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Investigation of Selected Heavy Metals Level in Top Soils Around Ajaokuta Steel Company, North Central Nigeria

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The concentration of selected heavy metals in top soils around Ajaokuta Steel Company was investigated in order to evaluate the environmental status level of the metals. Top soil samples were randomly collected around Ajaokuta Steel Company between 2003 and 2005. The samples were sorted; air dried, pulverized to < 2 mm grain size and digested using standard methods. The soil digest solutions were quantified for Cd, Cr, Mn, Ni, Cu, Zn and Pb using flame atomic absorption spectrometry. The mean concentrations (mg/kg) of the heavy metals were; Zn, 56.30 ± 11.94; Cu, 42.90 ± 5.84; Pb, 15.62 ± 3.06; Cr, 14.33 ± 2.38; Ni, 11.48 ± 2.13; Mn, 6.53 ± 1.68; and Cd, 0.13 ± 0.16, with soil concentration distribution in the order Zn > Cu > Pb > Cr > Ni > Mn > Cd. The soils were slightly acidic with mean pH 6.54 ± 0.67 and mean organic carbon levels of 2.03 ± 0.72 %. Significant correlation ($p < 0.05$) exists between the concentration of heavy metals in soils and organic carbon levels, with correlation coefficient for Mn; $\gamma = 0.51$ and Cr; $\gamma = 0.63$. The transport/availability of metals in soils is strongly influenced by pH and organic carbon levels, and this forms the basis of their fixation with plant growth nutrients. The retention of metals in soil organic matter proceeds by complexation. The stability of the metal-organic carbon complexes depends on the organic carbon type, nature of the complex formed and the degree of stearic effect.

Keywords: Heavy metals, Concentration, Top soil, Distribution, Availability, Fixation.

INTRODUCTION

The iron and steel industry is a crucial corner stone of growth, socio-economic advancement, technological development and overall industrialization of any nation[1,2]. Among its economic impact is the supply of basic raw materials and products to multitude of industries such as building, construction, machinery, equipment, automobile manufacturing and railways[3].

Metallurgical operations in the iron and steel industry involve series of complex processes, in which iron ore or metallic element is transformed into products[4]. The most vital conversion operation is the extraction process, which involves the reduction of iron ore (haematite/magnetite) to obtain pig iron, by the addition of coke, limestone and other materials in the blast furnace[5]. Other metallurgical operations include smelting, refining, steel rolling and casting.

These activities have been reported to be point sources of heavy metals release, with potential capacity for heavy metal pollution[6]. For instance, the conversion of iron ore to molten iron produces significant amount of particulate emissions and carbon monoxide. Considerable quantities of metal laden solid wastes *i.e.* slag; wastewater and air emissions may also be generated in the process of making iron and steel[7]. In addition, the wastewater may contain potentially toxic concentrations of phenols, cyanide, thiocyanate, ammonia, sulphide and chloride[8]. Air emissions may include visible smoke, coke-dust, ammonia, hydrogen sulphide, nitrogen oxides and carbon monoxide[7]. If these wastes are not adequately managed it can result into significant degradation of land, water and air with negative environmental impacts[9].

Soil may however become contaminated as a result of heavy metals release from metallurgical operations of the iron and steel industry[10,11]. Soils play major role in material cycling. Hence they could serve as medium of transfer of heavy metals to plants and animals and other environmental medium. Earliest concerns of occupational exposure were of the symptoms peculiar to metal workers of various kinds[12]. Classic effects of heavy metals can be as a result of toxic metal air emissions, which are suggested to be a factor in high lung cancer rates in some areas. Metals such as Hg, Pb, Cd, Cu, Zn and Mn may be deposited at levels toxic to humans, animals and plants[13,14]. According to ATSDR[15], Pb, Hg and As ranked top 3 toxins with most adverse effects on public, while Cd, Cr and Ni are listed among the deleterious toxic metals of concern.

The mitigation of the potential environmental impacts of iron and steel production operations require information and understanding of the environmental status of the location of the industry, vicinities near and further away. This is in order to put in place measures that will eliminate or reduce as much as possible the anticipated impact on the environment and guaranty environment health and safety. Information concerning the environmental status of Ajaokuta Steel Company is lacking. This is because an environmental baseline study was not conducted before the construction of the industry and no comprehensive post impact audit studies had been conducted. Such information is required, in order to put in place mechanisms for environmental protection, sustenance and monitoring.

In this study, the concentration of heavy metals in top soils around Ajaokuta Steel Company in North Central Nigeria was investigated. This is in order to acquire data on the status level of selected heavy metals in the soil environment. This is with the view to developing benchmark levels against which future monitoring can be compared when the plant become operational.

EXPERIMENTAL

Ajaokuta Steel Company is located along the bank of lower river Niger region in North Central Nigeria, with geo-reference coordinate N 070 32, 669", E 006^0 41, 550" and altitude range 74-187 metres of the river Niger alluvium at Ajaokuta, North Central Nigeria.

Samples collection: Top soil samples, 0-15 cm of A-horizon were randomly collected northward, eastward, westward and southwards by scooping surface soils in the study area using a stainless steel hand trowel between 2003 and 2005. Control soils were collected from farmlands in serene environment about 20 km away from Ajaokuta Steel Company. Each of the soil samples were stored in a nitric acid pre-treated and dried polypropylene bags and well labelled. The sampling points are presented in Table-1.

TABLE-1
GEO-REFERENCE COORDINATES OF SOILS SAMPLING POINTS AROUND AJAOKUTA STEEL COMPANY

Northward Ajaokuta		Eastward Ajaokuta	
N 07° 33,647"	E 006° 41,564"	N 07° 33,710"	E 006° 41,578"
N 07° 33,690"	E 006° 41,529"	N 07° 33,654"	E 006° 41,605"
N 07° 33,763"	E 006° 41,537"	N 07° 33,686"	E 006° 41,642"
N 07° 33,715"	E 006° 41,572"	N 07° 33,725"	E 006° 41,677"
N 07° 33,669"	E 006° 41,550"	N 07° 33,692"	E 006° 41,691"
Southward Ajaokuta		Westward Ajaokuta	
N 07° 32,653"	E 006° 41,542"	N 07° 33,648"	E 006° 41,539"
N 07° 33,594"	E 006° 41,580"	N 07° 33,652"	E 006° 41,476"
N 07° 33,537"	E 006° 41,551"	N 07° 33,705"	E 006° 41,428"
N 07° 33,482"	E 006° 41,519"	N 07° 33,593"	E 006° 41,367"
N 07° 33,440"	E 006° 41,548"	N 07° 33,624"	E 006° 41,295"

Sample preparation and analysis: The soil samples were manually sorted to eliminate pebbles and coarsy materials and air-dried under ambient conditions in the laboratory for 72 h. The dried soil samples were pulverized and sieved to obtain < 2 mm by screening through a nylon sieve of 2 mm mesh size. About 5 g each of soil samples were digested in 50 mL 2 M analar grade HNO_3 in a water bath for 2 h[16]. The resulting sample digests were filtered into 100 cm^3 volumetric flasks and made up to 100 cm^3 mark with distilled water. The digested sample solutions were quantified for the heavy metals Cd, Cr, Mn, Ni, Cu, Zn and Pb, using of flame atomic absorption spectrometry (FAAS).

Determination of soil pH: Hydrogen ion (H^+) concentration was determined using the method of McLean[17]. Briefly, 1:1 mixture of soil and distilled water and top soil samples were prepared (10 g of soil mixed with 10 mL of distilled water). The resulting solution was mixed on a mechanical shaker for 0.5 h and then allowed to stand for another 0.5 h and the pH determined using a pre-calibrated pH meter.

Determination of soil organic carbon: Soil organic carbon was determined using the method of Walkley-Black[18]. Each of the soil samples (2.5 g) were weighed into separate 250 mL teflon beakers and subjected to rapid dichromate oxidation by the addition of 0.5 M 50 mL $K_2Cr_2O_7$ acidified with 2 mL concentrated H_2SO_4 in 5 % $FeSO_4$. The solution was mixed and allowed to stand for 15 min to reduce the heat generated by exothermic reaction. This was followed by gentle boiling for 0.5 h at 150 °C. Water was added to the digestive mix to halt the reaction. Excess dichromate ($Cr_2O_7^{2-}$), were titrated with 0.25 M ferrous ammonium sulphate.

Recovery studies: Selected samples were spiked with different concentrations of standard solution of analytes in triplicates; at low, medium and high spike concentrations, in order to verify the efficiency of digestion procedure in analyte recovery. The spiked sample was then subjected to the same sample analysis procedures and method used in analyzing the unspiked samples.

The analyte recoveries obtained for the spiked samples were ranged 86.92-97.10 %, while relative standard deviation (RSD) of the replicate spiked samples lies between 1.52 % and 16.28 %. The percentage recoveries and the RSD for the selected metals were range as follows: Cd, 90.17-94.71, C.V 2.83-12.85 %; Mn, 91.62-95.48 %, C.V 2.18-3.42 %; Cr, 92.61-96.75 %, C.V 8.25-14.70 %; Ni, 89.30-92.73, C.V 4.09-16.28 %; Cu, 86.92-93.42 %, C.V 6.09-12.59 %; Zn, 93.62-96.74 %, C.V 1.52-7.54 % and Pb, 93.54-97.10 %, C.V 7.44-9.32 %. The values of the percentage recovery of each metal falls within the generally acceptable recovery 100 ± 20 %.

RESULTS AND DISCUSSION

The results obtained from the analysis of the topsoil samples consisting of sandy loam, silty loam and loam, collected during different seasons between 2003 and 2005 are presented in Table-2. The concentration levels of the selected heavy metals detected in soils around the vicinity of Ajaokuta Steel Company (ASC) were evaluated by comparing study results with guidelines concentration limits and other reported study results.

The measured heavy metals are heterogeneously distributed in soils around Ajaokuta Steel Company. Zn (39.15-76.15 mg/kg) was the most available with the highest seasonal mean concentration amongst other metals. The concentration of Cu ranged between 35.99-48.38 mg/kg, followed by Pb (11.87-21.22 mg/kg). The concentration of other metals were Mn, 4.60-9.54 mg/kg; Cr, 11.53-17.59 and Ni, 5.70-16.25 mg/

TABLE-2
RANGES AND MEAN CONCENTRATIONS (mg/kg) OF HEAVY METALS IN SOILS AROUND AJAOKUTA STEEL COMPANY

Sample identity	pH	Organic carbon (%)	Cd (mg/kg)	Mn (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)
AJK/SL/D/03-04									
Concentration range	5.37 – 7.39	0.90 – 4.00	0.04 – 0.99	3.80 – 9.52	12.42 – 22.13	9.85 – 18.07	37.94 – 57.26	48.47 – 78.06	12.93 – 25.18
Mean ± Standard Deviation	6.44 ± 0.57	2.24 ± 0.76	0.19 ± 0.28	6.01 ± 1.70	17.59 ± 2.72	13.54 ± 2.34	48.38 ± 5.56	65.59 ± 11.16	19.52 ± 3.12
AJK/SL/D/04-05									
Concentration range	5.30 - 7.51	0.50 – 2.90	0.06 – 1.07	6.80 – 12.54	11.53 – 19.92	11.83– 21.68	38.45 – 57.46	53.72 – 91.45	14.23 – 27.69
Mean ± Standard Deviation	6.30 ± 0.76	1.64 ± 0.61	0.23 ± 0.31	9.54 ± 1.61	15.78 ± 2.37	16.25 ± 2.81	48.36 ± 5.33	76.48 ± 14.39	21.22 ± 3.34
AJK/SL/W/03-04									
Concentration range	5.72 – 8.01	0.80 – 2.60	0.02 – 0.09	2.75 – 8.25	7.64 – 17.00	2.75 – 8.02	28.81 – 52.12	35.74 – 52.58	7.82 – 17.15
Mean ± Standard Deviation	6.72 ± 0.63	1.94 ± 0.59	0.05 ± 0.02	4.60 ± 1.48	12.42 ± 2.61	5.73 ± 1.28	35.99 ± 6.66	39.15 ± 10.01	11.87 ± 2.62
AJK/SL/W/03-04									
Concentration range	5.72 – 8.01	0.80 – 2.60	0.02 – 0.09	2.75 – 8.25	7.64 – 17.00	2.75 – 8.02	28.81 – 52.12	35.74 – 52.58	7.82 – 17.15
Mean ± Standard Deviation	6.72 ± 0.63	1.94 ± 0.59	0.05 ± 0.02	4.60 ± 1.48	12.42 ± 2.61	5.73 ± 1.28	35.99 ± 6.66	39.15 ± 10.01	11.87 ± 2.62
Control soil									
Concentration range	-	-	0.05 – 0.16	5.86 – 7.40	9.07 – 10. 21	6.91 – 9.52	30.29 – 32-74	40.55 – 57.25	18.60 – 23.17
Mean ± Standard Deviation	-	-	0.08 ± 0.02	6.49 ± 2.62	9.36 ± 2.05	8.04 ± 1.75	30.95 ± 4.12	49.83 ± 12.47	20.29 ± 3.05

Key: AJK – Ajaokuta; SL – soil; D dry season; W – wet season; 03-04 – year 2003/2004; and 04-05 – year 2004/2005

kg, with Cd having the least concentration (0.05-0.23 mg/kg). The overall mean concentrations (mg/kg) of the heavy metals in soils around Ajaokuta Steel Company were Zn, 56.30 ± 11.94; Cu, 42.90 ± 5.84; Pb, 15.62 ± 3.06; Cr, 14.33 ± 2.38; Ni, 11.48 ± 2.13; Mn, 6.53 ± 1.68; and Cd, 0.13 ± 0.16, with soil heavy metal concentration distribution sequence in the order Zn > Cu > Pb > Cr > Ni > Mn > Cd.

Results of the concentrations of the heavy metals were comparable with those of the control soil environments. The concentration of Cd, Cr, Ni, Cu and Zn in the control soils ranged 0.05-0.16; 9.07-10.21; 6.19-9.52; 30.29 - 32.74 and 40.55-57.25 mg/kg, respectively, were slightly lower than in Ajaokuta Steel Company environment soils, except for Pb, 18.60-23.17 mg/kg which were slightly higher. The higher Pb levels in control soils may be due to automobile emission from vehicular traffic. The concentration of Mn which ranged between 5.86-7.40 mg/kg in the control soils, were however within the range detected in soils around Ajaokuta Steel Company. The difference in concentration levels of heavy metals detected in control soils and soils around Ajaokuta Steel Company environment were not significant ($p > 0.05$). Thus, the levels of heavy metals in the soil samples lies within natural concentration ranges, which indicate that there was minimum or no impact from Ajaokuta Steel Company.

The levels observed in soils around Ajaokuta Steel Company are subject to enrichment or depletion depending on source inputs and environmental factors such as climate. Discharge of contaminants from source points may be localized and this can lead to considerable increase in heavy metals concentration in the immediate adjacent surrounding. Taylor *et al.*[19] reported that aerial dispersal for dust and particulates metal inputs can also enhance distance distribution. The redistribution of metals and their dynamics of translocation through soils and or availability to plant may be determined by selective retention and this may be competitive especially in soils with available multi-elements. This however depends on the properties of the metals and soil type on which they are retained[20,21].

Soil pH and organic carbon: The availability of metals in soil is strongly influenced by the pH, clay mineral assemblage and the level of organic carbon in soil[22-24]. Soils around Ajaokuta Steel Company are slightly acidic with soil pH ranged 4.39-8.01 (6.54 ± 0.67), while organic carbon levels in the soil samples ranged 0.50-4.00 % (2.03 ± 0.72 %) (Table-2). According to Lindsay[25] the pH of soils influences the availability, solubility and or mobility of heavy metals. There exists significant correlation ($p < 0.05$) between pH and heavy metals concentration levels in soils. Apparently, the concentration levels of the heavy metals in soils around Ajaokuta Steel Company are partly a function of the soil pHs[26].

The retention of metals in soil organic matter probably proceeds by complexation or carbon sequestration. Sorption of metals to nonpolar/nonionic organic solute in soils is controlled by partition[27], while sorption to polar/ionic organics is controlled by electrostatic forces. The stability of the resultant products *i.e.* heavy metal/organic matter complexes may be enhanced by high degree of stearic effects, the nature of the complex formed and the organic carbon compound type. There was a significant correlation ($p < 0.05$) between the concentration of heavy metals in soils and organic carbon levels, with correlation coefficient for Cr; $\gamma = 0.63$, Mn; $\gamma = 0.51$, Ni; $\gamma = 0.39$, Cu; $\gamma = 0.67$, Zn; $\gamma = 0.71$ and Pb; $\gamma = 0.76$ except for Cd; $\gamma = 0.27$. The soil-metal sorption interactions and metal stabilization forms the basis of the fixation of elements and thus their preoccupation with nutrition for plants growth.

Effect of seasonal climate condition on the concentrations of heavy metals and soil safety: The effect of climate change was apparent in the seasonal variation of soil concentration levels of the heavy metals except for Cd which were only slightly affected (Fig. 1). Concentration of heavy metals in the soils appears to increase during dry season, than observed in the wet season. Low metal concentration levels during wet seasons may be due to metal leaching, by precipitation or storm water, although this depends on soil surface/subsurface hydrodynamics and/or erosion processes.

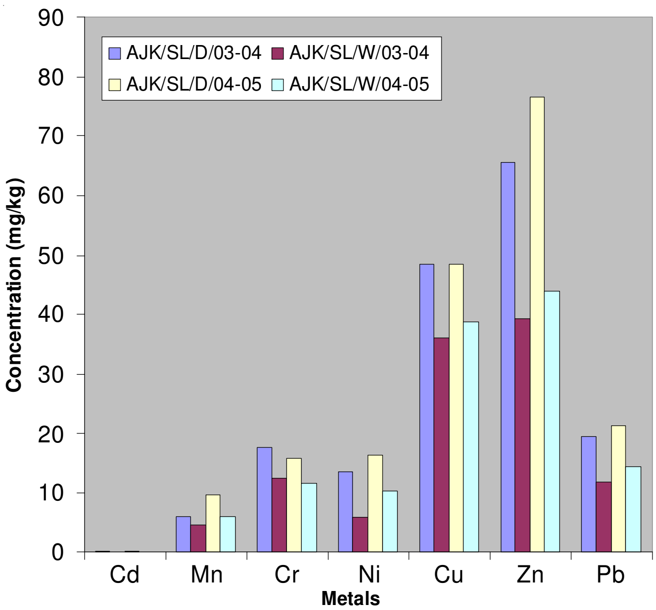

Fig. 1. Variation in soil concentration levels (mg/kg) of heavy metals around Ajaokuta Steel Company situated at North Central Nigeria during different climatic seasons

Also, the concentration levels of the heavy metals were slightly higher in 2004/2005 than 2003/2004, with soil heavy metals enrichment of about 9-30 %, except for Cd, which was fairly stable with concentration variation between 3-6 %. This may be due to the lower rainfall recorded during 2004/05 compared with 2003/04. Low soil water volume may probably result in increased biogeochemical processes which are known to enhance metal stabilization. Biological mediated processes of plant uptake and microbial activities as well as other environmental processes may partly account for concentration reduction on the other hand[28].

European Economic Community maximum acceptable concentration guideline threshold[29] for arable agricultural soils was used as basis for establishing the environmental status and implications of the analysed soil samples. Copper, 37.94-57.46 and Zn, 48.47-91.45 mg/kg have moderate concentrations compared to Cu, 140-300 and Zn, 150-300 mg/kg European Economic Community recommended maximum acceptable concentration, respectively. Manganese, 2.75-12.52 and Cd, 0.02-0.11 mg/kg, are low compared to Mn, 40-500 and Cd, 1-3 mg/kg maximum acceptable concentration.

The detected concentration levels of the metals were low when compared with findings from other studies around metallurgical environment[30], especially in soils contaminated by slag. Thus, the concentrations of the heavy metals in soils around Ajaokuta Steel Company environments were within uncontaminated soils levels (Table-3).

This implies that topsoil around Ajaokuta Steel Company environment are not polluted and contain the metals in concentrations below phytotoxic range suggested by Kabata-Pendias and Pendias[38] and are of no threat to the terrestrial ecosystem. The observed concentrations of the selected heavy metals in soils around Ajaokuta Steel Company may largely be attributed to nature or crustal processes contributions.

Conclusion

The concentration levels of heavy metals in soil environment around Ajaokuta Steel Company in North Central Nigeria are low and within natural concentration levels. The detected levels were below the European Economic Community maximum acceptable concentration limits for agricultural soils. Therefore, the soil environment are not negatively impacted by heavy metals, hence could be regarded as pristine. The acquired data may be of importance in making informed choices on the

TABLE-3
COMPARISON OF MEAN HEAVY METAL CONCENTRATIONS (mg/kg) IN SOIL SAMPLES WITH EEC MAXIMUM ALLOWABLE CONCENTRATION (MAC) IN AGRICULTURAL SOILS AND OTHER RESEARCH WORKS

Location	Cd	Mn	Cr	Ni	Cu	Zn	Pb	Reference
AJK/SL/D/2003-05 (mg/Kg)	0.04-1.07	3.80-12.54	11.53-22.13	9.85-21.63	37.94-57.46	48.47-91.45	12.93-27.69	This study
AJK/SL/W/2003-5 (mg/Kg)	0.02-0.11	2.75-10.73	7.64-17.00	2.75-14.35	28.81-52.12	35.41-56.27	7.82-20.50	This study
Concentration in some uncontaminated soil (mg/kg)	0.01-0.07		5.00-3000		2.00-100	10.0-300	2.00-200	
EEC Maximum allowable concentration (mg/kg)	1-3	40-500	50-150	30-75	50-140	150-300	50-300	29
USA maximum acceptable concentration (mg/kg)	20		1500	210	750	1400	150	31, 32
Heavy metal in contaminated soil (mg/kg)	117.0			17.0	4933.0		5067.0	33
Heavy metals in soil contaminated by slag (mg/kg)				34.0±2.0	18.0±1.0	110.0±4.0	20.0±2.0	34
Phytotoxic levels of heavy metals in soils	5-700		1-10	10-100		> 100	30-300	32, 35
Toxic element in soils of abandon waste dump site (mg/kg)	1.64±0.11		22.27±3.03	8.14±0.33			133.74±10.60	36
Dumpsite, wet, Port Hacourt, Nigeria (μg/g)	1.72±1.22			14.95±14.95			53.50±40.09	37
Mt Isa contaminated soils (mg/kg)					371.0±229.0	459.0±441.0	362.0±705.0	19

Code: AJK = Ajaokuta; SL = Soil; D = Dry season; W = Wet season; 2003-05 = Year 2003-2005 rational managements of steel production industries environment, as well as in the development environmental regulations concerning metallurgical operations/industries. Such information may also facilitate the choice of steel production operation technology that will not compromise environmental health and safety.

REFERENCES

1. B. Guibert, J. Laganier and M. Volle. Retrieved January 30, 2013 from http://ec.europa.eu/eurostat/ramon/other_documents/index.cfm?TargetUrl (1971).
2. A.J. Field, *J. Macroecon.*, **31**, 173 (2009).
3. I.H. Gonzalez and J. Kaminski, *Gospodarka Surowcami Mineralnymi*, **27**, 1 (2011).
4. GSA, Chapter 4: Mining and processing operations, Report of the Government of South Australia (2011).
5. R.I.L. Guthrie and J.J. Jonas, ASM Handbook, ASM International, vol. 1, p. 107 (1990).
6. K.M. Greaney, An Assessment of Heavy Metal Contamination in the Marine Sediments of Las Perlas Archipelago Gulf of Panama, A Master of Science Thesis submitted to the School of Life Sciences, Heriot-Watt University, Edinburgh (2005).
7. T.E. Norgate and W.J. Rankin, In Proceedings, Minprex 2000, International Conference on Minerals Processing and Extractive Metallurgy, pp. 133-138 (2000).
8. F.E.P.A. Nigeria, Federal Ministry of Environment of Nigeria Environmental Impact Assessment sectorial guidelines (Manufacturing Industries). 138pp (1995).
9. F. Sallaku and S. ShaIIari, *Méditerranéennes: Série A. Séminaires Médierranéens*, **57**, 55 (2003).
10. H.T. Shacklette and J.G. Boerngen, Retrieved March 31, 2013 from http://pubs.usgs.gov/pp/1270/pdf/PP1270_508.pdf (1984).
11. C.R. Evanko and D.A. Dzombak, Retrieved November 26, 2012 from http://www.gwrtac.org (1997).
12. R. Lauwerys, H. Roels, P. Genet, G. Toussaint, A. Bouckaert and S. de Cooman, *Am. J. Ind. Med.*, **7**, 171 (1985).
13. H.R. Casdorph, Toxic metal Syndrome, Avery Publishing Group, London (1995).
14. A. Bignert and E. Nyberg, Lead Concentrations in Fish Liver, Swedish Museum or Natural History, p. 35 (2002).
15. ATSDR, Agency for Toxic Substances and Disease Registry, U. S. Public Health services, Toxicology Profile for Mercury: March and April 1999 Media Advisory on elemental mercury vapour/inhalation/chronic & MRL: methyl mercury/oral/acute; Retrieved April 21, 2006 from http://atsdr.cdc.gov:8080/97list.html (1999).
16. P.C. Onianwa, *Soil Sed. Contam.*, **10**, 577 (2001).
17. E.O. McLean, Methods of Soil Analysis, Part 2, Agronomy. American Society of Agronomy Inc., Madison, Winconsin, USA, vol. 17, pp. 199-224 (1982).
18. A. Walkley and I.A. Black, *Soil Sci.*, **63**, 251 (1947).
19. P.M. Taylor, L. Stuart and F. Dustine, Heavy metal contamination of Mt. Isa-implication for the ecosystem (Isoconferences). Retrieved December, 23, 2005 from www. isoconferences.org.au (2002).
20. K. Fijalkowski, M. Kacprzak, A. Grobelak and A. Placek, *Inzynieria i Ochrona Srodowiska,* **15**, 81 (2012).
21. O.S. Olatunji, O.S. Fatoki, B.J. Ximba and B.O. Opeolu, *World Environ.*, **3**, 37 (2013).
22. N.E. Korte, J. Skopp, W.H. Fuller, E.E. Niebla and B.A. Alesli, *Soil Sci.*, **122**, 350 (1976).
23. G.F. Lee, Role of Hydrous Metal Oxides in the Transport of Heavy Metals in the Environment Session IV Transport Mechanism 2. Institute for Environmental Sciences, University of Texas, Dallas. Seminar paper 18 p. (1975).
24. M.E. Essington, Soil and Water Chemistry, CRC Press, Boca Raton, FL (2004).
25. W.L. Lindsay, Chemical Equilibra in Soils, John Wiley & Sons, New York (1979).
26. A. Lenart and K. Wolny-Koladka, *Bull. Environ. Contam. Toxicol*., **90**, 85 (2013).
27. O.E. Kile, R.L. Wershaw and C.T. Chiou, *Environ. Sci. Technol*., **33**, 2053 (1999).
28. O.J. Ogunsola, A.F. Oluwole, I.B. Obioh, O.I. Asubiojo, F.A. Akeredolu, O.A. Akanle and N.M. Spyrou, *Nucl. Instrum. Methods Phys. Res. B*, **79**, 404 (1993).
29. EEC, Agricultural Soil and the Environment (1993); Retrieved July 26, 2004 from www.ec.europa.eu/agriculture/publi/fact/envir/2003_en pdf.
30. E. Remon, J.-L. Bouchardon, B. Cornier, B. Guy, J.-C. Leclerc and O. Faure, *Environ. Pollut*., **137**, 316 (2005).
31. B.J. Alloway, Heavy Metals in Soil, Blackie Academic & Professional London (1995).
32. A. Kabata-Pendias and H. Pendias, Trace Element in Soils and Plants, edn 3, p. 492 (2000).
33. J.L. Gardea-Torresday, L. Polette, K.J. Tiemann, J. Bibb and J.H. Gonzalez, *Plant Cell Physiol*., **97**, 632 (2000).
34. K. Bunzl, M. Trautmannsheimer and P. Schramel, *J. Environ. Qual*., **28**, 1168 (1999).
35. A. Boularbah, C. Schwartz, G. Bitton, W. Aboudrar, A. Ouhammou and J.L. Morel, *Chemosphere*, **63**, 811 (2006).
36. N.E. Okoronkwo, S.A. Odemelam and O.A. Ano, *Afr. J. Biotechnol*., **5**, 1241 (2006).
37. T.J.K. Ideriah, V.O.T. Omuaru and U.P. Adiukwu, *Afr. J. Ecol*., **44**, 388 (2006).
38. A. Kabata-Pendias and H. Pendias, Trace Element in Soils and Plants, CRC Press, Boca Raton, FL, p. 425 (1984).