



## SPECIATION OF METALS IN SEDIMENTS FROM DAMS AND RIVERS ALONG GOLD MINING VICINITIES IN ZAMFARA STATE

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### ABSTRACT

Sediments samples from three dams and rivers in Zamfara State were analyzed for chemical association of the metals (Zn, Cd, Cr, Pb and Hg) using sequential extraction method to determine the amount of the heavy metals available for absorption. The concentrations were determined in four fractions. The concentration of heavy metals in the food crop (tomatoes) was also determined using atomic absorption spectrometry (AAS). The sequential extraction was carried out using (1.0 g) of powder sample weighed into a glass centrifuge (60 ml) and fractions were obtained. Comparing the way the metals were bound to the different fractions in the sediments, it showed clearly that the metals in the sediments are bound to different fractions with different strength. Cd and Cr were primarily in the carbonate bound fraction while Zn and Hg appear mainly in the residual phase. Pb was found in carbonate, exchangeable and water soluble fractions. The distribution of the five metals studied revealed their differences in mobility. From the five elements studied, Cd (14.739-39.931%) and Pb (0.105- 9.832%) appeared to be the most readily solubilized, thus making these elements the most potentially bioavailable. This may present a real threat as Cd and Pb are transferred into the food chain from soil contaminated by these metals. Zn and Cr levels in the tomatoes, were within international standard 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 standard for drinking water. Two indices such as contamination factor (CF) and pollution load index (PLI) were used to calculate the contamination level of the tomatoes samples. The result showed a high contamination level for Cd, Pb and Hg and a general high overall pollution load across all the locations.

**Keywords:** sediments, chemical speciation, dams, rivers, heavy metals

### INTRODUCTION

Research showed that from natural aquatic environment, many chemical parameters are available in low concentration. This concentration increases as a result of rapid growth of population, increased urbanization, industrial activities and exploitation of natural resources (Mehedi *et al.*, 1999). Pollution and contamination of natural water bodies by industrial discharge, agricultural practices and domestic activities have emerged as major challenges in a densely populated country like Nigeria. Contamination of the environment usually result from industrial activities, such as mining, electroplating, gas exhaust, energy and fuel production, fertilizer and pesticides application, and generation of municipal waste (Olaofe *et al.*, 2004). Gold mining and processing have been the main sources of heavy metal contamination in the environment (Duruibe *et al.*, 2007; Boamponsem *et al.*, 2010; Girigisu *et al.*, 2012). The uncontrolled dissemination of liquid waste to large water bodies has negatively impaired on both water quality and aquatic life (Abdulrahman *et al.*, 2008). The processing of the ores for gold produces poisonous heavy metals substances such as oxides and sulphides that are released into the environment (Boamponsem *et al.*, 2010). As a result, most of the water sources, particularly in Zamfara State, are gradually becoming polluted due to the addition of these foreign materials from the environment. Different aquatic organisms often respond to external

contamination in different ways, where the quantity and form of the element in water, sediment, or food will determine the degree of accumulation (Abdulrahman *et al.*, 2008; Olaoye and Onilude, (2009). Certain environmental conditions such as salinity, pH, and water hardness can play an important factor in heavy metals accumulation up to toxic concentrations in living organisms and cause ecological damage (Garba *et al.*, 2010). Thus, heavy metals acquired through the food chain as a result of pollution are potential chemical hazards that threaten consumers (Olaofe *et al.*, 2004). Artisanal mining is a vital economic sector in many developing countries. However, limited financial resources and technical training, and the availability of cheap, but potentially hazardous methods of extraction and processing of minerals can cause major threats to both miners and the environment (Bitala, 2008; Armah *et al.*, 2010). This is the experience in the mining locations in Zamfara State. At the peak of mining periods especially in Zamfara State, up to 5000 people invade the mining areas from within and outside the State. This usually produces devastating effects on health and environment. Surface waters in close proximity to the mining industries are at a great risk of contamination due to waste discharges from mining activities (UNEP, 2010). To assess the environmental impact of polluted sediments, information on metal concentrations alone is not enough to

understand the environmental behavior of heavy metals available in different chemical form in the sediments (Stecko and Bendell –Young, 2000; Bendell – Young *et al.*, 2002). Research on the distribution and separation of heavy metals in sediments can provide information on the degree of pollution and the actual environmental impact of metal bioavailability as well as their origin (Rauret *et al.*, 1988; Lopez-Gonzales *et al.*, 2006). The most labile are metals associated with water soluble ions, exchangeable and carbonate that can easily be remobilized by changes in environmental conditions such as pH, salinity etc. (Perez *et al.*, 1991). Therefore, a proper understanding of factors such as the mobility, transport rates, paths and sinks of sedimentary particles and associated contaminants will be necessary for predicting both the fate of substances that have been introduced into the dams and rivers as well as any risk associated with their presence.

### MATERIALS AND METHODS

**Sampling Points:** The sampling area are in Zamfara State which is located in the North Western region of Nigeria between Latitude 11° 40' E and Longitudes 7° 25' E at an altitude of 420 m. The dams are located in Gusau LGA (Gusau dam), Maradun LGA (Bakolori dam), and Maru LGA (Dangulbi dam). The rivers are located in Anka LGA of the state; they are Abare, Sunke and Bagega which are contaminated with lead poisoning coming from extensive gold mining in those villages.

**Sample Collection and Analysis:** About 1.0 kg of the sediment samples was collected at three different points in a location and five meters away from each other to form a composite sample. Samples were collected by scooping the topmost layer sediments using a plastic spoon and then stored in a pre-cleaned 1000 ml polyethylene container, labeled and taken to the laboratory for storage in freezers awaiting analysis. Samples were then air dried in the laboratory and crumbs in the sediment were removed. Sediments were also sieved through a 2 mm sieve to remove coarse particles.

**Water soluble fractions:** Approximately (1.0 g) sediment sample that has been air dried was weighed into a polythene container (60 ml); water (10 ml) was added and shaken for 1

hour. The soil colloids were then centrifuged a Baird and TatLock authobench centrifuging machine at 4000 rpm for 20 min. The supernatant was decanted and filtered through a Whatman No.42 filter paper into a volumetric flask (50 ml), which was then made up to the mark with water.

**Exchangeable fraction:** To the residual soil sample from F1, (10 ml) of  $MgCl_2$  (1.0 mol/l) at pH 7 for one hour with continuous agitation using magnetic stirrer.

**Carbonate –bound fraction:** To the residue obtained above. An aliquot (8 ml) sodium acetate (10 mol/l) (pH = 5.0, adjusted with acetic acid) was added while Continuous agitation was sustained for 5 hours.

**Residual fraction:** The residue from above step was digested with a 5:1 mixture of hydrofluoric and per chloric acids. The sediment was first digested in a platinum crucible with a solution of concentrated  $HClO_4$  (2.0 ml) and HF (10.0 ml) to near dryness; subsequently a second addition of  $HClO_4$  (1.0 ml) and HF (10.0 ml) was made and again the mixture was evaporated to near dryness. Finally,  $HClO_4$  (1.0 ml) alone was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in HCl (12.0 mol/l) and diluted to 25.0 ml. The resulting solution was then analyzed by flame atomic absorption spectrophotometry for metal using standard addition technique. About (1.0g) of grounded tomatoes sample was weighed into beaker (100.0 ml). Concentrated  $HNO_3$  (5.0 ml) and perchloric acid (2.0 ml) was added and heated in a fume cupboard to almost dryness. Then, distilled water (10.0 ml) was added and the solution was properly stirred and filtered with a whatman filter paper No. 42. The filtrate of the digestate was then transferred into bottle (50.0 ml) and was then made up to mark with distilled water (APHA, 2005). Blank samples were prepared in the same procedure with distilled water.

**Statistical Analysis:** Descriptive statistics (such as mean and standard deviation) were performed on all the data. Duncan Multiple Range Test was used to separate means where significant. Means were considered significantly different at  $P > 0.05$ .

RESULT AND DISCUSSION

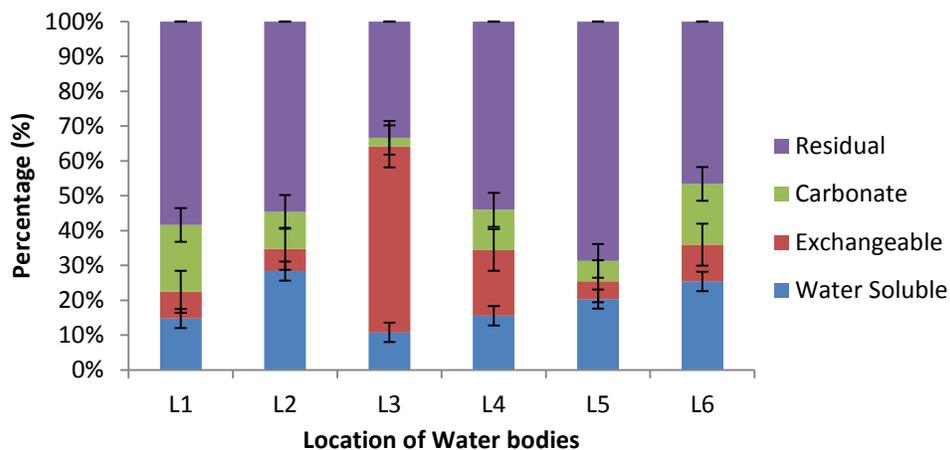


Fig. A Percentage Zn in different chemical fractions across all locations

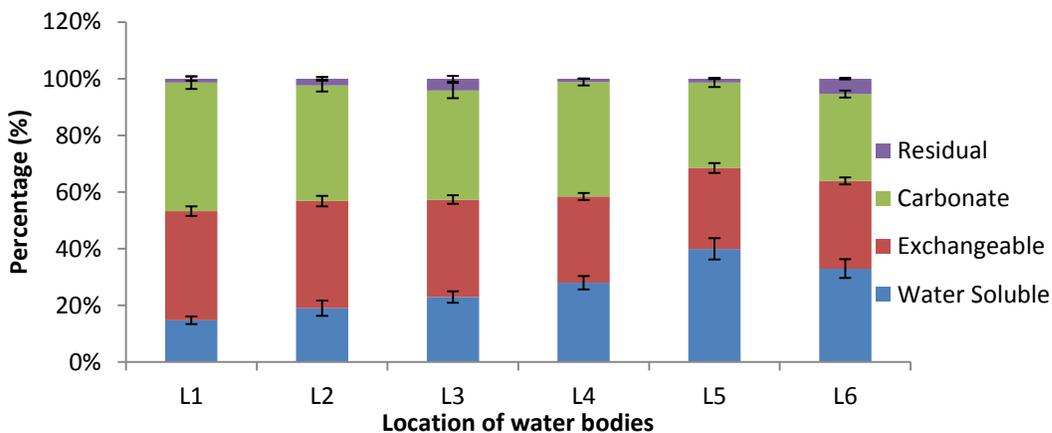


Fig. B Percentage Cd in different chemical fractions across all locations

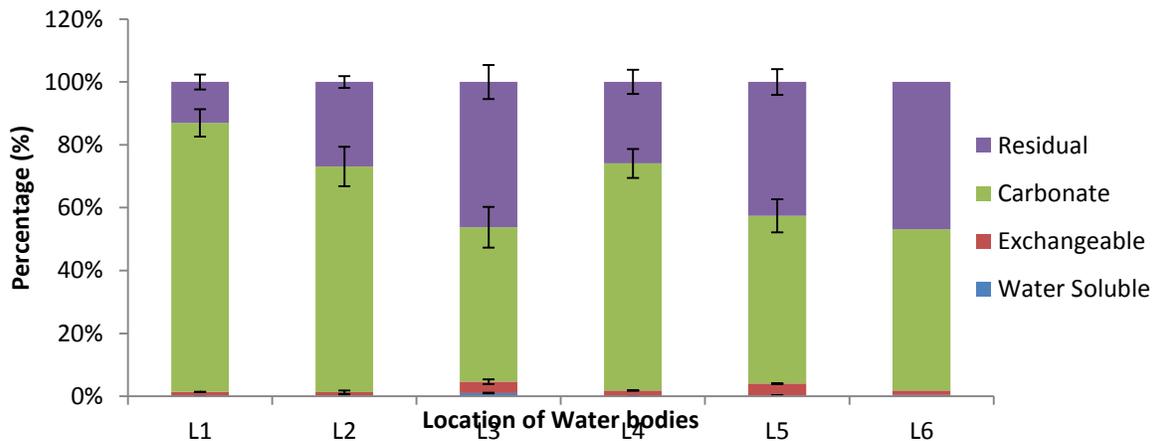


Fig. C Percentage Cr in different chemical fractions across all locations

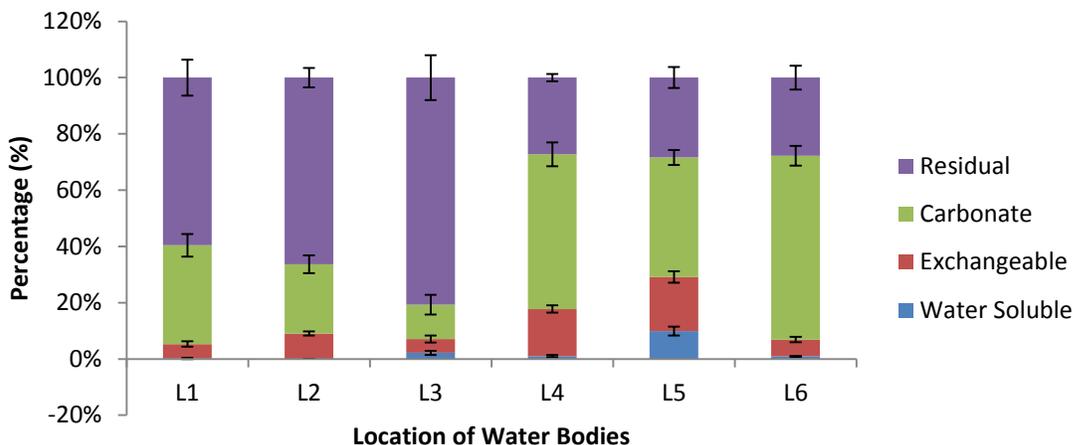


Fig. D: Percentage Pb in different chemical fractions across all locations

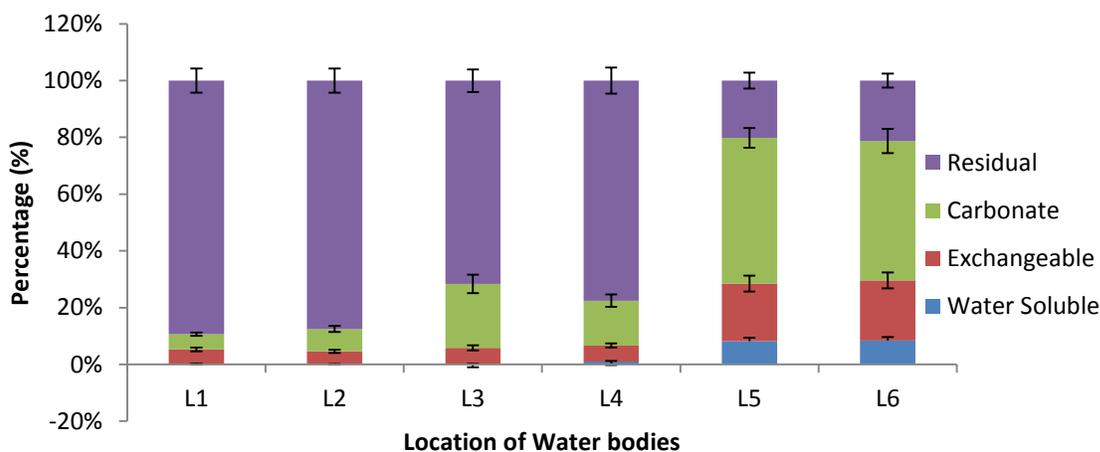


Fig. E: Percentage Hg in different chemical fractions across all locations

**Key:**

- |           |                     |           |                     |
|-----------|---------------------|-----------|---------------------|
| <b>L1</b> | <b>Gusau dam</b>    | <b>L2</b> | <b>Bakolori dam</b> |
| <b>L3</b> | <b>Dangulbi dam</b> | <b>L4</b> | <b>Bagega River</b> |
| <b>L5</b> | <b>Sunke river</b>  | <b>L6</b> | <b>Abare River</b>  |

The chemical fractionation of Zn, Cr, Cd, Pb and Hg in the sediments from all the dams and rivers under studied in the state are as presented in percentage starck graph in Fig. A--E. The three chemical fractions that constitute the non-residual fraction considered in this work are defined operationally as water soluble (F1), exchangeable (F2) and carbonate bound (F3) while the residual fraction is defined as F4. It was generally observed that the carbonate bound fraction (F3) recorded high Cr percentages across all the location with exception of location

L3, which recorded its highest percentage Cr in the residual fraction. The water soluble fraction F1 consistently recorded very low (below 1.5%) percentage fraction of Cr across all the six locations studied. It was generally observed that predominant percentage Hg was recorded in the residual fraction across all the location with exception of Sunke (51.316%) and Abare rivers (49.145%) with high percentage Hg in the carbonate bound fraction. Water soluble fraction generally recorded very low percentage Hg across all the locations.

**Table 1: Concentrations of Heavy Metals (mg/kg) in Tomatoes Samples for Two wet Seasons**

location	year	Zn	Cd	Cr	Pb	Hg
L1	2014	0.029 ±0.002	0.019±0.001	0.183±0.003	0.261±0.004	0.556±0.002
	2015	0.024±0.002	0.010±0.002	0.010±0.004	0.334±0.001	1.746±0.003
L2	2014	0.039± 0.001	0.019±0.003	0.261±0.003	0.125±0.002	0.163±0.000
	2015	0.049 ± 0.001	0.012±0.002	0.012±0.003	0.396±0.001	2.202±0.003
L3	2014	0.052± 0.002	0.014±0.001	0.157±0.004	0.271±0.002	0.446±0.000
	2015	0.056±0.003	0.016±0.005	0.016±0.002	0.511±0.002	0.600±0.003
L4	2014	0.044 ±0.002	0.032±0.001	0.157±0.003	0.021±0.004	0.953±0.000
	2015	0.048±0.002	0.019±0.002	0.019±0.004	0.386±0.001	1.050±0.003
L5	2014	0.092± 0.001	0.017±0.003	0.118±0.003	0.208±0.002	ND
	2015	0.097 ±0.001	0.019±0.002	0.019±0.003	0.188±0.001	1.103±0.003
L6	2014	0.128± 0.002	0.027±0.001	0.301±0.004	0.356±0.002	ND
	2015	0.124±0.003	0.022±0.005	0.022±0.002	0.396±0.002	0.896±0.003

Key: ND: not detected

**Table 2: Concentrations of Heavy Metals (mg/kg) in Tomatoes Samples for Two dry Seasons**

location	year	Zn	Cd	Cr	Pb	Hg
Gusau	2014	0.036 ±0.002	0.432±0.001	0.364±0.003	0.250±0.004	ND
	2015	0.031±0.002	0.256±0.002	0.369±0.004	0.365±0.001	4.363±0.003
Bakolori	2014	0.058± 0.001	0.216±0.003	0.324±0.003	1.074±0.002	ND
	2015	0.041± 0.001	0.334±0.002	0.314±0.003	0.500±0.001	2.527±0.003
Dangulbi	2014	0.093± 0.002	0.668±0.001	1.165±0.004	0.615±0.002	ND
	2015	0.071±0.003	0.354±0.005	1.150±0.002	0.644±0.002	1.343±0.003
Bagega	2014	0.059 ±0.002	0.668±0.001	0.199±0.003	0.354±0.004	ND
	2015	0.061±0.002	0.472±0.002	0.099±0.004	0.394±0.001	1.362±0.003
Sunke	2014	0.166± 0.001	0.729±0.003	0.126±0.003	0.511±0.002	ND
	2015	0.113 ±0.001	0.098±0.002	0.116±0.003	0.521±0.001	1.188±0.003
Abare	2014	0.420± 0.002	0.256±0.001	0.314±0.004	0.394±0.002	ND
	2015	0.293±0.003	0.491±0.005	0.334±0.002	0.719±0.002	1.293±0.003

Key: ND: not detected

**Heavy Metals in Tomatoes Samples:** The results obtained for metals in tomatoes samples from all locations around the dams and rivers in study area are presented in Table 1 and 2. Generally, the concentrations of Cr in the dry seasons were higher than in the wet season, a situation which suggests seasonal variation effect also the concentrations of Pb in the dry seasons were higher than in the wet season, a situation which equally suggests seasonal variation effect. However, it was generally observed that Hg concentrations are higher in the dry seasons than their corresponding wet seasons. While the concentration of Hg was mostly below detection limit but very pronounced concentration in year 2015.

**Table 3: Correlation matrix of Heavy Metals Concentrations (mg/kg) in Tomatoes Samples for Two Wet and Two Dry Seasons**

	Correlations					Correlations				
	For wet					For dry				
	Zn	Cd	Cr	Pb	Hg	Zn	Cd	Cr	Pb	Hg
Zn	1					1				
Cd	.416*	1				.416*	1			
Cr	.128	.471**	1			.128	.471**	1		
Pb	.166	-.350*	-	1		.166	-.350*	-	1	
Hg	-.375*	-.414*	.429**	-.709**	1	-.375*	-.414*	.429**	-.709**	1
	36	36	36	36	36	36	36	36	36	36

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

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

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

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

**Assessment of Heavy Metal Pollution in Tomatoes Samples:** Contamination factor calculated for heavy metal concentration in tomatoes are presented in Table 4. It revealed that only Hg had contamination factor (CF>>6) higher than 6 across all the location for both wet and dry seasons. The pollution load indices (PLI) for all the locations have values less than one (1) for both wet and dry season.

**Table 4: Heavy Metal Contamination Factors (CF) and Pollution Load Index (PLI) in Tomatoes for Wet and Dry Seasons.**

Location/Wet	Zn	Cd	Cr	Pb	Hg	PLI
Gusau	0.0026	0.1050	0.0029	0.0383	6.1667	0.0453
Bakolori	0.0005	0.0443	0.0016	0.0164	6.0033	0.0206
Dangulbi	0.0006	0.0653	0.0018	0.0354	2.4000	0.0225
Bagega	0.0024	0.1117	0.0026	0.0368	3.0500	0.0378
Sunke	0.0013	0.0733	0.0010	0.0159	12.7800	0.0283
Abare	0.0017	1.8083	0.0057	0.0526	10.3000	0.0992
Gusau	0.0053	1.5733	0.0132	0.1108	10.7567	0.1671
Bakolori	0.0015	2.4250	0.0054	0.0204	2.9867	0.0662
Dangulbi	0.0011	1.2450	0.0069	0.0430	8.5833	0.0915
Bagega	0.0029	2.4233	0.0143	0.1341	3.7967	0.1384
Sunke	0.0019	1.5400	0.0023	0.0199	12.7100	0.0705
Abare	4.1895	2.7166	0.0091	0.0862	11.4330	0.6328

ND: Below detection

**Chemical Speciation of Metals in Sediment**

**Zinc:** The distribution of Zn obtained in the four fractions by the extraction of sediment across all the six locations showed that Zn was mostly concentrated in the water soluble (FI) with the highest percentage of 28% in Bakolori dam and the least at Dangulbi dam (10.765%). The highest percentage concentration of Zn in the exchangeable was recorded in Dangulbi dam while Bakolori dam recorded the lowest level. The predominance of percentage Zn was mostly recorded in the residual fraction. This suggests that the greater percentage of Zn in the sediments is non-bioavailable. Literature revealed that High percentage of total Zn have been found to be associated with the reducible fraction in similar studies of polluted sediments, which was not determined in this present work (Fernandes, 1997; Li *et al.*, 1995; Fan *et al.*, 2002; Korfali and Davies 2004). The absorption of Zn onto oxides has higher stability constants than onto carbonates (Rao *et al.*, 1990). Several other works have also revealed that Zn is more associated with exchangeable and Fe-Mn oxides (Kuo *et al.*, 1983; Ramos *et al.*, 1994) which is

consistent with the result of this work. **Cadmium:** The predominant percentages of Cd were recorded in the carbonate bound fraction of Gusau dam 45.424%, Bakolori dam 40.820%, Dangulbi dam 38.446% and Bagega river 40.512%. The residual fraction generally recorded low Cd concentration across all the locations. This further suggests that a high concentration of Cd in this sediment might be easily available and can easily enter the food chain. This is in close agreement with the report of Ahumada *et al.*, 1999; Narwal *et al.*, 1999 who reported that Cd is distributed more as carbonate, reducible and as residual fraction. High concentrations of Cd in carbonate bound fractions have also been reported in sediments (Rao *et al.*, 1990; Korfali and Davies, 2004). The result obtained in this work were in accordance with previous studies by Adelan *et al.*, 2011 who highlighted that the potential risks caused by Cd were extremely associated with the acid-soluble fractions.

**Chromium:** Cr recorded the highest percentage level in the carbonate bound fraction across all the locations with exception of Dangulbi dam. The lowest percentage was generally recorded

in the water soluble fraction across all the six locations. This suggests that Cr was mostly concentrated in the carbonate bound fraction (72.234%) much more than its concentration in exchangeable fraction (1.828%). The residual fraction has concentration of 171.2 mg/kg i.e. about 25.937% while water soluble has the least value. This is consistent with reports of other researchers where large proportion of Cr was found in the carbonate bound fraction and the least fraction located in the water soluble fraction (Korfali and Davies, 2004; Naimo *et al.*, 2005). Chromium may not be easily mobilized, this is because of the small fraction found in the exchangeable phase (F2), and hence a more severe condition might be required for their released. This result was also in agreement with previous studies that the potential risks caused by Cr were extremely associated with acid – soluble fractions (Adelakan *et al.*, 2011). However, the potential ecological risks that still exist which cannot be ignored even with the attendant low percentage degree of association with the mobile fraction (Adelakan *et al.*, 2011).

**Lead:** The exchangeable fraction recorded some appreciable amount of Pb across all the locations with the highest being (16.714%) at Bagega river. The percentage of Pb distribution is in order: F3>F2>>F1. This is consistent with the results obtained by several authors (Jones and Turki, 1997; Li *et al.*, 1995; Fan *et al.*, 2002; Adelakan *et al.*, 2011 and Wong *et al.*, 2007).

**Mercury:** All three dams considered in this work and Bagega River recorded their highest percentage Hg concentration in the residual fraction while Sunke and Abare River recorded their highest percentage fractions in the carbonate bound fraction. The exchangeable also had some appreciable percentage Hg concentration across all the six locations. Water soluble fraction consistently had the lowest percentage Hg concentration across all the locations. Korfali and Davies, 2004; Naimo *et al.*, 2005 suggests that the mercury metal fractions are more associated with the alumino–silicate minerals. The relative metal concentration in non-residual fraction can be used as a measure of the contribution from natural and anthropogenic sources, including higher percentage in these fractions revealed a high level in pollution of sediments from the sampling zones (Cao *et al.*, 2014). Comparing the way the metals were bound to the different phases in the sediments, Cd and Pb appeared to be the most readily solubilized, thus making these elements the most potentially bioavailable. This may present a real threat as Cd is transferred into the food chain from soil contaminated by this metal. It is also clear that from the results and discussion so far that the metals in the sediments are bound to different fractions with varying strength (Duan *et al.*, 2014).

#### Heavy Metals Content in Food Crop (Tomatoes)

Correlation analysis conducted to examine whether there is a relationship between the heavy metal concentrations in the tomatoes revealed a significant positive relationship for Cr and Cd, Cd and Zn, Hg and Pb in the wet season and a significant and positive relationship for Cr and Cd, and Pb and Cr in the dry season. This may suggest reason for the consistent variation of these metals in all the locations across the seasons. Concentrations of heavy metal in tomatoes in this work revealed

spatial variation at all locations during the study periods. The relative abundance of different metals at the six locations during the wet and dry seasons varied with locations and with season in the tomatoes samples.

**Zinc:** All the metals investigated except Zn were measured in relatively high amount especially during the dry seasons across all the locations. This situation above is expected in view of the reduction in the pollution in the wet season arising from the increased dilution and water flow. Heavy metals are found naturally in the Earth, and they become concentrated as a result of human activities which include but not limited to industrial processes, mining, agriculture and transportation (Noor-ul *et al.*, 2015; Bassey *et al.*, 2014). These metals have both positive and negative roles in human life (Noor-ul *et al.*, 2015, Colak *et al.*, 2005; Oktem *et al.*, 2005).

**Cadmium:** Heavy metals such as Cd, Cu, Pb, Cr, Zn, Ni, As, Co and Hg cannot be degraded or destroyed and can be accumulated in living tissue through the food chain, causing various diseases and disorders (Manohara *et al.*, 2014). Fruits, vegetables and other foods are among pathways by which heavy metals enter the human tissues leading to deterioration of health (Manohara *et al.*, 2014). The presence and accumulation of the analyzed heavy metals in tomatoes plants could be traced to their presence in the wastes water used for their irrigation. Liu *et al.*, 2005 opined that the soil type, root stock, mulching, irrigation, fertilization, and other cultural practices has an influence on the amount of water and nutrient supply to plant and therefor affect the composition and quality attributes of the harvested plants.

**Chromium:** The result of this study agreed with the data reported by Liu *et al.*, (2005). Also report from some researchers (Muchuweti *et al.*, 2006; Sharma *et al.*, 2007) demonstrated that the plants grown on wastewater-irrigated soils are contaminated with heavy metals and that they pose a threat to health. The accumulation of these heavy metals in the tomatoes was as a result of the presence of the metals in the soil due to their irrigation with waste water.

**Lead:** The concentration of Pb in this study was in agreement with the submission of Liu *et al.*, 2005 who opined that the extractable Pb in both cultivated and uncultivated soils increased by increasing Pb concentration to the soil. Sharma *et al.* (2007) showed that the concentrations of exhaustible metals such as Zn, Cd, and Pb in the soil increased with increase in sludge application. This was supported by the submission of Sharma *et al.* (2007) who find a highly significant correlation between the chemical composition of irrigation water used and the soil chemical properties. The calculated contamination factor (CF) revealed that only Hg had CF values greater 6, which indicates a serious contamination of tomatoes harvested from all the location. The pollution load index (PLI) across all the locations had PLI values less than 1. This indicates that there is no serious overall pollution load on the tomatoes samples.

**Conclusion:** The speciation of heavy metals with selective extracting agents gives additional information about the fundamental reactions governing the behaviour of the metals in sediments. Comparing the way the metals were bound to the

different fractions in the sediments, it is clear that the metals in the sediments are bound to different fractions with different strength. Anthropogenic input of Cd and Cr was primarily in the carbonate bound fraction while Inputs of Zn and Hg appear mainly in the residual form. Inputs of Pb were found in carbonate, exchangeable and water soluble fractions. The distribution of the five studied metals in the various fractions confirms their differences in mobility. Of the five elements studied, Cd and Pb appeared to be the most readily solubilized, thus making these elements the most potentially bioavailable. This may present a real threat as Cd and Pb are transferred into the food chain from soil contaminated by these metals.

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