

Determination Of Physicochemical And Heavy Metal Content Of Soil Around Paint Industries In Kaduna

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Abstract: the increasing trend of environmental contamination by heavy metals is an issue of concern. The need for a continual monitoring of heavy metal content of soil around industrial areas becomes pertinent. The present study focuses on the physicochemical properties and heavy metal content of soil around vicinities of paint industries in Kaduna. The range of pH, EC and TOM obtained were 6.50 ± 0.20 to 8.03 ± 0.20 , 225 ± 20.1 to $520 \pm 14.0 \mu\text{S/cm}$ and 2.18 ± 0.01 to $3.10 \pm 0.01\%$ respectively. The percentage of sand was 61 to 89% while silt and clay were 12 to 29% and 0 to 10% respectively. The mean concentrations of the heavy metals were: Pb (30.80 ± 0.15 to $79.60 \pm 0.87 \mu\text{g/g}$), Zn (128.35 ± 2.16 to $273.00 \pm 0.92 \mu\text{g/g}$), Cu (15.45 ± 0.39 to $27.00 \pm 0.13 \mu\text{g/g}$), Mn (102.9 ± 1.47 to $237.2 \pm 0.75 \mu\text{g/g}$), Cd (ND to $1.30 \pm 0.20 \mu\text{g/g}$), Cr (28.50 ± 0.36 to $51.50 \pm 0.30 \mu\text{g/g}$) and Fe (1084.43 ± 3.58 to $6542.32 \pm 2.56 \mu\text{g/g}$). The metal content of the samples were generally higher when compared to those of the control which indicates contaminations mainly due anthropogenic contributions. The result of geoaccumulation index and enrichment factor also revealed moderate contamination in most of the samples. There was also a significant positive correlation ($p < 0.05$) among some of the metals investigated.

Index Terms: Contamination, enrichment factor, geoaccumulation index, monitoring, paint, industry.

I INTRODUCTION

Industrialization has long been identified as the bedrock of national development, hence the assertion that no nation can grow beyond its level of industrialization [1]. However, the soaring trend of industrialization has engendered significant environmental pollution. Various pollutants are discharged into the environments as waste from manufacturing processes [2]. Among these pollutants; heavy metals constitute a major threat. Industrial products such as paints, pesticides, fertilizers among others have trace metals as components in them [3]. Environmental contamination by heavy metals has become an issue of concern, due to the fact that heavy metals unlike some other pollutants are not biodegradable. Consequently, they are not detoxified but are bioaccumulated in the environment [4]. Heavy metal refers to any metallic element whose density is relatively high and is toxic or poisonous even at low concentration [5]. Such metals have density ranging from 3.5 to 7g/cm^3 . Heavy metals include copper, iron, mercury, zinc, arsenic, silver, lead, chromium among others [6]. The major challenge that is associated with the discharge of industrial waste is the contamination of soil and the immediate environment [3]. The soil is a natural storeroom for various environmental contaminants, since these pollutants eventually find their way into the soil.

Various researchers have opined the need for continual monitoring of the concentration of trace metals in soil. To this end, various studies have been carried out on determination of heavy metals in industrial areas. However most of these studies were carried out in industrial cities with long period of industrialization [7]. Much has not been done in the vicinities of paint industries in Kaduna. It is therefore necessary to carry out a study of this nature. Such study will no doubt accentuate the need for a more constant monitoring of heavy metal concentration of soil in industrial areas and also serve as relevant input into the existing global record on soil pollution by heavy metals in industrial areas.

MATERIALS AND METHODS

Sampling Method

Two paint industries were selected for this study, all located in Kakuri industrial area of Kaduna State. A total of 32 soil sub-samples were collected from the vicinity of the paint industries. At each of the sampling location, four subsamples were taken at a depth of 0-15cm, using a soil auger. The sub-samples were homogenized to form each of the composites. The collected samples were packed in a clean polythene bag. Decontamination of the sampling equipment was ensured between sites by washing with distilled water. A control sample was also collected from an uncontaminated area, away from the industries in line with [8].

Samples Preparation

The collected samples were air dried for 48 hours. They were then crushed using agate mortar and sieved using 2mm sieve and then 0.5mm sieve after further pulverization.

Physico-chemical Parameters Determined

The bioavailability of trace metals in soil is dependent on various physicochemical properties of soil [9]. Accordingly the soil properties that were determined include pH, particles sizes, total organic matter (TOM) and electrical conductivity (EC). The pH of the soil was determined using a pH meter in 1:1(soil: water suspension) in line with the method proposed by [8]. The electrical conductivity was determined using an electrical conductivity meter (Kent EIL5013 model) as

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described by [10]. Analysis of particle sizes was carried out using hydrometer method [9]. Soil organic matter content was determined using Walkley and Black method [11].

Digestion of samples

The samples of soil were digested using $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-HClO}_4$, following the procedure recommended by AOAC [9]. The concentration of Pb, Zn, Cu, Cd, Ni, Mn and Fe in the digest was determined using Fast Sequential Atomic Absorption Spectrometer (AA240FS).

Quality Assurance and Quality Control (QA/QC)

In order to ensure quality control in the course of the analyses, all the reagents used were analytical grades. Reagent blanks were also run in order to check purity of the reagents. Analyses were done in triplicate to ensure precision of the analytical procedure and the instruments used.

RESULT AND DISCUSSION:

The result of the physicochemical parameters of the soil

samples collected from the study area is presented in table 1. Soil pH has been identified as a principal factor that affects the mobility and availability of metals in soil [3]. The pH of the soil ranged from 6.50 ± 0.20 to 8.03 ± 0.20 , indicating a slightly acidic to slightly alkaline soil. Such pH values are characteristic of soils in areas where leaching is less pronounced due to low precipitation, resulting in the concentration of base forming cations in the place of acid contributing cations such as Al^{3+} and H^+ [10]. The electrical conductivity value of the soil ranged from 225 ± 20.01 to 520 ± 14.0 $\mu\text{S}/\text{cm}$. These were generally higher when compared to that of the control ($152.5\mu\text{S}/\text{cm}$). The disparity in the electrical conductivity values could be attributed to differences in the soluble salt content of the soils. The particle size distribution of the soil showed that the soil contained higher composition of sand than silt and clay in all the sampling sites. Trace metals have preferential accumulation in the clay and silt fraction of soil. Generally, the concentration of heavy metal in soil increase with decrease in the sizes of the soil particles.

Table 1: Physicochemical properties of the soil samples

Sampling point	pH	EC($\mu\text{S}/\text{cm}$)	OM (%)	Particle Sizes (%)		
				Sand	Silt	Clay
S1	7.86 ± 0.15	520 ± 14.0	2.54 ± 0.21	67	24	9
S2	8.03 ± 0.20	425 ± 7.07	2.77 ± 0.03	65	28	7
S3	7.66 ± 0.11	395 ± 7.07	2.57 ± 0.03	65	27	8
S4	7.16 ± 0.11	530 ± 28.2	2.41 ± 0.02	61	29	10
S5	7.03 ± 0.15	225 ± 21.2	2.31 ± 0.17	87	12	1
S6	7.02 ± 0.05	275 ± 7.00	3.10 ± 0.01	81	14	5
S7	7.76 ± 0.16	225 ± 20.1	2.25 ± 0.03	87	13	0
S8	6.50 ± 0.20	305 ± 21.2	2.18 ± 0.01	89	11	0
Control 1	7.01 ± 0.21	140 ± 28.3	2.32 ± 0.12	82	15	3

Results are expressed as mean \pm standard deviation of triplicate analysis. Soil organic matter is a principal variable that affects the spatial distribution of heavy metals in soil [12]. Increase in soil organic matter content lead to elevation of soil adsorption capacity hence enhancing the accumulation of trace metals. Organic matters can therefore be considered as an important medium through which heavy metals are incorporated into the soil [13]. Soil in all the sampling points generally contained low organic matter content with the highest being at sampling point 6 ($3.10\pm 0.01\%$). The organic matter content of the soil in the study area where generally higher when compared to that obtained by [8] in a similar study. They were however lower than that reported by [14].

Table 2: Heavy Metal Concentration in Soil Samples ($\mu\text{g}/\text{g}$).

	Pb	Zn	Cu	Mn	Cd	Cr	Fe
S1	45.35 ± 0.05^d	212.90 ± 1.08^g	21.35 ± 0.53^c	237.2 ± 0.75^h	ND	33.50 ± 0.40^c	1676.65 ± 1.76^e
S2	40.35 ± 0.15^b	197.25 ± 0.62^f	15.45 ± 0.39^a	167.2 ± 0.20^d	1.00 ± 0.10^a	38.00 ± 0.85^e	1339.15 ± 1.02^d
S3	44.80 ± 0.23^c	188.70 ± 0.30^e	26.80 ± 0.20^e	202.8 ± 0.90^g	1.30 ± 0.20^b	38.30 ± 0.36^e	1269.23 ± 2.24^d
S4	53.15 ± 0.06^f	273.00 ± 0.92^i	25.85 ± 0.23^d	196.0 ± 0.20^f	ND	37.50 ± 1.10^e	1119.66 ± 3.11^b
S5	63.65 ± 0.18^g	139.15 ± 1.23^b	27.00 ± 0.13^e	182.7 ± 0.72^d	1.00 ± 0.11^a	51.50 ± 0.30^f	6261.32 ± 7.60^f
S6	47.10 ± 0.10^e	142.30 ± 0.70^c	26.80 ± 0.35^e	152.9 ± 0.36^e	ND	32.00 ± 1.00^b	6323.43 ± 4.12^g
S7	30.80 ± 0.15^a	128.35 ± 2.16^a	17.0 ± 0.15^b	120.9 ± 0.26^b	ND	28.50 ± 0.36^a	1084.43 ± 3.58^a
S8	79.60 ± 0.87^i	184.60 ± 1.49^d	21.0 ± 0.05^c	102.9 ± 1.47^a	ND	35.50 ± 0.26^d	6542.32 ± 2.56^h
C1	18.90 ± 0.78	98.10 ± 0.95	8.10 ± 1.00	79.02 ± 0.57	ND	10.00 ± 0.11	842.55 ± 2.19

ND: Not Detected C: Control Results expressed as mean \pm SD for triplicate measurement. Values on the same column with same superscript do not differ significantly. From table 2 above, the concentration of Pb obtained at the various sampling sites is far greater than that of the control of $18.90\pm 0.7887\mu\text{g/g}$, which implies contamination. The mean concentration of Pb obtained ranged from 30.80 ± 0.15 to $79.60\pm 0.87\mu\text{g/g}$. The highest concentration of Pb obtained is $79.60\pm 0.87\mu\text{g/g}$. This elevated value at this site could be attributed to its proximity to the commercial road resulting to discharge from vehicular and other related sources [15]. The mean concentration of Pb obtained is higher than $49.53\pm 1.31\mu\text{g/g}$ reported by [12] in surface soil at Chitgar industrial area of Tehran. It is however within the range of $53\pm 0.32\mu\text{g/g}$ documented by [16] in their study of Pb, Cu and Zinc concentration in road side top soil of Niger state. Environmental contamination by Pb can constitute health problems especially in young children, due to its tendency to accumulate in the body and magnify to a toxic level as a result of continuous exposure [17]. The Index of geoaccumulation of Pb calculated ranged from -0.35 to 1.05 (table 3), this implies uncontaminated to moderate soil contamination by Pb. The maximum Enrichment factor (2.10) for Pb in the soil samples analyzed as shown in table 4, also showed that there is a moderate soil enrichment by the element (EF = 2-5). The various samples were observed to be enriched with zinc when compared with the control and findings from other studies. This implies soil enrichment with zinc due to anthropogenic contributions. Zinc is widely used in industries to make paint and dyes [17]. The concentration of Zn obtained ranged from 128.35 ± 2.16 to $273\pm 0.92\mu\text{g/g}$ and is higher than $60\mu\text{g/g}$ reported by [18] as the concentration of Zn in a typical soil. It was also higher when compared to $33.84\text{-}131.06\mu\text{g/g}$ reported by [19] as well as $49.37\pm 1.35\mu\text{g/g}$ by [12]. Elevated content of Zn at sampling point 4 could be due to higher clay content at this point. Incorporation of trace metals occur to a great extent with fine clay soil rather than with coarse soil [10]. The mean I-geo revealed that the soil falls into the category of uncontaminated to moderate contamination ($0 < \text{I-geo} < 1$). The EF obtained was generally low (0.26 to 2.04). The maximum EF (2.04) obtained also depicts moderate enrichment

Table 3: Geoaccumulation Index (I-geo) of the metals.

Metal	Range	Mean
Pb	-0.35 – 1.05	0.33
Zn	0.03 – 1.11	0.50
Cu	-0.85 – -0.02	-0.283
Mn	0.25 – 1.45	0.93
Cd	0.00 – 0.07	0.03
Cr	-0.02 – 0.83	0.32
Fe	0.08 – 2.64	1.16

The highest concentration of Cu obtained from this study is $27.0\pm 0.13\mu\text{g/g}$, which was obtained at sampling point 5. The elevated concentration of Cu at S5 suggests additive input from agricultural activities around this point. Copper is a

component of some agricultural fungicides [17]. The higher organic matter at this point could also be a contributing factor to the enriched concentration of Cu at this point. Increase in soil organic matter content lead to elevation of soil adsorption capacity hence enhancing the accumulation of trace metals. Organic matters can therefore be considered as an important medium through which heavy metals are incorporated into the soil [13]. The highest concentration of Cu ($27.00\pm 0.13\mu\text{g/g}$) obtained from this study is higher than $4.51\text{-}21.07\mu\text{g/g}$ reported by [11] and the mean concentration of $18.0\pm 4.0\mu\text{g/g}$ reported by [20]. All the soil samples had a negative I-geo for Cu (table 3). The maximum I-geo from all the soil studied was -0.02, which shows practical uncontamination ($\text{I-geo} \leq 0$). The mean EF of 0.72 obtained also showed deficiency to minimal enrichment. On average, soil contains $600\mu\text{g/g}$ of Mn and a concentration range of 200 – 3000 $\mu\text{g/g}$ (Akoji, 2010). The concentration of Mn in this study ranged from 102.9 ± 1.47 - $237.2\pm 0.75\mu\text{g/g}$. The lowest and highest concentrations among the industrial areas were obtained at S8 and S1 respectively. Comparisons of the result obtain with the normal background concentration of copper in soil shows less contamination. There was no significant difference in the concentration of Mn at S1 and S5. This could be as a result of similarity of the source of the metals. The concentration of Mn obtained in this study is within the range of $600\mu\text{g/g}$ documented by [21] as the background concentration of Mn in soil. Cd was not detected in most of the samples. The mean concentration of Cd obtained ranged from ND - $1.30\pm 0.20\mu\text{g/g}$. The highest concentration of Cd obtained in this study was 1.30 ± 0.30 which was at S3. The elevated concentration of Cd at this site could be due to its proximity to an electroplating and alloying company. Cd is known to be a major component in the manufacture of anticorrosive coatings for metals, solders and bearing alloys [17]. This is higher than the permissible limit of $0.1\text{-}1.0\mu\text{g/g}$ reported by [21]. The maximum value obtained for Cd in this study is twice the mean value of $0.7\mu\text{g/g}$ reported by [22]. It was however lower than ND- $7.02\mu\text{g/g}$ reported by [19]. The absence of Cd in some of the samples may be attributed to sampling sites, as the extent of heavy metal contamination is also affected by varying sampling sites. High concentration of Cd in soil could have deleterious effect to vital body organs in both human and livestock. It interferes with enzymes and accumulates in kidneys, spleen and liver [17]. From table 3, the I-geo 0.00 to 0.07 for Cd denotes that the soil samples were not contaminated by this metal. The EF of 0.00 to 0.13 for Cd also showed a deficiency of Cd in the soil.

Table 4: Enrichment Factor (EF) of the metals.

Metal	Range	Mean
Pb	0.29 - 2.10	1.06
Zn	0.26 - 2.04	1.30
Cu	0.18 - 1.33	0.72
Mn	0.28 - 3.08	1.89
Cd	0.00 - 0.13	0.11
Cr	0.26 - 2.49	1.21
Fe	1.0 - 1.00	1.00

The concentration of Cr in the samples range from 28.50 ± 0.36 to 51.50 ± 0.30 $\mu\text{g/g}$ (table 2). The concentrations of Cr obtained from samples around the vicinity of the industry were observed to be significantly higher than that of the control site. The value is within the range of 14.2 to 92.7 $\mu\text{g/g}$ report by [22] and [12] in their study. It is however higher than 1.64-22.36 $\mu\text{g/g}$ documented by [19]. The soil samples had I-geo range of 0.02 to 0.83, with a mean value of 0.32. Thus most of the soil samples analysed were observed to fall into the category of uncontaminated to moderately contaminated soil. The mean soil EF of Cr was 1.21 (table 4). There was minimal enrichment in the soil sample, with the exception of sampling point 4, where there was moderate enrichment. The concentration of 1084.43 \pm 3.58 to 6542.32 \pm 2.56 $\mu\text{g/g}$ obtained for Fe from this study is several times greater than of other elements studied. This could be ascribed to the relative abundance of the element on the earth crust [23]. This correlates with findings from similar studies [11]. The I-geo for Fe obtained showed moderate contamination. The highest enrichment factor obtained for Fe was 1.0 which denotes deficiency to minimal enrichment.

Table 5: Interelemental correlation of heavy metals in soil around the studied paint industries

	Pb	Zn	Cu	Mn	Cd	Cr	Fe
Pb	1						
Zn	0.47	1					
Cu	0.67*	0.59	1				
Mn	0.32	0.77*	0.74*	1			
Cd	0.14	0.15	0.33	0.42	1		
Cr	0.71*	0.48	0.75*	0.57	0.58	1	
Fe	-	-0.05	0.51	0.03	0.01	0.45	1
	0.75*						

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

A correlation matrix computed for the investigated heavy metals so as to determine their interrelationship with each other. From the result obtained from the computation, a significant positive correlation was obtained for some of the elements (Cu:Pb, Cr:Pb, Mn:Zn, Mn;Cu and Cr:Cu) at 0.05 level of significance. This strong positive correlation shows that the elements are closely associated, thus suggesting their common origin. A significant negative correlation was however obtained for Cu:Pb. There was also a negative correlation between Fe and Zn, although not significant. Thus Fe and Zn are not closely associated.

CONCLUSION

The result from this study showed that the heavy metal concentration of soil in the studied area were in the order

Fe>Zn>Mn>Pb>Cr>Cu>Cd. All the metals investigated were found to be present in all the soil samples with the exception of Cd which was not detected in most of the soil samples. The concentration of Fe was several times higher than other metals. The concentration of the metals in all the samples analyzed were far greater than the control, showing decreasing contamination with increase in distance from the industries. There was also a significant positive correlation among some of the elements analyzed. The result of geoaccumulation index and enrichment factor revealed moderate soil contamination by most of the metals investigated. Thus suggesting environmental contamination from industrial activities, vehicular emissions and related anthropogenic contributions. There is therefore need for continual monitoring of heavy metal content in soil around industrial areas.

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