Full Length Research Paper

Assessment of Soil-pollution by slag from an automobile battery manufacturing plant in Nigeria

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This study assessed heavy metals pollution of soil by slag from an automobile battery manufacturing plant in Nigeria to ascertain the potential danger they pose on the environment. 84 soil samples were randomly collected at 0 - 15 cm and 15 - 30 cm depths from the premises of the plant and an uncontaminated site as control for both dry and wet seasons. Samples were analyzed for lead, cadmium, chromium and nickel using standard analytical methods. Lead level in soil ranged from 243 to 126000 mg/kg on the premises of the manufacturing plant with about 98% of all soil samples analyzed having levels higher than 400 mg/kg permissible level for Pb in soil. Lead levels for both seasons and depths were statistically comparable (p > 0.05). Cadmium, chromium and nickel were within the permissible limits in soil. Speciation of Pb showed about 89% Pb in non residual phases implying high availability to ecological materials. Soil within the company's premises and the environs needs to be urgently cleaned up.

Key words: Heavy metals, automobile-battery, speciation, slag, pollution.

INTRODUCTION

In the global world today, various types of activities, including agriculture, industry and transportation produce a large amount of wastes and new types of pollutants. Since antiquity, soil has been the repository of society's wastes (Evans, 1989). The commonest kinds of waste can be classified into 4 types: Agricultural, industrial, municipal and nuclear (Alloway, 1995).

For thousands of years, people have extracted lead (Pb) from ores for use in a variety of products. World use of primary metallic Pb in 1999 showed that lead battery consumed the highest percentage of 71%, pigments 12%, extrusions 7%, ammunitions 6% and cable sheathing 3% (Technical Workshop Group, 2001).

Wastes from automobile battery manufacturing companies (ABMC) are known to release a high percentage of lead on soil (Greenpeace International, 1991 - 1993) and these wastes are reported to be responsible for some of the World's most polluted sites. The following are some of the reported cases. A recent survey showed that

Kabwe in Zambia, home to 300,000 people, is Africa's most polluted city and ranked as the world's fourth most polluted site (IRIN, 2007). Kabwe has Africa's largest lead mine with smelting operation that lasted till 1994, but have left a city poisoned from debilitating concentrations of lead in the soil and water from slag heaps that were left as reminders of the smelting and mining era (IRIN, 2007). A survey of a community near a previously active auto battery recycling smelter in Haina near Santo Domingo, Dominican Republic revealed this community as the World's third most polluted site with at least 28% of children requiring immediate health attention. Out of these, 5% (with lead levels >70 μg/dL) are at risk of severe neurological sequelae (Balkrishena et al., 1999).

High levels of heavy metal pollution at a site in southern France: A medieval metallurgical workshop has been reported by Evanhoe (2006). The lead, antimony, arsenic, copper and zinc residues left behind there more than 800 years ago still pose a potential health threat. A survey was also made of the concentrations of EDTA-extractable lead, zinc, cadmium and copper in surface soils at 472 sites surrounding an isolated lead smelter at Port Pirie, Southern Australia. Contamination declined exponentially with distance near the smelter, but was

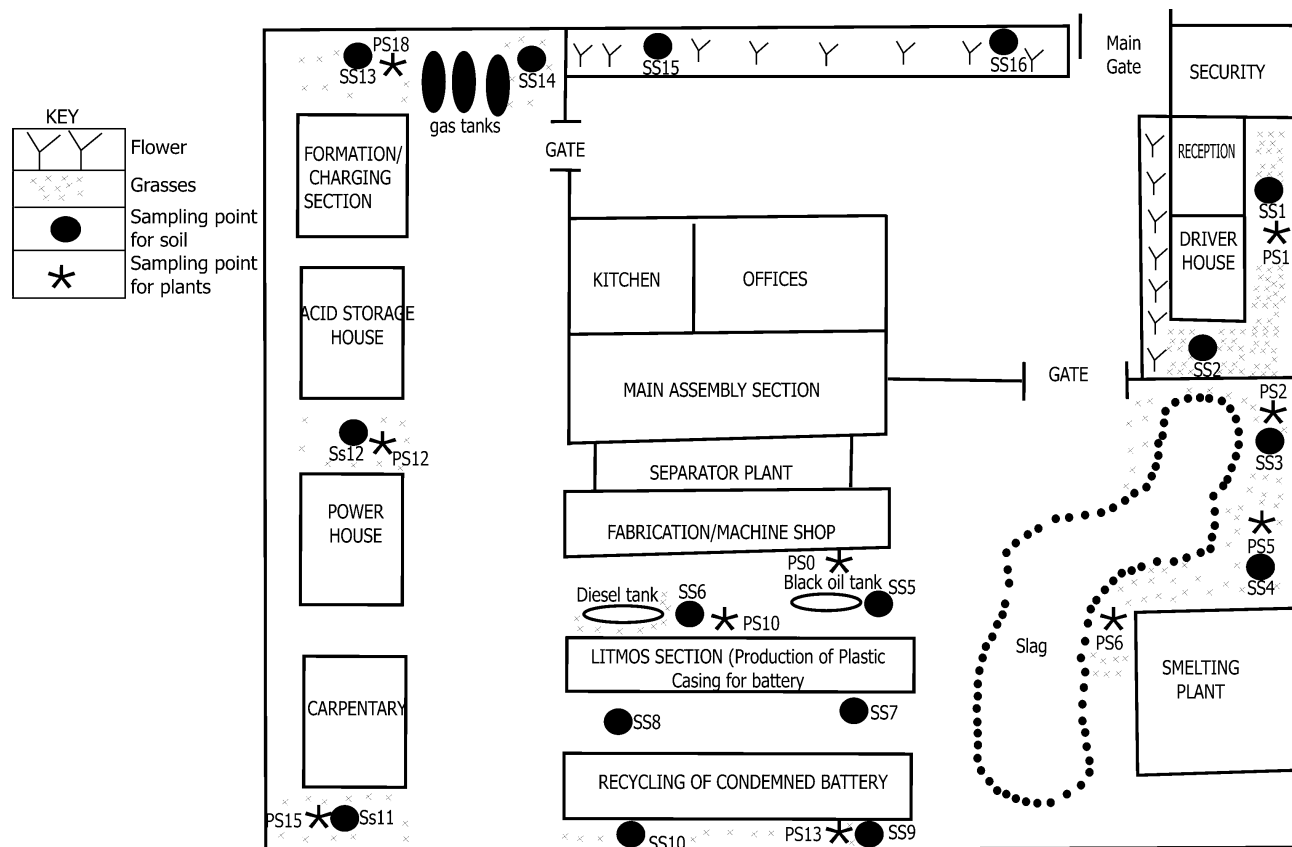*Corresponding author. E-mail: gildie1975@yahoo.com. Tel.: +2348059998665

Figure 1. A map showing the location of the sampling points.

detectable up to 40 - 65 km from the source depending upon direction of the surface winds (Cartwright et al., 1977). Composite soil samples taken from 91 allotments around the Hope Lead Mine area, which has become a residential district in Jamaica showed values of <2 – 220 mg/kg for cadmium, 6 – 38,000 mg/kg for lead and 66 – 40,000 mg/kg for zinc and blood lead levels for 33 children aged between ten months and 7 years were in the range 5.7 - 57 mg dL^{-1}. The soil contents of cadmium and lead in at least 2 areas suggested urgent remediation action (Anglin-Brown, 1995).

Slag from ABMC has been reported in Nigeria to contain about 6% upwards of lead (Basel Convention, Nigeria, 2004). Slag is a by-product formed from thermal reduction of metallic ores in the smelting plant. This term is also applied to similar materials produced in other operations like coal combustion, incineration, industrial waste sludge (Szente et al., 1998) and phosphorus production (Busch, 2000). Other sources of lead from ABMC are particulates that go off with smoke during smelting operations and later resettle on soil and lead that comes from scrap battery wastes (that is, batteries that fail the quality assurance tests and batteries that are returned from customers to be recycled).

Contamination of the environment with heavy metals from anthropogenic sources is of major concern because of their toxicity and threat to human life and the en-

vironment (Balkrishena et al., 1999; Caselles et al., 2004; Razo et al., 2004; Lu et al., 2005; Iwegbue et al., 2006; Chen et al., 2009; Hartley et al., 2009; Zhao et al., 2009).

Nigeria has 3 well-known automobile battery manufacturing companies. Exide Battery, Ibadan -The biggest in West Africa in the 90s, now abandoned; Union Battery Company, Nnewi and Metropolitan Battery, Ota still in operation. These companies dump the slag from smelting operations either in near- by bushes or on the premises. Enough work has not been done in the three sites to ascertain the pollution posed on the entire ecosystem by the slag. The objectives of this research were; (1) to determine the levels of lead and other heavy metals in the soil within the premises of the Metropolitan Battery Company in Ota and; (2) to proffer recommendations for the recycling and remediation of the slag and soil respectively.

MATERIALS AND METHODS

Description of study area

Metropolitan Battery Company (MBC), Ota, Ogun State, Nigeria is situated in the outskirt of a fast growing Ota town in the Western part of Nigeria. The company is surrounded by residential settlements. A map showing the location of the sampling points is shown in Figure1. The control site was an undeveloped area located about

Table 1. Summary of soil properties for dry and wet seasons.

Sample	Depth (cm)	pH	CEC (mmol$_c$/kg)	Organic carbon	Sand	Clay	Silt	Pb	Cd	Cr	Ni
				%				mg/ kg			
Control (n = 3)	0-15	5.81 ± 1.42 [5.78 ± 1.41]	2.01 [2.02]	0.74 ± 0.11 [0.75 ± 0.15]	72.0 [71.9]	21.1 [21.3]	6.9 [6.8]	9.61 ± 0.84 [6.31 ± 1.70]	0.25 ± 0.07 [0.35 ± 0.07]	131 ± 15.56 [135 ± 2.12]	BDL [BDL]
	15-30	5.82 ± 1.65 [5.30 ± 0.93]	4.21 [4.15]	0.87 ± 0.21 [0.83 ± 0.21]	72.6 [72.9]	20.4 [20.3]	7.0 [6.8]	9.78 ± 1.73 [4.85 ± 3.32]	0.15 ± 0.07 [0.33 ± 0.04]	135 ± 42.43 [130 ± 43.13]	BDL [BDL]
Premises (n = 18)	0-15	6.74 ± 0.74 [6.19 ± 0.92]	6.81 [6.49]	1.34 ± 0.67 [0.98 ± 0.51]	71.2 [69.4]	17.9 [21.9]	10.9 [8.9]	31485 ± 39562 [6289 ± 4370]	4.57 ± 8.91 [5.34 ± 8.21]	249 ± 52.81 [219 ± 76.31]	5.24 ± 18.71 [0.45 ± 1.66]
	15-30	6.75 ± 0.75 [6.10 ± 0.90]	4.18 [1.48]	1.11 ± 0.61 [0.74 ± 0.42]	66.2 [71.7]	23.3 [20.6]	10.5 [8.9]	5423 ± 4066 [4066 ± 3641]	3.10 ± 5.69 [1.56 ± 1.78]	236 ± 50.97 [208 ± 72.78]	1.44 ± 4.07 [BDL]

Dry season (wet season) BDL – below detection limit.

20 km from the site, but within the same geographical area as the site.

Soil sampling, preparation and analyses

Eighty soil samples were randomly collected within and around the polluted premises of MBC and 4 soil samples were collected from an uncontaminated site as control within the same geographical area for both dry and wet seasons and at 0 - 15 cm and 15 - 30 cm depths. Soil samples from the top layer (0 - 15 cm) and sub layer (15 - 30 cm) were sampled separately, dried for 8 days, ground using agate mortar and sieved with a 0.5 mm mesh size sieve to remove stones, plant roots and have soil of uniform particle size. Soil samples were packed in polythene bags and kept in a dry place until analyses.

Air dried soil samples (~1 g each) were accurately weighed into series of 100 ml beakers and 10 ml each of 2MHNO$_3$ was measured with a 10 ml pipette into each of the beakers (with watch glass covers) containing the soil samples. These were shaken properly and transferred to a water bath, which was now boiling at 100 ± 3^{0}C. There was intermittent shaking of the beakers with their contents after every 20 min. Acid - extractable Pb, Cd, Cr and Ni were leached for 2 h. The contents were filtered through Whatman's No.1 filter paper and diluted with deionized water to give final volumes depending on the suspected level of the metals. The metals were analyzed with Perkin Elmer Analyst 200 Flame Atomic Absorption Spectrophotometer (2003 model). A reagent blank sample was taken through the method, analyzed and subtracted from the samples to correct for reagent impurities and other sources of errors from the environment. Other parameters determined on the soil samples included: pH which was determined with a calibrated Jenway glass electrode pH meter on 1:1 soil: deionized water extracts (IITA, 1979), percentage organic carbon was determined using Walkey - Black method (1934), cation exchange capacity (CEC) was determined according to Stewart (1989), particle size analysis was determined using the hydrometer method (IITA, 1979) while Speciation of Pb in soil was done using Tessier et al. (1979).

Quality control/assurance

Soil samples were collected with plastic-made implements to avoid contamination. Samples were kept in polythene bags that were free from heavy metals and organics and well covered while transporting from field to the laboratory to avoid contamination from the environment. Reagent blanks were used in all analyses to check reagent impurities and other environmental contaminations during analyses. Analytical grade reagents were used for all analyses. All reagents were standardized against primary standards to determine their actual concentrations. All glassware used were soaked in appropriate dilute acids overnight and washed with teepol and rinsed with deionised water before use. All instruments used were calibrated before use. Tools and work surfaces were carefully cleaned for each sample during grinding to avoid cross contamination. Duplicate samples were analyzed to check precision of the analytical method and instrument. To validate the analytical procedures used, the spike recovery test was conducted on some soil samples for Pb, Cd, Cr and Ni.

RESULTS AND DISCUSSION

A statistical summary of soil properties for both dry and wet seasons at 0 - 15 cm and 15 - 30 cm depths is presented in Table 1. Table 2 presents the soil quality criteria in some countries. The assessment of heavy metal contamination using Geoaccumulation Index (Igeo) is presented in Table 3. Table 4 shows the speciation of Pb in some soil and raw slag samples. The correlation of the various parameters carried out on soil samples for both seasons and depths is presented in Tables 5 - 6. Tables 7 - 10 present comprehensive results of the recovery tests on some soil samples. A map showing the location of

Table 2. Soil quality criteria of some countries.

Country/Definition	Pb(mg/kg)	Cd (mg/kg)	Cr(mg/kg)	Ni (mg/kg)	Reference
Norway	50	1.0	100	30	Reimann et al.,1997
Netherlands (action level)	530	12	380	210	Reimann et al.,1997
Netherlands (further investigation)	310	6	240	120	Reimann et al.,1997
Switzerland (guide level)	50	0.8	-	-	FOEFL, 1987
Canada (residential)	140	10	64	50	CCME, 1999
Canada (agricultural)	70	1.4	64	50	CCME, 1999
Canada (commercial)	260	22	87	50	CCME, 1999
Canada (industrial))	600	22	87	50	CCME, 1999
This study (mean ± Standard deviation)*	4904 ± 3545	4.34 ± 1.14	228±18	1.78 ± 2.38	This study
This study (Range)*	243 - 129000	0.2 - 34.90	50-309	BDL - 18.7	This study
This study (Control)	7.64 ± 2.45	0.27 ± 0.08	131±2.6	BDL	This study

(Source: Onianwa, 2001).* Mean for both seasons and depths. BDL – below detection limit.

Table 3. Assessment of heavy metal contamination using Geoaccumulation Index (i_{geo}).

Code↓	Pb (mg/ kg)				Cd (mg/ kg)				Cr (mg/ kg)			
Season→	Dry		Rainy		Dry		Rainy		Dry		Rainy	
Depth (cm)	0-15	15-30	0-15	15-30	0-15	15-30	0-15	15-30	0-15	15-30	0-15	15-30
SS1	8.6	7.2	8.2	6.9	1.4	-1.3	1.4	1.8	-0.0	0.6	0.2	0.7
SS2	10.7	11.3	10.61	12.1	3.7	1.3	3.0	3.1	0.5	-0.0	-0.4	0.2
SS3	13.0	13.0	11.2	11.2	5.3	-0.01	4.4	3.8	0.5	0.4	0.3	-0.1
SS4	12.0	11.8	12.7	13.1	5.8	1.8	-0.9	-0.2	0.1	-1.1	0.2	-0.3
SS5	12.1	12.1	12.4	12.6	2.7	0.3	5.7	6.3	-0.7	-0.7	-0.8	0.6
SS6	11.8	11.8	12.6	12.4	0.9	-1.0	0.7	0.5	0.4	0.3	-0.7	-0.4
SS7	9.0	8.4	7.2	8.7	0.4	-1.8	3.5	2.8	0.4	0.3	-1.2	0.5
SS8	7.3	6.1	6.9	6.6	1.2	-0.8	1.8	2.1	0.5	0.3	0.1	-0.7
SS9	9.6	9.4	8.4	8.9	1.2	-0.3	2.6	4.2	0.6	0.4	0.5	-1.0
SS10	9.1	8.8	8.9	8.2	1.2	-1.8	1.8	2.5	0.6	0.3	0.6	-0.4
SS11	8.7	4.6	7.0	7.6	0.6	-2.0	0.1	0.4	0.3	0.3	0.2	0.3
SS12	11.4	11.1	11.7	10.5	0.8	-2.4	0.9	1.6	0.3	0.5	-0.8	-0.7
SS13	9.4	9.0	8.9	7.5	0.2	-2.0	0.9	1.2	0.4	0.3	-0.3	-0.3
SS14	9.4	9.3	10.2	10.3	1.2	-0.7	1.4	1.2	-0.5	0.2	0.6	-0.4
SS15	7.6	6.5	8.2	5.1	1.2	-1.8	0.9	1.6	0.5	0.2	0.1	0.2
SS16	8.3	7.4	7.6	7.6	3.8	-2.4	1.9	1.3	0.4	0.3	0.5	0.5
SS17	9.8	10.1	10.5	10.6	0.7	-2.0	2.0	2.5	0.6	0.3	0.6	0.6
SS18	13.1	13.1	11.5	11.5	5.1	-0.7	6.5	6.4	0.7	0.2	0.6	0.7
SS19	7.1	7.4	8.6	8.2	0.2	-0.7	0.4	1.9	0.03	-0.4	0.3	-0.3
SS20	5.4	5.7	8.7	6.4	1.7	-2.4	0.4	1.0	-0.7	-1.3	-0.8	-2.0
SS21	6.3	7.3	9.4	8.1	2.0	-2.0	2.4	1.8	-0.5	-0.9	-0.7	-0.6

I_{geo} is classified into six descriptive classes as follows: < 0 = practically uncontaminated; 0-1= uncontaminated to slightly uncontaminated; 1-2 = moderately contaminated; 2-3 = moderately to highly contaminated; 4-5 = highly to very highly contaminated; >5 = very highly strongly contaminated.

Table 4. Metal speciation of Pb in soil (% in the various phases)

	Exchangeable	Carbonate-bound	Reducible	Oxidisables	Residual	Total
	Pb (%)					
S_1	2.91	20.2	25.0	21.1	30.8	100
S_2	4.85	3.13	82.2	6.01	3.83	100
S_3	8.81	52.8	32.0	6.40	3.22	103
S_4	16.5	28.5	37.5	10.3	7.21	100
S_5	28.6	26.6	32.9	3.89	7.99	100
S_6	25.0	30.4	33.2	3.50	7.91	100
S_7	24.4	56.2	13.3	3.95	2.26	100
S_8	7.05	12.6	72.1	5.67	2.56	100
S_9	3.76	53.0	30.3	3.18	9.82	100
S_{10}	10.7	16.3	20.7	14.6	37.7	100
S_{11}*	1.58	2.10	11.3	19.0	66.0	100
Mean ± SD	13.3 ± 9.7	30.0 ± 18.0	37.9 ± 22.0	7.85 ± 5.85	11.3 ± 12.5	100 ± 1

* Raw slag SAMPLE (not included in the mean). All samples were analysed in duplicate with RSD <10%.

Table 5. Correlation of physico-chemical properties of soil for dry season at 0 – 15 cm depth.

	pH	O.C	CEC	Sand	Clay	Silt	Pb	Cd	Cr	Ni
pH	1	0.92	0.87	-0.17	-0.37	0.71	0.92	0.92	0.97	0.91
O.C	0.80	1	0.99	0.24	-0.72	0.38	0.69	0.85	0.79	0.67
CEC	-0.25	-0.78	1	0.35	-0.79	0.27	0.61	0.78	0.72	0.58
Sand	-0.74	-0.99	0.84	1	-0.85	-0.81	0.53	-0.32	-0.40	-0.56
Clay	0.63	0.97	-0.91	-0.99	1	0.37	0.00	-0.24	-0.15	0.03
Silt	0.87	0.99	-0.69	-0.98	0.93	1	0.93	0.81	0.86	0.94
Pb	0.99	0.76	-0.19	-0.70	0.58	0.84	1	0.97	0.99	0.99
Cd	0.99	0.86	-0.34	-0.80	0.70	0.91	0.99	1	0.99	0.96
Cr	0.90	0.98	-0.65	-0.96	0.91	0.99	0.87	0.94	1	0.99
Ni	0.96	0.94	-0.51	-0.90	0.82	0.97	0.94	0.98	0.97	1

Correlation of physico-chemical properties of soil for dry season at 15 – 30 cm depths. O.C – organic carbon, CEC – cation exchange capacity.

Table 6. Correlation of physico chemical properties of soil for wet season at 0 - 15 cm depth.

	pH	O.C	CEC	Sand	Clay	Silt	Pb	Cd	Cr	Ni
pH	1	0.78	0.46	-0.28	0.22	0.34	0.96	0.91	0.98	0.86
O.C	-0.07	1	0.92	-0.82	0.78	0.85	0.92	0.46	0.63	0.35
CEC	-0.39	0.94	1	-0.98	0.92	0.99	0.69	0.06	0.26	-0.06
Sand	-0.29	0.93	-0.77	1	-0.99	-0.99	0.53	0.14	-0.06	0.26
Clay	0.13	0.98	0.86	-0.99	1	0.99	0.48	-0.20	0.00	-0.31
Silt	0.97	0.17	-0.16	-0.51	0.36	1	0.58	-0.08	0.12	-0.20
Pb	0.98	0.26	0.57	0.10	0.07	0.91	1	0.77	0.88	0.69
Cd	0.96	-0.36	-0.65	0.00	-0.17	0.86	0.99	1	0.98	0.99
Cr	0.73	-0.74	-0.92	0.45	-0.58	0.55	0.85	0.90	1	0.95

Correlation of physico chemical properties of soil for wet season at 15 – 30 cm depth. O.C – organic carbon, CEC – cation exchange capacity.

Table 7. Recovery studies on lead (Pb) in soil.

Sample No.	Original Sample Concentration (µg/g)	Mass of sample Spiked (g)	Concentration of Standard spiked (µg/ml)		Volume of Standard spiked (ml)		Increased Concentration achieved (µg/g)		Total Concentration Expected (µg/g)		Recovery %	
			a	b	a	b	a	b	a	b	a	b
Sample 1	557	5	2500	5000	1.0	1.0	1090	1560	1060	1560	103	100
Sample 2	626	5	2500	5000	1.0	1.0	1190	1650	1130	1630	105	101
Sample 3	508	5	2500	5000	1.0	1.0	1120	1700	1010	1510	111	113
Av Recovery											106	105

a and b are two different concentrations used. Samples 1 –3 are replicates.

Table 8: Recovery studies on cadmium (Cd) in soil.

Sample No.	Original sample concentration (µg/g)	Mass of sample spiked (g)	Concentration of standard spiked (µg/ml)		Volume of standard spiked (ml)		Increased concentration achieved (µg/g)		Total concentration expected (µg/g)		Recovery %	
			a	b	a	b	a	b	a	b	a	b
Sample 1	0.35	5	50	100	1.0	1.0	11.7	21.5	10.4	20.4	113	105
Sample 2	0.25	5	50	100	1.0	1.0	11.6	19.8	10.3	20.3	113	98.0
Sample 3	0.25	5	50	100	1.0	1.0	8.65	21.4	10.3	20.3	84.4	105
Av Recovery											103	103

a and b are two different concentrations used. Samples 1 –3 are replicates.

Table 9. Recovery studies on chromium (Cr) in soil.

Sample No.	Original sample concentration (µg/g)	Mass of sample spiked (g)	Concentration of standard spiked (µg/ml)		Volume of standard spiked (ml)		Increased concentration achieved (µg/g)		Total concentration expected (µg/g)		Recovery %	
			a	b	a	b	a	b	a	b	a	b
Sample 1	15.0	5	50	50	1.0	1.5	22.2	27.4	25.0	30.0	89	91
Sample 2	12.8	5	50	50	1.0	1.5	20.4	23.8	22.8	27.8	89	86
Sample 3	13.9	5	50	50	1.0	1.5	24.4	26.1	23.9	27.9	101	94
Av Recovery											93	90

a and b are two different concentrations used. Samples 1 –3 are replicates

Table 10. Recovery studies on nickel (Ni) in soil.

Sample No.	Original sample concentration (µg/g)	Mass of sample Spiked (g)	Concentration of standard spiked (µg/ml)	Volume of standard spiked (ml)	Increased concentration achieved (µg/g)	Total concentration expected (µg/g)	Recovery %
Sample 1	3.54	5	50	1.0	12.6	13.5	93
Sample 2	3.50	5	50	1.0	12.1	13.5	90
Sample 3	3.54	5	50	1.0	12.2	13.6	90

Samples 1 –3 are replicates.

the sampling points for soil is presented in Figure 1. Figures 2 – 5 show Pb, Cd, Cr and Ni variations between sampling points and a line graph showing the variation in pH and organic carbon between the sampling points is presented in Figure 6.

Concentration of Pb in soil

Soil samples from the control (Table 1) showed background levels of Pb within the geographical region. These samples showed very low levels of Pb ranging from 2.50 - 11.00 mg/kg. The values were far lower than the maximum permissible limit of 400 mg/kg of Pb in soil (Chen et al., 2003). Other properties of soil were within the same ranges as those from the premises of MBC confirming that control and the MBC were within the same geographical region.

The premises of MBC showed Pb level ranging from 243 – 129000 mg/kg for both seasons and depths with about 97 and 94% samples higher than the maximum permissible level of 400 mg/kg of Pb in soil (Chen et al., 2003) and 1000 mg/kg of Pb in soil respectively defined by US EPA as level that correlates with the critical blood Pb level of 7µgdL-1 (US EPA, 1994) in children. Most soil

samples from MBC also exceeded the lead soil quality criteria of other countries like Norway, Netherlands, Switzerland and Canada as shown in Table 2.

Soil samples from sampling points SS2 – SS 6 (Figure 2) showed moderate to very high levels of Pb in soil. This from all likelihood could have been because of their closeness to the slag dumpsite within the company's premises (Figure 1). Soil from sampling points SS17 - SS18 (Figure 2) also showed high levels of Pb. This could certainly be because these samples were collected from an undeveloped portion of land within the premises of MBC which probably had served in the past as a dumpsite for the slag waste as pieces of weathered slag were found scattered everywhere within this site. The source of Pb in other portions of the premises could be due to leaching, run off or aerial depositions of particulate of Pb from smelting activities (Blair, 1980). Geoaccumulation index (Igeo) rating compares the concentrations in samples with background (control) concentration (Mueller, 1979). Soil samples from MBC premises showed Geoaccumulation index rating for Pb that ranged from 5.1 - 13 for both seasons and depths correlating to a rating of very highly strongly contaminated (Table 3). This confirms high contamination by Pb as seen in Table 7.

Concentration of Cd, Cr and Ni in soil

Cadmium, chromium and nickel levels on average were comparable with background concentrations for both seasons and depths (Table 1). This generally suggests that the sources of these metals may not have been anthropogenic, but rather associated with the natural weathering of the metalliferous parent rock that formed the soil. However, there were anomalously high levels of Cd in samples SS3 - SS4 and SS18 for 0 – 15 cm depth during the dry season and SS5 and SS18 during the wet season (Figure 3). Also, SS5 and SS18 for 15 – 30 cm depth during wet season showed high concentrations of Cd. The corresponding levels of Pb in these samples were also very high. The source could probably be associated with Galena (PbS) alloy as Cd often an impurity in the alloy (Holmes, 1976; Adriano, 1986). Chromium showed concentrations in the soil samples that fluctuated between 50 and 309 mg/kg (Figure 4) and they were comparable with the background levels (Table 1) implying that Cr was from the parent material that formed the soil not from the slag. Nickel was not detected in about 95% of all soil samples. Sampling points SS3 (0 - 15), SS11 (15 - 30), SS18 for 0 – 15 cm depth and SS18 for 15 – 30 cm depth during dry
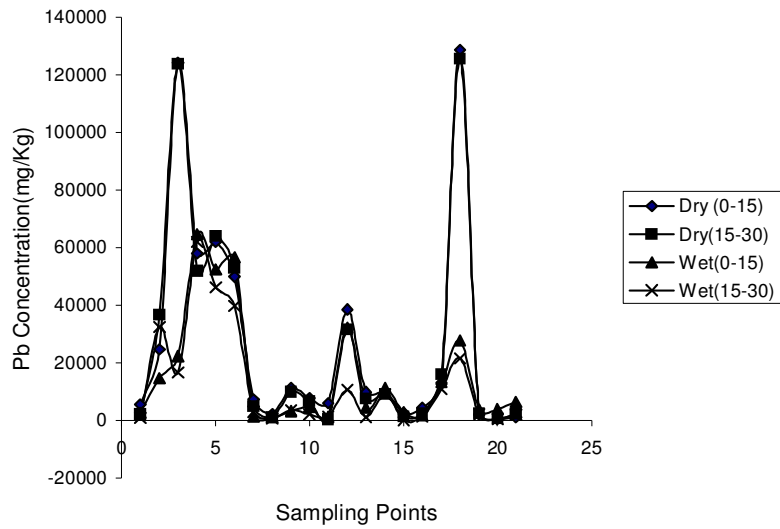
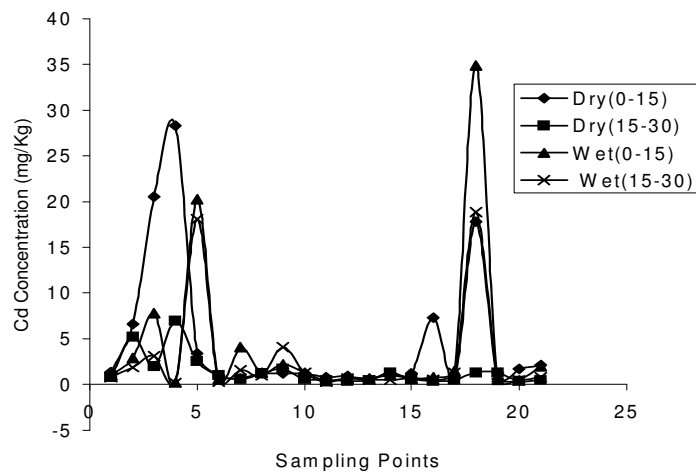**Figure 2.** Graph of lead variation between sampling points.

Figure 3. Graph of cadmium variation between sampling points.
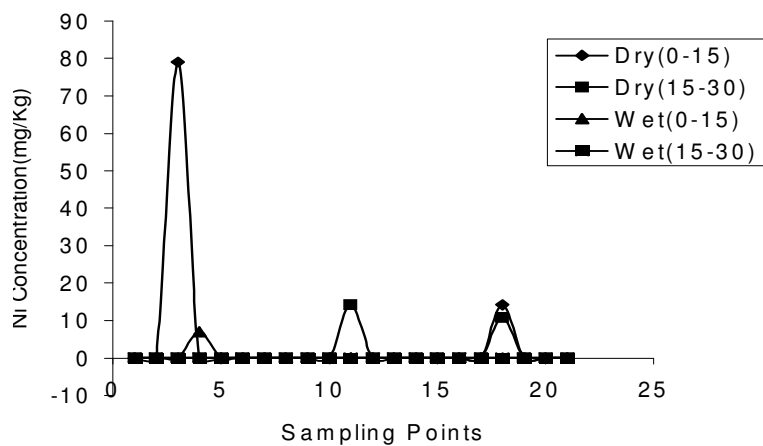
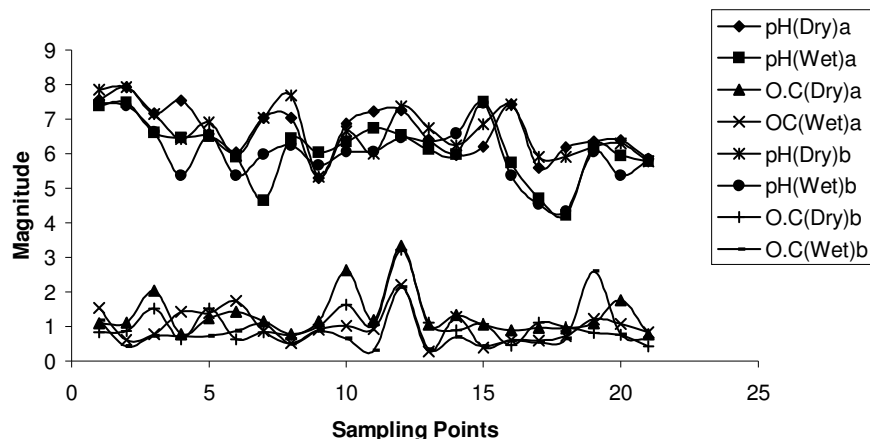**Figure 5.** Graph of nickel variation between sampling points.

Figure 6. Graph showing the variation in pH and Organic carbon within sampling points.
Note: a – 0 – 15 cm depth, b – 15 – 30 cm depth, O.C- organic carbon (%)

season showed Ni levels of 79.00, 14.30, 14.30 and 10.70 mg/kg respectively. Sampling point SS3 for 15 – 30 cm depth during wet season showed Ni level of 7.10 mg/kg (Figure 5). The sources of these Ni levels are non point sources probably associated with the slag because these points are close to the slag waste deposit. The levels of Cd, Cr and Ni were lower than the action limits set by Netherlands, but exceeded criteria set by other countries for certain metals (Table 2) (e.g., the Norwegian criteria for cadmium and chromium were exceeded).

Geoaccumulation index rating revealed that ≈ 45% of the soil samples analyzed showed no contamination of Cd; ≈ 32% showed moderate contamination and ≈ 23% showed high contamination of Cd. This assessment buttresses the explanation given. All the soil samples showed no Cr contamination by the Geoaccumulation index rating assessment.

Other physico – chemical parameters

The averages and ranges in parenthesis of other physico – chemical parameters carried out on soil samples for both dry and wet seasons at 0 – 15 cm and 15 – 30 cm depths for MBC premises were: pH - 6.45 (4.22 - 7.93); organic carbon - 1.04 (0.27 - 3.33%); cation exchange capacity (CEC) - 4.74 (1.48 - 6.8) mmol$_c$/kg; sand - 69.6 (66.2 - 71.7%); clay - 20.9 (17.9 - 23.3%) and; silt - 9.5 (7.7-10.9%) respectively (Table 1). Mobility of heavy metals from topsoil varies with a range of environmental conditions and soil properties. The effect of soil acidification and flooding has been extensively studied (Wenzel, 2005). It is well known that metal concentrations in soil solution and consequent leaching can be much enhanced in soils with low pH and/or low redox potential. Changes of land use such as deforestation or afforestation typically result in changes of pH, redox

potential and content of organic matter and subsequent mobilisation or immobilisation of metals (Evans, 1989; Wenzel, 2005). Droughts and changes in temperature can modify metal mobility as a consequence of changes of organic matter content, quality and solubility. These processes can even occur as seasonal phenomena, for instance the increased metal solubility during wet warm summers.

Most metals in the pH range of 6.0 - 9.0 are not always in the free form (Porteus, 1985). The pH range of all the soil samples in the present study is slightly acidic to neutral (Figure 2) implying that some metal ions may exist in the free form and hence could be leached into subsoil and subsequently into ground water. The soil organic carbon (matter) contains humic materials with highly complex functional groups, which have ability to complex metals thereby retaining them in the topsoil (Evans, 1989). The more organic carbon is present in soil, the more the functional groups available for complexation with the metals, hence, the more the retention. The organic carbon of soil in the present study was in the range of 0.27 – 3.33% for both seasons and depths (Tables 1, Figure 6), indicating low retention of metals in the topsoil. The retention of metals by CEC or non-specific adsorption mechanisms is complex because it is dependent on various factors like pH, concentration of metal ions etc. However, CEC of any soil is an important tool that could assist in explaining the retention capacity of many metals especially the alkali, alkaline earth and heavy metals in the soil. Metals bound by cation exchange mechanism are via electrostatic forces resulting in the formation of outer-sphere complexes. The ions in solution are always in equilibrium with counter ions that balance the surface charge of the colloids. In general terms, the more the CEC of soil, the more the active sites available for cation exchange. The affinity of soil colloid surfaces for cations increases as the valency increases

For cations of different valences, the affinity generally follows the order M^+, $M2^+$, $M3^+$. For cations of the same valence, the adsorption strength is usually determined by the hydrated radius of the ions (Ji and Li, 1997). Cation exchange capacity normally ranges from 1.0 –100 $mmol_c$/kg. It is least for sandy soils and most for clayey soils. The CEC of soil samples in the present study was low probably because of the sandy nature of the soil (Table 1). The same trend was observed by (Korte et al., 1976) who leached eleven different soil samples with a neutral leachate spiked with Pb and observed that Pb was immobile in all soils except one classed as ultisol with a loamy sand texture and a very low CEC (2 meq/100 g).

Speciation of Pb in soil and raw slag

10 soil samples of varying Pb concentrations and 1 sample of raw slag were speciated for Pb using the popular Tessier et al. (1979) method. About 89% of total Pb as shown in Table 4 was held in bioavailable phases (sum of % of exchangeable, carbonate-bound, reducible and oxidisable). The order of abundance of % Pb in the fractions was: reducible > carbonate- bound > exchangeable > residual > oxidisable. Stones and Marsalek (1996) and Onianwa (2001) also observed highest enrichment of Pb in the reducible phase (fraction bound to oxides of iron and manganese) of soil. It is well established that iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as coating on particles. These oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions (Tessier et al., 1979), hence, changes of anoxic conditions of the soil will either influence the release or retention of elements in the reducible phase (Charlatchka and Cambier, 2000). The most mobile phase of the bioavailable phases is the exchangeable phase. This is the fraction that indicates the most available of the metal to ecological materials. In the present study, this fraction showed a quite high percentage of Pb (13.26 ± 9.67%) compared to other speciation studies where the percentage concentrations of Pb in this fraction were the least (Onianwa, 2001; Sauve et al., 1997). The least percentage of Pb shown by the oxidisable phase(organic- boundphase) in this study could probably be as a result of low organic matter in the soil, which contains humic materials with highly complex functional groups with the ability to complex metals thereby retaining them in the soil oxidisable phase (Evans, 1989). The percentage of Pb in the various speciation fractions for the raw slag waste showed an enrichment order of Pb as residual > oxidisable > reducible > carbonate-bound > exchangeable. This spatial distribution showed 34% of Pb in the bioavailable phases and 66% in the residual phase implying that a greater % of Pb is not bioavailable, but is gradually released into the environment as conditions become favourable. The high levels of Pb in soil samples around the slag dumpsites justify the reason given.

The high concentration of Pb in soil within the premises of the company presents a serious menace to man as Pb with deleterious effect can get to man either directly by contact with the soil or through food chain with water, meat (grazing herbivores, bush meat) or food crops planted around this environment. This is evident in the analysis of some forage plants collected from the pre-mises of the polluted company soil which showed hyper accumulation of Pb in the shoots and roots of the plants.

Correlation of physico-chemical parameters of soil

The Correlation of the physico chemical properties of soil presented in Tables 5 - 6 showed strong negative correlation between CEC and percentage sand during wet season and both depths. All metals showed significant positive correlation with one another (0.687 – 0.999) during both seasons and for both depths. This possibly suggests a strong association among these metals as the metals could come from a common geogenic input which though sometimes is dependent on the chemical factors including solubility and mobility of each metal (Tijani et al., 2004).

One-way parametric analysis of variance (ANOVA) was used to compare the levels of heavy metals in soil sam-ples in the present study for both dry and wet seasons and 0 – 15 cm and 15 – 30 cm depths to check the seasonal and depths variations in the spatial distribution of Pb, Cd, Cr and Ni. Comparable concentrations (p > 0.05) of metals were observed between dry season and wet season and the 2 depths respectively (data not shown). This from all likelihood is connected to the close relationship in the properties of the soil explained above. A soil low in organic carbon (matter) and CEC, but high in sand is susceptible to high leaching because the retention power of heavy metals in its topsoil is low.

Spike recovery test was conducted on some soil samples to validate the analytical procedures used. The results of the spike recovery test conducted on some soil samples for Pb, Cd, Cr and Ni as presented in Tables 7 – 10 showed % recovery for all the metals within 100 ± 10% (Lena, 1997). This demonstrated that the uncertainties in the methods of analyses used in this study were within acceptable limits.

Conclusion

This research has confirmed that slag from the smelting plant of Metropolitan Battery industry in Ota, Nigeria contains high level of lead that pollutes the soil around its dumpsite to over several times the permissible limit. Other toxic metals like Cd, Cr and Ni were at the

background levels. There was no significant difference between the concentrations of these metals for both wet and dry seasons, top and sub levels. The soil was sandy loam in nature with low organic carbon, low CEC and pH around neutral point.

The soil within and around the premises of the plant needs urgent clean up to minimise contamination of ecological materials. The slag and soil can be recycled into bricks and tiles for building by mixing the soil/or slag with clay in an optimum proportion. The lead can be bound chemically using phosphate salts or plants known to bioaccumulate heavy metals could be introduced to pick up the metals.

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