ASSESSMENT OF SOME HEAVY METALS IN MACOBENTHIC INVERTEBRATE AND WATER SAMPLES COLLECTED FROM KUBANNI RESERVOIR ZARIA, NIGERIA

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A. B. Alhassan*, M.L. Balarabe and I.M.K. Gadzama

Department of Biological Sciences, Ahmadu Bello University Zaria, Nigeria

*Corresponding author: balahassan80@gmail.com;

Abstract: Heavy metal concentrations in water samples and macrobenthic invertebrate samples from Kubanni reservoir were investigated monthly between January and December, 2014 to determine the seasonal variation in heavy metal composition in the reservoir. Triplicate water samples were collected from 10 cm depth from three randomly selected sites into transparent amberedcoloured 250 ml reagent bottles. Macrobenthicinvertebrates were collected using an Ekman grab. Heavy metal concentrations of water samples and macrobenthic invertebrates were analysed using Air/Acetylene Flame Atomic Absorption Spectrophotometer (UNICAM 696 AA Spectrometer).Analysis of variance at $P \leq 0.05$ was used to analyse the result for heavy metal concentrations in macrobenthic invertebrates and students't – test was used to compare the seasonal variation in heavy metal concentrations in benthic macroinvertebrates as well as in the water sample. Principal component analysis (PCA) was use to determine the interrelationship between heavy metals andmacrobenthic invertebrate composition. In Macrobenthic invertebrates, high concentration of Fe (46.21 mg/L) was recorded in *Lumbriculid* sp and low concentration of Cd (0.09 mg/L) was recorded in *Lymnea*sp while in water samples, high concentration of Fe (86.84 mg/L) and low concentration of Cd (0.07 mg/L) were recorded respectively. Significant variations ($P \leq 0.05$) were observed in heavy metal concentrations inmacrobenthic invertebrateand water samples. Regular assessment of heavy metals in the reservoir should be carried out to monitor and track the trend of changes of its water quality and biodiversity.

Keywords: Invertebrate, macrobenthic, metals

Introduction

Macrobenthic invertebrate communities are known to respond to changes in the quality of water or habitat (Adeyemo *et al*., 2008). Because of their extended residency period in specific habitats and presence or absence of particular benthic species in a particular environment, these organisms can be used as bio-indicators of specific environment and habitat conditions (Sharma *et al*., 2013). Diversity, distribution and abundance of macrobenthos depend on the characteristics of their environment such as pollution condition, organic matter content, soil texture and sediment. Because they vary in their adjustment to environmental conditions and their tolerance or sensitivity to contamination, the parameters of benthic animals such as their community structure, dominant species, variety and abundance can be utilized to reflect environmental quality (Gao, 2011).

The pollution of the aquatic environment with heavy metals has become a worldwide problem during recent years because they are indestructible and most of them have toxic effects on organisms (MacFarlane and Burchett, 2000).

This contamination of aquatic ecosystems by heavy metals has been observed in water, sediment and organisms. Heavy metals may be directly absorbed by organisms but are also transferred from lower to higher trophic levels of the food chain. Adakole and Abolude (2012) observed that global concern about heavy metals in the environment stems from their persistence, toxicity and bioaccumulation in the trophic chain.The high accumulation of heavy metals in these components can result in serious ecological changes. One of the most serious results of their persistence is the biological amplification of metal in the food chain. Metals transferred through aquatic food chains and webs to fish, humans and other animals are of more environmental concern to human health (Farkas *et al*., 2001).

Among environmental pollutants, heavy metals are of particular concern due to their potential toxic effect and ability to bioaccumulate in aquatic ecosystems (Censi *et al*., 2006). The presence of heavy metals in aquatic ecosystems is the result of two main sources of contamination: natural process and or natural occurring deposit and anthropogenic activities. The main sources of heavy metal pollution to life form are invariably the result of anthropogenic activities (Kennish, 1992). In the freshwater environment, heavy metals are potentially accumulated in sediments and marine organisms and subsequently transferred to man through food chain. Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota (Cammusso *et al*., 1995).

Gadzama *et al*. (2013) reported 19 metals in the analysed soft tissues of the three species of bivalves (*Anodonta anatine*, *Anodonta marginata* and *Anodonta implicate*) studied in Kubanni reservoir. The elements vary in concentrations in the three bivalve species, with some of the elements falling below detection limit. The metals reported were Mn, Na, K, As, La, Sm, U, Sc, Cr, Fe, Co, Zn, Ba, Eu, Lu, Yb, Th, Sb and Rb. Amman *et al.* (2002) is of the view that anthropogenic activities like mining, final disposal of treated and untreated waste effluents containing toxic metals as well as metal chelates from different industries, such as tannery, steel plants, battery, industries, thermal power plants and the indiscriminate use of heavy metal containing fertilizers and pesticides in agriculture are some of the main causes of metal pollution in the aquatic ecosystem. Although some metals like Cu, Fe, Mn, Ni, Zn and Se are essential micronutrients for life processes in plants and animals, others like Cd, Cr and Pb have no physiological activity and have been proven detrimental beyond certain limit (Abolude, 2007). Trace elements constitute natural component of the earth crust and are not biodegradable, hence persist in the environment. Heavy metals may come from natural sources, leached from rocks and soils according to their geochemical mobility or come from anthropogenic sources as a result of human land occupation and industrial pollution (Abolude *et al*., 2009).

Materials and Methods

Study area

Kubanni reservoir is located on 11° 08ˈN and 7° 39ˈE south of Ahmadu Bello University Zaria Samaru campus, with an elevation of 2111 ft above sea level and reservoir area of 57 km^2 and mean depth of 6 meters (Fig. 1). The reservoir receives runoff and domestic waste waters from within the campus, nearby irrigation farms and Samaru community. Kubanni River which empties into the lake is known to play a major role in the disposal of industrial wastes accumulated from industries cited in Zaria (Abolude *et al*., 2009).

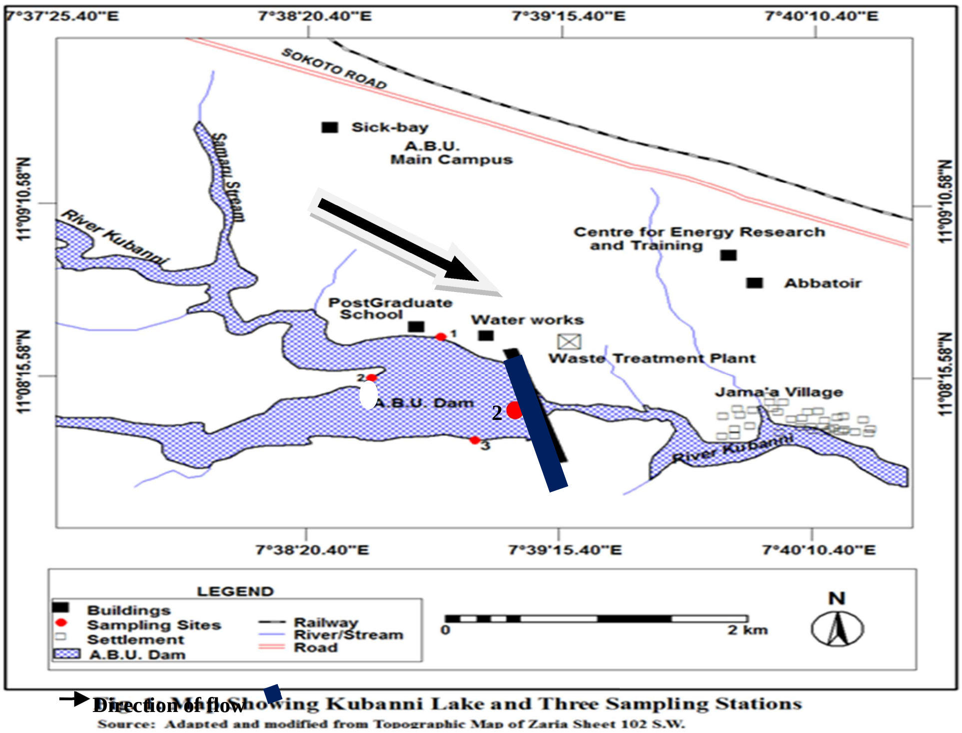

Fig. 1: Map of Kubanni reservoir showing three sampling stations

Sample collection

Samplings were done covering rainy and dry season in three stations based on accessibility, nearness to settlement and their suitability for future studies.

Collection, sorting and identification of benthic samples

Benthic sediment samples were collected between the hours of 8.00a.m. and 9.00a.m. using an Ekman grab (Model No. 923) measuring 19 cm by 14 cm with an area of 0.0266 m^2. The samples were collected twice a month. Three grab hauls were taken from each station, emptied into pre-labeled polythene bags and taken to the laboratory for sorting and identification. The collected materials were washed through a 0.5 mm mesh sieve. The residue in the sieve for each station was then preserved in 10% formalin solution for further analysis.Small portions of the sediment samples were washed in a 0.5 mm sieve to remove debris. Macrobenthic organisms were identified with the aid of dissecting microscope according to Odum (1971) and Pennak (1978). Thereafter, the organisms were grouped into different taxa in each sample.

Collection of water samples and analysis of heavy metals

Water samples were obtained by means of a tube sampler from the water surface in one liter bottles. The analysis of water samples was carried out according to methods describe by APHA (2005). Water samples were preserved by the addition of 1 ml of concentrated nitric acid per liter until the time of analysis. The water samples were filtered through 0.45µl membrane filter. The required volume (100 ml) of the filtrate was collected to measure heavy metals levels in water samples by using Air/Acetylene Flame Atomic Absorption Spectrophotometer (UNICAM 696 AA Spectrometer). This was done by comparing their absorbance with those of standards (solution of known metal concentration).

Some macrobenthic invertebrates collected were squashed using porcelain pestle and mortar, placed in a crucible and dried at 60°C for 36 h. The dried samples were weighed and ground into powdery form (enough to pass 1mm sieve) using porcelain pestle and mortar, and dissolved by wet chemical digestion in prepared 1 volume to 4 of 62% Perchloric acid and 70% Nitric acid.Heavy metal concentrations of macrobenthic invertebrates sample were analyzed by subjecting the digested samples to heavy metal analysis using Air/Acetylene Flame Atomic Absorption Spectrophotometer (UNICAM 696 AA Spectrometer).This was carried out at the Multi-user Laboratory, Ahmadu Bello University,Zaria.

Data analysis

Analysis of variance (ANOVA) was used to determine variations of heavy metal concentration in the macrobenthic invertebrates. The student t-test ($P \leq 0.05$) was used to determine the seasonal variations in heavy metal concentration of water samples. Principal component analysis was used to determine the interrelationship betweenheavy metals andmacrobenthic invertebrate composition. Statistics Analysis System (SAS) version 9.1.3 and Paleontological Statistics Software Package (PAST) V.2.17c were used for the analysis.

Results and Discussion

In this study the mean seasonal concentrations of heavy metal in macrobenthic invertebrate of Kubanni reservoir is presented on Table 1. Concentration of Fe in Kubanni reservoir ranged from 11.33 - 46.21 mg/L in dry season and 7.36 - 38.62 mg/L in wet season. *Lumbriculid sp* and *Cheumatopsychesp* recorded the highest concentration of Fe. However there was significant variation of Fe concentration in macrobenthic invertebrates for both seasons.

Mn concentration in macrobenthic invertebrate of Kubanni reservoir ranged from 1.19 - 4.70 mg/L in dry season and 1.13 - 2.73 mg/L in wet season while Zn concentration in macrobenthic invertebrate in the reservoir ranged from 1.67 - 3.43 mg/L in dry season and 1.62 - 2.92 mg/L in wet season. For Cd, concentrations ranged from 0.25 - 0.27 mg/L in dry season and 0.11 - 0.30 mg/L in wet season. Nickel concentration also show variation within the macrobenthic invertebrate with values ranging from 1.11 - 2.63 mg/L in the dry season and 1.11 - 2.81 mg/L in wet season while lead concentrations in macrobenthic invertebrates were found to be below detectable limit in both dry and wet seasons.

Table 1: Mean seasonal concentration of heavy metals in macrobenthic invertebrate of Kubanni reservoir

	DS						WS					
	Fe	**Mn**	**Zn**	**Cd**	**Ni**	**Pb**	**Fe**	**Mn**	**Zn**	**Cd**	**Ni**	**Pb**
***Lumbriculid*sp**	46.21 ± 5.26^{a}	4.70 ± 0.22^{a}	3.29 ± 0.14^{b}	0.27 ± 0.04^{a}	2.63 ± 0.76^{a}	BDL	38.62 ± 2.76^{a}	2.73 ± 0.66^{a}	2.92 ± 0.55^{a}	0.30 ± 0.11^{a}	2.76 ± 0.03^{b}	BDL
***Viviparus*sp**	22.32 ± 2.22^{bc}	3.21 ± 0.65^{b}	2.07 ± 0.99^{ef}	0.14 ± 0.01^{cd}	2.12 ± 0.04^{d}	BDL	17.56 ± 4.01^{c}	1.76 ± 0.05^{b}	2.07 ± 0.05^{d}	0.22 ± 0.01^{b}	2.61 ± 0.73^{c}	BDL
***Melanoides*sp**	20.76 ± 3.56^{c}	3.98 ± 1.32^{b}	2.12 ± 0.65^{e}	0.17 ± 0.03^{c}	2.32 ± 0.01^{c}	BDL	17.31 ± 1.98^{c}	1.57 ± 0.01^{c}	2.14 ± 0.74^{c}	0.19 ± 0.01^{c}	2.81 ± 0.03^{a}	BDL
***Anodonta*sp**	26.79 ± 2.34^{b}	3.69 ± 0.67^{b}	3.01 ± 0.87^{c}	0.18 ± 0.02^{c}	2.4 ± 0.13^{b}	BDL	18.91 ± 3.22^{b}	1.46 ± 0.45^{d}	2.15 ± 0.11^{c}	0.20 ± 0.06^{b}	2.16 ± 0.34^{e}	BDL
***Biomphalaria*sp**	17.61 ± 3.66^{e}	1.92 ± 0.13^{d}	2.02 ± 0.34^{f}	0.11 ± 0.01^{f}	1.29 ± 0.15^{f}	BDL	14.39 ± 2.34^{d}	1.17 ± 0.01^{e}	2.01 ± 0.33^{d}	0.13 ± 0.01^{cd}	2.61 ± 0.45^{c}	BDL
***Physa*sp**	18.74 ± 1.65^{de}	3.22 ± 0.34^{b}	2.41 ± 0.83^{d}	0.16 ± 0.01^{e}	2.39 ± 0.09^{c}	BDL	14.99 ± 1.45^{d}	1.42 ± 0.01^{d}	2.17 ± 0.54^{c}	0.16 ± 0.09^{c}	2.80 ± 0.66^{a}	BDL
***Lymnea*sp**	13.28 ± 1.11^{f}	1.19 ± 0.23^{d}	1.92 ± 0.45^{g}	0.09 ± 0.01^{g}	1.11 ± 0.01^{g}	BDL	10.51 ± 1.03^{e}	1.13 ± 0.01^{f}	1.62 ± 0.01^{f}	0.11 ± 0.04^{d}	1.16 ± 0.05^{f}	BDL
***Bulinus*sp**	19.31 ± 1.87^{d}	3.22 ± 0.01^{b}	3.43 ± 0.54^{a}	0.21 ± 0.04^{b}	2.43 ± 0.07^{b}	BDL	17.72 ± 2.67^{c}	1.75 ± 0.03^{b}	2.84 ± 0.06^{b}	0.25 ± 0.01^{b}	1.11 ± 0.01^{g}	BDL
***Hydrophilus*sp**	11.33 ± 3.39^{g}	2.34 ± 0.43^{c}	1.67 ± 0.01^{g}	0.13 ± 0.04^{d}	1.63 ± 0.01^{e}	BDL	7.36 ± 1.77^{f}	1.13 ± 0.01^{f}	1.75 ± 0.03^{e}	0.16 ± 0.02^{c}	2.53 ± 0.05^{d}	BDL
***Cheumatopsyche*sp**	40.05 ± 5.79^{a}	4.37 ± 0.22^{a}	3.12 ± 0.07^{bc}	0.25 ± 0.01^{a}	2.33 ± 0.08^{c}	BDL	-	-	-	-	-	-
MEAN	**23.65±3.07**	**3.19±0.41**	**2.50±0.40**	**0.18±0.03**	**2.06±0.12**	-	**17.48±2.35**	**1.56±0.03**	**2.17±0.03**	**0.18±0.04**	**2.29±0.02**	-
P value	**0.0001**	**0.0001**	**0.0001**	**0.0087**	**0.0001**		**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	

Means ±S.E with different superscripts along the same column were significantly different ($P \leq 0.05$); BDL = Below Detectable Limit; DS = Dry season; WS = Wet season

Table 2: Seasonal variation of heavymetal concentrations in Kubanni reservoir

Heavy metals (mg/L)	WS	DS	P value
Fe	28.16 ± 1.91^{b}	86.84 ± 7.32^{a}	0.00**
Mn	4.43 ± 1.64^{b}	9.13 ± 3.43^{a}	0.02*
Zn	1.56 ± 0.24^{b}	8.65 ± 1.94^{a}	0.00**
Cd	0.07 ± 0.02^{b}	0.25 ± 0.06^{a}	0.02*
Ni	2.09 ± 0.35^{b}	2.46 ± 0.58^{a}	0.05*
Pb	0.09 ± 0.01^{b}	0.67 ± 0.07^{a}	0.02*

Mean±S.E along row with different superscript were significantly different ($P \leq 0.05$); WS = Wet season; DS = Dry season; BDL = Below Detectable Limit; * =Significant; **= Highly significant

The concentrations of heavy metals were all higher in macrobenthic invertebrates during the dry season and Analysis of Variance ANOVA at $P \leq 0.05$ shows significant difference in concentration of heavy metals between the macrobenthic invertebrates. For concentration of heavy metals in water samples from the two reservoirs, comparing seasons in the two reservoirs, ANOVA shows significant difference in the concentrations of the heavy metals in dry and wet seasons with high concentrations in the dry season (Table 2).

However, the relationship between heavy metal concentrations in water samples and macrobenthic invertebrate in Kubanni reservoir for each heavy metal is shown in Fig. 2. There was significant variation in Fe and Zn concentration in water sample and macrobenthic invertebrates but no significant variation was observe for Mn, Ni and Cd concentrations in water samples and macrobenthic invertebrate in the reservoir while Pb concentrations in macrobenthic invertebrates were below detectable limit but detected in the water sample from the reservoir.

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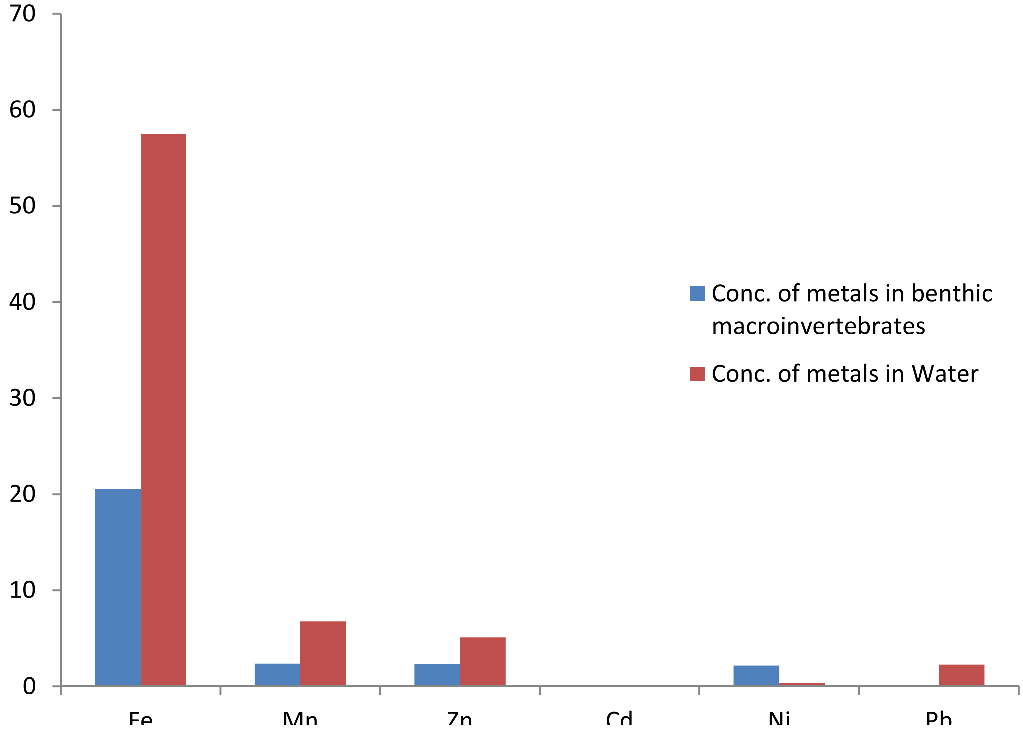
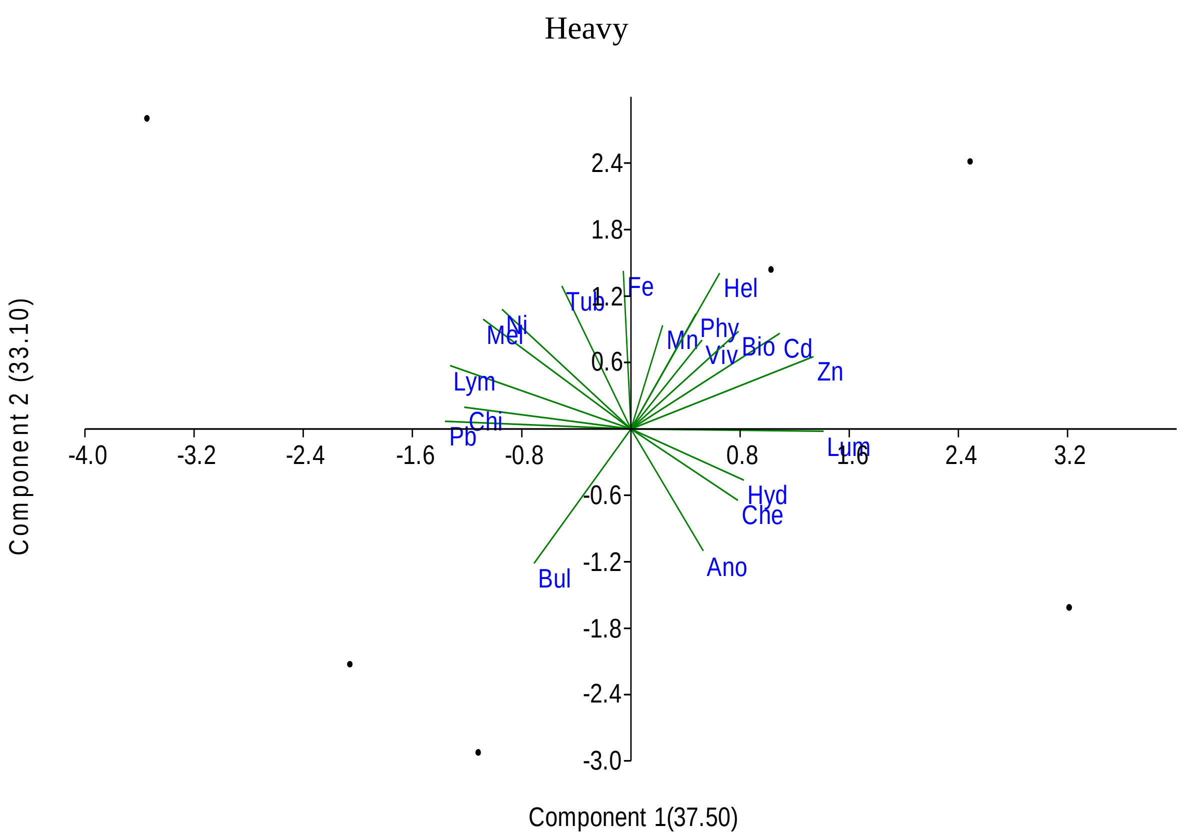


Fig. 2: Relationship between Heavy Metal Concentrations in Water Sample and Macrobenthic Invertebrate of Kubanni Reservoir



Tub =*Tubifex*sp, Lum = *Lumbriculid*sp, Hel = *Helobdella*sp, Viv = *Viviparus*sp, Mel = *Melanoides*sp, Bio = *Biomphalaria*sp, Phy = *Physa*sp, Lym = *Lymnea*sp, Bul = *Bulinus*sp, Ano = *Anodonta*sp, Chi = *Chironomus*sp, Hyd = *Hydrophilus*sp, Che = *Cheumatopsyche*sp

Fig. 3: Principal component analysis (PCA) biplot for heavy metal concentrations and macrobenthic invertebrate composition

Principal Component Analysis biplot (Fig. 3) showed the interrelationship between heavy metal concentrations and macrobenthic invertebrates composition. The first two components accounted for 70.60% of the total variation observed. Mn, Cd and Zn were positively correlated with *Physa*sp, *Helobdella*sp, *Viviparus*sp, *Biomphalaria*sp, *Cheumatopsyche*sp, *Lumbriculid*sp, *Hydrophilus*sp and *Anodonta*sp but with strong association with *Physa*sp, *Helobdella*sp, *Viviparus*sp, *Biomphalaria* sp. There was strong negative association between the metals Fe, Ni and Pb with *Chironomus*sp, *Lymnea*sp, *Melanoides*sp and *Tubifex* sp negatively.

Macrobenthic invertebrate and water samples from Kubanni reservoirin this study contained wide range of metals at different concentrations.These concentrations of heavy metals in macrobenthic invertebrate and the reservoir are primarily controlled by bedrock and overburden of the catchment (Adeyemo *et al*., 2008). The significant variation in metal concentrations in the macrobenthic invertebrates suggests that the different metals accumulate in different patterns and concentrations in the tissues of the macrobenthic invertebrates. The different forms (colloidal, particulate, and dissolved forms) that metals exist in water could have predisposed macrobenthic invertebrates to continuous metal intake. High concentration of heavy metals recorded in the dry season can be as a result of decrease dilution due to lack of rain, increase exposure to the metals and activities in the catchment areas. Below detectable limit of Pb in Kubanni reservoir in dry and wet season could be due to a difference in the catchment of the two reservoirs. So also Cd and Pb detected in water samples from the reservoir was above maximum permissible limit (Cd-0.005 mg/L and Pb-0.015 mg/L) by US EPA, 2008 and this could be due to the types of activities in the catchment of the reservoir (Shuman *et al*., 1997). Iron recorded the highest values above maximum permissible limit set by US EPA, 2008 (Fe-0.3 mg/L) in the reservoir and this can be due to smaller sized particleswhich remain suspended in the water column longer than larger particles, enhancing suspended metal concentrations. This is in line with the work of (Shuman *et al*., 1997).

The low levels of Cd and Pb relative to other heavy metal concentrations may be attributed to less industrial and mining operations in the catchment of the reservoir which is considered the main source of Cd in the environment (Iguisi*et al*., 2001). Zinc concentration in water was below maximum permissible limit in wet season and above maximum permissible limit in dry season. The most important reason for Zn pollution in the reservoir can be as a result of high human activities such as discharge of sewage, sludge and use of fertilizers. However, Zn is an essential element for plants and is taken up actively by roots (Khan *et al*., 2000).

The higher concentration of heavy metals in *Lumbriculid*sp relative to other macrobenthic invertebrates can be attributed to its body anatomy and physiology in response to concentration of the metals. Though the variation in concentrations of the metals in the species of macrobenthic invertebrate in this study may be due to differences in physiological ability to maintain internal metal concentrations or could be from species-specific capacity to regulate or accumulate trace metals (Reinfelder *et al*., 2013).

Positive and negative correlationthat exist between the macrobenthic invertebrate and some heavy metals in the reservoir can be as a result of their effectson macrobenthic invertebrate body physiology and survival of these organisms.

Conclusions

The study has established that 6 different types of metal contaminants; Fe, Mn, Zn, Cd, Ni and Pb exist in macrobenthic invertebrate and water samples from the reservoir in various levels of concentrations with influence on macrobenthic invertebrates composition.

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Conflict of Interest

There is no conflict of interest.

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