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Sequential extraction of cadmium, lead and zinc in soil profiles of Ifon and Environs, southwest Nigeria: Submission for their availability to terrestrial organisms

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Abstract

Soil profile at 5 agricultural areas within and around Ifon, southwest, Nigeria and at the sides of a major road in the region were investigated to determine the contents of Pb, Cd and Zn, in order to ascertain their availability to plants, animals and humans. The procedure used involved sequential extractions technique. Generally metal contents decrease with depth. Their concentrations are Cd (0.68-1.93 $mgkg^{-1}$), Pb (4.27-6.21 $mgkg^{-1}$) and Zn (33.16-46.63 $mgkg^{-1}$) except for the roadside soils with ranges of 114.32-141.96 $mgkg^{-1}$ for Pb, 9.71-11.78 $mgkg^{-1}$ for Cd and 123.13-132.25 $mgkg^{-1}$ for Zn. Sequential extractions show that the mobility factors are low for Pb at all sites under study while those of Cd are high in Ifon soils. Values of mobility factor are only high for Zn in site C. This study shows that rural areas with link-roads to urban cities are prone to heavy metals bioaccumulation. It recommends heavy metals status-depended selective use of soils and provides a programme for monitoring such environment.

Keywords: Heavy metals, bioavailability, soil use, Ifon.

Introduction

The solid geology of an area controls the metal contents in soils and hence determines the development of plants and the health of animals and humans in that environment. Contents of trace elements in the soil depend on the mineral composition and texture (Pospisilova & Lastincova, 1998) and on the parent substrate from which the soil was formed (Mengel & Kirby, 1979). Soils overlying mineralized rocks have inherent high concentration of particular elements. However in other areas where the metal contents are within the range (Alloway, 2005) considered healthy for agricultural soils, human activities can result in the production of higher than normal concentrations of elements including heavy metals in the soils. Zn and Cd are essential components of many alloys, wires, tires and many industrial processes and could be released into the roadside soils and plants as a result of mechanical abrasion and normal wear (Jaradat & Momani, 1999). Zn is also leached in high concentrations in the vicinity of its ore sites (Walker, 1971), while Cd is predominantly introduced in soil with mineral fertilizers, that is, cadmium containing phosphate raw materials (Forstner, 1980). Lead results from running automobile engines (Barbier, 1979).

Some heavy metals are essential for the healthy development of plants, animals and humans but they can be toxic and harmful if available in certain concentrations. The kidney and the liver are the major target organs of Cd accumulation and exposure to Cd leads to renal tubular dysfunction (Adaikpoh *et al.,* 2007), poor bone mineralization (Carisson & Lundholm, 1996) and testicular necrosis (Massanyi *et al.,* 2000). Accumulation of lead causes damage to the brain and nervous system. Cd and Pb are the elements in certain contaminated soils that are considered to constitute the widest possible health risk to humans through the plant uptake-dietary route (Alloway, 2005). The danger ensuing from these metals derives from their tendency to accumulate in the vital organs of humans, animals and plants (Simunic *et al.,* 2002). Unlike many organic pollutants, metal ions cannot be transformed into inert forms, so their environmental presence is permanent (Simunic *et al.,* 2002). Hence it is advisable to monitor the levels of these trace elements in the soils in areas of high population density and high human activities. Considerable studies have been carried out in developed countries to assess the heavy metals content in the soil. In developing countries, only few reports on such studies are available and these are done in urban areas. No study is known of these metals content in rural areas in developing countries where agricultural activities are domiciled.

However, knowledge of the total contents of heavy metals present in the soil provides limited information about their behaviour and bioavailability (Iwebue, 2007). The bioavailability and environmental mobility of the metals are dependent upon the form in which the metals are associated with the soil (Jaradat & Momani, 1999). Only metals dissolved in solution and those adsorbed to sediments by cation exchange processes are readily available to plants and organisms. While metals in some pedo-chemical phases may be available depending on several mobilization/immobilization processes, complexed or strongly bound metals are most likely unavailable to organisms (Horsfall & Stiff, 2005). This study assessed the contents of Pb, Cd and Zn in soils of Ifon area (with high agricultural & quarrying activities),

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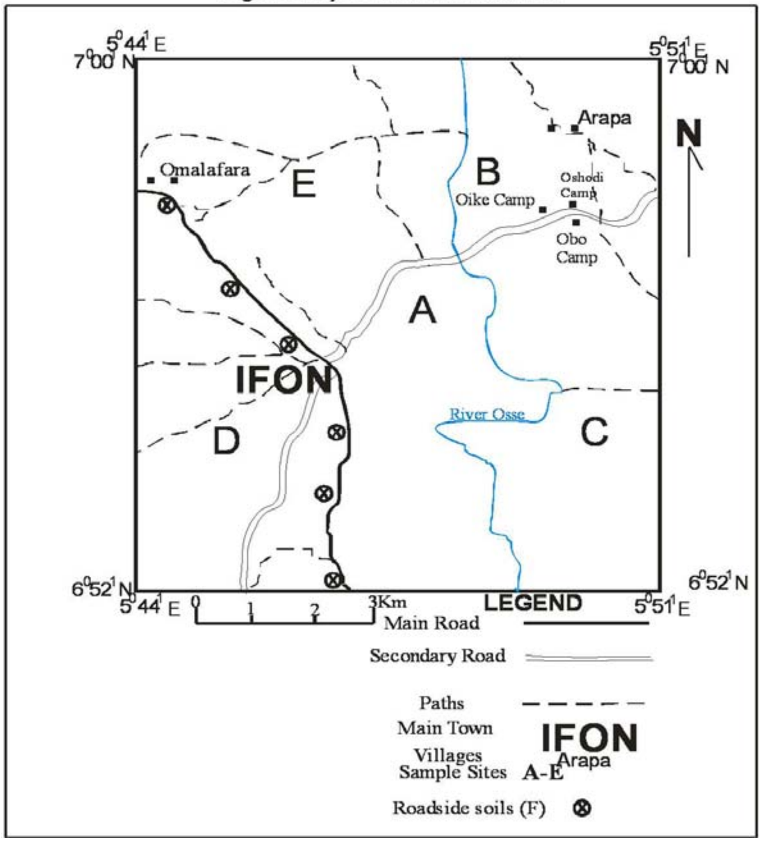
Fig. 1. Map of Ifon & Environs.



their pedo-chemical phase-distribution and hence their bioavailablity.

Study area

Ifon is a typical Nigerian town with low population density where the inhabitants live by subsistence farming with no major industrial activity except for quarries within its environs. It is transversed by a major and busy road linking western regions to the midwestern region of Nigeria. The area under study include Ifon and its environs bounded by Latitude $5^{o}44^{1}$ N and 5^{o} 51^{1} N and Longitude $6^{o}52^{1}$ E and $7^{o}00^{1}$ E (Fig. 1). It is underlain by sandstone ridges and shale of the Anambra formation which lie uncomfortably on the northeasterly basement complex migmatite gneiss, giving the area a rugged topography.

Method of study

Samples were collected from both sides of the road at six points to form the roadside composite sample (F) (Fig. 1). A minimum of 6 random samples were used as composite sample for other sampling areas (A-E), collected 10 m apart within 100 x 100 m of each of the area. At each sampling point, samples were taken from 0-15 cm, 15-30 cm and 30-50 cm depths. Soils collected from same depths were combined to form the representative sample for that horizon for that site. The samples were air-dried. Part of each was sieved for grain-size analysis while the other part was ground to pass through 2 mm sieve and used for chemical analysis. The procedure for the chemical analysis is as described by Tessier *et al*. (1979) and employed by Iwebue (2007). This procedure separates the metals into 6 fractions (F1-F6) described in the analytical procedure.

Analytical procedure

2 g of soil was placed in 50 ml polycarbonate centrifuge tube and subjected to the following extraction procedure:

Water soluble fraction F1; the metals in the soil was extracted with 20 ml of deionised water (DI) for 2 h; Exchangeable fraction F2; the metal from F1 residue were extracted wit 20 ml of 1 mol l^{-1}; $MgCl_2$, pH of 7 for 1 h; Carbonate-bound fraction F3; the metals from F2 residue were extracted with 20 ml of 1 mol l^{-1} NH_4Ac at pH of 5 for 5 h; Fe-Mn oxides-bound fraction F4; the metals from F3 residue were extracted with 20 ml 0.04 mol $l^{-1}NH_2OH.HCl$ in 25% (v/v) HOAc at $96^{0}C$ with occasional agitation; Organic-bound fraction F5; the metals from F4 residue were extracted with 15 ml 30% H_2O_2 at pH of 2 (adjusted with HNO_3) for 5.5 h (water bath, $85^{o}C$). After cooling, 5 ml of 3.2 mol l^{-1} NH_4OAc in 20% HNO_3 was added and shaken for 30 min before final dilution to 20 ml with DI. Residual fraction F6; the metals from F5 residue was digested using a HF-HCl/HNO_3 procedure.

All solid phases (except for F6) were washed with 10 ml of DI water before further extraction. The washes were collected and analyzed with supernatant from the previous fraction. After each extraction, the supernatant was separated by centrifugation for 30 min at 7500 x g. To verify the sum of the metals recovered in the sequential extraction steps, separate total concentrations of the metal were determined on the subsample after an HF/aqua regia digestion. Quality control was assured by the use of triplicates, standard reference materials (light s & soil CRM 142R) and the procedural blanks. For all elements analysed, the coefficient of variation on the triplicate analyses of the soil samples are less than 5%. The total concentrations of the metals in the supernatants from each step were analysed with atomic absorption spectrophotometer (Techtron). The recovery of trace metals in the sequential extraction steps was within 100±10%.

Result and discussion

Soils within this area are in some places immature, but generally characterized by yellowish red colour, 23.86±6.4% clay, 18.86±9.7% silt and 28.86±4.4% sand and 13.86±5.8% organic matter.

Total metal concentration: The total metal contents and the sum of metal contents from sequential extraction are presented for each horizon and each site in Table 1. Generally, metal contents decrease with depth. Their concentrations are Cd (0.68-1.93 $mgkg^{-1}$), Pb (4.27-6.21 $mgkg^{-1}$) and Zn (33.16-46.63 $mgkg^{-1}$) except for the roadside soils with ranges of 114.32-141.96 $mgkg^{-1}$ for

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Pb, 9.71-11.78 mgkg^{-1} for Cd and 123.13-132.25 mgkg^{-1} for Zn. These are within the range for agricultural soils (Lindsay, 1979; Kabata-Pendias & Pendias, 1992; Alloway, 1995; Adriano, 2001).

Table 1. Total metal contents in Ifon & sum of their sequential extracts.

Sites	Depth (cm)	Total content (mgkg^{-1})			Sum of extracts (mgkg^{-1})		
		Pb	Cd	Zn	Pb	Cd	Zn
A	0-15	4.61	1.47	47.37	3.38	1.31	46.32
	15-30	5.54	1.45	45.53	5.14	1.57	43.16
	30-50+	5.85	0.98	44.53	5.69	1.03	42.53
B	0-15	5.42	1.47	44.74	5.37	1.39	45.05
	15-30	4.44	1.01	42.63	4.51	1.12	42.21
	30-50+	4.28	0.98	41.47	4.34	1.03	41.58
C	0-15	6.21	1.93	48.42	5.52	2.05	46.63
	15-30	5.93	1.35	45.47	5.84	1.52	44.00
	30-50+	5.78	1.71	44.21	5.51	1.71	42.63
D	0-15	5.58	1.09	43.79	5.42	1.20	43.58
	15-30	5.24	0.99	42.95	4.87	1.05	43.37
	30-50+	4.98	0.87	42.02	4.84	1.03	42.32
E	0-15	5.48	0.87	40.21	5.33	0.88	38.95
	15-30	4.98	0.86	36.21	4.94	0.93	35.37
	30-50+	4.27	0.68	34.74	3.97	0.79	33.16
F	0-15	141.96	9.71	123.13	142.91	9.30	120.75
	15-30	133.32	11.78	132.25	131.45	11.04	128.75
	30-50+	114.32	10.50	123.27	115.55	9.33	125.21

Fig. 2. Percentage of lead in various geochemical phases of the soil from sequential extraction.

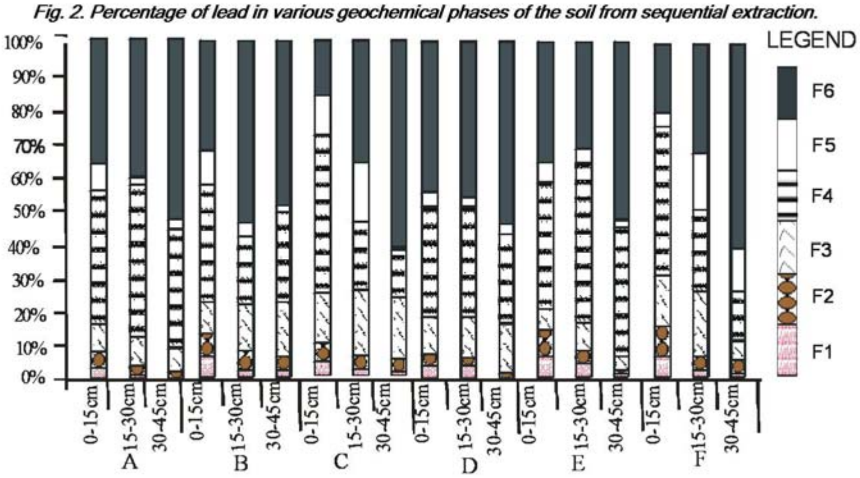
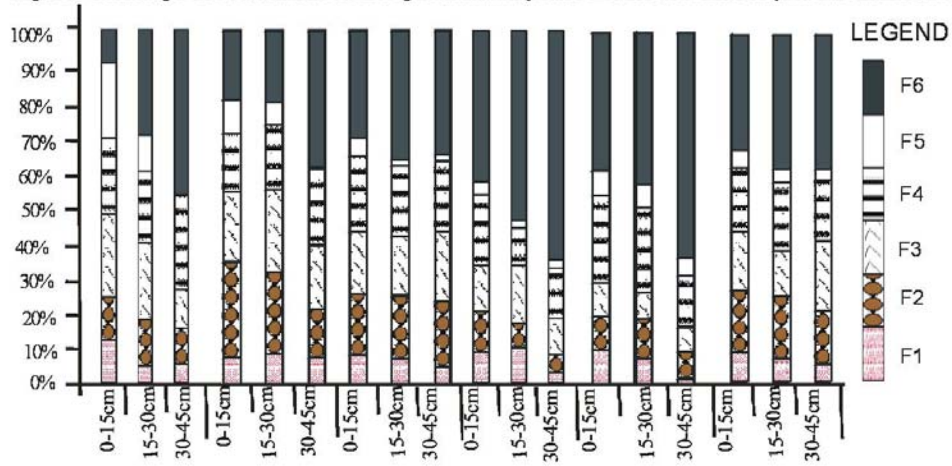


Fig. 3. Percentage of cadmium in various geochemical phases of the soil from sequential extraction.



Metal partition in soil: Results from sequential extractions are illustrated in Fig. 2-4.

Water soluble fraction (F1): This fraction represents those metals soluble in water. For the different sites, mean fractional content of the metals are Zn (1.27-6.71%), Cd (6.07-7.71%) and Pb (1.11-3.99%). Generally, all metals content of this phase decrease with depth.

Exchangeable fraction (F2): Mean fractional contents of metals for the sites in this pedo-chemical phase are Zn (4.05-13.50 %), Cd (7.96-21.72%) and Pb (2.36-6.00%). These values are higher than those of water soluble fraction.

Carbonate-bound fraction (F3): This pedo-chemical phase hosts 7.90-18.02 % of Zn, 8.10-20.72 % of Cd, and Pb (6.21-17.73%) as mean fractional contents for the sites.

Fe-Mn oxides-bound fraction (F4): Mean fractional contents of metals for the sites in this pedo-chemical phase are Zn (29.59-35.33%), Cd (15.29-22.37%) and Pb (27.09-41.57%).

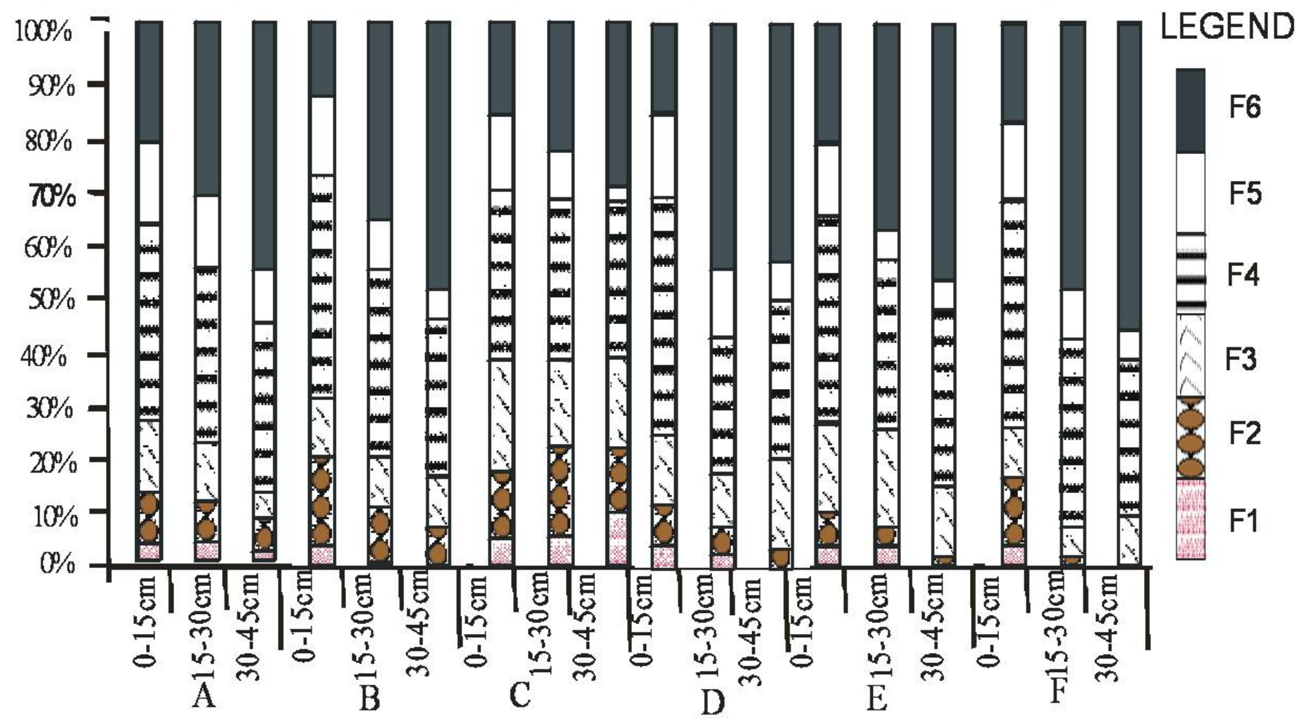
Organic-bound fraction (F5): 8.42-12.78% of Zn, 2.55-11.05% of Cd and 3.41-11.11% of Pb are the mean fractional contents of these metals captured in this phase for the sites.

Residual fraction (F6): Mean fractional contents of metals for the sites in this phase are Zn (23.34-40.61%), Cd (25.60-53.50 %) and Pb (36.74-48.19%). Cd and Pb have their highest percentages in this phase. Schintu *et al*. (1991) showed that most cadmium is bound to exchangeable site, carbonate friction, and iron-manganese oxide minerals which can be exposed to chemical changes at the sediment-water interface and are susceptible to remobilization.

Mobility factors of metals

The mobility factor was calculated according to Narwal *et al.* (1999) and Kabala and Singh (2001) as (F1+F2+F3) X 100% / (F1+F2+F3+F4+F5+F6). The mobility factors for sites and depths are shown in Table 2. The mobility factors are low for Pb at all sites under study hence it is not readily available, and poses no risk to the development of plants and human health. Except for site E and the lower horizon (30-45 cm) of site D, the mobility factors of Cd are high, hence high bioavailability in Ifon soils. This is a threat to the terrestrial ecosystem. Values of mobility factor are only high for Zn in site

Fig. 4. Percentage of zinc in various geochemical phases of the soil from sequential extraction.



C. High values of mobility factor for a heavy metal is an evidence of relative high bio-availability (Kabala & Singh, 2001). Zinc is released only when sediments are exposed to acidic environment or oxidized hence high abundance of soluble zinc are present under well oxidized conditions. Mobility factors decrease with depth for all metals and sites except for Cd (site A) and Pb (site C).

Table 2. Mobility factor for metals assayed for in Ifon, southwest Nigeria.

	Pb			Zn			Cd		
Depth (cm) / Site	0-15	15-30	30-45	0-15	15-30	30-45	0-15	15-30	30-45
A	15.98	14.78	9.24	24.95	22.55	11.13	41.55	39.45	25.72
B	29.27	24.78	11.17	26.33	8.05	9.33	40.83	33.66	38.95
C	25.04	24.67	23.33	34.77	35.09	32.22	43.22	42.44	41.64
D	19.25	19.06	16.3	23.55	18.88	19.05	35.17	35.93	28.32
E	20.12	17.13	6.10	25.96	24.37	15.31	27.66	25.36	26.53
F	21.85	19.15	22.45	29.64	21.16	16.41	44.28	48.13	38.96

Simunic *et al.* (2002) reported that the highest concentration of Pb and Zn in crop grains was recorded in the years of their highest availability to plants and similar results were obtained by Isermann (1983) and Christensen *et al.* (1998). Pb and Zn have low mobility factors in Ifon soils hence low bioavailability. They pose no environmental threat for now. Simunic *et al.* (2002) also reported that for Cd, the highest concentration in wheat grains were recorded at the lowest input to soil. Mortvedt (1987) opined that differences in the uptake and transport of Cd into the above-ground plants parts are considerable, depending on the species. Therefore, if such crops (or their species) are selected and solely grown in Ifon soils, Cd introduction into the food-chain through plant uptake-dietary route will be minimal.

Conclusion

Soils in Ifon and Environs generally have lead, zinc and cadmium contents that are within limits for agricultural unpolluted soils. However, the soils at the sides of the major road that transverse the area have very high values which can be adduced to the effluents from high vehicles traffic and spills from conveyed quarry products. The high concentration of metals at the road sides, and high mobility (high bio-availability) of Cd in the soil indicate potential risk to food-chain via the uptake in plants. Pb and Zn have low mobility factors in Ifon soils hence their low bioavailability. They pose no environmental threat for now. Since the uptake and transport of Cd into the above-ground plants parts are considerable, depending on the species, and the presence of these metals is permanent as they are not biodegradable; selective use of the soil is imperative. It is suggested therefore, that assessment of the levels of heavy metals in the soil should be considered as an essential parameter for the selection of crops (or species) that would be grown in an environment. The high values of metal content in roadside soils is also a matter of concern, hence continuous monitoring of heavy metals should not be limited to urban and industrial areas but be

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applied to rural or / and agricultural areas as well. Agricultural areas transversed by busy highways should be continuously monitored for changes of their metal contents, physico-chemical parameters, soil organic content, pH, PAHs, conductivity, temperature, etc. Sampling should be done on a seasonal basis of 4 months in wet season and 4 months in dry season. Samples should be collected from depths of 15 cm (where most of the plants' roots are). Sampling should be systematic with points parallel to the road with progressively increasing distance of 1, 50, 100, 150, 200 and 300 m from the road.

References

1. Adaikpoh M A, Orhue NE and Igbe I (2007) The protective role of *Scoparia dulcis* on tissue antioxidant defense system of rats exposed to cadmium. *Afr. J. Biotech*. 6(10), 1192-1196.
2. Adriano DC (2001) Trace elements in terrestrial environments (2nd ed.), Springer-Verlag, New York. ISBN 10: 0387986782 / 0-387-98678-2.
3. Alloway BJ (1995) Heavy metals in soils. (2nd ed.) Blackie academic and professional, London. pp:284-305.
4. Alloway BJ (2005) Bioavailabilty of elements in soil. In: Essentials of medical geology (ed.), Elsevier inc. pp347-372.
5. Barbier M (1979) Introduction to chemical ecology. Inst. Chim. Subst. Nattur. CNRS, Girf-Sur-Yvette, France, Long-man, London, NY.
6. Carisson L and Lundholm CE (1996) Characterization of the effects of cadmium on the activity of some enzymes from neonatal mouse calvaria in culture. *Comp. Biochem. Physiol. Pharmcol. Toxicol. Endocrinol*. 115(3), 251-256.
7. Christensen TH, Lorenz SE, Hamon RE, Dominigues HC, Sequeira EM and Megrath SP (1998) Matured soil water concentrations of cadmium and zinc in plant pots and estimated leaching outflows from contaminated soils. *Wat. Air Soil Pollut*. 102, 105-115.
8. Forstner UG (1980) Cadmium. In: Hatzinger O (ed.) Handbook of environmental chemistry, Part A. Springer-Verlag, Berlin, Heidelberg, NY. 3, 59-107.
9. Horsfall M and Spiff AI (2005) Speciation and bioavailabilty of heavy metals in sediments of Diobu River, PortHarcourt, Nigeria. *Euro. J. Sci. Res.* 6(3), 20-36.
10. Isermann K (1983) The extent to which agriculture is involved in environmental problems in modern industrial society. IFA Report A//83/60.
11. Iwebue CMA (2007) Metal fractionation in soil profiles at automobile mechanic waste dumps. Waste management and research, London. 25, 585-593.
12. Jaradat QM and Momani KA (1999) Contamination of roadside soils, plants and air with heavy metals in Jordan, a comparative study. *Turk. J. Chem.* 23, 209-220.
13. Kabala C and Singh BR (2001) Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter. *J. Environ. Quality*. 30, 485-495.
14. Kabata-Pendias A and Pendias H (1992) Trace elements in soils and plants. 2nd edn. CRC press Boca Raton Fl. p365.
15. Lindsay WL (1979) Chemical equilibria in soils. John Wiley & Sons, NY. ISBN 0-471-02704-9.
16. Massanyi P, Bardos L, Toman R, Hluchy S, Kovacic J and Lukai N (2000) Distribution of cadmium and its effects on the organ concenteation of retinoids on beta-carotene. 6th Int. World Congress for Biomed. Sci. Poster #38.
17. Mengel K and Kirby EA (1979) Principles of plants nutrition. 2nd ed. Int. Potash Inst., Bern. pp:436-437.
18. Mortvedt JJ (1987) Cadmium levels in soils and plants from some long-time soil fertility experiments in the United States of America. *J. Environ. Qual.* 16, 137-142.
19. Narwal RP, Singh BR and Salbu B (1999) Association of cadmium, zinc, copper and nickel with components in naturally heavy metal rich soils studied by parallel and sequential extraction. *Commun. Soil Sci. Plant Analysis*. 30, 1209-1230.
20. Pospisilova L and Lastincova J (1998) Determination of some trace elements in soil using ICP-AES method. *Rostl. Vyr*. 44, 427-429.
21. Simunic I, Tomic F, Kisic I and Romic M (2002) The content of Zn, Zn and Cd in hydroameliorated soil and drainage water and their uptake by plants. *Rostl. Vyr*. 48(9), 401-406.
22. Tessier A, Campbell PGC and Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51, 844-857.
23. Walker C (1971) Environmental pollution by chemicals. Hutchinson Educational, London. p:52.