



Original Research Article

Assessment of Heavy Metals Pollution in the Surface Water from Thomas Dam, Kano State, Nigeria

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ABSTRACT

The present study aimed to assess the level of heavy metals concentrations in the Thomas Dam, which is a recipient of wastes from agricultural, residential and industrial land uses. Six Heavy metals (Cd, Cr, Pd, Zn, Ni and Cu) were selected for the study primarily due to their chronic health effects on the public well-being. Samples were collected at three points, namely stations A, B and C, across the Dam during the rainy season (from August to October, 2018) and analyzed using standard laboratory procedures followed by Atomic Absorption Spectrophotometry (AAS). Results obtained showed that all the metals selected for this study were present in the water samples. However, Cr mean level was highest (1.51 mg/l), while Cu had the least mean concentrations (0.484 mg/l). Pb, Cd and Zn levels were also very high in concentrations with mean values of 0.066 mg/l, 0.173 mg/l and 0.762 mg/l respectively. There were no significant differences ($p > 0.05$) in the heavy metal concentrations between the three sampling points, an indication of spatial spread of contamination. Although Zn and Cu were below permissible limits for drinking water and safety levels for fish, efforts should be made to ensure that these element and other heavy metals are regularly monitored as well as activities leading to their presence in water and fish. This can be done through regular surveillance in order to detect changes in water quality of the dam and regulating of land uses within the reservoir which influence the introduction of contaminants into the river.

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1. INTRODUCTION

In most developing countries, the aquatic environment is on the receiving end of solid wastes and effluent discharge (Khadse *et al.*, 2008; Venugopal *et al.*, 2009; Islam, *et al.*, 2014; Edokpayi, *et al.*, 2014). These effluents usually contain high concentration of heavy metals which are regarded as serious pollutants of the

aquatic ecosystems, mainly because of their abundance, persistence and toxicity even at low concentrations (Sin *et al.*, 2001; Armitage *et al.*, 2007; Yuan *et al.*, 2011; Chowdhury *et al.*, 2016; Ali *et al.*, 2016). Across the world, the pollution of natural water by heavy metals has received considerable attention due to its risk to human health and ecology (UNICEF/WHO, 2011; WHO, 2011; Olukanni *et al.*, 2014). Although, heavy metals in rivers may originate from natural sources such as mineral weathering, anthropogenic processes agrochemicals, industrial and domestic municipal wastes, wastes from domesticated animals receiving metals in food supplements, and atmospheric deposition are of primary concern being the consequences of human population and economic activities (Reza and Singh, 2010; Butu and Ati, 2013). The increasing load of heavy metals cause imbalance in aquatic ecosystems and the biota growing under such habitats accumulate high amounts of heavy metals which in turn, are being assimilated and transferred within food chains by the process of magnification (Kuntal *et al.*, 2014). Although some of the metals like Copper (Cu), Iron (Fe), Manganese (Mn), Nickel (Ni) and Zinc (Zn) are essential as micronutrients for life processes in plants and microorganisms, other metals like Cadmium (Cd), Chromium (Cr) and Lead (Pb) have no known physiological activity, but instead are proven to be detrimental beyond a certain limit (Marschner, 1995; Bruins, *et al.*, 2000). Diseases like edema of eyelids, tumor, congestion of nasal mucous membranes and pharynx, stuffiness of the head and gastrointestinal, muscular, reproductive, neurological and genetic malfunctions caused by some of these heavy metals have been documented (Johnson, 1998; Tsuji and Karagatzides, 2001; Abbasi, *et al.*, 1998). Prolonged exposure to Pb has been linked to mental retardation, coma and eventual death (Rahman *et al.*, 2012). Ingestion of Cd on the other hand is known to cause chronic toxicity such as impaired kidney functioning, hypertension, hepatic dysfunction, breast and ovarian cancer whereas Cu and Zn may cause kidney problems such as nephritis and anuria (Rahman *et al.*, 2012; Hong *et al.*, 2014; Adams *et al.*, 2014). Further, interactions associated with exposure to multiple heavy metals may induce more severe human health consequences than might be expected from low individual metal concentrations alone (Liyin, *et al.*, 2018). Exposure to heavy metals from water bodies may also occurs through bioaccumulation of metals in human food sources (Baby *et al.*, 2010; Krishnamurti *et al.*, 2015; Fazio *et al.*, 2014). Thus, even if humans do not consume heavy-metal contaminated water directly, they are often exposed to high levels of heavy metals from plant and aquatic food sources grown in the polluted waters (Jiang *et al.*, 2016; Antoniadis *et al.*, 2017a; Antoniadis *et al.*, 2017b). This is especially important in rapidly developing areas of Nigeria where Fadama and subsistent farming represents a large fraction of the food supply to both rural and urban centers.

Thomas Dam is located near Danmarke village of Dambatta Local Government area of Kano State, 30 km away from the ancient Kano City. The contributing rivers/streams are Thomas and Kalebawa in Danbatta Local Government Area of Kano State. The dam and its location are socio-economically strategic being a source of drinking water supply to Makoda and some parts of Minjibir local government areas of Kano State. In addition, the reservoir is rich for fishing as well as houses holidays resort centres (Adamu *et al.*, 2016). Unfortunately, over the years, the areas have undergone intensive land use modifications (Butu *et al.*, 2019). At the moment agricultural activities, recreational activities, fishing, as well as residential and small-scale industrial activities are predominant in the study area, with agriculture being widely practiced and which rely heavily on organic and inorganic fertilizers, and this predisposes the study area to potential contaminations. It is against this background that the present study is conducted to investigate for the presence of heavy metals in the surface water of Thomas dam.

2. MATERIALS AND METHODS

2.1. Description of Study Area

The study area is Thomas Dam, situated in Kano State, North-Western Nigeria. The Dam is located at Latitude 12°16' N - 12°18' N and Longitude 8°30'E - 8°31'E (Figure 1). The dam is sited near Danmarke village of Dambatta Local Government area of Kano State, 30km away from the ancient Kano City (Kutama

et al., 2013). The contributing rivers/streams are Thomas and Kalebawa, while its discharge point is at Takwasa. The beneficiary settlements include Jalli, Dumawa, Ganduje, Rimi, Wailare, Madachi, Galoru, Shiddar, Takai, Marke and Kwasauri. Drinking water is supplied to Makoda and some parts of Minjibir local government areas of Kano State from the surface water of Thomas Reservoir (Adamu *et al.*, 2016). Generally, the area lies within the “wet and dry” climate with more dry than wet months (Olofin, 1987) which are categorized under the Tropical wet and dry climate (i.e AW according to Koppen’s climatic classification). It has a low mean annual rainfall of about 880 mm. In drought years, it could be lower than 450 mm as in the case of 1972/1973 drought. Agriculture is the primary land use in the study area, which can either be rainfall agriculture or irrigation agriculture. The farming systems in the study area are mainly subsistence and commercial. Other land use activities include residential house, markets, schools, government office for administration, motor parks, holiday resorts, communication network, roads and forest reserves (Olofin, 1987).

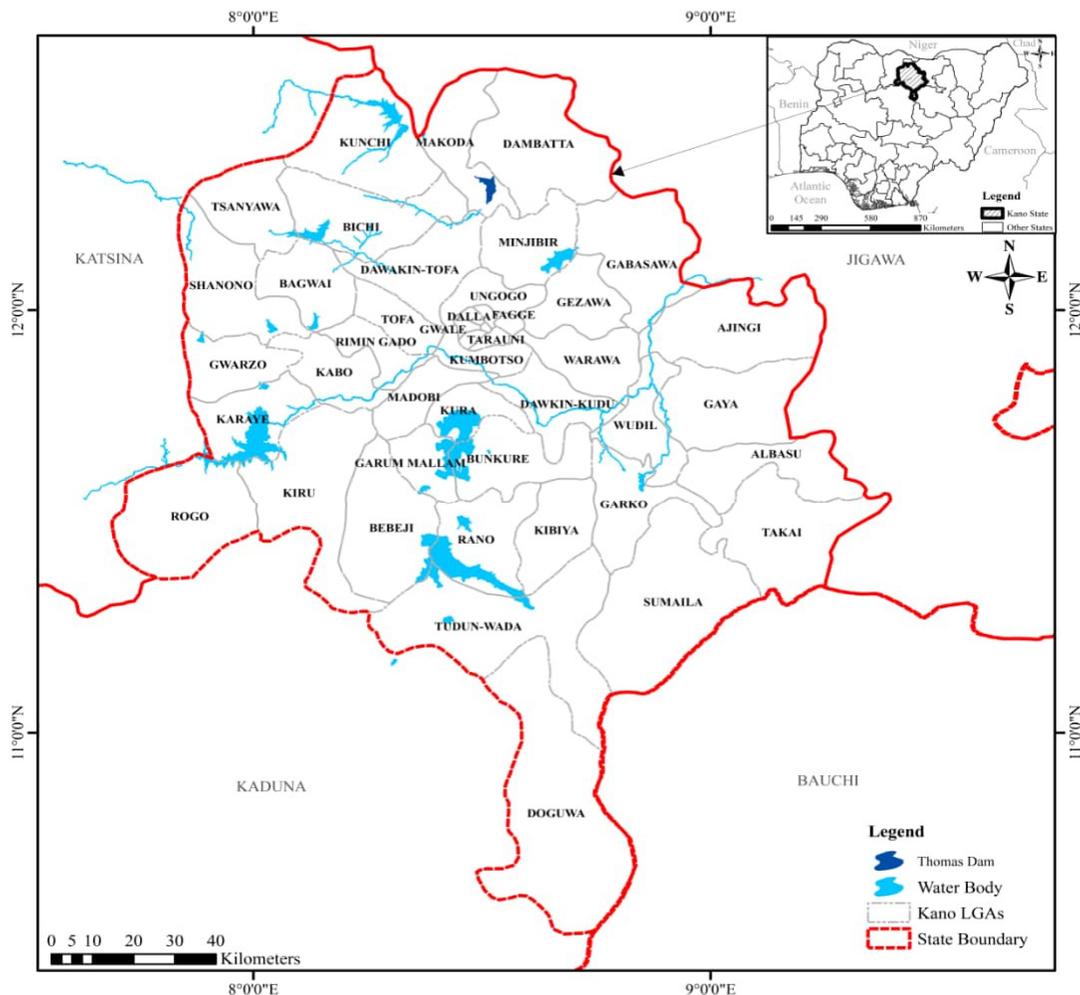


Figure 1: Map of Kano state showing Thomas dam (Source: Cartography unit, Geography Department, BUK 2018)

2.2. Sample Collection

Three (3) sampling points were selected along the water course of the dam and these sites were designated as stations A, B and C (Figure 2). The choice of the sampling points was informed by concentration of human activities which are potential sources of pollution and accessibility to sampling points. Each sampling point is hypothetically believed to receive different types of pollutants from diverse land use activities, though agricultural residues and solid wastes seem to be peculiar to all three stations. Station A, (named Rimi) is in the southern part of the dam. The station is one the shallow parts of the dam and irrigation activities take place around this point during the dry season and farming activities during the rainy season. At station B, (named Satame), human activities such washing of cars, motor bike, bathing and other laundry activities are common. Agricultural activities also occur at this station but sparsely. This station is also close to the highway which may be receiving particulate pollutants related to motor vehicles. Station C, is near the source point where water is being supplied to the dam. The contributing river/stream includes Thomas and Kalebawa rivers. These rivers are suspected to be contaminated due farming activities along the adjoining rivers. There are also two holiday resorts and a forest reserve along this area which may be releasing some form of wastes into the reservoir through direct release into the river/stream from the resorts or by run-off during the rainy season. Station C is named Babbanruga.

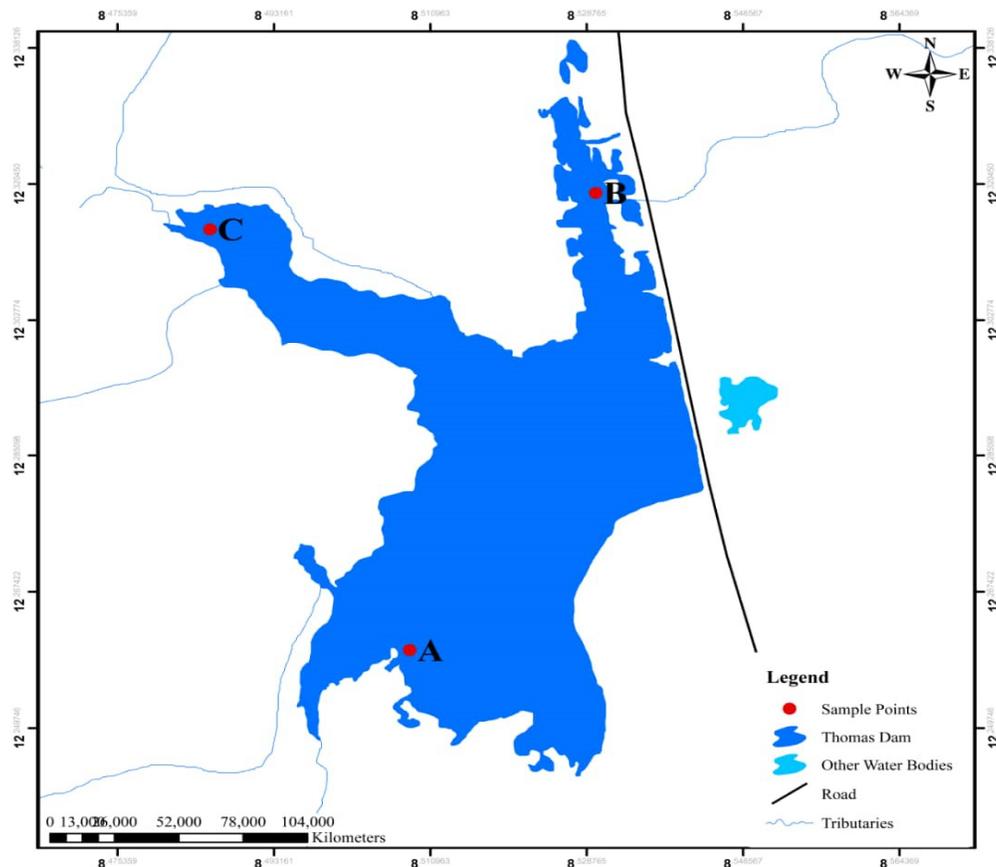


Figure 2: Thomas dam showing sampling points (Source: Cartography unit, Geography department, BUK 2018)

Water samples were collected on a monthly basis from August to October 2018 between the hours of 9:00 am to 4:00 pm. A total of 27 samples were collected from the three sampling stations. Three replicates of

surface water samples were collected. Method of sampling include lowering a pre-cleaned plastic bottles into the water at a depth of 30 cm below the water surface and allow to over flow before withdrawing (Lind, 1979; APHA, 2005). To ensure that no foreign substance was introduced into the samples, the plastic bottles were washed with water from the dam before collection. Samples were then transported in an iced box to the Laboratory at Soil Science Department, Bayero University Kano.

2.3. Sample Digestion and Metal Extraction

The three replicated samples for each site were composited for the procedures conducted in the laboratory. One hundred millimeter (100 ml) of the raw unfiltered water samples was transferred into Pyrex beakers containing ten millimeter (10 ml) of concentrated Nitric acid (HNO_3) and then boiled slowly till evaporated to 20ml on hot plate. The beakers were allowed to cool, while another 5ml of concentrated Nitric acid (HNO_3) was added and heated until digestion was completed. The samples were then evaporated again to dryness and the beakers were cooled, followed by the addition of 5ml of hydrochloric acid (Hcl) solution (1:1 v/v). The solution was warmed; 5ml of sodium hydroxide (NaOH) was added and then filtered. The filtrates were transferred to one hundred 100ml volumetric flasks and diluted with distilled water to be used for the elemental analysis. All the measurements were carried out in triplicate as a standard procedure by USEPA, (2006) as described by Agah *et al* (2009).

2.4. Preparation of Standard Metal Concentrations

Aqueous stock solutions were prepared for lead, chromium, cadmium, copper, nickel, and zinc using appropriate salts. Four working standards were prepared in triplicate for each metal by serial dilution of the stock solution. These and blank solution were aspirated into the Atomic Absorption Spectrophotometer (Agilent technologies model 200 series AA) as described by the manufacturers to obtain the absorbance of each of the samples and standard solutions for each of the metals. A calibration curve for absorbance versus concentration of the standard metal concentrations was prepared for each metal from which calibration graph for each of the metals in the sample was determined as described by Nnaji *et al.* (2007).

2.5. Detection Limit

Three replicate blank samples were digested following the same procedures utilized for digesting the fish and water samples. Each blank was assayed for its metal contents (Cr, Cd, Zn, Fe and Pb) by Flame Atomic Absorption Spectrophotometer (FAAS). The standard deviation (SD) of the three replicate blanks was calculated to determine the Method detection limit (MDL) (David and Terry, 2008). Method detection limit (MDL) was then calculated as shown in Equation (1) (David and Terry, 2008; Meseret *et al.*, 2013).

$$MDL = yB + 3SD \quad (1)$$

Where; yB = mean of the replicate blank and SD = Standard deviation of the blank

2.6. Recovery Test

Recovery is one of the most commonly used techniques utilized for validation of the analytical results and evaluating how far the method is acceptable for its intended purpose. In present study due to the absence of certified reference material for fish and water in the laboratory, the validity of the digestion procedure, precision and accuracy of AAS was assured by spiking fish and water samples with known concentration. The spiked and non-spiked fish and water samples were digested following the same procedure employed in the digestion of the respective samples and analyzed in similar condition. Then the percentage recoveries of the analytes were calculated as shown in Equation (2) (Kiflom and Tarekegn, 2015).

$$\text{Recovery} = \frac{\text{CM in spike samples} - \text{CM in non-spike samples} \times 100\%}{\text{Amount added}} \quad (2)$$

Where, CM = concentration of metal of interest.

According to Harvey (2000) the acceptable ranges of percentage recovery for heavy metals analysis were within 80 –120%.

2.7. Instrumental and Statistical Analysis

All samples were analyzed for the selected heavy metal concentrations using computer controlled Atomic Absorption Spectrophotometer (Agilent technologies model 200 series AA). The AAS was calibrated with standard solution settings and operational conditions were done in accordance with the manufacturers' specifications and instructions. After calibration of the instrument the samples were aspirated into the AAS instrument according to standard method (APHA, 1995). The samples were analysed in triplicates, and the blank determinations in triplicates were also run in the same manner during the analysis. Data was subjected to descriptive statistical analysis (95% confidence limit) using appropriate statistical tools to determine the mean and standard deviation values of metal concentration in the water. A student t test (paired two sample for means) was used to test if there were significant differences in the concentrations of heavy metals between water samples and fish tissues at different sampling sites at $p < 0.05$.

3. RESULTS AND DISCUSSION

Descriptive results of heavy metals levels are presented in Table 1. All the six heavy metals Cd, Zn, Pb, Cr, Cu and Ni were detected in the surface water from Thomas dam.

Table 1: Descriptive statistics of heavy metals concentration (mg/l) in water sample

	Cr	Cd	Pb	Ni	Zinc	Cu
Station A						
Mean±SD	0.484±0.109	0.173±0.027	0.013±0.027	1.026±0.108	0.427±0.035	0.032±0.007
SE	0.063	0.015	0.015	0.063	0.020	0.004
Station B						
Mean±SD	1.028±0.179	0.157±0.035	0.066±0.009	0.695±0.113	0.762±0.049	0.012±0.002
SE	0.103	0.020	0.005	0.065	0.029	0.001
Station C						
Mean±SD	1.51±0.345	0.135±0.027	0.044±0.008	0.182±0.0095	0.327±0.011	0.026±0.006
SE	0.199	0.016	0.005	0.006	0.006	0.004

Highest mean concentration of Cr (1.51 mg/l) was seen in Station C. This is followed by Station B (1.028 mg/l). Least Cr level was recorded in Station A (0.484 mg/l). For Cd, highest mean concentration was seen in station A (0.173 mg/l), while Station C recorded the least level (0.135 mg/l). Concentration of Pb was highest in station B (0.066 mg/l), followed by station C (0.044 mg/l). Ni level was highest in Station A (1.026 mg/l), with least concentration at station C (0.182 mg/l). Zinc mean level was highest in station B (0.762 mg/l), while station C (0.327 mg/l) recorded the least. For Cu, highest mean concentration was seen in station A (0.032 mg/l), followed by station C (0.026 mg/l). The fact that Cr was highest in Station C has a lot of implication for public health. This is due to the proximity of the station to water inlet into the dam. It therefore follows that water supply into the dam is already contaminated with Cr and unless there is any form of water treatment, it can be said that water supply to nearby communities is contaminated with chromium, lead, cadmium etc.

On the whole however, the presence of these heavy metals in the water sample could be attributed to discharge of Agricultural wastes, municipal wastes and the geological properties of the reservoir as shown by other studies (Obasohan, 2008; Kar *et al*, 2008). In a similar study, Butu (2013) detected the presence of heavy metals in surface water from Galma dam which he attributed to the presence to the anthropogenic activities and geologic processes within the catchment area. On the whole, Cr level was found to be higher in all the sampling stations when compared to other metals, while Cu recorded the lowest concentration. The fact that Cr level was elevated may be attributed to human activities taking place within and around the dam. For example, paint residue from buildings within the reservoir could be washed into the dam by rain, cement dust from building activities around the dam can also be washed into the dam (Al-Khatib *et al.*, 2019). Also air pollutants such as road dust from automobile emissions and emissions from asbestos brakes of automobile that ply the road along the dam can be deposited on the water. These air pollutants can fall directly on water as rain or dry particles or having fallen on land can be washed into a body of water as runoff (Narayana, 2007). Copper reaches aquatic systems through anthropogenic sources such as industry, mining, plating operations, usage of copper salts to control aquatic vegetation or influxes of copper containing fertilizers (Nusse, 1998). The absence of these copper contamination related activities within the study area could justify the low level of Cu as seen in the study. Furthermore, copper bioavailability increases with increasing salinity (Forstner *et al.*, 1989), although not tested in this study, an increase in the salinity of the water could be responsible for the low concentration of copper in the surface water in Thomas Dam.

In Table 2, the results of student's t test to determine the extent of spatial differences in the levels of metals are presented. On the whole it is found that there is no significant variation among the heavy metals concentration in the surface water from all three stations. Specifically, between stations A and B, levels of concentrations were not significantly difference at $p > 0.05$, $d = 0.242$ even though mean concentration level was more in station B. Similarly, concentration levels between stations A and C did not reveal any significant difference at $p > 0.05$, $d = 0.482$. Similar pattern was seen between stations B and C at $p > 0.05$, $d = 0.298$. These findings may suggest that the concentration level of the heavy metals across the sampling points are homogeneous, thus the reservoir is contaminated primarily by residential and agricultural land use activities. Dilution due to rainfall on the other hand may have also influenced the homogenous nature of the water in the dam since there as a result of mixing of the water through run-off.

Table 2: Paired Two Sample for comparison of means of heavy metals levels in water sample across sampling stations

Station	Sample	Mean	Variance	Obs.	df	Pearson Correl	t Stat	P(T<=t) one-tail	t Critical one-tail	P(T<=t) two-tail	t Critical two-tail
Station	A	0.359	0.145	6	5	0.72	-0.754	0.242	2.015	0.485	2.57
	B	0.453	0.183	6							
Station	A	0.359	0.145	6	5	0.31	-0.047	0.482	2.015	0.964	2.57
	C	0.371	0.323	6							
Station	B	0.453	0.183	6	5	0.77	0.564	0.298	2.015	0.597	2.57
	C	0.371	0.323	6							

The mean values of the concentrations of each of the selected heavy metal contaminants in water samples from the study area was compared with the World Health Organization (WHO) guidelines and Nigerian Industrial Standard (NIS) for drinking water in order to ascertain the pollution status of the chemical contaminants because of the harmful nature of these heavy metals and also see their health implications to humans (Table 3). In Table 3, it is seen that Cd, Cr, Ni and Pb levels were higher than both NIS and WHO limits; suggesting that the surface water of Thomas dam is polluted with Cd, Cr, Ni and Pb. Cd can be found in soils under agriculture from insecticides, fungicides, sludge and commercial fertilizers. In this case, its

presence in the surface water of Thomas dam could be attributed to the intense agricultural activities that occur around the dam as has been reported by (Reza and Singh, 2010).

Table 3: Comparison of mean values of concentration of selected heavy metals in the Surface water of Thomas dam with national and World Health Organization (WHO) standards.

Heavy metals	Mean values in mg/l (Surface water)	NIS (2007) Standard	WHO (2011) Standard
Cadmium (Cd)	0.16	0.003	0.003
Chromium (Cr)	1.01	0.05	0.05
Copper (Cu)	0.01	1.0	2.0
Lead (Pb)	0.04	0.01	0.01
Nickel (Ni)	0.63	0.02	0.02
Zinc (Zn)	0.51	NG	3.0

NG = No guideline

Cadmium has no biological functions to humans, it has been linked to a number of health problems including renal tubular dysfunction, pulmonary emphysema and possibly Osteomalacia, a situation where calcium in the bones is replaced by Cd in humans which results to cancer of the bones (Jarup and Jarup, 2003). Target organs include liver, placenta, kidneys, lungs, brain and bones (Reilly, 2002). Chromium (Cr) is very toxic and mutagenic when inhaled and is a known human carcinogen, and breathing high levels can cause irritation to the lining of the nose, runny nose and breathing problems (Dayan and Paine, 2001). Emissions of chromium-based automotive catalytic converters, and tobacco smoke as well as chromium compound leached by rain water could all be possible reason why Chromium is found to be higher than the NIS and WHO standards. The presence of Pb poses a high health risk of Pb poisoning as the element is known to be toxic even at low levels (Mwegoha and Kihampa, 2010). The higher levels of Pb observed in the surface water from the dam might be due to the closeness of some parts of the dam to the high way receiving pollutants that are related to vehicle emission. Some effects of Pb poisoning include deficiency in cognitive function due to destruction of the central nervous system, abdominal pain and discomfort, formation of weak bones as Pb replaces calcium and causes anaemia due to reduction of enzymes concerned with synthesis of red blood cells (Lars, 2003). Elsewhere in the sub-Sahara Africa studies have reported higher than the recommended limit of 0.01mg/l for drinking water (Wachira, 2007; WHO, 2008). Wachira (2007) reported that the water from Nairobi River was unsuitable for domestic use and attributed the higher level to discharge of untreated industrial and urban effluent to the river. The presence of Nickel in the surface water of Thomas Dam could be attributed to anthropogenic activities, old battery wastes, components of automobiles, old coins, and many other items containing stainless steel and other Nickel alloys. Elevated levels have been reported to cause sub-lethal effects (Nussey *et al.*, 2000). Among the known health-related effects of Ni are skin allergies, lung fibrosis, variable degrees of kidney and cardiovascular system poisoning and stimulation of neoplastic transformation. Nickel sulphide fume and dust is believed to be carcinogenic, and various other Ni compounds may be as well (Kasprzak *et al.*, 2003). Oguzie and Izevbigie (2009) reported that the anthropogenic sources as the major cause of pollution in the Nigerian aquatic environment. The difference in concentration with the current study was attributed to differences in geology and anthropogenic activities.

Mean concentration of copper (Cu) was found to be below the WHO and NIS standards of 2.0 and 1.0 mg/l respectively for human consumption. This agrees with Anim *et al.*, (2013) on the concentration of copper (1.2 mg/l) in Tono irrigation reservoir in Navrongo, Ghana which was below the WHO limits. The presence of copper in surface water and ground water is due to extensive use of pesticides containing copper compounds for agricultural purpose (Al-Weher, 2008), hence its choice as one of the heavy metals to be assessed in an agricultural dense area such as Thomas Dam. Copper is an essential element in human metabolism however, causes anemia, disorders of bone, and connective tissues and liver damage at excessive level. It is seen that the concentration of zinc (Zn) was below the WHO permissible limit of 3.0 mg/l. The

concentration of zinc may not pose immediate problem, however once it accumulates, it becomes an issue of concern because excessive intake of zinc may lead to vomiting, dehydration, abdominal pain and lethargy (Galadima *et al.*, 2011). Even though the zinc values are lower than the recommended limits, it is of paramount importance to safe guard the water bodies from excess zinc pollution, because zinc salts are intestinal irritants and can cause nausea, and abdominal pain (ATSDR, 2002). Prolonged exposure to high intakes of Zn results in copper deficiency and subsequent anaemia (Reilly, 2002). There is also a condition called the zinc shakes or "zinc chills" that can be induced by the inhalation of freshly formed Zn oxide formed during the welding of galvanized materials. It has been reported that zinc is able to damage nerve receptors in the nose, which can cause anosmia and recommended that consumers should stop using zinc based intranasal cold products and ordered their removal from store shelves (Johnson *et al.*, 2007; Safty *et al.*, 2008).

4. CONCLUSION

Results from the study showed high concentration of the heavy metal contaminants in the water samples. Cr recorded the highest mean concentrations in the study area, while Cu recorded the least mean concentrations. Mean levels of Cr, Cd, Pb, and Ni were above the NIS and WHO standards recommended limits for drinking water. This has implications for public health especially the nearby communities that depends on the Thomas Dam for drinking water supply and fish for consumption. The fact that ANOVA results showed no significant spatial variations in the concentration of the heavy metal contaminants among stations is an indication of the widespread pollution of surface water resources of Thomas Dam. The presence of these metals could be attributed to the intense agricultural activities that occur around the dam as well as effluent discharge from hotel resorts and settlements within the reservoir. In addition is it expected that emissions of chromium-based automotive catalytic converters, and tobacco smoke, old battery wastes as well as chromium compound leached by rain water may have also contributed to explain presence of Chromium and Pb in the surface water of Thomas Dam. In view of the importance of water to man, it is necessary that biological monitoring of the Dam's water and fish meant for consumption should be done regularly to ensure continuous safety of the dam and it resources. This is especially as the dam serves as source of drinking water, irrigation and fish for the local inhabitants in the study area.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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