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SPECIATION OF HEAVY METALS IN THE SIDMENTS OF GUBI DAM, BAUCHI STATE, NIGERIA

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ABSTRACT

Speciation of heavy metals in the sediments of Gubi Dam in Bauchi, Nigeria was carried out between December, 2001 and March, 2002. The mean total concentrations showed that Tatimari tributary has high Fe, Zn, and Mn, confirming it source and path. The spillway result suggest intensive farming activity along the dam runway. However, the physio-chemical forms of Fe, Pb, and Cr indicate that these metals are associated in high concentration with the mineral matrix of the sediment, as such it is most unlikely to become biologically available. High levels of Cu, Cd, Zn, Mn, Co and Ni are associated with the exchangeable carbonate bound fractions, indicating that they are in potentially available forms and many pose serious problems to the dam ecosystem.

KEY WORDS: Sediments, Speciation, Heavy metals, Gubi Dam, Nigeria

INTRODUCTION

Many drainage basins serve as sinks for metal contaminants and as a result there has been increasing concern about the levels of toxic metals in aquatic systems. Water quality studies have always focused on point source pollution with much attention being paid to dissolved contaminants (Sinclair *et al.,* 1989). However, the sediments and suspended load can be more significant in transportation of contaminants and nutrients than the dissolved load (Shear and Watson, 1977; Cullen *et al*., 1979; Allen 1986). The fact that large quantities of contaminants are transported in association with sediment suggest that problems may arise where contaminants are biologically available or can become biologically available.

The biological or chemical forms of species may affect all aspects of the metal behaviour and biological effects for different natural water systems which contain different proportion of the various species (Charles, 1989). The behaviour of these forms and species is governed by speciation, which influences heavy metal bioavailability and toxicity to biota, its transportation and mobilization and its interaction with the sediments and soil (Patrick, 1987). However, monitoring water quality using sediment has been associated with problems of heterogeneity (Abubakar and Ayodele, 2002). Nevertheless, adsorption of heavy metals by clay and organic fractions suggests that sediments can be used as pollution indicators. The heavy metal loads in water, suspended materials and sediments for rivers have been reported (Sinclair *et al*., 1989; Sarmani, 1989). The metal accumulation in trace sediments and in shells of mollusks have been reported for Tiga Lake in Kano, Nigeria (Abubakar and Ayodele, 2002).

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Birch *et al*., (2001) reported that heavy metals content of stream-bed sediments characterized environmental impacts in rural catchments and serve as sources of contamination. The sediments in a creek flowing through a country town was found to be enriched in Cr, Pb, and Zn over background concentrations.

Heavy metal-bearing sediments enter river systems by discharging of mine or processing waste, tailing dam failures, remobilization of mining areas and mine drainage (Hudson-Edwards, 2003). Lin *et al*., (2003) studied the mobility and toxicity of metals associated with sediments in Ke-ya and Ell-ren rivers in Taiwan. The result showed that the exchangeable, carbonate-bound and Fe/Mn oxide-bound forms were considered to be mobile and related with anthropogenic pollution. The impacts of domestic and industrial waste on water and sediments have been reported to be higher in the rainy season due to runoff, from contaminated sites, agricultural fields and industries (Gaur *et al*., 2005). The heavy metal levels in sediments in the coast of South-West Iberian Peninsula predominates (60%_ in the Fe and Zn at industrial and non-industrial areas (Saenz *et al.,* 2005). However, in some other industrial areas, Saenz *et al*., (2005) found less than 60% Cu, Zn and Cd in the residual fractions. The distribution of trace metals in sediments and water body have been reported to be influenced by season and flow conditions (Zhou *et al*., 2003; Cenci and Martin, 2004; Buck *et al*., 2005). In a study on three hard-water dams of Mooi River in South Africa, Van Aardt and Erdmann (2004) reported that the highest concentration of Cd and Cu were found in all the three dams, while highest lead was found in Potchfsroom dam.

Various methods have been used to assess the levels of meal contamination in sediments. The sequential chemical extraction schemes for heavy metals (Tessier *et al*., 1979; Sarmolloff *et al*., 1983; Kernsten and Forstner, 1987) and the chemical extraction and algae assay schemes for nutrient (Williams *et al*., 1980; Young and Depinto, 1982; Ellis and Standford, 1988) have been used for sediment-bound heavy metals in aquatic systems and soils. Trace metals in water and sediment was also studied using inductively couple plasma atomic emission spectrophotometer (ICP-AES) (Singh *et al*., 2005). This work therefore, determines the various forms and distribution of heavy metals in the exchangeable fractions of the sediments from Gubi dam. It is expected that the result obtained would provide the level of contamination and the likely effect on the water quality of the dam.

EXPERIMENTAL

Study Area

Gubi dam was constructed in 1979 to serve as a permanent water supply scheme for irrigation and dairy farming to Bauchi and its environs. It has a top water level of 577M and 3KM long. Tatimari (Shadawanka and Dinya), Suntum, Kumi and Larkarina provide the major tributaries to the dam. It is located in northern part of Bauchi, Nigeria (Fig 1). The dam lies within the boundary of longtitude $10^0 25^/$N to $10^0 26^/$N and latituide $9^0 51^/$E to $9^0 52^/$E. The region is classified as tropical, and the annual rainfall in the dam basin ranges from 970mm to 1400mm with about 50 to 60% of this rainfall occurring between July and August. Fishing, recreation, irrigation, dairy farming and water treatment take place around the dam (BASWAB, 1990).

Samples Collection and Preparation

Sediment samples were collected during an extensive environmental and aquatic pollution survey of Gubi dam. Samples were taken on two (2) occasions: high flow (September, 2001) and low flow (January, 2002) at the main entries (tributaries) of the dam and outlet (spillway) locations.

Sediment samples approximately 5 to 10cm depth were taken from both sides of the tributes and the spillway using a plastic scoop. The samples were stored in an acid washed, wide-mouthed, plastic bottles. It was air-dried for seven (7) days and then ground to find particles using a ceramic mortar and pestle. The ground samples were then sieve with a 2.00mm mesh (No.18) silk sieve to remove rubble or other dirty materials.

Analytical Methods

Determination of total metal concentration

0.5g of prepared sediment sample was weighed and transferred into a 500ml round bottom flask wetted with a few drops of deionized distilled water, 1oml of aquaregia was measured and transferred into the 500ml round bottom flaks containing sediment and the mixture was heated in a fume cupboard at low heat (120^oC) for one hour. The temperature was then increased to produce white dense fumes and mixture evaporated to approximately 0.5ml. The mixture was further digested with 1ml of percloric acid ($HClO_4$) and evaporated to dryness. The residue was dissolve with $20cm^3$ of 1% (v/v) nitric acid,

and transferred to 100ml volumetric flask. It was made up to the mark with dilute nitric acid 91% (v/v). The heavy metal concentrations in the digest were determined a Buck Scientific Model GP 210 using Atomic Absorption Spectrophotometer (AAS).

Metal Speciation

The method developed by Tessier *et al*., (1979) and Stone and Droppo (1996) were used to determined the physico-chemistry for each metal in the sediment as follows:

Exchangeable Metal- 1g of sediment samples was weighed and transferred into 250ml conical flask. The sample was extracted with 10ml of 1M NaOAC, adjusted to pH 8.2 with acetic acid and shaken for 2 hours using a mechanical shaker. It was filtered using Whatman No. 1 and the filtrate analyzed for metals.

Carbonate Bound Metals- the residue from exchangeable metal was leached three successive times with 10ml NaOAC adjusted to pH 5.0 with acetic acid and shaken for 30 minutes. This was also filtered using Whatman No.1 and the filtrate analyzed.

Mn-oxide bound metals- the residue from carbonate bound metal was leached with 10ml 0.1M NH_2OH, 0.01M HNO_3 adjusted to pH 2.0 with acetic acid and shaken for 3 hours. It was filtered using Whatman No.1.

Fe-Mn oxide metals-the residue from Mn-oxide bound metals extract was extracted with 10ml oxalate buffer [90.02M $(NH_4)_2$ C_2O_4, 0.02M H_2 C_2 O_4 pH_3] and was shaken for 12 hours at 90^oC in a water bath. This was filtered using Whatman No. 1.

Organic matter and sulfides bound metals- the residue from Fe-Mn oxide bound metals extract was extracted with 10ml 30% H_2O_2 adjusted to pH 2.0 with HNO_3 and then extracted with 1M NH_4OAC adjusted to pH 2.0 with HNO_3 at room temperature. The metals in the filtrate were determined.

Residual metal-the residue from organic matter and sulfides bound metals extract was digested with 10ml aqua-regia (3:1 HCl: HNO3).

Metal in fractions were determined using Buck Scientific Model GP210 Atomic Absorption Spectrophometer (AAS) GP210.

RESULTS AND DISCUSSION

The results of the total metal concentrations in Gubi dam sediments are shown in Figure 2. The result indicates that Tatimari site has the highest concentrations of Fe (2.26mgL^{-1}), Zn (0.53 mgL^{-1}) and Mn (0.50 mgL^{-1}). These concentrations could be as a result of sewage and other discharges of waste from the city which agreed with the work of Costal *et al*., (1991). The spillway is intensively farmed, thus justifying the relatively high concentration of Cr and Cd. This may be as a result of excessive washing away of inorganic fertilizer and herbicides by rain into the dam. The result of speciation of chemical fractions of heavy metals in Gubi dam sediments is shown in Table 1. The higher concentrations of iron and zinc and the low concentrations of chromium and nickel in most of the sediments show the changes in the metal content of the sediments with distance, thus suggesting that changes in the environment of deposition do occur along the dam. Consequently, this would result in metal accumulation in the sediment indicating the existence of localized metal pollution that is above the permissible concentration level recommended by the World Health Organization (WHO, 1984). These metals can be release by various processes of remobilization which give rise to the various forms of the metals in water, suspended matter and sediment.

The assessment of the extent of pollution in the dam may require the knowledge of the concentration of the various metal species in sediments. For representation of the dam, sediments at the tributaries, entry to the dam, and spillway were analyzed. The chemical forms of the heavy metals indicate the extent of their bioavailability and toxicity (Hart, 1982; Zhang, 1978). The higher the biologically active forms, the more polluted the water. The forms of each heavy metal in sediments taken from the dam (Fig.1) is shown in Table1. Highest percentages of Cu (31.42%) and Cd (62.39%) are associated with the exchangeable fractions while Zn (24.73%), Mn (32.73%), Co (48.02%) and Ni (32.92%) are associated with the carbonate fractions. These forms indicate that Cu, Cd, Zn, Mn, Co and Ni are in potentially available forms and may likely pose a serious problem to the ecosystem in the dam. This is because these fractions can be solubilized, and the metals become more available to broken in the dam. Despite the low levels of these metals (Fig.2), long residence time of the solubilized form can be threatening. The highest amount of Fe (23.71%) is associated with the organic and sulfide, and the mineral matrix of the sediment. Similarly, highest Cu (93.75%) is associated with the organic and sulfide pb (37.78%) is associated with the mineral matrix of the sediment. With the

Fe, Cr and Pb primarily associated with the mineral matrix, it is most unlikely these forms would become biologically available.

CONCLUSION

Heavy metals in Gubi dam occur in low concentrations. However, Cu, Cd, Zn, Mn, Co and Ni are in biologically active forms and may be of threat to the ecosystem. Nevertheless, it does not suggest serious pollution. Fe, Cr and Pb pose no threat to the living organisms in the water since they occur in non-potentially active forms.

Fig 1 The map of Bauchi showing Gubi Dam and Sampling Sites

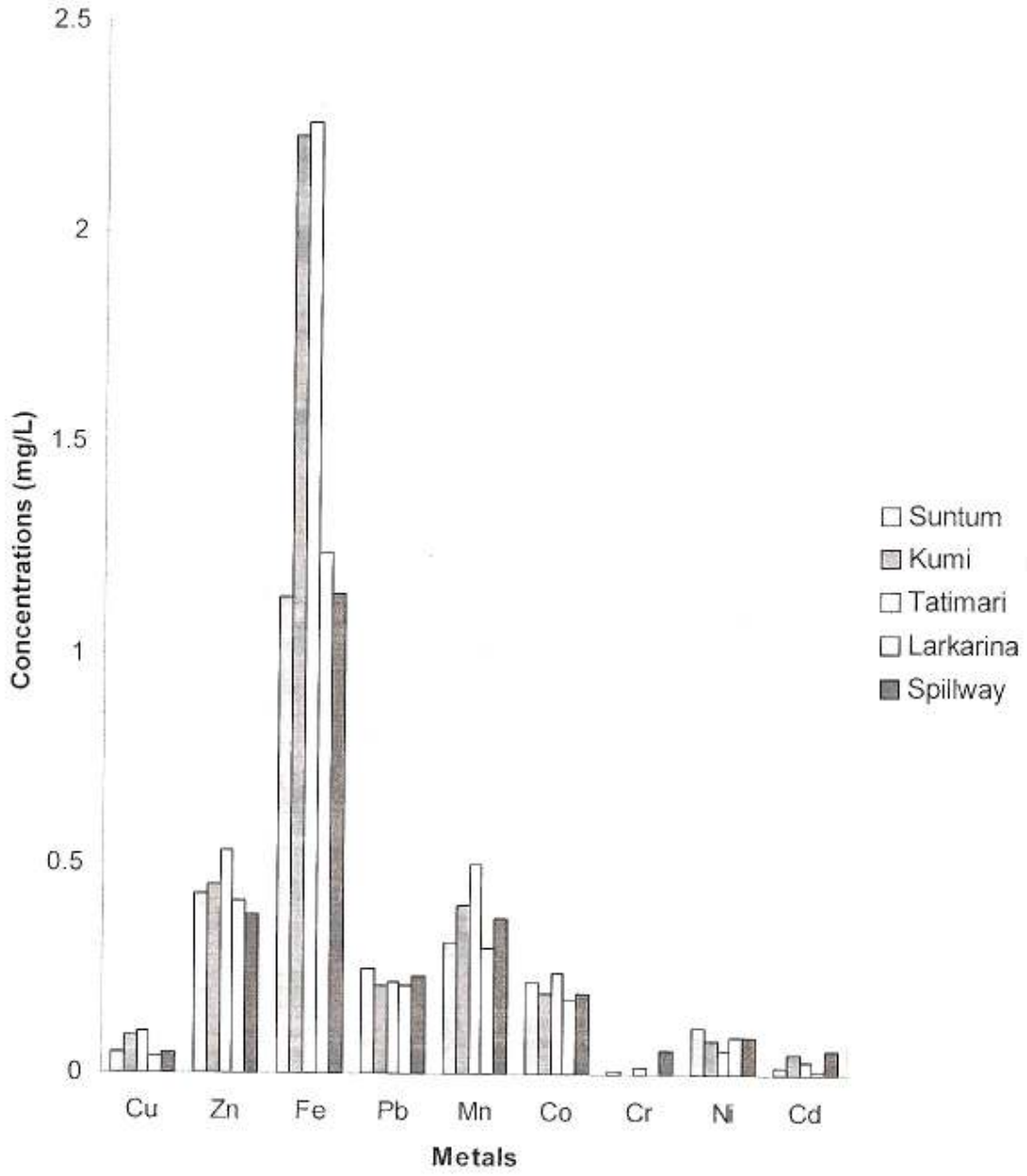

Fig.2 Mean Total Metal Concentrations (mg/L)

TABLE 1: Speciation of Chemical Fraction of Heavy Metals in Gubi Dam Sediments (mgL^{-1})

	Cu	Zn	Fe	Pb	Mn	Co	Cr	Ni	Cd
Exchangeable	0.33± 0.24 (31.42%)	0.77± 0.18 (21.15%)	1.22± 0.15 (12.31%)	0.44± 0.99 (24.44%)	0.68± 0.35 (20.61%)	0.48± 0.26 (14.59%)	0.004± 0.01 (4.17%)	0.23± 0.05 (28.05%)	2.14± 0.81 (62.39)
Carbonate	0.19± 0.10 (18.10%)	0.90± 0.10 (24.73%)	1.63± 0.33 (16.45%)	0.49± 0.03 (27.22%)	1.08± 0.23 (32.73%)	1.58± 0.32 (48.02%)	0.0± 0.00 (0.00%)	0.27± 0.03 (32.92%)	0.49± 0.02 (14.28%)
Mn-oxide	0.23± 0.01 (21.90%) (14.28%)	0.22± 0.06 (6.04%)	0.98± 0.34 (9.89%)	0.02± 0.02 (1.11%)	0.50± 0.51 (15.15%)	0.32± 0.00 (9.73%)	0.0± 0.27 (0.00%)	0.03± 0.49 (3.66%)	0.49± 0.02
Fe-Mn oxide	0.08± 0.02 (7.62%)	0.27± 0.11 (7.42%)	1.38± 0.076 (13.93%)	0.07± 0.04 (3.89%)	0.22± 0.22 (6.67%)	0.33± 0.02 (10.03%)	0.0± 0.00 (.0.00%)	0.02± 0.01 (2.44%)	0.25± 0.01 (7.29%)
Organic matter and sulfide	0.11± 0.42 (10.48%)	0.74± 0.08 (20.33%)	2.35± 1.00 (23.71%)	0.10± 0.31 (5.56%)	0.02± 0.28 (0.60%)	0.02± 0.54 (0.61%)	0.09± 0.01 (93.75%)	0.01± 0.20 (1.22%)	0.01± 0.02 (0.29%)
Residual	0.11± 0.04 (10.48%)	0.74± 0.08 (20.33%)	2.35± 0.81 (23.71%)	0.68± 0.11 (37.78%)	0.80± 0.07 (24.24%)	0.56± 0.11 (17.02%)	0.002± 0.004 (2.08%)	0.26± 0.08 (31.71%)	0.05± 0.006 (1.46%)

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