International Journal of Current Research in Applied Chemistry & Chemical Engineering
Vol. 3, Issue 1 - 2019

HEAVY METALS DISTRIBUTION AND POLLUTION INDICES OF SCRAPYARDS SOILS

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ABSTRACT

The research evaluated the levels and distribution of heavy metals (Mn, Cr, Pb, Cd and Fe) in two (2) metal scrapyard (Site A and Site B) and a control. The soil properties, level of metals concentration, speciation of metals and pollution indices were investigated. Standard techniques were employed in the appraisal. The level of each metal was detected low in the control site while the highest values were recorded for the first scrapyards (Site A). The metal concentration ranges between 0.25 mg/Kg (Cd of control) to 82,313 mg/Kg (Fe of site A). The speciation study also presented a trend showing that the major source of contribution of theses metals (Mn, Cr, Pb, Cd and Fe) were derived from anthropogenic activities of human. The geo-accumulation index ranged between 1.11 (Cr in Site B) to 9.97 (Pb in site A), this shows that the sites ranged from moderately contaminated to extremely contaminated. The other indices such as enrichment and mobility factors presented similarly interesting trends.

KEYWORDS: Scarp Yards, Heavy Metals, Speciation, Pollution Indices.

INTRODUCTION

Solid wastes include but are not limited to yard waste, household chemicals, building materials, and demolition materials. Solid waste does not include rock, or brick [1]. Once a product completes its useful product life, it becomes old scrap. Used beverage cans, junked automobiles and appliances are examples of old consumer scrap; used jet engine blades and vanes, junked machinery and ships, and metal recovered from commercial buildings or industrial plants are examples of old industrial scrap [2]. The heavy metals in waste or scraps are primarily a consequence of the intended use of heavy metals in industrial products. At the end of their useful life all products will end up in waste to the extent they are not attractive for recycling or in the scrapyard for recycling. Heavy metals may, however, also be lost to waste during production, use phases and during storage for recycling in scrapyard [3]. There is a growing concern about the possibility of contaminated soil to result in the introduction of metals in food chains through uptake by plants grown on contaminated soil and thereby affecting food safety [4]

The disposal of materials that contains heavy metals in scrap yards are of concern and pose dangers to people in contact with the soil and plants of these sites in which they are disposed. Metals exist in a number of different forms which influence their mobility and bioavailability [5].

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Since their toxicity is related to their existing species, their speciation is increasingly attracting more attention. It is very imperative to study different forms of heavy metal mobility and bioavailability rather than only the total concentration in order to obtain an indication of the bioavailability of metals. For this reason, sequential extraction procedures are commonly applied because they provide information on the fractionation of metals in the different lattices of the solid sample which serves as a good compromise to give information on environmental contamination risk [6]. In Nigeria, as a result of quest for more sources of income, there has been an increase in the number of minor scrapyards created at different location including within households without much concern to many people on consequences. This study aimed at assessing the heavy metals contents in two selected scrapyards and their distribution in the soil matrix (Speciation). It is expected that results obtained from this study will widen knowledge on the environmental risks associated with scrapyards soils.

MATERIALS AND METHODS

THE STUDY AREA

Two (2) metal scrapyards which are in constant relation with people were chosen for this study. The first scrapyard is located at Abeymotor Junction in Osun state Nigeria (Site A) on Latitude 7^{o} 38^{1} 38.8572 N and Longitude 4^{0} 45^{1} 29.3904 E (Figure 2.1). It has been in operation for over 10 years as a place where scavengers bring in scraps for sale. The second scrapyard is located at Oke-Oye, Osun state (Site B), on Latitude 7^{0} 37^{1} 14.1204 N and Longitude 4^{0} 44^{1} 45.28 E (Figure 2.2). It is located in front of a residential building and has been in existence for over 5 years. Over the time of its existence, the quantity of scrap has not been accumulating to a very large quantity before they are sold out to larger recycling centers.

Figure 2.1.Site A scrapyard

Figure 2.2.Site B scrapyard

SAMPLE COLLECTION AND PREPARATION

A total of twelve (12) soil samples were collected in a random system from each sites at a depth of 0-15 cm and a control sample at far distance free from pollution. The samples were transferred into polyethylene bags and labeled for easy identification. The samples for each of the sites were mixed to form a composite sample for individual site. They were put in black polyethene bags, tied and labeled. The soil samples were taken to the laboratory prior analysis. The soil samples were air-dried for seven days after which they were ground into powdered form with the aid of mortar and pestle. The samples were sieved through a 2.0 mm sieve to obtain a homogenous particle of same surface area, which was later kept in plastic containers and covered prior to analysis.

PHYSICO-CHEMICAL ANALYSIS

The pH of the soils were investigated using standard methods as described by [7] while the organic matter was expressed in terms of the organic carbon as:

$$\text{Organic matter} = \text{organic carbon} \times 1.729 \qquad \text{Equation 1}$$

Organic carbon was determined using the Walkley – Black method as described by [8]

HEAVY METAL ANALYSIS OF THE SOIL

The total metal content (Mn, Cd, Cr, Pb and Fe) was carried out by digesting Exactly 1 g of each soil samples using 20 ml of aqua regia mixture of concentrated nitric acid HNO_3 and concentrated hydrochloric acid HCl in a ratio of 1:3 as described by [9]. The experiments were carried out in triplicate and results expressed in the mean of the triplicates. The digests were analyzed using Atomic Absorption Spectrophotometer (AAS Buck Scientific model 210) in Ibadan, Oyo, Nigeria. The instrument setting and operational conditions were done in accordance with the manufacturers' specifications.

SEQUENTIAL EXTRACTION OF HEAVY METALS FROM SOIL

Exactly 1g of the soil sample was weighed and extracted into five fractions (Exchangeable fraction, carbonate fraction, Iron and Manganese fraction, organic matter fraction and Residual fraction) as described by [7, 10, 11].

DATA ANALYSIS

All determinations were performed in triplicate. The statistical analyses were conducted using One Way Analysis of Variance (ANOVA) and the mean value separated by Duncan's multiple range test (DMRT) using SPSS.

POLLUTION INDICES

GEO-ACCUMULATION INDEX

Geo-accumulation index (*Igeo*) was originally stated by [12] in order to determine and define metal contamination in sediments by comparing current concentrations with preindustrial levels [13]. Background concentration of heavy metals in the earth's crust was used as a reference value implicating pre-industrial environment. Igeo is calculated through the following equation:

$$Igeo = \text{Log}2\ (Cn / 1.5Bn) \qquad \text{Equation 2}$$

Where Cn is concentration of the element (n) in the soil sample and Bn is geochemical background value, which may be attributed to lithogenic variations in soils.

ENRICHMENT FACTOR

The enrichment factor (EF) was initially developed to speculate on the origin of elements in the atmosphere, precipitation or seawater [14], but it has been progressively extended to the study of soils and other environmental materials [15]. The enrichment factor is established on the basis of standardization of a tested element against a reference one characterized by low occurrence variability such as Al, Fe, or Zn [13].

$$EF = (M/Fe)\ \text{sample} / (M/Fe)\ \text{Background} \qquad \text{Equation 3}$$

Where (M/Fe) sample is the ratio of metal to Fe concentrations in the sample, and (M/Fe) Background is the ratio of metal to Fe concentrations of the background [16]

MOBILITY FACTOR

The operationally extraction sequence fractionates the heavy metals in the soil in order of decreasing solubility. As a result, the exchangeable and carbonate (F1 + F2) fractions which are the early fractions, capture the most reactive and presumably the most mobile and bioavailable fractions [17]. The relative index of metal mobility was calculated as a mobility factor (MF) [18] on the basis of the following equation.

$$MF = \frac{F1 + F2}{F1 + F2 + F3 + F4 + F5} \times 100 \qquad \text{.Equation 4}$$

Where, F1 = Exchangeable metal content fraction; F2 = Metal content bound to carbonate fractions; F3 = Metal content bound to Fe-Mn oxide fraction; F4 = Metals content bound to organic matter fraction; F5 = Residual metal content fraction

A high MF value for heavy metals in soil has been interpreted as evidence of relatively high liability and biological availability of the metal [18, 19].

RESULTS AND DISCUSSION

PHYSICO-CHEMICAL PROPERTIES OF THE SOIL

Table 3.1 shows the result of the physico-chemical properties of the soil samples. The pH values of the soils are 7.6 for Site A and 9.7 for Site B against the control pH value of 8.0. From the above pH result, it shows that all the soils are alkaline. It has been reported that most soils within the pH range of 6.0-9.0 have metals that are not always in the free form, hence not likely to be bioavailable [20]. The pH of all the soil samples investigated are within this range therefore, the metals investigated in this study possibly may not be bioavailable to the plant until when favourable conditions like acidic precipitation prevailed on the soil. pH plays significant role in solute concentration and in sorption and desorption of contaminants in soil [21].The soil organic matter enhances the usefulness of soils for agricultural purpose. It supplies essential nutrients and functions as source of food to microbes and thereby helps to enhance and control their activities [22]. The percentage organic matter of all the sites was found to be higher than the percentage organic matter of the control site. [23] reported that the organic matter content of soil contributes to the increase in the availability of mineral elements, nutrition to living organisms and acts as a buffer aqueous solution to maintain a neutral pH.

Table 3.1

Parameters	**Site A**	**Site B**	**Site C**
pH	$7.60^{a} \pm 0.60$	$7.90^{b} \pm 0.60$	$8.00^{c} \pm 00$
Organic matter	$0.10^{a} \pm 00$	$2.44^{c} \pm 0.01$	$1.34^{b} \pm 0.06$

TOTAL METAL CONCENTRATION IN SOIL

The Total concentration of metals analyzed for the two sites and the control site are presented in Table 3.2. The metals analyzed are Manganese (Mn), Chromium (Cr), Cadmium (Cd), Lead (Pb) and Iron (Fe). Results obtained showed that soils from the study sites have higher metal concentrations than their corresponding metals level at the control site which indicates that there is an anthropogenic contribution of metals to the studied sites than the naturally occurring metals. It could be attributed to the availability of metal containing wastes or scraps at the scrapyards which are eventually leached into the underlying soils. The metal concentrations of the selected heavy metals (Mn, Cd, Cr, Pb and Fe) were compared with Department of Petroleum Resources (DPR) and World Health Organization (WHO) standards.

Table 3.2

Metals	**Site A**	**Site B**	**Control**	**DPR T.V**	**DPR I.V**	**WHO MPL**
Mn	$987.50^{c} \pm 25.28$	$1610.00^{b} \pm 35.20$	$120.83^{a} \pm 0.76$	-	-	2000
Cr	$72.15^{c} \pm 0.88$	$68.72^{b} \pm 0.28$	$21.25^{a} \pm 0.17$	100	380	100
Cd	$13.42^{c} \pm 0.10$	$6.25^{b} \pm 0.13$	$0.25^{a} \pm 0.00$	0.8	12	3
Pb	$753.13^{c} \pm 5.10$	$520.23^{b} \pm 10.32$	$0.5^{a} \pm 0.00$	85	530	100
Fe	$82313.00^{c} \pm 189.79$	$50759.50^{b} \pm 3412.62$	$6362.83^{a} \pm 49.50$	-	-	50000

- All the values are in mg/Kg
- DPR T.V: Department of petroleum resources target value
- DPR I.V: Department of petroleum resources intervention value
- WHO MPL: World Health Organization maximum permissible level
- Source: [24, 25, 26, 27, 28].

Among all the metal studied in this research, the concentrations of Fe has the highest values throughout the sites. All the sites except the control site had Fe concentration values higher than the permissible limit set by World Health Organization (WHO). Although many researchers have earlier reported the high concentration of iron in Nigeria soil [29, 30] but the concentrations discovered in this study are much higher than the reported reports. Mean concentrations of lead (Pb) in the sites were higher than the control site and significantly different. While the Pb concentration at site B is above the DPR target value and WHO maximum permissible level limit but below the DPR intervention value. Site A Pb concentration was above both the DPR intervention value and WHO maximum permissible level limit for Pb in soil. Short-term exposure to Pb could result in diarrhea, vomiting, convulsion or coma, while long term exposure could result in kidney and nervous damage, cause brain and blood disorder and could leads to death [31]. Lead in the soils of the studied area could be from dry cell batteries disposals. The concentrations of cadmium from the scrapyards (Site A and Site B) are higher than the concentration discovered on some scrapyards in similar studies by [32] on soil and water around urban scrapyards. However, Cd concentration in Site A and site B were above the WHO maximum permissible level limit of Cadmium in soil. For metals like cadmium that have no biological function, this calls for public concern. The elevated levels of Cd and Pb in the soil profiles constitute a serious threat to both surface and ground water. Manganese and chromium concentration were found to be lower than WHO maximum permissible level limit and are considered to still be in a safe limit but needs to be monitored continuously. The result showed that there was significant difference in the concentration of the metals between the two sites and the control sites. Also, all metals except manganese had their highest concentration in Site A which may be attributed to the age and size of the scrapyard and regularity of scraps dumping.

SEQUENTIAL EXTRACTION OF THE METALS FROM SOIL

Tables 3.3 show the concentration of each metal found in the five different fractions; the exchangeable, bound to carbonate, bound to Fe - Mn oxide, bound to organic matter and residual fraction. The carbonate fraction contained the highest species of manganese. The relative percentage present in exchangeable and carbonate fractions suggest that manganese is available on the exchange sites [11, 33]. The Mn^{2+}ion is very soluble in water at pH less than 7 [34] and given the pH range of these soils (7.6 - 8.0), soluble exchangeable Mn^{2+} is not likely. This implies that the highest concentration is from anthropogenic activities. This was followed by the residual fraction. Though, this fraction may be considered relatively stable, it becomes more soluble under acidic conditions and so under oxidizing conditions [35, 36]. The high percentage of chromium was detected in the residual fraction. The metals found in this fraction are not bio-available and are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature [10]. There was no concentration of chromium detected at the exchangeable fraction throughout the study sites. The carbonate fraction suggests that this percentage of cadmium in these soils can be mobilized when favourable conditions like acidic pH prevailed. The concentration of cadmium in the carbonate fraction for both sites was higher than the exchangeable. The carbonate fraction suggests that this percentage of cadmium in the soil can be mobilized into plants and underground water when favourable conditions like acidic pH prevail. The percentage distribution of lead (Pb) showed that the highest percentage was found in the carbonate fraction which indicates that the concentration of lead (Pb) may have been from anthropogenic activities. Fe-Mn fraction and residual fractions had the least percentage and was detected only in site A and site B but below detection limit in the control site. Pb concentration was not detected in the Exchangeable and organic fraction in all the sites.

Table 3.3.Sequential extraction of the metals from soil

Metals	Sites	F1	F2	F3	F4	F5
Mn	SA	17.33 ± 0.29	475.17 ± 5.62	185.33 ± 10.28	8.17 ± 0.76	221.33 ± 1.53
	SB	42.33 ± 0.29	1076.67 ± 42.08	207.33 ± 6.37	9.83 ± 0.76	227.50 ± 10.83
	CNT	6.83 ± 0.29	26.67 ± 1.04	24.67 ± 2.52	1.17 ± 0.29	58.50 ± 2.65
Cr	SA	ND	5.20 ± 0.1	2.50 ± 0.25	10.63 ± 0.71	46.43 ± 1.37
	SB	ND	7.13 ± 0.10	7.55 ± 1.00	8.25 ± 0.29	42.20 ± 0.879
	CNT	ND	ND	ND	ND	19.65 ± 0.18
Cd	SA	0.62 ± 0.03	2.73 ±0 .08	1.27 ± 0.20	ND	7.88±0.58
	SB	0.77 ± 0.03	1.73 ± 0.08	2.70± 0.28	ND	ND
	CNT	ND	ND	ND	ND	ND
Pb	SA	ND	411.12 ± 10.02	212.85 ± 4.11	ND	76.78 ± 0.83
	SB	ND	253.10 ± 7.31	139.00 ± 9.64	ND	113.73 ± 5.28
	CNT	ND	ND	`ND	ND	ND
Fe	SA	1.00 ±0.00	4609.67 ±97.78	4965.00 ±102.50	11.00 ±1.32	70264.50 ±652.31
	SB	0.97 ±0.06	4784.17 ±112.87	4445.83 ±167.76	625.50 ±239.27	35796.67 ±383.88
	CNT	1.00 ±0.00	253.67 ±4.04	686.67 ± 20.97	ND	5083.33 ±125.83

- All the values are in mg/Kg

The lead in the carbonate fraction can easily leach in soils and could be carried away to contaminate food chain, groundwater and surface water. Therefore the Lead concentration obtained in the carbonate fraction pose a great risk to the environment because lead has toxic effects on living organism because they are non-required nutrient elements. Highest concentration of Iron was found in the residual fraction of site A. This result is consistent with numerous studies indicating that iron is insoluble in these types of soils [11, 37]. The metals in the residual forms are not available to the biota as it is considered to be held within the mineral matrix [38]. [10] suggested that metal concentrations in the residual fraction of soils or sediments may be indicative of background metal levels. Heavy metals in the residual fraction are probably associated with silicate minerals [39]. The lowest amount of iron found in the exchangeable is probably due to the fact that iron is easily absorbed and utilized by plants and other organisms in the soil environment.

POLLUTION INDICES

GEO-ACCUMULATION INDEX (IGEO)

Igeo levels of different metals in soil sample are given in Table 3.4. The Igeo of Pb in the two sites was the highest among all the metal which are extremely contaminated followed by the Cadmium which was heavily contaminated in the two sites. The result indicated that Mn and Fe were moderately contaminated while Cr had the lowest I_{geo} which are moderately contaminated.

Table 3.4

Metals	Site A	Site B
Mn	2.45	3.15
Cr	1.18	1.11
Cd	5.16	4.06
Pb	9.97	9.44
Fe	3.11	2.41

- Igeo<0, Practically uncontaminated
- 0< Igeo<1, Uncontaminated to moderately uncontaminated 1< Igeo<2
- Moderately contaminated
- 2< Igeo<3, Moderately to heavily contaminated 3< Igeo<4, Heavily contaminated
- 4< Igeo<5, Heavily to extremely contaminated 5< Igeo<6, Extremely contaminated
- Source: [12]

ENRICHMENT FACTOR OF METALS IN THE SOIL

Result of Enrichment factor is shown in Table 3.5. Mn and Cr in Site A indicated no enrichment which indicated that the Mn and Cr concentration is naturally occurring. Similarly, Cr in Site B also indicated no enrichment. Mn in Site B shows minor enrichment indicating that high percentage of concentration is naturally occurring than anthropogenic activities of man. Cd indicated moderate enrichment while Pb shows extremely severe enrichment indicating that the contamination is majorly anthropogenic activities of man.

Table 3.5

Metals	Site A	Site B
Mn	0.63	1.67
Cr	0.26	0.41
Cd	4.15	3.13
Pb	116.44	130.43

- EF < 1 indicates no enrichment,
- EF < 3 is minor enrichment,
- EF = 3 - 5 is moderate enrichment,
- EF = 5 - 10 is moderately severe enrichment,
- EF = 10 - 25 is severe enrichment,
- EF = 25 - 50 is very severe enrichment
- EF > 50 is extremely severe enrichment. Source: [40]

MOBILITY FACTOR OF METALS IN THE SOIL

The mobility factors (MF) of the metals for all the sites are presented on Table 3.6. In site A, the mobility factor (MF) values of the metals are in the decreasing order Pb > Mn > Cd > Cr > Fe. The relatively high mobility factor observed for lead is quite in agreement with the high percentage of carbonate fraction of lead recorded from the chemical fractionation results (Table 3.3) followed by the high percentage of Mn in the exchangeable and carbonate fraction in the sites. The low mobility factor observed in Fe is due to the high percentage of iron concentration in the Fe-Mn and residual fraction which are relatively stable over a long period of time. In site B, the mobility factor values of the metals in the sites differs from site A and following the order Mn > Pb > Cd > Cr > Fe. The Mn fraction in site B has high mobility percentage because of its much occurrence in the carbonate fraction and the mobility value of Fe is the lowest because of its high concentration in the residual fraction which interprets that the potential of the mobility and bioavailability of the metals decreases in the same manner Mn > Pb > Cd > Cr > Fe.

Table 3.6

Metals	Site A	Site B	Control
Mn	54.28	71.56	28.43
Cr	8.03	10.95	0
Cd	26.8	48.08	0
Pb	58.67	54.04	0
Fe	5.77	9.64	4.23

CONCLUSION

The study of the pH gave a negative indication of the mobility and solubility of metals and their bioavailability to plant. Generally, both in the total heavy metal (Mn, Cr, Cd, Pb and Fe) concentration and sequential fraction, the first scrapyards (Site B) show higher percentage value than the second scrapyards (Site B). Cd and Pb were revealed to be likely from anthropogenic sources and have caused severe contamination with very high mobility percentage while Mn and Cr are likely to be majorly from lithogenic sources than anthropogenic sources with moderate mobility.

ACKNOWLEDGEMENT

Miss Hammed Adebimpe, Your effort can never be forgotten, thank you so much for the continual prayer and encouragement toward the completion of this work.

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