

FULL LENGTH RESEARCH ARTICLE**EFFECTS OF pH AND TOTAL ORGANIC CARBON (TOC) ON THE DISTRIBUTION OF TRACE METALS IN KUBANNI DAM SEDIMENTS, ZARIA, NIGERIA***TUKURA, B. W.¹, KAGBU, J. A.² & GIMBA, C. E.^{2,3}¹Department of Chemistry
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tukurabitrus@yahoo.com**ABSTRACT**

The determination of Cd, Cr, Cu, Pb and Zn in the exchangeable, carbonate, Fe-Mn-oxides, organic matter and residual sediment chemical fractions of Kubanni Dam during dry and raining seasons was carried out using the spectrophotometric method after Tessiers' sequential scheme for speciation had been carried out. The pH and Total Organic Carbon (TOC) of the sediment samples were also determined to study their effects on the distribution of metals. The results indicate that pH influenced the release or adsorption of each metal in the different sediment fractions. At low average pH of 5.21 recorded during dry season, desorption of metals from the reducible sediment fraction into the water column occurred, which may have effect on aquatic organisms. Due to increased metal complexation at high pH, total extractable fractions of metals generally increased. Higher TOC levels during the rainy season indicated larger adsorption surfaces for Cr (19.92%) Pb (19.97%) and Zn (21.14%) on the organic matter fraction, which, under oxidizing condition, these metals may be remobilized into the aquatic environment. Cu correlated positively with the organic carbon content of the sediment samples. The positive correlation of Pb, Cd and Cr with sediment pH may reflect the tendency of cation adsorption to increase at high pH.

Key words: pH, TOC, Trace metals, Distribution, Sediments**INTRODUCTION**

Sediments are components of our environment that serve as repositories for deleterious chemical species (Korchayan *et al.* 2003) because of anthropogenic wastes discharged into water bodies (Jain 2004). Consequently, trace metals are frequently detected in water environment and have gradually become a major concern world-wide.

The bioavailability and toxicity of trace metals can be ascertained (Rate *et al.* 2000, Ackay *et al.* 2003) in the different sediment phases as exchangeable, carbonate (acid soluble), Fe-Mn oxides (reducible), organic matter bound (oxidizable), and residual bound species. The metals present in the inert fraction can be taken as a measure of contribution of natural sources (Kuang-chung *et al.* 2001) while the Fe-Mn oxides and the organic matter fractions have a scavenging effect and may provide a site for trace metals accumulation (Gutieres 2000).

Active remobilization of trace metals occurs through a series of post sedimentation processes that is abiotic, which may include diffusion, sorption and desorption, complexing, ion-exchange and dissolution or biotic (biodestruction and bioaccumulation (Korchayan *et al.* 2003). The relative importance of any solid phase for retaining a metal depends on the identity, concentration of the metal and the abundance of the solid phase (Gutieres 2000, Ackay *et al.* 2003). The solubility of the metal is principally controlled by pH, concentration, type of ligands, chelating agent, oxidation state of mineral component and the redox potential of the system (Gonzalez *et al.* 2000; Kuang-chung *et al.* 2001), with TOC enhancing metal adsorption to sediment phases.

The pH of sediment and the interstitial water affects metal retention by developing a pH-dependent charge at a weak acidic surface and determines the extent of ion-exchange reactions (Gundersen & Elime 2002). Similarly, protons and hydroxide ions compete with absorbing cations and anions respectively (Korfali & Davies 2003). A reduction in pH may allow the release of toxic metals that would otherwise be adsorbed to sediment (Mouvet & Borg 1983).

TOC is a measure of organic content in water and sediments (Yun 2003) and contributes significantly to the acidity of natural water and sediments through organic acids and biological activities due to the adsorption of light and water chemistry through the complexation of metals (Zoumis *et al.* 2001). Lopez-Sanchez *et al.* 1996 observed that both anthropogenic and natural processes have resulted in elevated concentrations of organic carbon in sediments. Sediment carbon increases with decreasing grain size because organic matter adsorbs onto mineral surfaces and have high affinity for fine grained sediments. High TOC levels, thus, entails larger adsorption surfaces and more metals are adsorbed to organic material (Nelson & Sommer 1982).

The Kubanni Dam was constructed in the early 1980s to supplement the water supply to Ahmadu Bello University community in Samaru, Zaria, Nigeria. Over time, the activities of man have resulted in the discharge of wastes into the dam. Despite the importance of the dam to the university community, no systematic study has been carried out on the effects of pH and TOC on the distribution of metal fractionation in sediments. This paper reports on the effects of pH and TOC on the distribution of extractable fraction of Cd, Cr, Cu, Pb, and Zn in bed sediments of Kubanni Dam.

MATERIALS AND METHODS

Study area: The Kubanni dam (Figure 1) is a fresh water dam constructed across Kubanni River within latitudes 11° 6' N - 11° N and longitudes 7°30' E - 7°40' E with a total catchment area of 57km²

Sample collection: Sediments samples were collected during the rain and dry seasons from the shallow water near the bank of Kubanni dam at five different points, as indicated in figure 1

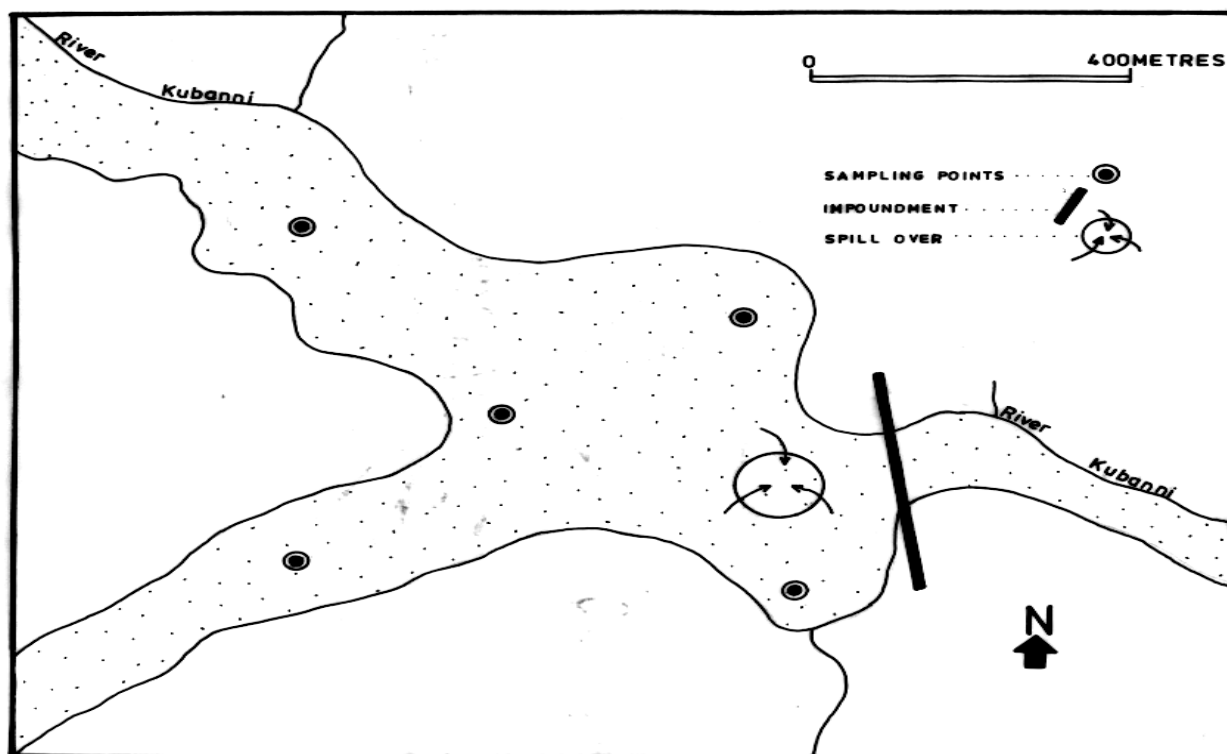


FIG. 1. KUBANNI DAM SHOWING SAMPLING POINTS

The samples were collected into decontaminated polythene bags using plastic scoops. The upper parts of the sediments were dried in an oven at 55°C for two days. In order to normalize the variation in grain size distribution, the dried sediments were ground in a porcelain mortar with a pestle and sieved to particle size of 150µm for analysis.

Determination of Ph: 5g of the air-dried sediments were weighed using an analytical balance and 25cm³ of distilled water added and agitated for 5 min and the solution left undisturbed for 1hr. The pH was determined using a digital pH meter (HI, 99100) by inserting the electrode in each of the sample solutions after the calibration of the pH meter.

Analysis of Total Organic Carbon (TOC): TOC in sediment samples were determined by wet oxidation-reduction titration method using acid dichromate and ferrous ammonium sulphate solutions (APHA 1998).

Metal Distribution: Direct determination of specific trace metal association is difficult due to great variety of solid phases that can bind trace metals and their amorphous character. The partitioning of trace metals were determined by sequential extraction method (Tessier *et al.* 1979) most often utilized for this kind of analysis to determine the following:

Exchangeable (FI): 1.0g sediment sample was extracted at room temperature for 1 hr with 16cm³ of 1.0mol dm⁻³ NaOAc (pH 8.2) with continuous agitation.

Bound to Carbonate (FII): The residue from (I) above was leached at room temperature with 16cm³ of 1.0 mol dm⁻³ NaOAc adjusted to pH 5.0 with acetic acid. The mixture was agitated for 1 hr.

Bound to Fe-Mn oxides (FIII): The residue from fraction (2) above was leached with 25cm³ of 0.1 mol dm⁻³ NH₂OH.HCl dissolved in 25%(v/v) HOAc for 2hrs at 96±3°C with constant agitation.

Bound to Organic Matter (FIV): To the residue obtained from fraction (3), 6cm³ of 0.02mol.dm⁻³ HNO₃ acid and 10cm³ of 30% H₂O₂, adjusted to pH 2.0 with nitric acid was added with continuous agitation for 2hr. A 6cm³ quantity of 30% H₂O₂ at pH 2.0 was further added and heated at 85 ± 2°C for 3hr and cooled.

A 10cm³ quantity of NH₄OAc in 20%(v/v) HOAc was added and the mixture diluted to 20cm³ and agitated continuously for 30 min.

Residual Metals (FV): Residue from fraction (4) above was digested with an acid mixture in the ratio 4:1:1:1 of HNO₃: HF: HClO₄: HCl for 3hr. The solution was diluted to 100cm³ with distilled water.

The selective extractions were conducted in centrifuge tubes to minimize losses of material. Between each successive extraction, separation was effected by centrifuging at 5000 rpm for 1hr. The supernatant liquid was decanted and analysed for trace metals whereas the residue was washed with 8cm³ of distilled de-ionized water. After centrifuging for 1hr, this second portion of supernatant liquid was discarded.

Metal analysis: Metal concentrations in the different sediments were determined using a Pye-Unicam 960 Atomic Absorption Spectrophotometer. The absorption measured is proportional to the concentration of the metal ion. Possible matrix effects were corrected by the standard addition method. All samples were analyzed in triplicates.

RESULTS

pH of sediments varied during the sampling periods (Table 1). Maximum pH 5.49 was observed at site 1 and the lowest at site 2 during the rainy and dry season respectively.

The highest TOC content (30.40mg kg⁻¹) was recorded in site 1 during rain season, and the lowest (800 mgkg⁻¹) at site 4 in dry season. The levels of total extractable metals over the 5 sampling points during the dry season follow the order in Table 3: Cd: residual > organic matter > exchangeable > carbonate ≈ Fe-Mn oxides; Cr: residueal > organic matter > Fe-Mn-oxides ≈ Carbonate > exchangeable; Cu: residual> carbonate ≈ Fe-Mn oxidws > exchangeable > organic matter; Pb: Fe-Mn oxides > carbonate > organic matter > residual > organic matter > exchangeable; Zn:Fe-Mn oxides ≈ residual > organic matter > carbonate > exchangeable, while for the rain season, it followed the order in Table 4: Cd: residual > Fe-Mn oxides > organic matter > exchangeable > carbonate; Cr: carbonate > exchangeable > organic matter ≈ residual > Fe Mn oxides; Cu: residual > carbonate ≈ Fe-Mn oxides > exchangeables > carbonate; Pb:Fe-Mn oxide > carbonate > organic matter > residual > exchangeable; Fe-Mn oxides ≈ residual > organic matter > carbonate > exchangeable.

Statistical analysis showed that all metals except Cu and Zn correlated positively with pH during the dry season (Table 5). In the rain season (Table 6), Cr and Cu showed a negative correlation with pH.

TABLE 1: SEASONAL VARIATION IN pH ACCORDING TO SAMPLING POINTS IN KUBANNI DAM SEDIMENTS.

Sampling Points (S)						
Season	S1	S2	S3	S4	S5	Average
Dry	5.19	5.02	5.40	5.16	5.26	5.21±0.12
Rainy	5.49	5.39	5.08	5.63	5.29	5.38±0.19

TABLE 2: DISTRIBUTION OF TOTAL ORGANIC CARBON (TOC) IN KUBANNI DAM SEDIMENTS.

Sampling Points (s)						
Season	S1	S2	S3	S4	S5	Average
Dry (mg/kg)	9.60	8.80	9.20	8.00	7.60	8.58±0.74
Rainy (mg/kg)	30.40	31.20	29.20	24.80	29.60	29.04±2.23

TABLE 3: PERCENT AND RANGE OF TOTAL EXTRACTABLE METALS IN SEDIMENT FRACTIONS (MG/KG-DRY WEIGHT) ACROSS 5 SAMPLING POINTS DURING DRY SEASON.

Fraction	Element									
	Cd		Cr		Cu		Pb		Zn	
(F)	Range	%	Range	%	Range	%	Range	%	Range	%
FI	3-18	19.44	0.37-2.25	7.41	0.08-1.41	31.81	2.01-2.64	18.35	0.03-1.09	6.14
FII	3-19	16.67	0.37-2.36	14.82	0.00-1.12	23.83	1.90-4.00	21.97	0.70-3.39	33.24
FIII	1-19	16.67	0.57-2.35	14.58	0.02-0.35	16.06	2.09-3.73	23.17	1.13-3.48	34.22
FIV	2-19	22.22	0.33-2.87	15.25	0.23-0.62	25.00	1.70-2.60	14.87	0.41-1.73	18.80
FV	3-19	25.00	0.41-8.53	47.94	0.01-0.08	3.30	1.81-3.90	21.63	0.29-0.63	7.60

TABLE 4: PERCENT AND RANGE OF TOTAL EXTRACTABLE METALS IN SEDIMENT FRACTIONS (MG/KG-DRY WEIGHT) ACROSS 5 SAMPLING POINTS DURING THE RAINY SEASON

Fraction (F)	Element									
	Cd		Cr		Cu		Pb		Zn	
	Range	%	Range	%	Range	%	Range	%	Range	%
FI	0.011-0.018	16.28	0.85-1.17	20.48	0.73-1.16	14.19	0.48-1.13	8.22	1.37-2.51	13.87
FII	0.003-0.021	13.95	0.36-2.50	23.83	1.74-1.50	19.69	1.47-2.85	24.22	1.20-3.64	18.20
FIII	0.014-0.028	23.26	0.34-1.22	16.33	0.94-1.54	19.18	1.64-3.71	31.79	0.70-3.70	23.09
FIV	0.007-0.027	19.77	0.20-1.66	19.94	0.70-1.44	13.91	0.79-3.08	19.97	1.91-2.97	21.74
FV	0.014-0.032	26.74	0.44-1.38	19.42	1.64-2.45	33.03	0.47-2.60	15.80	1.93-2.59	23.00

TABLE 5: PEARSON CORRELATION MATRIX OF TOTAL MEAN TRACE METALS WITH PH AND TOC IN SEDIMENTS DURING DRY SEASON

	Cd	Cr	Cu	Pb	Zn	pH	TOC
Cd	1	-0.783	-0.403	**0.831	0.009	0.098	-0.914
Cr		1	0.505	-0.811	0.321	0.197	*0.603
Cu			1	-0.718	**0.799	-0.676	0.078
Pb				1	-0.531	0.275	-0.700
Zn					1	-0.422	-0.208
pH						1	0.080
TOC							1

* Significantly related at 0.05

** Significantly related at 0.05 and 0.01

Critical value r ($P \leq 0.05$) at 9 degree of freedom = 0.602.

TABLE 6: PEARSON CORRELATION MATRIX OF TOTAL MEAN TRACE METALS WITH PH AND TOC IN SEDIMENTS DURING RAINY SEASON

	Cd	Cr	Cu	Pb	Zn	pH	TOC
Cd	1	-0.364	0.123	-0.045	0.207	0.117	-0.847
Cr		1	**0.854	-0.626	0.238	-0.841	0.522
Cu			1	0.383	0.211	-0.908	0.225
Pb				1	-0.658	0.434	-0.219
Zn					1	-0.183	-0.348
pH						1	-0.477
TOC							1

* Significantly related at 0.05

** Significantly related at 0.05 and 0.01

Critical value r ($P \leq 0.05$) at 9 degree of freedom = 0.602.

DISCUSSIONS

The pH values indicated acidic nature of the sediments during the periods of analysis. TOC levels (Table 2) increased during the rainy season due to high discharge of wastes with high contents of organic matter. Higher TOC content mean large adsorptive surfaces and thus, more metal adsorption to sediment.

pH variation in sediments influences the release or adsorption of each metal into sediment fraction. High pH lowers desorption of metals and possesses high buffering capacity against acidic conditions that may be created as a result of wastes accumulation. Association of metals with the carbonate, Fe-Mn-Oxides and organic fraction are affected by pH variations (Ikem *et al.* 2003). Cd, Cu and Zn are mostly bound to carbonate and Fe-Mn oxides fraction. Low pH is known to influence the sorption of Pb by organic fraction in sediments. Total extractable fraction of the metals studied generally increased during rainy season with a relatively higher average pH 5.38 due to increase in metals complexation and also increase in TOC contents. Under oxidizing conditions, metals present in both natural organic matter (due to complexation and peptization) and living organisms (as a result of bioaccumulation) may be remobilized into aquatic environment (Calmono *at al.*1993). Association with organic fraction is most probably affected by variations in TOC content. The concentration of Cr, Pb and Zn in the organic fraction was higher during rainy season with corresponding increase in TOC content. The levels of Cd and Cu in the organic matter fraction in rainy season was low despite of high TOC contents. Factors other than TOC level may explain the irregularity. Changes in TOC level seems to be responsible for shifting the pH to higher value.

The positive association of metals with sediment pH may reflect the tendency of cation adsorption to increase at high pH. Cr correlated with TOC during the dry season, while during rainy season, Cu and Cr correlated positively with TOC. Positive correlation with TOC implies that increase in TOC content may lead to increase in adsorption capacity of the organic fraction. The positive correlation of Cu concentration was expected on the basis of known strong complexation between copper and natural organic fraction (Mouvet *et al.* 1983).

In conclusion, the results revealed average pH values of 5.21 and 5.38 during dry and rain seasons respectively, reflecting the acidic nature of the sediments during the seasons. The average TOC level increased from dry season (8.58mgkg⁻¹) to rainy season (29.04mgkg⁻¹). Distribution of metals in sediment fractions at relatively low pH in dry season led to remobilization of Cd, Cr and Pb from the carbonate, Fe-Mn-oxides and organic fractions, as the levels of these metals decreased during the period. Association of Cr, Pb and Zn to the organic fraction increased during rainy season owing to increase in organic carbon content from plant, animal and domestic wastes discharged into the Kubanni Dam. Generally, the positive correlation of metals with pH reflects the tendency of metals immobilization at high pH. Changes in TOC concentration cause a shift in pH unit to some percentage changes in metal adsorption in sediment fractions. Irregularity observed in metals distribution in fraction suggests that parameters other than pH and TOC may also influence the metal speciation. Both pH and TOC appear to influence or co-vary with all metals.

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