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Profile of Heavy Metals from Automobile Workshops in Akure, Nigeria

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Abstract: Soil samples from five automobile workshops in Akure, Nigeria were analysed for heavy metals and pH. The samples taken at depths 0-15, 15- 30, 30- 45 and 45-60 cm were analyzed for Ba, Ni, Cr, Pb, Cu, Fe, Cd, Co and Zn metals. pH of soils ranged between 5.80 and 8.60. Cd was not detected in soil samples from all sites, Co was not detected in soils from Ilesha-garage. Fe and Zn were of high concentrations in all the sites considered; Cu and Cr had concentrations about 100 mg kg^{-1} in all sites. Ba, Cu, Zn and Fe were in high concentrations of 133.1, 151.4, 782.2 and 634.3 mg kg^{-1}, respectively at Ilesha-garage. Pb and Cr, have concentrations of 292.4 and 181.8 at Ijapo, respectively, while Ni and Co have 62.1 and 109.4 mg kg^{-1} at Oyemekun, respectively. Generally, many variations exist in concentrations within sites at different depths. However, applying an adopted C/P index value for determining total heavy metal pollution status within the depths and between the sites, the degree of heavy metal pollution was in the order: Ijapo > Ilesha garage > Ondo road > Oyemekun > Oke-ijebu.

Key words: Soils, heavy metal pollution, pH, automobile workshops

INTRODUCTION

Heavy metals are chemical elements found in all kinds of soils and mostly with density greater than 5 g dm^{-3}, the very low general level of their content in soils and plants as well as the biological role of most of them makes them microelements (Lacatusu, 1998).

Some heavy metals are essential to maintain human metabolism, however, many may be poisonous at higher concentrations, as they tends to bioaccumulate in human bodies making them dangerous and thereby poses great health and environmental risks (Lenntech, 2005).

Soil being an essential component of terrestrial ecosystem supports plant growth and the biogeochemical cycling of nutrients. Taking a ride from the surface to the bedrock, several distinct layers or horizons that form the soil profile (ground level, top soil, subsoil, the weathered material and the bedrock) has been identified (Lenntech, 2005). Heavy metal pollution refers to cases where the contents of these elements in soils are higher than the maximum concentration, which has potential harmful effects on vegetation.

Nigeria with a land area of approximately 950,000 km^2 is richly endowed with diverse resources. However, there are staggering environmental problems manifested in various forms to present a grim of woes across the lengths and breaths of the nation. Pollution with other types of degradation such as erosion, loss of fertility and the continuing speed of urbanization are major threat to the sustainability of soil resources in Nigeria (Bankole, 2005). Wide varieties of waste are dumped on soils, a dumpsite may consists of plastics, discarded cans and cartoons, tins, pail, motor and machine parts, dry cells, paints etc.

In addition, increased automobile repairs/workshops activities in Nigeria due mainly to large inflow of used Tokunbo vehicles into the country in the late 1990s contributed markedly to the problem of soil contamination in most cities. Automobile used (waste) oil contain oxidation products,

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sediments, water and metallic particles resulting from machinery wears, organic and inorganic chemicals used in oil additives and metals that are present in fuel and transferred to the crankcase during combustion (EEA, 2007). Wear metals are formed in lube oils under the harsh conditions of temperature and pressure that occur in heavy machinery. Under continuous heat and pressure, the surface of the metal piece becomes slightly oxidized, forms salts with the degradation products of the oil and becomes soluble in the oil. The friction of motion in machinery causes micro-fine particles to shear off the surface and become suspended in the oil (Anonymous, 1995a). These wastes including also waste oils used for cleaning during servicing, metal scraps, used batteries etc. indiscriminately discarded on soils by artisans contaminates the soil. Percolation of leachates from these materials poses threats to underground water. While other sources of ground water contamination have been well discussed (Anonymous, 2007), little is mentioned on the impact of automobile artisans' activities on the eco-system.

Earlier study by Kloke (1980), Kabata-Pendias (1995) and Ewer (1991) as quoted by Lacatusu, (1998) were aimed at interpreting the level of soil heavy metals. In addition, the standard employed for interpreting soil heavy metals contamination/pollution varies from country to country based on chosen factors (Lacatusu, 1998).

$$\text{C/P value} = \frac{\text{Actual measurement of metal concentration in soil}}{\text{Target values from reference table}}$$

In this study, similar comparison of heavy metals load in soils were made by using the method adopted by Lacatusu, (1998) in measuring the total heavy metals in soils with Atomic Absorption Spectrometry (AAS), a distinction between soil contamination and pollution range was established by means of the contamination/pollution index C/P (Table 1a). This index represents the metal content effectively measured in soil by chemical analysis and the reference value of contamination obtained using a standard table formulated by the department of petroleum resources of Nigeria (DPR, 1991) for maximum allowable concentration of heavy metal in soil (Table 1b). DPR is part of the governmental bodies concerned with soils and land pollution matters in Nigeria. C/P index values greater than unity (1) defines a pollution range and when lower than unity the contamination range.

Table 1a: Significance of intervals of Contamination/Pollution index (C/P) values

C/P	Significance	Symbols
<0.1	Very slight contamination	vsl
0.10-0.25	Slight contamination	sl
0.26-0.5	Moderate contamination	mi
0.51-0.75	Severe contamination	stl
0.76-1.0	Very severe contamination	vstl
1.1-2.0	Slight pollution	sp
2.1-4.0	Moderate pollution	stp
4.1-8.0	Severe pollution	stp
8.1-16.0	Very severe pollution	vstp
>16	Excessive pollution	ep

Source: Lacatusu (1998)

Table 1b: Department of Petroleum Resources (DPR, 1991) target and intervention values for metals in soil

Metals	Target values (mg kg^{-1})	Intervention values (mg kg^{-1})
Barium	200.0	5000
Cadmium	0.8	17
Chromium	100.0	380
Copper	36.0	190
Mercury	0.3	10
Lead	85.0	530
Nickel	35.0	210
Zinc	140.0	720
Cobalt	20.0	240

The aim of this study is to investigate the profile of heavy metal within mechanic workshops in Akure, with a view to determine the extent of heavy metal pollution. This will provide impetus on awareness of dangers that lies in indiscriminate disposal of used engine and automobile oils.

MATERIALS AND METHODS

The study area is within Akure, the capital of Ondo state, Nigeria (Fig. 1). Five mechanic workshops in the metropolis were selected for the study. The sites were chosen to span a wide area of the town, with ages (period of establishment >15 years, obtained by personal communications with

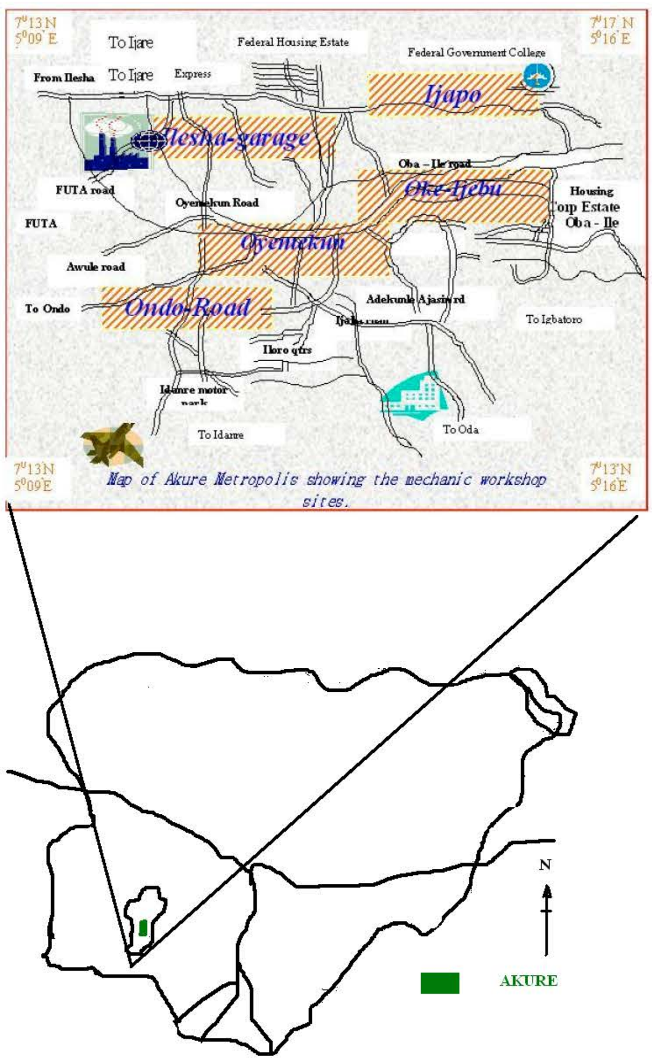

Fig. 1: Map of Nigeria showing the position of Ondo State and study area (Akure)

Table 2: pH of soils and mean concentration of metals (mg/kg) in dry soil samples of five sites

Codes	Site name	Depths (cm)	pH	Ba	Ni	Pb	Cr	Cu	Fe	Co	Zn
(A)	Oye mekun	0-15	8.55	54.02	62.06	70.80	42.50	76.40	561.53	74.44	391.57
07.25°N,			(0.02)	(0.15)	(0.84)	(0.16)	(0.31)	(0.80)	(0.18)	(0.72)	(0.36)
05.18°E		15-30	6.50	44.48	41.47	103.62	65.38	40.15	557.93	63.19	322.67
			(0.09)	(3.02)	(3.71)	(11.23)	(6.62)	(0.79)	(7.23)	(5.24)	(4.85)
		30-45	6.30	72.89	32.82	118.05	17.00	45.53	574.77	75.75	300.30
			(0.47)	(3.42)	(8.47)	(2.53)	(9.44)	(0.69)	(0.74)	(9.30)	(1.90)
		45-60	6.09	40.84	13.11	101.84	12.84	37.64	567.57	109.36	298.68
			(0.03)	(9.99)	(1.35)	(6.43)	(2.24)	(8.05)	(8.77)	(3.91)	(2.43)
(B)	Oke-Ijebu	0-15	8.41	77.57	28.79	101.4	81.60	85.58	384.08	6.70	489.7
07.28°N,			(0.02)	(1.13)	(8.49)	(8.72)	(1.33)	(0.43)	(3.40)	(1.60)	(9.08)
05.21°E		15-30	8.03	69.65	19.49	102.2	85.10	69.45	549.27	66.89	385.98
			(0.01)	(3.43)	(1.89)	(1.71)	(5.51)	(1.59)	(9.10)	(58.14)	(8.33)
		30-45	7.42	80.44	40.01	(0.37)	97.30	43.44	479.40	42.33	385.6
			(0.01)	(4.89)	(1.37)	133.3	(8.15)	(2.90)	(18.67)	(1.71)	(3.66)
		45-60	7.78	79.14	32.66	123.2	82.49	66.29	459.27	45.18	454.84
			(0.03)	(2.37)	(1.21)	(2.35)	(8.24)	(8.23)	(56.47)	(9.52)	(56.67)
(C)	Ijapo	0-15	7.77	32.24	51.73	192.03	181.80	113.18	581.33	23.55	755.37
07.26°N,			(0.26)	(8.22)	(2.90)	(59.42)	(2.31)	(36.15)	(4.89)	(4.79)	(5.64)
05.22°E		15-30	7.11	64.74	21.36	292.35	122.30	66.25	570.76	54.69	724.17
			(0.50)	(37.42)	(7.89)	(7.90)	(5.84)	(7.22)	(9.86)	(9.78)	(8.48)
		30-45	5.79	79.17	47.26	168.00	64.05	61.22	549.5	41.34	465.03
			(0.50)	(5.89)	(1.52)	(1.01)	(1.01)	(5.79)	(52.65)	(4.31)	(10.00)
		45-60	6.60	96.65	40.00	208.77	91.97	78.53	572.49	30.97	601.79
			(0.09)	(5.83)	(1.74)	(0.51)	(1.85)	(3.13)	(9.25)	(3.65)	(16.46)
(D)	Ilesha	0-15	7.98	113.45	28.21	170.57	21.50	151.43	634.30	ND	782.23
07.27°N,	Garage		(0.03)	(1.53)	(6.28)	(4.10)	(1.02)	(28.73)	(10.24)		(27.06)
05.17°E		15-30	7.57	115.38	53.78	200.13	19.60	130.50	614.50	ND	730.97
			(0.43)	(5.16)	(6.84)	(10.82)	(1.53)	(1.83)	(54.68)		(75.38)
		30-45	6.45	118.86	54.25	207.57	46.24	124.19	599.07	ND	627.27
			(0.41)	(9.43)	(1.50)	(2.70)	(1.31)	(6.27)	(7.02)		(13.87)
		45-60	5.96	133.09	38.03	215.44	26.67	93.26	597.10	ND	633.10
			(0.09)	(7.11)	(7.36)	(32.34)	(4.41)	(3.79)	(11.34)		(16.46)
(E)	Ondo	0-15	8.39	73.99	46.65	188.93	57.87	40.72	382.20	92.33	495.97
07.26°N,	Road		(0.07)	(4.89)	(2.89)	(6.72)	(1.31)	(1.82)	(4.31)	(3.46)	(2.64)
05.17°E		15-30	8.43	71.55	44.34	213.87	32.34	28.34	389.73	61.24	397.30
			(0.030)	(2.40)	(1.53)	(32.27)	(5.84)	(7.22)	(31.94)	(9.78)	(6.61)
		30-45	8.29	45.36	29.03	229.53	44.05	26.22	393.97	41.34	303.17
			(0.02)	(8.79)	(5.02)	(29.49)	(1.01)	(4.79)	(24.87)	(2.31)	(10.40)
		45-60	8.11	36.65	24.25	242.77	91.97	21.13	398.03	30.97	286.40
			(0.01)	(1.31)	(1.73)	(37.28)	(1.59)	(1.13)	(3.17)	(1.65)	(12.46)

ND: Not Detected; Values in brackets are standard deviation of triplicate measurements

the artisans working on these sites.). In this study, we have not considered the type of vehicle serviced in each station. Geographical coordinates (Table 2) were obtained using a global positioning system (Gamin GPS 12 model).

At each site, three different points were random systematically chosen for sampling. Four soil samples per points were collected at depths 0-15, 15-30, 30-45 and 45-60 cm using standard soil (Hand) Auger. The collected soil sample at each boring (about 10 kg) were transferred into a black polythene bag, properly labelled before transported into the laboratory (Aller, 1989). After series of quartering, 500 g of the collected soil samples were air-dried for a period of a week in a well-ventilated space (Boulding, 1994). However, we assume that there was no remarkably difference between soils from farmlands and soils from distances more than 100 m radius distance from automobile workshops.

Moisture content of the samples was determined using standard gravimetric procedures and pH was determined using a Corning 350 model pH meter.

Ten gram of the well-dried sample was ground in a mortal and sieved to fineness. Using the hydrofluoric acid-aqua regia system in a water bath at 60°C for 3 h, an acid digest was obtained. Twenty milliliter saturated boric acid mixture was added to complex with residual acid. The digested sample was filtered into a 50 mL standard flask using a Whatman No. 1 filter paper and made up to mark with distilled water.

Buck scientific model 200A Atomic Absorption Spectrophotometer (AAS) was used for metal analyses (Anil, 1986). The wavelength of metals determination ranges between 214 nm for Zn and 553 nm for Ba. Seven heavy metals; Cr, Cd, Co, Cu, Fe, Pb, Ni and Zn were analyzed in a premixed air-acetylene flame, while N_2O/acetylene flame was used for Ba. The signal levels for all determination were significantly higher than the detection limits of each metal calculated by the 3-sigma detectability method. Recovery test was not used the AAS method described above.

RESULTS AND DISCUSSION

The age of the mechanic workshops seems to have direct relationship with concentration of total heavy metal status for each site. Site B that has the lowest age of establishment (15 years) had the least pollution status (Table 2 and Fig. 2). Following the same line of argument, we expected site D with the highest age of 23 be ranked the most polluted site (Fig. 2), rather site C of age 18 years. This implies that other factors not determined in this study like volume of work done on each site, types of automobile serviced or repair and type of soil and so on might be important factors for consideration.

As shown in Table 3, the pH values vary from depths to depths on each site and within the sites. pH values ranged between 5.79 and 8.55. Highest pH was obtained in site A and the lowest from site C. The values obtained compared well with the results obtained previously for soils in Akure (Ogundare, 1998). It is a fact that pH is an important soil property, having great effects on solute concentration and sorption/desorption of contaminant in soil (Kadem *et al.*, 2004). High pH might reduce the mobility of some metal species down the soil strata while low pH values usually enhance metal distribution and transport in soil. The closeness of the pH values obtained for the soils may suggest an indication that pH effect on the availability of the metals is minimal and so do not affect site

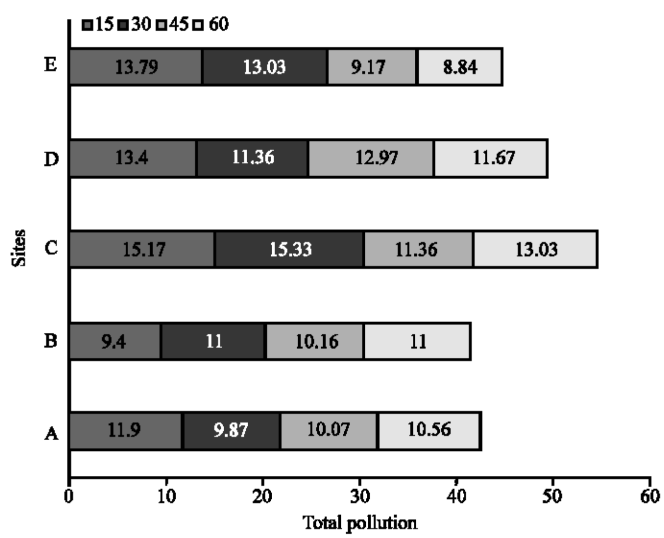

Fig. 2: Heavy metal pollution profile showing total pollution by sites and depths

Table 3: Total heavy metal concentrations in the five sites

Sites	Ba	Cd	Co	Cr	Cu	Fe	Ni	Pb	Zn
A	53.06^{a}	0.00	80.69^{c}	34.43^{a}	49.93^{ab}	565.45^{c}	37.37	98.58^{a}	328.31^{a}
B	76.70^{a}	0.00	40.28^{b}	86.62^{b}	66.19^{b}	428.00^{b}	30.24	115.04^{a}	429.03^{a}
C	69.70^{b}	0.00	37.64^{b}	115.03^{bc}	79.80^{b}	568.51^{c}	40.09	215.29^{b}	636.59^{b}
D	120.20^{b}	0.00	0.00^{a}	28.50^{a}	124.84^{c}	611.24^{c}	43.57	198.43^{b}	693.39^{b}
E	56.89^{a}	0.00	56.47^{bc}	56.56^{ab}	29.10^{a}	390.98^{a}	36.07	218.78^{b}	370.71^{a}

Data are means of four determinations (depths) in sites. Same superscripts in a row are not significantly different at ($p \leq 0.05$), Duncan multiple Range test

characterisation. It is worth noting that in sites C and D, the lower pH values may be responsible for the higher concentrations of some heavy metals between depths 30-60 cm and the resultant high pollution status rating obtained.

Table 3 shows the distribution of heavy metals within the sites and depths of the soils in all the sites. As observed, Fe and Zn are predominantly presents in all the sites with high concentrations of Fe being 634 mg kg^{-1} in site D at depth 15 cm while the lowest concentration is 382 mg kg^{-1} in site E, depth 15 cm. Zn highest concentration was found in site D at depth 15 cm to be 782 mg kg^{-1} while but with lowest concentration of 286 mg kg^{-1} found in site E, depth 60 cm. The abundance of these two metals might be due to their relative abundance in soil, or the anthropogenic source from the metal junkyard found in many of the auto mechanic site. Used oils that sink into the ground as leachates contain high proportions of these metals. Cu, Pb and Sb from babbit metal bushings, Cr and Mo from piston rings and seals, Cu and Sn from metal bearing wears, Ni and Fe from crankshafts wear and engine body damage (Anonymous, 1995).

Next in abundance to Fe and Zn is Pb. It is reported that Pb has the highest compositions of heavy metals in waste oil (Anonymous, 1995a) The highest concentration of Pb found in site E; depth 60 cm is 242.77 mg kg^{-1}, the lowest was in site A; depth 15 cm. Generally, lead added to gasoline in tetra ethyl form as anti-knock agent can be deposited from exhaust pipes in automobiles (Jensen, 1992). Unlike Fe and Zn, lead distribution follows a regular pattern of increase down the depths in all the sites with only few exceptions.

Ba, Co, Cr and Cu seem to have same concentrations in all sites but with irregular distribution down the depths. Cd was below the detection limit (not detected) of the instrument used for the metal analysis. Also Co was not detected from site D, this is surprising as all other sites had Co. Ni concentration was lowest in all the sites considerably compared with others (Table 1).

To understand the variation of the metal concentrations down the depths, Table 3 shows the statistical multivariate comparison of the metals using the Duncan multiple range test. Metals with the same superscript in a row are not significantly different at ($p \leq 0.05$). To explain the heavy metal profile on the sites, an appraising method by calculating the C/P index values for each metal in each site was calculated. Table 4 shows the C/P index distribution for different depths in all sites. Unlike the pattern observed in Table 2, there is much difference between the concentration of a metal in soils and the potential threat pose by them expressed through their C/P index value. Lacatusu (1998) established that the C/P value index is directly proportional to the level of contamination and pollution of specific metal species in each case. Higher values >1 indicate higher risks while lower values <1 connote minimal risk to the environment (Table 1).

Fe being relatively abundant in nature has no C/P value. As the lists of standards formulated by directorate for petroleum resources in Nigeria (DPR, 1991) also excludes Fe. However, discussion of Fe toxicity in this regards to environmental exposure does not exclude Fe as a heavy metal of great concern (Anonymous, 1995b), ingesting dietary iron supplements may acutely poison young children (e.g., as few as five to nine 30 mg iron tablets for a 30 lb child).

Table 4: Heavy metal pollution profile showing total pollution by sites and depths calculated from total heavy metals c/p index values (Lacatusu, 1998)

Depth/Site (cm)	Oyemekun	Oke-Ijebu	Ijapo	Ilesha garage	Ondo road
0-15	11.90	9.40	15.17	13.40	13.79
15-30	9.87	11.00	15.33	11.36	13.03
30-45	10.07	10.16	11.36	12.97	9.17
45-60	10.56	11.00	13.03	11.67	8.84
Total	42.40	41.56	54.89	49.40	44.83

Table 4 shows the profile of the heavy metals in the five sites. To obtain a profile, the total pollution ranges defined by multiple pollution found from contribution from each metal contamination/pollution status were used. The observed trend from site A, C to E, shows that the top is heavily loaded with heavy metals than the sub-soil. In contrast, site B profile shows that the sub-soil is heavily loaded than the topsoil. Site C has the highest total contribution to pollution by heavy metals, followed by sites D, E, A and B the least. Due to multiple pollutions, all the sites were characterized as severely polluted with respects to the eight heavy metals. It is one's candid opinion however that the observed trend in the profile is subjected to varying factors such as age of site, type of soil formation and possibly the workload of automobile activity on the sites.

CONCLUSIONS

Since the identification of type of contaminant, concentration and vertical distribution is an input for modelling, also the knowledge of type, depth, volume and concentration seems to be starting point for selection and design of remediation variables in modelling.

Mechanic workshops situated within the metropolis are anthropogenic sources of heavy metals in soil. They may pose serious threat to the underground water plume which will ultimately affects public health. Stricter environmental laws is to be observed in this regard to curb this menace and all stakeholders involved in the use of auto-mechanic workshops need be alerted of the impending dangers looming from indiscriminate heavy metal dumping. To be safe however, auto-mechanic workshops soil should be heavily cemented and proper drainage for used oils, lubricants and spilled gasoline constructed. As a waste to wealth approach, used oil and lubricants may be chemically re-processed to harness these heavy metals in them, under proper environmental practice.

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