

Trace Metal Composition of Soil around Selected Pharmaceutical Industries in Kaduna, Nigeria

¹Inobeme, A.; ¹ Adamu,A.; ¹Ajai, A.I.; ²Uwem, B. and ³Obigwa,P.A.

¹.Department of Chemistry, Federal University of Technology, Minna, Nigeria.

².Department of Environmental Science , Federal University of Petroleum Resources, Effurun, Delta State Nigeria.

³.Sheda Science and Technology Complex, Nigeria.

Abstract

The physicochemical properties and trace metal compositions of soil around selected pharmaceutical industries in Kaduna metropolis were investigated in this study. The mean pH, EC and TOM were 6.97, 341.3µS/cm and 3.11 respectively. Particle size analysis revealed a higher composition of sand fraction (78.7%). The concentration of the metals were in order Fe (1664.9 µg/g), Zn (155.17 µg/g), Mn (108.07 µg/g), Cr (34.62 µg/g), Pb (28.12 µg/g), Cu (12.21 µg/g) and Cd (0.04 µg/g). There was a significant difference in the concentration of these metals at most of the sampling point. Interelemental correlation analysis revealed a strong positive correlation between Cd and Zn, Mn and Cu, and Fe and Mn at $P < 0.05$. This implies a close association among them. The concentrations of the metals at the various sampling points were generally higher than the control which implies contamination from anthropogenic input. Result of relative pollution potential (RPP) and Contamination factor (CF) showed a similar trend: $Cr > Fe > Mn > Zn > Cu > Pb > Cd$. There was a moderate contamination of the soil by most of the metals investigated. There is need to continually monitor the concentration of trace metal in this area so as to ensure environment safety.

Keywords:

Trace Metal Composition, Pharmaceutical Industries, Kaduna, Nigeria, physicochemical properties, Environmental contamination,

INTRODUCTION

Environmental contamination by wastes from industrial and agricultural activities is a global issue (Sherene, 2012). Toxic wastes are discharged into the environment, thus constituting a deleterious effect on life (Seaward, 2004). Among the various wastes released into the environment, heavy metals make up one of the major class. Waste from pharmaceutical industries have also been reported to contain high concentration of heavy metals, which shows variation depending on the targeted drug, raw materials utilised as well as processes adopted (Olaitan, Nwaeze and Olabanji, 2013).

Discharge from pharmaceutical industries consists of organic substances such as phenolic compounds as well as inorganic materials which have heavy metals as their basic components and therefore toxic to humans (Momodu, 2010). Heavy metals are not acted upon by microorganism hence environmental contamination results to bioaccumulation and biomagnifications in living organisms (Campbell, 2006).

Soil has been identified as a geochemical sink for contaminants since all wastes from anthropogenic activities end up in the soil

(Romic and Romic, 2003). Heavy metals are released into the environment from various sources: agricultural activities; waste disposal; vehicular emission among others (Sayyed, and Sayadi, 2011). Heavy metals such as Zn, Cu, Fe, and Cu are essential trace element for proper functioning of the body system. Others such as Pb, Cr, Cd have no known functions in biological systems (Adakole and Abulude 2012; Butu and Egusi, 2013).

The need for monitoring continually the rising concentration of heavy metals in soil has been emphasized by various researchers (Iyaka and Kakulu 2012). The increasing concentration of heavy metals in soil is therefore a significant problem. Soils around industrial areas are more vulnerable to this. Though similar studies have been carried out in soil around pharmaceutical industries in different parts of the world, there is dearth of report on soil contamination by heavy metals around pharmaceutical industries in Kaduna, hence the need for this present study.

Study area

The present study focused on selected pharmaceutical industries in Kaduna metropolis. Kaduna is the capital of Kaduna state. It derived its name from the Hausa word 'Kaduna' meaning 'crocodiles' due to the large number of crocodiles in river Kaduna. The state occupies an area of approximately 48,473.2 square kilometres with a population of more than 6 million (2006 census). It lies along the Kaduna River, which is a tributary of the River Niger (Jonathan, 2010).

Kaduna is recognized as one of the major industrial and commercial center of northern Nigeria. Most of the industries are located in the south of Kaduna River near the main railway junction. The major industries in the area include textile industries, steel rolling plants, pharmaceutical industries, plastic industries, ceramic industries, paint industries, food

industries among others. Most of the industries are in active state of production while a few are dormant. The pharmaceutical industries studied were Arewa and Abumec pharmaceutical industries located around Kakuri and Sabon tasha all in kaduna town.

Sampling method

A total of eight samples were collected from soil in the vicinities of two pharmaceutical industries in the study area. At each sampling point, four sub-samples were collected. These were then homogenised to obtain the eight composite samples. The samples were obtained from a depth of 0-15cm using soil auger and stored inside clean polythene bags prior to pre-treatment and analysis.

Preparation of samples and determination of physicochemical properties

The samples collected were oven dried at 105°C for 24 hours. Plant materials were removed and the soil ground and sieved using 2mm and 0.5mm mesh sizes. The soil pH was determined using soil water suspension (1: 1) (Umoru, 2013). Particle size distribution was determined using hydrometer method. The soil electrical conductivity was determined using soil water suspension (1:5) in line with Akoji, 2010. The total organic matter content of the soil was determined using walkley black titration method as reported by Abolude, 2005.

Digestion of the soil samples

1g of the sample was digested using triacid mixture (HClO₄, HNO₃ and H₂SO₄) in the ratio of (2:10:1). This was then filtered into 100cm³ volumetric flask and made to the mark. The total metal content was determined using AAS.

Results

Physicochemical properties of the soil

The result on table 1 shows the physicochemical properties of the soil in the study area. The pH of the soil ranged from 6.23 to 7.55, with a mean value of 6.97. It is therefore apparent that the soils in this area have properties varying from neutral to slightly alkaline. Similar results have been reported for areas with low precipitation, thus preventing the leaching of cations that enhance soil basic properties (Akoji, 2010). Soil pH is a principal factor that dictates the uneven distribution of heavy metals in soil (Bozkurt *et al.*, 2000). Alkaline soil condition enhances the concentration of heavy metals on the surface soil, thus limiting their availability for plants uptake and underground water contamination (Nath, 2013). The pH at most of the sampling points differs significantly. The soil has a mean EC of 341.30 μ S/cm. The EC of the soil at different sampling points differ significantly. This shows the differences in the extent of dissolved compounds present in soil around

the areas. The highest EC of 488.63 μ S/cm was obtained at sampling point of 8. This could be due to presence of ionic compounds dissolved in this area. The result of particle size analysis reveals that the soil has higher percentage of sand compared to the clay and silt component. The mean composition of sand was 78.76% while clay and silt were 16.66% and 4.58% respectively. There was a significant difference in the percentage organic matter present at the different sampling points. The least TOM obtained was at S6 (2.16%). Soil organic matter is a principal variable that affects the differential distribution of heavy metals in soil. Increase in soil organic matter content lead to elevation of soil adsorption capacity hence enhancing trace metal accumulation and storage. Organic matters can therefore be considered as an important medium through which heavy metals are incorporated and reserved in the soil (Afshin, 2007).

Table 1: Physicochemical properties of soil in the study area

Sampling Point	Physicochemical parameters					
	pH	EC(μ S/cm)	Sand (%)	Silt (%)	Clay (%)	TOM
SP1	6.50 \pm 1.02ab	260.10 \pm 2.06b	70.11 \pm 1.23b	10.06 \pm 0.74g	19.20 \pm 0.61f	3.39 \pm 0.03e
SP2	7.02 \pm 0.07cd	300.16 \pm 0.94c	72.30 \pm 1.11c	9.54 \pm 1.07e	18.16 \pm 0.41e	3.72 \pm 0.09f
SP3	6.23 \pm 1.32a	305.81 \pm 1.26d	80.21 \pm 0.43e	4.58 \pm 0.66d	15.21 \pm 1.12c	3.21 \pm 0.97d
SP4	7.13 \pm 1.06d	235.52 \pm 2.31a	66.44 \pm 0.63a	5.17 \pm 1.00a	28.39 \pm 0.99h	3.85 \pm 1.01h
SP5	6.70 \pm 0.62bc	350.25 \pm 4.01e	73.21 \pm 0.61d	1.21 \pm 0.54	25.58 \pm 0.01g	3.20 \pm 0.19d
SP6	7.01 \pm 0.91cd	400.22 \pm 1.23g	81.87 \pm 1.63f	1.98 \pm 0.06c	16.15 \pm 1.04	2.16 \pm 0.69a
SP7	7.62 \pm 0.09e	389.70 \pm 2.06f	89.21 \pm 1.64g	1.51 \pm 0.90b	9.28 \pm 0.99b	3.09 \pm 1.00c
SP8	7.55 \pm 1.03e	488.63 \pm 3.04h	90.73 \pm 1.01h	1.07 \pm 1.61c	8.20 \pm 0.63a	2.27 \pm 0.95b
Mean	6.97	341.3	78.76	4.58	16.66	3.11
Control	7.10 \pm 1.10	290.15 \pm 0.97	87.20 \pm 2.14	3.10 \pm 0.93	9.70 \pm 0.45	2.59 \pm 0.02

Results are expressed as mean \pm SD. Values with the same superscript on same column do not differ significantly.

Heavy metal concentrations in soil

Pb

The concentration of Pb ranged from $23.25 \pm 0.71 \mu\text{g/g}$ to $36.43 \pm 1.01 \mu\text{g/g}$. The mean concentration of Pb was 28.12. The relatively higher concentration of Pb at sampling point 4 may be due to its closeness to a commercial road. Areas closed to commercial roads are prone to higher contamination by Pb, due to vehicular emission. The concentration of Pb obtained here is lower than $71.43 \pm 3 \mu\text{g/g}$ reported by Yan, *et al.*, 2013, $258.46 \pm 10.26 \mu\text{g/g}$ recorded by Adewoyin, *et al.*, 2013 and $49.53 \pm 1.31 \text{mg/kg}$ reported Sayyed and sayadi 2011. High concentration of Pb in the body can result to reduced intelligence and are toxic to vital body organs such kidney, liver, bone and heart (Bulinski and Libert, 1993).

Zn

There was a significant difference in the concentration of Zn at various sampling points. The highest concentration ($172.21 \pm 1.08 \mu\text{g/g}$) was obtained at SP2 while the least was at SP7 ($127.21 \pm 2.06 \mu\text{g/g}$). The mean concentration of Zn obtained was $155.17 \mu\text{g/g}$. The high concentration of Zn obtained at SP2 could be attributed to the high silt content of soil at this sampling location. Heavy metals have preferential accumulation in silt and clay fractions of soil than sand. The concentration of zinc obtained in this study is higher than $14.74 \pm 0.27 \mu\text{g/g}$ reported by Sayyed and Sayadi, 2011 in their study on soil around industrial area of Chitgar, Tehran. It is lower than 295- 553 $\mu\text{g/g}$ reported by Pam *et al.*, 2013 in their study.

Cd

The concentration of Cd varied across the various sampling points. Cd was absent in most of the sampling areas. The maximum concentration of Cd obtained was $0.14 \mu\text{g/g}$ which was at SP4. The presence of Cd could be due to the additive input from electroplating industry close to the vicinity of the pharmaceutical industry. The result obtained is within the range of 0.01 to 0.67mg/kg reported by Yan, Hong, Chong, and Fan, 2013 in a similar study. It is also lower than $2.25 \pm 0.06 \mu\text{g/g}$ reported by Sayyed and Sayadi, (2011) in a study on heavy metal accumulation in Chitgar industrial area, Tehran. Cd in soil is readily absorbed by plants and thus accumulates and passes along the food chain. Consumption of plants containing 3.0 ppm Cd can poison man and animals. It interferes with enzymes and other proteins and causes damages to body organs (David, 2008).

Cr

Chromium was observed to be present in appreciable quantity. With the exception of SP1 which had the least concentration of Cr, the concentration of Cr ranged from $27.00 \pm 1.21 \mu\text{g/g}$ to $43.71 \pm 1.92 \mu\text{g/g}$ with mean value of $34.62 \mu\text{g/g}$. The concentration of Chromium at various sampling areas exceeded that of the control ($34.62 \mu\text{g/g}$). The result obtained is higher than $0.05 \mu\text{g/g}$ reported as acceptable level by WHO. The result is higher than $16 \pm 9 \text{mg/kg}$ documented by Nwachukwu, Feng, and Alinno, 2010; $25.96 \pm 1.01 \mu\text{g/g}$ by Sayyed and Sayadi, 2011 and 4.82 to $16.48 \mu\text{g/g}$ reported by Patnaik, Raut, Behera, Nayak, Mishra and Swain, 2000 in soil around the industrial belt of Cuttack in Orisa.

Cu

Cu has a relatively low concentration when compared to some of the metals analysed. The concentration of Cu ranged from

7.29±0.94 µg/g to 18.03±2.01 µg/g. The mean concentration of was 12.2 µg/g. The result of Cu from this study is lower than 42.4±2.8 µg/g reported by Yan 2013 and 22.36±0.82 µg/g reported by Sayyed and sayadi, 2011.

Mn

The mean concentration of Mn was 108.07 µg/g. The least concentration 86.10±2.11 µg/g was obtained at SP3. With the exception of SP1, SP2, SP3 and SP4, the concentration at sampling sites was relatively higher than the control. The concentration of heavy metals shows variation at the various sampling areas. This is due to differences in the concentration and compositions of waste released at various point. The result obtained is lower than 378.3±207 mg/kg documented by Nwachukwu 2000 in his study and 4350-21252 mg/kg documented by Patnaiket et al.,2013 in his study on soil around industrial belt of Cuttack Orissa.

Table 2 : Concentration of heavy metals in soil (µg/g).

Sampling Point	Metals						
	Pb	Zn	Cd	Cr	Cu	Mn	Fe
SP1	23.25±0.71a	164.20±		27.00±	10.00±	90.24±2	1213.10±3.0
		2.01e	ND	1.21a	1.91c	.43b	8b
SP2	30.51±1.10g	172.21±	0.12±0	30.08±	11.23±	101.10±	1621.53±4.2
		1.08g	.01b	0.42c	0.21d	3.07d	2d
SP3	27.21±0.82d	141.21±		36.21±	7.29±0.	86.10±2	989.24±2.81
		0.72d	ND	2.01d	94a	.11a	a
SP4	36.43±1.01h	196.54±	0.14±0	43.71±	9.80±0.	91.12±0	1582.89±6.0
		2.06h	.09c	1.92f	91b	.88c	8c
SP5	30.05±0.93f	130.06±		30.02±	10.06±	120.23±	1863.21±8.1
		2.32b	ND	0.99c	0.83c	0.97f	4e
SP6	27.26±0.09e	140.89±		25.81±	16.47±	133.40±	2100.54±20.
		0.62c	ND	0.64a	1.33f	0.64h	01h
SP7	26.01±1.07c	127.21±		33.21±	14.92±	116.08±	1920.32±4.3
		2.06a	ND	2.06d	0.95e	3.41e	1f
SP8	24.24±0.64b	167.56±	0.09±0	27.96±	18.03±	126.29±	2029.09±8.4
		0.99f	.01	0.96b	2.01g	2.10g	2g

Fe

Fe was observed to be present in appreciable quantity among the analysed elements. The concentration of Fe was several times those of other elements. The result of Fe obtained is greater than 232.47± 24.53 µg/g reported by Adewoyin, Hassan and Aladesida, 2013 in their study on soil around automachanic workshop in Ibadan metropolis. The concentration of Fe obtained in this study is small when compared to the tolerable limit of 26,000 µg/g of Fe in soils (USEPA, 2004). The mean concentration of Fe in most of the site is within the range of 6761-6234 µg/g reported by Abida *et al.* (2009) for Indian soil. The concentration of Fe obtained is lower than the maximum value of 6000 µg/g reported by Yahaya *et al.* (2013).

Mean	28.12	155.17	0.043	34.62	12.21	108.07	1664.
Control	20.01±0.85	88.90±0	0.05±0	12.75±	8.32±0.	48.85±0	721±
		.46	.06	0.40	26	.38	1.66

Results are expressed as mean±SD for triplicate determinations. Values in the same column with the same letters do not differ significantly.

Result of interelemental analysis

The result on table 3 shows the interelemental correlation analysis of the metals analysed. There was a significant positive correlation between Pb and Cd. Zn also correlated positively with Cd at P<0.05 level of significance. Cu correlated positively with

Mn and Fe at P< 0.05. This shows a close association among such elements, which also points to related source.

Table 3: Result of interelemental correlation

	Pb	Zn	Cd	Cr	Cu	Mn	Fe
Pb	1						
Zn	0.464	1					
Cd	0.61*	0.86**	1				
Cr	0.57*	-0.007	0.117	1			
Cu	-0.394	-1.38	0.029	0.033	1		
Mn	-0.255	-0.45	-0.204	-0.059	0.84**	1	
Fe	0.008	-0.205	0.091	0.125	0.84**	0.93**	1

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

** Correlation is significant at the 0.01 level (2 tailed)

Pollution Assessment Indices

Various indices were used in order to ascertain the extent of environment contamination by the metals. These are

contamination factor (CF) and relative pollution Potential (RPP).

Contamination factor (CF) expresses the extent of contamination by metals by comparing the determined concentration of the studied soil with that of preindustrial era. This was calculated using the equation proposed by Kakanson (1980) and Dasaram *et al* (2011).

$$Cf = C^1_{0-1} / C^1_n$$

Where C^1_{0-1} is the mean concentration of the metal from at least 5 sampling point and C_n is the preindustrial concentration of individual

metal. The concentration of metals from control site was used as the preindustrial concentration (Victor *et al*, 2006).

Contamination factor	category
$Cf < 1$	low contamination
$1 < Cf < 3$	moderate contamination
$3 < Cf < 6$	considerable contamination
$6 < Cf$	very high contamination

The result of mean Cf shows that Cr had the highest contamination factor (2.72) which also implies that the soil was moderately contaminated with Cr. With the exception of Cd which had the least Cf (0.73), all the other metals showed a moderate contamination of

soil. Soil contamination by the metal based on this index was in the order: Cr > Fe > Mn > Cu > Pb > Cd.

Results of Indices of Soil Pollution Assessment

Metals	Pb	Zn	Cd	Cr	Cu	Mn	Fe
RPP	0.29	0.40	0.21	0.60	0.32	0.54	0.54
Cf	1.41	1.75	0.73	2.72	1.47	2.21	2.31

Relative Pollution Potential (RPP)

This index expresses the extent of chemical interaction between the pollutant and the recipient. This was determined using the formula suggested by Eghrevha and odjada (2008)..

$$Y = A-B / A$$

Where Y = relative pollution potential

A = metal concentration at impacted point

B = metal concentration at point away from impacted point

Positive values imply contamination at point source.

The result obtained from this study shows positive values for all the relative pollution potentials. Cr had the highest value (0.60) while Cd had the least (0.21). The general trend of pollution as revealed by this index is similar to that obtained from the contamination factor.

Conclusion

The present study has revealed the trace metal concentration of the soil around pharmaceutical industries in Kaduna. The result shows that Fe had the highest concentration among all the investigated elements while Cd had the least. The concentration of Fe was several time those of other element. Generally the concentration of the metals was in the decreasing trend: Fe > Zn > Mn > Cr > Pb > Cu > Cd. A significant positive correlation was obtained for some of the metals analysed: Pb and Cd; Zn and Cd; and Cu and Mn. Results from Contamination index and Relative pollution potential also revealed that the soils were moderately polluted by most of the metals determined. Consistent monitoring of trace metal content in soil around industries is pertinent in order to ensure a safe environment.

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