International Journal of Earth & Environmental Sciences
Vol. 7, No. 1, 2022, pp. 68-92

http://ijees.ielas.org
ISSN: 2545-4161

GEOCHEMICAL ASSESSMENT OF HEAVY METALS IN SURFACE SOIL FROM AUTO-WORKSHOPS IN ONITSHA, SOUTHEASTERN NIGERIA

[1]Iyi Emmanuel Chibuike; [2] Okoro Joel Ejiofor; [3]Anachuna, Nonyelum Geraldine

[1]Department of Geology and Mining Enugu State University of Science and Technology, P.M.B. 01660, Agbani, Enugu State, Nigeria.E-mail: emmanuel.iyi@esut.edu.ng
[2]Geology Department, Michael Okpara University of Agriculture, Umudike, P.M.B. 7267 Umuahia, Abia State, Nigeria.
[3]Department of Geology University of Calabar, P.M.B 1115, Calabar, Cross River State, Nigeria

Received: 2022-04-16 Accepted: 2022-06-22 Published online: 2022-07-01

Abstract

Core (0-60cm) samples were collected from ten (10) randomly designated auto-workshops within Onitsha and control site at Awka, Nigeria. Physiochemical parameters (particle size distribution, cation exchange capacity (CEC), pH, Organic Matter (%)) and heavy metals (Lead (Pb), Copper (Cu), Chromium (Cr), Zinc (Zn), Nickel (Ni), Aluminium (Al), Cobalt (Co), Molybdenium (Mo), Cadmium (Cd), Manganese (Mn) and Silicon (Si)) were analyzed by means of standard methods. The outcome of the physiochemical analysis show that the samples were generally sandy with very strongly to slightly acidic pH values (4.89-6.24); OM ranged from 5.693-27.71%; CEC varied between 0.072-0.211(Cmol/kg). Concentrations of these toxic contaminants were above those recorded at the control site. They were equally above national and international guidelines. Enrichment Factor (EF) values varied between no enrichment to extremely severe enrichment. Pollution load index (PLI) proved that all the sampled points within Onitsha were polluted while the ecological risk of heavy metals varied between low contamination to high contamination. The prevailing non-scientific method of handling wastes associated with repair and servicing of automobiles is the direct source of these contaminants. Appropriate and adequate scientific measures must be taken to minimize further deterioration as the contaminants pose serious deadly effects on human and soil organisms.

Keywords: Surface Soil, Heavy metals, Auto-Workshops, Pollution Load Index, Enrichment Factor, Potential Ecological Risk Index.

INTRODUCTION

The assessment of heavy metals in soil from auto-workshops/mechanic/auto-repair shops in Onitsha, Southeastern Nigeria is crucial. This is because of possible environmental and human health hazards associated with exposure to these contaminants. Soil is an important environmental medium due to its usefulness for the survival of life in Earth's ecosystems. It also serves as a medium for plant growth which underscores its importance to the survival of mankind. Soil may be polluted by the accretion of heavy metal through the dumping of high metal-containing wastes. Chokor (2016) reported that activities carried out at auto-mechanic workshops remain the most important sources of increased heavy metal concentration in the ecosystem.

Activities associated with auto-servicing are on the increase not just in Onitsha but most developing cities and countries. The undiscerning discarding of wastes associated with these auto-mobiles' servicing has worsened the problems associated with degradation of soil in most of the cities especially at Onitsha. Auto-workshops routinely deal with several hazardous materials. These may include fuels, lubricants, used batteries, used/spent oils/lubricants, asbestos (coming from brake pads), oxidation materials and metal. These can contaminate surrounding soils through leaks, spills and improper disposal practices. Consequently, different heavy metals may accumulate in the soil, threatening the ecosystems and human populations inhabiting the locality. Nonexistence of regulations and monitoring of the activities associated with auto-servicing contributes to elevated levels of heavy metals in the environment.

STUDY AREA

The study area is located within Latitudes 6^0 05' 56" and 6^0 12' 02"N, and Longitudes 6^0 46' 0" and 6^0 52' 30" E (fig. 1). It is found on the eastern bank of the Niger River, just south of its confluence with the Anambra River.

GEOLOGY

The main geologic units within the study area include Ameki Formation (Nanka Sand), Asaba-Ogwashi Formation. and Benin Formation (Coastal Plain Sand) (figure 2). The Ameki Formation, classified by Simpson (1955) into two lithological groups, comprises of a lower part which consists of fine to coarse grain sandstones and intercalations of calcareous shales and thin shelly limestone; the upper part comprises of course, cross-bedded sandstone with bands of fine, grey-green sandstone and fine – grained fossiliferous sandstone with thin limestone bands. The age of the Ameki formation has been deliberated to be either early Eocene according to Reyment (1965) or early middle Eocene according to the accounts of Berggren (1960) and Adegoke (1969). Faunal content has been used to interpret the depositional environment of the Ameki Formation. While White (1926) interpreted it as an estuarine environment for the reason that there was an occurrence of the fish species identified for its estuarine affinity, Adegoke (1969) favored an open marine depositional system, suggesting that the fish may perhaps have been washed into the Ameki sea from inland waters. On the other hand, Nwajide (1979) and Arua (1986) suggested an environment that alternated from nearshore to intertidal and subtidal zones. The Ameki Formation lie beneath the Imo shale (Paleocene) which conformably lie on top the Nsukka Formation according to Reyment (1965).

International Journal of Earth & Environmental Sciences
Vol. 7, No. 1, 2022, pp. 68-92
http://ijees.ielas.org
ISSN: 2545-4161

The Ogwashi–Asaba Formation is also exemplified within the Palaeocene Anambra Basin according to Oboh – Ikuenobe et al. (2005). This Formation, also called the Lignite "series", is characterized by broadly divergent lithologies encompassing a repetition of clays, sands, grits and lignites (Dessauvagie and Fayose, 1970; Whiteman, 1982; Parkinson, 1907). The work done by Reyment (1965) recommended Oligocene–Miocene age for this formation. However, palynological results from the work of Chene et al., (1978) assigned a Middle Eocene age to the basal part.

The Benin Formation also referred to as the Coastal Plain Sand comprises of an alternating series of gravel, sand, clay and alluvium originating from the neighboring Precambrian basement and Cretaceous rocks according to Short and Stauble (1967). The age is upper Miocene–Recent (Short and Stauble, 1967; Kogbe, 1976).

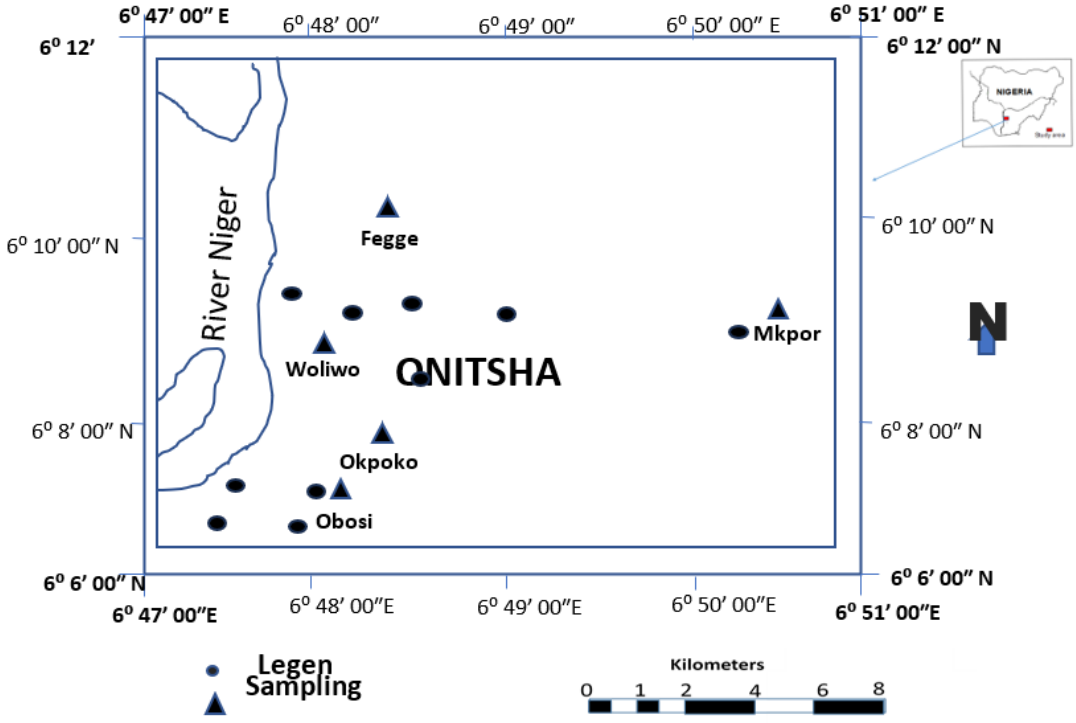


Fig. 1. Location of the study area showing some settlements and sample collection points (Drawn using Corel Draw)

International Journal of Earth & Environmental Sciences
Vol. 7, No. 1, 2022, pp. 68-92

http://ijees.ielas.org
ISSN: 2545-4161

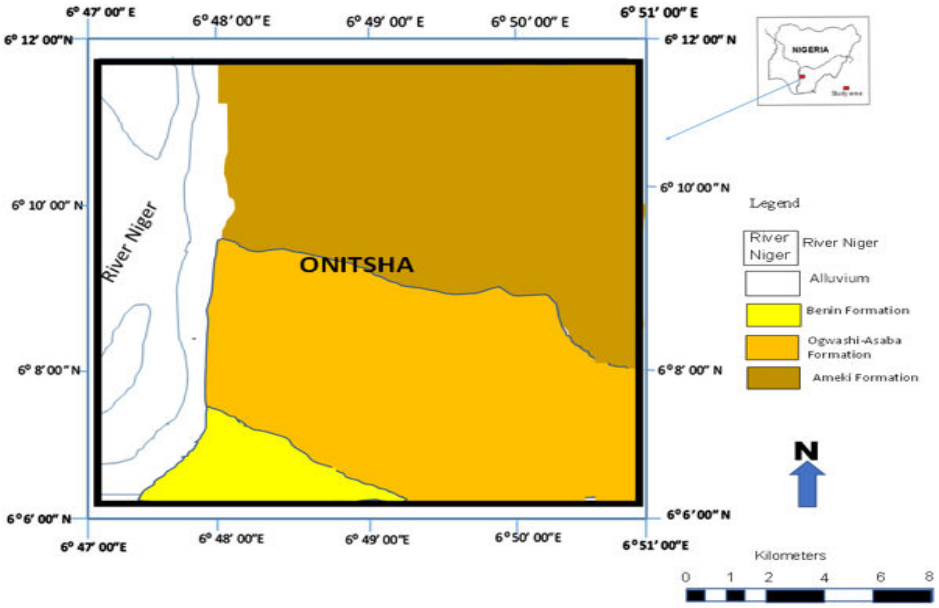


Fig. 2. The geologic map of Onitsha

LITERATURE REVIEW

Problems of environmental degradation and pollution by heavy metals in or near auto-workshops have been previously covered in many scientific publications. Among them include the work done by Agbaji *et al.* (2015) which assessed the heavy metals concentrations of soil in Kakuri industrial area of Kaduna State, Nigeria. This research made use of Mini Pal 4 version in PW 4030 X–ray spectrometer. The result of the research was compared with the control soil sample. It was also compared to national and international soil guidelines. It was revealed that the location was considerably polluted with heavy metals but below the intervention/alert level provided by the environmental protection agencies (DPR, 2002; Romanian Soil Guideline, 1997). Soil pollution assessment by means of Cf and Igeo indices confirmed the soils are uncontaminated. The result also showed that the availability and distribution pattern of heavy metals varied with the nature of industrial activities as indicated by the wide range of concentration values observed in virtually all the heavy metals in the soils analyzed across the sample locations.

Similarly, a study was undertaken by Chokor (2016) to evaluate the soil profile distribution of heavy metals in auto-workshops at Sapele, Nigeria using standard methods. He discovered that the levels of those considered heavy metals showed greater values than the recommended values by the DPR (2002), WHO (1996) and generally decreased with increase in depth.

Pam *et al.* (2013) evaluated the levels of heavy metals in soils around auto-workshop groups in Gboko and Makurdi, North-Central Nigeria using standard field and

laboratory methods. The aim was to evaluate the effects of auto-repair undertakings on the surface soils of the area. The result of this academic exercise discovered that for the bulk of heavy metals, the concentrations in the soils are above background concentrations. They were also above the permissible limits recommended for soils both within and outside Nigeria.

Ololade, (2014) worked on the assessment of heavy metal contamination in soils within mechanic workshops using enrichment and contamination factors as well as geo-accumulation indices. This study made use of standard field measurement and laboratory procedures. The results point out that the soils exhibited abnormally high levels of all the considered contaminants (Ni,Cu,Fe,Cr,Cd,Zn and Pb) above background concentrations.

Ogunkolu et al., (2019) worked on the evaluation of heavy metal contamination of soil around mechanic workshops in Anyigba, Northcentral Nigeria. Heavy metals contaminations at soil depth of (0-15 cm) in mechanic workshop in Anyigba were assessed and the laboratory result was subjected to statistical analysis using SPSS for descriptive statistics. It was discovered that the concentrations of the considered metals (Cadmium-0.32mg/kg, Zinc-4.31mg/kg, Iron-6.70mg/kg, Lead-1.43mg/kg, Nickel-0.44mg/kg, Chromium-0.23mg/kg, Copper-3.90mg/kg, Manganese -1.81mg/kg and Arsenic-0.026mg/kg) in the soil samples from experimental sites were greater than the corresponding concentrations from the control site (Cd-0.26mg/kg, Zn-3.80mg/kg, Fe-5.40mg/kg, Pb-1.23mg/kg, Ni-0.31mg/kg,Cr-0.16mg/kg, Cu-3.38mg/kg, Mn-1.35mg/kg, and As-0.012mg/kg). Also, they were higher than the recommended boundaries given by the World Health Organization (WHO). It was in the following order: Fe> Zn>Cu>Mn>Pb. This study concluded that the mechanic workshop soils represented potential sources of heavy metal pollution to the environment.

Additionally, a work done by Morka et al., (2016) titled 'Soil Contamination Due To Heavy Metals Within Auto-Mobile Workshop Clusters Along Mariere By T-Junction and Orubor by Prof. Ebie (B) Agbor, Delta State-Nigeria', the levels of heavy metals within two automobile clusters coded Alpha and Beta respectively in Agbor metropolis were presented. Heavy metal investigation of the soils in the two clusters (Alpha and Beta) exposed the occurrence of Cu, Mn, Ni, Zn, Cd, Pb, and Fe in abundance. Moreover, the levels of the considered pollutants were above the control values except for Cd at β cluster. This study confirmed that Cadmium at β cluster represented a contamination hazard that required some corrective action.

Though several similar studies have been carried out elsewhere as shown by the plethora of similar literatures, there seems to be no documented research on the geochemical evaluation of heavy metals in surface soil of mechanic workshops at Onitsha. This work, therefore, seeks to fill this knowledge gap and delve into this obscure field.

MATERIALS AND METHODS

Field procedure: Prior to the actual sampling activities, a reconnaissance survey was undertaken in order to identify possible sampling points and assess background information, site conditions and historical data. The reconnaissance survey was also used to identify variable possible routes, assess the topography, geology and traffic volume as well as economic land use (commercial and industrial activities) patterns within Onitsha and environs.The sample collection points were carefully chosen based on the information gathered during this reconnaissance survey.

Sample collection was carried out in May 2023 during which samples were collected at the depth of 0 - 60cm within the vicinity of eleven (11) randomly selected auto-workshops/mechanic workshops (MS) within the city using soil auger from the locations shown in figure 1. One soil sample was also collected from an undeveloped plot of land at Awka.

The instruments used for collecting the soil samples were a T- shaped manual soil auger, hand trowel, sampling bags. The sampling locations were auto-workshops at Obosi, Mgbuka auto-workshop/spare parts village, Fegge, Creek Road, Owerri Road, Ugwunabamkpa, Omagba and Mkpor. At each sampling location, the auger was decontaminated by cleaning the blades with white handkerchief soaked with methylated spirit and drilled into the soil in an anti-clockwise direction. When it penetrated the soil up to the pre-marked 60cm depth, it was brought out in a clockwise direction. The soil samples that stacked to the auger screw were collected using a decontaminated hand trowel before putting them separately into pre-labeled polyethylene bags. The control sample was collected at a similar depth in an undeveloped plot of land with a very low volume of traffic and no industrial activities at Awka and labeled. All the samples were preserved using an ice box to minimize degradation.

Spades of the soil auger and the hand trowel were cleaned with methylated spirit in between sample collection points in order to eliminate cross-contamination. In total, twelve samples were taken in a big ice box to the Springboard soil and water laboratory, Udoka housing Estate, Awka in Anambra State, Nigeria for various analyses.

Laboratory Procedure: Sample Preparation, Digestion and Analysis

The samples were air-dried at room temperature, lasting about sixteen days.

This was to eliminate excess moisture. The samples were disaggregated for quick dehydration. At the end of the period, the samples were pulverized using porcelain mortar and pestle, then thoroughly mixed (homogenized). The mortar and pestle were cleansed with methylated spirit using white handkerchief after crushing each sample to prevent cross contamination of samples.

The pulverized samples were sieved using a 2.0mm sieve. The stainless-steel sieve helped to remove stones, pebbles, plant debris etc. Some portions of the sieved samples were further crushed to fine powder before being passed through a 0.5mm

sieve for evaluating organic carbon and total metal contents. Mechanical analyses were made using serial sieves. The sieved samples were properly stored as sub-sample for the determination of various parameters. The digestion was done by weighing approximately 2.0g of the sample into a crucible, then heating it at a temperature of 550^0C for 3hours to get rid of the organic portion of the sample before being removed, then allowed to cool. After cooling, it was put into a 100ml beaker. Then 20ml of 20% H_2SO_4 was added, heated on a hating mantle and boiled vigorously for five minutes before being brought down. It was allowed to cool before being made up to 50ml with distilled water and filtered into a sample container for elemental analysis using atomic adsorption spectrophotometer.

The prepared samples were evaluated for heavy metal concentrations using Varian AA240 AAS at Springboard Research Laboratory, Udoka Housing Estate, Awka in Anambra State. Analysis for twelve (12) metals namely: Lead, Copper, Zinc, Chromium, Nickel, Cobalt, Molybdenum, Cadmium, Manganese, Mercury, Aluminium and Silicon were carried out in the digested soil samples.

Particle size analysis

Approximately 50g of the sample was carefully measured into a 250ml beaker. Approximately 200ml of distilled water was added. The mixture was vigorously stirred and allowed to stay for 10mins for sedimentation to take place. At the end of the 10mins, the water was siphoned and the process was repeated four times to wash the sample before 25ml of 25% hexametaphosphate was added and the mixture was allowed to stay for 24hrs. On the next day, the mixture was siphoned through a 75mm sieve and the sieved particles and the sieved liquid was dried using an oven before being allowed to cool and the following calculations made:

$$\%\text{Silt} = \frac{\text{wt of beaker + dried residue}}{\text{Wt. of sample}} \times 100 \quad (1)$$

$$\%\text{Sand} = \frac{(\text{wt of beaker + dried residue}) - \text{wt of empty beaker}}{\text{Wt. of sample}} \times 100 \quad (2)$$

$$\%\text{Clay} = 100 - (\%\text{Silt} + \%\text{Sand}). \quad (3)$$

Loss on Ignition (LOI)

The OM (%) of the samples were estimated from LOI. Approximately 2g of the sample was measured into a crucible. It was then dried in oven at 105^0C for 1hr before it was brought down and allowed to cool before the weight was recorded using an electric weighing balance. Then it was moved into a muffle furnace, then heated at 360°C for

about 3hrs. At the end of 3hrs, it was brought down and allowed to cool in a dessicator and the weight was recorded before the following calculations were made:

$$\text{LOI (\%)} = \frac{(\text{wt. at } 105^0\text{C}) - (\text{wt. at } 360^0\text{C})}{\text{wt. at } 105^0\text{C}} \times 100 \quad (4)$$

pH determination

A pH meter with glass electrode was used for this purpose. Approximately 1g of the prepared sample was measured and put into a beaker. Approximately 10ml of distilled water was then added. It was stirred continuously for 30mins. Then, it was allowed to stand for about 1hour. The digital pH meter was plugged, switched on and calibrated with a known buffer solution (buffer 7). After calibration, the pH electrode was dipped into the beaker containing the suspension. The reading was subsequently taken once the digital display became constant. The electrode was rinsed with deionised water between samples.

Cation exchange capacity (CEC)

Approximately 1g of the sample was measured into a 100ml beaker and 10ml of 1mol of potassium chloride (KCl) was added to it. Subsequently, the mixture was kept undisturbed for 30mins before being filtered. The filtrate was analysed for Mg, K, Ca and Na using AAS.

Then the concentration levels of these cations were converted from parts per million (ppm) to Cmol/kg using the following formulae:

$$\text{Mg(ppm)} \div 120 = \text{Mg (Cmol/kg)} \quad (5)$$
$$\text{K(ppm)} \div 390 = \text{K (Cmol/kg)} \quad (6)$$
$$\text{Ca(ppm)} \div 200 = \text{Ca (Cmol/kg)} \quad (7)$$
$$\text{Finally, the Cmol/kg results of Mg + K + Ca = CEC} \quad (8)$$

Quality control/assurance

As part of assurance and quality control, procedures were taken to prevent background contamination as well as to ensure reliability of data. Sequences of standard metal solutions in the peak concentration range were prepared. Preparations of reference solutions were achieved by diluting the single stock element solutions with water containing 1.5ml concentrated nitric acid/litre daily. Also, a calibration blank was prepared. This was done using all the reagents except for the metal stock solutions. For each metal, calibration curve was prepared by plotting the absorbance of standards versus their concentrations. Moreover, blank samples were analyzed after five samples. Duplicate analyses were performed on all samples using certified methods and the

analytical results reported on a dry weight basis. Finally, the precision and accuracy of analyzed metals were tested against stock reference material for every heavy metal.

Statistical analysis of data

SPSS Statistics and Microsoft Office Excel were the statistical method of data used in this work.

Microsoft Office Excel was used for statistical analysis which include range, mean, standard deviation (SD) and coefficient of variation (CV). Descriptive statistics were also employed to summarize the general trend in the data set and to identify main features of the parameters investigated. Bar Charts were used to analyze the levels of the physiochemical parameters and the heavy metals in order to obtain as well as compare their pictorial representations. The respective concentrations were compared with various national and international guidelines so as to ascertain the quality status of soils within the study area. Moreover, pollution indices (EF, PLI and ERI) were calculated to determine the level of heavy metal contamination in soil samples from the facilities. SPSS Statistics was employed to estimate the extent of interrelation between the heavy metals. Moreover, several pollution indices namely enrichment factor, pollution load index and potential ecological risk index were employed in order to ascertain the extent of contamination in the area.

Pollution Indices

The pollution indicators employed to assess the extent of pollution in the soils within the area include: enrichment factor (EF), Pollution Load Index (PLI) and Potential ecological risk index (Er^i).

The Enrichment Factor (EF)

The Enrichment Factor (EF) is applied in differentiating between metals that accumulate as a result of human/anthropogenic activities from those that accumulate owing to geogenic processes. In order to estimate the extent of contaminants in the environment, Enrichment Factors (EF) were calculated comparative to the abundance of species in source material to that found in the Earth's crust. Silicon (Si) is chosen as the element of normalization in this research. This is due to the fact that natural sources immensely dictate its availability. The following the equation as suggested by Simex and Helz (1981) was used:

$$EF = (C_M/C_{Si})_{sample} / (C_M/C_{Si})_{Background} \text{ (Simex and Helz, 1981)} \quad (9)$$

Where, $(C_M/C_{Si})_{sample}$ is the ratio of concentration of measured heavy metal (C_M) to that of Si (C_{Si}) in the soil sample and $(C_M/C_{Si})_{Background}$ is the same reference ratio in the Earth. The five contamination categories recognized and interpreted as suggested

by Birch (2003), adopted by Ololade (2014) and equally used in this research are as follows:

EF < 1 indicates no enrichment,
EF 1 < 3 indicates minor enrichment
EF between 3 < 5 show moderate enrichment
EF between 5 < 10 denotes moderately severe enrichment
EF between 10 < 25 denotes severe enrichment
EF between 25 < 50 denotes very severe enrichment
EF ≥ 50 refers to extremely severe enrichment

The Pollution Load Index (PLI)

The magnitude of pollution within the study area has been evaluated using the pollution load index (PLI) as was suggested by Tomlinson *et al*. (1980). PLI offers a simplified and comparative means for evaluating pollution status of a region. It is recommended as a consistent scheme for identifying pollution. It also permits an appraisal of pollution intensities between different sites and at different times.

The PLI for a single site is the *n*th root of *n* number multiplying the contamination factors (CF values) together as shown below:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots CF_n)^{1/n} \quad (10)$$

Where CF = contamination factor, n = number of metals at a given site

If PLI value is greater than 1 (> 1), it indicates pollution but if it is less than 1 (<1), it implies that the site is unpolluted

Potential Ecological Risk Index (Er^i)

The ecological risk index appraises the toxicity of elements in soils according to Hakanson (1980) and Xu *et al*. (2008). It is calculated as shown follows:

$$Er^i = Tr^i \text{ X } C^i_f \quad (11)$$

Where,

Tr = Toxicity coefficient of each metal

C^i_f [Contamination Factor] = Ci/Bi

[Where Ci = calculated conc. of pollutants and Bi= level of geological background. The average compositions of the metals in the control sample were used as background standards for the metals].

If Er is less than 40, it implies low contamination risk
If Er falls between 40 – 80, it implies moderate contamination risk
If Er falls between 80 –160, it implies considerable contamination risk
If Er falls between 160 – 320, it implies high

Standard values of Tr are Cd=30, Co=5, Cu=5, Ni=5, Pb=5, Cr=2, Zn=5 (as given by Hakanson, 1980; Xu *et al.,* 2008).

RESULTS AND DISCUSIONS

Physiochemical Parameters

The physiochemical parameters as shown in table 2 and figure 3 indicate that the sand fraction has mean±sd value of 50.2±6.59% and range from 37.84 - 58.72%; silt has a mean value of 22.4±3.8% and range from 16.74 – 29.37% while clay has an average value 27.4±5.2 and range of 19.48-37.39%. The sites were generally sandy as shown by the grain analysis values.

The pH in the mechanic workshops was very strongly acidic and range from 4.36 - 5.64 with a mean±sd value of 5.16 ±0.47. Soil pH values observed in these facilities were below the general mean abundance of 6.50 - 8.50 according to Rose *et al.,* (1979) and also below the observed pH of soil sample from control soil (6.72).

The Cation exchange capacity (CEC) values of samples from the auto-workshops range between 0.072 – 0.211 Cmol/kg with a mean±sd value of 0.2±0.04 Cmol/kg. At the control site, it was 0.56 Cmol/kg which implies lower CEC level at the control site.

The witnessed minor dissimilarities in the values of CEC can be ascribed to small differences in OM and clay content. The decline in CEC of the samples over that of the control may be as a result of nutrient draining wastes (Ololade, 2014). It could also be due to displacement by toxic metals which are incidentally introduced to the soil system through indiscriminate disposal of wastes and other pollutants. The CEC of soil can control the mobility of metals in soils. It also increases as pH increases in the soil (Pam *et. al.,* 2016).

The OM (%) ranges from 5.69 – 27.07% with an average value of 11.8±5.57 which is lower than what was recorded at the control site (17.3%). This is a clear indication that the disposal of wastes at the auto-workshops depletes the soils of organic matter. It could also be ascribed to the relatively limited and slow rate of biological breakdown of vegetation in the area.

Heavy metals concentrations

The heavy metals results (table 3 and fig. 4) show that Pb in the samples from the auto-workshops has a mean±sd value of 3.346±1.72mg/kg and range from 0.887 – 6.06mg/kg. The average Pb concentration in the samples is higher than the control sample value of 0.4mg/ kg but below the general mean abundance values of 17-30mg/kg according to Rose, *et al,* (1979), 20 mg/kg value of average composition of Shales (Turekian & Wedepohl, 1961), the EPA (1995) Ecological Screening Value of 30.2 mg/kg and the Dutch Soil Quality Standard ((MHSPE, 1994)) target and intervention values of 85 and 530 mg/kg respectively. It is also below the critical level of 300 mg/kg stipulated by FAO/WHO (2002) and 85 mg/kg recommended by the DPR (2002).

Pb with a CV value of 51% has a high variability rating in the auto-workshops. This high variability rating is an indication of relatively enhanced and uniform external influence on this heavy metal. Disposal of old and unusable automobile body parts, engine

servicing and combustion processes in the workshops, used lead acid batteries, used oil from automobile crankcases, burning of tires and disposal of solvents in the mechanic workshops could have introduced heavy metals including Pb in the soil within the facilities (Oladebeye, 2017). Other possible sources according to Abdulrashid *et al.,* (2013) include activities associated with welding and soldering, worn metal alloys in the combustion engine, paints, hydraulic fluids, lubricants as well as stripped oil sludge.

Cu has a range of 0.526–17.975 mg/kg and an average value of 4.713±4.774 mg/kg and highly variable (101%) in the studied surface soil samples. The high variability is an indication of a high external/anthropogenic influence on the availability of Cu in the samples possibly from an indication of relatively uniform external influence on this heavy metal and the likely homogeneity of its concentration throughout the study area. combustion of gasoline. Break wear, engine wear and tear, disposal of used lubricants are important sources of Cu in the soils at the auto-workshops (Abdulrashid *et al,* 2017).

Zn concentrations range from 1.023 - 19.501 mg/kg with a mean±sd value of 6.810±6.29 mg/kg. The high variability rating (92%) is as a result of external influence. In the control sample, the concentration of Zn was 2.05 mg/kg.

In the soil, pH and redox conditions govern the solubility of Zn (Iwegbue, 2013). In the pH range of 5.4-6.5 as within the range documented in this study, Zn is definitely more soluble in an oxidizing condition than in a reducing condition (Bhattacharya et al., 2002).

Zn level is above the control sample level of 2.05 mg/kg; the range of 36 – 100 mg/kg stipulated by Rose *et al.,* (1979) as the general mean abundance; below the target concentration value of 50 mg/kg and 140mg/kg set by WHO (1996) and DPR- EGASPIN (2002) respectively; below 95 mg/kg value of average composition of Shales (Turekian & Wedepohl, 1961). It is also below the EPA (1995) Ecological Screening Value of 124 mg/kg and the Dutch Soil Quality Standard values of 140 and 720 mg/kg for target and intervention values respectively (MHSPE, 1994).

Zinc is used in break lining because of its ability to conduct heat. It is released during break wear, mechanical abrasion of galvanized vehicle parts, as well as during wear and tear of tyres which are emitted into the environment as particles and subsequently deposited (Akande and Ajayi, 2007). Inputs from the metal junkyards that exist in most of the mechanic workshops remains suspect. Moreover, disposal of grease and spent lubricating oils which contain zinc as one of its many additives could also have introduced Zn in the soils within the auto-workshops (Jaradat and Momani, 1999).

The levels of Cr observed in the auto-workshops range from 1.211 – 7.023 mg/kg with an average value of 3.3193±1.62 mg/kg and also highly variable (49%). This variability rating is an indication that human activities have a high input in the observed level of this heavy metal in the auto-workshops. The observed values were higher than the concentration of 0.25 mg/kg in the control sample but below the general mean abundance range of 40 - 50 mg/kg according to Rose *et al.,* (1979); the EPA (1995) Ecological Screening Value of 52.3 mg/kg; average composition of Shales according to Turekian & Wedepohl (1961) which is 90 mg/kg; the Dutch Soil Quality Standard target

and intervention values of 100 and 380 mg/kg respectively, and the WHO (2008) permissible limit of 54 mg/kg. In spite of these, there is Cr enrichment in the auto-workshops as indicated by the difference in the control value and the value recorded at the samples. Also, the detected Cr levels at MS 2 (4.623mg/kg), MS 3 (4.523 mg/kg), MS 5 (7.023 mg/kg) and MS 10 (4.357 mg/kg) were above the average value (3.3193±1.62 mg/kg), signifying enhanced Cr contamination at those points.

The possible sources of Cr in the auto-workshops include wear and tear of car brake linings and chrome plated vehicular parts as well as from spilling of paints.

Ni has a range of 0.347 – 3.108 mg/kg with a mean±sd value of 1.58±0.749 mg/kg. The observed Ni values were above the background value of 0.66 mg/kg but below the Dutch Soil Quality Standard target and intervention values of 35 and 210 mg/kg respectively, the EPA (1995) Ecological Screening Values 15.9 mg/kg, the average composition of Shales according to Turekian & Wedepohl (1961) which is 68 mg/kg and the WHO/FAO (2001) permissible limit of 50 mg/kg for soils.

There is Ni enrichment in the samples within Onitsha as shown by the variability rating of 48%. This indicates highly variable anthropogenic sources of Ni within the area under study. Ni enrichment could be from the nickel-containing wastes such as batteries and welding wastes (Amadi and Nwankwoala, 2014). Ni is used as one of the fuel additives and burning of these fuels increases Ni concentrations in the soil as seen in the workshops (Iwegbue *et al,* 2013). Ni is also used in rechargeable or secondary power sources (batteries) because it has high output, long life, low maintenance as well as high tolerance to physical and electrical stress. Therefore, the disposal of these spent automobile batteries and various paint wastes in the mechanic workshops could account for the Ni levels observed within the facilities.

Cd concentrations range from 0.016 – 0.802 mg/kg with mean±sd value of 0.215±0.249 mg/kg. Cd also has a high variability rating of 116% which is an indication of high external influence on the observed Cd levels in the samples. The recorded average Cd levels were below the permissible limit of 3 mg/kg according to WHO/FAO (2001); the global average in surface soil which is 0.53 (Jones and Jarvis, 1981). It is also lower than the average composition of Shales according to Turekian & Wedepohl (1961) which is 0.3 mg/kg; the EPA (1995) Ecological Screening Value of 1.00 mg/kg; the DPR (2002) and WHO (1996) stipulated value of 0.8 mg/kg. It is also below the Dutch Soil Quality Standard (MHSPE, 1994) target value of 0.8 mg/kg and intervention value of 12 mg/kg.

However, it is within the general mean abundance range of 0.1 - 0.5 mg/kg given by Rose *et al.,* (1979).

Cd is incorporated as an anticorrosive on steel. Cd sulfide is also commonly used as pigments in batteries which eventually introduce the heavy metal into the soil in the auto-workshops soil (Amadi and Nwankwoala, 2013).

Mn ranges from 2.693 – 15.685 mg/kg with an average value of 10.129± 3.81 mg/kg and a high variability rating of 38%. The Mn level in the control sample was 2.522 mg/kg while the DPR (2002) stipulated a maximum value for Mn is 850 mg/kg. The average composition of Shales according to Turekian & Wedepohl (1964) is also 850

mg/kg. Due to their anti-knock value, Mn compounds are being added to a substantial portion of gasoline as an additive. This means that Mn compounds are being emitted from automobile exhausts and burning of fossil fuel according to Joselow *et al.* (1978). Mn could also come from batteries, discarded metallic/machinery parts and spray paintings of vehicles (Adebayo et. al., 2017).

Co concentrations range from 0.134 – 0.67 mg/kg with a mean±sd value of 0.309±1.66 mg/kg and a variability rating of 54% which is an indication of highly variable anthropogenic sources. The measured concentrations of Co were higher than the control level of 0.06 mg/kg and the acceptable range of 3 mg/kg for uncontaminated soil (WHO/FAO, 2003) but below 19 mg/kg value of average composition of Shales as reported in Turekian & Wedepohl, (1964). This signifies enrichment of Co in the auto-workshops which could have resulted from alloys of steels and electroplating-generated wastes disposed at the auto-workshops (Amadi, 2014).

Mo has a range of 0.055 - 0.67 mg/kg with a mean±sd value of 0.31±0.17 mg/kg and high variability rating of 53%. The measured concentrations of Mo are lower than the control level of 6.13 mg/kg and also below the acceptable range of 4 mg/kg for uncontaminated soil (WHO, 2003) and an average abundance value of 2.6 mg/kg as reported by Turekian & Wedepohl, (1964).

Hg was also detected and ranged from 0.022 – 0.303 mg/kg with an average value of 0.058±0.07 mg/kg and high variability rating (133%). It was not detected in the control sample. This implies that the auto repair activities are gradually enriching the surface soils in the study area with mercury. The high variability rating is also an indication of varied anthropogenic inputs.

Though the observed average Hg levels were below the DPR (2002), the European guideline (Romanian Soil Guideline, 1997) and the average composition of Shales according to Turekian & Wedepohl (1961) stipulated value of 4 mg/kg, there is a gradual Hg enrichment which could have come from the release of mercury from manometers used for measuring pressure and the use of hydraulic lifts attached to automobiles at the auto-workshops.

Al levels range from 3.654–17.516 mg/kg with mean±sd value of 8.643±4.646. The average shale abundance of Al is 80,000 mg/kg according to Turekian and Wedepohl (1964). It has a high coefficient of variability (54%) which signifies an enhanced influence from human sources. Possible sources include spray paintings, discarded metallic parts and burning of tires within the auto-workshops.

Si ranged from 3.54–18.4 mg/kg with a mean±sd value of 9.37±4.128 mg/kg. It has a high variability rating of 44%. The average shale abundance of Si according to Turekian and Wedepohl (1964) is 73, 000 mg/kg (Turekian and Wedepohl, 1964). According to Basile-Doelsch et al., (2005), the chemical weathering of silicate-bearing minerals is the ultimate source of dissolved Si which contributes to continental soil formation. This explains why Si was sufficiently detected in all the samples.

Table 1. Physiochemical parameters across the auto-workshops covered in this study

Site	%Sand	%Silt	%Clay	pH	CEC (Cmol/kg)	OM (%)
CONTROL	39.957	37.484	22.559	6.72	0.144	17.3
MS 1	57.621	22.535	19.848	5.36	0.151	11.848
MS 2	52.133	22.484	25.383	4.92	0.149	5.693
MS 3	50.523	19.284	30.193	5.74	0.144	11.492
MS 4	58.272	22.345	19.383	6.2	0.174	27.07
MS 5	52.235	19.382	28.383	6.24	0.199	8.6
MS 6	41.559	29.119	29.322	5.25	0.198	13.259
MS 7	50.14	21.282	28.578	5.6	0.199	8.604
MS 8	41.331	21.283	37.388	5.68	0.211	9.588
MS 9	37.839	29.373	32.788	4.89	0.143	8.77
MS 10	52.525	16.738	30.737	6.23	0.072	13.451
MS 11	57.535	22.621	19.84	5.26	0.15	11.4
Min	37.839	16.738	19.383	4.89	0.072	5.693
Max	58.272	29.373	37.388	6.24	0.211	27.07
Mean	50.2	22.4	27.4	5.6	0.2	11.8
SD	6.585	3.83623	5.2225	0.4835	0.0395146	5.5672

Table 2. Selected heavy metals levels (mg/kg) across the auto-workshops covered in this study

	Pb	Cu	Zn	Cr	Al	Cd	Hg	Ni	Co	Mo	Mn	Si
CONTROL	0.4	0.16	2.05	0.25	0.001	0.04	0	0.066	0.06	6.13	2.522	10.39
MS 1	0.887	0.536	3.509	2.692	9.424	0.016	0.303	0.347	0.134	0.354	9.848	11.35
MS 2	6.064	17.975	16.945	4.623	5.664	0.421	0.041	1.967	0.212	0.103	9.752	8.116
MS 3	4.471	1.011	19.501	4.523	17.235	0.802	0.031	1.1	0.197	0.055	14.574	8.883
MS 4	0.909	0.868	12.245	3.504	6.466	0.031	0.042	0.819	0.22	0.67	15.685	15.68
MS 5	3.09	7.409	8.771	7.023	4.664	0.558	0.03	3.108	0.67	0.194	11.003	18.4
MS 6	1.399	0.874	2.049	2.405	3.654	0.029	0.041	1.309	0.14	0.29	2.693	7.429
MS 7	4.325	2.598	1.3	1.211	9.23	0.075	0.022	1.539	0.54	0.303	11.125	6.495
MS 8	4.195	4.871	4.107	2.095	5.442	0.159	0.032	1.577	0.264	0.386	13.883	8.657
MS 9	4.809	6.268	1.023	2.503	10.908	0.101	0.022	1.84	0.366	0.461	9.425	5.687
MS 10	4.756	4.718	2.809	4.357	4.875	0.116	0.042	2.605	0.445	0.392	9.306	8.843
MS 11	1.904	4.718	2.648	1.577	17.516	0.06	0.033	1.172	0.212	0.212	4.12	3.542
Min	0.887	0.536	1.023	1.211	3.654	0.016	0.022	0.347	0.134	0.055	2.693	3.542
Max	6.064	17.975	19.501	7.023	17.516	0.802	0.303	3.108	0.67	0.67	15.685	18.4
Mean	3.346	4.713	6.810	3.319	8.643	0.215	0.058	1.580	0.309	0.311	10.129	9.371
SD	1.716	4.774	6.290	1.620	4.646	0.249	0.078	0.749	0.167	0.165	3.805	4.128
CV	51	101	92	49	54	116	133	47	54	53	38	44

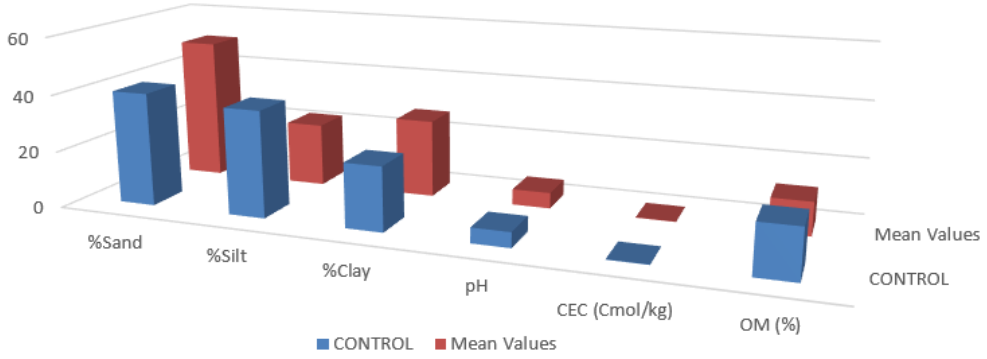
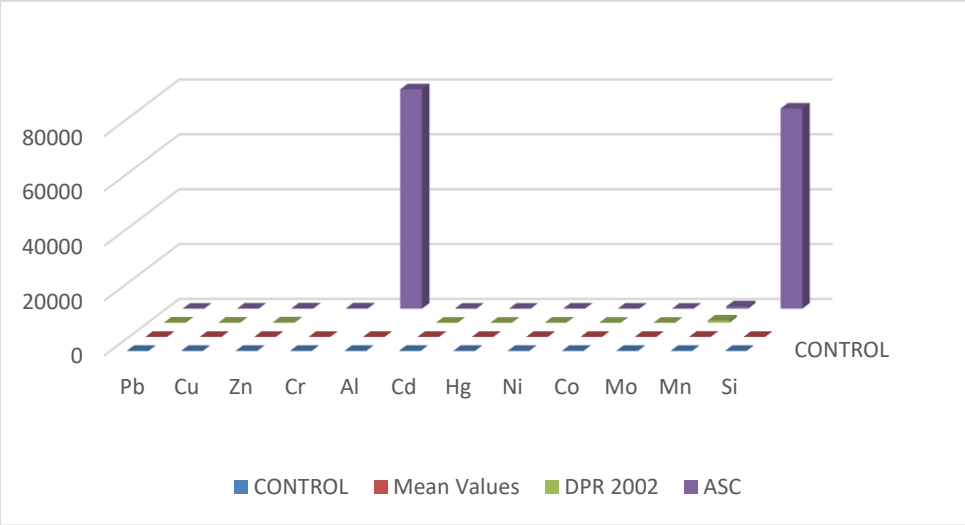


Fig. 3. Physiochemical parameters across the auto-workshops and the control



ASC= Average Shale Concentrations. DPR= Department of Petroleum Resources.

Fig. 4. Bar chart showing the concentrations (mg/kg) of heavy metals in study area and control compared with DPR (2002) and the Average Shale Abundance according to Rose *et al.* (1976).

SOIL QUALITY ASSESSMENT

Enrichment Factor, EF

The calculated Enrichment Factors (EF) shown in Table 4 indicate that there is Pb enrichment in all the sites. The enrichment was minor (1<3) in MS 1 and MS 4 but moderate (3<5) in MS 5 and MS 6. There is severe enrichment (10<25) of Pb in MS 2, MS 3, MS 5, MS 6, MS 7, MS 8, MS 9, MS 10 and MS 11. Cu enrichment is moderate in MS 1 and MS 4. Moderately severe enrichment of Cu was observed in MS 3 and MS 6, very severe enrichment in MS 5, MS 7 and MS 8; extremely severe enrichment in MS 2, MS 9 and MS 11.

There is Cr enrichment (moderately severe, 5<10) in MS 1, MS 4 and MS 7. There is severe Cr enrichment in MS 2, MS 3, MS 5, MS 6, MS 8, MS 9, MS 10 and MS 11.

Al enrichment in all the considered auto-workshops is extremely severe (>50) while there is no enrichment of Cd MS 1 and MS 4. It is minor in MS6 but moderate in MS 8, MS 9, MS 10 and MS 11. Cd enrichment in MS 5 is moderately severe. It is of severe enrichment in MS 2 and MS 3.

There is moderate Ni enrichment in MS 1; moderately severe enrichment in MS 4. Severe enrichment of Ni was observed in MS 3 while MS 2, MS 5, MS 6, MS 7, MS 8, MS 9 and MS 10 while extremely severe enrichment was observed in MS 11.

Co has minor enrichment in MS 1, MS 3, MS 4 and MS 6; moderate enrichment in MS 2, MS 6 and MS 8; moderately severe enrichment in MS 5, MS 8, MS 10 and MS 11.

There is minor Mn enrichment in MS 5 and MS 6; moderate enrichment in MS 1, MS 2, MS 4, MS 10 and MS 11. Moderately severe enrichment of Mn was observed in MS 3, MS 7, MS 8 and MS 9.

Pollution Load Index (PLI)

The Pollution Load Indices (PLI) of the samples in this study as shown in Table 5 ranges from 4.2 – 12.2. This is an indication that the study area is polluted.

Ecological Risk Index (Er^i)

The Er^i as shown in Table 6 indicate that the potential ecological risks of the heavy metals within the auto-workshops were mainly posed by Cd, Cu and Ni. The Er^i contribution to the RIs of these heavy metals were 29.94%, 27.32% and 22.2% respectively, while the contributions of Pb, Zn, Cr, Co were only 7.76, 3.08, 4.92 and 4.78% respectively. Based on the Er^i calculations, the order of the single ratio of the tested heavy metals in the study area for the total potential ecological hazard is Cd>Cu>Ni>Pb>Cr>Co>Zn. This analysis also shows that in the study area, the Er^i of all the heavy metals range from low to high ecological/contamination risk.

Correlation Analysis of Soil Heavy Metals

Pb has a moderate positive correlation (0.5-0.7) with Cu (+0.675) and Ni (+0.669). These substantial positive correlations between heavy metals imply that the sources of these metals are related to common anthropogenic inputs. There are some observed weak positive correlations (<0.5) between Pb and Zn (0.23), Cr (0.211), Co (0.063), Cd (0.063) and Mn (0.184). There is a weak negative correlation (<-0.5) between Pb and Al (-0.01), Mo (-042), Hg (-0.42) and Si (-0.29). The negative correlations show that the heavy metals have diverse source(s) of contamination in the environment.

Cu shows weak positive correlation with Zn (+0.304), Cr (+0.211), Co (+0.018) and Cd (+0.063); weak negative correlations with Mn (-0.083), Mo (-0.258), Al (-0.19) and Hg (-0.256).

Zn has a moderate positive correlation with Cr (+0.68), Cd (+0.563), and Mn (+0.546); weak positive correlation with Al (+0.171), Mo (+0.253) and Si (+0.365); weak negative correlation with Ni (-0.087), Co (-0.142) and Mo (-0.355).

Cr has strong positive correlation with Cd and Si with Cr/Cd having +0.718 and Cr/Si with +0.701. However, the correlation was weak and positive between Cr and Ni (+0.358); Cr/Mo (+0.103); Cr/Mn (+0.352) and Cr/Co (+0.154). It has a weak negative correlation with Hg (-0.086) and Al (-0.131).

On the other hand, Ni/Co, Ni/Mn and Ni/Si were had weakly positive correlation values of (+0.462), (+0.072), (+0.164) respectively. Ni/Mo (-0.026) and Ni/Mo (-0.228) showed a weakly negative correlation.

Co has weak positive correlation with Mn (+0.099) and Si (+0.307) but a weakly negative correlation with Mo (-0.149). Mo has a strong positive correlation with Si (+0.518) and a moderate positive correlation with Mn (+0.474) while Mn positively correlated strongly with Si (+0.545). Cd has a weak positive correlation with Ni (+0.1940, Co (-0.389), Mn (+0.342) and Si (+0.481). It was also weakly positive with Hg (-0.149) and Mo (-0.149).

Al has a weakly positive correlation with Cd (+0.239) and Hg (+0.025) while it is weakly negative with Ni (-0.409), Co (-0.168), Mo (-0.17), Mn (-0.0720 and Si (-0.451).

Table 3. Enrichment Factor values of heavy metals across the auto-workshops

	Pb	Cu	Zn	Cr	Al	Cd	Hg	Ni	Co	Mo	Mn	Si
MS 1	2.030	3.066	1.567	9.855	8625.243	0.366	277.318	4.812	2.044	0.053	3.574	1.000
MS 2	19.404	143.793	10.580	23.669	7249.585	13.471	52.478	38.146	4.522	0.022	4.949	1.000
MS 3	13.071	7.389	11.124	21.157	20155.035	23.447	36.252	19.490	3.840	0.010	6.758	1.000
MS 4	1.506	3.594	3.957	9.286	4283.725	0.513	27.825	8.221	2.429	0.072	4.120	1.000
MS 5	4.361	26.140	2.415	15.858	2632.846	7.875	16.935	26.583	6.304	0.018	2.463	1.000
MS 6	4.891	7.638	1.398	13.452	5109.403	1.014	57.330	27.733	3.263	0.066	1.493	1.000
MS 7	17.293	25.970	1.014	7.747	14762.316	2.999	35.186	37.295	14.394	0.079	7.055	1.000
MS 8	12.585	36.531	2.404	10.056	6530.149	4.770	38.399	28.672	5.280	0.076	6.605	1.000
MS 9	21.961	71.558	0.912	18.288	19924.794	4.612	40.186	50.924	11.142	0.137	6.826	1.000
MS 10	13.967	34.639	1.610	20.473	5726.733	3.407	49.338	46.366	8.712	0.075	4.335	1.000
MS 11	13.96	86.4811	3.7883	18.5	51371.036	4.3992	96.782609	52.0795	10.3626	0.10143	4.7911	1

Table 4. PLI of the different auto-workshops

Site	PLI
MS1	5.260
MS 2	6.099
MS 3	6.342
MS 4	5.590
MS 5	8.143
MS 6	3.734
MS 7	5.141
MS 8	5.802
MS 9	5.708
MS 10	6.476
MS 11	4.277

Table 5. PERI of heavy metals in the auto-workshops

	Pb	Cu	Zn	Cr	Al	Cd	Hg	Ni	Co	Mo	Mn	Si
Tri	5	5	5	2	-	30	-	5	5	-	-	-
MS 1	11.09	16.75	8.56	21.54		12.00		26.29	11.17			
MS 2	75.80	561.72	41.33	36.98		315.75		149.02	17.67			
MS 3	55.89	31.59	47.56	36.18		601.50		83.33	16.42			
MS 4	11.36	27.13	29.87	28.03		23.25		62.05	18.33			
MS 5	38.63	231.53	21.39	56.18		418.50		235.45	55.83			
MS 6	17.49	27.31	5.00	19.24		21.75		99.17	11.67			
MS 7	54.06	81.19	3.17	9.69		56.25		116.59	45.00			
MS 8	52.44	152.22	10.02	16.76		119.25		119.47	22.00			
MS 9	60.11	195.88	2.50	20.02		75.75		139.39	30.50			
MS 10	59.45	147.44	6.85	34.86		87.00		197.35	37.08			
MS 11	23.80	147.44	6.46	12.62		45.00		88.79	17.67			
	460.11	1620.19	182.70	292.10		1776.00		1316.89	283.33			
%	7.7573	27.3158	3.0803	4.9248		29.943		22.2023	4.77689			

Table 6. Correlation of heavy metals in the auto-workshops

	Pb	Cu	Zn	Cr	Al	Cd	Hg	Ni	Co	Mo	Mn	Si
Pb	1	.675*	.203	.211	-.010	.063	-.420	.669*	.063	-.420	.184	-.290
Cu		1	.304	.359	-.190	-.082	-.258	.468	.018	-.258	-.083	-.092
Zn			1	.680*	.171	.563	-.145	-.087	-.142	.253	.546	.365
Cr				1	-.131	.718*	-.086	.359	.154	.103	.352	.701*
Al					1	.239	.025	-.409	-.166	-.179	-.072	-.451
Cd						1	-.149	.194	.389	-.149	.342	.481
Hg							1	-.587	-.149	-.100	-.015	.128
Ni								1	.462	-.228	.072	.164
Co									1	-.149	.099	.307
Mo										1	.474	.518
Mn											1	.545
Si												1

*. Correlation is significant at the 0.05 level (2-tailed).

Environmental implications

It has been established that these heavy metals pose serious health concern for human; harmfully affects plant vigor, animal health, microbial processes and overall soil health. There is also the likelihood of surface and groundwater contamination. In human, the key pathways of contact to these potential pollutants include ingestion, inhalation and dermal contact but the effects from all the pathways are the same.

In men, Pb exposure causes mental retardation, high blood pressure, fertility problems; miscarriage in women, developmental delay as well as damage to nervous system in children (Oyeleke *et al.,* 2016). According to Needleman (1990), exposure to Pb also impairs physical and mental development as well as elevate hearing threshold and reduces serum levels of vitamin D.

Cr is associated with allergic dermatitis in humans according to Scragg (2006). Exposure to Cr has also shown to cause mutagenic, carcinogenic and teratogenic effects

on humans (Chokor, 2016). Zn exposure can result in gastrointestinal irritation and interference of physiological processes. High level of Zn adversely affects plant health (Chokor, 2016). Extreme Zn intake in human aggravates Cu deficiency (Hurley and Keen, 1987). It can also interrupt microbial activity in soils, as it harmfully influences the activity of microorganisms and earthworms and as a result, retards the breakdown of organic matter.

Ni compounds that are released to the environment will adsorb on soil particles and become immobile as a result (Oyeleke *et al.,* 2016). However, in acidic soils such as the ones within the study area, Ni becomes more mobile and often leaches down to the groundwater (Chokor, 2016). Microorganisms can also suffer from growth decline owing to the presence of Ni. The most common harmful health effect of nickel in humans is an allergic reaction or skin rash (dermatitis or eczema). Nickel inhalation can also cause asthma attacks.

Cd is another non-essential element for biota growth and development which is known to cause renal, prostate and ovarian cancers (Hartwig, 1998). Cd ingestion of any substantial amount also causes immediate poisoning, damage to the liver and the kidneys (Kalonel, 1976; Fasanya–Odewumi *et al.,* 1998) while ingestion in excess causes 'Itai – Itai', a disease that results in soft bones, shrinking body and death (Chorkor, 2016; Ademoroti, 1996; Kazantzis, 2004) and hypertension (Keller, 1981; Jensen, *et al*., 2003; Stoica, *et al*., 2000; Adamu and Nganje, 2010).

Mn is poisonous at high concentrations. The harmful effect in humans is always related with severe psychiatric disorder resembling schizophrenia, followed by permanently crippling neurological disorder clinically similar to Parkinson's disease (Klaassen, 2001; Chorkor, 2016). Mn has also been reported to impede synthesis of chlorophyll by obstructive Iron processes causing chlorosis and necrotic lesions on old leaves, dark brown or red necrotic spots and accretion of small particles of MnO_2 in epidermal cells of leaves or stems, drying leaf tips, and stunted roots (Clarimont *et al.,* 1986). On the other hand, exposure to high levels of Co results in lung and heart diseases and dermatitis (Olajide and Saeed, 2013).

Though Cu is a vital element, it may be injurious at high concentration. Cu restricts fatty acid and protein metabolism and inhibits respiration and nitrogen fixation process in plants (Chorkor, 2016; Konstantinidis *et al.,* 2003; Fernandez and Henrigues, 1991). Excessive dietary copper intake in mammals causes nausea, vomiting and diarrhea. It also causes pathological changes in brain tissue (Pizzarro *et al.,* 1999). Copper accumulates in the liver, kidney, cornea, and brain (Davis *et al.,* 2000). The accumulation of Cu in the brain leads to trauma and eventual death (Varela–Nallar *et al.,* 2006).

A number of studies have investigated the toxicity of Mo following inhalation exposure. Decreases in lung function, dyspnea, and cough were reported in workers exposed to fine or ultrafine Mo dust.

CONCLUSION

This research has been able to establish that surface soil within auto-workshops at Onitsha have been negatively impacted and degraded by these toxic elements which resulted from auto-repair activities. In the developed world like the United States of America, the Environmental Protection Agency (EPA) identifies the most serious hazardous waste sites in the nation. These sites are then placed on the National Priorities List (NPL) and are targeted for long-term federal clean-up activities. Nigeria should adopt this method because these heavy metals are harmful not only to the residents but also to the flora and fauna and can also alter the ecology of the area. This study will help in no small measures to create awareness about the inherent risks connected with non-scientific method of handling wastes and also complement other literatures/reference materials on urban soil geochemistry. It is recommended that auto technicians within the city of Onitsha should be educated on proper ways to handle wastes associated with their activities.

References

Adegoke, O. S. (1969). Eocene Stratigraphy of Southern Nigeria Collogue sur Eocene. Vol. III *Bur. Rech. Geol. Min. Mem*., No. 69, 23-48.

Adekola, F. A. and Eletta, O. A. (2007). A study of heavy metal pollution of Asia River, Ilorin, Nigeria: Trace metal monitoring and geochemistry. *Environ. Monit. Assess*. 125, 157-163.

Agbaji, E. B., Abechi, S. E. and Emmanuel, S. A. (2015). Assessment of Heavy Metals Level of Soil in Kakuri Industrial Area of Kaduna, Nigeria. *Journal of Scientific Research & Reports,* 4(1), 68-78.

Anegbe B., Okuo, B. J. M. and Okiemen, F. E. (2016). The Impact of Inorganic and Organic Pollutants in Soil from the Vicinity of Mechanic Workshops in Benin City. *International Journal of Chemical studies,* 4(3), 106-112.

Anzene, S. J. (2019). Determination of Heavy Metals in Waste Dumpsites in Lafia Town and Environs. *International Journal of Engineering Research & Technology (IJERT*), 8 (6), 2278-0181.

Arua, I. A. (1982). Borings and shell damage in Eocene gastropoda: Southeastern Nigeria. *Paleogeography, Paleoclimatology, Paleoecology.* 38, 3-4.

Aweto, A. O. (1982). Variability of Upper Slope Soils Developed on Sandstones in Southwestern Nigeria. *Nigerian Geographic Journal,* 25 (1&2), 27-37.

Basile-Doelsch, I. (2006). Si Stable Isotopes in the Earth's Surface: A Review. *Journal of Geochemical Exploration,* 88 (1-3), 252-256.

Benkhelil, J. (1987). Cretaceous Deformation Magmatism and metamorphism in the Lower Benue Trough, Nigeria. *Geol. Journ.,* 22, 467-493.

Bhattacharya, P., Mukherjee, A. B., Jack, G. and Nordquist, S. (2002). Metals Contamination at a wood preservation site: characteristics and experimental studies on remediation. *Science of the Total Environment,* 290, 165-180.

Birch, G. F. (2003). A test of normalization methods for marine sediments, including a new post-extraction normalization (PEN) technique. *Hydrobiologia,* 492, 5 – 13.

Bridget, Diagi E., Justin N. Okorondu, I. Ajiere Susan, Ekweogu Chinonye V., David O. Edokpa, Chidinma Acholonu, and Steven Edeh. 2023. "Assessment of Heavy Metal Contamination of Soil in Mechanic Workshops at Nekede and Orji, Owerri Zone, Imo State, Nigeria". *Journal of Scientific Research and Reports* 29 (7):8-16. https://doi.org/10.9734/jsrr/2023/v29i71755.

Chang, S. E., Stone, J., Demes, K. and Piscitelli, M. (2014). Consequences of oil spills: a review and framework for informing planning. *Ecology and Society,* 19(2), 26.

Chen, J. (2007). Rapid urbanization in China: A real challenge to soil protection and food security. *Catena*, 69, 1-15.

Chinda, A. C., Braide, A. S. and Sibeudu, O. C. (2004). Distribution of Hydrocarbon and Heavy Metals in Sediments and a Crustecean (shrimps-Penaeus notialis) from the Bonny/New Calabar Estuary Nigeria Delta. *Ajeam-Ragee,* 9, 1-14.

Chokor, A. A. (2016). Soil Profile Distribution of Heavy Metals in Automobile Workshops in Sapele, Nigeria. *International Journal of Basic Science and Technology,* 2 (1), 30 – 38.

Dessauvagie, T. F. and Fayose, E. A. (1970). Excursion A: Cretaceous and Tertiary rocks of Southern Nigeria. In: Dessauvagie, T. F. and Whiteman, A. J. (eds). *African Geol.*, 659 – 665.

Dian, C. (2018). Effects of heavy metals on soil microbial community. *Earth and Environmental Science, 68,* 113.

DPR (2002). Environmental guidelines and standards for the petroleum industry in Nigeria (revised edition). Department of Petroleum Resources, Ministry of Petroleum and Natural Resources, Abuja, Nigeria.

EPA, (1994). Environmental Regulations and Technology-managing used motor oil. United states environmental protection agency. Office of research and development, Washington, DC 20460. EPA/625/R-94/010

Ezeabasili, A. C. C., Anike, O. L., Okoro, B. U. and U-Dominic, C. M. (2014). Arsenic pollution of surface and subsurface water in Onitsha, Nigeria. *African Journal of Environmental Science and Technology,* 8 (9), 491 – 497.

FAO-UNESCO (1990). Soil map of the world. United Nations Educational, Scientific and Cultural Organization. Place de Fontenoy, 75700, Paris. Retrieved on August 3, 2018. www.fao.org/3/as360e.pdf

Garba, S. T. and Abubakar, M. A. (2018). Source and Distribution of Heavy Metals: Pb, Cd, Cu, Zn, Fe, Cr, and Mn in Soils of Bauchi Metropolis, Nigeria. *American Journal of Engineering Research (AJER)*, 7, (2), 13-23.

Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Res.,* 14(8), 975 – 1001.

Han, Y. M., Du, P. X. and Cao, J. L. (2006). Multivariate Analysis of Heavy Metal Contamination in Urban Dusts of Xi'an, Central China. *Science of the Total Environment,* 335, 176-186.

Jaishankar, M., Tseten, T., Anbalagan, N, Matthew, B. B. and Beeregowda, K. N. (2014). Toxicity, mechanism and health effects of some heavy metals. *Interdiscip. Toxicol.* 7(2), 60–72.

Karkarna, M. Z. and Matazu, M. J. (2021). Evaluation of Heavy metals pollution around Kano municipal solid waste Dumpsites, Kano state, Nigeria. *UMYU Journal of Microbiology Research,* 6(1), 146-152.

Kogbe, C. A. (1976). The Cretaceous and Paleogene Sediments of Southern Nigeria. In: Kogbe, C. A., Ed., Geology of Nigeria, Elizabethan Publishers, Lagos. 273-282.

Kogbe, C. A. (1989). The Cretaceous and Paleogene Sediments of Southern Nigeria: In Kogbe C. A. (Ed.), Geology of Nigeria. *Elizabethan Publ.*, Lagos, Nigeria. 273-286

Ministry of Housing, Spatial Planning and Environment (MHSPE) (1994). Intervention values and target values – soil quality standards. *Directorate-General for Environmental Protection, Department of Soil Protection, The Hague, The Netherlands.*

Ministry of Housing, Spatial Planning and Environment (MHSPE) (1994). Intervention values and target values – soil quality standards. *Directorate-General for Environmental Protection, Department of Soil Protection, The Hague, The Netherlands.*

Mozie, A. T. and Ayadiuno, R. U. (2008). The role of government in the degradation of landscape in Onitsha and its environs: Present state and future expectations. Nigeria *Journal of Geography and the Environment.* 1, 119-127.

Murat, R. C. (1972). Stratigraphy and Paleogeography of Lower Tertiary, Southern Nigeria, in Dessavagie, T. P. J. and Whiteman (Eds.), Afri-geol. University of Ibadan,Nigeria. 425.

Nganje, T. N. and Adamu, C. I. (2014). A Comparative Study of Element Cycling in the Soil-Plant System: A Case Study of Shaly and Calcareous Soils, Southern Benue Trough, Nigeria. *International Journal of Geosciences,* 5, 453-463.

Nwachukwu, M. A., Ntesat, B. and Mbaneme, F. C. (2013). Assessment of direct soil pollution in automobile junk market. Journal of Environmental Chemistry and Ecotoxicology. 5(5), 136 – 146.

Nwajide, C. S. (1979). A Lithostratigraphic Analysis of the NankaSand, Southeastern Nigeria. *Nigeria Journal of Mining and Geology,* 16, 103-109.

Nwajide, C. S. (1990). Cretaceous Sedimentation and Paleogeography of the Central Benue trough. In: Ofoegbu, C.O; (Ed.), The Benue. Tough structure and Evolution International Monograph Series, Braunschweig, 19-38.

Nwajide, C. S. (2014). Geology of Nigeria sedimentary basins. CSS Publisher, Lagos Nigeria. 520.

Nwajide, C. S. and Reijers, T. J. A. (1996). Geology of the Southern Anambra Basin. In: Reijers, T.J.A. (Ed), selected chapters on Geology, SPDC, Warri, 133-148.

Nwankwoala, H. O. and Ememu, A. J. (2018). Contamination Indices and Heavy Metal Concentrations in Soils in Okpoko and Environs, Southeastern Nigeria. *J Environ Sci. Public Health,* 2 (2), 77-95.

Oboh-Ikuenobe, Obi, C. G. and Jaramilo, C. A. (2014). Lithofacies, palynofacies and sequence stratigraphy of Palaeogene strata in southeastern Nigeria. *Journal of African Earth Sciences, 41 (1-2), 79-101.*

Odigi, M. I., Ukren, L. O. and Nwankwoala, H. O. (2011). Distribution of Heavy Metals in Soils of Port Harcourt and its Environs, Niger Delta, Nigeria. *Chin. J. Geochem.* 30, 415.

Ololade, I. A. (2014). An Assessment of Heavy Metal Contamination in Soils within Auto-workshops using enrichment and Contamination Factors with Geoaccumulation indexes. *Journal of Environmental Protection.* 5, 970-982.

Pam, A. A., Ato, R. S. and Offem, J. O. (2013). Contribution of Automobile Mechanic Sites to Heavy Metals in Soil: A Case Study of North Bank Mechanic Village, Makurdi, Benue State, Central Nigeria. *Journal of Chemical, Biological and Physical Sciences,* 3(3), 2337-2347.

Parkinson, J. (1907). The post – Cretaceous Stratigraphy of Southeastern Nigeria. *Quart. Jour. Geol. Soc. London.* 63,331 – 320.

Radha, R., Tripathi, R. M., Vidod, K. A., Sathe, A. P., Khandekar, R. N. and Nambi, K. S. V. (1997). Assessment of Pb, Cd, Cu and Zn exposures of 6 to 10 year old children in Mumbai. *Environ. Res.* 80, 215 -221.

Reyment, R. A. (1965). Aspects of the Geology of Nigeria. *Ibadan University Press, Ibadan, Nigeria,* 145.

Rose, A. W., Hawkes, H. E. and Webb, J. S. (1979). Geochemistry in Mineral Exploration, 2nd ed., *Academic Press London,* 562.

Sani, I. S. (2012). Health Risk Assessment of Heavy metals in Urban Soil. *Science Proceedings series,* 1(2), 16-18.

Short, K. C. and Stauble, A. J., (1967.) Outline of the geology of the Niger Delta. *Bulletin American Association of Petroleum Geologist 54*, 761-779.

Siegel, F. R. (2002). Environmental Geochemistry of Potentially Toxic Metals. Springer Verlag, Berlin, 218.

Simex, S. A. and Helz, G. R. (1981). Regional geochemistry of trace elements in Chesapeaker bay. *Environ. Geo.*, 3, 315 – 323.

Simpson, A. (1955). The Nigerian Coalfield: The Geology of Parts of Onitsha, Owerri and Benue Provinces. *Geology,* 103, 385 – 397.

Tomlinson, L. D., Wilson, J. G., Harris, C. R. and Jeffery, D. W. (1980). Problems in the assessments of heavy-metal levels in estuaries and formation of a pollution index. *Helgoländer Meeresuntersuchungen*, 33(1), 566-75.

Turekian, K. K. and Wedepohl, K. H. (1961). Distribution of the Elements in Some Major Units of the Earth's Crust. *Geological Society of America Bulletin,* 72, 175-192

Vashukevich, E. I., Kozlov, H. V. and Aprelkov, N. G. (2004). X-ray florescence determination of heavy metals in humic acids. *Journal of Analytical Chemistry*. 59, 1066-1072.

Environmental Protection Agency (EPA) (1995). "Ecological Screening Values" In: Supplemental Guidance to RAGS: Region 4. *Bulletin-Ecological Risk Assessment, Bull. 2,* Atlanta, Georgia. http://www.epa.gov/region4/wastepgs/ofiecser/otsguid.htm

VROM (2000). Circular on target values and intervention valuesfor soil remediation. The Hague, The Netherlands: Ministryof Housing, Spatial Planning and the Environment. *http://www.minvrom.nl/Docs/internationaal/annexS_I2000.*

Warren, H. V. (1972). Geology and medicine. *Western Miner*, 9, 34-37.

Whiteman, A. (1982). Nigeria: Its petroleum geology, resources and potential. *Graham and Trotman,* 1, 382.

WHO. (1996). Trace elements in human nutrition and health. WHO/FAO/IAEA. Geneva, 362.

Wuana, R. A. and Okieimen, F. E. (2011). Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. *Ecology,* 19.

Xu, Z. Q., Ni, S., Tuo, X. G. and Zhang, C. J. (2008). Calculation of heavy metal's toxicity coefficient in the evaluation of Potential Ecological Risk Index. *Environmental Science and Technology,* 31(2), 112 – 115.

Zhang, L., Ye, X., Feng, H., Jing, Y., Ouyang, T., Yu, X., Liang, R., Gao, C. and Chen, W. (2007). Heavy Metal Contamination in Western Xiamen Bay Sediments and its Vicinity, China. *Mar Pollut. Bull.,* 54, 974-982.