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An Assessment of Heavy-Metal Contamination in Soils within Auto-Mechanic Workshops Using Enrichment and Contamination Factors with Geoaccumulation Indexes

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Abstract

Soil characterization and heavy metals in different layers (0 - 15 cm; 15 - 30 cm and 30 - 45 cm depth) of automobile mechanic waste dumps were studied. The soils showed remarkably high levels of all the metals above background concentrations with most (Ni, Cu, Fe, Cr and Cd) decreasing with soil depth. The distribution pattern were in the following order Fe > Cu > Zn > Pb > Cr > Ni > Cd. Across all the sampling locations and profiles, Fe and Cd showed the highest (476.4 μg·g^{-1}) and least (37.5 μg·g^{-1}) mean concentrations respectively. Pollution load index (PLI) and index of geoaccumulation (I_{geo}) revealed overall high and moderate contamination respectively but the enrichment factors (EFs) for Pb Ni and Cd are severe. The inter-element relationship revealed the identical source of elements in the soils of the studied area. The accuracy of the results has been cheeked using the standard reference material; SRM (PACS-2). The mechanic waste dumps represent potential sources of heavy metal pollution to environment. The elevated levels of heavy metals in these soil profiles constitute a serious threat to both surface and groundwater.

Keywords

Heavy Metals, Soil Contamination, Soil Profiles, Automobile Mechanic, Enrichment Factor, Geoaccumulation Index

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1. Introduction

In Nigeria and most developing nations, increased automobile repairs/workshops activities are due to ever-increasing demand for personal vehicles, most of which are used "Tokunbo" vehicles. These have contributed markedly to the problem of soil contamination in most cities. Automobiles used (waste) oil contains oxidation products, sediments, water and metallic particles resulting from machinery wears, used batteries, organic and inorganic chemicals used in oil additives and metals [1]. Percolation of leachates from these materials poses threats to groundwater water. Unfortunately, information on the impact of automobile mechanics' activities on the ecosystem is still very rare.

The co-existence of toxic heavy metals and hydrocarbons (HCs) at many of the mechanics contaminated sites all over Nigeria and in other developing countries poses a severe threat to the environment. In fact, the significance of trace elements in soil chemistry is increasingly becoming an issue of global concern especially as soil constitutes a crucial component of rural and urban environment [2]-[4]. Heavy metals such as cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn) which are often contained as additives in some lubricants and gasoline are non-degradable in the soil. Some of them have been classified as priority pollutants by United State Environmental Protection Agency. At the moment, very few technologies, such as soil washing and bioremediation, are available to treat these mixed wastes [5].

High levels of heavy metals in soils do not necessarily reflect anthropogenic influence, but instead may be of a diagenetic origin [6] or grain size effects [7]. Since metals from both natural and anthropogenic sources accumulate in soils, it is often difficult to determine what fraction of soils metal load comes from which source. A crucial step for pollution assessment of soil is to establish the expected natural background concentration levels [8], from which various approaches can be used to quantify anthropogenic inputs.

A study of the distribution, enrichment and accumulation of heavy metals in soils within mechanic workshops is particularly important, especially in developing countries like Nigeria due to the unprofessional and lawless manner with which wastes are being disposed and to the assessment of the possible influence of anthropogenic activities on groundwater. In the present study, we carried out physicochemical characterization of soils from auto-mechanic workshops at different depths (0 - 15 cm; 15 - 30 cm, 30 - 45 cm), namely pH, clay, silt, sand, total organic carbon (TOC), exchangeable cations, and equally examined the distribution of heavy metals such as Pb, Cr, Cu, Zn, Fe, Ni, and Cd. Our assessment of soil contamination was based on degree of contamination using the enrichment factor (EF), the geo-accumulation index (I_{geo}) and the pollution load index [9]-[13]. In Nigeria, the pollution index represents the metal content effectively measured in soil by chemical analysis and the reference value of contamination obtained using a standard table formulated by the Department of Petroleum Resources of Nigeria, DPR [14] for maximum allowable concentration of heavy metals in soil (**Table 1**).

In addition, the standard employed for interpreting soil heavy contamination/pollution (C/P) varies from country to country based on chosen factors [15]

$$\text{C/P value} = \frac{\text{Actual measurement of metal concentration in soil}}{\text{Target values from reference table}}$$

The sampling site considered in this study (Ikare Akoko) is a major commercial city in Ondo State with well over 200 auto-mechanic workshops (big and small). After personal interview three locations were strategically considered due to the age of establishment, size and patronage. To date, there are scarce data pertaining to heavy

Table 1. Department of Petroleum Resources (DPR, 1991) target and intervention values for metals in soil.

Metals	Target values ($\mu g \cdot g^{-1}$)	Intervention values ($\mu g \cdot g^{-1}$)
Cadmium	0.8	17
Chromium	100.0	380
Copper	36.0	190
Lead	85.0	530
Nickel	35.0	210
Zinc	140.0	720

metals composition of soil profiles (0 - 15 cm, 15 - 30 cm and 30 - 45 cm depth) within and around auto-mechanic workshops in developing countries like Nigeria. Moreover, the available study has been limited to the top soil (0 - 15 cm depth) [3] [16] [17]. This is a major shortcoming considering the complex, porous nature of soil in retaining and releasing pollutants to groundwater [18]. The present study hopes to address some of these shortcomings. The ultimate aim of the study is to assess heavy metals status on soils around auto-mechanic workshops of this environment. Thus, the specific objectives include: 1) to study the vertical distribution of the various metals and 2) to assess the extent of anthropogenic contribution.

2. Material and Methods

2.1. Study Area and Sampling

This investigation was carried out within three auto-mechanic workshops in Ikare Akoko located in the northern geographical district of Ondo State, south-western part of Nigeria (**Figure 1**). Ikare is about 100 km from Akure, the Ondo State capital. Population as of 2006 was over 700,000. The temperature in Akoko land throughout the year ranges between 21˚C - 29˚C and humidity is relatively high. The climate is tropical with approximately 20% precipitation. The workshops used in this study were chosen based on age of establishment and strategic location within the city. Two of the three workshops (approx. 10 m^2 each in size) are located at a distance of about 250 m away from each other while the third workshop (approx. 15 m^2 in size) is located south of the two other locations at a distance of almost 1200 m away. At each of the workshop investigated were three designated sites for soil sampling. Thus, three samples were collected separately at each site and at each depth and analyzed separately. The control (background) sample was obtained from a location remote from industrial zone and far removed from the influence of industrial activities at the University Campus, Akungba-Akoko, Ondo State. Sampling design for this study was based on two premises: first, the need to spread sample sites objectively over the study area and second, the need to ensure that site characteristics are adequately depicted. Soil samples were collected from three sampling depths 0 - 15 cm, 15 - 30 cm and 30 - 45 cm, hereafter referred to as topsoil, subsoil and sub-sub soil respectively. The sampling was restricted to this zone because it provides the bulk of plant nutrients [19]. Samples were collected inside labeled polythene bags.

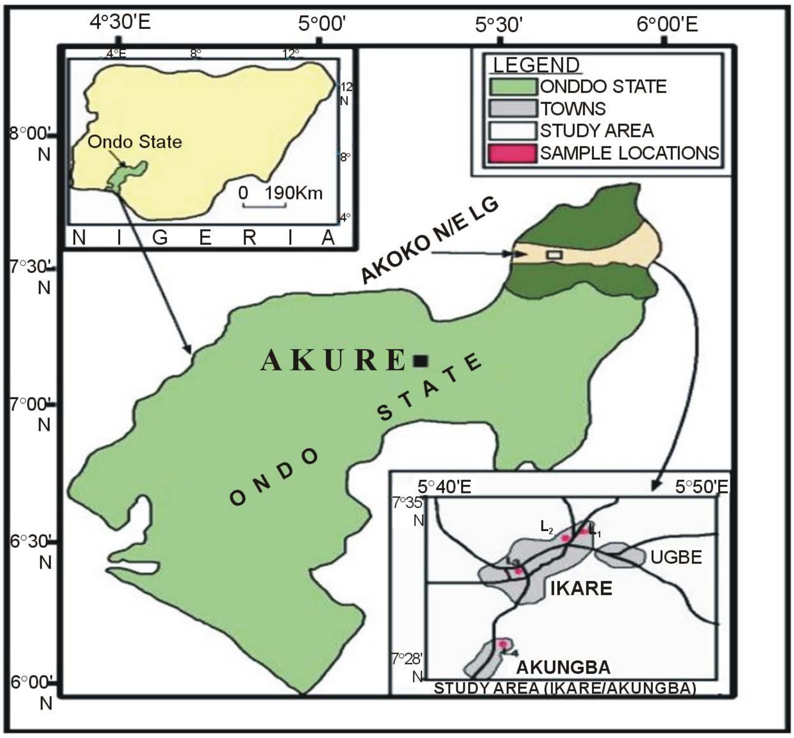


Figure 1. Map of the sampling locations (inserted is the area map of Nigeria and Ondo State showing the geographical locations).

2.2. Quality Assurance (QA)/Control (QC)

Quality assurance (QA)/control (QC) protocol prescribed by the U. S Environmental Protection Agency (EPA) for metal analysis was used. In order to control the analytical procedure, precision of the analytical results was estimated by replicate analysis. All laboratory equipments used for analysis were from Pyrex, washed with 0.1 N HNO_3, rinsed twice with distilled water and placed in a clean environment until dry. All reagents used were of analytical grade (BDH, Merk). Certified standard solutions 1000 $\mu g \cdot g^{-1}$ (BDH, Ltd.) of elements Pb, Cd, Cu, Cr, Fe, Ni, and Zn were used for Flame Atomic Absorption Analysis. In this study, the use of certified standard reference material PACS-2 (heavily contaminated marine sediment available from the Natural Research Council, Canada) was employed. The results are shown in **Table 2**. The percentage recoveries varied from 84.1% to 97.4% for all the metals excluding Fe.

2.3. Sample Preparation and Analysis

Soil samples were air-dried, sieved, and analyzed in the laboratory using standard techniques. Particle size composition was obtained by hydrometer method [20]. Soil pH was determined in water and 0.1 M KCl solution at 1.2:5 soil/solution ratios. Organic carbon content was found by the modified $K_2Cr_2O_7$ digestion of Walkley-Black method [21]. The value of organic matter was obtained by multiplying organic carbon by 1.724. The cation exchange capacity (CEC) was determined by adding the 1 M KCl extractable acidity to cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) exchanged by neutral 1 M $NH_4C_2H_3O_2$ (pH 7) as described in Barton and Karathanasis [22]. The K and Na were measured with flame photometer while the Mg and Ca were determined with atomic absorption spectrophotometer. The exchangeable acidity was determined by titration and the cation exchange capacity (CEC) was obtained by summation of exchangeable cations and exchange acidity.

For the total metals, a 0.5 g aliquot of the dried powder soil was taken into a 140 ml Teflon bomb and digested in 15 ml of a high purity concentrated 7 ml – HF + 5 ml – HNO_3 + 3 ml – HCl acid mixture on a hot plate at about 110˚C for 6 hours within a fume cupboard. After cooling to room temperature, the digest was diluted to 100 ml and dried and then again dissolved in 10% HNO_3 and made up to 20 ml by adding deionized water. Blank samples for soil were prepared. Each preparation of sample was repeated in triplicate.

2.4. Instrumentation

The determinations of the heavy metals Cd, Co, Cr, Pb, Fe, Ni and Zn) were performed with from the final solution with the use of Alpha 4AAS, Chemical Tech. Analytical Euro model atomic absorption spectrophotometer. The instrument's setting and operational conditions were done in accordance with the manufacturer's specifications. The instrument was calibrated with analytical grade metal standard stock solutions (1 $mg \cdot dm^{-3}$) in triplicate.

2.5. Statistical Analysis

We performed statistical analysis by using the raw data. Relationships between metals and other controlling factors were determined by bivariate correlation using the Pearson coefficient in a two-tailed test ($r < 0.01$ and 0.05). All analysis was performed using SPSS software (version 13.0).

3. Results and Discussion

Results

Table 3 shows the mean values and standard deviations of pH, organic matter (%), exchangeable cations ($\mu g \cdot g^{-1}$), and particle size distribution (*i.e.* percentages of sand, silt and clay) in soil samples from the areas

Table 2. Results of QA/QC analysis using PACS-2 SRM[a] (Trace Metals ($\mu g \cdot g^{-1}$) dry weight basis).

Sample	Cd	Fe	Cu	Pb	Zn
Certified-V	1.000	NI	310	183	364
Measured-V % Recovery	0.841 (0.11)	-	302 (14)	169 (8)	342 (18)

[*] The values in parentheses are standard deviations (SD); MDL = Method detection limit; SRM = Standard reference material; NI = Not indicated; a = Mean of triplicate analysis, V = Values.

Table 3. Chemical composition (Mean ± S.D, n = 9) of soil samples.

Specifications	Soil Depth (cm)	Soil 1	Soil 2	Soil 3	Control
pH (H_2O) 1.2:5	0 - 15	7.1 ± 0.2	6.9 ± 0.1	6.5 ± 0.2	6.7 ± 0.1
	15 - 30	6.7 ± 0.1	6.7 ± 0.1	6.4 ± 0.1	5.7 ± 0.1
	30 - 45	5.6 ± 0.2	6.6 ± 0.2	6.2 ± 0.2	5.7 ± 0.1
RH		61.4	56.5	58.3	59.0
OC (%)	0 - 15	1.74 ± 0.10	1.57 ± 0.12	1.22 ± 0.12	4.18 ± 0.13
	15 - 30	1.63 ± 0.21	0.75 ± 0.24	0.17 ± 0.16	3.08 ± 0.20
	30 - 45	0.75 ± 0.11	0.41 ± 0.13	0.12 ± 0.11	2.61 ± 0.11
CEC (cmol·kg^{-1})	0 - 15	10.7 ± 1.3	9.7 ± 1.9	9.9 ± 1.9	15.2 ± 0.2
	15 - 30	8..8 ± 1.0	7.1 ± 1.2	5.2 ± 0.8	12.3 ± 0.1
	30 - 45	6.7 ± 1.3	6.6 ± 1.2	3.3 ± 0.8	10.5 ± 0.1
PSD	Sand (%)	67 ± 3	63 ± 3	71 ± 4	55 ± 2
	Clay (%)	24 ± 3	26 ± 2	22 ± 3	34 ± 2
	Silt (%)	09 ± 2	11 ± 3	09 ± 3	11 ± 2
	T/C	SCL	SCL	SCL	SCL

S.D: standard deviation; T/C: textural class; SCL: sand clay loam; OM: organic matter; EC: electrical conductivity; CEC: cation exchange capacity; PSD: particle size distribution.

under study. The pH values ranged from 6.3 - 7.4 (0 - 15 cm); 6.2 - 6.9 (15 - 30 cm) and 5.1 - 6.7 (30 - 45 cm) while the sub-soils are basically slightly acidic. The relative Humidity (RH) of all soils ranged from 56.5 - 61.4. The total organic matter (TOM) content in the samples ranged from 1.8% - 3.3% (0 - 15 cm), 0.3% - 3.0% (15 - 30 cm) and 0.2% - 1.4% (30 - 45 cm). Based on total soils examined, the CEC (in cmol·kg^{-1}) ranged from 9.3 - 11.2 (0 - 15 cm); 5.1 - 9.7 (15 - 30 cm) and 2.9 - 7.2 (30 - 45 cm) across all studied soils with decreasing order down the profiles at each sample location. The soil samples show a variable admixture of sand, silt and clay. Results show that sand (>63 μm) was the main component of all soil samples, with a mean range from 63% to 71%. Mean clay contents were in the range of 22% to 24% and silt in the range 9% to 11%.

The distribution pattern of the metal across the various soil profiles is presented in **Figure 2** (details in supporting information). Across all the sampling locations and profiles, Fe and Cd showed the highest (476.4 μg·g^{-1}) and least (37.5 μg·g^{-1}) mean concentration respectively. In terms of concentration value across the various profiles, the highest mean concentration for Ni (99.2 μg·g^{-1}), Cu (399.3 μg·g^{-1}), Cr (79.8 μg·g^{-1}) and Cd (67.4 μg·g^{-1}) were recorded in the top soil (0 - 15 cm depth) with decreasing order down the soil profiles. However, the highest for Pb (210.1 μg·g^{-1}) and Zn (258.1 μg·g^{-1}) were recorded in the 30 - 45 cm depth with decreasing order up the soil profile.

4. Discussion

4.1. Soil Characterization

The data in **Table 3** shows that the pH across the entire study area ranged in a narrow interval. Top soils (0 - 15 cm) across the study area suggest slightly acidic to neutral condition while the middle (15 - 30 cm) and bottom layers (30 - 45 cm) suggest slightly acidic soil condition. pH plays significant role in solute concentration and in sorption and desorption of contaminants in soil [23] [24]. However, based on data in **Table 3**, the pH levels are very close at each soil layer which may suggest that, all other factors being equal, pH effects on the metal's bioavailability is insignificant.

The CEC is high in all top soils, followed by the middle soils and least in the bottom soils. The reduction in CEC down the soil profile makes the soil less suitable for tap rooted crops. This reduction in CEC of the studied soil over that of the control is a reflection of nutrient depleting wastes or displacement by toxic metals which are indirectly introduced through indiscriminate disposal of auto mechanic wastes. However, there are no significant mean differences ($p < 0.05$) in levels of CEC obtained at each soil layer from the various sampling locations. Soil-1 seems better enriched with macronutrients (Mg, Ca, Na and K) than the other two sites.

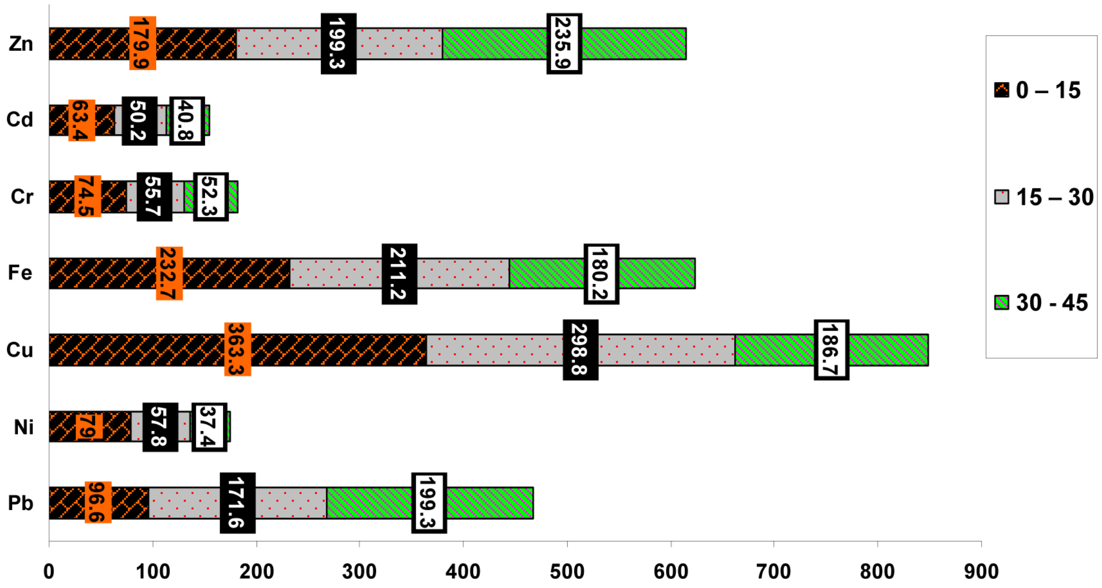


Figure 2. Distribution pattern of the mean concentrations of metals across soil depth (figure is generated from the cumulative data from all sites).

The OM decreases down the soil profile with Soil-1 and Soil-3 displaying the highest and least percentages respectively. The range in organic matter content of the control area (4.2% - 7.3%) is much higher than the range (0.2% - 3.3%) any of the samples from auto-mechanic workshops. The significant difference in the OM content of control and mechanic workshops sample indeed reflects a depletion of this parameter by wastes which are indiscriminately disposed within mechanic workshops. Previous studies have found that higher TOC (>3.0%) levels are typically associated with fine soils and lower TOC levels with coarse soils [25].

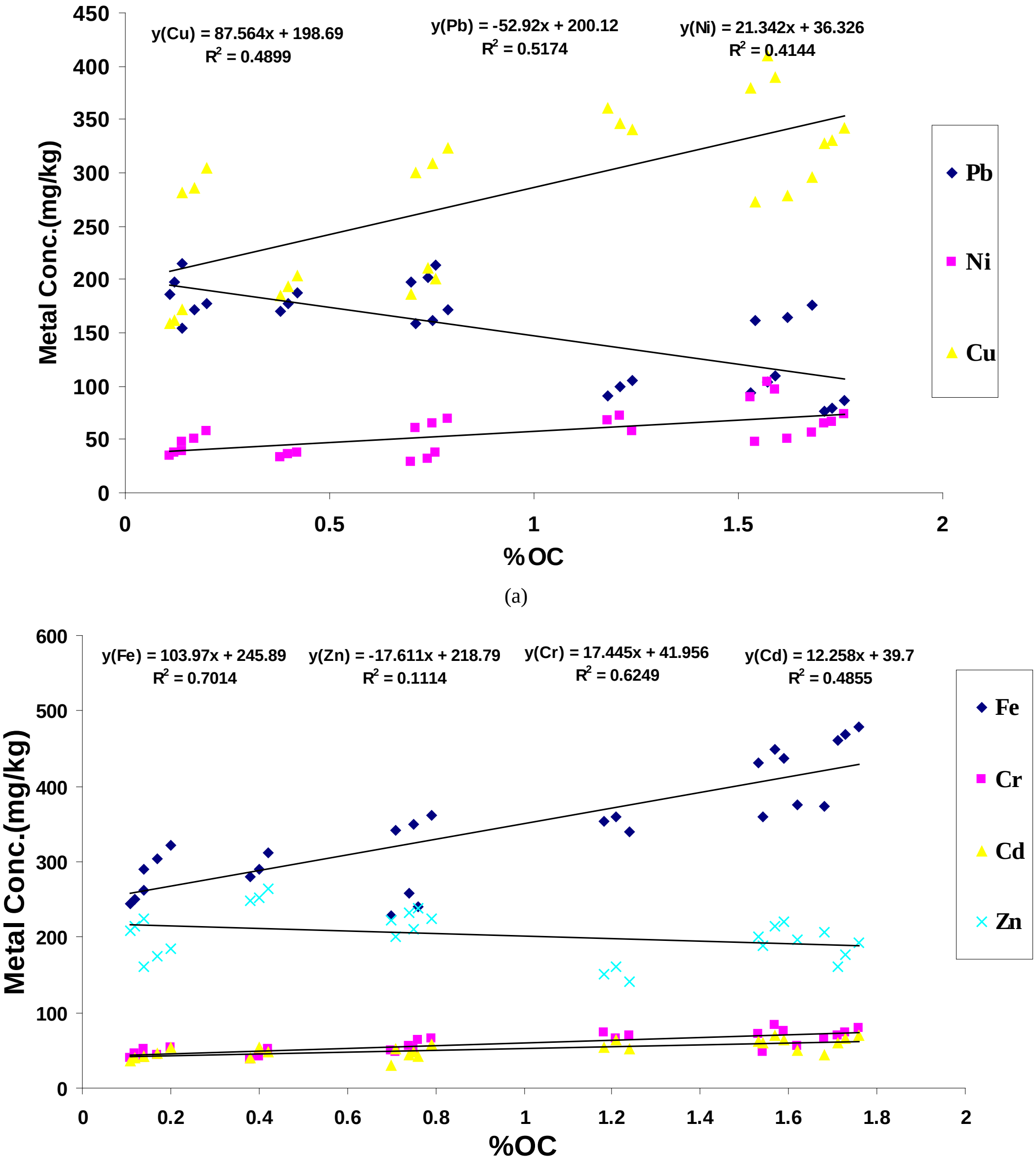
4.2. Heavy Metal Distribution

Metals in soils of the auto-repair workshop are not all retained within the profile depth of 0 - 15 cm (**Figure 2**). Average concentrations of Cd, Cr, Cu, Fe and Ni obtained from this study generally decreased vertically with soil depth while Pb and Zn increased with depth. This illustrates the mobility potential of heavy metals down the soil profile. The study on vertical variations of heavy metals concentrations in soils with depth was able to illustrate potential trends in heavy metals contaminations, which might draw a picture for the historical variations of local contaminations through the temporal analysis on soils. The enhanced concentrations of some of the metals may be attributed to the presence of additives (consisting of metals in various proportions) in lubricants used by auto mechanics.

Slight variation exists between the levels of individual metal across all sampling locations but without any significant mean differences ($\alpha \geq 0.95$). The variation may be due to factors such as age of the mechanic workshops, volume of work done on each site, types of automobile serviced or repair, type of lubricant commonly used, mode of wastes disposal and type of soil. However, significant variation and mean differences occur between levels of individual metals ($p < 0.05$).

Comparing metal concentrations with **Table 1** indicate that apart from Fe (where the DPR value is not indicated) and Cr, all the other metals are well above target values. For metals like cadmium and lead that have no biological function, this calls for public concern [26] [27]. The elevated levels of these metals in the soil profiles constitute a serious threat to both surface and ground water. Some of the metals correlated significantly with percent organic carbon with decreasing soil depth (**Figure 3(a)** and **Figure 3(b)**). This is indicative of the significance of organic matter in the sorption of micro pollutants in soil.

The total metal concentrations in the present study were compared to other studies, particularly in Nigeria. As noted earlier, the very few studies were based on top 0 - 15 cm soil depth. Apart from Pb which was found within the range reported [17], mean concentrations of all the other metals were above levels recorded in literature [3] [28].



(a)

(b)

Figure 3. (a) Correlation graph showing relationship between metal concentration (Cu, Pb and Ni) and OC with decreasing soil depth (figure is generated from the cumulative data from all sites); (b) Correlation graph showing relationship between metal concentration (Fe, Zn, Cr and Cd) and OC with decreasing soil depth (figure is generated from the cumulative data from all sites).

4.3. Indices of Pollution

In this study, the enrichment factor (EF), contamination factor (CF) and pollution load index (PLI) was applied to assess heavy metal contamination in soil located within automechanic workshops.

4.3.1. Pollution Load Index (PLI)

In order to give proper assessment of the degree of contamination, attempts were made to calculate the PLI using the Tomlinson's approach [9]. The PLI represents the number of times by which the metal content in the soil exceeds the average natural background concentration, and gives a summative indication of the overall level of heavy metal toxicity in a particular sample. The control samples were taken to represent natural background. According to Angula [29], PLI is able to give an estimate the metal contamination status and the necessary action that should be taken. The PLI is obtained as a contamination factor (CF) of each metal with respect to the natural background value in the soil [29] [30] by using Equations (1) and (2);

$$\mathrm{CF} = \mathrm{C}_{\mathrm{sample}} / \mathrm{C}_{\mathrm{background}} \tag{1}$$

$$\mathrm{PLI} = \left[\mathrm{CF}_1 \times \mathrm{CF}_2 \times \mathrm{CF}_3 \times \cdots \times \mathrm{CF}_n\right]^{1/n} \tag{2}$$

where,

CF: contamination factor, n = number of metals = 7;

$\mathrm{C}_{\mathrm{sample}}$: mean metal concentrate on in polluted soils;

$\mathrm{C}_{\mathrm{background}}$: mean natural background value of that metal.

In the study, the contamination factor and pollution load index are presented in **Table 4**. The CFs for the seven metals in the different soil layers are indeed very high ranging from 1.38 (Fe) to 67.50 (Ni). The trend is such that highest CFs was observed in Ni and Cd and least in Fe. In general, the increasing order of CFs is Fe < Cu < Zn < Ni <Cr < Pb < Cd. The CFs values decreases down the soil profile in Ni, Fe and Cu but increases down the soil profile in Pb, Cr and Cd. The pattern in Zn is undefined. The very high values of the CFs (>1) in all the metals can be due to influence of mechanic activities such as indiscriminate disposal of metal containing compounds such as used engine oil, vehicle spare parts, welding activities etc. The data on PLI of all the soil samples (**Table 3**) were far greater than unity (>>1). Consequently, soils from the mechanic workshops (as representatives of other workshops) are considered to be of pollution concern in view of indiscriminate disposal of used oils, vehicle spare parts and other wastes from their workshops.

Table 4. Elemental contamination factors (CFs) of soils and Pollution Load index (PLI) of metals in different soil layers.

Element	Soil Layers	Soil 1	Soil 2	Soil 3	Natural Background Concentration[a]
Pb	0 - 15	8.36	10.31	10.02	10.1 ± 0.2
	15 - 30	16.46	16.07	16.98	10.4 ± 0.6
	30 - 45	17.96	15.50	26.19	11.7 ± 0.3
Ni	0 - 15	48.85	67.50	45.01	14.7 ± 1.1
	15 - 30	17.01	20.36	17.59	13.4 ± 1.4
	30 - 45	14.14	16.38	14.96	10.2 ± 1.2
Fe	0 - 15	2.05	1.90	1.50	232.7 ± 8.4
	15 - 30	1.74	1.68	1.47	211.2 ± 8.9
	30 - 45	1.38	1.65	1.41	180.2 ± 9.7
Cu	0 - 15	2.56	3.05	2.70	131.1 ± 6.3
	15 - 30	2.31	2.52	2.40	124.6 ± 4.0
	30 - 45	1.68	1.63	1.36	120.1 ± 4.4
Cr	0 - 15	8.05	8.59	7.43	9.3 ± 0.4
	15 - 30	8.31	8.35	6.77	7.1 ± 0.4
	30 - 45	19.01	15.00	14.54	3.2 ± 0.2
Cd	0 - 15	29.68	30.64	26.18	2.2 ± 0.2
	15 - 30	44.82	48.91	43.18	1.1 ± 0.1
	30 - 45	53.57	64.71	56.71	0.7 ± 0.2
Zn	0 - 15	2.64	3.07	2.20	68.2 ± 4.3
	15 - 30	2.63	2.80	2.28	77.5 ± 4.7
	30 - 45	2.82	3.14	2.63	82.3 ± 5.3
PLI	0 - 15	5.41	6.13	5.00	
	15 - 30	5.92	6.29	5.54	
	30 - 45	6.32	6.43	6.26	

[a] Average natural background concentration (±SD, n = 3) obtained in the study.

4.3.2. Enrichment Factor and Index of Geo-Accumulation

The extent of soils contamination was assessed using the enrichment factor (EF) and geoaccumulation index (I_{geo}) [11]-[13]. EF was used in the study to assess the relative contributions of natural and anthropogenic heavy metal inputs to soils [31] [32]. It (EF) has also been used to indicate the degree of pollution or contamination or both [33]. Data from samples taken from the control site (University Campus) were used to establish metal-normalizer relationships to which the data generated from various mechanic workshops are compared. According to this technique metal concentrations were normalized to the textural characteristic of soils. Most commonly used reference elements include Sc, Mn, Al and Fe [34]. In this study, Fe was chosen as the geochemical normalizer because of its conservative nature during diagenesis [35]. Moreover, soils in Nigeria have been reported to be rich in Fe [36] [37]. Based on Rubio *et al*. [38], EF is defined as:

$$\mathrm{EF} = \left(\mathrm{X}/\mathrm{Fe}\right)_{\mathrm{soil}} \Big/ \left(\mathrm{X}/\mathrm{Fe}\right)_{\mathrm{background}} \tag{3}$$

where $\left(\mathrm{X}/\mathrm{Fe}\right)_{\mathrm{soil}}$ is the ratio of heavy metal (X) to Fe in the soil from mechanic workshops, and $\left(\mathrm{X}/\mathrm{Fe}\right)_{\mathrm{background}}$ is the natural background value of the metal-Fe ratio. The EF values close to unity indicate crusted origin, those less than 1.0 suggest a possible mobilization or depletion of metals, whereas EF > 1.0 indicates that the element is of anthropogenic origin [39]. Five contamination categories are recognized and interpreted as suggested by Birth [40]: EF < 1 indicates no enrichment, EF < 3 is minor enrichment, EF = 3 - 5 is moderate enrichment, EF = 5 - 10 is moderately severe enrichment, EF = 10 - 25 is severe enrichment, EF = 25 - 50 is very severe enrichment and EF > 50 is extremely severe enrichment. Details of the EF values of the metals studied with respect to the natural background concentration are presented in **Table 5**. Variation occurs in the EFs with Pb, Cd and Ni occurring at levels ≥ 9 while Cu, Cr and Zn occur at values < 1.0. Thus, based on Birth [40] interpretation, the EFs for Cu, Cr and Zn indicated no enrichment which suggested a possible mobilization of metals while all the auto-mechanic workshops are said to be severely enriched with Pb, Cd and Ni. Do these truly represent anthropogenic input? In a recent report, it has been shown that high EFs do not provide a reliable indication of the degree of human interference with the global environment [41]. In the report carried out in Czech Republic where five different elements were used as reference, the sequence of the EFs does not reflect the relative importance of the elements determined. It was concluded that other factors such as the choice of reference element may be responsible for high EFs. The variation in EFs from site to site may also reflect the age of establishment of the various workshops and indicative of the number of services each workshops render.

Table 5. Mean EF* and I_{geo}* classes of the metals studied with respect to the natural background.

Element	Soil 1	Soil 2	Soil 3
Enrichment Factor			
Pb	8.85	9.72	13.41
Ni	17.31	25.73	20.20
Cu	0.11	0.14	0.15
Cr	0.35	0.40	0.44
Cd	10.24	11.36	12.33
Zn	0.20	0.47	0.23
I_{geo} class^a			
Pb	1.01	1.02	1.11
Ni	1.28	1.40	1.26
Cu	1.71	0.31	0.25
Cr	0.73	0.76	0.69
Cd	1.30	1.31	1.24
Zn	0.49	0.56	0.41

*Values calculated based on soil layer 0 - 15 cm only. Normalizing element, Fe, with natural background value of 232.7 $\mu g \cdot g^{-1}$. a > 5, extremely contaminated; 4 - 5, strongly to extremely strongly contaminated; 3 - 4, strongly contaminated; 2 - 3, moderately to strongly contaminated; 1 - 2, moderately contaminated; 0 - 1, uncontaminated to moderately contaminated; <0, practically uncontaminated (Muller, 1979; Forstner *et al*., 1993).

4.3.3. Geoaccumulation Index

The geoaccumulation index (I_{geo}) as defined by Equation (4) was used to quantify the extent of heavy metal contamination associating with the soils from the various mechanic workshops. The I_{geo} values were calculated using the Muller's [41] expression:

$$I_{\text{geo}} = \log_2 C_m / 1.5 B_n \tag{4}$$

where C_m = measured total concentration of metals in soils ($\mu g \cdot g^{-1}$); B_n = geochemical background values of metals ($\mu g \cdot g^{-1}$); 1.5 = the background matrix correction factor due to lithogenic effects. The I_{geo} scale consists of seven grades (0 - 6) ranging from uncontaminated to very highly contaminated (**Table 5**). The results of the I_{geo} of the metals investigated in the study are presented in **Table 4**. Unlike the EFs, the I_{geo} values are generally low (< 2) in all cases. In all the soils, the six metals fall within two I_{geo} class based on Muller's [41] interpretation; moderate contamination (Pb, Cd and Ni) and uncontaminated to moderate contamination (Cu, Cr and Zn). This contamination can only result from anthropogenic activities considered to emanate from mechanic activities.

4.4. Correlation Matrix

The results of correlation between the various metals (**Table 6**) were calculated using the entire raw data. This was aimed at reducing possible bias that might result from mean values. The correlation coefficient data is important in order to deduce the possible sources of the metals in the soil samples. Based on the data in **Table 5**, the concentrations of several metals were strongly correlated with each other. Major correlations in soils were between Cu-Ni, Cu-Fe, Fe-Ni, Cd-(Ni, Fe and Cu) ($r \geq 0.95$; $p < 0.05$; $df = 20$). Other correlations between Cd-(Pb, Cr) and Cr-Cu ($r \geq 0.99$; $p < 0.01$; $df = 20$) were also obtained along with a strongly negative correlation between Fe-Pb ($r \geq 0.95$; $p < 0.05$; $df = 20$). The correlation coefficients between the concentrations of the different metals indicate strong links between them, which probably reflects their related origin. The wastes which are indiscriminately disposed within the various workshops are possible sources of these metals.

5. Conclusion

This survey has allowed the determination of the level of some important heavy metals at different layers of the soil. The combined use of different approaches for evaluating soil metal contamination facilitates a comprehensive interpretation of the soil characteristics in terms of the background influences. The mechanic environment is getting polluted particularly with Pb, Ni and Cd based on the enrichment factor. This is a reflection of anthropogenic contribution which might partly result from the use of metal-containing additives as lubricants. Based on the geoaccumulation index data, the soils can generally be classified as "moderately contaminated" by these heavy metals although the pollution index load indicate that the entire mechanic soils are considered to be of pollution concern. There was an indication of an uneven distribution of the metals in soils from various locations, though there was no significant difference in metal distributions between them.

6. Recommendations and Perspectives

This study assessed the extent of heavy-metal contamination in soils within auto mechanic workshops using some pollution indexes. Consequent upon our findings, it is recommended that government should provide appropriate places that will serve as automobile village where auto repairs are being carried out. This may not be

Table 6. Correlation matrix of metals.

Pb	Ni	Fe	Cu	Cr	Cd	Zn
1.000	−0.771*	−0.853**	−0.827**	−0.755*	0.789*	0.628
	1.000	0.840**	0.936**	0.774*	0.818**	0.359
		1.000	0.844**	0.757*	0.884**	0.382
			1.000	0.762*	0.805**	−0.566
				1.000	0.716*	0.313
					1.000	−0.315
						1.000

Significant /r/ *($p < 0.05$); **($p < 0.01$).

necessary in developed countries where measures are already put in place as appropriate. Education and legislation on management of wastes in the auto-mechanic workshops should be intensified to forestall the effects of waste oil related problems on the environment, particularly on groundwater. Also, modern waste disposal facilities should be acquired by relevant authorities and appropriate waste disposal sites be chosen to avoid the injurious effects of indiscriminate disposal of used oils/lubricants. In addition, continuous monitoring and further studies on the level of these heavy metals should be carried out in the near future to ascertain long-term effects of anthropogenic impact. This should also involve larger coverage with studies on ground water around such locations. In addition, metals speciation should be carried out so that the form and extent of metal bioavailability can be evaluated further.

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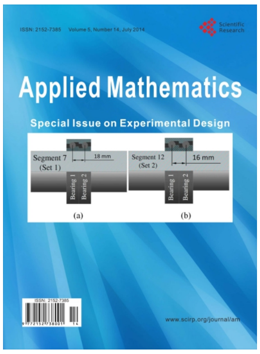
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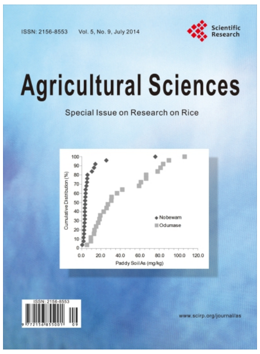
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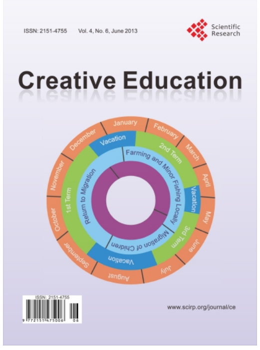
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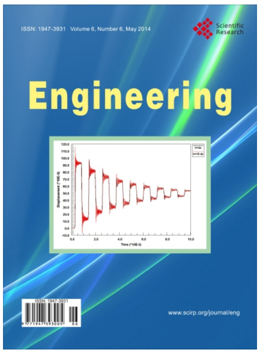
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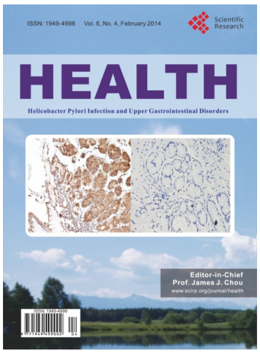
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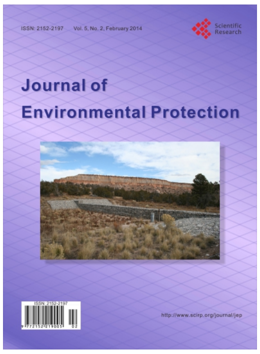
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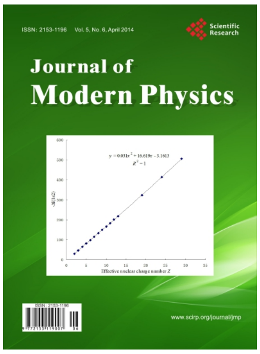
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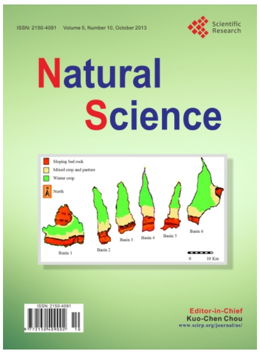
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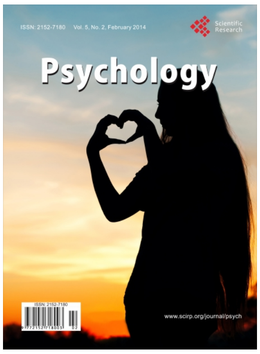
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