BIOAVAILABILITY AND BIOACCESSIBILITY OF TOXIC AND ESSENTIAL ELEMENTS IN URBAN WASTE DUMPSITE SOILS AND CONTROL WITHIN AKWA IBOM STATE, NIGERIA

Godwin Asukwo Ebong*[1], Offiong Effanga Offiong[2] and Bassey Offiong Ekpo[2]
[1]Chemistry Department, Unversity of Uyo, P. M. B 1017, Uyo, Nigeria
[2]Chemistry Department, University of Calabar, P. M. B 1115, Calabar, Nigeria.
*E-mail: g_ebong@yahoo.com, goddyebong2010@gmail.com

Abstract
Studies on speciation, bioavailability and bioaccessibility of toxic and essential elements were undertaken in some urban dumpsite soils and Control within AkwaIbom State, Nigeria. Soil samples were collected from six designated urban waste dumpsites namely: Uyo (Uyo); Utu Abak (Abak); Atabong (Eket); NdoEyo (Onna); NungUdoeItak (Ikono) and IkotObongErong (IkotEkpene). While Control samples were obtained from a forest in IkotUdobia (Etinan). Samples collected were extracted sequentially using the Modified BCR speciation procedures to obtain the different fractions of toxic elements lead (Pb); cadmium (Cd); arsenic (As) and essential elements iron (Fe); copper (Cu) and zinc (Zn). Concentration of metal fractions in dumpsite soils and Control were analyzed for using atomic absorption spectrophotometer (Unicam 939/959 model). Bioavailability and bioaccessibility models were employed for the determination of bioavailability factor and bioaccessibility index of these elements in dumpsite soils and Control. Results obtained indicated that, Pb and As existed mostly in the reducible fraction, Cd in acid extractable fraction while Fe, Cu and Zn existed principally in the residual fraction. Consequently, toxic metals were more available and assessible than the essential elements in both dumpsite soils and Control. Results obtained revealed that, the availability of these metals in the environment studied was basically controlled by the form they exist in soil.

Keywords: Dumpsite soil, Optimized BCR speciation, Spectrophotometer, Waste-impacted soil, Niger Delta and Pollution.

Submitted: 05.10.2014   Reviewed: 06.01.2015   Accepted: 20.02.2015

1. INTRODUCTION

It is a known fact that elements are natural components of the soil and their natural concentrations varied with the geological processes that formed the soil. According to Lokeshappa*et al.* (2012) some are nutritionally essential to plants, animals and man while some are toxic depending on the concentration. However, Lead, cadmium, manganese, arsenic and mercury are elements have no known physiological benefit when ingested (Park and Shin, 2006). Elements in soil pass through plants to human thus when their concentrations in soil is in minute quantities or in forms which are unavailable to plants, human exposure to them from soil is limited and vice versa. The issues of bioavailability and bioaccessibility in soil often determine whether or not the concentration at which an element is present will have effects on organisms (Peijnenburg and Jager, 2003). Consequently, these metals both toxic and essential are very poisonous when human is exposed to at very high concentrations (Khan *et al.*, 2010). Studies have shown that waste dumpsite soils have elevated levels of these toxic elements (Ebong*et al.*, 2008). It has also been reported that human exposure to toxic metals depends solely on their bioavailability for plants uptake (O' Halloran, 2006). This research work aimed at ascertaining the level of human exposure to toxic elements between waste impacted soils and Control within the study area. Thereby relating results obtained to the associated environmental and health implications. The study also aimed at comparing the bioavailability and bioaccessibility of toxic element and essential elements in area under study.

2. MATERIALS AND METHODS

2.1 Study Area

The study was undertaken in dumpsite soils in six (6) local government areas namely: Uyo, Abak, Eket, Onna, Ikono and IkotEkpene within AkwaIbom State, Niger Delta region of

Nigeria. A forest in Etinan local government area within the same State was chosen as the Control. AkwaIbom State locates in the coastal south-south part of the country, lying between latitudes 4º 32! and 5º 33! North and longitudes 7º 25! 8º 25! East. Soil samples were obtained from the following locations Uyo(Uyo) (007. 56 E and 05.02 N); Utu Abak (Abak) (007.59 E and 04.59 N); Atabong (Eket) (007.55 E and 04.38 N); NdonEyo (Onna) (007.51 E and 04.37 N); NungUdoeItak (Ikono) (007.06 E and 05.06 N); IkotObongErong (IkotEkpene) (007.42 E and 05.11N); IkotUdobia (Etinan) (007.50 and 04.52).

2.2 Sample collection, treatment and analysis

Surface soil (0 – 15cm) samples were obtained from six (6) waste dumpsite soils namely: Uyo, Ikono, IkotEkpene, Abak, Eket and Onna within AkwaIbom State, Nigeria using auger according to the methods of Aydinalp (2009). Top soil samples were also obtained from a forest in Etinan local government Area of the same State and used as Control. At each location, samples were collected from different locations of the site and pooled together to form composite sample (Anake*et al.*, 2009). These samples were collected for a period of one year (December, 2010 to November, 2011) to cover the dry and wet seasons of the study area. Samples collected were air dried for three (3) days and ground to pass through a 2mm mesh. An optimized BCR (Community Bureau of Reference of the European Commission) method of speciation was applied for the sequential extraction of elements into four (4) different fractions namely: acid extractable, reducible, oxidisable and residual fractions following the procedures of Prasanth*et al.* (2013). Bioavailability factors (BAF) was determined using the relationship between acid extractable fraction and other fractions of a particular element as reported by Adaikpoh (2011) while the association between bioavailability factor and recommended standard for each element was employed for the determination ofbioaccessibility index (BAI) of the elements (Ebong, 2014).

3.RESULTS AND DISCUSSION

Results for the bioavailability factor and bioaccessibility index of toxic and essential elements in dumpsite soils and Control between December, 2010 and November, 2011 are shown in Tables 1 and 2. Results for the sequential extraction of toxic elements (Pb, Cd and As) are given in Figures 1- 3, while Figures 4 - 6 show results for the speciation of iron, copper and zinc (Essential elements).

Table1: Mean values of bioavailability factor and bioaccessibility index of toxic elements in dumpsite soils and Control between December, 2010 and November, 2011.

	LEAD		CADMIUM		ARSENIC	
SAMPLE ID	BAF	BAI	BAF	BAI	BAF	BAI
1	24.96	24.66	49.22	49.02	21.43	21.00
2	26.05	25.75	46.34	46.14	23.08	22.65
3	21.50	21.20	52.54	52.34	23.08	22.65
4	24.44	24.14	51.30	51.10	18.18	17.75
5	21.65	21.35	50.00	49.80	18.18	17.75
6	22.87	22.57	45.28	45.08	20.00	19.57
7	31.04	30.74	41.10	40.90	10.00	9.57

Table 2: Mean values of bioavailability factor andbioaccessibility index of essential elements in dumpsite soils and Control between December, 2010 and November, 2011.

	IRON		COPPER		ZINC	
SAMPLE ID	BAF	BAI	BAF	BAI	BAF	BAI
1	13.74	– 411.76	12.49	– 60.81	19.31	– 80.09
2	13.93	– 411.57	18.45	– 54.85	19.48	–79.92
3	12.62	– 412.88	13.09	– 60.21	19.71	–79.69
4	12.25	– 413.25	14.32	– 58.98	18.52	– 80.88
5	11.85	– 413.65	13.41	– 59.89	17.23	– 82.17
6	11.76	– 413.74	9.16	– 64.14	19.97	– 79.43
7	12.24	– 413.26	10.07	– 63.23	16.29	– 83.11

Key: 1 = Uyo; 2 =Abak; 3 = Eket; 4 = Onna; 5 = Ikono; 6 = IkotEkpene and 7 = Etinan (Control).

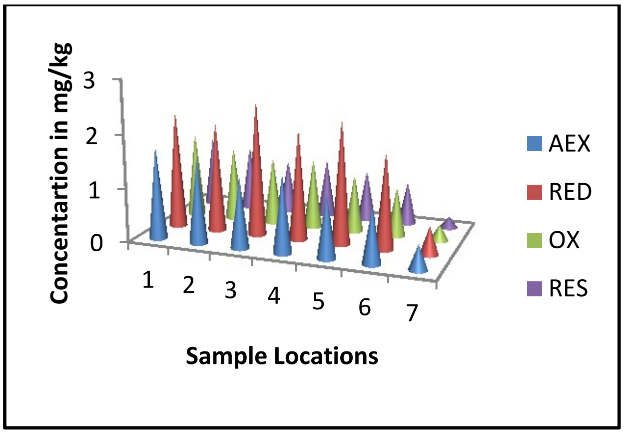

Fig. 1: Mean concentration of lead fractions in dumpsite soils and Control between December, 2010 and November, 2011.

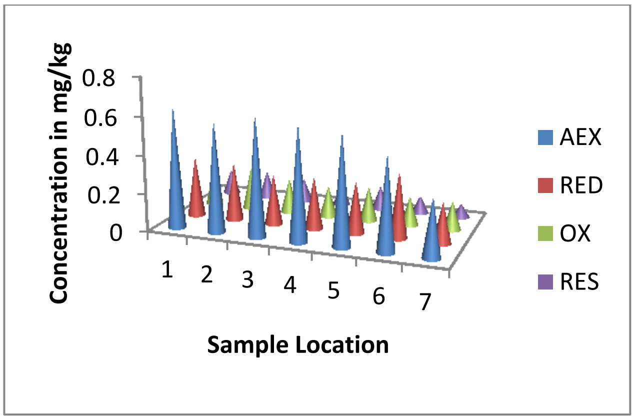

Fig. 2: Mean concentration (mg/kg) of cadmium fractions in dumpsite soils and Control between December, 2010 and November, 2011.

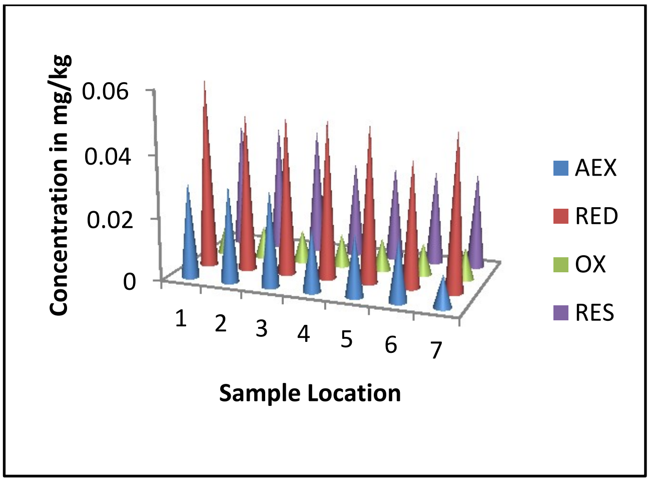

Fig. 3: Mean concentration (mg/kg) of arsenic fractions in dumpsite soils and Control between December, 2010 and November, 2011.

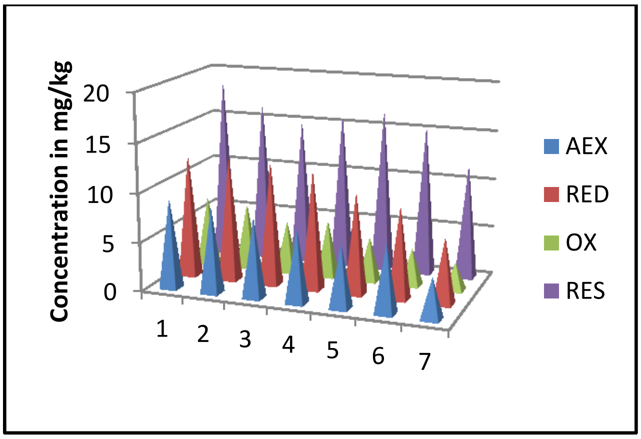

Fig. 4: Mean concentration (mg/kg) of iron fractions in dumpsite soils and Control between December, 2010 and November, 2011.

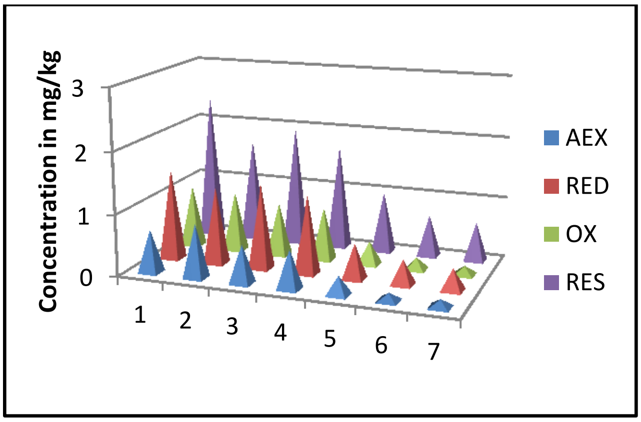

Fig. 5: Mean concentration (mg/kg) of copper fractions in dumpsite soils and Control between December, 2010 and November, 2011.

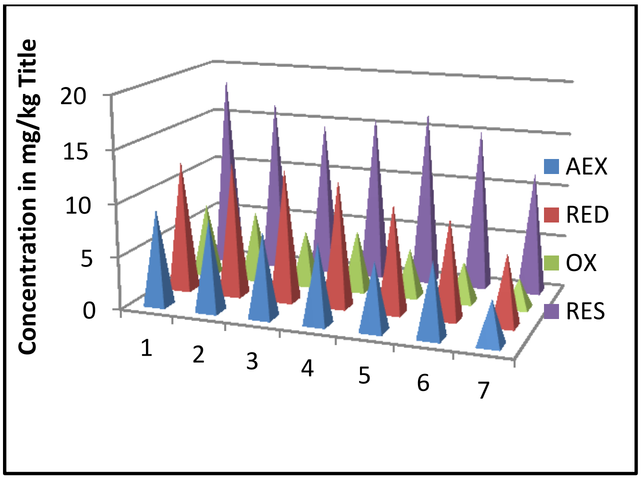

Fig. 6: Mean concentration (mg/kg) of zinc fractions in dumpsite soils and Control between December, 2010 and November, 2011.

3.1. Speciation, Bioavailability and Bioaccessibility of lead

Results in Figure 1 indicate concentrations (mg/kg) for acid extractable (Aex), reducible (Red), oxidisable (Ox) and residual (Res) fractions in the different dumpsite soils as 1.37, 2.13, 1.24 and 1.04 respectively. However, Control site indicated the following results (mg/kg): 0.45 Aex, 0.51Red, 0.29 Ox and 0.20 Res. Lead existed mostly in the reducible fraction at both dumpsite soils and Control between December 2010 and November 2011. The high Pb fractions recorded in dumpsite soils maybe attributed to waste materials found at these locations. Results obtained in this study is similar to that reported by Jie*et al*. (2009) .Higher concentration of each fraction of lead was found in dumpsite soils than at the Control, this maybe attributed to a higher level of total lead reported in dumpsite soils.The mean bioavailability (BA) and bioaccessibility (BAI) of lead in the different dumpsite soils were 23.58% and 23.28% respectively while 31.04% and 30.74% were recorded for mean BA and BAI respectively at the Control site(See Table 1). The study also revealed that, the proportion of lead readily available for plants uptake was higher in Control site than in dumpsite soils during the period. Thus, higher amount of the metal was accessible to human at Control site than in dumpsite soils.

3.2. Speciation, Bioavailability and Bioaccessibility of cadmium

Figure 2 shows the following concentrations: 0.58 (Aex); 0.29 (Red); 0.18 (Ox) and 0.12 (Res) for Cd in dumpsite soils while Control site indicated 0.30, 0.21, 0.15 and 0.07mg/kg for Aex, Red, Ox and Res fractions respectively. Concentration of each fraction of Cd was higher in dumpsite soils than at Control.Thus, waste materials at dumpsite may have contributed significant amount of cadmium to the underlying soil environment. Generally, Cd existed mostly in the Aex fraction at both locations thereby signifying that it was readily available for plant consumption in the area studied during the period. This is in agreement with findings by Kashem*et al*. (2011). Periodic assessment of Cd in the area should be encouraged to forestall Cd toxicity and underground water pollution. The mean BA and BAIin Table 1 at dumpsite soils are 49.11% and 48.91% respectively while Control site indicated 41.10% and 40.90% as mean BA and BAI respectively. These higher values in dumpsite soils may be credited to a higher proportion of Aex fraction of Cd at dumpsite soils. Consequently, human may have more accessible to Cd at dumpsite soils than in Control. Cadmium recorded the highest BA and BAI values in this study. This may be due to its high mobility in soil as reported by Ahumada*et al*. (1999).

3.3. Speciation, Bioavailability and Bioaccessibility of arsenic

Results of Asfractions in Figure 3 show the concentrations (mg/kg) in dumpsite soils between December 2010 and November 2011as 0.03 (Aex), 0.05 (Red), 0.01 (Ox) and 0.04 (Res). The Control site recorded mean concentrations of 0.01 (Aex), 0.05 (Red), 0.01 (Ox) and 0.03 (Res) during the same period. I this work, As existed principally in reducible fraction in both dumpsite soils and Control during the period, this is similar to reported by Khan *et al*. (2010). Arsenic fractions did not show significant variations between dumpsite soils and Control. Thus, the availability of waste materials at dumpsite soils may not have affected the geologic nature of As in the soil environment studied. The BA and BAI indices of As in dumpsite soils and Control within the period are given in Table 1. Dumpsite soils recorded 20.66% and 20.23% as BA and BAI respectively, while 10% and 9.57% were obtained as BA and BAI respectively at Control site. Accordingly, human beings were accessible to almost the same level ofAs in both locations during the period.

3.4.Speciation, Bioavailability and Bioaccessibility of iron

Concentration (mg/kg) of iron fractions in dumpsite soils studied between December 2010 and November 201 in Figure 4 are as follows: 156.28, 346.58, 226.76 and 459.22 for Aex, Red, Ox and Res respectively. The Control site recorded 121.07, 276.95, 175.12 and 415.96 for Aex, Red, Ox and Res fractions correspondingly. Iron existed primarily in the residual fraction thus, not readily available for plant uptake. This is consistent with results reported by Osakwe (2012). Table 2 shows results for the bioavailability and bioaccessibility of iron in dumpsite soils and Control within the period under study. Dumpsite soils recorded12.69% and –412.81% for mean BA and BAI respectively while Control site indicated 12.24% and –413.26% as mean BA and BAI respectively. Hence, the exposure of human beings to iron in the area was almost the same at both dumpsite soils and Control. Iron as an essential element to plants, animal and man has indicated a deficient status in the study area therefore supplementary sources of this element should be applied to elevate their presence and avert the effects associated with its deficiency.

3.5. Speciation, Bioavailability and Bioaccessibility of copper

The mean concentration (mg/kg) of copper fractions in dumpsite soils and Control between December 2010 and November 2011 is given in figure 5. Dumpsite soils recorded 0.54, 1.05, 0.69 and 1.53 for mean Aex, Red, Ox and Res respectively. The Control site indicated 0.12, 0.34, 0.14 and 0.62 as meanAex, Red, Ox and Res respectively. Copper existed mainly in the residual fraction in both locations studied; this is in agreement with findings by Achi *et al.* (2011). The existence of copper mostly in the unavailable form has greatly affected life in the area since the element is an essential element for plants and animals including man (Ozcan, 2003). Table 2 gives the mean bioavailable and bioaccessible copper in dumpsite soils as 13.49%and –59.81% respectively. While the Control site recorded 10.07% and –63.23% as mean BA and BAI correspondingly. Consequently, humanbeings were exposed to more copper at dumpsite soils than at Control. The general results indicated a deficient status of copper in the study area and as essential element a supplementary source of the element should be provided for normal plants and animal growth.

3.6. Speciation, Bioavailability and Bioaccessibility of zinc

Zinc fractions in dumpsite soils recorded the following concentrations: 7.79 (Aex), 11.49 (Red), 5.46 (Ox) and 16.15 (Res). However, zinc in Control station indicated 4.07, 6.60, 2.81 and 11.49 for the mean Aex, Red, Ox and Res fractions respectively. The element occurred mainly in residual fraction, this is consistent with the reports by Adekola*et al.* (2012). This study has also ascertained that the availability of zinc in the study area has been restricted immensely by its geologic nature. Table 2 shows the mean BA and BAI in dumpsite soils as 19.04% and –80.36% respectively while Control site recorded 16.29% and –83.11% for mean BA and BAI respectively. Thus, the accessibility of zinc to human was insignificantly higher in dumpsite soils than at Control site. Zinc according to Linder and Azam (1996) is one of the elements needed in the human body for proper growth and development, its deficiency may have some physiological effect on human thus additional source should be sought to complement the natural one.

4. CONCLUSION

Results obtained from his study have shown that toxic elements were readily available in dumpsite soils and Control than their essential counterpart in the study area. This revealed that, human beings were more exposed to toxic elements than essential ones in the area. This research work has also indicated that the availability of elements in an environment largely depend on their forms. Consequently, periodic assessment of the area studied should be carried out to forestall bioaccumulation of these toxic elements and underground water pollution since these elements are highly mobile.

5. ACKNOWLEDGEMENT

We wish to acknowledge the financial contributions by Education Trust Fund (ETF) in Nigeria for the successful completion of this research work. The technical assistance provided by the Technologists in Soil Science and Central Laboratories within University of Uyo, Uyo, Nigeria is highly commendable

6.REFERENCES

[1] Lokeshappa, B, Kandarp, S, Vivek, T and Anil, KD, Assessmentof Toxic Metals in AgriculturalProduce.**2**, 1,2012, 24-29.

[2] Park, JH and Shin, WS, Immobilization of Pb contaminated soil using modified Clay, **1**, 2, 2006, 1-10.

[3] Peijnenburg,, WJGM andJager, T., Monitoring approaches to assess bioaccessibility and bioavailability of metals: Matrix issues.**56**, 2003, 63–77.

[4] Khan, MA, Islam, MR, Panaullah, GM, Duxbury, JM., Jahiruddin, M, and Loeppert, RH., Accumulation of Arsenic in soil and rice under wetland condition in Bangladesh, **333**, 1010, 263-274.

[5] Ebong, GA, Akpan, MM and Mkpenie, VN, Heavy metal contents of municipal and rural dumpsite soils and rate of accumulation by *Carica papaya* and *Talinumtriangulare*in Uyo, Nigeria, **5**, 2, 2008, 281-290.

[6] O'Halloran, K., Toxicological considerations of contaminants in the terrestrial environment for ecological risk assessment, **12**, 2006, 74–83

[7] Aydinalp, C, Concentration and speciation of Cu, Ni, Pb and Zn in cultivated and uncultivated soils.**15**, 2, 2009, 129 –134.

[8] Anake, WU, Adie, GU and Osibanjo, O, Heavy metal pollution at municipal solid waste dumpsites in Kanoand Kaduna states in Nigeria. 23, **1**, 2009, 281-289.

[9] Prasanth, KM, Sreekala PP, Sandeep S., Kripa, PK and Sreejesh KK, HeavyMetals and its Fractions in Soils of Koratty Region, Kerala, **2,**2013,171-176.

[10] Adaikpoh, EO, (2011). Sequential extraction of cadmium, lead and zinc in soil profiles of Ifon and Environs, southwest Nigeria: Submission for their availability to terrestrial organisms, **4**, 2011, 399 – 403.

[11] Ebong, GA, Trace metal: levels, speciation, physicochemical determinants and bioavailability at dumpsite soils within AkwaIbom state, Niger Delta region of Nigeria. Ph.D. Thesis, University of Calabar, 2014.

[12] Jie, S., Zhao-hui, G., Xi-yuan, X., Xu-fengi, M. and Feng-yong, W, Environmental availability and profile characteristics of arsenic, cadmium, lead and zinc in metal contaminated vegetables soils, **19**, 2009, 765 – 772.

[13] Kashem, MA, Singh, BR., ImamulHuq, SM. and Kawai1, S, Fractionation and mobility of cadmium lead and zinc in some contaminated and non-contaminated soils of Japan, **3**, 2011,9, 241-249.

[14] Ahumada, I, Mendoza, J, and Ascar, L, (1999). Sequential extraction in soils irrigated with wastewater, **30**, 1999, 1057-1519.

[15] Osakwe, SA, Chemical partitioning of iron, cadmium, nickel and chromium in contaminated soils of south-eastern Nigeria, **2**, 5, 2012, 1-9.

[16] Achi, MM.,Uzairu, A., Gimba, CE. andOkunola, OJ. Chemical fractionation of heavy metals in soils around the vicinity of automobile mechanic workshops in Kaduna Metropolis, Nigeria,**3**, 7, 2011, 184 - 194

[17] Ozcan, M, Mineral Contents of some Plants used as condiments in Turkey, **84**, 2003, 437-440.

[18] Adekola, FA, Inyinbor, AA. and Abdul-Raheem, AMO. (2012). Heavy metals distribution and speciation in soilsaround a mega cement factory in North-Central Nigeria, **5**, 1, 2012, 11-19.

[19] Linder, C and Azam, MH, 1996, Copper biochemistry and molecular biology,**63**, 1996, 791-796.

[20] Kaasalainen, M. and Yli-Halla, M. (2003). Use of sequential extraction to assess metal partitioning in soils.*Environmental Pollution*, 126: 225-233.