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Concentration and Distribution of Some Heavy Metals in Urban Soils of Ibadan, Nigeria

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Abstract. Concentrations and distribution of seven heavy metals, namely, Pb, Cd, Zn, Cr, Co, Ni and Cu in the soil samples collected from 38 different sites from Ibadan Metropolis and its suburbs were investigated. The metals were extracted from the soil with HNO_3-$HClO_4$-HF combination for the elemental analysis using flame atomic absorption spectrophotometer. The results obtained for all locations indicated (μg g^{-1} dry weight): Pb (150±143); Cd (4.2±4.4); Zn (213±213); Cr (131±96); Co (38±19); Ni (79±56); and Cu (40±36). Zonal average of metal concentrations indicated the highest metal load in the environment of the urban high traffic (UHT) zone followed by the refuse dump sites. Interelemental association in the UHT-zone showed significant correlation between the pairs Pb-Cd (r = 0.521), Pb-Cu (r=0.412), Zn-Cr (r = 0.603), Zn-Cu (r = 0.334), Ni-Cr (r = 0.749), Ni-Co (r =0.324), and Cd-Cu (r = 0.408).

Keywords: heavy metals, environment pollution, metal contamination, metal-polluted soil

Introduction

Heavy metals are natural components of the environment. However, their pressence is a serious problem as they pollute the soil, water and air. Environmental contamination with toxic heavy metals has become an issue of global concern owing to their multiple effects on the ecosystem (Nriagu, 1990). Heavy metals may accumulate in rural and urban soils due to a variety of human activities. Potential pathways include municipal incinerators, metal processing industries, automobile exhausts, application of phosphate fertilizers to agricultural farmland, application of sewage sludge and animal manure (often high in copper) to agricultural land, and the deposition of paint flakes from buildings (Alan, 1993; Alloway, 1990; Ward *et al*., 1977; Lagerweff and Specht, 1970).

Automobile exhausts account for about 80% of the air pollution by heavy metals in Nigeria (Onianwa and Egunyomi, 1983). The market share of leaded gasoline in Nigeria is still 100%, which is known to have a very high lead content of 0.66 g per litre (WRI, 2000). Cadmium is released into the air as a result of incineration or disposal of Cd-containing products, such as rubber tyres, plastic containers and the wear of break-linings (David and Wiliiams, 1975). In non-polluted soils, the cadmium concentration is generally less than 1.0 mg kg^{-1}. Recently, Onianwa (2001) has reported a study on the levels of Pb, Zn, Cd, Cu, Cr, Co, and Ni in the roadside topsoils in lbadan. Variations in the levels of lead in the roadside soils and vegetation were attributed to the traffic volume. It has been reported that the level of soil lead increased as the traffic volume increased, and decreased significantly as the distance from the highway increased (Xiong, 1998; Onianwa and Adoghe, 1997; Olajire and Ayodele, 1997; Zupancic, 1997; Fergusson, 1990; Garcia and Millan, 1988; Ward *et al.*, 1977). Widespread use of Zn in galvanized products have also contributed to the contamination of soils with cadmium and zinc (Kabata-Pendias and Pendias, 1992).

Studies of various environmental media in lbadan, Nigeria, have highlighted the growing hazards of the heavy meta-lrelated pollution load (Onianwa, 2001; Onianwa and Fakayode, 2000; Onianwa and Adoghe, 1997; Onianwa and Egunyomi, 1983). The present study aims at further assessing the level of heavy metal load due to the increased traffic volume with the growing population and to identify the other major anthropogenic sources of these heavy metals in the environment.

Materials and Methods

Soil samples were taken from 38 sites from the Ibadan Metropolis and its suburbs during the dry season, November 2001-January 2002 (Fig. 1). For effective sampling, the city was subdivided into five zones: urban industrial ((UI); urban high traffic (UHT), urban low traffic (ULT), refuse dump sites (RDS), and rural zones (RZ). The samples were collected in polyethylene bags from 0-5 cm depth (topsoil), with a stainless steel hand trowel. Samples were air-dried at ambient temperature for four days in the laboratory and then ground in a porcelain mortar and passed through a 0.5 mm nylon sieve.

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For elemental analysis, 0.5 g of the ground samples were placed in 50 ml teflon beakers and then digested with 10 ml of HNO_3-$HClO_4$-HF to near dryness at 80-90 °C on a hot plate. The digests were filtered into a 50 ml volumetric flask by using Whatman No. 42 filter paper and analyzed for Pb, Cd, Zn, Cr, Co,Ni and Cu by using Buck Scientific Model 200A flame atomic absorption spectrophotometer.

All samples were analyzed in duplicate and the results reported are the averages of these duplicates. Blanks were prepared for all digestions, while two controls were also run during the analysis. A blank was also prepared for all the digestions. All glassware and polyethylene sample bottles were precleaned by soaking overnight in a 3M HNO_3 and then thoroughly rinsed with distilled deionized water. Analar grade reagents were used. The instrument calibration standards were made by diluting the commercial BDH standard (1000 ppm) with deionized water.

Results and Discussion

Results of the soil metal concentrations are shown in Table 1. The average content of heavy metals in the topsoil of the study area was in the order of Zn > Pb > Cr > Ni > Cu > Co > Cd. The total metal concentrations in all of the five surveyed zones were generally higher than the normal levels expected in unpolluted topsoil and agricultural soils (Kabata-Pendias and Pendias, 1992; Nriagu, 1990).

The zonal average soil metal concentration, with respect to different human activities going on in the area, is given in Table 2. Topsoil of the study area showed a substantialy high concentration of Cd, Pb and Zn (Table 2), as compared with the estimated natural concentration of these metals in arable soils of Poland (mg kg^{-1} dry weight): Cd (0.1-0.6), Pb (8.0-25) and Zn (14-100) (Dudka, 1992). However, it is pertinent to mention that merely exceeding the natural concentration does not cause deleterious biological or ecological effects. Nega-

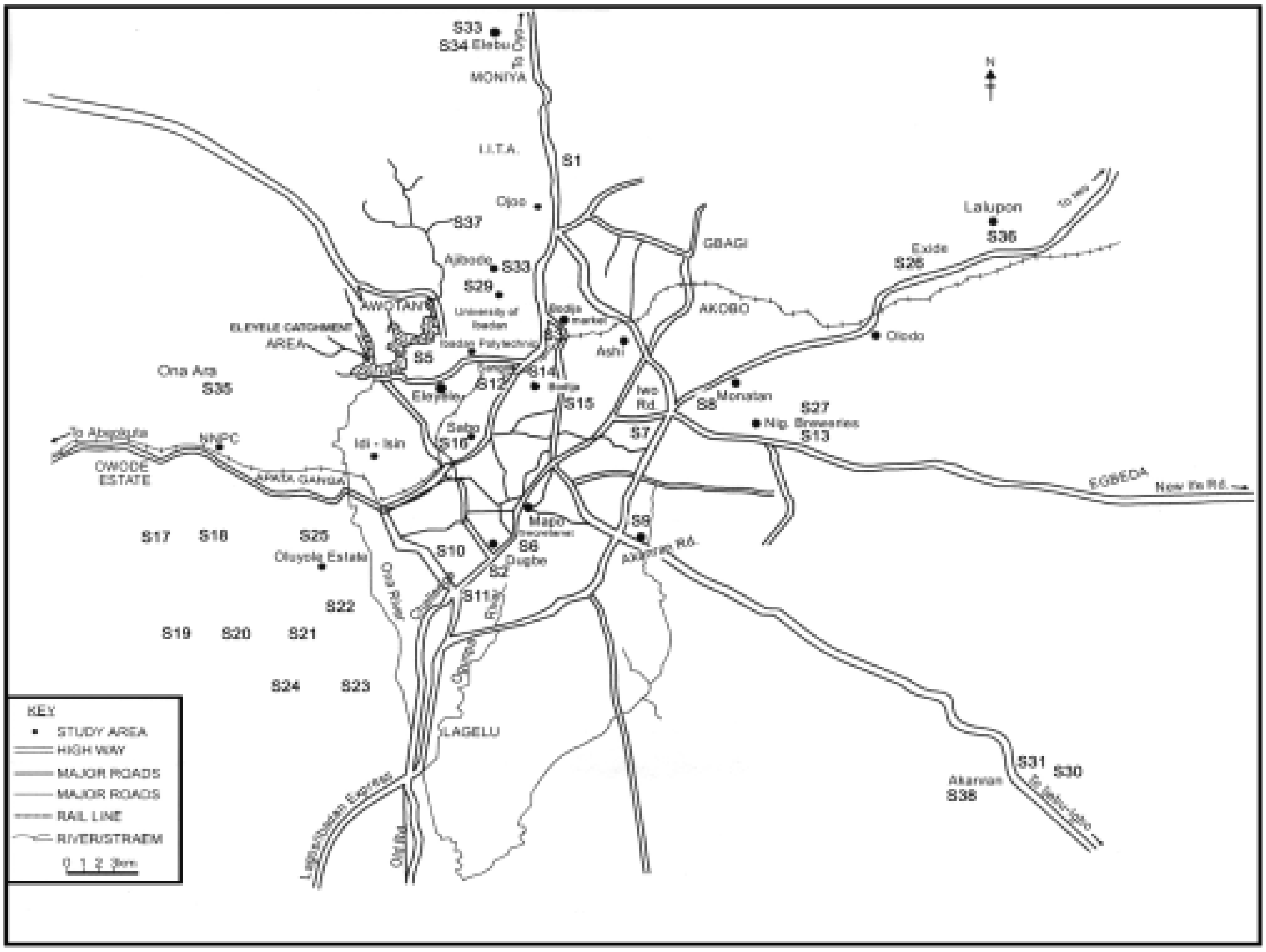

Fig. 1. Map of Ibadan Metropolis and its suburbs, Nigeria, showing the study area and the sampling points for study on the concentration and distribution of several metals (Pb, Cd, Zn, Cr, Co, Ni, and Cu).

tive effects of elevated concentration of metals in soils appear only when their critical (threshold) levels are exceeded. Maximum concentrations of these potentially toxic metals in the soils permitted under the European Community Regulations in mg kg^{-1} are: Pb (300), Cd (3.0), Zn (300), Ni (75), and Cu (140) (Kabata-Pendias and Pendias, 1992). Total average metal concentrations at all locations were (µg g^{-1} dry weight): Pb (150±143), Cd (4.2 ± 4.4), Zn (213±213), Cr (131± 96), Co (38±19), Ni (79±56), and Cu (40±36) indicating a significantly elevated level of pollution by these metals as compared with the data reported by Onianwa (2001).

Zonal distribution of the metals (Table 2) showed that the highest contamination of lead in the environment was traceable to the high traffic and refuse dumps zones, with an average level of 197±115 and 180 ± 49 µg g^{-1}, respectively.

Average cadmium level of 7.2 ± 7.7 µg g^{-1} was recorded from the industrial area of the city, which was about five times higher than the level in the rural zone. The highest concentration of 23 µg g^{-1} and 20 µg g^{-1} obtained for sample S18 and S19, respectively, was probably due to the proximity of two steel mills (Sanusi Steel Industries Ltd., and Steel Works Ltd.) located in the study sampling area (Table 1). Dudka *et al*. (1996) reported Cd level in arable soil in an industrial area of Upper Silesia, South Poland to be 3.20 mg kg^{-1}. Cadmium is released into the environment as a result of incineration or disposal of cadmium-containing products, such as rubber tyres, break-linings and plastic containers (David and Williams,1975), and as a bye-product in the refining of other metals, primarily zinc. Interelemental associations for the urban high traffic zone (UHT) were obtained by using the Pearson correlations (Table 3). These correlations were noted to be positive for the elemental pairs Pb-Cd (r = 0.521), Zn-Cr (r =0.603), Cr-Ni (r = 0.749), Co-Ni (r = 0.324), Pb-Cu (r = 0.412). The correlations were generally not too strong, though significant, probably due to the various sources of metal contaminants within the studied area. Open burning of municipal solid waste, indiscriminate dumping of refuse, indiscriminate siting of steel workshops are the common features of many locations in Ibadan. In the rural zone, however, where there was no significant pollution, the interelemental association showed a wide association between lead and other heavy metals, except for cobalt (Table 4). There was a positive correlation in the rural zone between Cd-Cr (r = 0.394), Cd-Co (r = 0.485), and Cd-Ni (r = 0.565).

The observed high concentration of zinc and chromium in the urban high traffic zone, 328±152 µg g^{-1} and 176±106 µg g^{-1}, respectively, may be due to the presence of these metals in the Zn-containing automobile additives, such as Zn-

Table 1. Metal concentration (µg g^{-1} dry weight of soil) in different soil sampling zones of Ibadan Metroplois and its suburbs, Nigeria

Soil sample number/zone	Connection of different metals Pb	Cd	Zn	Cr	Co	Ni	Cu
UHT(n=13)							
S1	480	4.8	210	151	26	80	75
S2	265	5.5	365	109	14	58	74
S3	262	3.5	112	179	28	166	30
S4	281	3.1	234	462	28	179	35
S5	171	2.0	347	171	18	69	19
S6	149	2.7	525	118	12	55	95
S7	166	3.0	367	94	53	51	54
S8	76	3.3	390	173	43	114	26
S9	100	3.8	617	260	47	228	41
S10	278	3.9	422	262	53	204	35
S11	84	3.7	68	64	30	60	24
S12	163	3.2	335	75	33	47	31
S13	83	2.9	277	174	44	54	27
ULT (n=4)							
S14	85	3.9	295	85	46	62	29
S15	44	3.1	53	76	41	51	20
S16	301	3.6	102	115	41	53	42
S17	116	3.2	480	197	39	52	34
Ul (n=11)							
S18	23	23	107	44	30	49	17
S19	19	20	25	224	35	87	15
S20	172	9.8	103	146	71	147	61
S21	72	8.4	348	130	104	117	116
S22	43	1.7	43	72	33	32	61
S23	60	1.8	27	168	91	113	20
S24	49	2.5	16	49	27	130	6
S25	67	1.9	101	189	46	96	14
S26	752	5.5	117	136	35	67	6
S27	236	1.7	636	68	36	76	40
S28	213	2.5	151	96	50	49	32
RDS (n=4)							
S29	232	1.7	60	39	21	16	12
S30	121	7.2	908	96	56	63	170
S31	205	5.4	103	416	37	202	137
S32	160	3.2	28	50	23	33	46
RZ (n=6)							
S33	27	1.4	22	38	30	21	21
S34	8	1.9	8	42	37	24	7
S35	32	2.0	23	41	26	21	23
S36	25	1.7	25	63	29	25	9
S37	66	2.2	25	55	15	25	14
S38	13	0.8	26	40	10	21	18
Control (n=2)							
S39	8	0.5	10	32	10	11	7
S40	6	0.4	13	15	11	14	9

UHT= urban high traffic; ULT= urban low traffic; UI= urban industrial; RDS= refuse dump sites; RZ= rural zone

Table 2. Metal concentrations (μg g^{-1} dry weight of soil) in different soil sampling zones of Ibadan Metropolis and its suburbs, Nigeria, showing their mean, standard deviation, range, and coefficient of variation

Zone	Pb	Cd	Zn	Cr	Co	Ni	Cu
UHT (n = 13)							
Mean	197±115	3.5±0.9	328±15	176±106	33±14	105±66	44±24
Range	76 - 480	2.0 - 5.5	68 - 617	64 - 462	12 - 53	47 - 228	19 - 95
cv (%)	58	26	46	60	42	63	55
ULT (n = 4)							
Mean	137±114	3.5±0.4	233±55	118±55	42±3	55±5	31±9
Range	44-301	3.1- 3.9	53 - 480	76 - 197	39 - 46	51 - 62	20 - 34
cv (%)	83	11	84	47	7	9	29
UI (n = 11)							
Mean	155±212	7.2 ± 7.7	152±185	120±59	51±26	88±37	35±33
Range	19 - 752	1.7 - 23	16 -636	44 - 224	27 - 104	32 - 147	6 - 116cr
cv (%)	137	107	122	49	51	42	94
RDS (n = 4)							
Mean	180±49	4.4±2.4	275±423	150±179	34±16	79±85	91±74
Rang	121 -232	1.7 - 7.2	28 - 908	39 - 416	21 - 56	16 -202	12 - 170
cv (%)	27	55	154	119	47	108	81
RZ (n=6)							
Mean	29±20	1.7±0.5	22±76	47±10	25±10	23±2	15±6
Range	8 - 66	0.8 - 2.2	8 - 26	38 - 63	10 - 37	21 - 25	7 - 23
cv (%)	71	29	32	21	40	8	40
Control							
Mean	7.0±1.0	0.5±0.1	11.5±1.5	23.5±8.5	10.5±0.5	12.5±1.5	8.0±1.0

UHT= urban high traffic; ULT= urban low traffic; UI= urban industrial; RDS= refuse dump sites; RZ=rural zone; ± =standard deviation; cv = coefficent of varation

diethylcarbamate used in vulcanization, and from engine wear and tear (Onianwa and Ajayi, 2002; Lageweff and Specht, 1970). The nickel level of 105±66 μg g^{-1} (for all locations) was obtained in this study, which was about 10-folds higher than the levels reported by Onianwa (2001). Nickel is used for the production of heat-resistant and special corrosion-resistant steels, Zn-Ni alloys. The wear and tear of automobile engines contributes significantly to the Ni and Zn load in the environment, especially in the urban high traffic density areas. Sampling period may, as well, contribute significantly to the high level of these metals in the soil. Sample collection was done during the dry season when there was heavy atmospheric fallout on the topsoils, hence very low dissolution, mobilization and leaching of the fallout of these metal.

The zonal metal distribution showed the highest distribution of Zn, Pb, Cr and Ni in the urban high traffic zone and the least distribution of all metals in the rural zone where there was no significant pollution.

The coefficient of variation (cv) for zonal distribution of metals in the city showed a very high variation (above 100%), which were: Pb (137), Cd (107) and Zn (122) in the industrial zone, and Zn (154), Cr (119) and Ni (109) at the refuse dumps (Table 2). The range of these metals in the urban industrial zone was 19-752 μg g^{-1}, 1.7-23 μg g^{-1}, and 16-636 μg g^{-1} for Pb, Cd and Zn, respectively. The high lead variation in the zone was due to the influence of an autobattery industry, located in the area, as shown by sample S26 (752 μg g^{-1}). The variation obtained for the refuse dumps showed higher values, above 100% for Zn, Cr and Ni, with a spread of 28-908 μg g^{-1} (cv=154), 39-416 μg g^{-1} (cv=119), and 16-202 μg g^{-1} (cv=108), respectively. The high Zn variation in the industrial zone was probably due to the high contribution made by sample number S21 (348 μg g^{-1}) and sample number S27 (636 μg g^{-1}), obtained from the power generation area of Nigerian Breweries Ltd., which were characterised by waste oil spill and along the effluent line of Sanusi Steel Mills, respectively. Generally, the poor coefficient of variation could be improved by increasing the number of observations.

Conclusion

The results obtained showed the highest distribution of zinc, lead, chromium and nickel in the urban high traffic zone, suggesting traffic volume as the major anthropogenic source of

Table 3. Interelemental association (Pearson correlation) in the urban high traffic zone soil samples taken from Ibadan Metropolis and its suburbs, Nigeria

	Pb	Cd	Zn	Cr	Co	Ni
Cd	0.521					
Zn	-0.272	-0.096				
Cr	0.231	-0.102	0.603			
Co	-0.233	-0.084	0.188	0.160		
Ni	0.142	0.111	0.231	0.749	0.324	
Cu	0.412	0.408	0.334	-0.214-	-0.426	-0.257

Table 4. Interelemental association (Pearson correlation) in the rural zone soil samples taken from Ibadan Metropolis and its suburbs, Nigeria

	Pb	Cd	Zn	Cr	Co	Ni
Cd	0.475					
Zn	0.651	-0.316				
Cr	0.422	-0.394	0.290			
Co	-0.356	0.485	-0.677		-0.060	
Ni	0.184	0.565	-0.214	0.855	0.186	
Cu	0.571	-0.262	0.553	-0.577	-0.288	-0.848

these heavy metals in the study area. The highest cadmium and cobalt concentration was obtained from the industrial zone, while copper was significantly higher at the refuse dumps.

References

Alan, W. 1993. *Soil and the Environment: An Introduction*, Cambridge University Press, Oxford, UK.

Alloway, B.J. 1990. The origins of heavy metals in soils. In: *Heavy Metals in Soils*, B. J. Alloway (ed.), pp. 29-39, Blackie, London, UK.

David, D.J., Williams, C.H. 1975. Heavy metals contents of soils and plants adjacent to the Home Highway near Marulan, New Soth Wales. *Aust. J. Exptl. Agric. Husb.* **15:** 414-418.

Dudka, S. 1992. Factor analysis of total elements concentration in surface soils of Poland. *Sci. Total Environ.* **121:** 39-52.

Dudka, S., Piotrowska, M., Terelk, H. 1996. Transfer of cadmium, lead and zinc from industrially contaminated soil to crop plants: a field study. *Environ. Pollut.* **94:** 151-188.

Fergusson, J. E. 1990. *The Heavy Metals: Chemistry, Environmental Impact and Health Effects*, pp. 1-309, Pergamon Press, Sydeny, Australia.

Garcia, R., Millan, E. 1988. Assessment of cadmium, lead and zinc contamination in roadside soil and grasses from Gipuzkoa (Spain). *Chemosphere* **37:** 1615-1625.

Kabata-Pendias, A., Pendias, H. 1992. *Trace Elements in Soil and Plants*, pp. 1-21, 2nd edition, Lewis Publishers, Boca-Raton, Florida, USA.

Lagerweff, J. V., Specht, A.W. 1970. Contamination of roadside soil with cadmium, nickle, lead and zinc. *Environ. Sci. Technol.* **4:** 583-586.

Nriagu, J.O. 1990. Global metal pollution poisoning the biosphere? *Envion* **32:** 7-33.

Olajire, A.A., Ayodele, E.T. 1997. Contamination of roadside soil and grass with heavy metals. *Environ. Int.* **23:** 91-101.

Oniawa, P.C. 2001. Roadside topsoil concentrations of lead and other heavy metals in lbadan, Nigeria. *Soil and Sediment Contamination* **10:** 577-591.

Onianwa, P.C., Adoghe, J.O. 1997. Heavy metal contents of roadside gutter sediments in Ibadan, Nigeria. *Environ. Int.* **23:** 893-897.

Onianwa, P. C., Ajayi, S.O. 2002. Heavy metals contents of roadside mosses in the northern and south-eastern regions of Nigeria. *Chem. Ecol.* **18:** 1-187-194.

Onianwa, P. C., Egunyomi, A. 1983. Trace metal levels in some Nigerian mosses used as bioindicators of atmospheric pollution. *Environ. Pollut. (Serices B)* **5:** 71-81.

Onianwa, P. C., Fakayode, S.O. 2000. Lead contamination of topsoil and vegetation in the vicinity of a battery factory in Nigeria. *Environ. Geochem. Health* **22:** 211-218.

Ward, N. I., Brooks, R.R., Roberts, E. 1977. Heavy metal pollution from automotive emission and its effect on roadside and pasture species in New Zealand. *Environ. Sci. Technol.* **11:** 917-920.

WRI. 2000. *Exposure to Air Polluted with Lead from Gasoline in Developing Countries*, World Resource Institute, retrieved December 12, 2000, world wide web: www.wri.org/ehi/dev-leaddev.html.

Xiong, Z. 1998. Heavy metal contamination of urban soils and plants in relation to traffic in Wuhan City, China. *Toxicol. Environ. Chem.* **65:** 31-39.

Zupancic, N. 1997. Lead pollution of Ljublana-Zagreb roadside soils. *Rud-Metal Sb.* **44:** 169-185.