



ISSN 2049-7318

Comparative Assessment of Levels of Heavy Metals in Earthworm Casts and Soils at Contaminated Sites

¹Iorungwa, M.S., ¹Wuana, R.A., ²Yiase, S.G.

¹Department of Chemistry and Centre for Agrochemical Technology, Federal University of Agriculture, P.M.B. 2373, Makurdi, 970001, Nigeria ²Department of Chemistry, Benue State University, P.M.B 102119, Makurdi, 970001, Nigeria

ABSTRACT

In this study, the levels of some metals in earthworm casts (EWC), surface organic matter (SOM) and the parent soil (PS) were compared to assess the bio-monitoring potential of earthworm casts. Samples of earthworm casts, surface organic matter (SOM) and the actual soil were collected from each of the randomly selected points (16) around an active dumpsite located at the North Bank Area of the River Benue in Makurdi, north-central Nigeria. The samples were assayed for Cd, Cu, Fe, Pb, Mn and Zn by flame atomic absorption spectrophotometry after aqua regia digestion. Results revealed that in the casts, metal concentrations (mg/kg) ranged as: Cd(0.20 - 2.93), Cu(5.00 - 20.00), Fe(0.52 - 1.90), Pb(26.00 - 83.00), Mn(52 - 130) and Zn(44.00 - 80.00). In SOM, the concentrations were Cd(0.30 - 2.00), Cu(95.00 - 15.00), Fe(0.30 - 1.50), Pb(31.00 - 88.00), Mn(63.00 - 122.00) and Zn(42.00 - 98.00). In the actual soil samples, metal concentrations were Cd(0.12 - 3.00), Cu(3.50 - 28.00), Fe(0.25 - 4.10), Pb(38.00 - 120.00), Mn(69.00 - 202.00) and Zn(35.00 - 112.00). Depending on the sample matrix, even though metal concentrations varied as parent soil > earthworm cast > SOM; on a whole they were well correlated indicating that earthworm cast may be adopted as surrogate in the bio-monitoring of soil contamination.

Keywords: Earthworm, metals, bio-monitoring, soil contamination

1. INTRODUCTION

Risk assessment in metal-contaminated soils is frequently done by performing bioassays. In certain cases, however, more information on the biochemical responses other than bioassays may be required to help elucidate the mechanisms involved in metal availability to biota. Earthworms play an important role in the soil macrofauna biomass and they are extremely important in soil formation, principally by consuming organic matter, fragmenting it, and mixing it intimately with soil mineral particles to form water-stable aggregates underscoring the particular bioaccumulation ability of earthworms which is essential for any bio-monitoring organism (Takeshi and Kazuyoshi, 2011).

A bio-monitoring method would be appropriate to evaluate metal toxicity, because of its sensitivity and availability for unknown metabolites. Organisms such as fish, snails, and plants have been employed as biomonitors. Although this approach is useful and promising, it is also somewhat limited, because it could be available only for a specific combination of a living organism with certain substances. Hence, the need unearth the right living organisms as bio-monitors for each type of assessment (Citterio *et al.*, 2002; Brulle, *et al.*, 2006).

To establish a bio-monitoring system using earthworms, the effects of various chemical pollutants on earthworms have been studied. The accumulation of both natural and depleted uranium in earthworms was analyzed to evaluate the corresponding biological effects (Giovanetti et al., 2010). The study showed that no effects were observed in terms of mortality or weight reduction, but cytotoxic and genetic effects were identified at quite low natural uranium concentrations. Among metals, methyl mercury might be more easily absorbed by and accumulated in earthworms, suggesting that the earthworm is an ideal candidate for monitoring methyl mercury. Lee et al, 2009 mentioned that metal bioaccumulation also by earthworms could be used as an ecological indicator of metal availability. On the other hand, metal pollution reportedly had no effect on earthworm communities.

Casting occurs when earthworms ingest soil and leaf tissue to extract nutrients, and then emerge from their burrows to deposit the fecal matter (casts), as mounds of soil on the surface. Earthworm cast consists of mixed inorganic and organic materials from the soils that are voided after passing through the earthworm intestine. Total cast production is an indicator of burrowing and soil turnover, because 99.9% of ingested material is egested as casts (Edwards, 2004). Mostly, earthworms were proven to be a good biological indicator; they can be sampled easily, have a wide distribution range and strongly accumulate pollutants. Their limited mobility means that they are representative of a precise site, which makes them suitable for monitoring the impact of contaminants. The presence of contaminants in earthworms poses a serious risk of secondary poisoning of vertebrate predators due to biomagnifications (Reinecke and Reinecke, 2004). The process of cast production and/or earthworm bioturbation causes soil mixing and surface casting may also contribute to a redistribution of contaminants in the soil profile (Zorn et al., 2005; 2008). Deep burrowing species can bring polluted soil from deeper layers to the soil surface and may increase metal availability in soil (Zorn et al., 2005). However, in the literature we can find only few studies on metal contents in earthworm casts compared to surrounding soil (Kızılkaya, 2004; Udovič and Leštan, 2007).

The objectives of our research were to determine the Cu, Pb and other metals content and dispersion in earthworm casts from active dump site around the mechanic village in the North Bank area of the Benue River and to compare them to the values in SOM and soil (0–10 cm) obtained from the same site. The main purpose was to assess the reflection of soil contamination in casts with the intention to estimate whether the data about cast contamination can tell us something about the distribution of contaminants in soil. The contents of 6 elements were determined in earthworm casts in order to establish increased values of any of these elements and to compare the values in casts to the contents in SOM and soil (0–10 cm) from investigated area.

2. MATERIALS AND METHODS

2.1 Study Area

The study was conducted at an active dumpsite located near the Mechanic Village in North Bank area of Makurdi which is one of the 23 Local Government Areas and the capital city of Benue State. It lies between the coordinates 7.44°N, 8.33°E in the Lower Benue River Basin, northcentral Nigeria. The soils are derived from Precambrian basement complex rocks and quartenary alluvial deposits of River Benue as parent materials. The range of annual rainfall is 1200 - 1650mm and is distributed between March/April and October/November, followed by marked dry season (of up to 4 months). The ranges of daily maximum and minimum temperatures during the rainy season are $30 - 34^{\circ}$ C and $22 - 24^{\circ}$ C, respectively and $33 - 34^{\circ}$ C 37° C and $18 - 24^{\circ}$ C, respectively in the dry season. Daily global irradiation and mean hours of insulation are 314 -433 cal.cm².day⁻¹ and 4.00 - 7.74h, respectively. The soils

here are subject to rural, peri – urban and urban agriculture and other human activities (Okezie, 1985).

2.2 Sampling, Pretreatment and Analysis

Earthworm casts, deposited on top of the soil, were collected at an active waste dump site located at the Mechanic Village North Bank of the Benue River in Makurdi. Sampling was performed at the area surrounding the dump site, on approximately 50×50 m area. Earthworm cast samples were collected from 16 sampling points in the research grid of about 30×30 m. At each sampling location on average 5 - 10 casts were collected in the 2.5 m radius to create the composite sample. About 16 soil sampling points surface organic matter-rich soil layer (SOM) and underlying soil layer (0 -10cm) were sampled in the 30 \times 30 m research grid. Earthworm cast samples were prepared in the same manner as SOM and soil samples in accordance with the method described by Teršič et al. (2011). The air-dried samples were gently crushed in a porcelain mortar, sieved through a 2 mm mesh sieve and pulverized prior to chemical analysis. All samples were collected and analyzed in June, 2012. The powdered earthworm casts as well as the soil and SOM samples were analyzed for Cu, Pb and 4 other chemical elements viz: Cd, Fe, Mn, and Zn. A 10g portion of the sample was weighed into a 100ml capacity beaker and digested with aqua regia (HNO₃ and HCl; 1:3) for 2 hrs. The mixture was filtered with a Whatman No 42 filter paper and 5ml of the digestate (filtrate) was made up to 100ml with de-ionized water in a volumetric flask and 10ml of this solution was used to evaluate the concentration the metal using a flame atomic absorption spectrophotometer (Buck Scientific 200A). Soil and SOM samples were determined in the same manner. Details of determining soil and SOM samples are as described by Teršič et al. (2010).

3. RESULTS AND DISCUSSION

Table 1 shows some physicochemical properties of the parent soil while the results of the concentration of some chemical elements present in earthworm cast, SOM and the parent soil samples around the active dumpsite at the mechanic village, North Bank Area of the Benue River is presented in Tables 2, 3 and 4 while table 5 shows the median values of heavy metals in earthworm casts, surface organic matter and parent soil samples.

In all the areas, it was observed that the metal with the highest concentration in all the three (cast, SOM and soil) samples is Mn with the lowest concentration of 52 mg/kg (in the earthworm cast) and the highest concentration of about 202 mg/kg (in the soil sample), the metal with the lowest concentration was found to be Cd with the minimum concentration of 0.70 mg/kg (found in the earthworm cast) and a maximum of 3.0 mg/kg (as obtained in the soil).

Property	Parent soil	Earthworm cast		
	6 2 1 0 0	6 8 0 1		
pri Particle Size Distribution (%) Sand:	0.5±0.0 55 0+1 1	53+00		
Silt:	12.6±0.2	12.6±0.0		
Clay:	32.4±0.3	27.6±0.2		
Cation exchange capacity (%):	0.82±0.02	0.84±0.3		

Table 1. Some physicochemical properties of the soil and cast around an active dump site in
Mechanic Village, North Bank, Benue State

Mean value for triplicate determinations \pm standard deviation

The general trend of metal concentration was however determined to be in the following order: Mn > Zn > Pb >Cu > Cd. The content of Mn, Zn and Pb is relatively high apparently because of the activities such as panel beating, painting and dumping of alloy metals which contain these metals at the site. Zn has a median value of 50 mg/kg in both the earth worm cast and the SOM with a minimum of 42 and 44 and a maximum of 80 and 98 mg/kg respectively. The median value in the soil was however 49 mg/kg with the minimum value at 35 mg/kg and a maximum 112 mg/kg. The relatively high concentration of the metal in the cast could be explain from the ability of earthworms to accumulate certain heavy metals, the case with the SOM is against the backdrop that organic matter in the soil has the capability of complexing with the metal thereby immobilizing the metals. Recent studies have that the immobilizing ability of SOM makes it useful for reducing the phyto-availability of heavy metals (Wuana *et al*, 2009, Osakwe, 2009.). Considering numerousness of earthworm casts on the surface of investigated area, it does not seem that these highly elevated metal contents would have a harmful effect on earthworms and their activity.

 Table 2. Concentration (mg/kg) of metals in earthworm cast samples around the mechanic village in

 North Bank area of the Benue River (n=16)

EWC			Elements						
	Cd	Cu	Fe	Pb	Mn	Zn			
А	1.80±.012	17.0±0.00	1.3±0.10	60.1±0.21	130.0±0.15	65.0±0.20			
В	0.25±0.01	6.2±0.12	0.62±0.18	38.0±0.15	72.0±0.31	45.0±0.00			
С	0.20±0.04	5.3±0.11	0.58±0.12	29.0±0.18	58.1±0.08	44.3±0.02			
D	0.65±0.00	7.8±0.18	0.71±0.91	40.1±0.21	90.0±0.00	46.3±0.21			
E	2.80±0.11	20.0±0.12	1.88±0.31	83.1±0.27	130.0±0.17	78.1±0.07			
F	0.70±0.02	9.8±0.00	0.88±0.12	43.1±0.11	112.0±0.01	48.4±0.15			
G	2.40±0.23	19.5±0.19	1.71±0.11	72.0±0.15	130.0±0.17	76.3±0.05			
Н	0.70±0.12	10.1±0.13	0.93±0.01	43.0±0.19	128.0±0.13	48.5±0.12			
Ι	0.50±0.03	6.5±0.13	0.67±0.12	39.1±0.17	75.0±0.00	45.2±0.03			
J	0.71±0.11	15.9±1.20	1.07±0.25	44.0±0.13	129.0±0.22	51.5±0.11			
К	2.93±0.12	20.0±0.41	1.90±0.19	108.0±1.00	130.0±0.20	80.0±0.11			
L	1.61±0.09	16.8±0.14	1.17±0.03	58.0±0.14	130.0±0.12	60.1±0.00			
М	0.67±0.01	9.2±1.12	0.79±0.00	42.3±0.18	112.1±0.12	48.1±0.00			
Ν	1.83±0.91	18.2±0.23	1.52±0.07	65.2±0.00	130.0±0.15	70.2±0.10			
0	1.42±0.16	16.1±0.90	1.12±0.02	55.0±0.11	130.0±0.11	55.0±0.28			
Р	0.20±0.01	5.0±0.21	0.52±0.01	26.0±0.12	52.0±0.01	44.0±0.01			

Mean value for triplicate determinations ± standard deviation

SOM	Elen	Elements									
	Cd	Cu	Fe	Рb	Mn	Zn					
А	1.42±0.16	11.1±0.90	1.12±0.02	55.0±0.11	112.0±0.11	53.0±0.28					
в	1.95±0.11	14.0±0.12	1.48±0.31	73.1±0.27	121.0±0.17	88.1±0.07					
С	0.89±0.11	10.1±1.20	0.93±0.25	53.0±0.13	110.0±0.22	51.5±0.11					
D	1.80±.012	12.0±0.00	1.2±0.10	60.1±0.21	119.0±0.15	57.0±0.11					
E	0.32±0.04	9.3±0.11	0.38±0.12	31.0±0.18	68.1±0.08	44.4±0.02					
F	0.55±0.00	9.8±0.18	0.51±0.91	35.1±0.21	80.0±0.00	45.8±0.21					
G	1.61±0.09	11.8±0.14	1.19±0.03	58.0±0.14	117.0±0.12	55.1±0.00					
н	0.30±0.01	9.0±0.21	0.30±0.01	31.0±0.12	63.0±0.01	42.0±0.11					
I	2.00±0.12	15.0±0.41	1.50±0.19	88.0±1.00	122.0±0.20	98.0±0.11					
J	0.48±0.03	9.5±0.13	0.47±0.12	34.1±0.17	73.0±0.00	45.0±0.03					
К	1.87±0.23	13.5±0.19	1.31±0.11	68.0±0.15	120.0±0.17	76.3±0.05					
L	0.67±0.01	9.9±1.12	0.59±0.00	36.3±0.18	92.1±0.12	46.1±0.09					
М	0.70±0.12	9.9±0.18	0.93±0.01	43.0±0.19	106.0±0.13	49.5±0.12					
Ν	0.70±0.02	9.9±0.14	0.68±0.12	40.1±0.11	100.0±0.01	48.0±0.15					
0	1.83±0.91	12.2±0.23	1.22±0.07	62.2±0.00	120.0±0.15	70.2±0.10					
Р	0.45±0.01	9.4±0.12	0.42±0.18	32.0±0.15	71.0±0.31	44.8±0.00					

 Table 3. Concentration (mg/kg) of metals in Surface organic matter (SOM) samples around the mechanic village in North Bank area of the Benue River (n=16)

Mean value for triplicate determinations ± standard deviation

 Table 4. Concentration (mg/kg) of metals in parent soil (PS) samples around the Mechanic Village in North Bank area of the Benue River (n=16)

PS	Elements							
	Cd	Cu	Fe	Pb	Mn	Zn		
А	1.80±0.09	20.8±0.14	2.17±0.03	48.0±0.14	135.0±0.12	55.1±0.00		
В	2.90±0.11	27.0±0.12	3.88±0.11	85.1±0.27	189.0±0.17	108.1±0.07		
С	0.50±0.00	8.8±0.18	0.41±0.91	40.1±0.21	92.0±0.00	46.3±0.21		
Ν	0.67±0.01	9.0±1.12	0.89±0.00	44.0±0.18	115.1±0.12	48.1±0.00		
с	2.83±0.23	25.5±0.19	3.71±0.01	79.0±0.15	173.0±0.17	86.3±0.05		
F	0.91±0.02	9.5±0.00	0.88±0.12	44.0±0.11	123.0±0.01	48.4±0.15		
D	0.15±0.04	4.3±0.11	0.28±0.12	40.0±0.18	70.1±0.08	38.3±0.02		
E	2.53±0.91	25.2±0.23	3.52±0.07	70.2±0.00	160.0±0.15	75.2±0.10		
н	0.012±0.01	3.5±0.21	0.25±0.01	⁺ 38.0±0.12	69.0±0.01	35.0±0.01		
F	0.91±0.02	9.5±0.00	0.88±0.12	44.0±0.11	123.0±0.01	48.4±0.15		
I	1.15±0.16	18.1±0.90	2.13±0.02	47.0±0.11	133.0±0.11	50.0±0.28		
J	0.92±0.11	13.9±1.20	1.87±0.25	45.0±0.13	132.0±0.22	49.5±0.11		
К	1.90±.012	24.0±0.00	2.83±0.10	50.1±0.21	158.0±0.15	65.0±0.20		
L	0.18±0.01	5.2±0.12	0.32±0.18	41.0±0.15	75.0±0.31	40.0±0.00		
0	3.00±0.12	28.0±0.41	4.10±0.10	120.0±1.10	202.0±0.20	112.0±0.11		
P	0.25±0.03	6.0±0.13	0.37±0.12	41.1±0.17	76.0±0.00	45.2±0.03		

Mean value for triplicate determinations \pm standard deviation

Metal	EWC	SOM	PS	
Cd	0.70	0.82	0.92	
Cu	13.0	10.0	12.0	
Fe	1.0	0.93	1.40	
РЬ	43.0	48.0	44.0	
Mn	120.0	108.0	131.0	
Zn	50.0	50.0	49.0	

Table 5.	Median	values o	of heavy	metals in	earthworm	casts.	surface	organic	matter and	parent s	soil (mg/k	(g
								01 5 00000		P			~ n /

The concentration of Pb and Cu on a general note were slightly high with Pb being more on the higher side compared to that of Cu, the median value recorded the its highest figure of 48 mg/kg in the SOM with the minimum value of 31 mg/kg and a maximum of 88 mg/kg, next to the SOM was the concentration of Pb in the soil which had a median value of 44 mg/kg Pb with a minimum value of 38 mg/kg Pb and a maximum of 120 mg/kg Pb; the median concentration of Pb in the earthworm cast was found to be slightly lower than those of the soil with a of 43 mg/kg, a minimum of 26 mg/kg Pb and a maximum of 108 mg/kg Pb. This concentration in the cast though not as high as that of the soil still showed a close relationship to the concentration obtained from the soil establishing the fact that the cast could be a perfect tool for biomonitoring giving the fact that it recorded its highest points where the concentration in the parent soil was found to be the highest (Oyedele et al., 2006). The median value of Pb in the three media could be postulated to have followed the trend; SOM > Soil > Earthworm cast, but in terms of the metal concentration, the trend takes the dimension of soil > earthworm cast > SOM. The concentrations of Cu however, were found to be relatively lower than those of Pb; here the earthworm cast recorded the highest median concentration of 13 mg/kg Cu with a minimum value of 5.0 and a maximum of 20 mg/kg Cu. Closely following the median concentration in the cast was that of the soil sample with a median concentration of 12 mg/kg, a minimum of 3.5 and maximum of 28 mg/kg Cu. It can clearly be seen in this case that the cast properly indicated the concentration of Cu in the area; the slightly higher value could be attributed to the heavy metal bio - accumulative potential of earthworm reflecting in the cast as stated elsewhere (Buck et al., 1999; Schrader and Zhang, 1997; Chadhuri et al., 2009; Ash and Lee, 1980). The result here underscores the fact that the earthworm cast reflects the heavy metals status of the soil to a great extent. However, Chadhuri et al. (2009) reported lower Ca and Mg values in casts compared to surrounding soil, suggesting that the elevated levels of Ca often observed in earthworm casts in the field are probably due to selective feeding by earthworms on materials enriched in those cations.

Among all the metals considered, Cd recorded the lowest metal concentration. It had a median concentration in cast

as 0.70 mg/kg Cd and the minimum and maximum values stood at 0.20 – 2.93 mg/kg Cd. The SOM had a comparatively higher median concentration value of 0.82 mg/kg and the range was found to be 0.30 - 2.0mg/kg Cd. The highest concentration was found in the parent soil with a 0.92 mg/kg median concentration and a range of 0.12 - 3.0 mg.kg Cd, the trend could presented as: parent soil > SOM > Earthworm cast. The fact that the elemental median values for casts are mostly in between SOM and soil median values is indicating that the material from casts is to a certain part a mixture of soil and SOM material.

4. CONCLUSION

In this study the comparison between elemental contents in earthworm surface casts, soil and SOM was shown at highly Mn contaminated area with the intention to assess the reflection of soil contamination in casts. Highly elevated Mn contents were determined in earthworm casts reaching as much as 130 mg/kg. In general the Mn values determined in casts are slightly higher compared to the values in SOM (122 mg/kg) and somewhat lower compared to the Mn contents in soil (202 mg/kg). For most of the analyzed elements, the determined contents were in the order of soil > cast > SOM, indicating that the material from casts is a mixture of material from soil and SOM. Only Ca, Mg, Cu and Zn contents were higher in earthworm casts compared to soil, which was observed also in earlier investigations by other authors (Nahmani et al., 2005). The results show that at the investigated site Mn contents and distribution in soil are strongly reflected in Mn contents and dispersion in earthworm casts. Therefore, earthworm casts proved to be a suitable sampling media for determining soil contamination at this particular area. However, to confirm these findings assessed in the presented research, investigations at other mining site locations are necessary.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Centre for Agrochemical Technology (CAT), Federal University of Agriculture, Makurdi-Nigeria for permission to use its facilities.

REFERENCES

- Giovanetti, A., Fesenko, S., Cozzella, M.L., Asencio, L.D. & Sansone, U. (2010). Bioaccumulation and biological effects in the earthworm *Eisenia fetida* exposed to natural and depleted uranium. *Journal of Environmental Radioactivity*, 101:509-516.
- [2] Reinecke, A.J. & Reinecke, S.A. (2004. Earthworm as Test Organisms. Ecotoxicological Assessment of Toxicant Impacts on Ecosystems. In *Earthworm Ecology*; CRC Press LLC: Boca Raton, FL, USA, pp. 299-320.
- [3] Buck, C., Langmaack, M. & Schrader, S. (1999). Nutrient contents of earthworm casts influenced by different mulch types. *European Journal of Soil Biology*, 35:23-30.
- [4] Okezie, C.N. (1985). Geological map of Nigeria, Div. Geological survey, Lagos, Nigeria.
- [5] Edwards, C.A. (2004). The Importance of Earthworms as Key Representatives of the Soil Fauna. In *Earthworm Ecology*; Edwards, C.A., Ed.; CRC Press LLC: Boca Raton, FL, USA, pp. 3-11.
- [6] Ash, C.P.J. & Lee, D.L. (1980). Lead, cadmium, copper and iron in earthworms from roadside sites. *Environmental Pollution*, A22:59-67.
- [7] Oyedele, D.J., Schjønning, P. & Amusan, A.A. (2006). Physicochemical properties of earthworm casts and uningested parent soil from selected sites in southwestern Nigeria. *Ecological Engineering*, 28:106-113.
- [8] Brulle, F., Mitta, G., Coquerelle, C., Vieau, D., Lemière, S., Leprêtre, A. & Vandenbulcke, F. (2006). Cloning and real-time PCR testing of 14 potential biomarkers in *Eisenia fetida* following cadmium exposure. *Environmental Science and Technology*, 40, 2844-2850.
- [9] Takeshi, H. & Kazuyoshi, T. (2011). Earthworms and Soil pollutants. *Journal of Sensors*, 11:11157-11167.
- [10] Nahmani, J., Capowiez, Y. & Lavelle, P. (2005). Effects of metal pollution on soil macroinvertebrate burrow systems. *Biology and Fertility of Soils*, 42:31-9.

- [11] Udovič, M. & Leštan, D. (2007). The effect of earthworms on the fractionation and bioavailability of heavy metals before and after soil remediation. *Environmental Pollution, 148*:663-668.
- [12] Zorn, M.I., Van Gestel, C.A.M. & Eijsackers, H. (2005). The effect of *Lumbricus rubellus* and *Lumbricus terrestris* on zinc distribution and availability in artificial soil columns. *Biology and Fertility of Soils*, 41:212-215.
- [13] Zorn, M.I., Van Gestel, C.A.M. & Eijsackers, H. (2008). Metal redistribution by surface casting of four earthworm species in sandy and loamy clay soils. *Science of the Total Environment,* 406:396-400.
- [14] Chaudhuri, P.S., Nath, S., Pal, T.K. & Dey, S.K. (2009). Earthworm casting activities under rubber (*Hevea brasiliensis*) plantations in Tripura (India). World Journal of Agricultural Science, 5(4):515-521.
- [15] Kızılkaya, R. (2004). Cu and Zn accumulation in earthworm *Lumbricus terrestris L*. in sewage sludge amended soil and fractions of Cu and Zn in casts and surrounding soil. *Ecological Engineering*, 22:141-151.
- [16] Wuana, R.A., Okieimen, F.E. & Iorhemen, D.A.T. (2009). Chemical speciation of heavy metals in a spiked soil in the vicinity of the Benue Industrial Layout and assessment of uptake by maize (*Zea mays L.*). *Journal of Chemical Society of Nigeria*, 34(1):5-14.
- [17] Citterio, S., Aina, R., Labra, M., Chiani, A., Fumagalli, P., Sgorbati, S. & Santagostino, A. (2002). Soil genotoxicity assessment: A new strategy based on biomolecular tools and plant bioindicators. *Environmental Science & Technology*, 36:2748-2753.
- [18] Schrader, S. & Zhang, H. (1997). Earthworm casting: stabilization or destabilization of soil structure? *Soil Biology & Biochemistry*, 29:469-75.
- [19] Osakwe, S.A. (2009). Heavy metal distribution and bioavailability in soils and cassava (Manihot esculenta Grantz) along Warri – Abraka Expressway, Delta State, Nigeria. Journal of Chemical Society of Nigeria, 34(1): 211-217.
- [20] Teršič, T. (2010). Environmental influences of historical small scale ore processing at Idrija area Okoljski vplivi starih žgalnic na Idrijskem (Ph.D. thesis). Ljubljana: University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology.