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Temporal variability of selected heavy metals in automobile soils

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ABSTRACT: Studies on seasonal changes of heavy metal concentration in soils provide vital information for best management options at all times. The study investigated temporal variation in concentration of heavy metals in three towns having automobile service centres in Imo State. The study site is characterized by two major seasons in a year. Heavy metals were found in both arable and automobile soils, but more concentrations were recorded on the latter. Mean values of Cd, Cr, Ni, Hg and Pb were 6.2 mg/kg, 4.7 mg/kg, 6.5 mg/kg, 0.02 mg/kg and 71.9 mg/kg respectively in the dry season while 2.9 mg/kg Cd, 2.2 mg/kg Cr, 1.9 mg/kg Ni, 0.01 mg/kg Hg and 51.9 mg/kg Pb were recorded during the rainy season of the experimental period. Higher values of heavy metal concentration were found in automobile soils as follows: 18.1 mg/kg Cd, 12.0 mg/kg Cr, 16.3 mg/kg Ni, 4.8 mg/kg Hg and 312.8 mg/kg Pb in rainy season, and 15.1 mg/kg Cd, 8.1 mg/kg Cr, 11.9 mg/kg Ni, 2.7 mg/kg Hg and 267.9 mg/kg Pb. However, Cd showed highest variability in arable soils during the dry season (CV=79%) while Hg varied widely in automobile soils in the rainy season (CV=54%).

Key words: Temporal variability, heavy metals, automobile soils, dry and wet seasons

INTRODUCTION

Heavy metals are naturally present in soils (Ojanuga, *et al.*, 1996) but anthropogenic activities have resulted in high concentrations in the environment (He, *et al.*, 2004). Motor vehicle servicing centres popularly called 'mechanic villages' are sources of automobile wastes in urban and peri-urban areas of Imo State, Nigeria. In these locations, fossil fuel products are used leading to excess accumulation of various forms of heavy metals. These accumulations deteriorate nearby farms and cause non-point-source pollution. But these heavy metals vary with seasonal changes (Aiyesanmi, 2005). The major objective of this study was to assess the status of heavy metals in soils with seasonal changes. The assumption is that heavy metal concentration in excess of critical levels could lead to agronomic and environmental problems.

MATERIALS AND METHODS

Location

The study site is Imo State, southeast Nigeria, bounded by Latitudes 4°40' and 8°15' N and longitudes 6°40' and 8°15' E. It lies within the humid tropics. Temperatures are high and change slightly during the

year (mean daily temperature is about 27 °C). The average annual rainfall is about 2400 mm. There is a distinct dry season of about 3 months of dryness. Imo State has a rainforest vegetation characterized by multiple tree species.

Geology and geomorphology

The predominant parent material underlying Imo State from which most of the soils are formed are the coastal plain sands popularly known as "Acid Sands" (Orajaka, 1975). A greater proportion of the land surface of Imo State is of flat topography.

Soils

Soils of the study site have been classified as Typic Paleudult/Dystric Nitosol for Owerri and Orlu towns; and Plinthic Tropudult/Plinthic Acrisol for Okigwe town (Federal Department of Agricultural Land Resources, 1985). They are acidic, have low cation exchange capacity, low base saturation, and low fertility status, usually suffering from multiple nutrient deficiencies. Soil fertility is maintained by fallow, whose length is fast reducing due to high demographic pressure (Onweremadu, 1994). Farming is a major economic activity even in urban areas where patches of subsistence farms are found.

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Field survey

Sixty soil surface samples were collected from the study, 30 of which were from automobile-waste-affected soils while the rest 30 soil samples were from nearby, unaffected arable land. These soil samples were collected from three locations, namely Owerri, Orlu and Okigwe, and in the months of January and July 2005 for dry and rainy seasons respectively. Soil samples were prepared by air-drying and sieving using 2-mm aperture.

Laboratory methods

Particle size distribution was determined by hydrometer method according to the procedure of Gee and Bauder (1986). Total porosity was calculated from values of bulk density obtained by clod method (Blake and Hartge, 1986), at an assumed particle density of 2.65g/cm³. Mathematically, it is expressed as follows:

$$f = 100\% - \frac{(BD \times 100)}{PD} \dots (\text{Vomocil, 1965; Foth 1984})$$

Where f = total porosity (%)

BD = bulk density (g/cm³)

PD = assumed particle density (2.65g/cm³)

Moisture content was determined gravimetrically thus:

$$\theta m_s = \frac{\text{Wet Soil sample} - \text{dry soil sample}}{\text{Dry soil sample}} \times \frac{100}{1}$$

Where θm_s = gravimetric moisture content (saturated) (%)

Exchangeable basic cations were estimated by complexometric titration and flame photometry (Jackson, 1958). Exchangeable acidity was measured by the procedure of McLean (1965). Cation exchange capacity (CEC) was determined by the neutral ammonium acetate method as described by Chapman (1965). Percent base and aluminium saturations were calculated as follows:

$$\text{Base saturation} = \frac{\text{Total exchangeable basic cations}}{\text{CEC}} \times \frac{100}{1}$$

$$\text{Aluminium saturation} = \frac{\text{Exchangeable aluminium}}{\text{CEC}} \times \frac{100}{1}$$

These calculations on the basis of their proportion of the total exchanging capacity allow for simpler comparisons between soils of contrasting cation

exchange capacity (Billet and Cresser, 1996). Total carbon was measured by Walkley and Black wet digestion method (Nelson and Sommers, 1982) and organic matter was obtained by multiplying total carbon by a factor of 1.724. Total nitrogen was determined using micro-kjeldahl (Bremner and Mulvaney, 1982), while available phosphorus was estimated using Bray II method (Bray and Kurtz, 1954). Soil reaction was measured according to the procedure of Henderson, *et al.* (1993). Digestion of soil samples for heavy metals was carried out with a mixture of concentrated HClO₄ and HNO₃ at a ratio of 2:1 and heavy metals were extracted using 0.5M HCl (Lacatusu, 2000). The heavy metals concentrations in the supernatant were determined using Atomic Absorption Spectrophotometer Alpha 4 model.

Statistical analyses.

Mean and coefficient of variation were used to ascertain seasonal variability of metals. Ranking of variability was done using the method of Aweto (1982) as follows:

Little variation (CV = less than 20%)

Moderate variation (CV = 20-50%)

High variation (CV = greater than 50%)

RESULTS

Temporal variability in soil properties

Soil properties in arable and automobile soils are shown in Tables 1 and 2 respectively. Total sand dominated the other size fractions in the study site. Silt content decreased by 50% in rainy season in both arable and automobile soils. Exchangeable bases were generally higher in dry season in both arable and automobile soils. Higher values of total carbon were recorded in the rainy season which could be as a result of lower soil temperatures leading to reduced pedogenic process of decomposition. There were higher values of total carbon in automobile soils. Available phosphorus was also higher in rainy season in both arable and automobile soils. Organic carbon content may have influenced the distribution pattern of available phosphorus which is associated with low solubility.

Temporal variability of heavy metals concentration

Occurrence and distribution of heavy metals with seasons are shown in Tables 3 and 4 for arable and automobile soils respectively.

Table 1: Average values soil properties in arable soils

Soil property	Dry season	Rainy season
Total sand (%)	80	82
Silt (%)	3	2
Clay (%)	17	15
Textural class	SL	SL
Total porosity (%)	43	40
Gravimetric soil moisture (%)	33	35
Exchangeable Ca (cmol/kg)	2.00	1.70
Exchangeable Mg (cmol/kg)	0.80	0.50
Exchangeable K (cmol/kg)	0.30	0.10
Exchangeable Na (cmol/kg)	0.03	0.01
Exchangeable H (cmol/kg)	0.99	1.20
Exchangeable Al (cmol/kg)	2.40	2.89
Effective cation exchange capacity (cmol/kg)	6.52	5.40
Base saturation (%)	48.00	42.27
Aluminium saturation	36.80	53.52
Total carbon (%)	1.73	1.98
Organic matter (%)	2.98	3.41
Total nitrogen (%)	0.13	0.22
Available phosphorus (mg/kg)	8.64	9.13
Soil pH (KCl)	4.00	3.82

SL=Sandy loam

Table 2: Average values of soil properties in automobile waste soils

Soil property	Dry season	Rainy season
Total sand (%)	85	86
Silt (%)	2	1
Clay (%)	13	13
Textural class	SL	SL
Total porosity (%)	40	36
Gravimetric soil moisture (%)	29	30
Exchangeable Ca (cmol/kg)	1.10	0.60
Exchangeable Mg (cmol/kg)	0.40	9.20
Exchangeable K (cmol/kg)	0.20	0.10
Exchangeable Na (cmol/kg)	0.02	0.02
Exchangeable H (cmol/kg)	2.31	2.53
Exchangeable Al (cmol/kg)	4.38	5.05
Effective cation exchange capacity (cmol/kg)	6.69	8.50
Base saturation (%)	25.71	10.82
Aluminium saturation	65.47	59.41
Total carbon (%)	2.11	2.63
Organic matter (%)	3.63	4.53
Total nitrogen (%)	0.22	0.28
Available phosphorus (mg/kg)	5.82	8.87
Soil pH (KCl)	3.86	3.50

In both soils, higher values of heavy metals were reported in the dry season. Similar results were observed by Aiyesanmi (2005) in the Rivers State, Nigeria. Results showed that as pH lowers to 3.82 (arable soils) and 3.50 (automobile soils) in the rainy season, heavy metals generally decrease.

Agronomic Implications

Automobile wastes are hazardous wastes with serious agronomic and environmental implications. Soil properties varied widely and temporally in automobile soils (Table 5) especially in aluminium saturation (CV

=62%), effective cation exchange capacity (CV=53%), base saturation (CV =50%) and soil pH (CV=50%). Heavy metals varied moderately but temporally in automobile soils (Table 6) except in mercury (CV=54%) but Cd varied widely and temporally in arable soils (CV =79%).

DISCUSSION AND CONCLUSION

Sandiness of soils is attributable to the sandy nature of parent material, being derived from coastal plain sands. High rainfall status of the site also favoured washing away and leaching of silt-sized and clay-sized

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Table 3: Heavy metal concentration (mg/kg) in arable soils

Sample	Dry season					Rainy season				
	Cd	Cr	Ni	Hg	Pb	Cd	Cr	Ni	Hg	Pb
1	8	6	9	0.02	86	4	4	4	0.01	
2	7	7	9	0.02	80	4	3	5	0.01	
3	6	6	6	0.02	60	5	2	2	0.01	
4	5	5	8	0.02	70	6	2	3	0.01	
5	8	3	8	0.01	60	4	2	3	0.01	
6	9	3	6	0.02	60	3	2	2	0.01	
7	8	4	7	0.02	80	2	2	3	0.01	
8	7	5	8	0.03	70	4	3	4	0.02	
9	9	6	6	0.02	90	6	4	2	0.01	
10	8	5	5	0.02	80	7	3	3	0.01	
11	10	3	4	0.02	88	4	2	2	0.01	
12	8	2	1	0.02	75	5	1	2	0.01	
13	6	6	2	0.02	65	3	2	Trace	0.01	
14	7	4	6	0.02	48	2	3	Trace	0.01	
15	6	5	8	0.02	50	5	4	Trace	0.01	
16	4	6	7	0.01	56	4	3	2	Trace	
17	3	3	4	0.03	62	6	2	1	Trace	
18	2	2	2	0.02	64	7	2	Trace	0.01	
19	2	2	4	0.01	71	2	1	2	Trace	
20	3	4	7	0.02	78	4	2	2	0.01	
21	4	5	8	0.03	81	Trace	1	2	0.00	
22	6	6	9	0.02	54	Trace	2	1	Trace	
23	8	7	10	0.02	66	Trace	2	1	0.01	
24	5	8	11	0.02	98	Trace	2	1	Trace	
25	6	9	10	0.02	101	1	2	2	Trace	
26	7	1	6	0.02	108	1	2	2	Trace	
27	8	3	7	0.01	78	1	2	3	Trace	
28	3	4	8	0.02	76	2	2	2	Trace	
29	4	5	6	0.01	76	Trace	2	1	0.01	
30	4	6	5	0.03	88	Trace	1	Trace	0.01	
Mean	6.2	4.7	6.5	0.02	71.9	2.9	2.2	1.9	0.01	51.9

fractions. Slight seasonal textural differences as experienced in arable soils could be due to continuous cultivation. Silt-sized fractions are readily transported in space. Dry season porosity values were higher in both soils than in the rainy season while soil moisture took a reverse trend. Rain drops increased bulk density (Bresson, *et al.*, 2004) in the rainy season by clogging pore spaces in soils. Seasonal changes are attributed to heavy annual rainfall that lasts for about 9 months and estimated to be 2400 mm (Oti, 2002). Movement of water through pores in rainy season leads to eluviation and leaching losses of exchangeable bases, leaving behind acidic cations of H and Al. This could be the reason for the high aluminium saturation in rainy season (arable soils) although the reverse was the case in automobile soils in the same season. The higher values of soil carbon in automobile soils could be accounted for by regular supply of automobile wastes, most of which are of fossil origin. These wastes killed and/or inactivated soil organisms in the automobile soils, hence they

pile up in the sites as autochthonous decomposers have been rendered extinct. The reverse was the case in arable soils where there were lower values of organic components which Foth (1984) attributed to cultivation and pronounced activities of soil organisms. Although automobile soils were more acidic, they had higher available phosphorus which could be as a result of P-uptake by crops in arable soil. Again, the buffering of the soil system by organic matter may have prevailed over the activities of iron and aluminium at such low pH values. The relatively lower values of heavy metals obtained in the rainy season may not be unconnected with dilution by rainwater, which influences concentration and heavy metal dynamics in soils. Low pH increases solubility and percolation into deeper horizons of the pedon. However, He, *et al.* (2004) reported that mobility of heavy metals depends not only on the total concentration in the soil but also on the soil properties, metal properties, and environmental factors.

Table 4: Heavy metal concentration (mg/kg) in automobile waste soils

Sample	Dry season					Rainy season				
	Cd	Cr	Ni	Hg	Pb	Cd	Cr	Ni	Hg	Pb
1	20	12	15	5	300	18	8	12	3	298
2	15	9	16	4	200	13	7	12	2	180
3	21	11	18	4	280	19	8	10	1	260
4	17	12	15	5	270	18	9	11	1	250
5	18	11	13	3	290	16	9	13	3	220
6	16	10	16	2	285	15	6	14	2	280
7	15	14	17	7	260	11	8	6	3	275
8	23	16	21	8	300	18	9	17	4	259
9	20	8	23	5	345	16	4	18	5	300
10	22	8	18	3	280	16	5	11	6	333
11	12	7	17	2	262	10	5	12	2	270
12	16	6	20	2	200	17	5	11	3	250
13	20	8	21	3	198	16	6	8	1	200
14	19	12	18	4	188	15	7	18	6	201
15	21	13	16	6	198	17	14	15	2	170
16	17	11	15	7	345	14	13	13	1	160
17	19	12	18	8	400	16	11	10	1	300
18	15	14	12	8	446	10	11	11	4	350
19	17	11	13	6	126	14	9	11	5	280
20	16	11	15	4	444	11	8	14	3	300
21	24	20	23	5	286	16	16	18	2	305
22	20	16	12	3	288	17	11	10	2	380
23	14	10	16	4	363	11	10	12	2	280
24	12	8	16	3	348	10	6	13	2	222
25	17	12	17	8	323	14	6	15	1	250
26	18	13	14	6	404	15	7	11	4	260
27	19	13	16	8	565	18	8	13	4	300
28	23	16	15	3	288	20	12	9	2	350
29	21	14	13	6	298	17	9	9	4	280
30	16	12	13	4	306	14	8	10	2	276
Mean	18.1	12.0	16.3	4.8	312.8	15.1	8.1	11.9	2.7	267.9

Table 5. Seasonal variability of soil properties

Soil property	Coefficient of variation (%)	
	Arable soil	Automobile soil
Total sand (%)	2	2
Silt (%)	1	1
Clay (%)	2	0
Total porosity (%)	3	12
Gravimetric soil moisture (%)	8	15
Exchangeable Ca (cmol/kg)	15	21
Exchangeable Mg (cmol/kg)	13	18
Exchangeable K (cmol/kg)	10	14
Exchangeable Na (cmol/kg)	8	12
Exchangeable H (cmol/kg)	22	28
Exchangeable Al (cmol/kg)	26	51
Effective cation Exchange capacity (cmol/kg)	29	53
Base saturation (%)	18	50
Aluminium saturation	29	62
Total carbon (%)	11	28
Total nitrogen (%)	18	35
Available phosphorus (mg/kg)	12	40
Soil pH (Kcl)	17	50

Table 6: Seasonal variability of heavy metal concentration (mg/kg)

Heavy metal	Coefficient of variation %			
	Arable dry season	Soil rainy season	Automobile dry season	Soil rainy season
Cd	35	79	17	34
Cr	31	37	25	35
Ni	37	48	18	25
Hg	1	0	49	54
Pb	20	36	32	20

The sandy nature of soils which implies high value of macro-porosity coupled with heavy rainfall characteristics of the area may have caused lower values of heavy metals in the wet season. Water-soluble, exchangeable, carbonate- associated, oxide-associated, organic-associated and residual forms were not determined as to ascertain the effect of metal form in influencing transportability within the pedosphere. Lower values of heavy metals in the rainy season may be related to the oxidation state. Cadmium has been reported to be soluble in soil under oxidized conditions but is precipitated as cadmium sulphate as reduction takes place (Wang and Liao, 1999). It is also possible that other heavy metals behave like cadmium in the study area, characterized by long duration rainfall. The variations as found in Tables 5 and 6 tend to spell the degree of instability of soil properties hence of outstanding limitations in crop production. Most crops may not tolerate wide variability in the availability of essential nutrients in the growth and developmental stages but the presence of these heavy metals will certainly truncate crop demands. High levels of heavy metals above critical levels result in human health hazards. Concentrations of heavy metals in crops depend on availability in the soil and crop uptake. However, Federal Environmental Protection Agency (1991) set up critical limits for these heavy metals which vary according to metals. Values above critical levels of 100 mg/kg were found in Pb, having mean values 312.8 mg/kg (dry season) and 267.9 mg/kg (rainy season). Similar results ranging from were 174.55 -1685.45 ppm were reported by Nriagu *et al.* (1983) and Ano (1994). Government of Taiwan sets the critical levels for heavy metals in soils as follows: 10 mg/kg Cd, 16 mg/kg Cr, 100 mg/kg Ni and 120 mg/kg Pb. By these values, automobile soils are polluted in terms of Cd and Pb. Yet, certain plants have been found to accumulate more than 20,000 mg/kg Ni, 40,000 mg/kg Zn and 1000 mg/kg Cd hence referred to as hyper-accumulating plants (Brady and Weil, 1999). Such plants pose serious health hazards to humans and animals. Heavy metals are naturally present

Tin soils but of higher concentrations in automobile soils. The heavy metals influenced soil properties especially soil pH, aluminium saturation, base saturation, and effective cation exchange capacity. Moderate and high variations in heavy metals were encountered in both arable and automobile soils irrespective of season. These variabilities influence crop growth. However with the exception of Cd and Pb all other investigated heavy metals were below critical levels of toxicity.

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