The Impact of Heavy Metals on the Soil in Calabar Metropolis Lemna Area

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Abstract:- Soil samples were collected from the dumpsite soil located at Lemna Road, Calabar Municipality, Cross River State, Nigeria to investigate the speciation and bioavailability of some trace metals namely: iron, cadmium, copper, zinc and lead. Extract from the soil were obtained by sequential extraction. This involved Acid extractable fraction, Oxidisable fraction, Reducible fraction and Residual fraction. These fraction were then analyzed for Pb, Cd, Cu, Fe and Zn using acetylene flame atomic absorption spectrophometer. The results obtained, showed that the metals occurred with the following percentage bioavailability: Fe (33.57%), Zn (43.59%), Cd (67.23%), Cu (82.98%) and Lead (69.96%). Acid extractable 5.57% reducible fraction accounted for over 9.33% of the total fractions, metal bound to residual and oxidisable fraction accounted for 10.90% and 13.05% respectively. Fe has the highest distribution in all the fractions followed by Zn while Cd has the least in all the fractions. The results of these findings indicates that the trace metals with exception of Cd were readily bioavailable in the dumpsite soil therefore, phytoremediation is advocated.

I. INTRODUCTION

Contamination of the soil by trace metal is a far more serious problem than either water or air pollution because they are usually tightly bound by the soil and may persist for centuries depending on the conditions. Hence the environmental problem of soil pollution by trace metals has received increasing attention in the past decades in both developed and developing countries of the world. Metal toxicity though dependent on their chemical forms, can cause several diseases affecting almost all the vital organs and functions of the human body· However, trace metals such as Zn, Cu, Cr, Fe, and Mn are required by the body in small amount, but can be toxic in larger quantities. It has been reported that the determination of total trace metal content in soil cannot indicate the comprehensive pollution status of the environment but metal speciation can identify the bioavailability, mobility and toxicity of trace metal in soils. Unlike the single extraction technique, sequential extraction gives information about both mobile and stable fraction of

metals in soil, which evaluates the actual potential mobility in metals and according to Bashir et al.. (2013). The understanding of metal bioavailability and mobility in soil is important for evaluating its potential environmental and health effects. Environmental reports have also shown that, pollution of soil environment is ascertained by calculating the enrichment factor, the contamination factor/degree of contamination and index of geoaccumution. However, previous studies in dumpsite soils within the area concentrate on the determination of total metal content without assessing the polluting status of the dumpsite and metal. These elements are usually associated with the principle component of the samples (Carbonates, Organic Matter, Fe –Mn Oxides and Minerals) and they are available to living organism when the dissolved in environmental materials. The information about the physiocochemical properties of the elements is required for understanding their environment behavior, including mobility and bioavailability, the determination of total metal content in the samples after digestion with aqua regia does not provide sufficient criteria for estimating their ecological and biological effects. The sampling area was mainly influenced from three sources natural phenomenon, namely industrial, traffic and natural sources. The mobilization of metal, in particular toxic heavy metals has caused the increase of their concentrations in the environment. Investigation of metal contents of the dust samples of car parking areas are vital for heavy metal pollution originated from traffic particularly lead and recently the elements of platinum group, used in catalytic convertors for the purpose of reducing the pollutants coming from automobile emissions. This study aimed at using metal speciation to identify the forms, mobility, bioavailability toxicity and sources of trace metals in Lemna dumpsite soils. It is also aimed at establishing the pollution status of the Lemna dumpsite soil and its environ and compared result obtained at control site with that of Lemna dumpsite soil thereby stressing the possible factor, and effect for any difference observed.

Nowadays soil pollution is main problem to agriculture. Soil pollution may arise and mainly from industrial waste, sewage water, pesticides, fertilizers (chemical based), mining and smelting, fuel production,

automobile les etc. Industrial activities are also caused of land pollution like chemical industries, paper and pulp mills, steel industries, pharmaceuticals industries, mining industries, refineries. pesticides and fertilizer industries. thermal and nuclear power plants, food processing industries, tanneries. textile industries etc. releases their effluents direct into lands.

Srinivas N. *et al.,* (2005). reported the concentration of Pb. Zn. Ni and Cu in air, soil and vegetables analyzed by using ICP-ES. The work done mainly in industrial areas, sub urban and rural areas of Vishakhapatnam. The P b c o n c e n t r a t i o n (*1.*46μg/m^3) is higher in industrial area. The Ni, Zn and Cu concentrations is higher in semi urban area than with industrial area. The concentration of Pb in vegetable rural area 0.88 to l.02μgis and sub urban area 3.55μg/g.

Metals in the environment may be present in the solid, liquid or gaseous state. They may be present as individual elements and as organic and inorganic compounds. The movement of metal between environmental reservoirs may or may not involve changes of state. The geosphere is the original source of all metal (except those that entered the atmosphere in the form of meteorites and cosmic dust.) Within the geosphere, metals may be present in minerals, glasses and melts. In the hydrosphere metals occur as dissolved ions and complexes, colloids and suspended solids.

In the atmosphere, metals may be present as gaseous elements and compounds and as particulate and aerosols (Nriagu; 1989). Gaseous and particulate metals may be inhaled and solid and liquid (aqueous-phase) metals may be ingested or absorbed, thereby entering the biosphere. In addition to being the original source of all terrestrial metals. The atmosphere and hydrosphere also constitute sinks for metals however, from a geological perspective, they are more likely to be considered as agents of transport.

The main source for metal input to plants and soils is atmospheric deposition. Volatile metalloids such as As, Hg, Se, and Sb can be transported over long distance in gorgeous form or enriched in particles, while trace metals such as Cu, Pb, Zn are transported in particulate phases (Adriano, 200l. Adriano *et of ..* 2005) in terrestrial ecosystem, soils are the major recipient of metal contaminants. while in aquatic systems sediments are the major sink for metals (Spark. 2005). Freshwater system are contaminated due to runoff and drainage via sediments or disposal, while groundwater is impacted through leaching or transport via mobile colloids (Adriano, 200l). A number of biological processes take place at the heterogeneous interface between the rock, soil, water, air and living organisms. (Spark. 2005). The process or interaction ill turn controls the solubility, mobility. bioavailability and toxicity of metals (Sparks, 2005). Metals are found in solution as free ions or complexes to inorganic or organic liquids. Both the free ions and the metal· ligand complexes can be; taken up by plants, retained on minerals, natural organic matter, microbes, transport through the soil

profile into ground water via leaching or by colloid-facilitated transport, precipitated as solid phases, diffused in porous media such as soils.

This research work was carried out in the dumpsite soil at Lemna Road, Calabar, Cross *River* State, Niger Delta region of Nigeria. The state is located in the coastal south-south part of the country, lying between S' 45°N 8'30°E *I*5. 750°N 8.SOO'E. The state has basically two distinct seasons namely the dry and the wet. The wet season fasts between 8 to 9 months starting from mid-march till the end of November. The dry season has a short duration of between the last week of November or early December and last till early march. This study was undertaken during April when the rain was not yet much to avoid the leaching of the heavy metals to the soil. During the sampling the surface soil samples were obtained from the following location within the dumpsite at Lemna Road, Calabar.

Table 1 Coordinates Samples Location

S/N	Locations	Coordinate
1	Location 1	N 5°01'59.4'' E8°21'59.3
2	Location 2	N5°01'59.7'' E8°21'49.9''
3	Location 3	N5°01'57.2'' E8°2157.5''
4	Location 4	N5°01'58.7'' E8°21'58.8''
5	Location 5	N5°02' 1.7'' E8°21'59.3''
6	Location 6	N5°02' 1.9'' E8°21'47.6''

II. SAMPLE COLLECTION AND TREATMENT

Top soil (0-15 cm) samples were collected at six (6) different locations including the control sample. A W-shape format was employed in collecting samples in order to cover a transverse of the dumpsite soil while the soil auger was use to pick samples at six (6) different location.

➢ *All samples were air dried for three (3) days and grounded to pass through a 2rnm mesh. While trace metals speciation was done using 3.3 procedures for optimized BCR sequential extraction of trace metals were as described by Rauret et al,(2000) and Umoren et al, (2014).*

● Acid extractable fraction: 40ml of 0.11rnol/L acetic (CH$_3$COOH) was added to 1 g of dry soil sample in a 50ml polypropylene tube. The mixture was shaken overnight (16hr) in an end to end mechanical shaker at room temperature. The mixture was centrifuged at 3000rpm for 20mins to separate the extract from residue.

● Reducible fraction: 40ml of 0.5mol/L hydroxyl ammine hydrochloride (NH$_2$0HHCl) containing 2.5ml 2m HNO$_3$ (pH = 1.5), was added to residue from step 1, shaken for 16hr at 22 ± 5^0c .The mixture was centrifuged as per step 1.

- Oxidisable fraction: the residue from step two (2) was treated twice with 10ml of 8.8mol/L hydrogen peroxide (H_2O_2) and allowed to digest for one (1) hour with intermittent manual mixing. The mixture was evaporated to dryness, then 50ml of 1 mol/dm3 ammonium acetate (NH_4OAC) adjusted to pH = 2 with 2m HNO3 was added, shaken for 16hr at 22 $\pm$ 5^{0}C and centrifuged to separate the extract from residue.

Residual fraction: To the residue from step iii, 5ml 16mol/L HCl on a hot plate cooled for 2hr and filtered through Whatman no. 50 filter paper into a volumetric flask for analysis. Determination of total trace metal 1g of sieved soil sample was digested with 5ml conc. HNO3 and 15ml conc. HCl on a hot plate. After cooling, the digest was filtered using (Whatman type 50 filter paper) into a 100ml volumetric flask and diluted to the mark with distilled water. Concentration of Cd, Cu, Fe, Zn, and Pb, in the extract from both sequential extraction method and total metal extracts were determined using air acetylene flame atomic absorption spectrophotometer (Unicam 939/959 model) Rauret *et al.*, 1999, Mmolawa *et al.*, 2011, Udousoro *et al.*, (2010).

III. CHEMICAL ANALYSIS

All the supernatant solution from stage (i) to (iii) and the residual digest (iv) were analyzed for the following trace metals: Lead (Pb), Cadmium (Cd), Copper (Cu), iron (Fe), and Zinc (Zn) using air acetylene flame atomic absorption spectrophotometer (Unicam 939/959 model).

➢ *Apparatus / Equipment used in the project.*
- Soil auger
- Crucible
- Filter
- Filter funnel
- Mechanical shaker
- Centrifuge / fume cupboard
- Atomic Absorption Spectrometer (AAS).
- Viii) Conical flask
- Reagent bottle
- Beaker
- 3.5 Chemical / Reagents
- Acetic Acid (CH_3COOH)
- Polypropylene tube
- Hydrogen peroxide (H_2O_2)
- Nitric acid (HNO_3)
- Hydroxyl ammonium chloride ($NH_2OH.HCl$)
- Ammonium acetate (NH_4OAC)
- Aqua regia (tri-oxonitrate and nitric acid)
- Hydrochloric acid (HCl)

IV. RESULT

Table 2 Total Concentration of Trace Metal Ions (M/Kg) in Calabar Dumpsite Soil and Control.

Location	Pb	Cd	Cu	Fe	Zn
A	238.25	1. 32	37.40	2506.01	1169.47
B	241.07	1.45	43.26	2495.39	1246.32
C	225.63	1.23	40.38	2673.85	1072.38
D	232.94	1.29	36.74	2594.17	1350.53
Control	5.78	0.42	4.72	306.55	12.06

Table 3 Different Fractions of Lead

Location	Acid extractable	Reducible	Oxidisable	Residual
A	66.85	98.30	33.48	37.62
B	67.52	99.01	34.15	38.27
C	63.65	95.16	30.32	34.46
D	65.52	96.73	32.18	36.16
Control	1.37	2.11	1.24	0.92

Table 4 Different Fractions of Cadmium

Location	Acid extractable	Reducible	Oxidisable	Residual
A	0.50	0.35	0.23	0.19
B	0.51	0.37	0.26	0.22
C	0.47	0.33	0.21	0.17
D	0.48	0.34	0.22	0.18
Control	0.16	0.10	0.07	0.06

Table 5 Different Fractions of Copper

Location	Acid extractable	Reducible	Oxidisable	Residual
A	4.92	14.24	10.28	6.21
B	7.54	16.36	11.41	6.12
C	6.82	15.62	9.69	6.40
D	5.91	14.69	9.78	4.49
Control	0.90	1.82	1.12	0.82

Table 6 Different Fractions of Iron

Location	Acid extractable	Reducible	Oxidisable	Residual
A	315.21	492.12	614.30	1012.32
B	312.51	489.40	611.58	1009.62
C	357.13	534.02	656.20	1054.24
D	337.21	514.10	636.28	1034.32
Control	47.75	61.06	78.23	114.51

Table 7 Different Fractions of Zinc

Location	Acid extractable	Reducible	Oxidisable	Residual
A	179.18	304.03	407.20	224.25
B	198.39	323.24	426.38	243.42
C	155.00	279.75	382.83	199.89
D	224.43	349.28	425.35	269.43
Control	1.87	3.13	4.38	2.06

Table 8 Percentage Concentration of Metal Ions in Different Fractions

S/N	Fractions	Pb	Cd	Cu	Fe	Zn
1	Acid extractable	0.66%	0.005%	0.063%	3.31%	1.89%
2	Reducible	0.97%	0.003%	0.15%	5.07%	3.14%
3	Oxidizable	0.33%	0.002%	0.10%	6.30%	4.17%
4	Residual	0.37%	0.0019%	0.06%	10.28%	2.34%

Table 9 Shows the Mean Value, Total Concentration and % Bioavailability

S/N		Pd	Cd	Cu	Fe	Zn
1	Mean value	234.47mg/kg	1.32mg/kg	39.45mg/kg	2567.36mg/kg	1209.68mg/kg
2	Total conc.	2.34%	0.013%	0.39%	25.67%	12.10%
3	%bioavailability	69.96%	67.23%	82.98%	33.57%	43.59%

V. DISCUSSION

The tables above shows the result t of partitioning or trace metals in the soil sample. Figures 1-5 also represent the percentage composition of each trace metal accumulated in t he four fractions. Taking location I as a case study the total conc. of trace metals are partitioned in the sediment in the order : Fe>Zn> Pb> Cu> Cd which followed same for all the location. Iron have the total concentration of trace metal which was 2506.01mg/kg and percentage concentration of 33.57% while cadmium have the lowest concentration with 1.32mg/kg. Both the oxidizable and residual fraction of lead (Pb) are closely related to values obtained for the same metal by Tessier *et al, (1999)* (0.8µg/0.81g/g) and Horowitz (1 .3µg/g,0.8µg.lg) in the Ruzin sediment leachates. The concentration of lead in residual fraction was 0.37%. The high value may not pose any threat to human and its environment considering. the fact that metals in this form are not readily released into solution but incorporated in the crystal lattices of clay minerals and silicate. Conversely, the distribution of lead in acid extractable (0.66%) and 0Kidi1ablc (0.33%) forms. which are known as the major contributors to the mobility and bioavailability of the metals in the soil were very high. Copper had the highest percentage bioavailability of 82.98% widely followed by lead 69.96% and has the least value of 33.57%. Percentage bioavailability fraction range from 35.57% to 82.98%. The values were moderate but most parts of the trace metals were absorbed or found in the exchangeable fractions. This small amount entering biota may not pose immediate environmental hazards. It was also found that the percentage bioavailability or trace metals studied followed the order Cu (82.98%) >Pb (69.96%)>Cd (67.23%) >Zn (43.59%) > Fe (33.57%). The percentage bioavailability of Fe was found to be 33.57%. The result of this investigation was on high side when compared with the findings of distribution pattern of Fe in the top soil within Awkuzu area of Anarnbra State, Nigeria *as* reported by Omuku et al., (2009).

➢ The concentration of trace metals evaluated in residual form were relatively high. Fe had the highest concentration of 2506.01mg/kg, Cd had concentration of 1.32mg/kg, and this value is low and tolerable but should be monitored.

➢ In the metals bound to organic matter (oxdisable) Fe also had the highest concentration in all locations followed by Zn in all the locations.

➢ For the selected trace metals evaluated, they occurred in the fraction in the order: for iron; Residual > Oxidisable > Reducible > Acid extractable. For zinc; Oxidisable > Reducible > Residual > Acid extractable. For lead; Reducible > Acid extractable > Residual > Oxidisable. For cadmium; Acid extractable > reducible > Oxidisable > Residual. For copper; Reducible > Oxidisable > Residual > Acid extractable.

➢ In acid extractable the occurrence of the Cd is least followed by Cu and Pb, while in reducible fraction Cd is still the least widely followed by Cu and Pb. Fe is the highest in the entire fraction that shows the high concentration of iron in the Lemna dumpsite soil.

➢ Also in oxidisble fraction the percentage occurrence of Cd is the lowest (0.002%) followed by Cu (0.1%) and Pb (0.33%). Fe had the highest with (6.30%).

➢ In residual fraction, Fe still had the highest occurrence with 1028% with a high margin from closest Zn, which had 2.34%.

VI. CONCLUSION AND RECOMMENDATION

The result obtained and presented in this project revealed that the concentration of Fe and Zn in the dumpsite soil at Lemna Road, Calabar is high. The high concentration of Fe and Zn could be as a result of iron scraps and zinc metals which when rust and decompose increased the concentration of the dual in the area. The mean value concentration of zinc, though essential to maintain the metabolism of organism, has to be monitored, because at high concentration. It can lead to poisoning and may cause anemia and copper deficiency as a result of bioavailability. The total concentration of cadmium in the fractions though minimal must also be monitored considering the fact that it is relatively mobile in solution and has no nutritional benefit to both animal and plant. Soluble in anoxic environment and readily available to biota Reducible metals which arc the most important scavengers represented only a minor fraction of the sediment (0.003%). Bound to organic matter fraction also bounded small portion of the trace metals instigated. Residual metals, that is those that bound to crystal lattices and silicates, were found to be 10.28%. This portion is not easily released into ecosystem over a time frame, therefore the

easy of bioavailability is negligible. The continuous dumping of solid waste of these metals into ecosystem increases their concentration levels, consequently their toxicity. The metals may be made insoluble possibly by the use of chelating agents.

Periodic monitoring of the area studied should be carried out to forestall bioaccumulation of these toxic elements and underground water pollution since this elements are highly. Most especially given the rapid development of Residential houses surrounding the dumpsite.

Dumpsite should only be allowed to be in landfill in open place where the waste should not be allowed to now into streams.

Treatment like phytoremediation should be carried out early, that is using plants to extract toxin from the soil. Plants can extract or remediate toxin from the soil through their root systems. Open air burning. should be control because this might expose people living around the dumpsite to high level of diseases caused by the heavy metal oxides. Therefore, government should employ the use of incinerator in future, during burning.

REFERENCES

[1]. Adrian F.I. Domy C. (2001), trace Elements in terrestrial Environments, Bioecochemistry and its risks of metals. Journal of Organic Chemistry India. 7 (2) 49 – 56.

[2]. Akcay H., A. Oguz and C. Karapie, study of heavy metal pollution and speciation in Buyak Menders and Gedis river sediments, Water Res., 37, 2003, 813 – 822.

[3]. Amal F. A. Mannsour, Amany F. Zayed and Ola A.A. Basha M.A (2008), Contamination of the shell and internal content of the table eggs, south Australia, International Journal of Food Microbial146 (3): 219 – 27

[4]. ATSDR: Agency for Toxic Substances and Disease Registry 4770 Bufford HWYNE Atlanta, GA 30341 800-CDC-INFO (800-232-4636) TTy: (888) 232 – 6348.

[5]. Bashir F.H., M. S Othman, A. G. Mazlan, S.M. Ralim, K. D. Simon (2013) Heavy metal concentration in fishes from the costal water of Kapar and Mersing, Malaysia, Turkish. Journal of Fisheries, 13 (2), 375 – 382.

[6]. Chonkar P. K., S. P. Datta, H. C. Joshi, Surendra Patha, (2000), Impact of industrial effluents on soil health and agriculture, India, Journal of Scientific and industrial research 59/5: 350 – 361.

[7]. Colbourn, P., and Thornton (1978). Lead pollution in agricultural soils. Journal of Soil Science 29:513 – 526.

[8]. Culbard, E. B. and L.R. Johnson. (1984). An assignment of arsenic in household and garden soils from South West England and their implications for human health. P. 276 – 281. In Environment Contamination. CEP, Edinburg.

[9]. Cullbard, E. B., I Thornton, J., Watt, S. Moorcroft, and K. Brooks, 1983. Sources and distribution of Lead and Cadmium in United Kingdom dust and soil. P. 426 – 429.

[10]. Davies, B. E. and R. C. Ginnever (1979). Trace metal contamination of soils and vegetable in slipham somerest. Journal of Agricultural Science. Comb 93: 753 – 756.

[11]. Dubey Vinods K., A. K. Chopra, A. Kumar, (2006). A review on sewage sludge (Bio-solids) A Resource for Sustainable Agriculture Journal of Scientific and industrial research 3: 23 – 543.

[12]. Ebong G. A. (2014), trace metal: levels, specification, physiochemical determination and bioavailability at dumpsite within Akwa Ibom State, Niger Delta region of Nigeria Ph.D. thesis, University of Calabar.

[13]. Edet A. E., B. J. Merkel, Offiong E. Offiong (2003). Trace element hydrochemical assessment of the Calabar Coastal Plain Aquifer, Southeastern Nigeria Using Statistical Methods. Environmental Geology 44 (2) 137 – 149.

[14]. Edet A. E., Offiong E. Offiong (2002), Evaluation of water quality population indices for heavy metal contamination monitoring, Geojournal. 57(4),295-304 en.wikipedia.org/wiki/Enugu.Retrieved07/09/2011.

[15]. Ferguson, J. E., R. W. Hayes, S. Y. Tan. And H. T. Sim (1980). Heavy metal pollution by traffic in Christchurch, New Zealand: Lead and Cadmium content of dust, soil and plant samples. N. Z. J. Sci. 23: 753 – 756.

[16]. Ferguson. J.E. 1990.The heavy elements: chemistry, environmental impact and health effects. Oxford, Pergmon Press.

[17]. Garcia-Miragaya, J., (1984), Levels, chemical Fractionation and solubility of Lead in roadside soils of Carcas, Venezuela Soil Science. 138: 147 – 152.

[18]. Gibson, M. J, and J. G. Farmer.{1983). A survey of trace metal contamination in Glasgow urban soils. In proc.4th Int. Conf. on Heavy metals in the Environment. 2: 1141 - 1144.

[19]. Haines, R. C., and Pocook, R. L., (1980). Heavy Metal and contamination: Background levels and site case histories in the London Borough of Greenwich. Res. Note 16. Birmingham, Joint unit for Research on the Urban Environment. University of Aston. Birmingham.

[20]. Horowitz A.J., (1999). A primer on sediment – trace element chemistry (Chelsea: Lewis Publ. Inc., 1991).

[21]. http://www.lenntech.com/processes/heavy/heavy-metals/heavy-metals.htm#ixzz1a059jjv9.Retrived20/08/2011.

[22]. Imperator, M, P. Adama. D. Naimo, M. Arienzo, D. Stanzione and P. Violante. Spatial distribution of heavy metals in urban soils or Naples city, Italy, Environmental pollution, *124,* 2003, *247-256*

[23]. In proc. Of 4th Int. Conference on Heavy Metal in the Environment, CEP Edinburg.

[24]. Iwegbue C. M. A. Emuh. F. N., N. 0.and Egun, A. C. (2007). Fractionation, characterization and speciation of heavy metals in compost and compost-amended soils. *Africa Journal of Biotechnology* 6 (2):067-078.

[25]. Jareth D and Sahai A., (2017). Impact of industrial effluents on soil health and agriculture, India, *Journal of Scientific and industrial Research 5975:350-361.*

[26]. Joan M. Njaji, Daniel N. Akunga, Martin M. Njaji Mathew P. Ngugi, Eliud M. M. Njaji (2017). Heavy Metal Concentration in Vegetable Grown around Dumpsites in Nairobi City County, Kenya. Work environmental. 7 (2) 495.

[27]. Lagenverff, J. V., and A. W. Specht, (1970). Contamination of roadside soil and vegetation with Cadmium, Nickel, Lead and zinc. Environment Science technology. 4: 583- 586.

[28]. Nemeth T., E. Molnar, J. Csillag, K. Bujtas. A. Lukacs, G. Partay, J. Feher and G. T. van Genuchten. Mobil ily of some heavy metals in soil-plant systems studied on soil monoliths. *Wat. Sci. Tech.*, 28 (3 - 5), 1993, 389 – 398.

[29]. Nor-ul Amin and Taused Ahmed, (2005). contamination of soil with heavy metals from industrial effluents and their translocation in green vegetables of Peshawar, Pakistan. RSC Advances *5* (19). Nriagu J.O. and Pacyca. J. M. 1988. Qualitative assessment of worldwide contamination of air. Water and soils by trace metals. Nature 333: 134-140.

[30]. Nriagu J.O., Cadmium in the environment. *Ecological Cycling,* Part, 1, John Wiley, 1980, 682. Odukoya O. O., Bamgbose 0. Arowolo T.A (2007). Heavy metals in topsoil of Abeokuta dumpsites. *Global Journal of Pure and Applied Science.* 7: 467 -472.

[31]. Omuku P., P.A.C. Okoye. H. A. Onwumelu and S.O. Ogoc. (2009). Distributions of chromium and nickel in the topsoil within Awkuzu area of Anarnbra State, Nigeria. *Anachem Journal, 4(1)*, 61l-617.

[32]. Papafilippaki A. K., M. E. Kotti, and G.G. Stavroulakis, (2008), Seasonal variation in dissolved heavy metals in the Keritis River, Chania, Greece. *Global NEST Journal*, 10 (3), 320 – 325.

[33]. Parry, G. D. R., M. S. Johnson and R. M. Bell., (1981). Trace metal survey of soil as a component of strategic and local planning policy development. Environment Pollution Series. B 2, 97 – 107.

[34]. Pawan K. Bharti, Pawau Kumar, Vijender S. (2013). Impact of industrial effluents on ground water and soil quality in the vicinity of industrial area of Panipat City, India, Journal of Applied Natural Science.

[35]. Prusty B.G.. K.C. Sahu and G. Godgul, (1994) Metal contamination due to mining and milling activities at the Zawar zinc mine. Rajasthan, India, Chemical Geology. 112, 275 – 292.

[36]. Rauret G.,Lopez-sachez JF, Sahaquillo A.,Barahona E., Lachica M., (2000). Application of a modified BCR Sequential extraction (three - step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil. Allan, *C* 2(3). 228 – 233.

[37]. Skvaria. J., (1991). A study on the trace metal speciation in the Ruzin reserviour sediment. *Acta Montanistica Slovaca Rochik.* 3(2), 177-182.

[38]. Sparks. D. L., (2005). Toxic metals in the Environment *The Role of Surfaces.* Article in Elements 1 (4): 193. Dol: 1 0. 2 1 13/gse/elements.l4.I 93.

[39]. Stevovic S. V.S. Mikovilovi c and D. Calic-Dragosavac, (20 I 0). Environmental impact of site location on m acro- and micro- elements in Tansy, African *J. of Biotech,9(16).* 2408-241 2.

[40]. Sumanta Roy and Srimanta (2013) a comparative study of heavy metals accumulation in soil irrigated with well water and waste water in sub-urban region of Asansol. West Bengal, Article in focus (San Francisco, California), 4:89 – 95

[41]. Tessier A. Campbell P. G.C. and M.. Bisson, (1 979). Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry, 51(7), 844 – 851. http://www.lenntech.com/recommended-daily-intake.htm#ixzz1a0coc7D2.retrived07/09/2011. Thornton, J., Applied Environmental Geochemistry (London: Academic Press, 1983), 501.

[42]. Turkmen A. and M. Turkmen, (2004). The seasonal variation of heavy metals in the suspended particulate material in the lskenderum Bay (North- Eastern Mediterranean sea, Turkey). *E. U. journal of Fisheries & Aquatic Sciences,* 2 1 (3-4), 307-31 1.

[43]. Urnoren U.Ini., Arthur Valbon, Marcelo A Neves., Aurea Echevarria., (2014). Pollution status and chemical speciation in surface water and sediments of two Rivers in Akwa Ibom. *J0urnal of Environmental Monitoring* 2(3), 228 -233.

[44]. USATD. 1 990. Strategies for linking water and sanitation programmes to child survival. Washing DC: United State Agency for international Development.

[45]. US-EPA. 1984. MINTQA2, A geochemical assessment data base and test cases for environmental systems: ver. 3.0 user's manual. EPA/600/3-91/-21. Athens, GA. Allison, J., D. S. Brown and K. J. Novo-Gradac.

[46]. Wyzkowski M., and J. Wyszkowska, (2003) Effects of soil contamination by copper on the content of macro-elements in spring barley, *Pol. J. Nat. Sci.* 14, 309-320.

[47]. Zhang, C., S. Zhang, (1995) background contents of heavy metals in sediments of the yantze river system and their calculation methods. Journal of Environmental Science. 7: 422-429.