



**ANALYSIS OF HEAVY METALS CONCENTRATIONS IN WATER SAMPLES, THE SHELLS
AND MUSCLES OF *MUTELA RUBENS* IN RIVER WUDIL, KANO STATE NIGERIA**

AZUBUIKE ADAMS, (Ph.D)

Department of Biological Science, Faculty of Science,
Nigeria Police Academy, Wudil, P.M.B 3474, Kano – Nigeria.
Author for correspondence: dr.azubuikeadams@yahoo.com



ABSTRACT

The heavy metal concentrations in water samples, the shell and flesh of *Mutela Ruben* were evaluated. Samples were collected from three different sites. About (15-20) samples of heaving Bivalves and 2 plastic bottles of water samples each were collected fortnightly over a period of four months at three identified stations and analyzed for their metal contents and concentrations.

The study revealed the accumulation of Zn, Cr and Cu by *Mutela Rubens* from river Wudil concentrations of heavy metals (zinc, Zn, copper (Cu), chromium (Cr), lead (pb), and nickle (Ni) in water samples, the shells and flesh of *Mutela Rubens* were determined using Atomic Absorption spectrophotometry (AAS). The order of concentration in water were Cr>Zn>Cu>Ni>pb while their mean values were (1.87mg/1, 0.754mg/1, 0.61mg/1, 0.39ml/1 and 0.38mg/1) respectively.

The order of concentration in the flesh were (Zn>Cr>Cu>pb?Ni while their mean values were (6.19ug/g, 1.65ug/g, 0.91ug/g, 0.36yg/g and 0.35ug/g) respectively.

The concentration factor for Cr, Zn and Cu were higher than one and this means that the shells and flesh of *Mutela Rubens* have preferentially accumulated these metals. Zn showed highest accumulation by the flesh at the 3 sampling sites (Zn, 7.59ug/g, 8.37ug/g and 8.82ug/g) respectively. The order suggests that *Mutela Rubens* accumulate metals according to biological importance. The accumulation of metals confirmed that *Mutela rubens* can be used as bio-indicator of heavy metal pollution (bio-monitor) for heavy metals in river Wudil.

Keywords: Heavy Metals, shells, concentrations, atomic Absorption spectrophotometer, Bioaccumulation.

©KY Publications

1.1 INTRODUCTION

Many studies have been carried out to determine the levels of pollutants and their temporal fluctuation in coastal areas. Such studies include the use of water, sediments and living organisms to describe the environmental behaviour of pollutants or to monitor the levels of contamination in those compartments (Simpson 1979, Phillips 1977, 1980, Dekock and Kuiper 1981, Windows *et al* 1981, Karez *et al* 1994). Fresh water molluscs, such as bivalves, have been used as bio-indicators of pollution because they are abundantly available, easy to harvest, characterized with long life span, accumulation ability and high concentration factors for several xenobiotics within their



environment (Phillips and Rainbow, 1993) Reports on the molluscs that can be used as bio-indicators for heavy metal contamination have been summarized by Elder and Collins (1991). However, studies on heavy metal contamination in Molluscs from fresh water in Nigeria are lacking. Ayodele and Abubakar, (2001) suggested that the study of heavy metal contamination in bivalves found in Tiga lake is important in order to consider them as bio-indicators for heavy metal contamination and to serve as background data.

Pollution of lakes and rivers may occur from a variety of sources. Regarding heavy metals, various processes influenced by anthropogenic activities may contribute to increase concentration (Singh and Sternns. 1994). They include run-off from agricultural and urban areas, discharges from mining, factories and municipal sewer systems, leaching from dumps, and former industrial sites and atmospheric depositions (Martin *et al*, 1999). The pollutants are carried from the source and tend to sink thereby polluting the aquatic organisms.

Contaminations by heavy metals are found in lakes and rivers. (Bowen, 1979). Cases of serious pollution appear to be due to Cadmium, Copper, Mercury and Zinc. Cadmium pollution has caused painful illness and death among the Japanese (Friberg *et al* 1971). Acute copper pollution killed the local floral and fauna in the river Churnet (Butcher, 1946) while chronic pollution by copper caused the flesh of Oysters to turn green (Bryan. 1976) and salmon are known to avoid streams contaminated by copper (Sprague *et al* 1965). Streams draining lead and zinc mines have reduced algal growth and have no invertebrate fauna (Jones, 1940). Walford (1980) reported that copper, arsenic, lead, zinc, cadmium, cobalt, nickel and manganese which could be found in environment could present health risks. Human toxicity from metals have been reported as a result of contamination of food (Hui, 1992). High intakes, acute or chronic low intakes in food may lead to toxicity which may be due to the body's inability to detoxify their metals contaminations. Prasad (1978), observed that high levels of copper in the blood result in haemolysis, hepatic necrosis, gastro-intestinal bleeding, haematuria, convulsion, coma and death Murphy, (1970), reported drowsiness and renal failure in case of zinc toxicity. Similarly, renal dysfunction, hypertension and lung damage have been linked to cadmium toxicity.

Bryan (1983) suggested that metal contamination in some algal species have been reported for the temperate regions. Although information on contaminated regions in the tropical areas are lacking, studies on pollution monitoring in fresh water lakes environment have been reported using different indicator species (Imevbore 1970, Nwaidairo and Umehan 1985, Ayodele and Abubakar,2000)

Water sediments, the shells of bivalves and gastropods have been used for describing the behaviour of heavy metal and to monitor their levels of contamination in these compartments (Phillips, 1977 Ayodele and Abubakar, 2000; Martins *et al* 1999). In the present work , the metal contents of water samples, the shells and flesh of *Mutela rubens* were analysed for Zn, Cu, Cr, Pb and Ni in accordance with standard techniques (Parsons *et al*, 1984, Ayodele and Abubakar, 2001) and metal concentration was determined by Atomic Absorption spectrophotometer (AAS).

1.2 Justification

The research is intended to determine the level of pollution of the aquatic environment. It is important to point out that there is the need to identify the indicators that will be used and the parameters that should be monitored. There are criteria that will enable one determine the sensitivity and usefulness of an indicator for monitoring of pollution. This study is imperative because of the high concentration of industries that use heavy chemical within Kano metropolis which eventually drain into river Wudil. There is no enforcement of laws that guide against waste discharge from this industries. Heavy metals are sources of heavy pollution around Kano environment, bearing in mind the tanning industry, plastic industry, mining sites, textile



industry and leather industry and intensive agriculture (wet and dry season farming where fertilizers are heavily used). Industry employs heavy chemicals for its processes. The effluents or liquid/semi liquid waste from this industries are discharged into the environment which finds their way into storm water or streams that feed the river that flow into river Wudil. Because of the intensity of chemicals as stated above, it will be worth while to consider the pelagic aquatic animals as bio indicator in the river Wudil which exist in abundance while heavy metals as components of the heavy chemical can be the indicators since they are easily ingested by aquatic life eg. Mollusc

1.3 Aims and objectives

1. To investigation the presence of heavy metals such as Zn, Cu, Pb, Cr, and Ni in water samples, the shells and flesh of *Mute la rubens* collected from river Wudil.
2. To evaluate the concentrations of these metals (Zn, Cu, Cr, pb, and Ni) in water and their accumulation by fresh water bivalves of river Wudil Kano- Nigeria.
3. To established its suitability as bio-indicators that can be used to monitor heavy metals pollution in river wudil.

2.0 MATERIALS AND METHODS

2.1 Sampling

The sampling exercise carried was out between February to May 2013. All samples were analysed for Zn, Cr, Pb, Ni in accordance with standard technique (Parsons *et al* 1984, Ayodele and Abubakar 2001) Three sampling sites were selected (site 1, 11 and 111).

2.3 Collection of samples

The water samples, the shells and flesh of *Mutela rubens* were collected from Rurum water side in river wudil. Water samples were collected in plastic bottles, pre-rinsed with distilled water. Each sample was preserved by adding 4m nitric acid and stored in a freezer prior to chemical analysis.

Mutela rubens were collected by hand picking. The bivalves were chosen by harvesting only large but similar sizes whole and healthy. A total of (15-20) samples were collected fortnightly over a period of 4 months at 3 identified sites. They were then kept in plastic containers filled with water. In the laboratory, samples were stored under room temperature in an open environment.

2.4 Chemical analysis of the shells and flesh of *Mutela rubens*

In the laboratory after taking the biometric measurements (length & width), the soft tissue of each composite sample of (15 - 20) were scooped out and cleansed in water. The samples were later dried in an oven at 95°C overnight. The dry shells were also cleaned in water and later dried in an oven at 95° C overnight. Each sample of flesh and shell were grounded to fine power in a tehplon mortar and sieved through a 20um sieve before drying at 105° C to constant weight and preserved in a polythene bottle prior to ashing. 1.0g of sample was ashed at 450°C for six hours

2.5 Chemical analysis of water samples

A 0.25 litre of the water sample was transferred into a 500cm³ beaker. Sample was heated to dryness. It was redissolved in 0.1m nitric acid in a 100cm³ volumetric flask. The volume was made up to mark with distilled water (Ayodele and Abubakar, 2000 and Parson *et al* 1984)

The metal concentration were determined by flame atomic absorption spectrophotometer (AAS). Distilled water used as blank was digested using the above procedure. A calibration curve of Absorbance versus concentration was plotted for the standards. The concentration of metal under investigation in (mg/ litre) were determined from the calibration curve of its standard.



2.6 Ashing of the shell and flesh of *mutela rubens*

One gram of each sample (the shells and flesh of *Mutela rubens*) were accurately weighed in a silica crucible and transferred to a muffle furnace and heated at 450°C for 6 hours, the ash obtained was cooled in a desiccator prior to analysis. The ash was then used for determination of metals present within.

2.7 Determination of metals

One gram of the samples each were ashed as described above and the ash was dissolved in 10cm³ of concentrated nitric acid. The volume was made up to 50ml with distilled water. This solution was then used for AAS reading to determine the relevant metals present (Cr, Cu, Zn, Ni, and Pb) in it using suitable lamps and standard solution for each metal. The standard solution readings from (AAS) was obtained. A calibration curve of absorbance versus concentration was plotted for the standards. (figure 2-6). The concentration of each metal under investigation in (mg/litre) were determined from the calibration curves.

2.8 Statistical analysis

A one way analysis of variance (Anova) was carried out to determine significant difference between the mean concentration of heavy metals in the flesh, shell and water samples collected from various sampling sites in the lake studied.

3.0 RESULTS

Plates 1 and 2 show the shells and flesh of *Mutela rubens*.

3.1 The Calibration Curves

The calibration curve of metal concentration versus absorbance plotted for standard solutions of Zn, Cu, Cr, Pb, and Ni with their calculated gradient are presented in (fig. 2-6).

The concentration of each metals under investigation in (mg/l) or (µg/g) for the water, shell and the flesh samples are presented in (tables 1-5).

3.2 The results of analysis of water samples.

The calculated mean values for the concentration of the heavy metals in mg/l for water samples collected at the various sampling station at the lake is presented in (Table 1).

Concentration of Zn Ni and Cr were high in water:- Cr showed the highest concentration in water while Pb showed the least concentration. The order of concentration in water were Cr >Zn>Ni>Cu>Pb while their mean values were (1.87mg/l, 0.75mg/l, 0.61mg/l, 0.39mg/l, and 0.38mg/l) respectively. These values were high -when compared with standards for water quality (drinking).

Table 1 : Mean monthly heavy metal concentration (mg/l) in water collected at the various sampling site in the river (mead, sd, standard values)

Station	Metals	Feb.	March	April	May	Mean	SD	Mean for 3 sites ÷ 3	Drinking water
I	Zn	0.73	0.83	0.92	0.85	0.83	0.08	0.75	5.0
II		0.67	0.70	0.79	0.80	0.74	0.06		
III		0.65	0.63	0.68	0.79	0.69	0.07		
I	Cu	0.40	0.40	0.37	0.37	0.37	0.02	0.39	0.1
II		0.40	0.40	0.36	0.46	0.41	0.04		
III		0.40	0.40	0.38	0.46	0.41	0.03		
I	Cr	2.06	2.27	1.93	1.80	2.02	0.20	1.87	0.05
II		2.06	1.60	1.80	1.80	1.82	0.19		

Research Article

Copy Right ©KY Publications
Journal of Advanced Studies in Agricultural, Biological and Environmental Sciences (JABE) www.jabe.in



A Peer Reviewed & Refereed, International Open Access Journal

Vol.2.Issue.4.2015 (Oct-Dec)

ISSN:2455-0221(P)2394-2606(O)

III		1.86	1.67	1.74	1.80	1.77	0.08		
I		1.00	0.60	0.60	0.60	0.70	0.29	0.61	0.05
II	Ni	1.00	0.40	0.40	0.40	0.55	0.26		
III		1.00	0.40	0.40	0.40	0.55	0.21		
I		0.36	0.38	0.43	0.43	0.40	0.09	0.38	0.05
II	Pb	0.35	0.36	0.38	0.38	0.37	0.02		
III		0.37	0.37	0.41	0.34	0.36	0.04		

The calculated mean values for the concentration of the heavy metals in (Uglg) for the shells of mutela rubens collected at various sampling sites is presented in Table 2

The order of magnitude for heavy concentration in shells was Cr > Zn > Cu > Ni > Pb while their mean concentration was (1.90 ug/g, 1.26 ug/g, 0.69 ug/g, 0.39 ug/g, and 0.37 ug/g) respectively.

Cr 1.90 ug/g showed highest concentration in the shells while the lowest concentration in shell wa Pb 0.37 ug/g

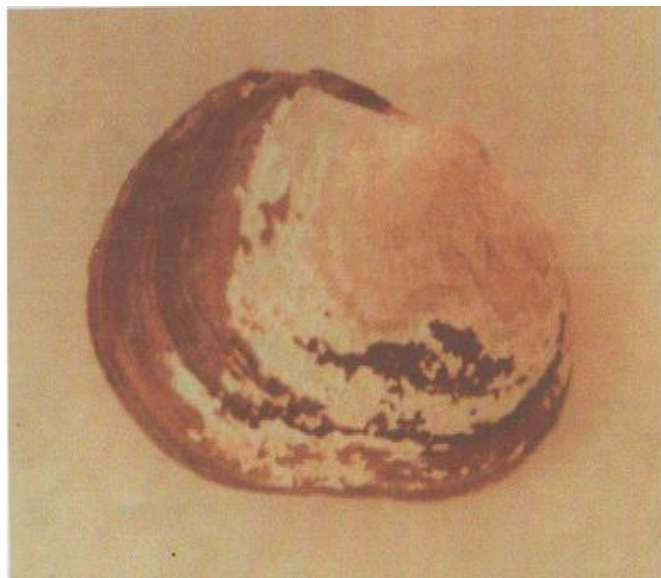
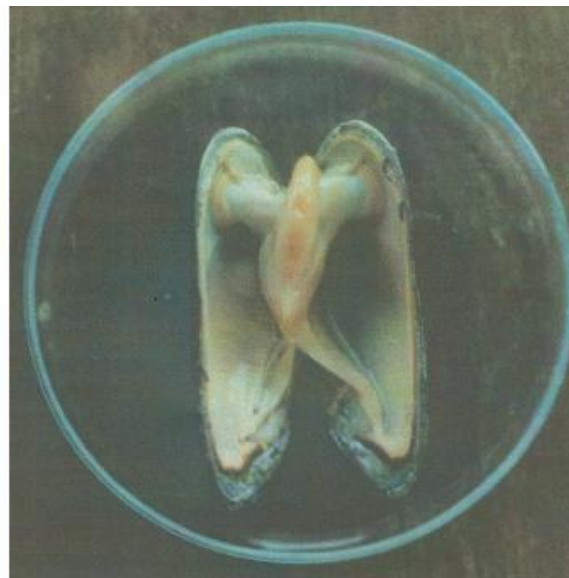


PLATE 1: The Shells of *Mutela ruben*



The inside view of the flesh of *Mutela ruben*

Table 2: Mean monthly heavy metal concentration (mg/l) in mutela rubens shell at various sampling site the river (mean and standard deviation)

Station	Metals	Feb.	March	April	May	Mean(x)	SD	Mean for 3 sites ÷ 3
I				2.44	2.09	1.17	0.28	1.26
II	Zn	1.53	1.43	1.83	1.45	1.56	0.19	
III		1.03	0.93	1.33	0.96	1.06	0.18	
I		0.56	0.56	0.88	0.90	0.70	0.19	0.70
II	Cu	0.54	0.56	0.84	0.86	0.70	0.20	



III		0.56	0.56	0.84	0.86	0.67	0.19	
I		1.81	1.73	1.93	2.13	1.92	0.17	1.90
II	Cr	1.93	1.73	1.93	2.13	1.93	0.16	
III		1.80	1.73	1.87	2.02	1.85	9.12	
I		0.30	0.40	0.50	0.60	0.45	0.04	0.38
II	Ni	0.30	0.40	0.40	0.50	0.38	0.03	
III		0.30	0.40	0.30	0.30	0.30	-	
I		0.38	0.39	0.37	0.35	0.37	0.03	0.37
II	Pb	0.38	0.40	0.38	0.36	0.38	0.03	
III		0.38	0.38	0.36	0.34	0.37	0.03	

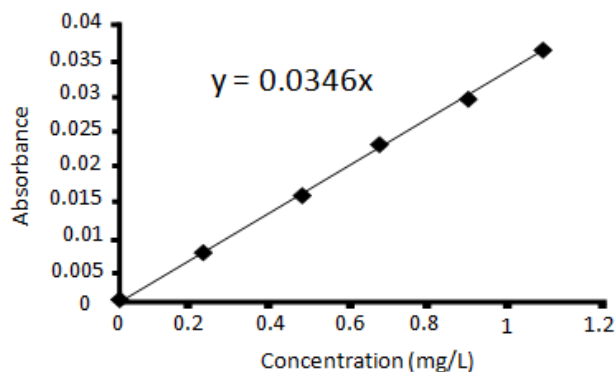


Figure 2: Calibration curve for standard Zinc Metal

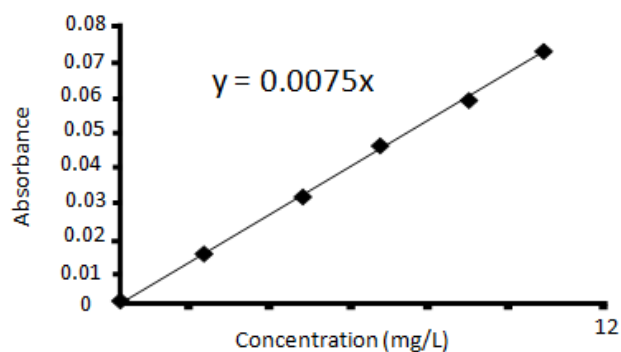


Figure 3: Calibration curve for standard Chromium Metal

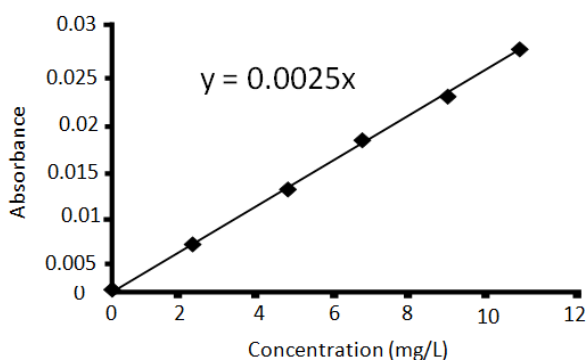


Figure 4: Calibration curve for standard Copper Metal

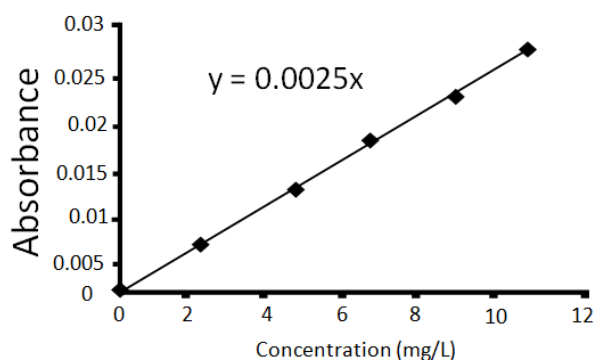


Figure 5: Calibration curve for standard Nickel Metal

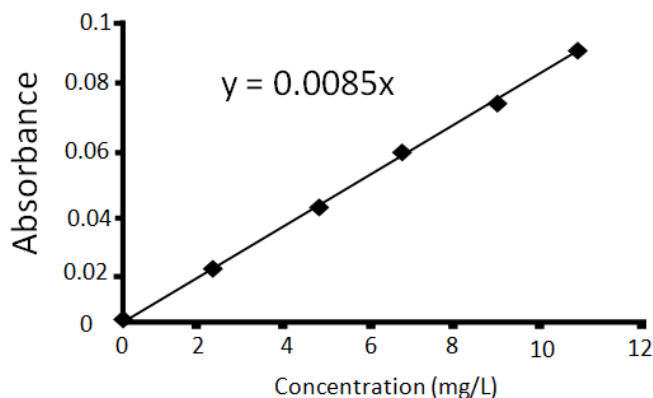


Figure 6: Calibration curve for standard Lead Metal

3.3 The result of analysis of the flesh of *Mutela rubens*

The calculated mean values for the concentration of the heavy metals in ug/g for the flesh of *Mutela rubens* collected at the various sampling site in the Lake (mean, sd) is represented in Table 3

Zn showed highest concentration in the flesh (6.19ug/g). ni had lowest concentration in the flesh (0.35ug/g). the order of concentration were Zn > Cr > Cu > Ni while their mean values were (6.19ug/g, 1.65ug/g, 0.69ug/g, 0.36ug/g and 0.35ug/g) respectively.

Table 3: Mean monthly heavy metal concentration (ug/g) in *Metula rubens* flesh at the various sampling site in the river (mean, standard deviation)

Station	Metals	Feb.	March	April	May	Mean	SD	Mean for 3 sites ÷ 3
I	Zn	5.27	5.46	5.99	8.49	6.30	1.48	6.19
II		4.96	5.37	5.95	8.49	6.20	1.68	
III		5.00	5.26	5.77	8.28	6.09	1.50	
I	Cu	1.00	0.90	0.92	1.00	0.90	0.05	0.91
II		0.94	0.86	0.92	1.00	0.93	0.06	
II		0.90	0.64	0.88	0.96	0.90	0.05	
I	Cr	2.01	2.02	2.01	2.00	2.10	0.02	1.65
II		1.97	1.77	1.87	1.67	1.83	0.19	
III		1.97	1.78	1.68	1.88	1.83	0.12	
I	Ni	0.30	0.30	0.40	0.05	0.45	0.04	0.35
II		0.30	0.30	0.30	0.03	0.30	-	
III		0.30	0.30	0.30	0.03	0.30	-	
I	Pb	0.40	0.48	0.42	0.40	0.41	0.04	0.36
II		0.38	0.36	0.36	0.34	0.36	0.03	
III		0.32	0.30	0.34	0.32	0.32	0.02	

The mean metal concentration (ug/g) in the flesh of *Metula rubens* compared with their concentration in water sample from the lake and the shell is presented in Fig. 7.



From Observation, Zn showed highest mean heavy metal concentration in the flesh compared to the concentration, in shells and water samples their mean values were (Zn 6.19 ug/g, 1.26 ug/g and 0.75 ug/g) respectively. There was a significant difference ($p > 0.05$) in the concentration of Zn in flesh compared to its concentrations in shells and water samples collected at the .3 various sampling sites

Concentration of Cr. was higher in shells (1.90 ug/g), compared to those in the flesh. (1.65 ug/g) and water samples (1.87 ug/g). There was no significant difference ($p < 0.05$) for concentration of Cr and Cu in shells compared to flesh and water samples collected from the sampling sites.

The Concentration Factor (CF) calculated to show whether the organism have accumulated the metal or not. When concentration is less than one, there is no accumulation. The CF for Zn, Cu and Cr were higher than one, this means that Zn, Cu, and Cr have been preferentially accumulated. Ni and Pb were not accumulated by *Mutela rubens* flesh.

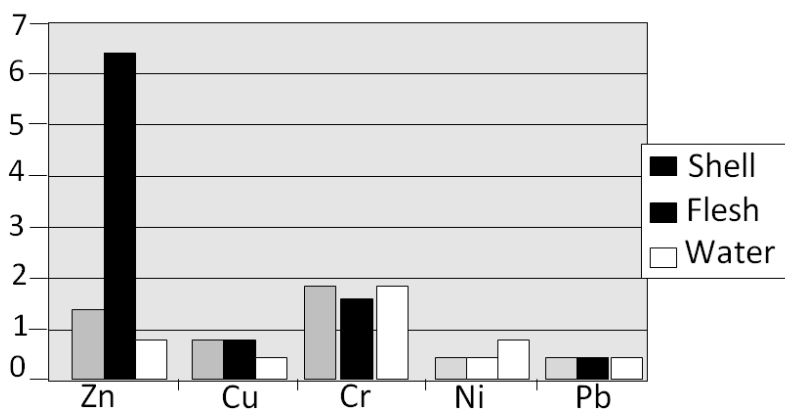


Fig 7: Mean trace Metal concentration (Ppm) in mutela ruben flesh compared with their concentration in water and shell.

Table 4: Concentration Factor (CF) of heavy metals in mutela rubens shells compared to their levels in water samples at the various sampling stations.

Site	Samples	Mental Concentration (ppm)				
		Zn	Cu	Cr	Ni	Pb
I	Water	0.83	0.39	2.02	0.83	0.40
	Shell	2.17	0.73	1.17	0.45	0.37
	CF	2.61	1.87	0.59	0.54	0.93
II	Water	0.74	0.41	1.82	0.55	0.37
	Shell	1.56	0.78	1.93	0.38	0.38
	CF	2.11	1.90	1.06	0.69	1.03
III	Water	0.66	0.41	1.77	0.55	0.36
	Shell	1.06	0.67	1.85	0.30	0.37
	CF	2.61	1.68	1.04	0.54	1.03

$$CF = \frac{\text{shell conc.}}{\text{Water}} = \frac{2.17}{0.83} = 2.61 \text{ for Zn at site I}$$



At $CF < 1$ Means no accumulation

Table 5: Concentration Factor (CF) of heavy metals in mutela rubens flesh compared to their levels in water samples at the various sampling site.

Site	Samples	Mental Concentration (ppm)				
		Zn	Cu	Cr	Ni	Pb
I	Water	0.83	0.39	2.02	0.83	0.40
	Flesh	6.30	0.90	2.10	0.45	0.36
	CF	7.59	2.31	1.03	0.64	0.90
II	Water	0.74	0.41	1.82	0.55	0.37
	Flesh	6.20	0.93	1.83	0.30	0.36
	CF	8.37	2.27	1.00	0.55	0.97
III	Water	0.69	0.49	1.77	0.55	0.36
	Flesh	6.09	0.9	1.83	0.30	0.32
	CF	8.83	2.20	1.03	0.55	0.86

$$CF = \frac{\text{Flesh conc.}}{\text{Water}} = \frac{6.30}{0.83} = 7.59 \text{ for Zn at site I}$$

At $CF < 1$ Means no accumulation

4.0 Discussion

Around the world, coastal zones are subject to the direct release of Urban and industrial discharges and such inputs are known to contain heavy metals, which may increase heavy metal concentrations in the coastal zone, some of which are toxic and can endanger human health (Al-madfal *et al*, 1988). The mean heavy metal concentrations in river water sample were high. Abdulahi (1997), reported that the high level of these metals in the lake may be related to their concentration in the stream and rivers discharging into the lake. The high level of Cr, Zn, Ni, Cu and Pb in the river indicates the quality of the water prevailing at the period of sampling.

The mean metal concentration (Pb, Cu, Zn) were similar to the observed levels for many fresh water lakes. For example, the level of Pb in the water is in agreement with the work of Anderson and Salbut (1982), who reported high level of Pb, Cu, Zn when compared with standard values by World Health Organisation (WHO) and limits of Federal Environmental Protection Agency (FEPA, 1991), thus high-lighted the possible danger of utilizing such water for drinking and other domestic activities.

Direct comparison with other river of industrialized area show that river wudil was less polluted as data obtained from this study were in sharp contrast to that of Salanki *et al*,_ (1982), who reported high levels in lake Balaton, due to the discharge of pollutants from industries surrounding the place. Imevbore (1970), reported that concentration of Pb, Cu, Zn and Ni were high in Kainji Lake. Studies on pollution monitoring in fresh water lake environment has been reported using different indicator species (Imevbore 1970; Nwadiaro and Umeham,1988; Ayodele and Abubakar,2001). High level of bioavailable contaminants (Cu and Zn) using *Mytilus edulis* from lake Vecre have been reported (Kock,1983).

Nwadiaro and Umeham, (1985) reported high concentration of metals cation and anions in Oguta lake while Abdulahi, (1979) reported fluctuations in cation and anions in river wudil.



River wudil is considered free from pollutants since human activities are minimal up stream . Contamination due to anthropogenic activities probably comes from fertilizer and pesticides used in rice, maize fields (fertilizer are a source of heavy metals chromium Cr, Lead Pb, Arsenic As and Cadmium Cd); domestic derived pollutants and transport activities to the agricultural fields and neighbouring states (Olofm. 1988; Abdullahi, 1992) The concentration of these metals in river wudil are within the levels of many fresh water lakes (Klein 1975) and their metal concentration were in the order of Cr > Zn > Ni> Cu> Pb which indicates the quality of the river water prevailing at the period of sampling. Observation from this study show that there were little variations in the metals concentration as Cr, Ni, and Zn were slightly higher than Cu and Pb and this could be connected with the sources of this metals to the river: there have been reports of seasonal differences in elemental concentrations throughout the year. These could be associated with natural variation of trace metals in aquatic environment. This has to be monitored continuously for a number of years.

Observation shows that the mean heavy metal concentrations (Cr 1.90ug/g and Cu,0.70ug/g, Pb, 0.38ug/g and Ni, 0.37ug/g) in the shells *Mutela rubens* were high when compared with standard values (Fepa, 1991) That of Zn, 1.26ug/g was low. Thesevariation in metal concentration of the shells can be related to concentration in the water. The high concentrations of Cu and Cr in the shells show that bivalves are accumulating them as the shells may be capable of metal uptake and retention, for example, Cr is important in protein metabolism while Cu as copper carbonate increases shell strength (Purchson, 1977; Bernard and Lauwerys, 1984). The order of metal accumulation in the shell, Zn> Cu> Cr> Pb> Ni suggests that metal uptake decreases with its toxicity. The observed order of Cr and Cu concentration in the shells agrees with the observed results of (Moore and Ramamoorthy,1984) who reported the bio accumulation of heavy metals by Molluscs in a fresh water environment. Other authors have reported similar observations (Qing hui and Yang, 1985 Metcalfe -Smith *et al*,1992;. Ayodele and Abubakar, 2001) in the different species of mussels studied from different parts of the world.

The concentration of metals were high (Zn, 6.19ug/g Cr, 1.65ug/g Cu, 0.91 ug/g, Pb 0.36ug/g, Ni, 0.35ug/g) in the flesh of *Mutela rubens* This indicates that the organism is accumulating the metals; accumulation takes place when concentration in the organism is higher than concentration in water. These metals were in the order of Zn> Cr> Cu> Pb> Ni. The concentration of Ni and Pb was low in the flesh of *Mutela rubens*. Strike *et al*, (1995) stated that some metals are required for life (essential elements) and some metals are not known to have any essential function in organism and they can give rise to toxic manifestation when intakes are only slightly higher than normal.

In this study, essential metals were accumulated in amounts higher than non-essential metals (Ni and Pb). This order suggests that *Mutela rubens* accumulate heavy metals according to their biological importance. Zn and Cu are biologically essential and play important role as co-factors in enzymatic processes (Singh and Steinnes,1994; loyld,1963). Zn (6.19ug/g) showed highest concentrations. Generally Oysters have been considered as strong accumulators of Zinc, and these organism accumulate high concentration of zinc in detoxified granules (George *et al*, 1978). With regard to Cu, Eisler, (1981) observed that some species could exhibit high Cu concentrations due to proximity to anthropogenic source or biotic /a biotic factors capable of modifying Cu uptake and retention.

Rainbow (1988), reported that heavy metal are taken up and accumulated by marine invertebrates with tissue and body concentrations usually higher in a wet weight basis than concentrations in the surrounding seawater.



The mean metal concentration ($\mu\text{g/g}$) in *Mutela rubens* flesh compared with their concentration in the shell and water sample were high (Zn, Cr, were higher in the flesh and shells than in the water samples). This indicates *Mutela rubens* to be good accumulator of these metals as confirmed by Singh and Steinnes, (1994). The mean concentration of Cr was higher than those of Cu in the shells. This suggest that the ability of *Mutela rubens* to concentrate Cr is larger than for Cu and that Cr have been accumulated to play certain physiological and protective function (Ayodele and Abubakar 2001). However there was no significant difference ($P < 0.05$) in heavy metal concentration for Cr and Cu in the flesh, shells and water samples collected from the three various sampling sites. Accumulation of Ni and Pb were lower in flesh than in shells. Ni and Pb may be toxic and less beneficial to the organism Strike *et al.* (1995) reported that some metals are not known to have any essential function in organism and they can give rise to toxic manifestation when intake are only slightly higher than normal. Zn showed highest concentration in the flesh compared to those of the shell and water samples. (Martins et al 1995; Ayodele and Abubakar 2001) The concentration factors of metals in flesh were in most cases higher than in shells in all the sampling areas. Thus, the accumulation of heavy metals by *Mutela rubens* flesh or shells shows that *Mutela rubens* is a very suitable species as an indicator of heavy metal pollution. Mollusc such as bivalves have been used as bio-indicators of pollution because they are abundantly available, easy to harvest and have the ability to concentrate heavy metals to several other magnitude above ambient levels

Concentrations of metals were low compared to other polluted areas but when compared with the National water quality for human consumption (FEPA, 1991), these concentration are higher and this may pose a health risk if taken as drinking water presently, According to the Federal Ministry of Environment the maximum allowable limits for metals in aquatic life should not exceed their limit depending on the metals, for chromium 0.02 $\mu\text{g/l}$, Zinc 50 $\mu\text{g/l}$ and lead 1.7 $\mu\text{g/l}$ (Appendix v) excess of essential metals like copper, zinc, Manganese and cobalt are toxic (Strike *et al.*, *et al* 1916). Lead is associated with mental retardation, premature loss of teeth and others.

The high concentration factors for Zn, Cu and Cr in shells and flesh of *Mutela rubens* indicates that the metals have been accumulated therefore the species can be used as bio-indicator.

4.1 Summary

Water samples, the shells and flesh of *Mutela rubens* were collected from river wudil between February to May 2013. The samples were analyzed for their metal content in laboratories of chemistry and Biological Sciences Departments of Bayero University, Kano-Nigeria. The result have shown that, the shells and flesh of *Mutela rubens* accumulated all the metals analysed (Zn, Cr, Cu but not Ni and Pb). Hence mollucs can provide useful information on the availability of metals deposited on the shells and flesh. The shells and flesh can serve as a bio-indicators for some of the heavy metals analyzed.

One way of monitoring contaminants in the fresh water environment is to make use of appropriate bio-accumulating organisms, indicting the relative amounts of potentially harmful compounds that are available. This is important since toxic physiological effects are related to the internal concentrations of the compound.

4.2 Conclusion

Based on the monitoring survey of chromium and copper, zinc, lead and nickle concentrations in water and the bivalves collected from river wudil the following conclusion could be made.

The Oyslers (*Mutela rubens*) can be used as a bio-indicator to monitor pollution in ^EtgLlafce. This can be inferred based on the amount of these heavy metal present in the samples and the amount required in normal water quality. Although chromium, copper and zinc concentrations were elevated in bivalve and water, these may not pose



any threat to the river fauna except Pb and Ni since they do not have any essential function and their level in water (aquatic life) is not above the recommended limit.

From this study, the concentrations of these metals in the river within those that may be found for the unpolluted regions.

Therefore a continuous monitoring of the area is recommended considering that the river is a site of important fishing, aquaculture activities, irrigation, mechanized farming and future increased loading of agro-industrial effluents and domestic waste to ascertain their long term effects which may not yet have been revealed.

REFERENCES

- [1]. Abdullahi, B.A (1979) *zoo Plankton studies of river wudil, kano-nigeria*. Unpublished Msc thesis, Bayero University, Kano, M.Sc. Thesis.
- [2]. Anderson, B. and Salbu, U. (1982) Determination of trace element in sea water using Mg (OH)₂ scavenger as a pre-concentration agent. *Brit. Radiochem. Lett.*, 52(1) pp. 19-28 (CA:101 1084 68^a).
- [3]. Ayodele, J.T and Abubakar M.B (2000) Trace metal levels in river wudil, Kano Nigeria *Trop. Journ of Environ. Res.* 3:230-237.
- [4]. Ayodele, J.T and Abubakar M.B (2001) *Cleopatra bulimode and Mutela rubens* as bio-indicators of heavy metals in river wudil, Kano Nigeria. *Research Journal of Science*, 7: Nos. 1 & 2.
- [5]. Ayodele J.T. and Abubakar M.B (2002) Metal accumulation in sediment and in the shells of two species of fresh water mollusc in river wudil, Kano Nigeria. *Nigeria Journal of Basic and Applied Science*. 11:81-90.
- [6]. Ayodele J.T, Abubakar M.B and Ogunga E.O (2002) lake chemistry: trends in river wudil, Kano-nigeria *environs. Res.* 4:255-266.
- [7]. Bernad, A and Lauwerys, R. (1984), Trace metals:- Exposure and health effect, *Experiential*, 40:145.
- [8]. Bowen, H.J.M (1979) *Environmental chemistry of the elements*; Academic Press, London. 2:222 – 225.
- [9]. Bryan, C.R (1983) The occurrence and seasonal variation of trace metals in the scallops *pectin maximus* (L) and *Chlamys opercularis* (L), *J. Mar. Biol. Ass. U.K* 53: 145-166.
- [10]. Bryan, - Smith, D. (1871) Lead Pollution a growing hazard to public health chemistry in Britain *Afri Journ. Of Nat. Sci.* (2) 54-56.
- [11]. Eisler, E. (198) *Trace Metal Concentration in marine organisms*. Plergamon, New York, 685.
- [12]. Elder J.F. and Collins, J.J (1991) Fresh water mollusc as indicator of bio availability and toxicity of metals in surface water system *Environmental Contamination and Toxicology* 12: 37-79.
- [13]. FEPA, (1991) Federal Ministry of Environment. National guidelines and standards for water quality in Nigeria pp. 14.
- [14]. Friberg L; piscator, M and Nordberg G. (1971) Cadmium in the environment, Chem Robber Co. Cleveland, Ohio.
- [15]. George, S. G Pirie B.J.S; Cheyne, A.R., Coombs, T.L and Grant P.T. (1978) Detoxification of metals by marine bivalves: An ultra structural study of the compartmentation of copper and zinc in the oyster *ostrea edulis* *Mar. Biol.* 45: 147-156.
- [16]. Hui, H.Y. (1992) *Encyclopedia of food science and technology*. John Willey and sons Inc. USA 1 452 – 482, (3). [1805 – 1819, 42587 – 2597].
- [17]. Imevbore, A.M.A; (1970): The chemistry of the River Niger in the Kainji Reservoir area *Arch. Hydrobiol.* 67:112- 131.
- [18]. Jones, M.J. (1992) *Foods safety*, Eagan press.



- [19]. Kock, W. (1983) Monitoring bio-available marine contaminants with mollusks (*Mytilus edulis*) in the Netherland: *Environment Monitoring and Assessment* 1. 209-220.
- [20]. Martin, G. F, Monica A.O, Isidro O.J (1999) Heavy metal in the rock oyster *Crassostrea Irridescens* Mazatlan, Mexico., *Revista de Biologia Tropical*. 10:1-9.
- [21]. Metcalfe-Smith, J.R; Merriman, J.C and Batchelor (1992); Relationship between concentration of metals in sediment and two species of fresh water mussels in Ottawa River; *Jour of water pollut. Res*, Canada, 27(4): 845 – 869.
- [22]. Nwadiaro, C.S and Umeham S.N (1985): The chemical hydrology of Oguta Lake, Imo Sate Southern Nig. *Arch. Hydrobiol*. 105.251 – 269.
- [23]. Philips, D.H.J (1977) The use of biological indicator organisms to monitor trace metal pollution in marine and estuarine environments. A review: *Environ, pollut* 13. 281 – 317.
- [24]. Philips, D.J.H and Rainbow P.S (1993) *Bio monitoring of trace aquatic contaminants*. Elsevier, New York 371.
- [25]. .Prasad, A.S (1978) *trace elements and iron in human metabolism*. Plenum publishing corporation U.S.A,
- [26]. Purchson, R.D (1977): *Biology of the Mollusca*, 2nd Ed. Academic Press London. 105 – 109.
- [27]. Quinghui, X. U. and Yang C. (1985) Heavy metal content in mussel's flesh and shell: *Heiyang Nuebao* 7 (5): 646 -619.
- [28]. Rainbow, P.S (1988) The Significance of trace metals concentration in decapods. *Symp of London, Soc*. 59:291-299.
- [29]. Rainbow, P.S (1993) The Significance of trace metals concentration in marine invertebrate, R. Dallinger and rainbow P.S (eds) *Ecotoxicology of metals in invertebrates*. Levis, Boca Raton, Florida.
- [30]. Salanki, J.K Balogh. V. and Berta, E. (1977) Heavy metals in animals of Balaton *Water Res*. 16:1142 – 1152.
- [31]. Simpson, R.D (1979) Uptake and loss of zinc and lead by mussels (*mytilus edulis*) and relationships with body weight and reproductive cycle *Marine pollut*. Bull 10:74-74.
- [32]. Singh, B. R. and Steinnes E. (1994) Soil and water contamination by heavy metals in R.Lai and Steinnes, process and water quality. Lewis Boca Raton. Florida.
- [33]. Strike, J.J.T.A.; Leeuwangle P. and Musch A. (1995) *Ecotoxicology handbook*. 17 – 28.
- [34]. Watling, H.R and Watling R.J (1976). Trace metals in [*Chloromytilus meridionali mar pollution Bull*] 7.3 – 24.
- [35]. Widows, J. Phelps, D. K. and Galloway W. (1981) Measurement of Physiological conditions of mussels translated along a pollution in Noir angansett Bay. *Mar Environ Res*. 4.181 – 194. `