



INFLUENCE OF HEAVY METAL AROUND GOLD MINING CITES ON WATER, FISH AND SEDIMENT.

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Abstract:

*The concentrations of heavy metals in water, sediment and fish (*TillapiaMonsambicus*) in the three major dams in Zamfara State along gold mining vicinities were determined using standard methods for two years (four seasons). The concentration of heavy metals determined in water, sediment, and fish were generally high during the dry season with exception of Hg which recorded its highest concentration across the seasons. Zn and Cr levels in the water, sediment, and fish were within international safe limits while Cd (0.1022 mg/l), Pb (0.2104 mg/l) and Hg (1.8818 mg/l) levels were far above (0.01, 0.01 and 0.001mg/l) USEPA safe limits respectively for drinking water. Two major pollution indices such as contamination factor (CF) and pollution load index (PLI) were used for determining the contamination level of water, sediment, and fish samples. The result showed a high contamination factor for Cd, Pb and Hg in all the six locations accessed and a general overall pollution load across all the locations. Generally, the concentration of the analyzed heavy metals in mg/l for water and sediments were in the order of $Hg > Pb > Cd > Cr > Zn$. Correlation analysis revealed a significant and positive relationship for Cd and Zn and Hg and Cr during the wet season and a significant positive relationship at the ($p > 0.05$) for Cr and Zn in the dry season. The pollution index value of the water samples across all the three dams indicated that there is need for immediate intervention to ameliorate pollution particularly in the dry season.*

Keyword: Dams, Heavy metals, sediments, fish and gold mining.

Introduction: The increasing artisanal mining at low and large scale is now being paralleled with a corresponding challenge of waste management and disposal in Nigeria particularly in Zamfara State. This is to say that the hitherto clean, fresh and safe ecological setting is today exposed to the hazard of environmental pollution which has a potential deleterious effect to

both biota, flora and the fauna of the ecosystem as a whole (Mukhtar et al, 2007). Gold mining and processing have been the main sources of heavy metal contamination in the environment (Duruibeet *al.*, 2007; Boamponsemet *al.*, 2010; Girigisuet *al.*, 2012). The uncontrolled dissemination of waste effluents to large water bodies has negatively affected both water quality and

aquatic life (Abdulrahman, *et al.*, 2008). During the processing of the ores for gold, poisonous substances such as oxides and sulphides of heavy metal pollutants are released into the environment Boamponsemet *et al.*, (2010). Artisan gold mining is an important economic sector in many developing countries, especially Nigeria. However, limited resources and lack of training, and the availability of cheap, but potentially hazardous methods of extraction and processing of the minerals can cause significant threats to both miners and the local environment (Bitala, 2008; Armahet *et al.*, 2010). Such is the scenario being experienced in mining locations in Zamfara State. At the peak mining periods, up to 5000 people invade the mining areas from outside the State. This has devastating effects on health and environment.

It is observed that artisan mining in these areas conforms to neither mining laws nor regulations governing mining operations and environmental management. Studies in a similar region, in Tanzania revealed that symptoms of heavy metal poisoning such as sensory disturbance, hyporeflexia, tremor, gingivitis, metallic taste, neuroasthenia and night blindness are common (Harada *et al.*, 1997; Akabzaa, 2000; Lottermoser, 2007). There have been several reports on acute lead (Pb) poisoning outbreak among the dwellers of some remote villages of Zamfara State, Nigeria. This has been linked to the illegal mining operations by the people in the remote communities (Galadima, 2012).

Mercury as a pollutant in artisan mining is due mainly to gold processing, when mercury is used to amalgamate gold. Cadmium, which is another common toxic metal, occupying position seven in the priority list of hazardous substances (ATSDR, 1999), generally occurs as an isometric trace element in sphalerite. Cadmium levels are likely to be quite low. Large amounts of Hg are released into the

environment as a result of its usage in gold extraction. About 1.32 kg of Hg is lost for every 1 kg of gold produced which goes directly into water, soil and streams as inorganic Hg and later converted into organic forms (Matshusa *et al.*, 2012). The aim of the research is to investigate the levels of heavy metals in water, fish and sediment in dams around the vicinities of gold mining areas in Zamfara State, Nigeria.

MATERIALS AND METHODS

In the preparation of solution, analytical reagent grade chemicals and distilled water were used. All glassware were washed with detergent and rinsed in water before immersion in 10% nitric acid solution. (Ayodele *et al.*, 1994).

Description of the Sampling Area

The dams selected for this analysis are located in Gusau LGA (Gusau dam), Maradun LGA (Bakolori dam), and Maru LGA (Dangulubi dam). The dams are considered for investigation as a result of lead poisoning epidemic that struck the state sometimes around year 2012. The dams became very necessary to investigate because mining activities are still going on across the state in which water from the dams are used in the mining processes coupled with livestock seen drinking from the dams and fishes are also being harvested both for consumption and commercial purposes.

Collection of water, sediment and fish Samples from the Dams

The water samples were collected by dipping a two litre plastic bottle just below the water surface at a depth of one meter from each of the six sampling locations. Sediment samples were collected using a plastic spoon by scooping the top layer sediments and then stored in a pre-cleaned 1000 ml polyethylene container, labeled and transported to the laboratory for storage in freezers awaiting analysis. Nine (9) pieces of Tilapia (*Oreochromis mossambicus*) fish samples of 28 cm average length and 52 g

average weight, three from each of the three sampling locations was collected by a local fisherman. The fish samples were rinsed with distilled water immediately to remove any adhering contaminants and were stored in a frozen pre-cleaned polythene bags. Digestion of Water Samples for Heavy Metal Analysis and sediments including fish

samples was done according to the method by APHA, 2005.

Contamination factor (CF): The Contamination factor (CF) is the ratio obtained by dividing the concentration of each metal in the sediment, water and fish samples by

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times CF_4 \dots \times CF_n}$$

RESULTS AND DISCUSSION

Table 1a: Heavy Metals Concentrations (mg/l) of Water Samples for Two wet and dry Seasons

location	season	Zn	Cd	Cr	Pb	Hg
L1	Wet 1		0.0040±0.0001	0.0210±0.0003	0.0918±0.0004	0.2638±0.0000
	Wet 2	0.0024±0.0001	0.0036±0.0002	0.0262±0.0040	0.0029±0.0001	1.5532±0.0030
L2	Wet 1	0.0060±0.0001	0.0064±0.0003	0.0078±0.0003	0.0476±0.0020	ND
	Wet 2	0.0066±0.0001	0.0024±0.0002	0.0044±0.0003	0.0068±0.0001	0.5005±0.0030
L3	Wet 1	0.0042±0.0002	0.0024±0.0001	0.0014±0.0004	0.0126±0.0002	ND
	Wet 2	0.0049±0.0003	0.0066±0.0005	0.0042±0.0002	0.0480±0.0020	0.5308±0.0030
L1	Dry 1	0.0244±0.0002	0.0904±0.0001	0.0682±0.0030	0.1376±0.0040	ND
	Dry 2	0.0112±0.0020	0.2044±0.0020	0.0694±0.0040	0.0062±0.0001	1.5570±0.0030
L2	Dry 1	0.0068±0.0001	0.0740±0.0003	0.0034±0.0003	0.0876±0.0020	ND
	Dry 2	0.0266±0.0010	0.0744±0.0020	0.0304±0.0030	0.1314±0.0010	0.5573±0.0030
L3	Dry 1	0.0076±0.0002	0.0550±0.0010	0.1090±0.0040	0.0334±0.002	ND
	Dry 2	0.0118±0.0030	0.0140±0.0050	0.1098±0.0020	0.0668±0.0020	0.8506±0.0030

n = 3; mean ± S.D .key: L1= Gusau dam, L2= Bakolori dam and L3= Dangulbi dam

Table 1b: Correlation matrix of Heavy Metals Concentrations (mg/l) in Water Samples for Two Wet seasons

Correlations	For wet				
	Zn	Cd	Cr	Pb	Hg
Zn	1				
Cd	.394*	1			
Cr	-.130	-.074	1		
Pb	-.021	-.128	-.102	1	
Hg	-.023	.280	.365*	.034	1
	36	36	36	36	36

*Correlation is significant at the 0.05 level (2-tailed)

Table 1c: Correlation matrix of Heavy Metals Concentrations (mg/l) in Water Samples for Two Dry seasons

Correlations	For dry				
	Zn	Cd	Cr	Pb	Hg
Zn	1				
Cd	-.023	1			
Cr	.565**	-.247	1		
Pb	.243	-.306	.056	1	
Hg	-.017	.233	.025	-.189	1
	36	36	36	36	36

** . Correlation is significant at the 0.01 level (2-tailed).

Table 1d: Heavy Metal Contamination Factors (CF) and Pollution Load Index (PLI) in Water for Wet and Dry Seasons.

Location/WET	Zn	Cd	Cr	Pb	Hg	PLI
Gusau dam	0.0004	0.3800	0.2360	0.9470	90.8500	0.3206
Bakolori dam	0.0013	0.4400	0.0610	0.5440	50.0500	0.2486
Dangulbi dam	0.0009	0.4500	0.0280	0.6060	53.0800	0.2053
DRY						
Gusau dam	0.0035	14.7400	0.6880	1.4380	155.700	1.5188
Bakolori dam	0.0033	7.4200	0.1690	2.1900	557.300	1.3858
Dangulbi dam	0.0019	3.4500	1.0940	1.0020	850.600	1.4423

Table 2a: Heavy Metals Concentrations (mg/kg) of sediment Samples for Two wet and dry Seasons

location	season	Zn	Cd	Cr	Pb	Hg
L1	Wet 1	0.258 ±0.002	0.034±0.001	0.209±0.003	0.469±0.004	ND
	Wet 2	0.238±0.002	0.029±0.002	0.379±0.004	1.063±0.001	1.850±0.003
L2	Wet 1	0.058± 0.001	0.022±0.003	0.183±0.003	0.396±0.002	ND
	Wet 2	0.044± 0.001	0.004±0.002	0.144±0.003	0.261±0.001	1.801±0.003
L3	Wet 1	0.054± 0.002	0.027±0.001	0.072±0.004	0.896±0.002	ND
	Wet 2	0.059±0.003	0.011±0.005	0.288±0.002	0.521±0.002	0.720±0.003
L1	Dry 1	0.571 ±0.002	0.256±0.001	1.933±0.003	2.471±0.004	ND
	Dry 2	0.432±0.002	0.688±0.002	1.903±0.004	1.960±0.001	3.227±0.003
L2	Dry 1	0.165± 0.001	0.944±0.003	0.545±0.003	0.450±0.002	ND
	Dry 2	0.111± 0.001	0.511±0.002	0.541±0.003	0.365±0.001	0.896±0.003
L3	Dry 1	0.123± 0.002	0.472±0.001	0.690±0.004	1.135±0.002	ND
	Dry 2	0.080±0.003	0.275±0.005	0.694±0.002	0.584±0.002	2.563±0.003

n = 3; mean ± S.D .key: L1= Gusau dam, L2= Bakolori dam and L3= Dangulbi dam

Table 2b: Correlation matrix of Heavy Metals Concentrations (mg/kg) in sediment Samples for Two Wet seasons

Correlations	For wet				
	Zn	Cd	Cr	Pb	Hg
Zn	1				
Cd	.319*	1			
Cr	.636**	.624**	1		
Pb	.189	.504**	.231	1	
Hg	.125	.499**	.389*	-.177	1
	36	36	36	36	36

** .Correlation is significant at the 0.01 level (2-tailed), * .Correlation is significant at the 0.05 level (2-tailed).

Table 2c: Correlation matrix of Heavy Metals Concentrations (mg/kg) in sediment Samples for Two Dry seasons

Correlations	For dry				
	Zn	Cd	Cr	Pb	Hg
Zn	1				
Cd	-.273	1			
Cr	.422*	.251	1		
Pb	.332*	.073	.797**	1	
Hg	.066	.449**	.130	-.194	1
	36	36	36	36	36

*.Correlation is significant at the 0.05 level (2tailed), **.Correlation is significant at the 0.01 level (2tailed).

Table 2d: Heavy Metal Contamination Factors (CF) and Pollution Load Index (PLI) in sediment for Wet and Dry Seasons.

Location/WET	Zn	Cd	Cr	Pb	Hg	PLI
Gusau dam	0.0005	1.4500	3.9650	29.7500	1151	2.5333
Bakolori dam	0.0009	1.5500	1.3650	118.2500	1183	3.0417
Dangulbi dam	0.0011	1.2000	0.8650	39.1000	0523	1.8709
DRY						
Gusau dam	0.0007	34.4000	7.3300	30.7500	4363	7.4314
Bakolori dam	0.0010	27.5000	3.1900	78.7000	2527	7.0383
Dangulbi dam	0.0016	51.1000	11.575	62.9500	1343	9.6111

Table 3a: Heavy Metals Concentrations (mg/kg) of fish Samples for Two wet and dry Seasons

location	season	Zn	Cd	Cr	Pb	Hg
L1	Wet 1	0.055 ±0.002	0.024±0.001	0.098±0.003	0.240±0.004	ND
	Wet 2	0.057±0.002	0.198±0.002	0.261±0.004	0.198±0.001	0.887±0.003
L2	Wet 1	0.010 ± 0.001	0.014±0.003	0.092±0.003	0.177±0.002	ND
	Wet 2	0.040 ± 0.001	0.438±0.002	0.235±0.003	0.438±0.001	0.796±0.003
L3	Wet 1	0.021± 0.002	0.028±0.001	0.059±0.004	0.177±0.002	ND
	Wet 2	0.028±0.003	0.448±0.005	0.072±0.002	0.448±0.002	0.476±0.003
L1	Dry 1	0.077 ±0.002	0.845±0.001	0.810±0.003	0.907±0.004	ND
	Dry 2	0.075±0.002	0.201±0.002	0.850±0.004	0.479±0.001	1.176±0.003
L2	Dry 1	0.024± 0.001	0.904±0.003	0.430±0.003	0.292±0.002	ND
	Dry 2	0.019 ± 0.001	0.538±0.002	0.433±0.003	0.677±0.001	0.871±0.003
L3	Dry 1	0.026± 0.002	0.826±0.001	0.682±0.004	0.187±0.002	ND
	Dry 2	0.036±0.003	0.609±0.005	0.697±0.002	0.477±0.002	0.871±0.003

n = 3; mean ± S.D .key: L1= Gusau dam, L2= Bakolori dam and L3= Dangulbi dam

Table 3b: Correlation matrix of Heavy Metals Concentrations (mg/kg) in fish Samples for Two Wet seasons

Correlations	For wet				
	Zn	Cd	Cr	Pb	Hg
Zn	1				
Cd	-.083	1			
Cr	.055	.266	1		
Pb	.162	.633**	.111	1	
Hg	.118	.763**	.530**	.137	1
	36	36	36	36	36

**Correlation is significant at the 0.01 level (2-tailed),

Table 3c: Correlation matrix of Heavy Metals Concentrations (mg/kg) in fish Samples for Two Dry seasons

Correlations	For dry				
	Zn	Cd	Cr	Pb	Hg
Zn	1				
Cd	.228	1			
Cr	.823**	-.023	1		
Pb	-.334*	-.206	-.371*	1	
Hg	-.040	-.828**	.025	.082	1
	36	36	36	36	36

*.Correlation is significant at the 0.05 level (2tailed), **.Correlation is significant at the 0.01 level (2tailed).

Table 3d: Heavy Metal Contamination Factors (CF) and Pollution Load Index (PLI) in fish for Wet and Dry Seasons.

Location/WET	Zn	Cd	Cr	Pb	Hg	PLI
Gusau dam	0.0011	11.0000	1.7950	21.9000	887	3.3621
Bakolori dam	0.0005	22.6000	1.6350	30.7500	796	3.4103
Dangulbi dam	0.0005	23.8000	0.6550	31.2500	476	2.5769
DRY						
Gusau dam	0.0015	52.3000	8.3000	69.300	1176	8.8331
Bakolori dam	0.0004	72.1000	4.3150	48.4500	871	5.6278
Dangulbi dam	0.0006	71.7500	6.8750	33.200	585	5.6886

Water

The concentration of Pb and Hg in the water samples (Table 1a) from this water bodies exceeded the permissible limit of 0.05 and 0.001 mg/L respectively set by (WHO, 2004; USEPA, 2002). In this work, the concentration of the analyzed heavy metals in mg/l was in the order of Hg>Pb>Cd>Cr>Zn. The abnormal high contamination factor (CF) level (table 1d) of Hg was expected across all the three dams since gold processing is still very active in these areas. The higher contamination factor for all the heavy metals during the dry season might be due to seasonal rainfall which dilutes some

concentration of the metal concentration during the wet season. The pollution load index value of the water samples across all the three dams indicated that there is need for immediate intervention to ameliorate pollution particularly in the dry season. This is in agreement with the work of (Ashokkumaret al., 2009). Correlation analysis (Tables 1b and 1c) showed a significant and positive relationship for Cd and Zn and Hg and Cr during the wet season and a significant positive at the (p>0.05) relationship for Cr and Zn in the dry season. Similar observation was reported on the study of heavy metals in Ureje dam in Ado-

Ekiti by Adefemiet *al.* (2007) and in Kanji dam (Amooet *al.*, 2005) and other studies on surface water (Chapman, 1999; Asaolu *et al.*, 1997; Karadede *et al.*, 2000). **Sediments:** Concentration of heavy metals in sediment (table 2a) showed spatial and temporal variation at all the locations during the study period. The relative abundance of different metals at the three locations during the study period varied with location and with season. All the metals examined except Zn were measured in relatively high concentration across all the locations during the period of investigation. A significant positive relationship was established for Cr and Zn, Cr and Cd, Pb and Cd, Hg and Cd and Hg and Cr respectively during the wet seasons. While during the dry season it showed a significant and positive relationship for Cr and Zn, Pb and Zn, Pb and Cr and lastly Hg and Cd (table 2b and 2c). The levels of Zn were generally low and the values were lower than the mean (0.73 mg/kg) reported by Ado *et al.* (2012) and much lower than 7.8 - 830 mg/kg reported by Ajao *et al.* (1991) and 128-308 mg/kg reported by Ong and Kamaruzzaman, (2009) and 76 -1200 mg/kg in surface sediment across Stockholm (Sebastien, 2007).

The concentrations of Zn in the sediment of this water bodies was observed to be higher than the permissible limits of 123 $\mu\text{g/g}$ set by (CPCB, 2010; USEPA, 2002). The levels of cadmium in the sediment samples from the three sampling locations in this work were above the (WHO, 2004) standard value of 6 $\mu\text{g/g}$. The acute toxicity of chromium to saltwater organisms is extremely variable Manceet *al.* (1984). Aderinola *et al.* (2009) reported a mean value of 0.66 mg/kg which is lower than the mean obtained from most of the locations. According to WHO guideline value for sediment, the concentration of 25 $\mu\text{g/g}$, Cr is acceptable (Radojevic *et al.*, 1999). The Cr concentrations in sediment samples did exceed this limit, indicating pollution of this water bodies in the state. The concentration recorded for Pb in all the location was between 0.229 – 2.831 mg/kg. The mean for some locations were higher than the average

(0.45 mg/kg) reported by Aderinola *et al.* (2009) for the Ijora section of the lagoon. The levels of lead in the analyzed sediment samples showed that the limiting value set by USEPA of 10 $\mu\text{g/g}$ was exceeded. The level of Pb in the sediment samples from this water bodies might be attributed to heavy agricultural run-off which contains fertilizers, mining activities, agrochemicals and pesticides (Bassey *et al.*, 2014). The abnormal high contamination factor (CF) level (table 2d) of Hg was expected across all the three dams since gold processing is still very active in these areas. The higher contamination factor for all the heavy metals during the dry season might be due to seasonal rainfall which dilutes some concentration of the metal concentration during the wet season. The pollution load index value of the sediment samples across all the three dams indicated that there is need for immediate intervention to ameliorate pollution particularly in the dry season.

Fish: Fish is widely acceptable for consumption because of its high palatability, low cholesterol and tender flesh (Ado *et al.*, 2012) and also a cheap source of protein. Medhiet *al.*, (2012) linked the accumulation of the toxicants in the fish to the possibilities of the fish to accumulate metals and thus could serve as indicators of pollution. The concentration of Zn in fish in this work, fall below the maximum zinc level permitted for fish (50 mg/kg) according to Food Codex and WHO, 2004. The values recorded for this work are lower compared to Zn values reported for freshwater fishes in China (Du *et al.*, 2012). United States environmental protection agency and the European Commission (US-EPA and EC) have not considered any standards or limits for the zinc concentrations in fish (WHO, 2008). The concentration of Cd was generally high across all the six locations especially in the dry season. Gusau and Bakolori dams also showed very high Cd concentration of 0.845 mg/kg and 0.904 mg/kg respectively. This may have come from natural sources, run-off from agricultural soils around the dams and rivers where phosphate fertilizers are in use,

and more so, during the dry season when the volume of water of ponds and wells has reduced, miners relocate the mining processing closer to the dams and rivers where there is large volume of water, this was also in agreement to the report of (Stoeppler, 1991; Dimariet *et al.*, 2008). The concentration of Cr was generally high across all the locations especially in the dry season. Gusau and Dangulbi dams also revealed high Cr concentration of 0.850 mg/kg and 0.697 mg/kg respectively. The concentrations of lead across all the locations are generally high when compared with the 0.01 mg/kg maximum permissible level (NIS 554, 2007; WHO, 2003). The observed heavy metal concentrations in this fish are above the 0.001 mg/kg recommended limit for human consumption (Davies *et al.*; 2006; Olowuet *et al.*, 2010; WHO, 2003). The public health implication of this work seems to show possibility of acute toxicity of the heavy metal of edible fishes consumed at these locations (Oshisanja and Oshisanya, 2009). This is more so because levels of Cd, Cr, Pb and Hg were above normal range in minimum allowable in the diet of man. Correlation analysis was conducted to examine whether there is a relationship between the heavy metal concentrations in the fish sample for two wet and dry seasons. The result revealed a significant positive relationship for Pb and Cd, Hg and Cd and Hg and Cr respectively for wet seasons. This may explain the consistent variation of these metals in the locations in different seasons.

CONCLUSION: The levels of the metals in the water bodies were generally high with exception of Zn metal which should cause trepidation to both the aquatic lives and human health, hence calling for urgent regular monitoring of the dam and control of anthropogenic input into the water bodies. The pollution level of all the three dams and sample was accessed using the contamination factor (CF) and pollution load index (PLI), which revealed that all the water bodies have suffered from metal pollution particularly of Pb, Cd and Hg.

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