http://www.pjbs.org

PJBS

ISSN 1028-8880

Pakistan Journal of Biological Sciences

ANSInet
Asian Network for Scientific Information
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Pakistan Journal of Biological Sciences 17 (10): 1136-1140, 2014
ISSN 1028-8880 / DOI: 10.3923/pjbs.2014.1136.1140
© 2014 Asian Network for Scientific Information

Trace Elements in Water, Soil, Earthworm and Fishes from Otokutu End of Warri River, Delta State, Nigeria

Embbey K. Ossai, Chukwujindu M.A. Iwegbue and Godwin E. Nwajei
Department of Chemistry, Faculty of Science, Delta State University, P.M.B. 1, Abraka, Nigeria

Abstract: Selected environmental samples such as water, fishes (*Tilapia mariae* and *Clarias gariepinus*), earthworm (*Libyodrillus violaceous*) and soils were obtained from the Otokutu end of Warri River, digested with acid mixtures and analyzed for trace metal concentrations using the atomic absorption spectrophotometry. The trace metals measured include; zinc, lead, copper, arsenic, iron, cadmium and mercury. The results obtained showed variations in the concentrations of metals in the entire samples analyzed. Lowest metal concentrations were recorded in the water samples. Trace metal concentrations in *Tilapia mariae*, *Clarias gariepinus* and *Libyodrillus violaceous* were higher than levels recorded in water and soil samples, respectively. The elevated concentrations of lead, arsenic, iron, cadmium and mercury were traceable to anthropogenic wastes and activities of industries operating in Warri and its environs.

Key words: Bioaccumulation, earthworm, fish species, industrial activities, soil pollution, water pollution, Warri River

INTRODUCTION

The major sources of pollution in streams and rivers are the effluents from industries and untreated wastes (Okafor and Nwajei, 2006). High levels of cadmium were found in tissues of fish which may be traceable to industrial pollution in Asaba and Onitsha areas of the River Niger (Nwajei and Oruvwuje, 2001). Human exposure of mercury via global cycle is likely to be greatest in the Arctic where natives depend on freshwater marine fish and marine mammals for much of their diet (Gobeil *et al*., 1999). As river receive discharges from the oil and gas industries, urban water storm and agricultural water runoff from the farming communities along the river course. Contamination of the sediment matrix by heavy metals may be accumulated in fishes and other aquatic resources which may eventually get into human food chains (Iwegbue *et al*., 2007). Heavy metal pollution in the Rio San Juan is a major concern in the Rio Bravo as well (Schmandt *et al*., 2000; IBWC, 1994). De La Garza (1995) observed that 89% of discharges to the Rio San Juan by the 10000 industries in the Rio San Juan watershed exceeded the standards. Therefore, degradation of water quality in the Rio San Juan watershed may involve two factors: (1) Increasing water withdrawal demands to meet domestic and industrial water supplies and (2) Increasing loads of pollutants into the river. The aquatic communities of fish, insects and other organisms are already under stress. The susceptibility of fish to damage by toxic substances such as heavy metals increases when the level of dissolved oxygen depletes (Brooks *et al*., 1992). The accumulation of heavy metals or their compounds in an aquatic environment has direct consequence to man and to the ecosystem (Pickering and Owen, 1994).

Trace elements and organic matter pollutants are predominantly transported in association with suspended particulates with heavy metals and organic matter pollutants in low turbulent river, leading to the formation of highly polluted river bottom sediments in industrialized areas (Haag *et al*., 2001). Study has revealed that nearly all metal contents in aquatic environment reside in water sediments while the fractions in biota are small (Ademoroti, 1996).

Earthworms constitute the largest terrestrial faunal biomass (Vandecasteele *et al*., 2004). Earthworms were found to have a high potential for cadmium accumulation in polluted floodplains (Hendriks *et al*., 1995). They have been considered useful for assessing heavy metal pollution in soils (Menzie *et al*., 1992) because earthworm biomass and abundance were found to be more sensitive to pollution in comparison with other indicator taxa (Spurgeon *et al*., 1996).

MATERIALS AND METHODS

The samples collected from Otokutu River include water, *Tilapia mariae*, *Clarias gariepinus* (fish) *Libyodrilus voilaceous* (earthworm) and soil. These

Corresponding Author: Chukwujindu M.A. Iwegbue, Department of Chemistry, Faculty of Science, Delta State University, P.M.B. 1, Abraka, Nigeria

samples were collected in the day time for the period covering October 2008 to March 2009. Two water sample locations were chosen (i.e., sample station A and B). The water samples were collected at a depth of about 15 cm in clean white polyethylene stoppered bottles which have been washed with soap solution, rinsed three times with pure water and then rinsed another three with 1% HNO_3. The water to be collected was used to rinse the bottles and stoppers for three times before the final collection. The water samples were stoppered and labeled A and B, respectively. Filtration was done on location by passing water samples through a 0.45 μm millipore membrane filter. The membrane filters had been washed with 1% HNO_3, followed by rinsing in high purity water prior to filtration (Bordin *et al*., 1992). The water samples were taken to the laboratory and stored in cold at 4°C prior to digestion. Then, 100 mL of each water sample was transferred into a beaker and 5.0 mL of concentrated HNO_3 was added. The beaker containing the solution was placed on a hot plate and evaporated to near dryness making sure that the sample does not boil. The beaker containing the residue was cooled. Then, 5.0 mL of the concentrated HNO_3 was further added. This was returned to the hot plate until digestion was completed. Then 2.0 mL of concentrated HNO_3 was added and the beaker was warmed slightly to dissolve the residue (APHA, 1990; Ahn *et al*., 1996). The digested sample was filtered. The filtrate was made upto 50 mL with deionised water. The solution was returned to the laboratory and kept in the refrigerator prior to metal analysis. The blank was also prepared using the same procedure of digestion as in samples.

Soil sample was collected at depth of 0-15 cm by the bank of Otokutu River. The soil was air-dried and was sieved to pass through a 2 mm sieve. The 5.0 g of dried surface soil sample was accurately weighed into a clean dry beaker. The 10 mL of concentrated HNO_3 was added and left for 10 min. 5 mL of concentrated $HClO_4$ was added and left for another 10 min. The digest was heated on a hot plate regulated to 120°C for 30 min, stirred to attain a uniform mixture with the liberation of hydrogen chloride gas from the sample. The digest was transferred to fume cupboard where it cooled over night (Darmody and Marlin, 2002) and filtered through Whatman filter No. 42 study into 100 mL volumetric flask and made to mark with deionised water. A blank sample was also prepared using the same procedure. The solution was stored in the refrigerator prior to metal analysis.

Earthworm (*Libyodrillus violaceous*) sampling was done on the bank of Otokutu River according to the combined method of Bouche and Aliaga (1986). While, the fish (*Tilapia mariae* and *Clarias gariepinus*) samples were collected using the method adopted by Ney and van Hussel (1983). Earthworm and fishes collected were taken to the Department of Animal and Environmental Biology Delta State University Abraka for identification. The samples were dissected with a clean stainless steel knife and were then oven-dried at 60°C. The whole body of *Libyodrillus violaceous*, *Tilapia mariae* and *Clarias gariepunis* was crushed in each case, in clean mortars with pestle. Five gram each of the dried *Libyodrillus violaceous*, *Tilapia mariae* and *Clarias gariepunis* were weighed in clean beakers and digested concentrated acid mixture containing 20 mL HNO_3 and 5 mL $HClO_4$. The resultant solution was placed on a hot plate with constant stirring for 30 min until the liberation of nitrous oxide gas from the sample was observed. The digest was transferred into the fume chamber overnight. On cooling, the digest was filtered through Whatman filter No. 42 into 100 mL volumetric flask and made to mark with deionized water (Heikens *et al*., 2001). The blanks were prepared for each case following the same procedure but omitting the samples using atomic absorption spectrophotometry (Perkin Elmer Analyst 200, Norwalk, CT, USA).

RESULTS AND DISCUSSION

Environmental samples such as water, soil, *Libyodrillus violaceous*, *Tilapia mariae* and *Clarias gariepinus* obtained from Otokutu River were analyzed for selected metals (zinc, lead, copper, arsenic, iron, cadmium and mercury). The results are presented in Table 1. The results revealed that there were variations in metal concentrations in all the samples studied. The results further revealed that metal concentrations in *Clarias gariepinus*, *Tilapia mariae*, *Libyodrillus violaceous* and soil were elevated when compared to metal concentrations in water samples. The aquatic vertebrates and invertebrates metal values exceeded those in the soil sample. The bioaccumulation of trace metals in the aquatic vertebrates (fishes) and invertebrates (earthworm) may have accounted for the elevated values.

Tilapia mariae contained higher concentration of trace metals compared to those obtained in *Clarias gariepinus* from the same river. Also, the trace metal concentrations in *Libyodrillus violaceous* (earthworm) were lower than those obtained in *Tilapia mariae* and *Clarias gariepinus* except for iron, cadmium and mercury concentrations which were considered high. This study revealed that vertebrates and invertebrates in rivers are the major indicator for metals accumulation.

The concentrations of zinc, lead, copper, arsenic, iron, cadmium and mercury in water from the two sampling

Table 1: Mean and range of trace metal concentrations in water, soil earthworm and fishes from otokutu river

	Metals (mg kg^{-1} dry weight except water samples in mg L^{-1})						
Sample	Zinc	Lead	Copper	Arsenic	Iron	Cadmium	Mercury
Clarias gariepinus (Fish)	(24.00)	(0.67)	(1.04)	(0.56)	(0.59)	(0.48)	(0.44)
	20.00-28.00	0.45-0.78	0.92-1.24	0.49-0.66	0.42-0.71	0.39-0.59	0.30-0.52
Tilapia mariae (Fish)	(28.80)	(0.74)	(1.10)	(0.61)	(0.65)	(0.53)	(0.52)
	22.04-34.00	0.51-0.97	0.82-1.39	0.40-0.83	0.50-0.80	0.42-0.76	0.40-0.64
Libyodrillus violaceous	(1.16)	(0.77)	(0.68)	(0.50)	(10.40)	(0.60)	(0.57)
(Earthworm)	0.92-1.38	0.62-0.89	0.56-0.80	0.45-0.55	10.00-10.80	0.50-0.70	0.50-0.64
Soil	(0.64)	(0.52)	(0.43)	(0.28)	(8.00)	(0.31)	(0.28)
	0.54-0.70	0.50-0.56	0.40-0.49	0.24-0.32	7.00-9.00	0.28-0.33	0.26-0.30
Water sample 1	(0.28)	(0.01)	(0.02)	(0.003)	(0.01)	(0.002)	(<0.002)
	0.20-0.36	-	0.01-0.05	-	-	0.00-0.012	-
Water sample 2	(0.284)	(0.011)	(0.02)	(0.004)	(0.01)	(0.01)	(<0.002)
	0.204-3.60	0.009-0.018	0.01-0.04	0.003-0.006	0.004-0.03	-	-

Table 2: Concentration range of metals in water, soil, earthworm and fishes in different rivers in Nigeria

		Metals (mg kg^{-1} dry weight except water sample in mg L^{-1})							
Sample	Location	Zinc	Lead	Copper	Arsenic	Iron	Cadmium	Mercury	Reference
Tilapia zilli (fish)	Warri river	19.80-26.00	0.92-1.45	-	-	-	0.38-0.80	-	Nwajei and Okrija (2004)
Clarias gariepinus (fish)	Warri river	23.50-32.30	1.30-1.90	-	-	-	0.52-1.60	-	Nwajei and Okrija (2004)
Libyodrillus violaceous (earthworm)	Warri river	25.00-30.00	1.36-2.02	-	-	-	0.66-1.10	-	Nwajei and Okrija (2004)
Soil	Warri river	6.50-9.50	0.42-0.60	-	-	-	0.18-0.45	-	Nwajei and Okrija (2004)
Ilisha africana (fish)	Lagos Lagoon	2.42±0.53	0.09±0.02	0.10±0.01	-	-	0.01±0.001	-	Tomori *et al.* (2004)
Pseudotolithus elongates (fish)	Lagos Lagoon	2.46±0.62	0.09±0.05	0.25±0.07	-	-	0.03±0.02	-	Tomori *et al.* (2004)
Tilapia zilli (fish)	River Niger	66.08	68.36	ND	-	84.42	-	-	Obodo (2002)
Synodontis membranaceus (fish)	River Niger	55.82	80.77	5.92	-	93.39	-	-	Obodo (2002)
Water	Landzu river	0.62	-	0.19	-	0.96	0.03	-	Adekola and Saidu (2005)
Soil	Landzu river	17.30	-	22.10	-	99.40	3.73	-	Adekola and Saidu (2005)
Water	River waters within Okitipupa	ND -0.12	ND -0.047	0.007 -0.902	ND -1.400	0.063 -4.597	ND -0.004	ND -0.238	Aiyesanmi (2006)
Soil	Calabar river	-	-	-	-	-	2.50	0.68	Uwah *et al.* (2006)
Synodontis membranaceus (fish)	Ora river	1.891	2.806	0.566	1.528	4.425	0.26	0.033	Okafor and Nwajei (2007b)
Water	Ora river	0.195	0.32	0.102	0.486	1.58	0.047	0.221	Okafor and Nwajei (2007a)
Synodontis membranaceus (fish)	Ebe river	2.50	1.27	0.57	-	1.29	0.10	-	Okafor and Nwajei (2007a)
Water	Ebe river	0.174	0.384	0.12	0.405	1.84	0.062	0.115	Okafor and Nwajei (2007b)
Water	Ethiope river	1.27	0.72	0.37	-	-	0.03	-	Omuku *et al.* (2008)
Tilapia (fish)	Ethiope river	0.10	0.11	0.14	-	-	0.06	-	Omuku *et al.* (2008)
Catfish	Ethiope river	0.18	0.14	0.15	-	-	0.05	-	Omuku *et al.* (2008)
Water 01	This study	0.281	0.01	0.020	0.003	0.01	0.002	<0.002	
Water 02	This study	0.284	0.011	0.020	0.004	0.01	0.01	<0.002	
Soil	This study	0.64	0.52	0.43	0.28	8.00	0.31	0.28	
Libyodrillus violaceous (Earthworm)	This study	1.16	0.77	0.68	0.50	10.40	0.60	0.57	
Tilapia mariae (fish)	This study	28.80	0.74	1.10	0.61	0.65	0.53	0.52	
Clarias gariepinus	This study	24.00	0.67	1.04	0.56	0.59	0.48	0.44	

ND: No detected, -: Parameter not measured

stations (samples 1 and 2) were below the water quality guideline values for metals in water (WHO, 2006). The concentrations of zinc, copper, iron and cadmium in water, in this study were lower than those values obtained in Ora River around Nigerian cement factory by Okafor and Nwajei (2007a). Table 2 represent the results of the present study in comparison with published data on the metal concentrations in water and fish species from some Nigeria waters.

The concentrations of lead and cadmium in *Tilapia mariae*, *Clarias gariepinus*, *Libyodrillus violaceous* and soil in this study were lower than those

values obtained by Nwajei and Okrija (2004) from Warri River. The accumulated metal concentrations in the tissues of *Tilapia mariae* and *Clarias gariepinus* may be passed on through the food chain to man thereby causing food poison. These high concentrations of trace metals are traceable to various activities of industries operating in Warri and its environs.

In general, cadmium is the most important pollutant for food chain transfer whereas copper is the most element for earthworm survival. The knowledge of trace metal concentrations in earthworm is essential for risk assessment of trace metal biomagnifications. Earthworms have been considered useful for assessing heavy metal pollution in soils (Menzie *et al*., 1992). However, trace metal pollution has two major effects on the ecosystem. For example, accumulation of cadmium as measured in this study, can lead to risks of poisoning whereas low concentrations of copper in soil can lead to earthworm disappearance, thereby, causing food scarcity for earthworm predators such as fishes.

CONCLUSIONS

Water, soil, *Libyodrillus violaceous*, *Tilapia mariae* and *Clarias gariepinus* samples obtained from Otokutu River were analyzed for metals such as zinc, lead, copper arsenic, iron, cadmium and mercury. The results obtained revealed that there were metal variations among the samples measured. Lowest metal levels were obtained in water samples in comparison with other samples studied. The results further revealed that *Libyodrillus violaceous* depends on soil for survival. Secondly, it serves as food for predators such as fishes. This is an indication that metal pollution through the food chain can be passed to human. Soil metal levels being lower than the metal concentrations in earthworm and fishes being lower than that of water are indication of bioaccumulation. This implies that vertebrates and invertebrates can serve as bioaccumulators of trace elements in Nigerian rivers. The presence of trace metals in Otokutu River are traceable to anthropogenic wastes and activities of various industries operating in Warri and its' environs.

ACKNOWLEDGEMENT

The author is thankful to Mr. G.C. Ndinwa for his assistance in sample collection and metal analysis.

REFERENCES

APHA, 1990. Standard Methods for the Examination of Waters and Wastewaters. 16th Edn., American Public Health Association, Washington, DC., USA.

Adekola, F.A. and M.M. Saidu, 2005. Determination of pollution level of water and sediment samples of Landzu River, Bida, Nigeria. J. Chem. Soc. Nigeria, 30: 181-186.

Ademoroti, C.M.A., 1996. Environmental Chemistry and Toxicology. 1st Edn., Foludex Press Ltd., Ibadan, Nigeria.

Ahn, L.Y., S.H. Lee, K.T. Kim, J.H. Shim and D.Y. Kim, 1996. Baseline heavy metal concentration in the antarctic clain, lutemula elliptica in maxwell bay, King George Island, Antarctic. Mar. Pollut. Bull., 32: 592-598.

Aiyesanmi, A.F., 2006. Baseline concentration of heavy metals in water samples from rivers within Okitipupa southeast belt of the Nigerian bitumen field. J. Chem. Soc. Nigeria, 31: 30-37.

Bordin, G., J. Mccourt and A. Rodrignez, 1992. Trace metals in the marine bivalve macoma balthican the water schelde eastuary (The Netherlands) Part I: Analysis of total copper, cadmium, zinc and iron concentrations-occasional seasonal variations. Sci. Total Environ., 127: 280-285.

Bouche, M.B. and R. Aliaga, 1986. Contre une degradation physique et chimique des soil et pour leur optimization economique, I'echantillonage des lombriciens: une urgente necessite. La Defense des Vegetaux, 242: 30-36.

Brooks, K.N., P.F. Ffolliot, H.M. Gregersen and J.L. Thames, 1992. Hydrology and The Management of Watersheds. Iowa State University Press, Ames.

Darmody, R.G. and J.C. Marlin, 2002. Sediments and sediment-derived soils in Illinois: Pedological and agronomic assessment. Environ. Monit. Assess., 77: 209-227.

De La Garza, J., 1995. Incumplen normas 89% de industries. Resumen Noticoso. Revista Calidad AMbiental Vol. 11 Monterrey, Nuevo Leon, Mexico.

Gobeil, C., R.W. MacDonald and J.N. Smith, 1999. Mercury profiles in sediments of the arctic ocean basins. Environ. Sci. Technol., 33: 4194-4198.

Haag, I., U. Kern and B. Westrich, 2001. Erosion investigation and sediment quality measurements for a comprehensive risk assessment of contaminated aquatic sediments. Sci. Total Environ., 266: 249-257.

Heikens, A., W.J.G.M. Peijnenburg and A.J. Hendriks, 2001. Bioaccumulation of heavy metals in terrestrial invertebrates. Environ. Pollut., 113: 385-393.

Hendriks, A.J., W.C. Ma, J.J. Brouns, E.M. de Ruiter-Dijkman and R. Gast, 1995. Modelling and monitoring organochlorine and heavy metal accumulation in soils, earthworms and shrews in Rhine-delta floodplains. Environ. Contam. Toxicol., 29: 115-127.

IBWC, 1994. Binational study regarding the presence of toxic substances in the Rio Grande/Rio Bravo and its tributaries along the boundary portion between the United States and Mexico. Final Report, International Boundary and Water Commission, United States and Mexico, September 1994.

Iwegbue, C.M.A., G.E. Nwajei and F.O. Arimoro, 2007. Assessment of contamination by heavy metals in sediments of Ase River, Niger Delta, Nigeria. Res. J. Environ. Sci., 1: 220-228.

Menzie, C.A., D.E. Burmaster, J.S. Freshman and C.A. Callahan, 1992. Assessment of methods for estimating ecological risk in the terrestrial component: A case study at the Baird and McGuire superfund site in Holbrook, Massachusetts. Environ. Toxicol. Chem., 11: 245-260.

Ney, J.J. and J.H. van Hassel, 1983. Sources of variability in accumulation of heavy metals by fishes in a roadside stream. Arch. Environ. Contam. Toxicol., 12: 701-706.

Nwajei, G.E. and B.O. Okrija, 2004. Cadmium, chromium, lead and zinc concentrations in Fishes, earthworm and soil from Warri River. Proceedings of the 27th International Conference of the Chemical Society of Nigeria, September 20-24, 2004, Benin, pp: 155-158.

Nwajei, G.E. and J.U. Oruvwuje, 2001. Assessment of heavy metals in *Clarins buthopogon* (fish) parts and *Nymphaea lotus* (aquatic plant) in River Niger, Delta State of Nigeria. Pak. J. Sci. Ind. Res., 44: 333-337.

Obodo, G.A., 2002. The bioaccumulation of heavy metals in fish from the lower reaches of river Niger. J. Chem. Soc. Niger., 27: 173-176.

Okafor, E.C. and G.E. Nwajei, 2006. Assessment of the levels of trace elements contamination in Sediments from Ebe and Ora Rivers South Eastern Nigeria. Niger. J. Sci. Environ., 5: 44-49.

Okafor, E.C. and G.E. Nwajei, 2007a. Heavy metals in water and fish (*Synodontis membranmaceus*) from Ora and Ebe Rivers in the Vicinity of Nigerian cement factory Nkalagu. Biosci. Biotechnol. Res. Asia, 4: 185-192.

Okafor, E.C. and G.E. Nwajei, 2007b. Metal contents in water and aquatic plant (Macaranga Heudelotic) from Ora river around Nigerian cement factory, Nkalagu. Res. Biol. Sci., 2: 85-88.

Omuku, P., A.K. Asiagwu and A.J. Chinweuba, 2008. Assessment of heavy metal load of Owah-Abi, Ethiope River Delta State. Proceedings of the 31st International Conference of the Chemical Society of Nigeria, September, 22-26, 2008, Effurun-Warri, Delta State of Nigeria, pp: 640-647.

Pickering, K.T. and L.A. Owen, 1994. An Introduction to Global Environmental Issues. Routledge, London, UK., ISBN-13: 9780415102278, Pages: 390.

Schmandt, J.I., N. Aguilar, L. Armstrong, S. Chapa and R. Contreras *et al*., 2000. Water and sustainable development. Executive Summary, USEPA Research, Agreement R 824799-01-0, USEPA, Washington, DC.

Spurgeon, D.J., R.D. Sandifer and S.P. Hopkin, 1996. The Use of Macro-Invertebrates for Population and Community Monitoring of Metal Contamination-Indicator Taxa, Effect Parameters and The Need for a Soil Invertebrate Prediction and Classification Scheme (SIVPACS). In: Bioindicator Systems for Soil Pollution, Van Straalen, N.M. and D.A. Krivolutsky (Eds.). Kluwer Academic Publishers, Dordrecht/Boston/London, pp: 95-110.

Tomori, W.B., A.F. Aiyseanmi and O.A. Obijola, 2004. Heavy metal quality assessment of marine fishes of lagos lagoon. Proceeding of the 27th International Conference of the Chemical Society of Nigeria, September 20-24, 2004, Benin, pp: 252-256.

Uwah, I.E., E.E. Ntekim and R.A. Etiuma, 2006. Distribution of Hg and Cd in the sediment from Calabar River Estuary, S.E. Nigeria. J. Chem. Soc. Nig., 31: 63-67.

Vandecasteele, B., J. Samyn, P. Quataert, B. Muys and F.M. Tack, 2004. Earthworm biomass as additional information for risk assessment of heavy metal biomagnification: A case study for dredged Sediment-derived soils and polluted floodplain soils. Environ. Pollut., 129: 363-375.

WHO, 2006. Guidelines for Drinking-Water Quality: First Addendum to Third Edition, Volume 1: Recommendations. World Health Organization, Geneva, Switzerland, ISBN-13: 9789241546744, Pages: 68.