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THE DISTRIBUTION OF Mn, Zn, Cu, Cr, Ni, AND Pb AROUND TWO MAJOR REFUSE DUMPSITES IN BENIN CITY, NIGERIA

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The concentration of Zn, Pb, Mn, Cu, Cr and Ni around two major refuse dumpsites in Benin City have been determined. This was done in order to ascertain the suitability of these area of land for residential and agricultural purposes when eventually reclaimed. In all, 18 soil samples were collected at distances of 0 m, 50 m and 100 m (9 top soil; 0 to 15 cm and 9 bottom soil; 15 to 30 cm) from each dumpsite. Sample solutions were prepared and analysed using atomic absorption sepectrophotometry. Results obtained indicate that top-soil samples from Ugbowo dumpsite contain as much as 1.10 - 8.88 mg/kg Mn, 0.68 - 2.30 mg/kg Zn, 5.90 - 8.70 mg/kg Cu, 0.08 - 0.16 mg/kg Cr, 0.50 - 77 mg/kg Ni and 0.10 - 0.45 mg/kg Pb. Bottom soil samples from the same dumpsite gave ranges of 4.44 - 15.26 mg/kg Mn, 0.84 - 6.59 mg/kg Zn, 5.30 - 7.70 mg/kg Cu, 0.11 - 0.20 mg/kg Cr, 0.66 - 1.57 mg/kg Ni and 0.20 - 0.60 mg/kg Pb. For Evbuotubu dumpsite, concentration ranges obtained for the top soil samples are 5.72 - 18.33 mg/kg of Mn, 2.10 - 5.23 mg/kg of Zn, 1.96 - 12.22 mg/kg of Cu, 0.22 - 0.56 mg/kg of Cr, 0.27 - 0.83 mg/kg of Ni and 0.72 - 1.20 mg/kg of Pb. Bottom soil samples gave concentration ranges of 3.24 - 17.96 mg/kg of Mn, 1.46 - 6.20 mg/kg of Zn, 4.33 - 10.93 mg/kg of Ni and 0.69 - 1.51 mg/kg Pb. The heavy metal levels were found to decrease in both top and bottom soils with distance from the dumpsites.

Key words: Heavy metals, Top soil samples, Absorption spectrophotometry.

Introduction

Benin city which lies between latitudes 6°, 00'N and longitudes 5°, 40'E is located in the Southern part of Nigeria. The ancient city is urban and has witnessed an overwhelming influx of people from the rural areas in the last few decades. This has resulted in a tremendous increase in population in the city. Population explosion is always inevitably accompanied with environmental pollution. In order to meet man's daily myriad demands, large quantities of solid wastes are generated from industrial, domestic and commercial activities. If not properly disposed and managed, the resulting environmental impact from these wastes can be disastrous.

As a result of prohibitive cost and manpower requirement to operate standard solid waste management machines such as incinerators, waste disposal and management in Benin City is by the less attractive method of open dumping in designated locations. Population explosion in the city and other factors have necessiated the re-developing of some of these dumpsites covering a expanse land for residential and agricultural purposes. It is, therefore, essential that the levels of heavy metals in these dumpsites are assayed, because uncontrollable inputs of heavy metals are undersirable. Once accumulated in the soil, these elements are generally very difficult to remove and potentially harmful effects may arise in the future.

Soil metal contamination has occurred since prehistoric times, but the extent and pace of contamination has increased during the last century as a result of rapid industrialization and population explosion. Toxic metals are of considedrable environmental concern due to their toxicity and accumulative behaviour (Purves 1985). Trace quantities of some of the heavy metals are essential for animal and plant growth. However, they are easily assimilable and tend to accumulate in materials in the environment (Nurberg 1984). Metal contamination of soils became a world-wide concern when it was observed that rice paddy fields irrigated with wastewaters from a Zinc mine caused excessive cadmium (Cd) intake and adverse health effects in farmers who had consumed rice grown in this contaminated soils (Kobayashi 1978). This first observation of human disease caused by a heavy metal in the environment has stimulated research on the potential adverse effect of Cd and other metals in soils and in agricultural and dietary systems. During the 1980s, the risks of young children suffering from neuropsychological effects because of excessive lead (Pb) ingestion appeared to be more serious than had been previously recognized (Needlemann *et al* 1979; Needlemann *et al* 1990). Increased bioavailability of heavy metals may inhibit root growth and uptake of macronutrients by trees and

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these effects have been shown to be synergistic (Burton *et al* 1983; Breckle and Kahle 1992). Most recently, it has been reported (Dudka *et al* 1996) that addition of Pb - Zn smelter flue dust strongly contaminated the test soil with Cd, Pb and Zn, although there were relatively low metal concentration in crop plants, the crop yield reduction indicated the presence of phytotoxic conditions in the studied soil.

As a result of the potentially harmful effects of long-term accumulation of heavy metals on plant growth, the evaluation of ecological significance of heavy metal pollution requires most importantly an assessment of the relative concentration level of the metals. The present study was therefore, focused on establishing the levels of Mn, Zn, Cu, Pb, Cr and Ni in the soil around two major refuse dumpsites in Benin City.

Materials and Methods

With the aid of soil auger and a trowel, 18 composite soil samples were collected at the distance of 0 m, 50 m and 100 m (9 top soil; 0 to 15 cm and 9 bottom soil; 15 to 30 cm) from each dumpsite (Fig 1). The soil samples were stored in polyethylene bags and labelled property.

The samples collected were air dried, ground in an agate mortar and then sieved through a 1.73 mm nylon sieve. Soil pH was determined using H_2O according to Folson *et al* (1981). The soil/solution ratio was 1:2. Soil organic carbon was determined by Walkey Black rapid dichromate oxidation technique (Nelson and Sommers 1982) with the use of correction factor 1.3 to account for incomplete oxidation of organic compound and a multiplying factor 1.724 to convert organic carbon to organic matter (%). Particle size analysis was achieved according to the method of Bouyoucos (1962).

Metal determination. A 1g sub-sample of the processed soil was weighed into a 125 cm^3 hard - glass digestion tube, a few drops of high-purity HNO_3 were added slowly. After the effervescence, 5 cm^3 of high-purity HNO_3 and 15 cm^3 of $HClO_4$ were added slowly and kept overnight. The samples were then heated in a digester at 120°C for 3 hours. The contents were allowed to cool for 15 minutes after the appearance of white fumes, filtered into a 100 cm^3 volumetric flask and diluted to volume with distilled water (Allen *et al* 1974). Concentrations of Mn, Zn, Cu, Cr, Ni and Pb were determined using a Varian spectra AAIO Atomic Absorption Spectrophotometer.

Results and Discussion

The levels of selected physiochemical properties of the soils from the two refuse dumpsites are shown in Table 1, while the measured concentration ranges, the average levels and standard deviations for Mn, Zn, Cu, Cr, Ni and Pb in both bottom and top soil samples from Evbuotubu and Ugbowo refuse dumpsites are summarized in Table 2 and 3. Soil organic matter was observed to be generally higher at Ugbowo dumpsite than at Evbuotubu dumpsite. This may be attributed to varied rates of microbial decomposition or degradation associated with different types, quality and quantity of waste in the two locations. A number of organic wastes, such as tree bark, leaf mold, city and urban refuse, sewage sludge and sawdust simultaneously undergo humification in both controlled systems (composing) and open refuse dumpsites (Inbar *et al* 1990).

Mn gave the highest level with a range of 3.24 - 17.96 mg/kg and a mean of 12.22 mg/kg at the base (0 m) of the dumpsite at Evbuotubu, while the total concentration of Mn reduced to a mean of 6.07 mg/kg at 100 m away from the site. The reduction in the amount of Mn with distance from the dumpsite also exhibited an increase in pH (Table 1). The high concentration of Mn at the base 0 m of the site corresponds to a lower pH of 4.8. High organic matter in the soil causes a flush of microbial activity, which adds complexing agents to the soil and affects the redox condition of the soil. Controlled oxidation - reduction experiments have shown that more Mn is present in soil at low pH and Eh (reducing conditions) than at high pH (Shuman 1988). This same trend was observed at Ugbowo dumpsite where the amount of Mn decreased with distance from the dumpsite as the pH increased. On the other hand, there may have been little lateral migration of the waste containing sources of Mn.

Cu had the next highest concentration with a range of 1.42 - 6.20 mg/kg and a mean of 8.16 mg/kg just at he periphery (0 m) of the dumpsite at Evbuotubu. At Ugbowo, total concentration of Cu ranged between 5.90 and 8.0 mg/kg (Table 3) also at the base of the dumpsite. The concentration of Cu decreased with distance away from the dumpsites. The relatively high organic matter content of the soil at both locations associated with increased Cu concentrations is consistent with previous reports (Ducaroir *et al* 1990; Baker 1990; Ramos *et al* 1994), that even in metal speciation studies, the greater amount of Cu occurs in the organic fraction. Since the refuse dumpsites contain high organic matter, it could be opined that the distribution of the metals studied are affected basically by the organic matter content and the soil pH.

Zn had a mean concentration of 3.28 mg/kg at Evbuotubu and 2.79 mg/kg at Ugbowo dumpsite. Zn has been shown to occur mostly in the residual fraction (87-90 %) even in acid soils with high loadings of organic material or sludge (Xiang *et al* 1995). Similarly, Chlopecka *et al* (1996) reported a non-correlation between the total concentration of Zn and organic fraction associated with increasing contamination of soils in areas where metallurgical industries are located in Poland.

Table 1
Selected physicochemical properties of the soils from the two refuse dumpsites

Distance (m) from dumpsite	Depth (cm)	% C	% Organic matter	pH	% Sand	% Silt	% Clay
Ugbowo							
0	0 - 15	2.91	5.01	4.70	79.6	7.00	13.40
50	0 - 15	2.64	4.55	4.50	80.4	7.90	11.70
100	0 - 15	1.77	3.05	5.20	84.9	6.10	9.00
0	15 - 30	1.18	2.03	5.00	80.1	9.20	10.70
50	15 - 30	1.13	1.94	5.60	83.5	4.20	12.30
100	15 - 30	1.05	1.81	5.70	82.7	7.50	9.90
Evbuotubu							
0	0 - 15	1.56	2.68	4.80	84.90	3.90	11.20
50	0 - 15	1.39	2.39	5.30	84.30	7.20	8.50
100	0 - 15	1.24	2.13	5.60	85.70	3.90	10.40
0	15 - 30	0.97	1.67	5.20	82.10	5.10	12.80
50	15 - 30	0.95	1.63	5.40	80.50	8.80	10.70
100	15 - 30	0.88	1.51	5.40	83.20	5.90	10.90

Table 2
Concentration of Mn, Zn Cu, Cr, Ni and Pb in top and bottom soil samples around the Evabotubu refuse dumb site

Distance from dumpsite		Concentration mg/kg					
	Top soil	Mn	Zn	Cu	Cr	Ni	Pb
0 m	Average conc.	12.02	3.22	7.22	0.44	0.64	0.98
	S.D	6.32	1.74	5.13	0.19	0.32	0.24
	Range	5.72 - 18.33	2.10 - 5.23	1.96 - 12.22	0.22 - 0.56	0.27 - 0.83	0.72 - 1.20
	Bottom soil						
	Average conc.	12.22	3.28	8.16	0.40	0.78	1.22
	S.D	7.88	2.56	3.43	0.19	0.49	0.46
	Range	3.24 - 17.96	1.42 - 6.20	4.33 - 10.93	0.18 - 0.52	0.23 - 1.17	0.69 - 1.51
50 m	Top soil						
	Average conc.	8.23	1.62	5.29	0.22	0.36	0.64
	S.D	5.07	0.61	1.03	0.03	0.23	0.18
	Range	2.46 - 12.00	0.93 - 2.07	4.24 - 6.30	0.18 - 0.24	0.13 - 0.58	0.47 - 0.83
	Bottom soil						
	Average conc.	8.12	2.04	6.17	0.28	0.32	0.72
	S.D	3.42	1.22	3.56	0.03	0.16	0.41
	Range	4.26 - 10.98	1.09 - 3.41	3.99 - 10.28	0.26 - 0.32	0.14 - 0.43	0.25 - 1.00
100 m	Top soil						
	Average conc.	5.33	0.76	2.78	0.99	0.21	0.31
	S.D	2.55	0.59	1.09	0.01	0.03	0.17
	Range	3.42 - 8.23	0.14 - 1.31	1.98 - 4.02	0.08 - 4.02	0.19 - 0.24	0.13 - 0.47
	Bottom soil						
	Average conc.	6.07	0.91	2.42	0.18	0.28	0.33
	S.D	1.07	0.09	1.40	0.05	0.02	0.16
	Range	5.18 - 7.25	0.18 - 0.99	1.26 - 3.97	0.13 - 0.22	0.26 - 0.30	0.23 - 0.51

Table 3
Concentration of Mn, Zn Cu, Cr, Ni and Pb in top and bottom soil samples around the Ugbowo refuse dumb site

Distance from		Concentration mg/kg					
Dumpsite	Top soil	Mn	Zn	Cu	Cr	Ni	Pb
0m	Average conc.	6.07	1.27	6.83	0.13	0.61	0.31
	S.D	4.32	0.89	1.62	0.04	0.13	0.19
	Range	1.10 - 8.88	0.68 - 2.30	5.90 - 8.70	0.80 - 0.16	0.50 - 0.75	0.10 - 0.45
	Bottom soil						
	Average conc.	9.45	2.79	6.17	0.16	0.97	0.44
	S.D	5.45	3.29	1.33	0.05	0.52	0.21
	Range	4.44 - 15.26	0.84 - 6.59	5.30 - 7.70	0.11 - 0.20	0.66 - 1.57	0.20 - 0.60
50m	Top soil						
	Average conc.	4.10	0.36	3.22	0.17	0.47	0.22
	S.D	1.01	0.56	1.14	0.06	0.11	0.16
	Range	3.08 - 5.09	0.02 - 1.01	2.06 - 4.34	0.01 - 0.12	0.38 - 0.59	0.19 - 0.39
	Bottom soil						
	Average conc.	3.96	0.39	4.13	0.06	0.53	0.25
	S.D	0.87	0.58	0.65	0.04	0.11	0.14
	Range	3.03 - 4.76	0.02 - 1.05	3.50 - 4.80	0.02 - 0.07	0.42 - 0.64	0.13 - 0.41
100m	Top soil						
	Average conc.	2.80	0.14	2.42	0.04	0.31	0.11
	S.D	1.06	0.12	1.32	0.02	0.15	0.07
	Range	1.96 - 4.01	0.06 - 0.20	1.35 - 3.89	0.02 - 0.07	0.19 - 0.48	0.06 - 0.19
	Bottom soil						
	Average conc.	3.02	3.03	2.74	0.04	0.38	0.14
	S.D	1.12	0.14	1.23	1.23	0.16	0.10
	Range	2.07 - 4.26	0.08 - 0.33	1.92 - 4.16	0.03 - 0.06	0.21 - 0.52	0.07 - 0.26

The pattern of decrease in metal concentration of Ni, Pb and Cr away from the two dumpsites were equally obtained (Table 2 and 3). The similarities in the distribution pattern of these heavy metals at the two refuse dumpsites is as a result of similarities in the composition of the solid waste dumped at both locations, since the wastes are from different quarters of the same ancient city with the populace have identical dietary pattern and living conditions. Results available equally indicate that metal concentrations were slightly higher at Evbuotubu dumpsite which is attributed to high population density at Evbuotubu. This means the utilization of more materials and the generation of more refuse.

Correlation analysis was carried out to determine the extent of relationship between the elements investigated (Table 4 and 5). The correlation matrix shows that the highest correlation was obtained between Mn and Ni (r = 0.92) at Evbuotubu dumpsites. The high level of organic matter present in the soils suggests amongst other things the presence of humic substances (humic and fulvic acids). Generally, phenolic compounds present in these substances enhance sorption of metallic cations such as Ni, on soil materials containing high concentration of Mn (Gagnon *et al* 1992). Increased competition for complexing or adsorption sites are perhaps responsible for high correlation between Cu and Ni (r = 0.86) obtained at the Ugbowo dumpsite. Correlation decreases and increases between the various metals studied are presented in Table 5. The entire correlation increases and/or decreases between the metals can be better understood by postulating a scheme of what happens in a typical waste deposit. Since waste deposits contain a complex mixture of different compounds, their morphology is also very variable and over time the wastes change considerably. The processes are in many case similar to those found in soil formation where organic material degrades by biologically mediated anaerobic and aerobic processes (Bozkurt *et al* 1999). There is a strong competition for the metals by the organic acids and between the metals for other complexing agents. Also colloids formed by the release of the little soluble part of the solid humus phase can carry considerable amounts of these metals which have been sorbed. It is thus not certain that even reducing phase there will be negligible release of the metals of concern (Zn, Mn, Cu, Cr, Pb and Ni) (Bozkurt *et al* 1997).

Comparison of data obtained in this study with previous results concerning heavy metal pollution in road side sedi-

Table 4
Correlation between the elements Mn, Zn Cu, Cr, Ni and Pb in both layers (Evbuotubu dumpsite)

	Mn	Zn	Cu	Cr	Ni	Pb
Mn	1.00	0.56	0.47	0.65	0.92	0.77
Zn		1.00	0.51	0.61	0.55	0.72
Cu			1.00	0.59	0.50	0.67
Cr				1.00	0.66	0.82
Ni					1.00	0.74
Pb						1.00

Table 5
Correlation between the elements Mn, Zn Cu, Cr, Ni and Pb in both layers (Ugbowo dumpsite)

	Mn	Zn	Cu	Cr	Ni	Pb
Mn	1.00	0.73	0.75	0.63	0.76	0.83
Zn		1.00	0.78	0.85	0.80	0.82
Cu			1.00	0.67	0.86	0.80
Cr				1.00	0.60	0.58
Ni					1.00	0.84
Pb						1.00

ments and soil in the same city (Ihenyen 1998; Ndiokwere 1984) indicate very much lower concentrations in this study. While the highest concentration of 1.22 mg/kg Pb was obtained in the present study, previous studies gave 753.14 ppm Pb (Ihenyen 1998) and 11.70 ppm (Ndiokwere 1984). One main reason that may explain these differences in the levels of heavy metals obtained previously and now is that most of these metals especially Pb and Zn are directly associated with emissions from vehicles exhaust which run solely on leaded gasoline, activities of road side mechanics along motorways and the presence of these metals as additives which form components of some lubricating oils. The dumpsites investigated in this study are located in areas remote from high human activities covering a distance about 4km from a major road. In addition, a substantial part of waste dump at the sites are food waste and other household waste. It is important to emphasize that more remote agricultural areas and settlements may also be receiving contaminating metals, not only from industries, but also from sewage sludge, fertilizers and gasoline used in powering local milling machines. It has been estimated that 2 - 4% of arable soils in Poland are contaminated at least to some extent by Cd, Pb, and Zn due to these mentioned activities (Kabata - Pendias *et al* 1992). The values obtained in this study are, however, similar to those reported for soils at Ekpan (Omgbu and Kokogho 1993), but lower in concentration.

Table 6
Environmental quality criteria in the UK. Soil quality criteria recommendations to the National government (Visser 1993)

Element	Soil (mg / kg) Threshold	
	Domestic gradens, play areas	Landscapes buildings
Cd	3	15
Cr	600	1000
Cu	-	130
Pb	500	2000
Ni	-	-

Table 7
Environmental quality criteria in Canada. Interim environmental quality criteria for contaminated sites. Recommendations to sub-national authorities (CCME 1991)

Element	Soil (mg / kg)		
	Agriculture	Residential	Commercial/ Industrial
Cd	3	5	20
Cr	750	250	800
Cu	150	100	500
Pb	375	500	1000
Ni	150	100	500

Conclusion

Soil contaminated with heavy metals are not only a problem with respect to plant nutrition and the food chain, they may constitute a direct health hazard as well. However, levels of heavy metals obtained in this study when compared with standards giving critical concentrtion of various pollutants in soils (Table 6 and 7), suggest no serious environmental problems at the moment. The dumpsites can, therefore, be effectively utilized for residential and agricultural purposes when eventually reclaimed. It is equally strongly recommended that dumping of refuse in these locations be discontinued and the sites be allowed to go follow for a period of time. Furthermore, it is suggested that further studies be carried out in the dumpsites to ascertain the forms or species in which the heavy metals occur. This will equally guarantee the safe use or otherwise of the decomposing wastes as soil amendment materials especially in organic farming.

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