

Distribution and Concentration of Trace Elements in Kubanni Reservoir in Northern Nigeria

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Abstract: The distribution and concentration of trace elements in Kubanni Reservoir in Zaria (7°38' and 11°11') were investigated between November 2002 and April 2004 using Atomic Absorption Spectrophotometer (AAS). The trace elements detected in the water were Magnesium, Calcium, Iron, Manganese, Zinc, Chromium, Cobalt, Nickel, Copper, Cadmium and lead. Mean monthly concentrations of trace elements that ranged from 0.021-1.00mg/L were Cd, Cu, Cr, Zn and Mn. While trace elements that ranged from 1.22-2.36mg/L were Pb, Ni, Co and Fe. Elements like Zn, Cu, Ni and Pb had higher concentrations in the dry season than the rainy season. ANOVA showed that there were significant variations between the months, stations, seasons, months versus stations and seasons versus stations. On the other hand, the concentrations of Fe, Mn and Cr were significantly higher in the rainy season than the dry season. Water temperature showed high significant positive correlation with Fe, Mn, Cr, Co and Pb ($P < 0.01$). Furthermore, water temperature showed significant negative correlation with Zn and Ni ($P < 0.01$). A note worthy observation was the fact that seven (Fe, Mn, Cr, Co, Ni, Cu and Pb) out the nine trace elements determined exceeded maximum permissible concentration for drinking water.

Key words: Concentration, drinking water, heavy metals, Kubanni Reservoir and Nigeria

INTRODUCTION

Trace elements constitute a natural component of the earth crust. They are not biodegradable, hence persist in the environment. Trace elements may come from natural sources, leached from rocks and soils according to their geochemical mobility or come from anthropogenic sources, as the result of human land occupation and industrial pollution. Depending on their solubility, these metals may eventually become associated with suspended particulate matter and/or accumulate in the bottom sediments. The increase of industrial activities has intensified environmental pollution problems and the deterioration of several aquatic ecosystems with the accumulation of metals in biota and flora. Although trace metals at low concentrations are essential to life, at high concentrations, may become hazardous. Trace elements are dangerous because they tend to bio-accumulate resulting in heavy metal poisoning. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain.

Many trace metals are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into food chains. The chemical behavior of these elements in water (i.e. speciation) and accompanying transformations

in sediments e.g. through methylations, Mercury (Hg) and Tin (Sn) result in even more toxic forms. Sediments and water provide pathways for trace metals. Metals may become bio-available to aquatic organisms, after deposition and translocation from various diffuse and point sources apart from geological sources (Mwanburi and Oloo, 1996/97). Various metals from industrial, agricultural, domestic and urban wastes may enter river and lake waters through leaching, runoff, effluents and dry deposition (Biney *et al.*, 1991; Okoye *et al.*, 1991).

Kubanni River which empties into Kubanni Reservoir is known to play a major role in the disposal of industrial wastes accumulated from industries cited in Zaria and irrigation of farms. There is a great concern that trace elements contained in the wastes may end up being accumulated in plants and animals (including fish) which calls for a comprehensive trace elements investigation of the water to add to the baseline data of the trace elements in the water. This research was borne out of a need to establish a good surveillance data for elemental parameters for Kubanni Reservoir and its effluents in order to protect the resident aquatic organisms. The findings of this research will serve as a prelude to the comprehensive analytical data that might later be forwarded to the newly constituted Federal Environmental Protection Agency (FEPA) which will form a part of the extensive data bank for the evaluation and monitoring of pollution sources in the country – a task to which FEPA has been assigned (FEPA, 1991).

The importance of Kubanni Reservoir to the residents of Ahmadu Bello University, Zaria and Environs cannot be over emphasized. Apart from being the source of potable water to some communities, Ahmadu Bello University and Samaru Village in particular, a lot of vegetables and farm produce being consumed in Zaria and beyond are grown along the banks and tributaries of this Reservoir. In return, Kubanni Reservoir receives polluted discharges from urban, agricultural and industrial point and non-point sources of pollution. The objective of the present study was therefore to determine the speciation and concentrations of Trace elements in water of the Reservoir.

MATERIALS AND METHODS

Study area: Zaria, is situated in the Northern Guinea Savanna zone. The climate condition is a tropical continental with distinct wet and dry seasons. The rainy season is between May to October. Zaria has a settlement pattern which consists of Island of cultivation surrounded by woodland which is being transferred into a sea of cultivation with residual island of bush, on shallow laterite rocks and in gullies. Kubanni lake, also called Ahmadu Bello University reservoir supplies water to the University community and environs. The reservoir has a catchment area of 57Km² with a width of 122 meters (400 feet) and the mean depth of 6 meters. The lake lies approximately within latitude 11°11'N and longitude 7°38'E in Samaru, Zaria. It is located within the premises of Ahmadu Bello University, main campus. The lake's two major tributaries are the Kampagi and Samaru stream. Kampagi stream, which originates from a rural settlement, has a seasonal flow whereas Samaru stream that originates from a semi-urban settlement has an all-year-round flow due to its sustenance by urban runoffs and seepages.

Sampling stations: Five fixed sampling stations were selected and marked along the Kubanni Reservoir within an approximately 600 meters section and about 100 to 200m distance between locations.

Station 1 is located close to Institute of Development Research (IDR) which takes care of agricultural, domestic and other wastes from the university. It is the point where Kubanni River enters the reservoir.

Station 2 is half way between the point where Kubanni River and Kampagi stream join the reservoir. Takes care of agricultural, chemicals and other wastes from the adjacent farmland.

Station 3 is just below the point where Kampagi stream enters the reservoir.

Station 4 is located at the southern end point of ABU reservoir. Takes care of the wastes from the adjacent farmland settlements.

Station 5 was chosen along same axis occupied by Center for Energy Research and Training (CERT). It is a point along the Kubanni River just before the entry point of sewage (from the treatment plant of the Ahmadu Bello University) into the Kubanni river.

Sampling duration: Sampling was done on a bimonthly basis from November 2002 to April 2004. Water samples were collected about the middle of the Kubanni reservoir from all stations between 9.00am and 4.00pm. A small sailing boat with a fisherman and a technician were employed throughout the sampling period especially during the rainy season when water levels were high. During the dry season sampling period, one walked to the sampling point without the aid of a boat. Surface water samples from each station were collected from about 0.2-0.5m below the surface of the water and stored in a pretreated two (2) litre plastic (polyethylene) bottle (Lind, 1979; APHA, 1998), 20 to 30 meters away from the shore.

Physicochemical analysis of water samples: At each sampling station, Temperature (°C), pH, Electrical conductivity and Total Dissolved Solids were determined in situ using Hannah Portable Meter model HI991300.

Elemental analysis of water samples: Water samples were analysed using Atomic Absorption Spectrophotometer (AAS). The use of AAS because it has advantage over flame photometry and colorimetry methods due to its high sensitivity, detection limit, degree of accuracy and reproducibility with the ease of sample preparation and handling (Allen *et al.*, 1974). From each 2 litre plastic water sampled, 150ml of water was taken, this was preserved by adding 1.0ml conc. HNO₃ pooled and then stored in a refrigerator to stabilize the metals for up to 2 weeks. From the pool 100 ml water sample was filtered and concentrated to about 60ml in 100ml standard flask to which 5.0ml HNO₃ was added. This was made up to 100ml mark with deionized water followed by elemental analysis with Unicom 969 Atomic Absorption Spectrophotometer (AAS) using 1% HNO₃ as blank. The metal concentration was read off from a standard curve.

$$\text{Metal concentration, mg/l} = A \times B/C$$

Where

A = Concentration of metal in digested solution (mg/l)

B = Final volume of digested solution (ml)

C = Sample size

The use of AAS was based on Beer-Lambert's law:

$$\text{Log } I_0/I_t = (abc) \quad (1)$$

Where:

I₀ = Intensity of incident light

I_t = Intensity of transmitted light

a = Molar absorptivity

b = Thickness of medium

c = Concentration

Thus, the concentration and the logarithmic of the transmittance are proportional.

The procedures employed are as indicated in the AAS manufacturer's manual.

Statistical analysis: Analysis of variance was used to test for the difference between observed mean concentrations of metals between months, stations and seasons. Least Significant Difference (LSD) was the post hoc test used to separate significantly different means.

RESULTS

Among the Trace elements recorded, Fe had the highest concentration with a mean monthly concentration of 2.36 ± 0.16 mg/L. The highest concentration of Fe was in the rainy season (3.93 mg/L) than the dry season (0.80 mg/L). Generally, Fe concentration of the stations ranged from 2.13 mg/L (station 5) to 2.45 mg/L (station 4) (Table 1). All elements except Cd significantly differed in their concentrations from month to month throughout the study period (Table 2). Mean monthly concentrations of trace elements that ranged from 0.021-1.00 mg/L were Cd, Cu, Cr, Zn and Mn. While trace elements that ranged from 1.22-2.36 mg/L were Pb, Ni, Co and Fe. Elements like Zn, Cu, Ni and Pb had higher concentrations in the dry season than the rainy season. These trace elements with significantly higher concentrations in the dry season had a concentration range from 0.08-2.61 mg/L. On the other hand, the concentrations of Fe, Mn and Cr were significantly higher in the rainy season than the dry season. In this case the concentrations ranged from 0.07 to 3.93 mg/L. The only trace elements that showed no significant difference between seasons were Co and Cd. A very interesting observation was in Station 4 where five (Fe, Mn, Cr, Co and Cu) of the Nine trace elements recorded in this study had the highest concentrations. Zn had the highest concentration (0.51 mg/L) in station 1 and the least (0.37 mg/L) in station 4. For Ni, the highest concentration was in station 5 (1.80 mg/L) while the least (1.47 mg/L) in station 1. In addition, the highest level (0.041 mg/L) of Cd was recorded in station 3 and the lowest concentration (0.007 mg/L) was in station 5. The least concentration of Pb was 1.15 mg/L in station 4 while the highest concentration was 1.26 in station 2. A note worthy observation was the fact that seven (Fe, Mn, Cr, Co, Ni, Cu and Pb) out of the nine trace elements determined exceeded USEPA (2002) maximum permissible concentration for drinking water. Significant interactions between months and stations were observed in all the trace elements except Mn and Cd. Contrary to what was observed in the case of month-station interaction, season-station interaction showed that only Co had a significant interaction between season and station while the other elements showed no significant interaction.

Mean monthly water temperature was 24.97 ± 0.29 °C (Table 3). Water temperature showed significant seasonal difference with higher values in the rainy season (mean = 28.48 °C) than the dry season (mean = 23.21 °C). pH ranged was circumneutral between seasons in the reservoir with no significant difference between the dry

and rainy seasons. Station 5 had the highest mean pH of 7.76 while station 2 had the lowest (7.19) recorded pH. Total Dissolved Solids (TDS) was not significantly different between seasons. Mean monthly TDS was 34.42 mg/L with the highest value (39.39 mg/L) recorded in station 1 while the minimum (28.03 mg/L) was in station 4. Generally, electrical conductivity was low throughout the study period. The maximum observed value (212 μ S/cm) for EC was in the station 1. Mean monthly EC was 69.2 ± 1.72 μ S/cm for all stations. Seasonally, EC differed significantly with higher value (71.02 μ S/cm) in the dry season than the rainy season (65.57 μ S/cm). TDS and EC showed significant interactions for month-station and month-season interactions in this study. Water temperature showed high significant positive correlation with Fe, Mn, Cr, Co and Pb ($P < 0.01$). Furthermore, water temperature showed significant negative correlation with Zn and Ni ($P < 0.01$) (Table 4). Significant negative correlation was observed between pH with Fe, Mn and Pb. In addition, TDS had significant negative correlation with the concentration of Cr.

DISCUSSION

Mg, Ca, Fe, Mn, Zn, Cr, Co, Ni, Cu, Cd, Pb and Cl were the Trace elements detected in the water from the reservoir. There were variations in the concentrations of these metals from the various stations and from season to season. Their sources may be attributed to the nature of the catchment area, industrial waste discharges, municipal or domestic wastes, urban storm-water runoffs such as batteries and other electrical, agricultural wastes (fertilizers), groundwater leaching including leaching of metals from garbage and solid waste dump and geological weathering of parent rocks, metal inputs from rural areas (metals contained in pesticides and herbicides) and atmospheric sources (which include burning of fuels). Abernathy *et al.* (1984), Ajao and Fagade (1990) and Okoye *et al.* (1991) reported anthropogenic heavy metal enrichment of the Lagos lagoon with Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn and implicated land-based urban and industrial waste sources. All the stations examined had similar underlying rocks. Thus, low concentrations that were obtained for various metals may be attributed to domestic and agricultural effluents.

Fe and Mn, among the minor elements detected, concentrations followed almost the same pattern. The concentrations of both metals increased gradually from November to August (forming a plateau). The presence of influx of erosion and soil wash from catchments added to their concentrations until July or August when dilution from the rain greatly reduced their concentrations. Oniye *et al.* (2002) in their work on Zaria dam, Nigeria reported higher concentrations of Fe in the rainy season sampling period. So also, Mwanburi and Oloo (1996/97) in their investigation on concentration levels of trace metals in water and sediments of Lake Victoria, Kenya obtained higher concentrations of Fe and Mn during the rainy

Table 1: Summary of Trace element distribution and concentrations (mg/l) in water obtained from Kubanni Reservoir, Zaria, Nigeria

Metals	Station 1			Station 2			Station 3			Station 4		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
*Fe	2.44	0.19	8.01	2.40 ^a	0.25	7.63	2.41 ^a	0.15	8.12	2.45 ^a	0.12	8.05
*Mn	0.98 ^a	0.01	1.63	0.95 ^a	0.022	1.61	1.00 ^a	0.00	1.69	0.99 ^a	0.00	1.63
Zn	0.51 ^a	0.001	2.49	0.40 ^{ab}	0.00	1.43	0.42 ^{ab}	0.002	1.19	0.37 ^{ab}	0.00	1.24
*Cr	0.73 ^d	0.06	2.50	0.84 ^c	0.14	2.65	0.78 ^c	0.22	1.97	1.00 ^a	0.35	2.91
*Co	1.15 ^c	0.28	1.92	1.35 ^{ab}	0.34	2.08	1.21 ^{bc}	0.29	2.24	1.33 ^a	0.18	2.04
*Ni	1.47 ^b	0.02	4.63	1.51 ^b	0.12	4.57	1.49 ^b	0.07	4.87	1.76 ^a	0.12	5.20
*Cu	0.74 ^b	0.03	1.75	0.79 ^b	0.00	1.99	0.92 ^b	0.10	2.32	1.03 ^a	0.09	2.31
Cd	0.026 ^a	0.001	0.253	0.02 ^a	0.001	0.035	0.041 ^a	0.00	0.30	0.014 ^a	0.001	0.102
Pb	1.18 ^a	0.18	2.33	1.26 ^a	0.00	2.59	1.26 ^a	0.17	2.66	1.15 ^a	0.39	1.91

Table 1 Continued

Metals	Station 5			Monthly			Seasons	
	Mean	Min	Max	Mean±SE	Min	Max	Dry	Rainy
*Fe	2.13 ^b	0.22	8.62	2.36±0.16	0.00	8.64	0.80 ^b	3.93 ^a
*Mn	1.07 ^a	0.09	1.82	1.00±0.04	0.00	1.83	0.66 ^b	1.32 ^a
Zn	0.18 ^{ab}	0.001	1.41	0.11±0.05	0.00	4.63	0.80 ^a	0.07 ^b
*Cr	0.96 ^b	0.35	2.96	0.86±0.04	0.05	2.99	0.67 ^b	1.05 ^a
*Co	1.27 ^{ab}	0.41	2.16	1.26±0.05	0.06	2.45	1.16 ^a	1.36 ^a
*Ni	1.80 ^a	0.08	4.75	1.61±0.14	0.00	5.37	2.61 ^a	0.41 ^b
*Cu	0.91 ^{ab}	0.09	3.01	0.88±0.05	0.00	3.02	1.12 ^a	0.64 ^b
Cd	0.007 ^a	0.001	0.013	0.021±0.006	0.00	1.00	0.02 ^a	0.02 ^a
Pb	1.22 ^a	0.23	2.23	1.22±0.05	0.00	3.78	1.60 ^a	0.83 ^b

Note: Means with same alphabets along rows are not significantly different at P<0.05, Dry Season Sig. > Wet Season = Mg, Ca, Zn, Cu, Ni and Pb, Rainy Season Sig. > Dry season = Fe, Mn, Cr, Min = Minimum; Max = Maximum, * = Exceed maximum permissible concentration (USEPA, 2002).

Table 2: Mean squares of Analysis of Variance (ANOVA) for Trace elements in water from Kubanni Reservoir, Zaria, Nigeria

Source of Variation	Df	Fe	Mn	Zn	Cr	Co	Ni	Cu	Cd	Pb
Month	11	66.03**	4.13**	4.16**	4.35**	4.45**	60.73**	5.52**	0.006 ^{NS}	4.79**
Station	4	0.25*	0.02 ^{NS}	0.17 ^{NS}	0.34**	0.71**	1.06**	0.41*	0.005 ^{NS}	0.33 ^{NS}
Season	1	391.44**	17.20**	20.91**	5.87**	1.52*	230.90**	9.48**	0.001 ^{NS}	24.05**
Season*Station	44	1.42**	0.01 ^{NS}	0.26*	0.14**	0.56*	0.32**	0.52**	0.008 ^{NS}	0.27 ^{NS}
Season*Station	4	0.91 ^{NS}	0.005 ^{NS}	0.15 ^{NS}	0.21 ^{NS}	1.36*	0.20 ^{NS}	0.05 ^{NS}	0.011 ^{NS}	0.72 ^{NS}

** = Highly significant at P<0.01, * = Significant at P<0.05, NS = Not Significant at P<0.05

Table 3: Summary of Physicochemical parameters of Kubanni reservoir, Zaria, Nigeria

Metals	Station 1			Station 2			Station 3			Station 4		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
WT(°C)	24.86 ^a	19.50	30.50	25.17 ^b	20.25	31	24.89 ^a	20.50	30	24.94 ^a	20.00	32
TDS (mg/L)	39.39 ^a	26.00	106.00	33.47 ^b	26.00	45	33.83 ^b	26.00	45	28.03 ^c	19.50	46
pH	7.33b ^c	6.90	7.65	7.19 ^c	6.80	7.50	7.45 ^b	7.10	7.65	7.51 ^b	7.10	7.85
EC (µS/cm)	79.56 ^a	51.00	212.00	66.94 ^a	51.00	90	67.61 ^b	50.00	90	57.22 ^c	41.00	92

Table 3 Continued

Metals	Station 5			Monthly			Seasons	
	Mean	Min	Max	Mean±SE	Min	Max	Dry	Rainy
WT(°C)	24.97 ^a	20.00	30	24.97±0.29	18	33	23.21 ^b	28.48 ^a
TDS (mg/L)	37.39 ^a	20.00	56	34.42±0.88	15	109	35.23 ^a	32.80 ^a
pH	7.76 ^a	7.30	8.10	7.45±0.03	6.5	9.00	7.51 ^a	7.34 ^a
EC (µS/cm)	74.67 ^a	39.00	112	69.2±1.72	38	215	71.02 ^a	65.57 ^b

Note: Means with same alphabets along the rows are not significantly different at P<0.05, Dry Season sig. > Rainy Season = EC; Rainy Season sig. > Dry Season = WT
WT = Water Temperature; TDS = Total Dissolved Solids; EC = Electrical Conductivity

Table 4: Mean squares of Analysis of Variance (ANOVA) for physicochemical parameters of Kubanni reservoir, Zaria, Nigeria

Source of Variation	Df	WT (°C)	TDS (mg/L)	pH	EC (µS/cm)
Month	11	216.00**	389.00**	0.48*	1515.00**
Station	4	0.50 ^{NS}	681.00**	1.61**	2594.00**
Season	1	1113.00**	237.00*	1.12*	1188.00**
Season*Station	44	2.00 ^{NS}	289.00**	0.06 ^{NS}	1160.00**
Season*Station	4	1.58 ^{NS}	420.00**	0.02 ^{NS}	1593.00**

** = Highly significant at P<0.01, * = Significant at P<0.05, NS = Not significant at P<0.05, WT = Water Temperature; TDS = Total Dissolved Solids, EC = Electrical Conductivity

period. The mean monthly concentrations of Fe, Mn, Zn, Cr, Co, Ni, Cu and Pb were high than the recommended value by USEPA (2002). Cr Used in metal alloys and pigments for paints, cement, paper, rubber, etc through many human activities might have been washed into the reservoir.

While the concentrations of Zn, Ni, Cu and Pb were significantly higher (P<0.05) during the dry season, the presence of any runoff or rainfall could have accounted for the dilution in concentration of Zn, Ni, Cu and Pb

observed in the dry season. Zn, Cd and Pb through anthropogenic activities are transported atmospherically as particles (Environmental Encyclopedia, 2001). The concentration of Cu however was boosted by the influx of rain. Copper and Zinc are also released to the soil solution by mineral weathering. The usage of Copper sulphate (CuSO₄) as Beauoudeux mixture used in spraying grapes around the catchment areas might have been washed into the reservoir during the rainy season. The concentrations obtained for Co were insignificantly different (P>0.05)

irrespective of season, that is Co and Cd concentrations were not dependent on seasons but Co concentrations in the rainy season was higher than that obtained during the dry season which could be an addition through incoming erosion (soil wash).Cd from electroplating steel, Cadmium storage batteries, paints and inks as impurities in several products like phosphate fertilizers, detergents and refined petroleum products could be other sources of Cd. The concentrations of Mn, Zn, Cr, Cu and Cd were generally low with Cd being the least in this study. This results compare favourable with those of Tukura (2005) on same reservoir. Henry and Semili (2005) in their works on the levels of heavy metal pollution in water and sediments in Simiyu wetland of Lake Victoria Basin (Tanzania) also reported higher concentration of Cd, Cu, Pb, Cr and Zn in the dry season than was obtained in the rainy season.

The low temperatures observed for all stations between late December and February during the sampling periods could be due to the prevailing North-East trade wind called Harmattan. The high temperatures observed from April till October in all stations are indications of "rainy" periods. These findings agree with those of Holden and Green (1960), Oladimeji and Wade (1984), Wade (1985), Awanda (1987), Adakole (2000) and Tukura (2005) who reported that water temperatures were low during this Harmattan period of the year in their studies on related aspects of some water bodies of Northern Nigeria. The high significant relationship between water temperature with Fe, Mn, Cr, Co and Pb is indicative of the fact that their solubility or concentrations in water is/are determined by temperature respectively. It is well established (Fausey *et al.*, 1995) that the mineral content of the water expressed as Total Dissolved Solids (TDS) can be used as a rough indicator of the edaphic conditions which play a fundamental role in determining the biological productivity of water bodies. Electrical conductivity found to be significantly lower in the rainy season than the dry season could be due to dilutions of the reservoir during the rainy season and possibly the precipitation of the metallic ions during this period coupled with the low water level in the dry season period (Chapman and Krammer, 1991; Akin-Oriola, 2003). Data observed for TDS and EC from these study show that values of these parameters fall midway between values obtained for standing water bodies in Nigeria and some African countries (Hare and Carter, 1984; Adeniji and Mbagwu, 1990; Odhiambo and Gichuki, 2000; Magadza, 2003; Ndebele and Magadza, 2005). Water pH here was observed to be circumneutral with values around 7. This value is optimum for growth and development of most aquatic organisms as deviations from this could have severe negative impact on the populations of susceptible organisms (Kadiri, 2006).

The levels of the trace elements in this reservoir are of concern as contaminants to aquatic systems because of their toxicity at low concentrations. This is supported by the fact that seven (7) of the nine (9) trace elements were

above permissible levels for portable drinking water. Plants, animals and man drinking or using this reservoir stand the risk of heavy metal poisoning.

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