



Risk Assessment of Selected Heavy Metals in Water and Sediment of Shika Dam, Zaria, Nigeria

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Abstract

*The purpose of this study was to assess levels of contamination and risk assessment of water and sediment in Shika Dam, Zaria Kaduna State. The levels of physicochemical parameters and some toxic heavy metals in the dam's water and sediments were determined using standard analytical methods adopted from USEPA and WHO (1994, 2012). A questionnaire was developed, validated by experts and used for the collection of data for risk assessment test. The results and data collected from the water and sediment samples were subjected to statistical analysis at $p \leq 0.05$ level of significance. Student *t*-test (ANOVA) statistics was used to test the relationship between the physicochemical parameters and the toxic heavy metals in both water and sediments samples. The findings of the study indicated that, the mean concentrations of Pb, Cd, Cu, Co, Cr, and Ni in the water samples were: 0.140, 0.046, 0.010, BDL, 0.100 and 0.013 mg/L respectively. However, the mean concentrations recorded in the sediment samples were: 0.166, 0.005, 0.013, BDL, BDL, and 0.009 mg/L respectively. It also indicated that, concentrations of Cu and Co both in water and sediment samples were found to be lower than WHO/USEPA (2012), permissible limits. The levels of concentration of Cr were found to be higher in water but lower in sediments samples. However, the level of concentration of Ni was lower in water samples but, higher in the sediment samples while the concentrations of Pb and Cd in the water and sediment samples were found to be higher than the WHO/USEPA (2012), guidelines, indicating pollution of these portions of Shika dam water and sediments. The high level of Pb and Cd in water and sediment samples might be attributed to runoff of wastewater from agricultural activities within the study area. The findings from the results of this study revealed that, the concentrations of all the parameters studied were statistically significant ($P \leq 0.05$) among the sampling points which clearly indicates common pollution source. Similarly, concentrations of physicochemical parameters in both the water and sediments samples revealed that pH, TSS, alkalinity, PO_4^{3-} -P, NH_4^+ -N, NO_3^- -N, NO_2^- -N, SO_4^{2-} -S in water samples are lower than the recommended limits but higher in the sediment samples from the four sampling points used for this research. Results of the risk assessment test carried out in both the water and sediment samples revealed that, the analyzed toxic metals have the following risk assessment indices: $Pd >$, $Cd >$, $Cu >$, $Co >$, $Cr >$, and Ni.*

Keywords: Risk assessment, Dam Water, Sediment, Heavy Metals, Shika Dam, Nigeria.

1. Introduction

Physicochemical parameters of water are of extreme significance in the distribution of aquatic life and also in the breeding of aquatic life. They control chemical, biological and physical processes taking place in the environment (Mohamaden *et al.*, 2017). They also have influences on domestic life while physical and chemical parameters of



soil affect many processes such as microbial activities, plant growth and mineral uptake by plants; cations exchange capacity and compactness of soil etc (Rehman et al., 2016). Various physicochemical parameters like temperature, transparency, pH, total hardness, biological demand, nitrates, phosphates etc. are regulating the planktonic biomass and productivity of the freshwater bodies (Tamilnadu, 2010).

Heavy metals are considered to be point or nonpoint pollutant sources of dams, lakes, seas, and rivers. In general, heavy metals originate from terrestrial flows, atmospheric deposition and waste water discharge in water. High levels of these metals in dam water and sediments are considered as good indicator of man-made pollution in the area. Pollution of heavy metals in aquatic ecosystem is growing at alarming rate and has become an important worldwide problem. Increase in population, urbanization, industrialization and agricultural practices have aggravated the situation. As heavy metals cannot be degraded, they are deposited, assimilated or incorporated in water, sediment and aquatic animals and thus, causing heavy metal pollution in water bodies (Akan *et al.*, 2012). Many efforts have also been made to analyses risk associated with heavy metals in dam water and sediments. Various studies have proposed procedures to assess the total risk of dam water and sediments (Saha, 2011).

Metals trapped in aquatic ecosystems have an effect on the environment and can even threaten human health through the food chain due to their abundance, environmental toxicity, persistence, and bioaccumulation (Abolude, 2012). One of the major sources of heavy metals to aquatic ecosystems is the increasing industrial densely inhabited areas in the whole basin. It has great significance to understand the heavy metal pollution status in the surface water and sediment in dam (Uzairu A., Uba S., Sallau M. S., & Hamza A., 2013).

The aim of this research was therefore to determine the risk assessment of selected heavy metals in water and sediment of Shika Dam, Zaria, Nigeria.

Risk Assessment of Water and Sediment in Dam

Many efforts have also been made to analyses risk associated with heavy metals in dam water and sediments. Various studies have proposed procedures to assess the total risk of dam water and sediments. There are two main approaches to quantitatively analyzing dam overtopping caused by flood: probabilistic risk analysis and indicator-based risk analysis. While the probability estimation relies on large samples of historical data, the indicator-based method solves the non-linear problems inherent to risk assessment in a complex manner. Bureau's methods can deal with these problems (Srikanth, *et al.*, 2013). The widely known method recommended by Bureau (1989) quickly rates total risk and evaluates the seismic hazard of a dam site and the risk rating of the structure separately. The method was developed by Bureau, who combined these two factors to define the total risk factor (TRF) and established the type of dam as an important parameter impacting the TRF (Zoynab, *et al.*, 2013). The method was subsequently applied to dams in South Carolina and neighboring states and to the Euphrates Basin in Turkey. According to Bureau's method, the total risk rating is based on the capacity of the reservoir, the height of the dam, the evacuation requirements, and the potential downstream damages (Ghrefat and Yusuf, 2006).

In recent years, many researchers developed different methods to evaluate heavy metal contamination in aquatic ecosystems. With regard to sediment, geochemical normalization and pollution indices were applied in risk assessment; i.e., contamination factor (CF), sediment quality guidelines (SQGs), geoaccumulation index (IGeo), modified degree of contamination (mCd), pollution load index (PLI), metal pollution index (MPI), enrichment factor (EF), and potential ecological risk index (PERI). Although reviewing literature revealed that applying those methods on metals assessment was a controversial issue, geochemical normalization with conservative elements had been effectively used for evaluating the pollution degree of metal pollutants and identifying their anthropogenic and natural sources (Rinklebe J., & Shaheen S. M. 2014).

Compared with sediment, relatively few methods have been applied in evaluating water quality. The heavy metal pollution index (HPI) was always used for evaluating drinking water quality, while the hazard index (HI) and excess cancer incidence (ELCR) were applied for human health risk assessment associated with the ingestion and dermal absorption of metals through water. The latter method under a residential scenario was frequently used for evaluating heavy metals in water (Zoynab, *et al.*, 2013).



In China, a great deal of research has focused on heavy metals enrichment in riverine systems since 2000. Unfortunately, few research studies have focused on assessing the levels of heavy metal contaminants in the Gan River, with only a few investigations reporting data on a certain metal or river section. The Gan River, one of the main tributaries of Poyang Lake and similar to other rivers in China, is the only surface water source for local drinking water and is suffering from frequent anthropogenic impacts due to the pressure of severe mining plus ore dressing and smelting activities upstream; the metal-associated industry downstream; severe metal pollution in the environment, especially in aquatic ecosystems.

Metals trapped in aquatic ecosystems have an effect on the environment and can even threaten human health through the food chain due to their abundance, environmental toxicity, persistence, and bioaccumulation. One of the major sources of heavy metals to aquatic ecosystems is the increasing industrial densely inhabited areas in the whole basin. It has great significance to understand the heavy metal pollution status in the surface water and sediment in dam (Saha and Hossain, 2011).

Physicochemical Parameters in Water and Sediments

Physicochemical parameters of water are of extreme significance in the distribution of aquatic life and also in the breeding of aquatic life. They control chemical, biological and physical processes taking place in the environment. They also have influences on domestic life while physical and chemical parameters of soil affect many processes such as microbial activities, plant growth and mineral uptake by plants, cations exchange capacity and compactness of soil etc. (Zubia, *et al.*, 2015).

Water, the dynamic abiotic component is directly related to human beings for different purposes (Bastami, *et al.*, 2015). The quality of water is described by the physical, chemical and biological characteristics (Adarshkumar *et al.*, 2006). Seasonal variation in physicochemical characters of water prevailing in the pond ecosystems was reported by many researchers (Singh, 2000; Ramachandra *et al.*, 2005; Papastergiadou, *et al.*, 2007 and Whelan *et al.*, 2008). Water quality has a direct impact on species specificity, composition, distribution pattern, stability and productivity of an aquatic ecosystem (Pendse *et al.*, 2000 and Radhika *et al.*, 2004).

Various activities of man on aquatic ecosystem create water pollution. According to WHO (1995), 30 – 80% of human diseases occur due to the use of impure water. The chemistry of water is influenced by the different types of inputs containing minerals, rainfall pattern, depth of water, soil properties, human impact and contamination from several sources, which are the major ecological crisis today. Begum and Harikrishnan (2008) has reported the untreated sewage affect the primary productivity and pollution status of the aquatic ecosystems in India.

Several biotypes with acute contamination of pollutants are the outcome of dumping off domestic, agricultural, municipal and industrial wastes into these aquatic system of life (Srivastava *et al.*, 2003; Khan and Shah, 2004; Usha and Ramalingam, 2006; Zuber and Sharma, 2007 and Parray *et al.*, 2009). As water is the basic necessity of life, such resources need to be managed for human survival. Physico-chemical characteristics not only reflect the quality of an aquatic ecosystem but also its biological diversity (Ghavzan *et al.*, 2006). Seasonal variation in ecological parameters exerts a profound effect on the population density of both animals and plant species (Odum, 1971).

Various physicochemical parameters like temperature, transparency, pH, total hardness, biological demand, nitrates, phosphates etc. are regulating the planktonic biomass and productivity of the freshwater bodies (Adeyemo *et al.*, 2008). Nutrients from different sources were drawn into the ponds, which in turn have a direct influence on the aquatic vegetation (Harikrishnan and Azis, 2000 and Mandol *et al.*, 2003).

For the maintenance of ecological balance, physicochemical parameters are required and different ecological conditions highlight the limnological studies. Raushankumar and Ramachandra (2010) has reported the global values of wetlands (\$ 3.2 trillion per year) rivers and lakes (\$ 1.7 million per year) which indicate the key importance of freshwater to human beings. Contamination of water bodies leads to a change in their trophic nature and several factors could act as stressors. Agarkar and Thombre (2005) highlighted the biological assessment is a useful alternative tool for assessing the ecological quality of an aquatic ecosystem since biological communities integrate the environmental effects of water chemistry.



In recent years, intensive agricultural and other developmental activities meet the needs of the escalating population affecting the surface and ground water sources at an alarming rate throughout the country (Karunakaran and Ramalingam, 2008). Remarkable changes were made on nutritional levels by the increase in urbanization, industrialization and over exploitation of natural resources (Eswari and Ramani, 2002 and Sawant and Telave, 2009).

Studies were made throughout India regarding the physicochemical parameters of ponds Ada, F.B., Ayotunde, O. and Ofem, B.O., 2012). Shanthi *et al.* (2003) have reported the nutrient analysis of Singanallur lake in Coimbatore. Seasonal variation of hydrological parameters and distribution of nutrients in the Veli Akkulam lake was highlighted by Jacob *et al.*, (2008). Murugesan *et al.* (2004) has pointed out the importance of water bacteria in maintaining the water quality. The ecological variation of a freshwater pond was studied by Sasmal *et al.*, (2005). Thirumala *et al.*, (2006) presented the diurnal variation in water quality of Ayyanakere lake, Western Ghat region of Chikmangalore, Karnataka.

The freshwater habitats have their own characteristic features which was moulded by local conditions and physiographic features (Abida, *eta al.*, 2008). Variation in dissolved oxygen and biological oxygen demand in two freshwater bodies of Bodhan, Andhra Pradesh was studied by Solanki *et al.* (2007). They reported the different pollutants in the water system determine the quality of water. As suggested by Raina and Vobra (1996) the freshwater ecosystems required conservation to maintain the physicochemical and biological quality of water. Hence, the present study is selected to know the annual and seasonal variations of physicochemical parameters of water and its influence on the distribution and seasonal abundance of Chlorophyta.

2. EXPERIMENTALS

Description of the Study Area

Shika dam is the zoned type it was constructed in 1975 on the river Shika to cater for the township water supply and other benefits. The dam has the following characteristics: It covers 18.8 hectares of land with catchment area of about 3200Km². It has gross storage capacity of 16.0x106 m³ and its maximum height is about 14.9m. The dam's length crest is approximately 640m with a lengthy lake of about 32Km – 35 Km at maximum flood water level. The dam has about 872 million liters of water supply capacity (WADPCO, 1991; in Butu & Bichi, 2013). Although the dam was constructed mainly for water supply, farming activities mainly by people living around the reservoir has been substantial over the years. The dam is located on latitudes 11°07'45"E to 11°08'20"E and longitudes 07°46'N to 07°48'N (Akan *et al.*, 2012).

Quality Assurance

Blank samples were scrutinized after every three samples for the purpose of ensuring a quality data. The levels of heavy metals were calculated based on a dry weight and all the determinations were carried out in triplicate so as to calculate the percentage error that might emanate from the measurement.

(a) Water: Plastic bottles which was washed with detergent, rinsed and soak in 10% HNO_{3(aq)} for 24hours and finally rinsed with distilled water was used to collect the samples.

Samples Collection

(i) Water: The plastic containers were rinsed three times and filled to brim at the depth of one meter below the water. the samples were collected from six sampling points by dipping the plastic bottles in the water before the sediment is reached and also at the surface to make a composite sample. The samples were collected for a period of two weeks intervals labeled and it was stored in a refrigerator prior to analysis.

(ii) Sediment: Sediment samples were collected at four set of locations (East, West, North, South, bottom- side layer of the dam). The top layer of the sediment was first collected from 0-15cm (Akan *et al.*, 2012). All the



sediment samples after decantation of overlying water and isolation of pore water were kept in polythene bags, labeled and transported to the laboratory for analysis.

Samples Pre-Treatment

(a) Water Samples

Water samples for metal analysis were treated immediately with few drops of conc. nitric acid and it was stored in a laboratory refrigerator prior to analysis.

(b) Sediment Samples

The sediment samples collected were air dried to constant weight and a composite sample was made and kept prior to determination of physicochemical parameters and digestion for heavy metals analysis.

Samples Digestion

(a) Water Samples: 100ml of each water sample was transferred into a 250ml beaker and 5ml conc. HNO_3 was added to it and it was placed on a hot plate to evaporate down to about 20mL at 100°C . The sample was allowed to cool and another 5ml conc. HNO_3 was added. It was covered with a watch glass and resumed heating with addition of a portion of conc. HNO_3 to the mixture until the solution appear light yellow in colour and clear. The sample was filtered while hot to remove insoluble materials that could clog the atomizer, the filtrate was allowed to cool and it was diluted to the mark in 1000cm^3 volumetric flask with distilled water. The sample was subjected to AAS analysis in accordance with (Enders & Lehmann, 2012).

(b). Sediments: 2.0g of the sediment samples was weighed into a previously acid-washed glass beaker and it was digested by the adding 20cm^3 of conc. aquaregia followed by 10cm^3 of 30% H_2O_2 which was added in small portions to avoid any possible overflow leading to loss of materials. The beaker was covered with watch glass, and heated over a hot plate at 90°C for about 2hours. The sample was filtered and diluted to 100cm^3 with distilled water which was transferred to 1000ml flask and diluted further to the mark. It was stored in plastic containers prior to laboratory analysis (Saha, 2011 and Akan *et al.*, 2012).

Analysis of Samples

Six samples of both water and sediments were analyzed in triplicate for Pb, Cd, Cu, Co, Cr and Ni, with AAS machines at National Research Institute of Science and Technology (NARICT) Laboratory, Zaria.

Determinations of Physicochemical Parameters

In this study, the following physicochemical parameters were determined: pH, Electrical Conductivity (EC), Cation Exchange Capacity (CEC), Total Suspended Solids (TSS), Turbidity, Alkalinity, Anions: (Cl^- , PO_4^{3-} , NH_4^+ , NO_3^- -N, NO_2^- -N & SO_4^{2-} ions) and cations (Pb^{2+} , Cd^{2+} , Cu^{2+} , Co^{2+} , Cr^{2+} & Ni^{2+}) were determined in accordance with the standard analytical methods below:

(i) Determination of pH Values

The pH meter was calibrated using standard solutions (pH 4, 7, and 10 buffers are recommended, by (Monica Z. Bruckner, 2016). pH of the water was taken directly at the dam sampling points. The probe of the pH meter was submerged into the water and wait until the pH reading stabilizes and the pH values were recorded immediately. The pH of the water was taken twice from the 3 sample sites in the dam. The results of the pH values are presented in form of table in chapter four.



(ii) Electrical Conductivity of the Water Samples

The electrical conductivity meter used was calibrated with a standard solution of known conductivity. The probe was thoroughly rinsed before and after calibration with distilled water and carefully wipe with tissue paper. About 200ml of the water sample was placed in plastic beakers so that the probe tip can be deeply submerged in to it; the probe was carefully submerged into the samples and wait until the EC readings on the meter to stabilizes and the values was recorded immediately.

(iii) Total Suspended Solids in Water Samples

In this method, filter papers were used which was initially washed with distilled water and cool dry, after which it was pre-weight and recorded the mass as (W_1). Filtration apparatus was assembled, 200ml water sample was measured and placed in a glass beaker, and the sample was stirred with a magnetic stirrer. A pipette was used to measure 50ml of the water samples while vigorously stirring and it was transferred on same pre-weight filter paper on the filtration set up and filter the water after which the filter paper was placed on a suction funnel of a vacuum pump and rinse three times with distilled water it was allowed to cool dry by suction and later in the oven at 105°C for about 20minutes. The paper was removed with a forceps and place in a desiccator for cool dry and re-weights to get the actual mass of the paper plus the dissolved particles. The process was repeated three times in order to take average of the determination. Total suspended particles in the water samples were determined by calculation using the relation: Amount of suspended solids = (weight of filter + sample - (weight of filter)) x $100/\text{Volume of Sample} = (W_2 - W_1) \times 1000$ in mg/ L.

(iv) Turbidity of Sediment Samples

For testing the sediment and the water samples, a control was prepared by dissolving 1.0g hydrazine sulphate in a beaker and transferred to a 100mL flask and 10.0g hexamethylenetetramine was also measured and dissolved in 100mL volumetric flask which was make up to the mark with distilled water. 5mL of hydrazine sulphate and 5mL of hexamethylenetetramine solutions was measured and mixed in another 100mL flask the mixture was allowed to stand for 24 hours which was used as standard working solution and it was used to calibrate the instrument. Turbidity meter (DR/890) model was used set and it was used to measure the test samples small portion of water samples was poured in to the sample cells of the meter a up to the horizontal mark and the cell was covered with lid. Readings was checked when the meter stabilized after some minutes and t was recorded directly as displayed by the meter.

(v) Determination of Alkalinity of the Water Samples

100mls of each sample was taken with a pipette and it was placed into a clean dry glass beaker on a magnetic stirrer. Burette was charged with 0.02M sulphuric acid solution followed by 5drops of phenolphthalein indicator was also added to the mixture. The solution was monitored for a colour change from colourless to pink and the acid solution was added slowly till the pink colouration totally disappears. Volume of acid consumed was recorded as (VP). Few drops of methyl orange indicator were also added to the same sampling at the end of first titration and 0.02 M sulphuric acid was added slowly till orange colour turns to pink (Zhang, *et-al.*, 2009).

(vi) Determination of Chloride ions (Cl⁻)

Chloride level was determined by argentometric titration method according to Ademoroti, (2009); in Mohr, (1879). It is the most significant methods for determination of chloride in water (Wang *et al.*, 2008) and (Zucci, *et al.*, 2012). Blank titration was conducted with distilled water prior to the major titration. 50ml of each water samples were measured and placed in a clean dry 250ml conical flask, followed by few drops of 1M NaOH solution to adjust the pH to 8.0 and 1cm^3 of K_2CrO_4 solution was added to the mixture as indicator. The mixture



was titrated against standard solution of AgNO_3 solution (0.01M) to end-point (from light yellow to bricks red colouration). The chloride ions concentration was calculated using the relation:

$$\text{Conc. of Cl}^- (\text{mg/L}) = (V_{\text{SN}} \times M_{\text{SN}} \times 35.45) \times \frac{1000}{V_w}, \text{ Where:}$$

V_{SN} = volume of titrant used

M_{SN} = molarity of AgNO_3 solution

V_w = Volume of water sample used in (ml) and (35.45) is constant.

(vii) Determination of Phosphate ions (PO_4^{3-} -P) ions

Quantitative method to determine the amount of phosphate present in water samples (Deniges, 2005) was used. 20ml of each water sample was measured and poured in a mixing tube and ammonium heptamolybdate reagent was added drop-wise. The tubes were stoppered and shake vigorously with a mechanical shaker followed by addition of a freshly prepared stannous chloride solution. The solutions produce a blue colour (due to the formation of molybdenum blue) and the depth of the blue colour indicates the amount of phosphate in the sample. Absorbance of the blue solution was measured with a (JENWAY 7315 model) spectrophotometer and the concentration of phosphate in the original solution was calculated. Similarly for the sediments samples, 10.0g was sieved and it was dissolved in 100ml of water to get a homogenous suspension. Concentration of 0-P was measured following the method of Murphy & Riley (2013). The Tot-P concentration in the samples was measured after digestion as follows:

A standard stock solution of phosphorus of approximately 100mg P/dm^3 was prepared by dissolving 0.11g of KH_2PO_4 in distilled water and dilute in 250ml volumetric flask (Stock Solution A), 10cm^3 of the solution was measured and transferred to another 250ml volumetric flask labelled as (Stock solution B). The stock solution B was used to prepare working standards of approximately: 0.20, 0.40, 0.60, 0.80 and 1.0 mg P/dm^3 , by pipetting 5, 10, 15, 20 and 25 cm^3 portions respectively to separate a labelled 100ml volumetric flasks. 50cm^3 distilled water was placed into a 100ml flask as a blank solution and then all the analytical working solutions was subjected for analysis of PO_4^{3-} - p. Absorbance was determined at 740nm. The pH of the suspensions was controlled immediately after the dilution and before measuring the absorbance of the solution after 15min (Rehman, *et al.*, 2016).

(viii) Determination of Ammonium (NH_4^+ -N) ions

Ammonium sulphate is an inorganic salt with a high solubility that disassociates into ammonium (NH_4^+) and sulphate (SO_4^{2-}) ions in aqueous solutions. Ammonium sulphate is especially useful as a precipitant because it is highly soluble, has a relatively low density. The adsorptive removal of ammonium ions (NH_4^+) from the sediment aqueous solution and the water samples using surfactant-modified alumina. The equilibrium concentration of NH_4^+ was measured using a spectrophotometer (JANWAY 715) model (Murphy & Riley, 2013).

(ix) Determination of Nitrate (NO_3^- -N) ions

De-ionized water free of nitrite and nitrate was used in preparation of all reagents and standards used for this determination. 30% sodium chloride solution and (1:4) solution of sulphuric was used. A brucine-sulphanilic acid which was prepared by dissolving 1.0g brucine sulphate [$\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4$] $\cdot 2\text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$] and 0.1g sulphanilic acid ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$) in 70mL hot distilled water, plus 3mL conc. HCl was added to the mixture, it was allowed to cool, mixed and diluted to 100mL with distilled water. 0.1mg potassium nitrate stock solution was also prepared with distilled water in 1liter flask. The stock was preserved with 2mL chloroform and 1molar solution of glacial acetic acid was also prepared this is in accordance with method recommended by Dwivedi and & Vankar (2014).



The pH of the samples was adjusted to approximately 7 with acetic acid (6.7). Test tubes containing the solutions were set up in the water bath and 10.0mL of both the standards and samples were taken with a micro-pipette and diluted to 20.0mL in a sample tubes the solution was mixed by swirling the tubes and it was placed in a rack in ice-cold water. 10.0mL sulphuric acid solution was added into each tube and mixed thoroughly. The mixture was allowed to come to thermal equilibrium in the cold water followed by another 0.5ml brucine-sulphanilic acid was also added to each tube (except the interference control tubes). The mixture was carefully mixed by swirling, and then the rack containing the tubes was placed in water bath at 100°C for about 25minutes, it was then removed from the hot water bath and it immediately immersed in a cold-ice water bath and allowed to reach thermal equilibrium (20-25°C). The tubes containing test samples was taken to AAS for analysis and absorbance was measured at 410nm against the reagent blank. A calibration curve was used to obtain the amount of NO₃-N in the test samples.

(x) Determination of (NO₂⁻-N) ions

Quantitatively (NO₂⁻ -N) ions was measured through the following process:

Reagents preparations: NO₂⁻ free water was prepared as follows:

1.0g crystal each of KMnO₄ and Ca(OH)₂ was dissolved in 1000ml of distilled water and the solution was redistilled. 50ml of distillate was discarded to obtain clearer fraction of the distillate which was free of permanganate. 1ml of conc. H₂SO₄ and 0.2ml MnSO₄ solution (36.4 g MnSO₄·H₂O/100 mL distilled water) was added to each 1L distilled water, and turns pink with 3ml KMnO_{4(aq)}. The solution was also redistilled to obtain standard solution of (NO₂⁻ -N) ions. Nitrite-free water was used in making all reagents and dilutions for this test for (NO₂⁻ -N) ions in the samples under study. Photometric measurement between 10 min and 2h after adding colour reagent to samples and standards was carried out and the absorbance was measured at 543nm. As a guide, the following light paths was used as indicator for NO₂⁻ -N concentrations:

Light Path Length (cm)	NO ₂ ⁻ -N (µg/L)
1	2 – 25
5	2 – 6
10	< 2

Self & Waskom (2013).

Calculations: A standard curve was prepared by plotting absorbance of standards against (NO₂⁻ - N) concentration and the sample concentration was compute directly from curve.

(xi) Determination of (SO₄²⁻) ions

250ml of the unknown sample was measured into a 500ml beaker and 3ml of 1:1HCl solution was added. A colourless solution was formed, the solution was heated to near boiling point and 80ml of 0.05M BaCl₂ was added slowly to it with continuous stirring. Cloudiness was formed and later a white precipitate of BaSO₄ formed beneath the solution.

The precipitate was digested for about 30mins in a water bath. Test for completeness was done by adding two drops of BaCl₂ to the solution, when cloudiness was noticed; 40ml of BaCl₂ was also added to the solution and allowed to digest for about 20mins. There was cloudiness when two drops of BaCl₂ was added to the solution. A filter paper of constant weight and cooled in a desiccator was weighed and its mass noted. The recorded mass was 1.048g. The precipitated of BaSO₄ was filtered with suction pump. A white crystalline precipitate of BaSO₄(s) was left on the filter paper and the filtrate obtained contained white gelatinous precipitate suspected to be BaCl₂ and lost BaSO₄ precipitate. The filter paper and the residue (BaSO₄) were dried for about 6mins and weighed. The recorded weight was 3.5363g.



(xii) Cation Exchange Capacity (CEC)

2g of sediment sample was taken in 10mL centrifuge tube which was used to obtain up to three washings with 1M sodium acetate. The excess sodium was also removed by washing thrice with 95% ethanol and sodium on the exchange was replaced in three washings with 1M ammonium acetate. The sodium content in ammonium acetate extracted was determined using a flame photometer and CEC of sediments was expressed as meq/100gms.

Three drops of a test solution onto the mixture and the dilution of the sample to a 2mL after colour development (3min). The absorbance of solutions was measured after 15min at 740nm. three drops (0.10 ± 0.01mL) of a KH₂PO₄ solution and water and sediment samples were added to a 2mL graduated test tube with a dry reagent mixture (100mg). The sediment suspension was diluted by a factor of 20. The test sample was also diluted to a volume of 2mL with twice-distilled water. Absorbance was determined at 740nm after 15min and the pH of the solution was controlled immediately after the dilution and before measuring the absorbance of the solution after 15 min (Gupta, 2014).

Risk Assessment Test

Hazardous Index (HI) was used to estimate the risk to human health through the hazard index (THI) developed (Gupta *et al.*, 2014). The hazard index is the sum of the hazard quotients which was calculated as follows:

THI = ΣHQ, -----(eqn 1), and
ΣHQ = (HQ_{Pb} + HQ_{Cd} + HQ_{Cu} + HQ_{Co} + HQ_{Cr} + HQ_{Ni}).-----(eqn 2)

Where: THI = Total Hazardous Index and HQ = Hazard Quotient for the metals
The following equation is used to represent daily exposure route as modified by (USEPA and Chrostowski adopted by Kavcar *et al.*, 2012)

CDI = C X DI/BW -----(eqn 3)

Where: CDI = Is the Chronic Daily Intake (mg/kg/d),
C = Concentration of the water contaminant (mg/L),
DI = Is the Average Daily Intake rate of the water (l/d), and
BW = Is the Body Weight in (kg).

The hazard quotient, (HQ) was calculated using the following equation:

HQ = CDI/RfD . -----(eqn 4)

Where: HQ = Hazard Quotient and RfD = Is the Reference Dose (mg/kg).

The RfD values employed in this study were obtained from the USEPA (2012).
when the values are less than 1 (i.e if HQ or THI < 1) it means there is no risk and generally, the greater the values, the greater is the risk level of the toxicants manifesting long term health hazard effects increasing (Klamath, 2011; Potter & Wimsatt, 2012 and USEPA, 2012).

Contamination Assessment

Contamination of heavy metals in sediment was determined according to contamination factor (Cf) and degree of contamination (Cd). The Cf is calculated according to method described by (Achadu *et al.*, 2015; Sulaiman *et al.*, 2019 in Thomilson, *et al.*; 2008) and the degree of contamination (Cd) was determined as the sum of all contamination factors using the relation: Cf = Measured Concentration / Background Concentration Where, Background value of the metal= world surface rock average given by (Asa *et al.*, 2013).

Statistical Analysis

One-way ANOVA statistics was used to assess whether the samples varied significantly between physicochemical parameters and the heavy metals in water and sediment samples at $p < 0.05$ level of significant.

Results and Discussion

The results obtained were presented in the forms of Tables. The data were analysed using SPSS at $P \leq 0.05$ level of significance adopted for the research.

Table 1: The Physicochemical Parameters Determined in the Analyses Samples

Parameters	mean conc. in Water	mean Conc. in Sediment	WHO permissible limits
pH	8.5	6.2	6.5-8.5
E.C ($\mu\text{g}/\text{cm}$)	60.3	28.6	NG
C.E.C (mol/kg)	19.5	18.63	NG
TSS (mg/L)	54.5	73.73	500
TURB. (F.A.U)	79	106.8	NG
ALK. (mol/L)	0.073	0.1	200
Cl-	143	466	250
PO_4^{3-} - P	8.47	343	5.0
NH_4^+ -N	45	125	2.50
NO_3^- -N	58.72	627	45
NO_2^- -N	22.40	252	5.30
SO_4^{2-}	117.43	815	30

Key: NG= No guideline, BDL = Below detection Limit, (APHA, 2012)

Table 2: Concentration (in mg/L) of Heavy Metals in Water Samples

Samples	Pb	Cd	Cu	Co	Cr	Ni
A1	0.1748	0.0101	0.0142	BDL	0.0964	0.006
A2	0.1126	0.007	0.0012	BDL	0.1296	0.0148
A3	0.1315	0.1211	0.0147	BDL	0.0727	0.0178
Mean	0.140±0.032	0.046±0.065	0.010±0.008	BDL	0.100±0.029	0.013±0.006
WHO (Standard)	0.01	0.003	2	NG	0.05mg/L	0.02mg/L

Table 3: Concentrations (in mg/L) of Heavy Metals in Sediment Samples

Samples	Pb	Cd	Cu	Co	Cr	Ni
B1	0.2128	0.0047	0.014	BDL	BDL	0.0194
B2	0.2292	0.0082	0.0135	BDL	BDL	0.0006
B3	0.0557	0.002	0.0126	BDL	BDL	0.0057
mean conc.	0.166±0.032	0.005±0.065	0.013±0.008	BDL	BDL	0.009±0.006
WHO (Standard)	0.01	0.003	2	NG	0.05	0.02



Table 4: ANOVA for the Selected Heavy Metals in Water and Sediment Samples

		Sum of squares	df	mean square	F	Sig.
Pb	Between Groups	.001	1	.001	.203	.676
	Within Groups	.020	4	.005	-	-
	Total	.021	5	-	-	-
Cd	Between Groups	.003	1	.003	1.197	.335
	Within Groups	.008	4	.002	-	-
	Total	.011	5	-	-	-
Cu	Between Groups	.000	1	.000	.564	.494
	Within Groups	.000	4	.000	-	-
	Total	.000	5	-	-	-
Co	Between Groups	0.000	1	0.000	-	-
	Within Groups	0.000	4	0.000	-	-
	Total	0.000	5	-	-	-
Cr	Between Groups	.015	1	.015	36.406	.004
	Within Groups	.002	4	.000	-	-
	Total	.017	5	-	-	-
Ni	Between Groups	.000	1	.000	.420	.552
	Within Groups	.000	4	.000	-	-
	Total	.000	5	-	-	-

Table 4: ANOVA for the Selected Heavy Metals in Water and Sediment Samples (Continued)

Metals		Sum of squares	Df	mean Square	F	Sig.
Pb	Between Groups	.001	1	.001	.203	.676
	Within Groups	.020	4	.005	-	-
	Total	.021	5	-	-	-
Cd	Between Groups	.003	1	.003	1.197	.335
	Within Groups	.008	4	.002	-	-
	Total	.011	5	-	-	-
Cu	Between Groups	.000	1	.000	.564	.494
	Within Groups	.000	4	.000	-	-
	Total	.000	5	-	-	-
Co	Between Groups	.000	1	.000	-	-
	Within Groups	.000	4	.000	-	-
	Total	.000	5	-	-	-
Cr	Between Groups	.015	1	.015	36.406	.004
	Within Groups	.002	4	.000	-	-
	Total	.017	5	-	-	-
Ni	Between Groups	.000	1	.000	.420	.552
	Within Groups	.000	4	.000	-	-
	Total	.000	5	-	-	-



Table 5: Correlation Matrix of Heavy Metals in Water and Sediments from Shika Dam

Metals	PbW	CdW	CuW	CrW	NiW	CdS	CuS	CoS	NiS	pHw	ECW
PbW	1										
CdW	-.198	1									
CuW	.712	.548	1								
CrW	-.387	-.828	-.923	1							
NiW	-.854	.679	-.241	-.150	1						
CdS	.137	-.998*	-.599	.861	-	1					
					.633						
CuS	-.366	-.840	-.914	1.000*	-	.872	1				
					.172						
CoS	.550	-.927	-.195	.557	-	.902	.575	1			
					.905						
NiS	.999*	-.232	.686	-.354	-	.172	-.333	.580	1		
					.872						
pHw	.947	.128	.900	-.663	-	-.189	-.646	.253	.935	1	
					.641						
ECW	.999*	-.246	.676	-.340	-	.186	-.320	.591	1.000**	.930	1
					.878						
CECW	-.058	-.967	-.743	.943	-	.981	.950	.801	-.023	-	-.009
					.470					.376	
TSSW	-.761	-.486	-.997*	.893	.311	.539	.883	.123	-.737	-	-.728
										.929	
TURW	.309	-.993	-.449	.758	-	.984	.772	.964	.342	-	.355
					.759					.014	
ALKW	.799	.431	.991	-.863	-	-.486	-.852	-.062	.777	.950	.768
					.369						
ECS	-.906	.594	-.347	-.040	.994	-.543	-.062	-.852	-.920	-	-.926
										.722	
CECS	-.999*	.146	-.748	.434	.825	-.084	.415	-.506	-.996	-	-.995
										.962	
TSSS	-.535	-.722	-.974	.986	.017	.764	.982	.411	-.505	-	-.492
										.778	
TURS	.817	-.727	.176	.217	-	.683	.238	.931	.837	.588	.844
					.998*						
ALKS	-.904	-.241	-.944	.744	.548	.301	.730	-.140	-.888	-	-.881
										.993	

Table 5. Cont.....

Metals	CECW	TSSW	TURBDYW	ALKNTYW	ECS	CECS	TSSS	TURBDTYS	ALKNTYS
CECW	1								
TSSW	.692	1							
TURW	.932	.382	1						
ALKW	-.647	-.998*	-.325	1					
ECS	-.370	.415	-.682	-.470	1				
CECS	.111	.794	-.258	-.830	.882	1			
TSSS	.875	.955	.638	-.935	.127	.579	1		
TURS	.529	-.247	.801	.306	-	-.785	.051	1	
					.984				
ALKS	.480	.965	.128	-.980	.638	.925	.845	-.491	1

Correlation Significant at P ≥ 0.05 level.

Table 6: Results of Risk Assessment Contribution to Total Risk Factor

Risk Factor	Extreme	High	Moderate	Low
CRF/(10 ⁴ m ³)	>6170 (6)	6170–123 (4)	123–12.3 (2)	<12.3 (0)
HRF/(m)	>70 (6)	70–30 (4)	30–15 (2)	<15 (0)

Adopted from (Kacholi, 2018) in *Journal of Chemistry/hindawi.com/jchem/*.

Discussion of Results

Physicochemical Parameters

The physicochemical parameters determined in water and sediment samples were: pH, E.C., C.E.C, TSS, turbidity and alkalinity. The mean pH value of water 8.5 and sediment 6.2 were all within the normal pH range of dam's water as recommended standard for drinking and domestic purposes of 6.5–8.5 (WHO, 2008). This is in line with the findings made by (Adamu *et al.*, 2014) in his summary of descriptive statistics of physical parameters and trace elements in pond and stream water samples which he found that, they were moderately acidic with mean pH values of 5.50 for pond water and 5.86 for stream water respectively. E.C mean values 60.3 in water and 28.6 in sediment samples, CEC mean values were 19.5 and 18.63 in both water and sediment samples respectively.

But, TSS mean values in water were 54mg/L and 73.73mg/L in sediment samples. These concentrations were lower than the WHO recommended standard values 500mg/L. The TSS result for this study is contrary to the findings conducted by Adamu C. I., Nganje, T. N., and Aniekan E., (2014). In their research, the mean values of TSS were 154.08 for pond water and 259.28 mg/l for stream water. They concluded that, the high TSS in stream water relative to pond water is due to the fact that pond water is mainly from the mine site, while stream water includes water from the mine sites in addition to activities and these activities include runoff from agricultural lands, bush burning areas, etc. Higher concentration of TSS were recorded in the sediment samples, it might be attributed to high discharge and draining of waste into the dam. However, turbidity in sediment (106 NTU) out weight that in water samples (79 NTU). The alkalinity values in water (0.073) and sediment (0.10) is lower than WHO recommended values (200 mg/L).

Results of contamination levels of heavy metals revealed that, the dam water has little contaminants with range values of (8-12 x10⁴ yuan/km²) which is less than the considerable limit of high contamination of (100-500x10⁴ yuan/km²). The results in in line with the research findings of Benyassine, *et al*, (2013). They discovered that, exposition of wastes and their leaches leads to the contamination of surrounding pit lake waters and soils. Chemical analysis of lakes shows low contamination by heavy metals except for Arsenic and explained by the low mobility of these elements in alkaline solutions, their sorption by clay minerals and iron hydroxides. The high concentration of Arsenic is due to its great mobility and its methylation by organic matter.

Generally, the results revealed that Pb and Cd contents in water were higher than the WHO/USEPA standards. In water and sediment samples the two heavy metals levels were above the set standards. The findings on the average daily intake (ADI), hazard quotient (HQ), and hazard index (HI) revealed that consumption of water direct from the dam could pose risks to human health due to high level of lead Pb and cadmium Cd respectively. No matter how low levels of heavy metals are present in water and or sediments, their presence is not desirable. The parameters analyzed from the dams show variable concentrations in heavy metals (Pb, Cd, Co, Cu, Cr & Ni), some concentrations are much higher in comparison to (USEPA/WHO), while others samples show lower contents than standards.

Heavy Metals in Water and Sediments Samples

Table 2: Shows mean concentration (in mg/L) of the heavy metals in water samples in the following order Pb (0.140), Cd (0.046), Cr(0.10) which are higher than the WHO/USEPA recommended limit values of (0.01),



(0.003), (0.05) and (0.02) respectively. This means Shika dam' water is contaminated with those three metals (Pb, Cd & Cr). But conc. of Cu, Co, and Ni are insignificant in the water samples used for this study.

Similarly, Table 3: Shows mean concentration of heavy metals in the sediment samples which indicates that only two metals Pb (0.166mg/L), Cd (0.05mg/L) has higher concentrations than the WHO/USEPA recommended limit values of (0.01) and (0.003) respectively. This means Shika dam' water is contaminated with those three metals (Pb, Cd & Cr). But concentration of Cu, Co, Cr and Ni are lower than the WHO, USEPA recommended limit and therefore they are considered insignificant in the sediment samples.

Table 4 shows the summary of data subjected to ANOVA statistics to assess whether there are significant variations between physicochemical parameters and the heavy metals in water and sediment samples at ($P \geq 0.05$) probability level of significant. The results indicate that, some parameters and heavy metals shows positive correlation while others show negative correlations. It implies that, positive correlation means both heavy metals and the parameters are from the same source while negative correlations revealed that, the metals and the physical parameters are from different sources.

Risk Assessment

The average daily intake each metal was calculated as a product of average vegetable and water daily consumption from the dam area per person, percentage of dry weight of vegetables, and average heavy metal concentration per dry weight as shown in the equation (4) above. The average daily consumption of vegetables suggested by WHO guidelines in human diet is 300 to 350 g per person (Singh *et al.*, 2010 in FAO/WHO, 1989). The mean of 325 g/person/day was used in calculating the ADI values. An average weight of person was considered to be 60 kg.

The hazard quotient (HQ) was calculated with assumption that, when the quotient is <1 , this means no potential health effects are expected from exposure, but when it is >1 , it signifies that there are potential health risks due to exposure (Bermudez *et al.*, 2010). The HQ was calculated as a fraction of determined dose to the reference dose as shown in equation (6) where ADI is the average vegetables intake per day (mg/kg/day) and is the oral reference dose of the metal (mg/kg/day). is an approximation of daily tolerable exposure to which a person is expected to have without any significant risk of harmful effects during a lifespan. for Pb, Zn, Cu, and Fe is 0.004 mg/kg/day, 0.3 mg/kg/day, 0.04 mg/kg/day, and 0.7 mg/kg/day, respectively (Benyassine & Dekayir, 2012; FAO/WHO, 2013 and Ede, 2014).

Hazard Index (HI) was calculated as an arithmetic sum of the hazard quotients for each pollutant

The findings show that hazard quotient (HQ) values for all heavy metals under this study were <1 in all the samples. When HQ exceeds one, this means there are potential health effects from exposure. The high HQ for Pb and Cd were observed in both water and sediment samples and both has significant health risk, while for other metals like Co and Cr, are nearly absent in the samples. High HQ for Pb was also observed in the sediment samples. Although there may no health risk effects to the community due to insignificant interactions with the dam's sediments.

The result is in line with findings of (Ya *et al.*, 2017). In their findings on health risk analysis based on the EDI and THQ revealed that the dietary intake of Cu, Cd, Cr, Pb and Ni was low as compared to the provisional permissible tolerable daily intake set by (Yahaya *et al.*, 2010) (Abdel-Satar *et al.*, 2017). The THQ for Cu, Cd, Cr, and Pb were less than 1 while Ni was greater than 1 in the intestine, muscles, rumen and liver of the cows.

In summary, the results revealed that Pb and Cd contents in the dams' water were higher than the WHO/USEPA standards. The findings on the average daily intake (ADI), hazard quotient (HQ), and hazard index (HI) revealed that consumption of water direct from the dam could pose risks to human health due to high level of lead Pb and cadmium Cd respectively. The parameters show varied concentrations in heavy metals, some are much higher in comparison to (USEPA/WHO), while some show lower concentrations than the standards.



Conclusions

In this study the contamination factor and risk assessment of the selected heavy metals in both water and sediments of Shika dam of Kaduna state revealed that; concentrations of Cu & Co in both water and sediment samples were lower, conc. of (Cr) was higher in water but lower in sediment while conc. of (Ni) was found to be lower in water but, higher in the sediment samples. However, the conc. of Pb and Cd in both water and sediment samples were higher than the WHO/USEPA guidelines limits, indicates pollution of water and sediments in the dam.

Results of ANOVA revealed that concentrations of all the parameters studied were statistically significant among the sampling points at ($P < 0.05$). Furthermore, the concentration factors of the analysed metals in both the sediment and water revealed that; heavy metal contents of water were high in water while that of copper is below but cobalt conc. was below detection limits in every case. Similarly, in the sediment samples, both cobalt and chromium was found to be below detection limits and finally, the results show both positive and negative correlations between physicochemical parameters and conc. of the heavy metals used for this research.

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