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HEAVY METAL CONTAMINATION AND PHYSICOCHEMICAL CHARACTERISTICS OF SOILS FROM AUTOMOBILE WORKSHOPS IN ABRAKA, DELTA STATE, NIGERIA

Osakwe Stephen Anapuwa[1]
[1]*Department of Chemistry, Delta State University, Abraka, Delta State, Nigeria*

ABSTRACT
Soils samples were collected from selected automobile workshops in Abraka, Delta State, Nigeria, at the depths of 0 – 15cm, 15 – 30cm and 30 – 45cm representing top,- sub- and bottom soils respectively and also from control site and 20m away from the point of impact. The soils were analyzed for their physicochemical characteristics and heavy metal levels. The p^H values of the soils in all the sites ranged from 3.6 to 6.7 with mean value of 5.97 showing that the soils were moderately acidic. The electrical conductivities of the soils ranged from (μScm^{-1}) 202.0 to 478.0 with mean value of 306.28 indicating significant presence of soluble inorganic substances with their corresponding ions. Total Organic Carbon content ranged from (%) 29.56 to 77.76 with mean value of 42.07 signifying presence of degradable substances and increased microbial activities in the soil. Total nitrogen contents ranged from (%) 2.03 to 9.35 with mean value of 4.19 which may be attributed to presence of some organic matters. Soil textural classification showed that the soils were sandy loamy. The heavy metal levels had the mean values of ($mgkg^{-1}$) 40.05 for Fe, 16.74 for Zn, 34.39 for Mn and 0.66 for Cu showing the abundance trend of Fe>Mn>Zn>Cu. The Relative Pollution Potential and contamination/Pollution Index values revealed that the soils were slightly contaminated by heavy metals. Although the present level of heavy metal contamination of the soils does not call for any alarm, proactive steps must be taken to minimize gradual accumulation of these metals. It is hereby recommended that a separate portion of land be set apart for automobile workshops which can be called mechanic village as it is in some cosmopolitan areas in this country.

Keywords: Heavy metal, Physicochemical characteristics, Automobile workshops, Contamination, Soil, Abraka.

1. INTRODUCTION

Most automobile workshops in Nigeria consist of mechanics, panel beaters, spraying painters and vulcanizers and in some cases, car wash personnels. The activities of each of these workers generate gaseous, liquid and solid pollutants which affect the immediate environment. Among these pollutants, contamination of heavy metals in the environment is of major concern because of toxicity and threat to human life and environment [1].

Automobile emission is perhaps the greatest single source of contamination and it has been shown to contain lead, zinc, cadmium and nickel, the most important being lead from fuel and zinc from tyres [2] and it accounts for about 80% of their pollution by heavy metals in Nigeria [3].

Repairs and servicing of automobiles and other types of machinery in mechanic workshops are sources of heavy metals in the environment. Automobile mechanic works wastes have been implicated for elevated concentration of cadmium, chromium, copper, lead, nickel and zinc in soil profile in the vicinity of automobile waste dumps in Nigeria [4]. Automobile used (waste) oil contain oxidation products, sediments, water and metallic particles resulting from machinery wears, organic and inorganic chemicals used in oil additives and metal that are present in fuel and transferred to the crankcase during the combustion. These vehicle servicing centres may constitute sources of soil contamination in Abraka metropolis and in these locations fossil fuel products accumulation of various forms of heavy metals deteriorate nearby vegetation causing non-point source pollution [5].

The aim of this study was to investigate the profile of heavy metals in the soils within the automobile workshops in Abraka, with a view of assessing the effect of the workshop activities on the soil quality.

2. MATERIALS AND METHODS

2.1. Description of Study Area

Abraka situated in Ethiope East Local Government Area of Delta State, Nigeria, lies between latitude 5^0 48^1 and 5^060^1 North of the equator and longitude 6^000^1 and 6^0 15^1 East of the Greenwich Meridian. The parent topography consists of rolling low land plain generally above 45m sea level. It lies within the tropical rainforest region. The soil type is made up of precisely red and brown soils with abundant free iron oxide.The presence of the State University in this town attracts a large population of people and presence of many automobile vehicles, which in turn gives a boost to automobile workshop activities.

2.2. Samples Collection

Soil samples were collected from four selected automobile workshops within Abraka metropolis using soil auger, at the depths of 0-15cm 15-30cm and 30-45cm representing the top, sub and bottom soils, respectively. At each location, the soil samples were taken from three different points and the anger borings of the same depths from the three points were bulked and representative samples were finally got after series of coning and quartering [6]. The control samples were collected from the outskirts of the town at location far removed from the influence of any industrial or traffic activity.

2.3. Sample Preparation

The soil samples were air dried for a period of one week in a clean well-ventilated laboratory, crushed in a clean porcelain motar, sieved through a 2mm stainless sieve and stored in labeled plastic cars.The soil samples for heavy metal analysis were digested using a mixture of 2cm^3 of 60% perchloric acid, 15cm^3 of concentrated nitric acid and 1cm^3 of concentrated sulphuric acid. The samples were stirred at intervals until complete digestion was achieved [7]. All the digests were cooled and filtered through Whatmann No 42 filter paper. The filtrates were labeled and kept for metal analysis.

2.4. Sample Analysis

Soil p^H was measured in a soil water ratio of 1:25 [8]. Electrical conductivity (EC) was determined by the method of Chopra and Kanzar [9]. Total organic carbon (TOC) was analyzed using the methods described by Nelson and Sommers [10], while total nitrogen (TN) was measured using micro-kjedahl method [11]. Particle size analysis to separate sand, silt and clay was achieved according to the method of Boujouiuos [12]. The digested soil samples were analysed for Fe, Mn, Zn and Cu, using Atomic Absorption Spectrophotometer of Perkin Elmer. A. Analyst 2002 Model fitted with deuterium lamp for background correction.All reagents used in this study were of pure analytical grade and were checked for possible trace metal contamination. All glasswares were previously soaked in 14% nitric acid for 24 hours to remove possible entrained metals, washed with detergent and rinsed with deconized water. Quality control was assured by the use of triplicates standard reference materials and procedural blanks.

3. Results and Discussion

3.1. Physicochemical Properties

The physicochemical properties of the samples are presented on Table 1.

Table- 1. Physicochemical Characteristics of the Soil Samples.

Sites	Soil Depth(cm^3)	p^H	TOC (%)	T.N (%)	EC(UScm^{-1})	Particle Size		
						Sand	Silt	Clay
A	0 – 15	3.6	77.15	205	422.0	72.6	27.6	-
	15 – 30	5.4	77.76	2.20	310. 0	84.2	15.8	-
	30 – 45	5.6	72.62	2.24	332.0	85.2	10.8	4.5
B	0 – 15	4.8	36.15	9.35	326.0	62.3	37.2	-
	15 – 30	4.9	34.84	7.20	346.0	65.3	28.3	6.4
	30 – 45	5.1	32.83	6.15	478.0	87.7	12.3	-
C	0 – 15	5.4	29.56	2.03	202.0	69.6	30.4	-
	15 – 30	5.9	30.05	2.69	231.0	73.4	26.0	0.06
	30 – 45	6.0	33.72	4. 84	218.0	63.0	34.2	2.8
D	0 – 15	5.2	30.03	3.64	252.0	64.7	35.3	-
	15 – 30	6.0	40.70	4.40	272.0	85.3	14.7	-
	30 – 45	6.7	36.40	3.44	279.8	92.3	5.2	2.5
Mean		5.39	42.07	4.19	306.23			
Control	0 – 15	6.5	24.07	0.28	25.8	92.5	7.5	
	15 – 30	6.7	24.95	0.34	24.4	60.8	39.2	
	30 – 45	7.0	26.61	0.30	28.0	60.5	39.5	
Mean		6.73	25.21	0.31	26.07			

The p^H of the soils ranged from 3.6 to 6.7 with mean value of 5.97 indicating that the soils were moderately acidic. The acidity of the soils in all the sites decreased with depth. The range of values obtained in this study are consistent with those reported by Oguntimehin and Ipinmoroti [13], Osakwe [14], but lower than those reported by Obasi, et al. [15], Okoye and Agbo [16], Tukura, et al. [17],Osakwe [18], Badejo, et al. [19]; and higher than those reported by Oviasogie and Ofomaja [20]. The p^H values in the control of site were relatively higher than those of studied sites which suggest that the activities in the automobile workshops contributed to the acidity of the soils. The levels of acidity of the soils could be attributed to spilled acid from discharged motor batteries. Since the availability and mobility of trace heavy metals are greatly favoured by reduced soil p^H, the values obtained in this study favour plant uptake of heavy metals which will eventually affect humans through food chain.

Electrical conductivity values ranged from ($UScm^{-1}$) 202.0 to 478.0 with mean value of 306.23. There was no regular trend with depth and these values are higher than the values obtained in the control samples. Similar range of values has been reported [14, 19]. However these values are by far higher than the values reported by Obasi, et al. [15]. The implication of high electrical conductivity in soils is that there are reasonable or significant presence of ions [21]. The observed electrical conductivity values could be attributed to the reactions between some spilled acids from batteries and some metals from vehicle scraps leading to formation of some soluble and ionizable inorganic salts in the soils.

Total Organic Carbon (TOC) values in the sites ranged from (%) 29.56 to 77.76 with mean value of 42.07. These values are relatively high and may be attributed to discharge of used oil and is also suggestive of presence of degradable and compostable substances and increased microbial activities in the soils [22].

Total Nitrogen (TN) values ranged from (%) 2.03 to 9.35 with mean value of 4.19. These values are relatively higher than those reported by Osemwota [23]. Goi and Kurihara [24] observed that the presence of Nitrogen in the soil could be due to Nitrogen mineralization as a result of organic matter in the soil. Nitrogen is an essential constituent of metabolically active compounds such as amino acids, proteins, enzymes and some non-proteinous compounds [25].

For particle size distribution, sand size fraction predominates while clay was not available in some samples. Similar observation of absence of clay in some samples was reported by Egharevba and Odjada [26]. The textural classification was sandy loamy for all the soil samples. This is expected as soil texture is mainly inherited from the soil forming material [17]. The proportion of sand, silt and clay suggests that the soils were coarse. Coarse – textured sandy soils usually have a low supply of nutrients and moisture but provide physical support to plants. Fine textured soils on the other hand, have sufficient water holding capacity, good aeration and often a high supply of nutrients [27].

3.2. Heavy Metals

The results of heavy metal analyses are presented on Table 2.

Table- 2. Vertical Distribution of Fe, Zn, Mn, and Cu in the Soil Profile (mgkg-1).

Sites	Soil Depth (cm3)	Fe	Zn	Mn	Cu
A	0 – 15	48.80	20.25	50.00	1.10
	15 – 30	47.45	18.33	45.50	1.00
	30 - 45	47.00	17.665	45.00	0.70
B	0 – 15	50.00	25.75	47.70	1.20
	15 – 30	49.72	23.68	46.75	0.90
	30 - 45	49.00	21.43	45.33	0.75
C	0 – 15	40.00	13.75	25.00	0.50
	15 – 30	39.33	11.93	24.00	0.40
	30 - 45	38.40	11.00	23.25	0.25
D	0 – 15	29.00	13.58	22.13	0.45
	15 – 30	23.45	12.08	20.33	0.35
	30 - 45	18.40	11.50	17.70	0.30
Mean		40.05	16.74	34.39	0.66
Control	0 – 15	10.73	4.00	7.50	0.50
	15 – 30	13.20	4.42	5.33	0.30
	30 - 45	12.80	4.83	4.25	0.25
Mean		12.24	4.42	5.69	0.35

The results of heavy metal analyses revealed that the concentrations of all the metals studied decreased with depth in all the sites and were significantly higher than the levels obtained in the control site. This indicates that the soils studied had some heavy metal enrichments and surface soil which is the point of impact bears the metallic burden. Previous studies have shown that surface soils are better indicators of metallic burdens [28].

Iron levels in the soil samples from all the sites varied from (mgkg-1) 18.40 to 50.00 with mean value of 40.05. High levels of iron obtained in this study can be rationalized from the fact that natural soils contain significant concentrations of iron [29]. These iron levels obtained in this study could therefore be an additive result of lithological or crustal origin and anthropogenic effects. The presence of iron could also be attributed to automobile crankshafts wear and vehicle body damage. The levels obtained in this study are in agreement with those reported by Urunmatsoma and Ikhuoria [30]. The values are however lower than those reported by Eddy, et al. [31], Oguntimehin and Ipinmoroti [13], Osakwe [32], Abidemi [33]. Acute exposure of iron in humans leads to vomiting, cardiac depression and metabolic acidosis [34].

Manganese concentrations ranged from (mg/kg-1) 17.70 to 50.00 with mean values of 34.39 Manganese levels obtained in this study are relatively lower than the values reported by Eddy, et al. [31], and higher than those reported by Oviasogie and Omoruyi [35],Osakwe [32], Kaur and Mehra [36].The high manganese levels could be attributed to the fact that manganese in the form of oxide is a component of subsoil material [37]. In addition, the levels of manganese could be from used batteries, discarded metal rails, machinery parts and wastes from welding works and spray paintings of the vehicles. Manganese in trace amounts is an essential element for both plants and animals. High concentration of manganese results in kidney failure, liver and pancreas malfunctioning but its optimum concentration is very essential for respiratory enzymes and connective tissues development [38]. Exposure to abnormally high concentration of manganese particularly in form of dust and fumes is known to have resulted to adverse effect on humans

[39]. Copper levels varied from (mgkg-1) 0.25 to 1.20 with mean value of 0.66. Similar range of values have been reported [4].The levels are however lower than those reported by Nnabo, et al. [40], Okoye and Agbo [16], Kaur and Mehra [36], Ekpete and Festus [41] and higher than the levels reported by Osakwe [14]. Used oils that sink into the ground as leachates contain high proportions of copper as well as lead and antimony. Metal bearing wears are also a possible source of copper. Copper cables are used as electrical light source. Although copper is essential for plant growth, a very small amount of copper is required for plant growth. At lower concentrations, copper ions cause headache, nausea, vomiting and diarrhea and at high concentrations they cause anaemia, gastrointestinal disorder and also lead to liver and kidney malfunctioning in extreme cases [42].

Zinc levels ranged from (mg/kg-1) 11.00 to 27.75 with mean value of 16.74. The levels recorded in this study are relatively lower than the levels reported by Qishlaqi and Moore [43], Jung [44], Al-Trabulsy, et al. [45], and higher than the levels reported by Osemwota [23], Osakwe [46], Kaur and Mehra [36]. Zinc in form of zinc oxide is a component of paint, so zinc levels in the soils could be as a result of the activities of the spray painter and also vehicle body paints. It is also a component of crude oil tyre and automobile exhaust [2] and so its concentration could also be attributed to this. Zinc is involved in various metabolic activities of many organisms and is also one of the micronutrients essential for normal plant growth, but its increased level can cause many health disorders. Pillai [47]. Zn can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter [48, 49].

The lateral distribution of the heavy metals is presented on Table 3.

Table-3. Lateral Distribution of the Metals in Soils 20m away from the Workshops

Metals	Sites	Point of Impact	20m Away
Fe	A	47.75	43.78
	B	49.57	48.18
	C	39.24	30.84
	D	23.62	16.69
Zn			
	A	18.74	15.59
	B	23.62	20.64
	C	12.22	9.03
	D	12.38	8.86
Mn			
	A	46.83	33.07
	B	46.59	42.58
	C	24.08	19.57
	D	20.05	15.36
Cu			
	A	0.93	0.82
	B	0.95	0.88
	C	0.38	0.22
	D	0.37	0.35

Lateral distribution of the materials showed that the soils at the point of impact had higher average concentrations of the metals than 20 meters away. This is consistent with some other reports [50, 51].

3.3. Relative Pollution Potential of the Metals

Relative Pollution Potential of a Pollutant is a measure of the level of chemical interaction between the pollutant and the recipient. This was computed using the following scheme Egharevba and Odjada [26].

$$Y = \frac{A - B}{A}$$

Where: Y = Relative Pollution Potential

A = Metal concentration at Impacted Point

B = Metal Concentration at Point away from the Impacted Point.

The Relative Pollution Potential values of the Metals are presented on Table 4.

Table-4. Relative Pollution Potentials of the Metals

Sites	Fe	Zn	Mn	Cu
A	0.10	0.30	0.20	0.12
B	0.03	0.10	0.13	0.10
C	0.21	0.19	0.26	0.42
D	0.30	0.23	0.28	0.05

The results gave positive values for all the metals in all the sites indicating that the soils were contaminated at the point of impact.

3.4. Contamination/Pollution Index (C/P) of the Metals

The Contamination/Pollution Index (C/P) of the metals in the soils was calculated using the scheme formulated by Lacatusu [52].

$$C/P = \frac{\text{Concentration of the Metals in the Soil}}{\text{TargetValue}}$$

The target value was obtained by using the standard formulated by the Department of Petroleum Resources of Nigeria (DPR)/cluster abundant values for maximum allowed concentrations of heavy metals in soil in mg/kg^{-1} (5000Fe, 476Mn, 140Zn, 36Cu). Contamination/Pollution Index value greater than 1, defines pollution range, but when it is less than 1, it defines contamination range. The Contamination/Pollution Index values of the metals in the soils are presented on Table 5.

Table- 5. Contamination/Pollution (C/P) Index of the Metals in the Soil Samples.

Sites	Fe	Zn	Mn	Cu
A	0.01	0.33	0.04	0.030
B	0.01	0.33	0.5	0.030
C	0.008	0.17	0.03	0.010
D	0.005	0.14	0.03	0.010

On individual basis, the values for all the metals were in the range that fall within contamination range (less than 1). Following the categorization of the contamination/pollution index, all the metals were in the range that showed very slight contamination (<0.1) except Zn which showed slight contamination (0.1 – 025) in sites C and D and moderate contamination (02.6 – 0.5) in sites A and B.

5. CONCLUSION

The results from the analysis of the physicochemical properties of the soils revealed that the values from the studied soils were higher than the values obtained from the control sites except for p^H values. This show that the activities taking place in the automobile workshops contributed significantly to increase in acidity dissolved inorganic substances, compostable and degradable substances and other organic matters.

The relative pollution potentials of the metals shows that the soils were contaminated and contamination/pollution index values confirmed that the soils had very slight metal contamination for all the metals except for Zinc which showed moderate contamination in sites A and B. The overall conclusion is that the activities in the automobile workshops contributed to the contamination of the soils. However the level of contamination of the soils by the metals is not high at present, so there is no serious implication for health hazard.

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