Journal of Environmental Science and Technology

ISSN 1994-7887

science alert

ANSInet
an open access publisher
http://ansinet.com

Journal of Environmental Science and Technology 4 (4): 437-443, 2011
ISSN 1994-7887 / DOI: 10.3923/jest.2011.437.443

Correlation Analyses of Organically Bound Trace Metals and Sediment in Kubanni, Dam, Zaria, Nigeria

[1]B.W. Tukura, [2]J.A. Kagbu and [2]C.E. Gimba
[1]Department of Chemistry, College of Education Akwanga, P.M.B. 05, Akwanga, Nasarawa State, Nigeria
[2]Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

Corresponding Author: B.W. Tukura, Department of Chemistry, College of Education Akwanga, P.M.B. 05, Akwanga, Nasarawa State, Nigeria

ABSTRACT

Surface bed sediments were collected from Kubanni dam during dry and rainy seasons. Concentrations of trace metals bound to carbonates, Fe/Mn-oxides and Organic Matter (OM) were determined using atomic absorption spectrophotometer. Correlations between any two trace metals binding fractions and the correlations between sediment matrices were also determined. Fe/Mn-oxides provided more binding sites for trace metals in dry season (1.64 mg kg^{-1}) and rainy season (1.97 mg kg^{-1}).Correlations analyses show that Cr significantly correlated with Fe/Mn-oxides (r = 0.7971) during rainy season, while Cr and Zn-carbonates (r = 0.8925), Cu and Zn-OM (r = 0.8314) and Pb and Zn-OM (r = 0.7626) in dry season. Significant correlations imply same source of pollution. Correlation analyses of organically bound trace metals and sediment phases show that organically bound Zn in dry season and Cu in rainy season strongly correlated with carbonates and OM, respectively, implying that the predicted amount of these metals are more accurate than those of other organically bound trace metals. The results generally indicate competitions of various sediment phases whenever binding with trace metals do occur. Fe/Mn-oxides and OM are the more accessible to trace metals than other sediment matrices.

Key words: Statistical analyses, trace metals, speciation, sediments

INTRODUCTION

The pollution of the aquatic environment with trace metals has become a world-wide problem during recent years (Benjamin and Mwashote, 2003) because they are non-biodegradable and are toxic to aquatic organisms (Ikem *et al*., 2003; Krissanakriangkrai *et al*., 2009; Ozturk *et al*., 2009).

Trace metals are introduced into the water systems both form point and nonpoint sources (Ghaffar *et al*., 2009). Once metals are introduced into water, they undergo interactive reactions with water bodies through series of processes which are influenced by allochthonous and autochthonous processes. The allochthonous influence is made up of natural and civilizations effects, while autochthonous influence is as result of precipitation, absorption, enrichment of organisms and organ metallic complexing during sedimentation as well as the post depositional effects of diagnosis (Forstner and Salomons, 1991; Zoumis *et al*., 2001; Tukura *et al*., 2007).

Bed sediments in water systems are repositories for various elements acting bot as sinks and sources of supply for the elements to overlying water column (Begum *et al*., 2009; Ghaffar *et al*., 2009; Abdul *et al*., 2009). Trace metals adsorbed onto sediment can be remobilized either by physical disturbance like flood or changes in geochemical parameters such as pH, redox potential, dissolved oxygen and ionic strength (Ali and Fishar, 2005; Chang *et al*., 2007; Ghaffar *et al*., 2009).

The bioavailability and subsequent toxicity of trace metals depend on metal speciation in sediments (Ewa-Szarek *et al.*, 2006). Trace elements are associated with Organic Matter (OM), adsorbed onto Fe/Mn oxides or complexed with hydroxides, sulphides and carbonates (Tessier *et al.*, 1979). High contents in the exchangeable and soluble and easily reducible fraction may indicate pollution from anthropogenic origin. Even high contents in the more resistant fractions, the residual, may be significant in the long term. OM and Fe/Mn oxides in the sediment matrices are the two most important sediment components for metal partition under aerobic conditions (Murray *et al.*, 1999; Yu *et al.*, 2001). During the last decade studies on resolving the mechanisms of mobility and bioavailability of trace metals by exploring various fractions of trace metals in sediments are numerous (Tsai *et al.*, 1998; Yu *et al.*, 2001; Hlavay *et al.*, 2004).

Correlations between binding fractions of trace metals and the sediment matrices are being explored on quantitative basis. Correlations study of trace metals in sediment matrices can not only provide a fundamental assessment of the relationship among different binding forms of trace metals (speciation), but also serve as a means of prediction of pollution sources of trace metals (Yu *et al.*, 2001). Effect of pH on the partitioning of trace metals in the bed sediments of Kubanni dam has been reported (Tukura *et al.*, 2007), but data on correlation analysis of trace metals with bed sediment matrices are not available. Seasonal correlations of binding fractions of trace metals (Cr, Cu, Pb and Zn) and sediment matrices of Kubanni dam were considered in this study. Kubanni dam serves as the major source of water supply to Ahmadu Bello University (ABU) community and its environs and also use for fishing and irrigation farming.

MATERIALS AND METHODS

This research project was conducted from 2002 to 2005.

Study area: Kubanni dam (Fig. 1) which was constructed in the early 1970s has its source from Kubanni river, bounded by latitude11° 06' to11° 11' N and longitudes 7° 30'E (Tukura *et al.*, 2009).

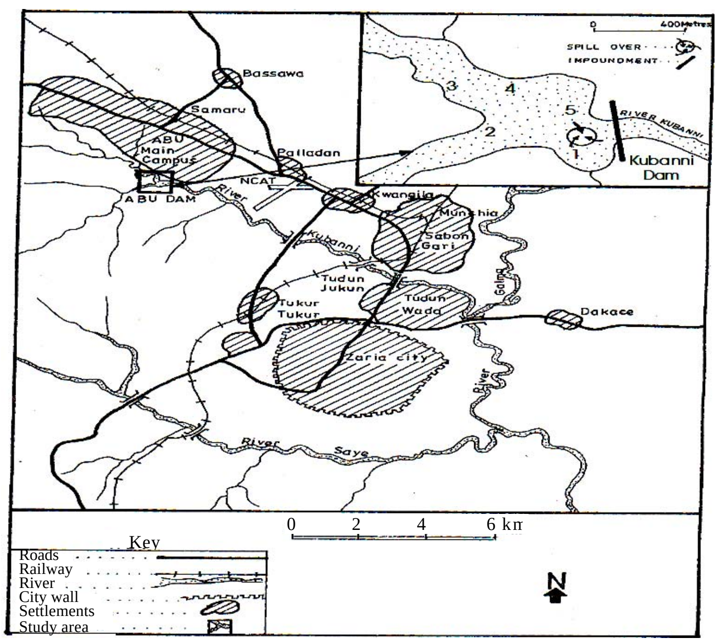

Fig. 1: Map of Zaria showing the study area

The dam has a catchment area of 57 km^2 and is the major source of water supply to Ahmadu Bello University, main campus, Zaria, Nigeria and its environs. Fishing is carried out in the dam and irrigation farming is witnessed along banks of the dam during dry season (Tukura *et al.*, 2007).

Sampling and sample preparation: Bed sediment samples at the depths of 0-5 cm were collected in the months of June and September (rainy season) and in January and March (dry season), into previously treated polythene containers using a perforated container to allow water to drain. The sediments were dried at 50°C for two days, then grind in acid-washed porcelain mortar with pestle. The samples were sieved through a150 μm sieve in order to normalise variations in grain size distributions. The samples were store in polythene containers with caps for further analysis.

Carbonates and Organic Matter (OM) contained in sediments were analyzed. Carbonates were analysed using the approximate gravimetric method (Raad, 1978) while OM was determined using the Walkley- Black wet combustion (Nelson and Sommers, 1982; Tukura *et al.*, 2009). Fractionation of trace metals was carried out using the sequential extraction procedure (Tessier *et al.*, 1979). All the five operationally defined geochemical binding fractions (exchangeable, bound to carbonates, bound to Fe/Mn-oxides and bound to OM could then be determined by the sequential extraction procedure. After each extraction step, the solution was centrifuged to separate the extracts from the solid. The obtained extracts were used to determine the binding amounts of Cr, Cu, Pb and Zn by an atomic absorption spectrophotometer.

Chemicals used for the extraction processes were of analytical grades. All glasswares were washed in 10% HNO_3 (w/v) prior to each experiment.

Statistical analysis: Statistical methods have many applications in environmental studies, providing a scientific basis for monitoring trace metals accumulation. For instance, statistical analysis combining the Principal Component Analysis (PCA) and the Hierarchical Ascending Classification (HAC) techniques was usually employed to determine the natural and anthropogenic sources of trace metals, by grouping them into significant groups. Correlation Analysis (CA) is used to establish relationships among environmental data (Qishlaqi and Moore, 2007).

Fundamental knowledge of the fate and the chemical speciation and distribution of trace metals in a complicated system is essential but hard to be understood. Statistical analysis can not only provide a fundamental assessment of the relationship among different binding forms of trace metals but also serve as a prediction of pollution sources of trace metals (Yu *et al.*, 2001).

Means, maximum values, minimum values and standard deviations of the trace metals and sediment matrices were calculated. Correlation was used to determine the correlations between any two binding fractions of trace metals and with the sediment Organic Matter (OM) and carbonate phases. Data analysis was performed using STATISTICA for windows 6.0 work package.

RESULTS AND DISCUSSION

Seasonal variations in mean, maximums, minimum and standard deviations of sediment matrices are presented in Table 1. The mean values of trace metals concentration in the sediment matrices are in the decreasing order of Fe/Mn-oxides (1.64 mg kg^{-1}) >OM (1.18 mg kg^{-1}) >carbonates (1.09 mg kg^{-1}) during dry season and Fe/Mn-oxides (1.97 mg kg^{-1}) >carbonates (1.75 mg kg^{-1}) >OM (1.58 mg kg^{-1}) for rainy season. The results indicate that Fe/Mn-oxides fraction provided more binding sites for trace metals than other sediment phases for both seasons, contrary

Table 1: Seasonal statistical results (20 sets of data) of the sediment matrices

	Sediment matrices (mg kg^{-1})					
	Carbonates		Fe/Mn-oxides		Organic matter	
Statistical parameter	Dry season	Rainy season	Dry season	Rainy season	Dry season	Rainy season
Mean	1.09	1.75	1.64	1.97	1.18	1.58
Max.	2.64	3.64	3.73	3.70	2.87	1.58
Min	0.02	0.37	0.02	0.02	0.33	0.23
SD	0.97	0.93	1.20	1.37	0.96	1.00

Table 2: Positive correlations between any two trace metals binding to sediment fractions during rainy season

Bound to cabonates	Cr-carbonates	Cu-carbonates	Pb-carbonates	Zn-carbonates
Cr-carbonates	-	-	0.5659	0.1888
Cu-carbonates		-	-	-
Pb-carbonates	-	-	-	--
Zn-carbonates	-	-	-	-
Bond to Fe/Mn-oxides	**Cr-Fe/Mn-oxides**	**Cu-Fe/Mn-oxides**	**Pb-Fe/Mn-oxides**	**Zn-Fe/Mn-oxides**
Cr-Fe/Mn-oxides		-	0.7971	-
Cu-Fe/Mn-oxides	-	-	-	0.5304
Pb-Fe/Mn-oxides	-	-	-	0.1034
Zn-Fe/Mn-oxides	-	-	-	
Organic Matter (OM)	**Cr-OM**	**Cu-OM**	**Pb-OM**	**Zn-OM**
Cr-OM	-	0.7971	-	-
Cu-OM	0.6410	-	-	-
Pb-OM	-	-	-	0.0704
Zn-OM	-	-	-	-

Blank cells represent negative and non-significant correlation values at $p<0.05$

to results reported by Ikem *et al.* (2003) for five different rivers in southern Taiwan. Adekola *et al.* (2010) indicated that contribution of metals bound to organic matter was high and the same magnitude as those bound to Fe/Mn- oxides. Variations in physicochemical parameters may account for the differences in available bounding metal sites in sediment matrices.

The binding behaviour of the four trace metals bound to the three sediment phases could also be known by performing correlation matrix. Results in Table 2 and 3 represent correlation matrices for trace elements in carbonates, Fe/Mn-oxides and OM for dry and rainy seasons respectively. The results in Table 2 show that Cr correlated moderately with Pb-carbonates ($r = 0.5659$) and weakly with Zn-carbonates ($r = 0.1889$) in dry season, while a significant correlation was observed for Cr with Cu-carbonates ($r = 0.7971$) and moderately between Cu and Zn- Fe/Mn-oxides ($r = 0.5304$). Table 2 shows a high correlation of Cu with Cr-OM ($r = 0.6412$). Table 3 indicated that Cu strongly correlated with Zn-Carbonates (0.8925) and weakly with Cr-carbonates ($r = 0.0264$). Association of trace metals with the Fe/Mn-oxides (Table 3) shows a weak correlation between Cr and Zn-Fe/Mn-oxides ($r = 0.1904$) and a moderate relationship between Cu and Pb-Fe/Mn-oxides ($r = 0.6036$). Table 3 shows a significant correlations of Cu ($r = 0.8314$ and Pb ($r = 0.7629$) with the Zn-OM and a moderate correlations between Cu and Cr-OM ($r = 0.5639$) and Pb-OM ($r = 0.4540$).

Significant correlations between some trace metals and some sediment phases imply that the variations in total concentration of complexed metal in solution comply well with the input of trace metals discharging into the dam.

Table 3: Positive correlations between any two trace metals binding to sediment fractions in dry season

Bound to cabonates	Cr-carbonates	Cu-carbonates	Pb-carbonates	Zn-carbonates
Cr-carbonates	-	0.0264	-	-
Cu-carbonates	-	-	-	0.8925
Pb-carbonates	-	-	-	-
Zn-carbonates	-	-	-	-
Bond to Fe/Mn-oxides	Cr-Fe/Mn-oxides	Cu-Fe/Mn-oxides	Pb-Fe/Mn-oxides	Zn-Fe/Mn-oxides
Cr-Fe/Mn-oxides	-		-	0.1904
Cu-Fe/Mn-oxides	-	-	-	0.6036
Pb-Fe/Mn-oxides	-	-	-	-
Zn-Fe/Mn-oxides	-	-	-	-
Organic Matter (OM)	Cr-OM	Cu-OM	Pb-OM	Zn-OM
Cr-OM	-	-	-	0.2846
Cu-OM	0.5639	-	0.5639	0.8314
Pb-OM	-	-	-	0.7626
Zn-OM	-	-	-	-

Blank cells represent negative and non-significant correlation values at $p<0.05$

Table 4: Seasonal Pearson's correlations between carbonates and carbonates bound trace metals and OM and organic matter bound trace metals

Carbonates	Dry season	Rainy season	Organic matter	Dry season	Rainy season
Cr-carbonates	0.4794	0.0639	Cr-OM	0.4114	-0.0421
Cu-carbonates	0.1817	-0.3847	Cu-OM	0.5108	0.7096
Pb-carbonates	-0.3671	-0.4481	Pb-OM	-0.7946	-0.7474
Zn-carbonates	-0.3671	0.9546	Zn-OM	-0.2529	-0.1602

Significant at $p\leq 0.05$

To determine the effects of OM and carbonates on the binding behaviour of the four trace metals, the correlation coefficient (r) was determined (Table 4). The results show that the correlations between organically bound Cr (r = 0.4794) and Zn (r = 0.9546) with carbonates were highest during dry and rainy seasons, respectively; while correlations of organically bound Cu (r = 0.7096) with OM was highest in rainy season and Cr (r = 0.4114) in dry season. Yu *et al.* (2001) reported negative and insignificant correlations between carbonates and carbonates bound Cr, Cu, Pb, Ni and Zn. Accordingly, regarding the sediment phases, the predicted amount of organically bound Zn in carbonates and Cu in Fe/Mn-oxides are more accurate than those of other organically bound trace metals. The significant correlation between organically bound Cu and OM is due to the high affinity of Cu for OM (Warran and Zimmerman, 1993).

CONCLUSION

Fe/Mn-oxides provided more binding sites for trace metals in dry season (1.64 mg kg^{-1}) and rainy season (1.97 mg kg^{-1}). Correlations analyses show that Cr significantly correlated with Fe/Mn-oxides (r = 0.7971) during rainy season, while Cr and Zn-carbonates (r = 0.8925), Cu and Zn-OM (r = 0.8314) and Pb and Zn-OM (r = 0.7626) in dry season. Significant correlation imply same source of pollution. Correlation analyses of organically bound trace metals and sediment phases show that organically bound Zn in dry season and Cu in rainy season strongly correlated with carbonates and OM, respectively, implying that the predicted amount of these metals are more accurate than those of other organically bound trace metals. Generally, the results indicate competitions of various sediment phase whenever binding with trace metals do occur and Fe/Mn-oxides and OM are the more accessible to trace metals than other sediment matrices.

ACKNWLEDGMENTS

The authors wish to thank the Federal Scholarship Board, Abuja, Nigeria, for partially sponsored the research work (FSBA/FGSS: PG/130/F1) and National Research Institute for Chemical and Technology (NARICT), Zaria, for the AAS analysis of samples.

REFERENCES

Abdul, R., M. Javed, M. Ubaidullah and S. Abdullahi, 2009. Assessing heavy metals in sediments of the River Ravi, Pakistan. Int. J. Agric. Biol., 11: 197-200.

Adekola, F.A., N. Abdus-Salama, R.B. Baleb and I.O. Oladejia, 2010. Sequential extraction of trace metals and particle size distribution studies of Kainji lake sediment, Nigeria. Chem. Speciation Bioavailability, 22: 43-49.

Ali, M.H.H. and M.R. Fishar, 2005. Accumulation of trace metals in some benthic invertebrate and fish species relevant to their concentration in water and sediment of Lake Qarun, Egypt. Egypt J. Aquat. Res., 31: 289-301.

Begum, A., S. Harikrishna and I. Khan, 2009. Analysis of heavy metals in water, sediments and fish samples of Madivala Lakes of Bangalore, Karnataka. Int. J. Chem. Tech. Res., 1: 245-249.

Benjamin, M. and M. Mwashot, 2003. Levels of caesium and lead in water, sediment and selected fish species in Mombasa Kenya Western Indian. Oceanic J. Mar. Sci., 2: 25-34.

Chang, M.L., Y.C. Sun, R.A. Doong, S.C. Wu and C.T. Fu, 2007. Concentrations and correlations of trace metals in estuarine sediments -interpretation by multivariate statistical analysisand elemental normalization. J. Environ. Eng. Manage., 17: 143-150.

Ewa-Szarek, G., A. Amrowiez and R. Gwazda, 2006. Trace elements concentration in fish and bottom sediments of autotrophic dam reservoir. Int. J. Hydrol., 35: 331-352.

Forstner, U. and W. Salomons, 1991. Mobilization of Metals from Sediments. In: Metals and their Compounds in the Environment: Occurrence and Analysis and Biological Relevance, Merian, E. (Ed.). VCH, Germany, pp: 379-398.

Ghaffar, A., M. Tabata,Y. Eto, J. Nishimoto and K. Yamamoto, 2009. Distribution of heavy metals in water and suspended particles at different sited in Ariake Bay, Japan. Electron. J. Environ. Agric. Food Chem., 8: 351-366.

Hlavay, J., T. Prohaska, M. Weisz, W.W. Wenzel and G.J. Stingeder, 2004. Determination of trace elements bound to soils and sediment fractions. Pure Applied Chem., 76: 415-442.

Ikem, A., N.O. Egiebog and K. Nyavor, 2003. Trace Elements in water, fish and sediment from Tuskegee Lake, Southeastern USA. Water, Air Soil Pollut., 149: 51-75.

Krissanakriangkrai, O., W. Suparpacboon, S. Juwa, S. Chacwong and W. Swaddiwudhipong, 2009. Bioavailable cadmium in water, sediment and fish, in a highly contaminated area of Thai-Myammy border. Thammasat Int. J. Sci. Technol., 14: 60-68.

Murray, K.S., D. Cauvent, M. Lybeer and J.C. Thomas, 1999. Particle size and chemical control of heavy metals in bed sediments from the Rouge River, Southeast Michigan. Environ. Sci. Technol., 33: 987-992.

Nelson, D.W. and L.E. Sommers, 1982. Total Carbon, Organic Carbon and Organic Matter. In: Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties, Wiscosin, A.L. (Ed.). 2nd Edn., ASA, SSSA, Madison, WI., pp: 539-579.

Ozturk, M., G. Ozozen, O. Minareci and E. Minareci, 2009. Determination of heavy metals in fish, water and sediments of Avsar dam Lake in Trukey. Iran J. Environ. Health Sci. Eng., 6: 73-80.

Qishlaqi, A. and F. Moore, 2007. Statistical analysis of accumulation and sources of heavy metals occurrence in agricultural soils of Khoshk river banks, Shiraz, Iran. Am. Eur. J. Agric. Environ. Sci., 2: 565-573.

Raad, A.A., 1978. Carbonates. In: Manual on soil Sampling and Methods of Analyses. Mckeage, J.A. (Ed.). 2nd Edn., CSSS, Ottawa, Canada.

Tessier, A., P.G.C. Campbell and M. Bisson, 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem., 51: 844-851.

Tsai, L.J., K.C. Yu, J.S. Chang and S.T. Ho, 1998. Fractionation of heavy metals in sediment cores from the Ell-Ren River, Taiwan. Water Sci. Technol., 37: 217-224.

Tukura, B.W., J.A. Kagbu and C.E. Gimba, 2007. Effects of pH and Total Organic Carbon (TOC) on the distribution of trace metals in kubanni dam sediments, Zaria, Nigeria. Sci. World J., 2: 1-6.

Tukura, B.W., J.A. Kabgu and C.E. Gimba, 2009. Effects of pH and seasonal variation on dissolved and suspended heavy metals in dam surface water, Zaria, Nigeria. Chem. Soc. Nigeria J., 6: 27-30.

Warran, L.A. and A.P. Zimmerman, 1993. Trace Metal-Suspended Particulate Matter Association in a Fluvial System: Physical and Chemical Influences. In: Particulate Matter and Aquatic Contaminants, Rao, S.S. (Ed.). Lewis Publishers, Chelsea. MI., USA., pp: 127-155.

Yu, K.C., L.J. Tsai, S.H. Chen and S.T. Ho, 2001. Correlation analysis on binding behaviour of heavy metals with sediment matrices. Water Res., 4: 2417-2428.

Zoumis, T., A. Schmidt, L. Groove and W. Calmono, 2001. Contaminants in sediments: Remobilization and demobilization. Sci. Environ., 266: 195-202.