

## Determination of Heavy Metals in Scrapped Car Paint Dust and Auto Repair Workshop Soil from Southeastern Nigeria: Soil Contamination Assessment

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**Abstract:** Automobiles imported into Nigeria are fairly used and rickety, the net effect is that high automobile waste dot the Nigerian landscape, amidst poverty the vehicles are taken to the workshops for reworking (panel beaten, welding, old paint scrapping, finishing and repainting). Therefore we used integrated pollution index, enrichment factor and geo-accumulation index to establish contamination profiles of used vehicle reworking workshop soil. Scrapped car paint dusts matrix from 55 vehicles and workshop soil were collected from eight (8) car reworking workshops in south eastern Nigerian. They were homogenized, mixed and divided into fine particles that can pass through 0.5mm sieve and digested by standard methods. The filtrates were assayed for cadmium, chromium, lead, manganese, nickel, copper and iron with atomic absorption spectrophotometry (AAS 200A) at their respective wavelength. Result of paint dust shows highest value (mg/kg) Cd  $(3.36\pm0.02)$ , Cr  $(2.95\pm0.01)$ , Pb  $(4.21\pm0.03)$ , Mn  $(3.31\pm0.01)$ , Ni  $(3.84\pm0.02)$ , Cu  $(7.11\pm0.01)$  and Fe  $(13.25\pm0.04)$  for vehicles in workshops D, G, B, A, A, D and H while that of workshop soil were Cd  $(3.93\pm0.01)$ , Cr  $(3.53\pm0.02)$ , Pb  $(5.19\pm0.05)$ , Mn  $(4.05\pm0.01)$ , Ni  $(4.57\pm0.01)$ , Cu  $(7.31\pm0.01)$  and Fe  $(16.12\pm0.08)$  were reported in workshops F, F, B, A, F, D and G. Contamination assessment [integrated pollution index (IPIn), enrichment factor (EF) and geo-accumulation index (I-geo)] calculated using standard equations were compared with established reference standard showed that workshop soils were anthropogenically polluted with heavy metals from scrapped waste car paint. Reworking used vehicles may contribute to environmental heavy metal burden with its associated public health risks.

Keywords: Paint Dust, Soil Heavy Metal Levels, Soil Contamination Assessment, Automobile Waste, Auto-Workshops, Southeastern Nigeria

## **1. Introduction**

Environmental contamination by heavy metal is posing serious challenge globally because of its human health implication [1]. The concentration of these toxic metal in the environment have significantly increased due to increased human activities through emissions from industrial plants, thermal power stations, waste disposal, soil amendments and fertilization, vehicular traffic and road infrastructure [2], mining, smelting and refining of ores. The implication is that these toxic metals has been associated with human activities for decades, been common industrial metals, they are wide spread in air, water, dust, soil, and food. A compilation has been made of 120 occupations e.g. auto-mechanic, painting, printing, welding etc. that involves exposure to metals such as lead [3]. It has been established that all humans have lead in their bodies, primarily as a result of exposure to man-made sources [4]. This is because consumable products are laden with chemical elements, this is of interest because they are either essential or toxic in nature [5], contaminated food [6], pediatric syrups [7, 8]. Dairy products [9], canned and noncanned beverages [10], herbal preparations [11] and cosmetics [12] are exposure pathways of metals, nonconsumable goods and others include flaking paints in old houses [13, 14], industrial effluents [15, 16], earthenware pottery and ceramic utensils [17], fugitive dusts and roadside surface soil [18, 19] also contain high amount of toxic metals. Studies has also shown that fairly used electronics such as computers and its accessories, TV sets, fax machines, cell phones, telephones, photocopy machines and printers, dryers, wireless devices, video cameras, chips, motherboards, cathode ray tubes and peripheral items, kitchen equipment, electronic toys, washing machines, refrigerators etc. are veritable sources of metal exposure in Nigeria and indeed Africa, because large volumes of these materials imported into the country are irreparable junks which the country lacks the technology to safely dispose, more than 75% of them wind up in landfills and informal dumps that dot the Nigerian landscape where they decompose and release toxic metals into the environment [20-22]. The irony is that most modern cars/vehicles are fitted with some of these electronic devices. Also mechanical components of vehicles/cars are made of metals and metalloids that contain arsenic, cadmium, chromium, lead, mercury etc. Since the automobile trade like electronics is associated with high volume of importation into Nigeria from Europe, America and some Asian countries, there are concerns that toxic chemicals will leach from electronic and mechanical devices when disposed [23]. High percentage of this vehicles and their parts are wornout, rickety and not road worthy and with an alarming rate of vehicular road accident in Nigeria coupled with deplorable road conditions, humidity and high ambient air temperature that cause expansion and contraction, corrosion, the net effect is that the vehicles constantly break down and are taken to the workshops for re-working by scrapping old paint, panel beaten and welding body parts, finishing and repainting.

Reworking automobiles can become important sources of toxic metals like lead, manganese, cadmium, nickel; chromium etc., and of public health concern in a country that lacks appropriate technology to deal with automobile/electronic waste and with no legislation on life span of imported vehicles. Where legislation exists, its weak implementation or non-compliance with standard makes the Nigerian environment especially soil and water great reservoir of heavy metals. Artisans at automobile workshops and the general population especially support and ancillary workers have highest exposure risk to heavy metals mainly by ingestion, inhalation and dermal contact with its attendant health implication as it concerns occupational/life time exposure. This may lead to a worst case scenario, given the juxtapositioning and indiscriminate citing of these automobile workshops, the metals may end up in adjacent farmlands where vegetables and other produce are planted leading to entry of toxic heavy metals into food web.

The aim of this study is to assess the average soil metal levels and that of scrapped car paint matrix to ascertain

lithogenic or anthropogenic metal contamination of the workshop soil using various indices such as enrichment factor (EF), geo-accumulation index (GI) and pollution load index.

## **2. Materials and Methods**

We used drive-by exercise to identify panel beating/automobile workshops, through friendly discussions and explanation; we were allowed to collect scrapped car paint dust with white cardboard sheet from cars of over 10 years and soil samples of the eight (8) workshops [A-H] located at Nnewi, Awka, Onitsha and Enugu all in Southeastern Nigeria. Figure 1. The soil and paint flakes/dusts were stored in black polythene bags before digestion and analysis. They were ground and sieved using meshes (metric test sieve BS 4 WS Tyler) with geometric diameters of 100 and 45µm on a mechanical shaker (Retsch AS 200) for 15 min at amplitude of 10 mm/g to separate them into two particle size fractions. Paint/soil dust size fraction below 100 µm were used in the study. Digestion was done by placing 2g of soil/paint dust separately in a conical flask, adding 15ml of concentrated nitric acid and perchloric acid at a ratio 1:1 and heating in a fume cupboard at a temperature of 105°C until the volume went down to less than 1ml, it was allowed to cool, and 10 ml of de-ionized water was added, stirred, filtered and made up in a standard volumetric flask. Heavy metals (cadmium, chromium, nickel, lead, manganese, copper and iron), each of soil/paint were assayed at their respective wavelengths (227, 358, 231 285.1, 278, 323, 247 nm) with atomic absorption spectrophotometry (AAS 200A), with a detection limit set at 0.001 mg/l, with blank values readings as 0.00 mg/l in deionized water and with an electrical conductivity value of lower than 5µs/cm. Samples were analyzed in triplicates and results shown in Tables 1 and 2 reported in SD and Mean  $\pm$ SEM. The calibration curves were prepared for each of the metals investigated using the least square fitting method. The accuracies of these methods have been evaluated by analysis of NBS standard reference materials and were better than  $\pm 10\%$ . A quality control programme, including reagent blanks, replicate samples and standard reference material, were used to assess data precision and accuracy. Blanks were prepared in a procedure similar to that used for the dust samples and routinely analyzed before each measurement. The result of Table 1 is the mean value of the number of vehicles per workshop. Percentage organic matter (carbon) of surface soil at the workshops was determined according to Emedo et al [24]. Exchangeable cations, such as potassium, sodium, and calcium were determined on a flame photometer, cation exchange capacities were determined according to Brady and Weil [25]. Soil pH was determined by weighing 20 g of airdried soil (passing through a 2-mm sieve) into a 50-ml beaker, then adding 20 ml of distilled water, allowed standing for 30 min, while stirring occasionally with a glass rod. An electrode of the pH meter was inserted into the partly settled suspension and pH measured; the result was reported as "soil pH in water".

Table 1. Showing average metal levels from scrapped car paint dust matrix of all the vehicles.

| Workshops | No of vehicles<br>per workshop | Data<br>presentation | Cd              | Cr              | Pb              | Mn              | Ni              | Cu              | Fe          |
|-----------|--------------------------------|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-------------|
| ٨         | 7                              | SD                   | 0.03            | 0.02            | 0.06            | 0.02            | 0.04            | 0.01            | 0.03        |
| А         | /                              | Mean + SEM           | $2.25 \pm 0.03$ | $2.43 \pm 0.02$ | $3.25 \pm 0.05$ | 3.31+0.01       | 3.84 + 0.02     | 2.12 + 0.01     | 7.66+0.03   |
| р         | 7                              | SD                   | 0.07            | 0.03            | 0.03            | 0.02            | 0.02            | 0.05            | 0.05        |
| Б         | 1                              | Mean + SEM           | 2.74 + 0.01     | $2.45 \pm 0.02$ | 4.21+0.03       | $2.32 \pm 0.01$ | 3.30+0.01       | $4.42 \pm 0.04$ | 10.94+0.22  |
| C         | 7                              | SD                   | 0.10            | 0.03            | 0.04            | 0.05            | 0.07            | 0.11            | 0.06        |
| C         | 1                              | Mean + SEM           | $2.03 \pm 0.07$ | $2.84 \pm 0.02$ | $2.74 \pm 0.11$ | 2.24 + 0.03     | 3.23+0.03       | $2.28 \pm 0.07$ | 5.27+0.04   |
| D         | 7                              | SD                   | 0.04            | 0.03            | 0.03            | 0.03            | 0.03            | 0.02            | 0.03        |
| D         | /                              | Mean + SEM           | 3.36+0.02       | $2.63 \pm 0.05$ | $3.65 \pm 0.02$ | $2.05 \pm 0.01$ | 2.34 + 0.02     | 7.11+0.01       | 6.57+0.01   |
| Б         | 7                              | SD                   | 0.04            | 0.04            | 0.07            | 0.02            | 0.03            | 0.05            | 0.07        |
| Е         | 1                              | Mean + SEM           | 2.54 + 0.02     | $2.48 \pm 0.02$ | $1.92 \pm 0.04$ | 1.80 + 0.01     | $2.75 \pm 0.02$ | 3.76+0.04       | 9.99+0.04   |
| F         | 7                              | SD                   | 0.02            | 0.06            | 0.01            | 0.01            | 0.01            | 0.02            | 0.03        |
| T.        | /                              | Mean + SEM           | $3.58 \pm 0.01$ | $2.87 \pm 0.05$ | 3.46+0.01       | 3.04+0.01       | 3.52+0.01       | $2.68 \pm 0.01$ | 8.98 + 0.04 |
| C         | 7                              | SD                   | 0.08            | 0.02            | 0.02            | 0.03            | 0.02            | 0.05            | 0.07        |
| G         | 1                              | Mean + SEM           | 2.37 + 0.05     | $2.95 \pm 0.01$ | $2.85 \pm 0.01$ | $1.35 \pm 0.02$ | $2.88 \pm 0.02$ | 4.49+0.03       | 13.25+0.04  |
| ц         | 6                              | SD                   | 0.02            | 0.02            | 0.04            | 0.02            | 0.05            | 0.01            | 0.06        |
| 11        | 0                              | Mean + SEM           | $1.67 \pm 0.01$ | $2.27 \pm 0.01$ | $2.86 \pm 0.02$ | $1.62 \pm 0.02$ | 3.41+0.03       | 3.31+0.01       | 12.48+0.03  |

[N= 3, SD= standard deviation, SEM = standard error of mean]



Figure 1. Showing location of the workshops in Municipal cities of Southeastern Nigeria.

## 2.1. Soil Contamination Assessment

Integrated pollution index

The integrated pollution index (IPI) is defined as the mean value of the pollution index (PI) of an element

The integrated pollution index of heavy metals in soil samples were calculated using

 ${\rm IPI}_{N}\mbox{-} C_n / B_n$  according to Chen et al [26] and Wei et al [27]

Where  $C_n$  = Determined concentration of element in the

environment.

 $B_n = Background value$ 

IPIn was classified as:

IPI  $\leq$  I: Low level of pollution;

 $I < IPI \le 2$ : Moderate level of pollution;

2 < IPI < 5: High level of pollution;

IPI > 5: Extreme high level of pollution [26, 27]

The result of Table 2 was used to calculate the integrated

| poll | ution | index | (IPI) | presented | in | Table | 3 |
|------|-------|-------|-------|-----------|----|-------|---|
|------|-------|-------|-------|-----------|----|-------|---|

| Table 2. | Showing meta | al concentration of | f soil samples | from different | workshops |
|----------|--------------|---------------------|----------------|----------------|-----------|
| Inone #. | Showing more | a concentration c   | j son sumpres  | from alfferent | mornops.  |

| S/No | Workshops | Data<br>presentation | Cd              | Cr              | Pb              | Mn              | Ni              | Cu              | Fe               |
|------|-----------|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|------------------|
| 1    | А         | SD                   | 0.04            | 0.03            | 0.03            | 0.02            | 0.01            | 0.01            | 0.01             |
|      |           | Mean $\pm$ SEM       | $2.63 \pm 0.05$ | $2.69 \pm 0.02$ | $3.89 \pm 0.04$ | $4.05 \pm 0.01$ | $4.31 \pm 0.01$ | $2.64 \pm 0.01$ | $9.47 \pm 0.03$  |
| 2    | в         | SD                   | 0.14            | 0.04            | 0.04            | 0.02            | 0.01            | 0.06            | 0.06             |
| 2    | Б         | Mean $\pm$ SEM       | $2.93\pm0.02$   | $2.72 \pm 0.03$ | $5.19\pm0.05$   | $2.43 \pm 0.01$ | $3.84 \pm 0.01$ | $4.68\pm0.05$   | $11.94 \pm 0.03$ |
| 2    | C         | SD                   | 0.02            | 0.03            | 0.02            | 0.06            | 0.06            | 0.15            | 0.02             |
| 3    | C         | Mean $\pm$ SEM       | $2.81\pm0.02$   | $3.11\pm0.02$   | $2.97\pm0.01$   | $2.60\pm0.03$   | $3.56\pm0.03$   | $4.74\pm0.09$   | $7.62\pm0.02$    |
| 4    | D         | SD                   | 0.05            | 0.03            | 0.04            | 0.02            | 0.03            | 0.02            | 0.03             |
| 4    | D         | Mean $\pm$ SEM       | $3.63\pm0.03$   | $2.80\pm0.02$   | $4.17\pm0.02$   | $2.41\pm0.01$   | $2.80\pm0.02$   | $7.31\pm0.01$   | $6.70\pm0.02$    |
| 5    | Б         | SD                   | 0.07            | 0.05            | 0.02            | 0.03            | 0.05            | 0.05            | 0.09             |
| 3    | E         | Mean $\pm$ SEM       | $3.58\pm0.04$   | $3.00\pm0.03$   | $2.92\pm0.01$   | $2.67\pm0.01$   | $3.68\pm0.03$   | $4.90\pm0.03$   | $11.94\pm0.05$   |
| (    | Г         | SD                   | 0.03            | 0.07            | 0.01            | 0.01            | 0.01            | 0.03            | 0.04             |
| 6    | F         | Mean $\pm$ SEM       | $3.93\pm0.01$   | $3.53\pm0.02$   | $3.21\pm0.01$   | $3.37\pm0.01$   | $4.57\pm0.01$   | $3.76\pm0.02$   | $10.08\pm0.06$   |
| 7    | C         | SD                   | 0.16            | 0.02            | 0.01            | 0.04            | 0.02            | 0.09            | 0.13             |
| /    | G         | Mean $\pm$ SEM       | $2.82\pm0.10$   | $3.45\pm0.02$   | $4.03\pm0.01$   | $1.59\pm0.03$   | $3.56\pm0.01$   | $5.54\pm0.05$   | $16.12\pm0.08$   |
| 0    | 11        | SD                   | 0.02            | 0.03            | 0.01            | 0.02            | 0.08            | 0.03            | 0.08             |
| 8    | Н         | Mean $\pm$ SEM       | $2.04\pm0.01$   | $2.63\pm0.02$   | $3.07\pm0.00$   | $1.84\pm0.01$   | $3.32\pm0.04$   | $3.91\pm0.02$   | $15.40\pm0.04$   |

[N= 3, SD = standard deviation, SEM = standard error of mean]

Table 3. Showing result of integrated pollution index of metals in workshop soil samples.

| S/NO | Workshop | Data presentation          | Cd     | Cr    | Pb    | Mn    | Ni    | Cu    | Fe     |
|------|----------|----------------------------|--------|-------|-------|-------|-------|-------|--------|
| 1    | А        | Integrated Pollution Index | 8.767  | 0.030 | 0.195 | 0.005 | 0.063 | 0.059 | 0.0002 |
| 2    | В        | Integrated Pollution Index | 9.767  | 0.030 | 0.260 | 0.003 | 0.057 | 0.104 | 0.0003 |
| 3    | С        | Integrated Pollution Index | 9.367  | 0.035 | 0.149 | 0.003 | 0.052 | 0.105 | 0.0002 |
| 4    | D        | Integrated Pollution Index | 12.100 | 0.031 | 0.209 | 0.003 | 0.041 | 0.162 | 0.0001 |
| 5    | Е        | Integrated Pollution Index | 11.933 | 0.033 | 0.146 | 0.003 | 0.054 | 0.109 | 0.0003 |
| 6    | F        | Integrated Pollution Index | 13.100 | 0.039 | 0.161 | 0.004 | 0.067 | 0.084 | 0.0002 |
| 7    | G        | Integrated Pollution Index | 9.400  | 0.038 | 0.202 | 0.002 | 0.052 | 0.123 | 0.0003 |
| 8    | Н        | Integrated Pollution Index | 6.800  | 0.029 | 0.154 | 0.002 | 0.049 | 0.087 | 0.0003 |

# 2.2. Determination of Enrichment Factors (EF)

The enrichment factor is calculated by comparing the concentration of a test element with that of a reference element [28]. In this study, the value of the enrichment factor was calculated using modified formula based on the equation suggested by Buat-Menard and Chesselet [29]. The most common reference elements are Sc, Mn, Ti, Al and Fe. [30, 31, 32]. According to Sutherland [32], five contamination categories are generally recognized on the basis of the enrichment factor. These are:

- Ef < 2: Deficiency to mineral enrichment
- Ef = 2-5: Moderate enrichment
- Ef = 5-20: Significant enrichment
- Ef = 20-40: Very high enrichment
- Ef > 40: Extremely high enrichment

Enrichment factor was determined using the formula;

## $Ef = [(C_{n(sample)}/C_{ref(sample)}]/B_{n(background)}/B_{ref(background)}]$

Where,  $C_n$  (sample) is the concentration of the examined element in the study site,  $C_{ref(sample)}$  is the concentration of the reference element in the study site;  $B_n$  (background) is the concentration of the examined element, an average shale value described by Turekian and Wedepohl, [33] and  $B_{ref(background)}$  is the concentration of the reference element. In this study, Fe was used as the reference element as it the most naturally abundant element in the soil and average shale value described by Turekian and Wedepohl, [33] was used as the reference value.

The result of Table 2 was used to calculate the enrichment factor (EF) presented in Table 4.

| S/No | Workshop | DataPresentation       | Cd     | Cr   | Pb    | Mn  | Ni   | Cu   | Fe   |
|------|----------|------------------------|--------|------|-------|---|------|------|------|
| 1    | А        | Enrichment Factor (EF) | 1622.5 | 6.26 | 40.9  |   | 13.3 | 12.3 | 0.04 |
| 2    | В        | Enrichment Factor (EF) | 3015.0 | 10.6 | 90.9  |   | 19.8 | 36.4 | 0.09 |
| 3    | С        | Enrichment Factor (EF) | 2702.5 | 11.3 | 48.6  | Used as reference metal for the calculation | 17.1 | 34.5 | 0.05 |
| 4    | D        | Enrichment Factor (EF) | 3765.0 | 11.0 | 73.6  |   | 14.5 | 57.3 | 0.05 |
| 5    | Е        | Enrichment Factor (EF) | 3352.5 | 10.6 | 46.5  |   | 17.2 | 36.7 | 0.08 |
| 6    | F        | Enrichment Factor (EF) | 2915.0 | 9.80 | 40.5  |   | 17.0 | 21.1 | 0.05 |
| 7    | G        | Enrichment Factor (EF) | 4435.0 | 20.5 | 272.7 |   | 28.0 | 65.9 | 0.18 |
| 8    | Н        | Enrichment Factor (EF) | 2772.5 | 13.5 | 71.0  |   | 22.6 | 40.2 | 0.15 |

## 2.3. Determination of Geo-accumulation Index

The geo-accumulation index (I-geo) introduced by Muller has been used since late 1960s, and has been widely employed in European trace metal studies [34]. The  $I_{geo}$  was used to calculate different metals in different workshops. Geo-accumulation index is expressed as follows:

$$I-geo = \log_2 \left( C_n / 1.5 B_n \right)$$

Where  $C_n$  is the measured concentration of the heavy metal "n" in the sample;  $B_n$  is the geochemical background for the element n which is either directly measured in precivilization sediments of the area or taken from the literature (average shale value described by Turekian and Wedepohl [33] and 1.5 is the background matrix correction factor due to lithogenic effects. In this study we adopted the Turekian and Wedepohl [33] value. Muller [34] proposed seven grades or classes of the geo-accumulation index.

Class 0 (practically uncontaminated): I-geo  $\leq 0$ 

Class 1 (uncontaminated to moderately contaminated): 0 < I-geo < 1;

Class 2 (moderately contaminated): 0 < I-geo < 2;

Class 3 (moderately to heavily contaminated): 2 < I-geo < 3;

Class 4 (heavily contaminated): 3 < I-geo < 4;

Class 5 (heavily to extremely contaminated): 4 < I-geo < 3;

Class 6 (extremely contaminated): 5 < I-geo.

Class 6 is an open class and comprises all value of the index higher than class 5. The elemental concentration in class 6 may be hundred fold greater than the geochemical background [35]

The result of Table 2 was used to calculate the geoaccumulation index (I-geo) presented Table 5.

|      | -        | -                      | -    | -       | -    |         | -       | -       |         |
|------|----------|------------------------|------|---------|------|---------|---------|---------|---------|
| S/No | Workshop | Data                   | Cd   | Cr      | Pb   | Mn      | Ni      | Cu      | Fe      |
| 1    | А        | Geo-Accumulation Index | 1.76 | 6.02E-3 | 0.04 | 9.60E-4 | 1.25E-2 | 1.17E-2 | 4.03E-5 |
| 2    | В        | Geo-Accumulation Index | 1.96 | 6.02E-3 | 0.05 | 5.73E-4 | 1.14E-2 | 2.08E-2 | 5.09E-5 |
| 3    | С        | Geo-Accumulation Index | 1.88 | 6.92E-3 | 0.33 | 6.14E-4 | 1.05E-2 | 2.11E-2 | 3.25E-5 |
| 4    | D        | Geo-Accumulation Index | 2.43 | 6.32E-3 | 0.04 | 5.69E-4 | 8.13E-3 | 3.25E-2 | 2.85E-5 |
| 5    | Е        | Geo-Accumulation Index | 2.40 | 6.62E-3 | 0.03 | 6.29E-4 | 1.08E-2 | 2.20E-2 | 5.09E-5 |
| 6    | F        | Geo-Accumulation Index | 2.63 | 7.83E-3 | 0.03 | 7.95E-4 | 1.35E-2 | 1.69E-2 | 4.27E-5 |
| 7    | G        | Geo-Accumulation Index | 1.89 | 7.83E-3 | 0.04 | 3.76E-4 | 1.05E-2 | 2.47E-2 | 6.86E-5 |
| 8    | Н        | Geo-Accumulation Index | 1.36 | 5.72E-3 | 0.03 | 4.33E-4 | 9.93E-2 | 1.75E-2 | 6.38E-5 |

Table 5. Showing geo-accumulation index of soil from different workshops.

### 3. Results

Table 1: shows average heavy metal concentration in the scrapped car paint dust matrix, from vehicles in all the workshops, average result of 7 vehicles per workshops, except workshop H with 6 vehicles. Iron has the highest concentration of all the metals in the workshops, its value in workshops G and H were as follows:  $13.25 \pm 0.04$  (mg/kg) and  $12.48 \pm 0.03$  (mg/kg). Highest cadmium concentration were in workshops D and F ( $3.36 \pm 0.02$  and  $3.58 \pm 0.01$  mg/kg), that of chromium were in workshops F and G ( $2.87\pm 0.05$  and  $2.95\pm 0.01$  mg/kg), lead in workshops B and D ( $4.21\pm0.03$  and  $3.65\pm 0.02$  mg/kg) while the highest manganese values of  $3.31\pm0.01$  and  $3.04\pm0.01$  (mg/kg) in workshops A and F but that of nickel and copper were  $3.84\pm0.02$ ,  $3.52\pm0.01$  (mg/kg) and  $7.11\pm0.01$ ,  $4.49\pm 0.03$  (mg/kg) (workshops A,G and D and G respectively)

Table 2: shows the highest soil cadmium values of  $3.63\pm0.03$  and  $3.93\pm0.01$  (mg/kg) at workshops D and F, highest soil chromium values of  $3.53\pm0.02$  and  $3.45\pm0.02$  in workshops F and G. Soil lead values of  $5.19\pm0.05$  and  $4.17\pm0.02$  were in workshops B and D. Workshops A and F had soil manganese of  $4.05\pm0.01$  and  $3.37.\pm0.01$  (mg/kg). Highest soil nickel concentration of  $4.31\pm0.01$  and  $4.57\pm0.01$  (mg/kg) were in workshops A and F. Soil copper occurred highest in workshops D and G with  $7.31\pm0.01$  and  $5.54\pm0.05$  (mg/kg).

Table 3: shows the results of integrated pollution index of

all the metals in the different workshops. The IPIs of chromium, lead, manganese, nickel, copper and iron were within IPI  $\leq 1$ , indicating low level of pollution by these metals, in all the workshops, cadmium is the highest pollutant, and its IPI is in the highest pollution level of IPI > 2.

Table 4: shows the results of the enrichment factor of the soil samples of the workshops. Iron is in the contamination category of EF < 2 (deficiency to mineral enrichment), chromium is in the category of EF= 5-20 (significant enrichment), with the exception of workshop G which is in EF= 20-40 category (very high enrichment). Enrichment factor for nickel in workshops A-F were in category of EF=5-20 (significant enrichment) while that of workshops G and H were in the category of EF= 20-40 (very high enrichment). Enrichment factor for copper in workshop A is EF= 5-20 (significant enrichment). Workshops B, C, E and F were in the category EF= 20-40 (very high enrichment) while workshops D, G and H were in category EF > 40 (extremely high enrichment).

Table 5: shows the geo-accumulation index of all the metals in all the workshops. The I-geo of Cr, Pb, Mn, Ni, Cu and Fe were in the class of 0 < I-geo < 1 (uncontaminated to moderately contaminated), but the geo-accumulation index of cadmium for workshops A, B, C, G and H were in the class of 1 < I-geo < 2 (moderately contaminated) while that of workshops D, E and F were in the class of 2 < I-geo < 3 (moderately to heavily contaminated).

## 4. Discussions

Scanty literatures if any may exist on the contributions of automobile reworking workshops to environmental heavy metal burden in Nigeria. The value of heavy metals from scrapped car paint dust matrix (Table 1) is considered high for a developing country like Nigeria without adequate technology for sustainable environmental remediation and public health care services. The number of old vehicles taken to automobile workshops for body work (scrapping old paint, panel beating, re-welding, finishing and re-painting) keep rising, because fairly used vehicular importation into Nigeria is reputed to be the highest in Africa. By inspection, it is evident that metal values of soil from all the workshops (Table 2) were higher than that of paint dust matrix (Table 1), this is in addition to the fact that soil heavy metal is subject to infiltration into the soil or washing into drainage system by surface run-off en-route to surface water, others may be absorbed by plant root when they are washed into nearby farmland, this can be attributed to the fact that as vehicles are repaired and taken away, more are brought into the workshop for repair, the workshop soil therefore keep accumulating these metals as against control samples taken 200 m away with insignificant metal value, Table not shown. Numerous automobile reworking workshops dot the Nigerian landscape and has created direct and indirect employment opportunities for self-employed several young artisans. The authorities in Nigeria consider these a means of poverty alleviation but the environmental and public health consequences are not given adequate attention. Artisans, ancillary or support worker at auto-repair workshop may be exposed to heavy metal poisoning through ingestion, inhalations or dermal contact. In view of poor hygiene exhibited by these informal sector workers especially during eating, ingestion becomes a sure means of exposure. Children of artisans in these workshops are often indirectly exposed through take-home paint/soil dust (car keys, car and clothes washing, breast feeding, hand shaking, hogging, etc.). Indiscriminate citing of automobile reworking workshop cluster is a common feature of both urban and rural communities in Nigeria. Through anthropogenic process, metals are concentrated and transformed into various products. These processes often lead to much more concentrations of different chemicals than they are naturally present in the environment.

Surveying numerous literatures revealed that anthropogenic sources of heavy metals can be generally classified into three categories; 1) urban elements, 2) natural element and 3) elements of a mixed origin, implying that some metallic pollutants undergo geochemical reactions which alter their significant features [36]. It has been established that vehicular emission, industrial production and weathered materials are the three main sources of heavy metals in urban areas [37, 38]. Our present work is an addition to the lists of emerging heavy metal pollution through automobile/electronic waste, especially in urban centers [20]. The integrated pollution index (IPIs) of all the analyzed soil samples from the different workshops (A-H) varied, Cd (6.800-13.100); Cr (0.029-0.039); Pb (0.146-0.260); Mn (0.002-0.005); Ni (0.041-0.67); Cu (0.059-0.162) and Fe (0.0001-0.0003). The analysis of the data revealed that the IPIs of the heavy metals in all the soil samples from the different workshops, implied that chromium, lead, manganese, nickel, copper and iron were below one (1), meaning that the workshop soils were minimally polluted and that pollution was not from anthropogenic emission (may not be from scrapped car paint dust alone) but the workshop samples were highly polluted with cadmium (IPIs > 5) and are from anthropogenic origin (probably scrapped car paint dust) (Table 3). These agreed with IPIs international classification [26, 27]. The enrichment factor (spatial distribution) of metal concentration is an important aid to assess the possible sources of enrichment and to identify areas with high metal concentration [39, 40]. It was calculated to evaluate anthropogenic source of the studied metals. The EF values for cadmium in all the workshop soil implied that the soil samples were enriched significantly with cadmium metal when compared with the background level (0.3) (Table 4). The EF value for copper < 2 showed deficiency to mineral enrichment. The EF for Cr, Pb, Ni and Cu showed significant enrichment, very high enrichment, extremely enrichment and extremely high enrichment, this agrees with Sutherland [32] classification. EF value for lead and copper from workshop G were higher than their background values of 20 and 45 (Turekian and Wedepohl, [33]. Apart from Fe with EF < 1, others have an EF value of > 1.5 (Table 4) suggesting that a significant portion of all the metals in all the workshops were derived from non-crustal material, or non-natural weathering process, therefore anthropogenic sources (scrapped paint dust) becomes an important contributing factor [41]. These agree with Sutherland's classification [32]. Therefore, for most heavy metals, anthropogenic sources contribute more to pollution than natural sources [42]. In this work, except for iron, all other metals in all the workshops showed anthropogenic origin, probably from scrapped car paint dust (Table 1). Applying Muller [34] classification, the geo-accumulation index (I-geo) values (Table 5), showed that chromium, lead, manganese, nickel, copper and iron were in between 0 and 1 (0 < I-geo < 1), implying uncontaminated to moderately contaminated. The I-geo value for cadmium in workshops A, B, C, G and H were in the range of 1 < I-geo < 2, which is moderately contaminated while that of workshops D, E and F were in the range of 2 < I-geo < 3, implying moderate to heavily contaminated (Table 5). The IPIs, EF and I-geo for all the workshops showed that cadmium most especially and other metals were from anthropogenic sources (scrapped car paint dust, Table 1). This study equates with other works were industrial activities such as petrochemical factory, textile mill [27], mining, smelting, waste disposal, wastewater irrigation [43, 44] and old power generation station [2] were all implicated as an anthropogenic contributor to heavy metal pollution. Previously Ahmed and Ishiga [45] reported that rapid urbanization, industrialization and increased vehicular emissions to the atmosphere may be responsible for increase in anthropogenic trace metals in the environment (as seen in our study). The implication is that artisans directly or indirectly engaged in menial jobs at automobile reworking workshop in Nigeria and the general public may be exposed to heavy metal poisoning through inhalation, ingestion or dermal contact with fugitive paint dust, roadside soil/paint dust or by eating agricultural produce from adjacent farmlands. Most of the heavy metals assessed in this study are initiators or promoters of carcinogenic activity in human and animals [46, 47]. Heavy metals are one of the greatest disease burden in the world, as they affect gastrointestinal tract, respiratory tract, liver, cardiovascular, hematopoietic and nervous system [48], including cancers of various viscera such as lung, bladder, kidney and liver [49]. This is exemplified by five (5) year study at the University of Port-Harcourt, Nigeria, which documentation showed that 56.2% of medical admissions were cases of various non-communicable diseases [50]. Chemical tests of workshop soil samples revealed the presence of exchangeable cations and exchange capacity (Table 6) higher than the values we previously reported at refuse dumpsites [51]

in an amount that will make nutrient available to plants. Cation exchange capacity (the sum total of the exchangeable cations that a soil can absorb) is a function of a variety of soils and materials; humus soil (with high organic matter) has high cation exchange capacity (CEC) (Table 6). This is evident in our result and supported by literature [51, 25]. The CEC of most soils tend to increase with increasing pH (alkalinity), CEC is commonly determined at a pH of 7 or above so as to obtain the maximum retentive capacity (Table 6) but minor variation exist due partly to influence of heavy metal from paint dust which positively correlates with electrical conductivity. Soils composed of mineral constituents, organic matter (humus), living organisms, air and water, are of vital necessity to human health and well-being. Anthropogenic contamination of soil by heavy metal is the most serious environmental challenge that poses significant implication to human health [52]. The very minimal or near zero values of control (Tables not shown) shows that automobile reworking workshops is anthropogenic contributor to soil heavy metal load in Nigeria.

Table 6. Showing some physicochemical parameters of soils from different workshops.

| S/No | Workshop | Data presentation | рН           | % Organic Matter | Cation Exchange capacity (cmol./kg) | Electrical Conductivity |
|------|----------|-------------------|--------------|------------------|-------------------------------------|-------------------------|
| 1    |          | SD                | 0.07         | 0.03             | 0.17                                | 1.16                    |
| 1    | А        | Mean $\pm$ SEM    | $5.8\pm0.04$ | $7.50\pm0.02$    | $10.52 \pm 0.10$                    | $332.7 \pm 0.67$        |
| 2    | D        | SD                | 0.10         | 0.02             | 0.18                                | 1.53                    |
| 2    | Б        | Mean $\pm$ SEM    | $6.6\pm0.06$ | $7.03\pm0.01$    | $11.59 \pm 0.10$                    | $316.3 \pm 0.88$        |
| 2    | C        | SD                | 0.12         | 0.02             | 0.06                                | 0.58                    |
| 3    | C        | Mean $\pm$ SEM    | $6.6\pm0.07$ | $6.82\pm0.01$    | $10.39 \pm 0.03$                    | $281.3 \pm 0.34$        |
| 4    | D        | SD                | 0.10         | 0.02             | 0.04                                | 0.58                    |
| 4    | D        | Mean $\pm$ SEM    | $6.6\pm0.06$ | $7.69\pm0.01$    | $11.79 \pm 0.02$                    | $353.7 \pm 0.34$        |
| 5    | F        | SD                | 0.17         | 0.01             | 0.06                                | 0.58                    |
| 5    | Б        | Mean $\pm$ SEM    | $6.7\pm0.10$ | $7.49\pm0.01$    | $9.48 \pm 0.03$                     | $252.3 \pm 0.34$        |
| 6    | F        | SD                | 0.1          | 0.01             | 0.15                                | 0.58                    |
| 0    | 1.       | Mean $\pm$ SEM    | $7.5\pm0.06$ | $9.13\pm0.01$    | $7.70 \pm 0.09$                     | $197.7 \pm 0.34$        |
| 7    | G        | SD                | 0.07         | 0.02             | 0.04                                | 1.00                    |
| '    | U        | Mean $\pm$ SEM    | $7.7\pm0.04$ | $7.56\pm0.01$    | $8.77 \pm 0.02$                     | $233 \pm 0.58$          |
| 8    | н        | SD                | 0.1          | 0.02             | 0.03                                | 1.00                    |
| 0    | 11       | Mean $\pm$ SEM    | $6.7\pm0.06$ | $8.57 \pm 0.01$  | $10.91 \pm 0.02$                    | $346 \pm 0.58$          |

[N= 3, SD = standard deviation, SEM = standard error of mean]

#### 5. Conclusion

Reworking of used vehicles imported into Nigeria is a major source of environmental heavy metal burden. Dilapidated road network, relative high ambient air temperature and humidity in Nigeria hastens expansion and contraction, corrosion, coupled with alarming high rate of vehicular accident in addition to weak and rickety components of vehicular parts that are imported, the end result is that large volume of vehicles end up at automobile reworking workshops. Corrosion rusts from metallic component and paint dust release heavy metals into the environment. Heavy metal contamination assessment [integrated pollution index (IPIs), enrichment factor (EF) and geo-accumulation index (I-geo)] revealed that cadmium and most other metals were anthropogenically released and these could pose health risk to numerous artisans at used vehicles repair workshop.

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