjobi.²³ The values obtained were above the permissible level for soil as recommended by USEPA²⁴ and this is a serious environmental concern which needs urgent attention. Lead in the soils according to Chokor and Ekanem²⁵ had an average top-soil value of 36.61 mg/kg. This value was higher than the critical soil Pb limit for Canada (25 mg/kg), and Eastern Europe (32 mg/kg); but lower than those of Finland (38 mg/kg), Denmark (40 mg/kg), Czech Republic (70 mg/kg), Netherland (85 mg/kg), and Switzerland and Ireland (50 mg/kg). Heavy metals load in soils could be attributed to sources and activities taking place at most of the automobile workshops. Lead poisoning could result from the common usage of lead batteries, metal products, paint coatings, and pipes around the workshops. Battery specialists, "battery chargers" as they are popularly called across Nigeria, are usually present around automobile workshops, and they are a major source of lead. Other sources is gas exhaust of most automobiles under service at these automobile workshops (use of leaded petrol and additives are still common).²¹ The arsenic content in MMY was below detection level, the control sites of OMV and NMAV were below detection levels. Arsenic, an element that is found in several environmental matrices at low concentrations²⁶ occur either in the organic form as methylated metabolites or in inorganic forms as pentavalent or trivalent arsenate. Tchounwu et al.,²⁷ and Centeno et al.,²⁸ have reported that arsenic compounds form part of the therapy used for the treatment of trypanosomiasis, syphilis, amoebic dysentery, and other parasitic diseases. A lot of factors like genetic and nutritional factors, individual proneness,

gender, age, and biological species all influence arsenic toxicity. Chromium concentrations in all the workshops were below their baseline values and were comparable to their control values. Adelekani and Abegunde,¹⁹ reported an increase in chromium content at a location in their study. Chromium is one of those heavy metals in the environment whose concentration is gradually increasing due to industrial growth, especially the development of metal, chemical and tanning industries. Air and water erosion of rocks, power plants, liquid fuels, brown and hard coal, and industrial and municipal waste are some other sources through which chromium permeate the environment. Local permeation of the chromium to soil, water or the atmosphere might result in excessive amounts in biogeochemical circulation although there is no risk of chromium contamination on a global scale. Ghosh and Singh,²⁹ observed that persistence of chromium in the environment is because of its non-biodegradability. Once chromium is mixed in the soil, it ends in the environmental sink after having undergone transformation into various mobile forms.³⁰ The cadmium contents of all the automobile workshops soils exceeded their baseline values but the control values of OMV, MMY and AMY were comparable to their baseline values. This present finding did not corroborate the study by Adelekan and Abegunde,²⁹ that reported that for 50% of the samples, the cadmium content was below the detection limit and this situation was found spread through all the locations and at various depths. It was also true for the control soil where cadmium was found to be $< 0.002 \text{ mg/kg}^{-1}$ at all the depths investigated according to their study. Cadmium tends to be more mobile in soil systems than many other heavy metals. Although the measured values in their study showed a range of 0.41 to 17.23 mg/kg^{-1} , the majority however are less than 1.0 mg/kg^{-1} .

Kidney damage, band cardiovascular problems and bone deformities occur as a result of chronic cadmium exposures.

The highest pH value was observed in NMAV while the lowest pH value was seen in MMY in Table 2. It is a fact that pH is an important soil property, having great effects on solute concentration and sorption/desorption of contaminant in soil.³¹ Availability of the heavy metals was minimal in NMAV but was profound in MMY. Low pH increases mobility of metals. Increasing the soil pH to 6.5 or higher is a measure in the remediation of heavy metal polluted soils.¹⁹ It reduces the mobility of some metal species down the soil strata while low pH values usually enhance metal distribution and transport in soil.³²

Table 2. pH and temperature levels of automobile workshops in Owerri Metropolis.

Site	Temp (⁰ C)	pH	Inference
OMV	33.8	7.7	Slightly alkaline
NMV	32.5	6.8	Slightly acidic
NMAV	34.1	8.2	Alkaline
MMY	31.8	5.7	Acidic
AMY	31.5	5.9	Acidic

Table 3 shows the contamination status of the automobile workshops studied. All the automobile workshop soils revealed low cobalt and chromium contaminations. Low nickel contamination was observed in OMV, NMV and MMY. However there was moderate nickel contamination in NMAV and AMY, but lower than the reports of Ogunka-nnoka *et al.*³³ There was also moderate mercury in OMV, NMV, and NMAV whereas there was low contamination at MMY and AMY. There was moderate silver

contamination in MMY and with arsenic in NMV and AMY. Further, very high cadmium and lead contaminations were observed in all the automobile sites. There was also very high silver contamination at OMV, NMV and NMAV and with arsenic at OMV and NMAV. Various toxicities to humans through uptake of crops which leads to unsafe foods that compromise food security can be caused by soils contaminated with substances like heavy metals.¹²

Table 3. Contamination Factor (CF) for automobile workshop soils in Owerri Metropolis.

Metals	OMV	NMV	NMAV	MMY	AMY
Ag	6.50	7.75	9.75	2.00	-
Co	0.42	0.16	0.71	0.33	0.45
Ni	0.93	0.62	1.20	0.80	1.07
Hg	1.23	1.30	1.92	0.53	0.46
Pb	20.94	18.23	24.22	10.51	16.95
As	9.33	1.31	6.68	-	1.06
Cr	0.22	0.08	0.57	0.14	0.49
Cd	110.30	144.65	58.50	45.55	102.60

The results obtained for the enrichment factor (Table 3, 4) shows that only the deposition of mercury at NMV was as a result of natural activities, while all other results showed depositions due to anthropogenic activities. In line with the observations of Bini and Bech,³⁴ a point-like mode of contamination where the deposition of each metal is particular to a given site, and varies from site-to-site could be suggested.

Table 4. Enrichment Factor (EF) for automobile workshop soils in Owerri Metropolis.

Metals	OMV	NMV	NMAV	MMY	AMY
Ag	5.2	10.33	4.33	-	-
Co	7.24	2.97	8.18	-	9.29
Ni	7.85	14.62	7.68	4.27	13.01
Hg	1.33	0.94	2.77	-	1.5
Pb	174.55	31.13	27.17	30.83	43.85
As	-	8.77	-	-	1.12
Cr	13.60	3.33	9.75	12.58	3.67
Cd	157.57	23.71	13.76	25.30	89.21

The I_{geo} values are represented in Table 5. According to the classification above, the results revealed that there were no cobalt and chromium pollutions in all the sites. There was also no nickel pollution in all the sites except in AMY and no mercury pollution in all the sites except in NMAV. Also, no arsenic pollution was observed in NMV and AMY. The result however indicates that there were slight silver, nickel and mercury pollutions in MMY, AMY and NMAV respectively. There was moderately severe silver pollution in OMV, NMV and NMAV. Further, there was moderately severe arsenic pollution in OMV and NMAV and lead at MMY. There was severe lead pollution in OMV, NMV and AMY. However, a severely extreme lead pollution was observed in NMAV. All the automobile sites were extremely polluted with cadmium. The highest I_{geo} value was obtained for cadmium at NMV. Automobile workshops are found scattered all over most cities where all categories of wastes are indiscriminately dumped on every available space ranging from lubricating oil, junked cars, tyres, spare parts are always been found to litter all parts of

the workshop. Waste from automobile workshop activities can be categorized into maintenance and materials handling wastes. Some of the soluble metals may find their way to lakes, rivers, streams and soil resulting into pollution since heavy metals in soil are toxic.¹⁵ Brain damage and disorder as well as stunted growth in plants could occur as a result of high lead level.³⁵

Table 5. Index of geoaccumulation (I_{geo}) for automobile workshop soils in Owerri Metropolis.

Metals	OMV	NMV	NMAV	MMY	AMY
Ag	2.11	2.36	2.70	0.41	-
Co	-1.81	-3.18	-1.07	-2.16	-1.71
Ni	-0.68	-1.26	-0.31	-0.89	-0.47
Hg	-0.28	-0.19	-0.35	-1.47	-1.70
Pb	3.80	3.60	4.01	2.80	3.49
As	2.63	-0.18	2.15	-	-0.49
Cr	-2.74	-4.17	-1.37	-3.39	-1.58
Cd	6.20	6.59	5.28	4.92	6.09

The results of Table 6 show the daily intake levels of heavy metals from the automobile workshop soils. Average daily intake of lead and specifically at NMAV was highest among all other metals and automobile workshops investigated. The levels of these heavy metals were found within the reference dose provided by ATSDR.³⁶ It is very vital to have a daily intake level of these heavy metals below their oral reference doses.

Table 6. Average Daily Intake (ADI) (Mg/kg/day) of heavy metals on automobile workshop soils in Owerri Metropolis.

Metals	OMV x10⁻⁶	NMV x10⁻⁶	NMAV x10⁻⁶	MMY x10⁻⁶	AMY x10⁻⁶	Reference Dose
Ag	0.44	0.53	0.66	0.13	-	5 x10 ⁻³
Co	4.59	1.78	7.71	3.61	4.94	3 x10 ⁻²
Ni	37.83	25.33	49.06	32.71	43.86	2 x10 ⁻²
Hg	0.27	0.29	0.42	0.21	0.10	4 x10 ⁻⁵
Pb	718.64	625.44	831.22	360.74	581.85	3.5 x10 ⁻³
As	9.60	1.35	6.98	-	1.09	3 x10 ⁻⁴
Cr	31.27	11.61	80.45	19.86	69.66	3 x10 ⁻³
Cd	37.84	49.62	20.07	15.62	35.19	1 x10 ⁻³

Table 7. Non-Cancer Hazard Quotient of heavy metals on automobile workshops soils in Owerri Metropolis.

Metals	OMV	NMV	NMAV	MMY	AMY
Ag x10 ⁻³	0.08	0.10	0.13	0.02	-
Co x10 ⁻⁴	1.53	0.59	2.57	1.20	1.64
Ni x10 ⁻⁴	18.93	12.66	24.53	16.35	21.93
Hg x10 ⁻¹	0.06	0.07	0.10	0.03	0.025
Pb x10 ⁻³	205.32	178.69	237.49	103.06	166.15
As x10 ⁻²	3.4	0.11	2.32	-	0.36
Cr x10 ⁻³	10.42	3.87	26.81	6.62	23.22
Cd x10 ⁻³	37.84	49.62	20.07	15.62	35.19

The non cancer hazard quotient shown in Table 7 indicates that no significant health hazard could result from the levels of metals deposited at the automobile workshops soils, as the levels did not exceed the reference

level at 1.0. Also, THI (Fig. 1) indicates that all the depositions of the heavy metals in the automobile workshops cumulatively would not cause any significant long-term health hazards as their values were below the standard value of 1. The greater is the value of HQ and THI, the greater is the level of concern, thus indicating higher concerns at NMAV than other automobile workshops.³⁷⁻³⁸

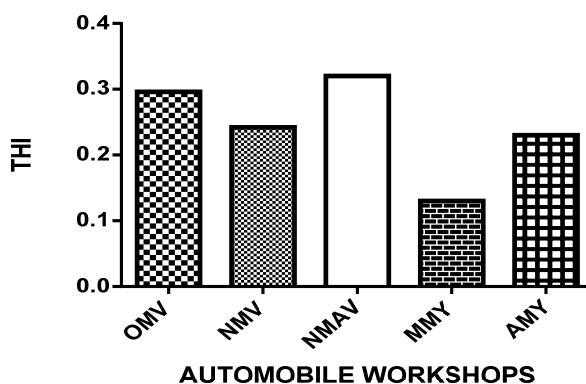


Figure 1. Total Hazard Index (THI) of heavy metals on top soils of automobile workshops in Owerri Metropolis.

Experimental

Description of area of study

The study comprised five automobile workshops within Owerri Metropolis in Imo State Nigeria. These workshops were chosen because they are located within the metropolis, as well as being the workshops with the highest level of activities and attendant infrastructural collapse.

Two sampling points in each of the locations were applied, which represented the control and test samples. Soil samples collected from points where the major activities occur in the workshops represented the test

samples. Soil samples used as control were collected 100m farther than the test sites as recommended by Agomuo and Amadi.¹²

The automobile workshops used for this study include:

- ❖ OMV: Orji Mechanic Village by Orji Fly Over, Okigwe Road
- ❖ NMV: Naze Mechanic Village, Off Aba Road, Owerri West
- ❖ NMAV: New Market Automobile Workshop, along Douglas Road, Owerri Municipal
- ❖ MMY: Matrix Mechanic Yard Umunwonyeali Owerri North
- ❖ AMY: Alvan Mechanic Yard Akwakuma Owerri North

Preparation of samples

With the aid of an auger, soil samples (100 g) were randomly collected (in dry season) from the top soils (0-15 cm) in each of the study sites. The soil samples were put in a container and any debris contained were removed before being tightly covered with an aluminium foil and conveyed to the laboratory for further preparation. The soil samples were air dried at room temperature, checked again for any stones or pellets, and then ground using a mechanical electric grinder. The ground soil samples were further sieved through a mesh (2 mm).

Sample analysis

Determination of soil pH

The pH analysis was carried out following the methods of Okereke and Amadi.¹³ Briefly, a suspension of soil and water (1:2) was obtained and analyzed for the pH using a calibrated pH meter.

Heavy metal analysis

The method of Agomuo and Amadi,¹² was applied for the determination of Silver (Ag), Cobalt (Co), Nickel (Ni), Mercury (Hg), Lead

(Pb), Arsenic (As), Chromium (Cr), and Cadmium (Cd) contents of the collected soil samples. Briefly the soil samples were measured, and 1g collected and put in a beaker was mixed with 15ml mixture (ratio of 5:1:1) of Nitric acid (HNO₃), Perchloric acid (HClO₄), and Sulfuric acid (H₂SO₄). After gently stirring the mixture, it was heated at 80⁰C to obtain a clear solution. The solution was allowed to cool, then, 2% nitric acid (30 ml) was added. Afterwards, this solution was subjected to spectrophotometric analysis (Shimadzu AA-670, Japan) and interpreted in line with a prepared reference solution.

Determination of index of geoaccumulation (I_{geo})

To obtain the I_{geo}, the formula of Muller below was applied.¹⁴

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n}$$

C_n means the heavy metal concentration of the samples, B_n means the background/baseline value of the heavy metal. Specific for this study, the background/baseline values used were as described by Agomuo and Amadi.¹²

I-geo was classified into seven grades as shown by Okereke and Amadi,¹³ I-geo ≤ 0 (grade 0), unpolluted; 0 < I-geo ≤ 1 (grade 1), slightly polluted; 1 < I-geo ≤ 2 (grade 2), moderately polluted; 2 < I-geo ≤ 3 (grade 3), moderately severely polluted; 3 < I-geo ≤ 4 (grade 4), severely polluted; 4 < I-geo ≤ 5 (grade 5), severely extremely polluted; I-geo > 5 (grade 6), extremely polluted.

Contamination factor (Cⁱf)

To calculate the contamination factor, the formula below was applied

$$C^i f = \frac{C_n}{B_n}$$

C_n and B_n were as described for the I_{geo}.

Four grades are recognized for the contamination factor values as described by Agomuo and Amadi.²²

$C^i_f < 1$ represents low contamination factor indicating low contamination, $1 \leq C^i_f < 3$ represents moderate contamination factor, $3 \leq C^i_f < 6$ represents considerable contamination factor, and $6 \leq C^i_f$ represents very high contamination factor.

Estimation of enrichment factor (EF)

The enrichment factor was computed using the following relationship:

$$EF = \frac{\text{Heavy metal concentration in the soil at the workshop}}{\text{Heavy metal concentration in the soils at the control site}}$$

When EF values < 1 the origin of the source of contamination is natural whereas an anthropogenic source is suggested when EF values ≥ 1 .

Health risk assessment

The risks associated with oral ingestion of the heavy metal at the automobile workshops were calculated as the daily intake of the metal, non cancer hazard quotient, and total chronic hazard index, shown below following the methods of Agomuo and Amadi.¹²

$$\text{Daily oral intake (DI) (mg/kg/day)} = \frac{C \times IR \times EF \times ED}{BW \times AT}$$

C means the heavy metal concentration at the sampling points

IR = Ingestion rate

EF = Exposure frequency (day/year)

ED = Exposure period (year)

BW = Body weight (kg)

AT = Average time for non-carcinogens

The IR, EF, ED, BW and AT were standard USEPA values adopted from the study of Qing et al.,¹⁵ while the mean bodyweight of occupants of the vicinity was 56.6 kg.

To calculate the systemic toxicity or non-carcinogenic hazard for the heavy metal at the sites was according to the formula below:

$$\text{Non-cancer Hazard Quotient (HQ)} = \frac{\text{DI}(\text{mg}/\text{kg}/\text{day})}{\text{ORfd}}$$

DI = Daily oral intake of soil

ORfd = Oral reference dose for the heavy metals.

In some cases where ORfd is unavailable the substitute oral reference concentration was used ORfc.

Total chronic hazard index was calculated as:

$$\text{Total Chronic Hazard Index (THI)} = \sum_{i=1}^n \text{HQ}$$

When HQ and THI > 1, the level of concern is high since the acceptable standard is 1.0, and it is deemed that at this point there will be no significant health hazard.

According to Agomuo and Amadi,¹² the higher the THI value, the more the probability of experiencing long term health hazards.

Statistical analysis

Experimental data was presented as mean ± SD of triplicate determinations. Data was analyzed using the least standard deviations (LSD) of the one way analysis of variance, and deemed significant at 95 % confidence interval.

Conclusions

According to this study, the concentration, ingestion and potential health hazard of lead were higher when compared to the other heavy metals investigated. The high levels obtained for lead could have been because

there are common usages of lead batteries, metal products, paint coatings, and pipes around the workshops. However, there was higher cadmium pollution and contamination when compared to the other metals. This could have been as a result of the immobility of cadmium at the automobile sites being known to possess high mobility through the soil layers. The Average Daily Intake (ADI) of the metals at all the study locations was below the reference doses. No significant health hazard could result from the levels of metals deposited at the automobile workshops soils, as the levels did not exceed the reference level at 1.0 as well as the Total Hazard Index (THI). Prevention of soil contamination is far better than any form of remediation process. In order to prevent heavy metals toxicity on soils, attempts should be made to regulate the heavy metals contents of sludge that can be directly released to the soil in automobile workshops. There is currently no enforced regulation in place at most automobile workshops. Although regulation of waste disposal at automobile workshops will not remove the heavy metal contaminants, it will enable their immobilization in the soil, reducing their potential for severe effects in the environment. This study has shown the necessity to periodically monitor and apply measures that can halt the environmental decay, occurring at the automobile workshops.

References

1. McLaughlin, M.J.; Parker, D.R.; Clarke, J.M. Metals and micronutrients-food safety issues. *Field Crop Research* **1999**, *60*, 143–163.
2. Lenntech, W.T. Chemical Properties, Health and Environmental Effects of Copper. Lenntech Water Treatment and Purification Holding 2009.

3. Gazso, L.G. The Key Microbial Processes in the Removal of Toxic Metals and Radionuclides from the Environment. A review. *CEJOEM*. **2001**, 7(3), 178–185.
4. Kosolapov, D.B.; Kuschik, P.; Vainshtein, M.B.; Vatsourina, A.V.; Wiebner, A.; Kasterner, M.; Miler, R.A. Microbial Processes of Heavy Metal Removal from Carbon Deficient effluents in constructed wetlands. *Eng. Life. Sci.* **2004**, 4(5), 403–411.
5. Begum, A.; Ramaiah, M.; Harikrishna, K. I.; Veena, K. Analysis of Heavy Metals Concentration in Soil and Lichens from Various Localities of Hosur Road, Bangalore, India. *Orbital: Electron. J. Chem.* **2009**, 6(1), 13-22.
6. Huerta-Diaz, M.D.; Morse, J.W. Pyritization of Trace Metals in Anoxic Marine Sediments. *Geochimica et Cosmochimica Acta* **1992**, 56, 2681-2702.
7. Cooper, D.C.; Neal, A.L.; Kukkadapu, R.K.; Brewé, D.; Coby, A.; Picardal, F.W. Effects of Sediment Iron Mineral Composition on Microbially Mediated Changes in Divalent Metal Speciation: Importance of Ferrihydrite. *Geochimica et Cosmochimica Acta* **2005**, 69, 1739-1754.
8. Hamilton-Taylor, J.; Smith, E.J.; Davison, W.; Sugiyama, M. Resolving and Modeling the Effects of Fe and Mn Redox Cycling on Trace Metal Behavior in a Seasonally Anoxic Lake. *Geochimica et Cosmochimica Acta*. **2005**, 69, 1947-1960.
9. Imevbore, A.A.A.; Adeyemi, S.A. Environmental monitoring in relation to pollution and control of oil pollution. *Incorporated Proceedings of Seminar on the petroleum industry and the Nigerian environment*. **1981**, 6, 135-142.

10. Adeniyi, A.A.; Afolabi, J.A. Determination of total petroleum hydrocarbons and heavy metals in soils within the vicinity of facilities handling refined petroleum products in Lagos metropolis. *Environ. Int.* **2002**, *28* (1-2), 79-82.
11. Europe Environmental Assessment Agency, (E.E.A). Progress in Management of contaminated sites (CSI 015), Kongan, 6DK- 1050, Denmark, **2007**.
12. Agomuo, E.; Amadi, P. Accumulation and toxicological risk assessments of heavy metals of top soils from markets in Owerri, Imo state, Nigeria. *Env. Nano. Monit. Mgt.* **2017**, *8*(1), 121-1126.
13. Okereke, C.J.; Amadi, P.U. Accumulation and risk assessment of heavy metals contents of school playgrounds in Port Harcourt metropolis, Rivers State. *J. Chem. Health Saf.* **2017**, *24*(5), 11-22.
14. Muller, G. Index of geoaccumulation in sediments of the Rhine River. *J. Geol.* **1969**, *2*, 108–118.
15. Qing, X.; Yutong, Z.; Shenggao, L. Assessment of heavy metal pollution and human health risk in urban soils of steel industrial city (Anshan) Liaoning, Northeast China. *Ecotoxicol. Environ. Saf.* **2015**, *120*, 377–385.
16. Olayiwola, O.A. Levels of Pb, Fe, Cd and Co in Soils of Automobile Workshop in Osun State, Nigeria. *J. Appl. Sci. Environ. Mgt.* **2011**, *15*(2), 279 – 282.
17. Environmental Agency. Environmental Concentrations of Heavy Metals in UK Soil and Herbage. UK Soil and Herbage Pollutant Survey. *Bristol: Environ. Agency* **2007**, p. 7.
18. Berrow, M.L.; Reaves, G.A. Total Chromium and Nickel Contents of Scottish Soils. *Geoderma* **1986**, *37*, 15-27.

19. Adelekani, B.A.; Abegunde, K.D. Heavy metals contamination of soil and groundwater at automobile mechanic villages in Ibadan, Nigeria. *Int. J. Phys. Sci.* **2011**, *6(5)*, 1045-1058.
20. Gillette, B. Nickel named 'Allergen of the Year'. ACDS adds to list of substances warranting more attention. *Dermatology Times* **2008**, *4*, 15-16.
21. Olanrewaju, L.; Arokoyu, S.B.; Udeh, I.I. Assessment of Automobile Workshops and Heavy Metal Pollution in a Typical Urban Environment in Sub-Saharan Africa. *Environ. Res. Eng. Mgt.* **2015**, *71(1)*, 27-35.
22. Ano, A.O. Trace metal studies on soils of the Nigerian coastal plain sands: Status of Cu, Zn, Pb, Fe and Mn. *J. Soils and Crops.* **1994**, *4(1)*, 1-5.
23. Nwoko, C.O.; Egunjobi, J.K. Lead contamination of soil and vegetation in an abandoned battery factory site in Ibadan, Nigeria. *J. Sust. Agric. Environ.* **2002**, *4(1)*, 91-96.
24. United States Environmental Protection Agency. Test methods of evaluation of soil waste. USEPA Washington, D.E. USEPA S/W, 846 (1986).
25. Chokor, A.A.; Ekanem, E.O. Heavy Metals Contamination Profile in Soil from Automobile Workshops in Sapele, Nigeria. *World Journal of Analytical Chemistry* **2016**, *4(2)*, 26-28.
26. Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Arsenic TP-92/09. Georgia: Center for Disease Control, Atlanta **2000**.
27. Tchounwou, P.B.; Wilson, B.; Ishaque, A. Important considerations in the development of public health advisories for arsenic and arsenic-containing compounds in drinking water. *Rev. Environ. Health* **1999**, *14(4)*, 211-229.

28. Centeno, J.A.; Tchounwou, P.B.; Patlolla, A.K.; Mullick, F.G.; Murakat, L.; Meza, E.; Gibb, H.; Longfellow, D.; Yedjou, C.G. Environmental pathology and health effects of arsenic poisoning: a critical review. In *Managing Arsenic In the Environment: From Soil to Human Health*. R. Naidu, E. Smith, J. Smith, P. Bhattacharya, Eds.; CSIRO Publishing Corp: Adelaide, Australia **2005**.
29. Ghosh, M.; Singh, S.P. Comparative Uptake and Phytoextraction Study of Soil Induced Chromium by Accumulator and High Biomass weed Species. *Appl. Ecol. Environ. Res.* **2005**, *3(2)*, 67-79.
30. Bartlett, R.J. Mobility and Bioavailability of Chromium in Soils. *Adv. Res. Environ. Sci. Tech.* **1988**, *20*, 267-304.
31. Kadem, D.E.D.; Rached, O.; Krika, A.; Gheribi-Aoulmi, Z. Statistical analysis of vegetation incidence on contamination of soils by heavy metals (Pb, Ni and Zn) in the vicinity of an iron steel industrial plant in Algeria. *Envirometrics* **2004**, *15*, 447-462.
32. Oguntimehin, I.; Ipinmoroti, K. Profile of Heavy Metals from Automobile Workshops in Akure, Nigeria. *J. Environ. Sci. Tech.* **2008**, *1(1)*, 19-26.
33. Ogunka-Nnoka, C.U.; Assor, K.C.; Onuoha, S.C.; Amadi, P.U. A Study of the Toxicants and Biomarkers of Oxidative Stress in Soils, Plants, and Sea Foods from Ebubu and Elele-Alimini Communities in Rivers State. *Ovidius Annals of Chemistry* **2018**, *29(1)*, 1-7.
34. Bini, C.; Bech, J. PHEs, Environment and Human Health Potentially Harmful Elements in the Environment and the Impact on Human Health. Springer, Netherlands **2014**.
35. Somer, E. The toxic potential of trace metal in foods. A review. *J. Food. Sci.* **1994**, *39*, 215-217.

36. Agency for Toxic Substances and Disease Registry (ATSDR). Case Studies in Environmental Medicine - Lead Toxicity. Atlanta: Public Health Service, U.S. Department of Health and Human Services 1992.
37. Grzetic, I.; Ghariani, R.H.A. Potential health risk assessment for soil heavy metal contamination in the central zone of Belgrade (Serbia). *J. Serb. Chem. Soc.* **2008**, 73(8-9), 923-934.
38. Wang, X.; Wang, F.; Chen, B.; Sun, F.; He, W.; Wen, D.; Liu, X.; Wang, Q. Comparing the health risk of toxic metals through vegetable consumption between industrial polluted and non-polluted fields in Shaoguan, South China. *J. Food Agric. Environ.* **2012**, 10(2), 943-948.