



Distribution and Health Risk Assessment of Metal Species and Physicochemical Parameters of Water and Sediments of River Sasa, Ife North Local Government Area, Nigeria

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Article Info	ABSTRACT
Article type: Research Article	This study determined extent of contamination and total concentration of some potentially toxic elements in sediment and water samples obtained from River Sasa. Sequential extraction protocol was used to fractionate Mn, Cr, Cu, Zn, and Fe to specific phases in sediment and water samples. Atomic Absorption Spectrophotometry was used to quantify the metals while physicochemical parameters were determined using standard techniques. Overall mean concentrations of anthropogenic-related metals in sediments for the dry season was highest for Cr ($66.7 \pm 3.34 \mu\text{gg}^{-1}$) and lowest for Zn ($39.6 \pm 1.30 \mu\text{gg}^{-1}$), while for the wet season, the mean concentration was highest for Cr ($82.3 \pm 6.34 \mu\text{gg}^{-1}$) and lowest for Zn ($43.1 \pm 4.33 \mu\text{gg}^{-1}$). Generally, the metal levels followed the order: Fe > Cr > Cu > Zn > Mn. Physicochemical parameters of the water samples for dry and wet seasons were within the stipulated limit set by regulatory agencies. Speciation results indicated high bioavailability for Cr, Cu, and Zn in water samples while relatively low bioavailability was indicated for all the studied metals in sediment samples. Health risk assessment indicated that water quality was unsuitable for drinking in its present status without further treatment. Results of the pollution load index (PLI) indicated a deterioration level that called for concern in the quality of the river sediments. The results of this study showed that River Sasa was polluted with high bioavailable metals such as Cr, Zn, and Cu in the water which could pose threatening toxicity concerns to plants and animals.
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INTRODUCTION

Globally, the effect of potentially toxic elements (PTEs) on the aquatic ecosystem is enormous (Nazeer et al., 2014; Paudyal et al., 2016). Unfortunately, these elements are mentioned among the persistent environmental contaminants (Iqbal and Shah, 2013) of grave health concern. Generally, there are PTEs, such as Cu, Zn, and Co that are required in trace amounts for proper body functioning. However, in excessive amounts, they tend to cause severe hazards similar to those caused by toxic metals, such as Pb, As, and Hg to the health of the ecosystem. They could migrate to the aquatic ecosystem via bedrock, agricultural runoffs, water drainage, and

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atmospheric deposition (Iqbal and Shah, 2013; Paudyal et al., 2016) and this can subsequently lead to health risks to the aquatic ecosystem and the general biota (Wu et al., 2009). Also, the carcinogenicity, mutagenicity and cell damage of PTEs have been established (Ayannuga et al., 2015; Mishra et al. 2019; Wallace and Djordjevic 2020).

That increased human activities have translated to an upsurge in the metal levels of the environment is no gainsaying. Anthropogenic activities are believed to be the main cause of the contamination of water sources, according to certain studies carried out in Nigeria to assess the potability of diverse water sources (Egbueri, 2018, Ekere et al., 2019, Egbueri & Mgbeonu, 2020, Ukah et al., 2020).

The main pathways for transporting potentially toxic elements (PTE) are riverine systems as they can move metals through the hydrological gradient within a short timeframe. With their attendant toxicity effects, metals can build up gradually in the environment over time. The toxicity of these potentially toxic elements depends on their ability to imitate and displace essential metals in living organisms (Jaishankar et al., 2014; Jan et al., 2015). However, the mobility, solubility, and distribution of potentially toxic elements are dependent on physicochemical properties such as redox potential, dissolved oxygen, and pH. In the aquatic ecosystem, only about 1% of environmental contaminants spread in water, the sediments act as the final repository for the remaining 99% (Paramasivam et al., 2015; Nazneen and Patel, 2016). This means that metal levels in sediments would be higher than that of the water column (Li et al., 2013).

The study of PTEs in sediments is of prodigious significance due to its possible incorporation into the food chain which could be hazardous to human consumers and aquatic biota (Bo et al., 2014; Mohammad et al., 2015; Parween et al., 2017). The use of PTEs as indicators of aquatic system alterations is made possible by their susceptibility to groundwater dissolution from surface runoff, atmospheric depositions, sediments, and anthropogenic sources. The anthropogenic sources include wastewater irrigation, municipal and industrial wastes, agricultural runoff, traffic emission, smelting effluents, excess agrochemicals application on farmlands, mining, and fossil fuel combustion among others (Cengiz et al., 2017).

The analysis of sediments is an effective instrument of source apportionment and risk assessment (Varol, 2011; Li et al., 2013). However, measuring total elemental levels alone cannot account for the chemical forms of potentially toxic elements in sediments, which necessitates the use of a sequential extraction approach (Gutiérrez et al., 2004). Metal speciation can reveal important details about metal mobility and biological availability (Huang et al., 2013; Oyekunle et al., 2014). Many exciting studies have been conducted on metal levels in water and sediments of different water bodies all over the globe (Bhuyan and Bakar, 2017; Torregroza-Espinosa et al., 2018; Pandey et al., 2019; Lin et al., 2020; Muneer et al., 2021). However, there is a paucity of data on the study area that simultaneously addressed the physicochemical parameters, metal levels of water and sediments, and health risk assessment as a result of exposure to PTEs via ingestion, inhalation, and dermal contact.

The study area (River Sasa) serves as a main drain in Ife North Local Government Area and water from the river is utilized by the residents for all domestic applications, while subsistence farming is practiced along the river bank. The present study aimed to carry out a pollution or contamination assessment of River Sasa flowing through Ife North Local Government Area of Osun State and its associated sediments with respect to physicochemical properties and PTEs levels. This is because no previous study has been carried out to ascertain the occurrence and levels of metal species in the sediments and surface water of the aquatic ecosystem of this river, hence this study.

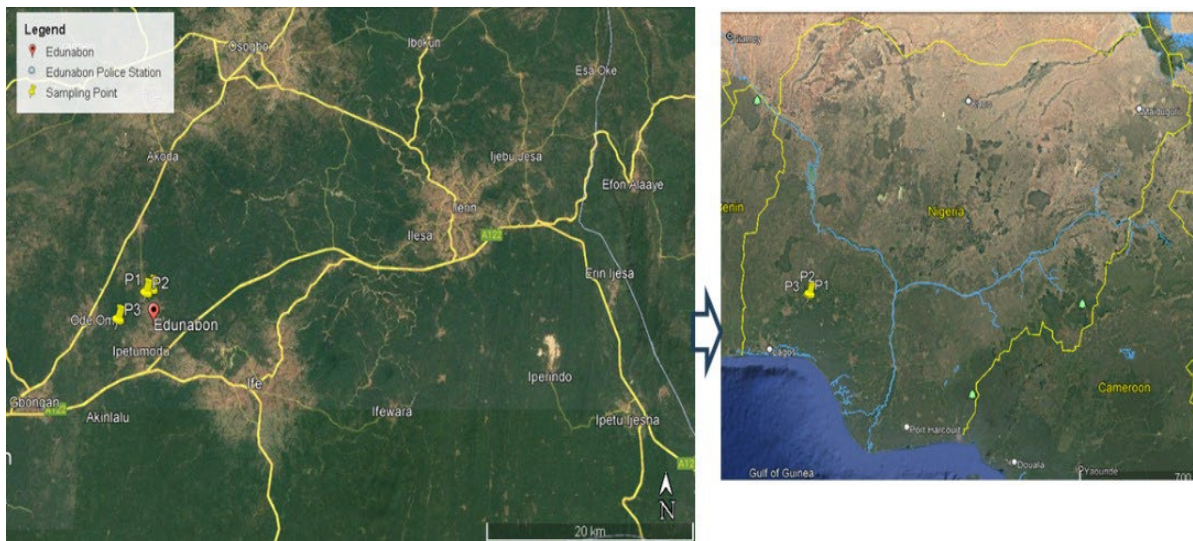


Fig. 1. Map of the study area showing the sampling points.

MATERIALS AND METHODS

Description of the Study Area

A map with the locations of the sample spots is shown in Figure 1.

People living in Ife North LGA have agriculture as their major source of income, with crops such as cassava, palm trees, vegetables, etc. Three locations along the stream were chosen for the studies, the distance from point 1 to 2 is 1.5 km and from point 2 to 3 is 1.5 km apart respectively. Point 1 (N07° 33.409'; E004° 27.094') located upstream, has a sandy substrate and a fairly constant flow rate. Local palm kernel oil production takes place on the stream's right flank, and water for daily activities is regularly collected from the stream. Fishing, laundry, and bathing are among the other human activities here. Point 2 (N07° 33.242'; E004° 26.784') was characterized by a fine-grain sediment bottom and swift-flowing current. This location was surrounded by grasses, plants, and shrubs, which enticed cattle farmers to graze their livestock in the nearby grassland. Point 3 (N07° 31.943'; E004° 25.287') downstream was characterized by a rocky bed and very a slow-flowing current. Activities at this point include farming and fire fetching, this point had less direct human contact than Points 1 and 2. Generally, the research location was chosen because of the vibrant human activity along the Sasa River's watercourse (Adekunle et al., 2020).

Reagents Used and their Sources

Reagents used for this research are Acetone (BDH Analar), Anhydrous Na_2SO_4 (MandB Laboratory chemical), n-hexane (BDH Analar), MnSO_4 , Silica gel 60-120 mesh (Oxford Laboratory Reagent), nitric acid, HNO_3 , hydrochloric acid, HCl , acetic acid, CH_3COOH , hydrogen peroxide, H_2O_2 , hydroxylamine hydrochloride, sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_7$ (BDH Chemical Ltd, Poole, England), hydrofluoric acid, HF (Riedel-deHaën, Germany), ammonium acetate, $\text{CH}_3\text{COONH}_4$, magnesium chloride, MgCl_2 , sodium acetate, CH_3COONa (MandB Ltd, Dagenham England), Amberlite XAD-16 resin (Sigma, USA), NaOH pellets (Merck, Darmstadt, Germany). The solutions were prepared with distilled water.

Sample Collection and Preparation

Detailed sampling procedures have been reported in previous research (Adekunle et al. 2020). However, a hand trowel was used to collect the sediment samples in a linear manner

along the river bed and around human activities, while 2.5 L pre-treated Winchester bottles were used to collect the water samples. Three samples were collected from three selected points along the river course, during January, February, and March (dry season) and July, August, and September (rainy season). The sediment samples collected were wrapped up in aluminum foil and transferred into polyethylene bags.

Analysis of Trace Metal Species in Water Sample

The procedure of Tokalioglu *et al.* (2002) was employed. It follows the determination of metals such as Cd, Ni, Cu, and Zn in water samples after sorption on Amberlite XAD-16 resin. Amberlite XAD-16 resin was ground to enlarge the sorption surface. It was then washed with methanol, distilled water, 1M HNO₃ in acetone, distilled water, 1 M NaOH, and distilled water. The water sample was filtered using a 0.45 μm membrane filter. The residue obtained was evaporated to near dryness with concentrated HNO₃ and was reconstituted with 2 mL of 2 M HNO₃. The metals in suspended particles were determined using FAAS. The filtrate was passed through a column packed with amberlite XAD-16 resin and the effluent obtained was adjusted to a pH of 9.8 using borate buffer solution and subsequently passed through a second column packed with amberlite XAD-16 resin. Both columns were then eluted with 1M HCl in acetone. The eluate from both columns was evaporated to near dryness, and 2M HNO₃ was added to about 1 mL of what was left. Analysis of trace metal species in the water sample was carried out using the FAAS instrument to determine free metal ions and metals bound to humic substances respectively.

The Water Quality Index (WQI) is a rating that reflects the composite influence of various water quality parameters, such as trace elements and heavy metals (Xiao *et al.* 2014). In this study, the weightings (w_i) were assigned based on the relative importance of the various water quality parameters in the overall quality of the water for drinking.

WQI is calculated by using the formula $WQI = \sum [W_i X C_i / S_i] X 100$

Where, $W_i = w_i / \sum w_i$, w_i is the weight of each parameter, and $\sum w_i$ is the sum of the weightings of all parameters. The calculated WQI are classified accordingly; excellent water (WQI < 50), good water (WQI = 50 – 100), poor water (WQI = 100 – 200), very poor water (WQI = 200 – 300), and water unsuitable for drinking (WQI > 300)

Analysis of Trace Metal in Sediment

The procedure of Tessier *et al.* (1979) was employed in the determination of the metal forms in the sediment samples. One gram of the sediment sample was thoroughly ground to afford a larger surface area. The addition of 20 mL of 1M MgCl₂ with agitation and filtration gave the exchangeable fraction. The addition of 20 mL of 1M NaOAc to the residue with agitation and filtration gave the carbonate bound fraction. 40 mL of 0.04 M NH₂OH.HCl in 25% HOAc was added to the residue from the second fraction to obtain the Fe-Mn oxide bound fraction. The organic bound fraction was gotten by adding 7.5 mL of 0.02 HNO₃, 12.5 mL of 30% H₂O₂ followed by heating, 7.5 mL of 30% H₂O₂ followed by heating then 3.2M NH₄OAc in 20% HNO₃ followed by agitation and filtration. To the residue from the organic bound fraction, 15 mL of concentrated nitric acid was added followed by heating and the addition of 10 mL of 3 M HNO₃ followed by agitation and filtration to give the residual fraction.

Determination of Physicochemical Parameters of Water

pH, Electrical Conductivity, Total Dissolved Solids, Temperature, and Oxidation Reduction Potential Determination

The pH of the water sample was determined in situ using an “ATC” hand pH meter (Eutech Instruments Pte Ltd Singapore). Before use, the pH meter was calibrated using freshly prepared buffer solutions of pH 4.0 and 9.0. The pH of each sample was determined at the sample

collection point by dipping the electrode of the pH meter into the sample. The pH measurement was done in triplicate.

Electrical Conductivity (EC), Total Dissolved Solids (TDS), temperature, and Oxidation Reduction Potential (ORP) of the water samples were determined by using a calibrated water instrument analyzer (Ultra meter II™ 6Psi serial 620769, U.S.A). The parameters of the water samples were determined in triplicate.

Dissolved Oxygen (DO) Determination

DO is the amount of oxygen measured in a water sample at the moment of collection. The method of measurement was done using Winkler's titration method.

The sample was put in a 250 mL BOD bottle and 2 mL MnSO₄ solution and 2 mL alkali-iodide-azide reagent below the surface of the liquid were added. The bottle was stoppered with care to exclude air bubbles, and the content was mixed by inverting the bottle several times until uniform supernatant water was obtained at the site. Following this, 2 mL conc. H₂SO₄ was added, stoppered, and mixed by gentle inversion until complete dissolution was observed. Accurately measured 201 mL of the sample was then titrated with 0.0125M Na₂S₂O₃.5H₂O solution to a pale straw colour. A 2 mL volume of starch solution was added and the solution turned blue. Titration was continued by adding more thiosulphate solution drop wisely till disappearance of the blue colour.

The DO was then calculated using the formula:

$$\text{DO (mg / L)} = \frac{16,000 \times M \times V}{V_1 - 2.0} \quad (1)$$

Where M = Molarity of the thiosulphate solution

V = Volume of the thiosulphate used for titration

V₁ = Volume of the bottle, with stopper in place

Biochemical Oxygen Demand (BOD) Determination

BOD was evaluated by measuring the dissolved oxygen present in the water sample before and after incubation in the dark at 20 °C for 5 days (Ademoroti, 1996). Following the procedure described for dissolved oxygen determination, the BOD₅ value was then calculated from the relationship:

$$\text{BOD}_5 \text{ (mg / L)} = \frac{(\text{DO}_o - \text{DO}_d) \times \text{Volume of BOD bottle}}{\text{mL of samole used}} \quad (2)$$

where DO_o = Dissolved oxygen determined in the sample on the initial day

DO_d = Dissolved oxygen determined in the dilutions of the samples after the titration on the fifth day.

Determination of Sulphate Ion (SO₄²⁻), Phosphate Ion (PO₄³⁻), and Nitrate Ion (NO₃⁻)

The determination SO₄²⁻, PO₄³⁻, and NO₃⁻ was carried out using turbidimetric, colorimetric, and ultraviolet techniques respectively. These procedures adopted are as reported elsewhere (Ademoroti 1996; APHA 1995).

Validation of Adopted Analytical Procedures

The efficiency of the digestion method, the precision, and the accuracy of the atomic absorption spectrophotometer were validated by a spiking experiment. The results as shown in Table 1

Table 1. Percentage Recovery (%R) values for the Metals in Sediment Samples

potentially toxic elements	Calibration curve, r^2	Amount spiked (μg^{-1})	Amount recovered (μg^{-1})	% Recovery
Fe	0.995	25	22.5	90.2
Zn	0.999	25	22.1	88.6
Mn	0.999	25	22.1	88.3
Cu	0.997	25	21.6	86.5
Cr	0.996	25	21.4	85.7

Table 2. Levels of Physicochemical Parameters of Water Samples of River Sasa

Parameter	Dry season			Wet season		
	P1	P2	P3	P1	P2	P3
pH	8.7±0.1	8.7±0.0	8.6±0.0	8.5±0.1	8.5±0.0	8.5±0.0
Temperature (°C)	28.3±0.4	28.2±0.5	28.0±0.4	24.5±0.3	24.7±0.3	24.3±0.1
TDS (mg/L)	112.9±4.0	118.1±12.2	128.9±10.2	144.3±18.2	149.2±19.4	147.8±10.6
ORP (mV)	335.8±7.4	336.9±5.3	340.0±1.8	343.8±3.6	345.4±4.1	348.1±4.6
EC (μScm^{-1})	179.8±5.4	187.6±19.3	198.2±15.8	216.7±22.5	236.1±30.6	233.2±16.9
DO (mg/L)	6.0±0.6	6.2±0.6	6.4±1.2	6.2±0.4	6.6±0.2	6.8±1.1
BOD (mg/L)	3.1±0.8	2.9±1.5	2.4±1.0	2.9±0.9	2.8±0.9	2.3±0.1
SO_4^{2-} (mg/L)	5.6±5.0	5.2±3.7	8.0±8.3	17.5±2.5	22.8±1.6	17.3±1.5
NO_3^- (mg/L)	1.9±1.4	1.8±1.7	1.1±0.6	4.3±0.1	4.4±0.8	4.1±0.2
PO_4^{3-} (mg/L)	4.3±0.1	3.8±0.2	1.3±0.3	3.0±1.4	3.3±0.9	0.8±0.2

revealed that the percentage recovery for the aqua-regia digestion ranged from 85 to 90 % for all the metals, with Fe having the highest and Cr having the lowest. The standard calibration curve developed under the experimental conditions showed a high linearity level with r^2 values ranging from 0.9958 to 0.9998 for sediment samples. The percentage recoveries for the metals showed that the uncertainties in the methods of analyses used were within acceptable limits (75 – 125 %) and that the procedure adopted was effective (Rashid *et al.*, 2016).

RESULTS AND DISCUSSION

Physicochemical Parameters of River Sasa

The physicochemical parameters of River Sasa collected during the wet and dry seasons are presented in Table 2. The values obtained for River Sasa were compared with the World Health Organization (WHO, 2006) and Standard Organization of Nigeria (SON, 2008) drinking water guideline values.

pH

Most of the metabolic activities of aquatic organisms are pH-dependent, hence their sensitivity to the pH of their environment (Wang *et al.* 2002). The pH of an aquatic system is a key indicator of water quality and pollution levels in watershed areas (Kumar *et al.* 2011). In the present study, the mean pH values obtained are alkaline, ranging from 8.5 ± 0.0 (during the wet season) to 8.7 ± 0.1 (during the dry season). These values were within the permissible limit of 6.5 - 8.5 WHO (2008) set for drinking and irrigation purposes respectively, consequently perfect for the sustenance of aquatic life such as fish. The findings corroborate with earlier reports by Idowu *et al.* (2013) and Kamran *et al.* (2003). The mean values of pH obtained for all the samples fell within the WHO range but were above 7.0, this increase may be due to the presence of drained domestic waste discharge, bicarbonates in the water, organic pollution, and dissolved carbonates (Araoye 2009). Photosynthesis increases the pH due to the consumption of free CO_2 and the dissociation of bicarbonates into carbonates. The carbonates are much stronger alkalis than the bicarbonates (Goel 2009).

Electrical Conductivity (EC)

EC is a measure of the dissolved ionic substances in water (Yilmaz and Koc 2014). Conductivity was highest at point 3 during the dry season with a mean value of $198 \pm 15.8 \mu\text{scm}^{-1}$ and the highest value of $236 \pm 30.6 \mu\text{scm}^{-1}$ was recorded for point 2 in the wet season. The wet season influences higher conductivities than the dry season. The surface runoff from farmlands emanating from the heavy rainfall during the wet season is likely responsible for this observation, as reported by Shabalala *et al.* (2013) and Anhwange *et al.* (2012). The observed EC values were below the maximum permissible limit of $1,000 \mu\text{scm}^{-1}$ (NIS 2007). Rapid ion exchange between soil and water, and minimal dissolution of solutes in the water samples are probably responsible for the observed EC values.

Total Dissolved Solids (TDS)

The composition of total dissolved solids in water includes chlorides, bicarbonates, phosphates, carbonates, and nitrates of manganese, salt, calcium, organic matter, sodium, magnesium, and other particles (Mahananda 2010). Surface runoff dilutes the levels of TDS in water at high flows (Charkhabi and Sakizadeh 2006). The mean TDS values for the surface water studied ranged from 112 ± 4.0 to $129 \pm 10.2 \text{ mgL}^{-1}$ in the dry season while values in the wet season ranged from 144 ± 18.2 to $149 \pm 19.4 \text{ mg/L}$, in consonance with the findings of Agale and Patel (2013). WHO (1996) recommends 1000 mgL^{-1} for the protection of fisheries and aquatic life while NIS (2007) recommends 500 mgL^{-1} as the maximum permissible limit for domestic water supply. The values obtained in this study were below the acceptable limits of 1000 mgL^{-1} for domestic use (WHO 2017). Based on these findings, water from River Sasa is desirable for drinking and is not harmful to humans and aquatic life.

Temperature

The temperature was found to be highest at point 1 during the dry season with a value of 28.3°C and the highest value of 24.7°C was observed at point 2 during the wet season. The relatively high-water temperature during the dry season might be due to low water levels, higher temperatures, and a clear atmosphere. Similar findings were reported by Jayabhaye *et al.* (2006) and Salve and Hiware (2008). The overall annual mean value of the surface water temperature was $26.3 \pm 2.59^\circ\text{C}$ and this was found to be slightly above the WHO maximum limits of 25°C for drinking water (WHO, 2011; Sixtus *et al.*, 2016). However, the temperature levels of water samples reported in this study were in consonance with previously published reports that temperatures in the tropics vary between 21°C and 32°C (Idowu *et al.* 2013; Ayoade *et al.* 2006; Kamran *et al.* 2003).

Dissolved Oxygen (DO)

DO is vital for aquatic life. Lower DO levels in water are usually contributed by industrial waste, agricultural runoffs, dissolved gases, mineral waste, and decomposing organic matter (Srivastava *et al.* 2011; Addo *et al.* 2013). The DO values obtained ranged from 6.0 ± 0.6 to $6.4 \pm 1.2 \text{ mgL}^{-1}$ in the dry season, while the wet season values ranged from 6.2 ± 0.4 to $6.8 \pm 1.1 \text{ mgL}^{-1}$. The DO concentrations obtained in the wet season were generally higher than values obtained in the dry season. Aquatic life is severely affected at DO levels below 5.0 mgL^{-1} (Sinha and Biswas 2011). However, the DO values reported in this study exceeded the critical limit (5 mg/L) and are within permissible limits suitable for aquatic life as determined by WHO (2008). Similar DO values were reported in other studies (Karikari *et al.* 2007; Jayalakshmi *et al.* 2011; Addo *et al.* 2013). DO values are relatively lower in systems with high rates of organic decomposition and respiration (Mishra *et al.* 2009). The pollution of the water by a large amount of organic matter will result in the rapid consumption of a high quantity of dissolved oxygen during aerobic decay and water quality will be affected in the process (Chhatwal 2011).

Oxidation Reduction Potential (ORP)

ORP is the ability of water to oxidize contaminants and measures the strength or activity of oxidizers or reducers relative to their concentration. The ORP mean values for the dry season ranged from 335 ± 7.4 to 340 ± 1.8 mV while the mean values in the wet season ranged from 343 ± 3.6 to 348 ± 4.6 mV. The relative upsurge in ORP during the wet season was probably a reflection of the presence of more dissolved oxygen to favor oxidative processes. The high ORP values obtained show that river Sasa has good disinfection quality. Similar results were obtained by Köse *et al.* (2014).

Biological Oxygen Demand (BOD)

BOD is the determination of the oxygen in the water that is needed by aerobic organisms (Abida 2008). BOD tests measure the only biodegradable fraction of the total potential DO consumption of a water sample. In this study, the BOD_5 values obtained for the surface water ranged from 2.3 ± 0.1 mgL⁻¹ in the wet season to 3.1 ± 0.8 mgL⁻¹ in the dry season. The BOD_5 values of the water samples were well within the recommended values (5 mg/L) set by regulatory agencies (WHO 2008). Similar findings have been reported by Arvind Kumar and Singh (2002), in the Mayurakshi River (Jharkhand State). The relative upsurge in BOD values at Point 1 during the dry and wet seasons is most likely due to the closeness of the sampling point to a refuse dumpsite. The maximum value of BOD was observed during the dry season and this might be due to the higher rate of decomposition of organic matter at higher temperatures and less water current (Sanap *et al.* 2006).

Nutrient Level in River Sasa

(a) Sulphate ion

The highest sulphate ion concentration (22.8 mg/L) was recorded during the wet season and the minimum concentration (5.2 mg/L) during the dry season. The relatively high SO_4^{2-} concentrations observed in the wet season could be due to sulphate minerals being carried into the river by increased surface runoff from roads. A high concentration of sulphates stimulates the action of Sulphur reducing bacteria, which produces hydrogen sulphide, a gas highly toxic to fish life. The sulphate concentration for both seasons was within the stipulated value of WHO for domestic water use of 250 mgL⁻¹ (WHO 2008). Sulphate is found in water naturally as a result of gypsum and other common minerals leaking into it. Its concentration tends to rise as a result of the discharge of industrial wastes and home sewage (Manivasakam 2005). The reported sulphate ion concentrations in River Sasa can be concluded to be from natural sources and it is, therefore, safe for drinking purposes and would not harm human or aquatic life.

(b) Phosphate ion

In the present study, the maximum phosphate (4.3 mg/L) was recorded during the dry season and the minimum (0.8 mg/L) during the wet season. The concentration of phosphate in water samples from the study area is generally within the SON (2008) standard of 5 mgL⁻¹ for phosphate in drinking water. The increased rate of decomposition of organic waste during the dry season could be the reason for the high phosphate level. Low water circulation during the dry season could also be responsible for the relatively high phosphate ion (Putz 2008). Although the concentrations of phosphate ions in the studied river might not pose any immediate threat to any form of life, they tend to cause eutrophication-related problems.

(c) Nitrate ion

Nitrate is a form of nitrogen and a vital nutrient for the reproduction, growth, and survival of organisms. The concentration of NO_3^- in the dry season ranged from 1.1 ± 0.6 to 1.9 ± 1.4 mgL⁻¹ while there was an observed increase in the mean values in the wet season ranging from 4.1

± 0.2 to 4.4 ± 0.8 mg/L. These values fell within $50 - 100$ mgL⁻¹ recommended SON standard of underground water (well) waters. High nitrate levels above 10 mgL⁻¹ are unsuitable for aquatic life (Efe *et al.* 2005). High levels above 10 mgL⁻¹ can result in methemoglobinemia or “blue baby syndrome” in infants and recent research has suggested a link between high nitrate levels and cancer. (EPA 2014). The seasonal variation could be likely due to the wash-off of nitrogen-rich fertilizers from farmlands during the rainy season as well as increased utilization of nitrate by phytoplankton, activity of denitrifying bacteria, and macrophytes as evidence of high photosynthetic activity during the dry season.

Total Metal Levels in Water and Sediments

The results of total heavy metal concentration in sediments and water of River Sasa are presented in Tables 3 and 4 respectively. In the dry season, the results ranged from 135 to 138 μgg^{-1} for iron, 63.0 to 69.4 μgg^{-1} for chromium, 38.7 to 41.1 μgg^{-1} for zinc, 46.3 to 64.5 μgg^{-1} for copper, and 24.1 to 27.6 μgg^{-1} for manganese; while in the wet season, concentrations ranging from 116 to 127 μgg^{-1} for iron, 78.5 to 89.6 μgg^{-1} for chromium, 38.3 to 46.6 μgg^{-1} for zinc, 50.9 to 62.7 μgg^{-1} for copper and 26.1 to 34.5 μgg^{-1} for manganese were recorded for the sediment samples. However, for water samples, the results ranged from 17.7 to 38.1 μgg^{-1} for iron, 8.25 to 9.9 μgg^{-1} for chromium, 2.35 to 17.05 μgg^{-1} for zinc, 0.8 to 1.85 μgg^{-1} for copper, and 1.75 to 2.95 μgg^{-1} for manganese in the dry season while in the wet season, it ranged from 18.5 to 31.1 μgg^{-1} for iron, 16.15 to 18.35 μgg^{-1} for chromium, 2.7 to 7.9 μgg^{-1} for zinc, 1.3 to 1.75 μgg^{-1} for copper, and 2.65 to 3.05 μgg^{-1} for manganese. The major reason for this discrepancy is because sediments have greater potentials to serve as sinks for metals and other pollutants than water. The amounts of metals found in the water medium are basically dependent on the soluble salts of the metals and those that are adsorbed unto suspended particulate, while the sediments harbour metals that form ligands and complexes with fulvic and humic acids, along with those in insoluble ores and detrital silicates. Nigeria Standard for Drinking Water (NIS 554) recommended a maximum permissible level of 0.3 , 0.05 , 3.00 , 1.00 , and 0.2 mgL⁻¹ for drinking water respectively, concentrations of iron, Cr, Cu, and Mn in the water samples are above the maximum permissible level. It was generally observed that the metal levels in sediments were relatively higher in the dry season except for Cr and Zn while the metal levels in water samples were relatively higher in the wet season except for Fe and Zn. The relative upsurge in Cr and Zn of the sediment samples during the wet season could be a reflection of increased anthropogenic inputs over dilution effects during this period (Oyewale and Musa 2006). The levels of Cr reported in this study were lower than the earlier reports of Shanbehzadeh *et al.* (2014). Sediment levels of Zn in this study were also lower than the previous findings of Banu *et al.* (2013) and Rahman *et al.* (2014). The order of predominance of the metals in the river sediments is $\text{Fe} > \text{Cr} > \text{Cu} > \text{Zn} > \text{Mn}$. Corrosion of commercial waste products could further increase the amount of Cr in the environment (Al-Hiyaly *et al.* 1988). Cr could also be emitted by lubricants such as braking fluids, especially in the case of broken engines (Nagajyoti *et al.* 2010). These leaked fluids from these broken engines (Holm *et al.* 2002) are possible in the rivers as residents were commonly seen washing motorcycles at the river banks. The observed elevated levels of Cu during the dry season agreed with the observations of earlier researchers which claimed that high-temperature could result in decreased oxygen levels and subsequently lead to high metabolic rate causing aquatic organisms to take up a greater amount of Cu (Aderinola *et al.*, 2009; Ogru *et al.* 2011). A high pH value during the dry season facilitates the accumulation of metals in sediments (Singh *et al.* 2005; Kumar *et al.* 2013). This could be attributed to the fact that metals tend to form precipitate of oxides at higher pH values.

Table 3. Seasonal Variation in Total Metal Levels of Sediment Samples of River Sasa

Metal	Dry season				Wet season			
	P1	P2	P3	Mean	P1	P2	P3	Mean
Fe (μgg^{-1})	135.76 \pm 12.83	138.79 \pm 6.53	137.98 \pm 17.43	137.51 \pm 1.57	118.68 \pm 17.74	127.67 \pm 17.68	116.11 \pm 15.85	120.82 \pm 6.07
Cr (μgg^{-1})	67.79 \pm 3.61	69.45 \pm 8.17	63.02 \pm 1.80	66.75 \pm 3.34	78.85 \pm 4.17	89.66 \pm 10.20	78.50 \pm 4.57	82.34 \pm 6.34
Zn (μgg^{-1})	38.79 \pm 1.54	38.95 \pm 12.20	41.12 \pm 1.33	39.62 \pm 1.30	38.35 \pm 6.93	44.55 \pm 7.50	46.68 \pm 2.80	43.19 \pm 4.33
Cu (μgg^{-1})	64.56 \pm 3.94	60.80 \pm 2.53	46.31 \pm 7.61	57.22 \pm 9.64	62.77 \pm 3.61	57.79 \pm 7.58	50.92 \pm 2.19	57.16 \pm 5.95
Mn (μgg^{-1})	26.1 \pm 4.65	24.13 \pm 2.06	27.61 \pm 1.69	25.95 \pm 1.75	32.79 \pm 2.72	26.12 \pm 3.07	34.59 \pm 2.99	31.17 \pm 4.16

Table 4. Seasonal Variation in Total Metal Levels of Water Samples of River Sasa

Metal	Dry season				Wet season			
	P1	P2	P3	Mean	P1	P2	P3	Mean
Fe (μgg^{-1})	38.1 \pm 7.3	17.75 \pm 9.3	29.65 \pm 6.6	28.5 \pm 7.73	31.1 \pm 1.8	18.5 \pm 14.35	28.05 \pm 2.55	25.8 \pm 6.23
Cr (μgg^{-1})	9.9 \pm 7.7	8.25 \pm 6.9	9.25 \pm 7.15	9.13 \pm 7.25	18.35 \pm 1.8	16.15 \pm 1.2	17.15 \pm 2	17.21 \pm 1.66
Zn (μgg^{-1})	8.5 \pm 0.5	2.35 \pm 0.5	17.05 \pm 16.15	9.3 \pm 5.71	7.9 \pm 5.2	8.8 \pm 3.65	2.7 \pm 1.3	6.46 \pm 3.38
Cu (μgg^{-1})	1.85 \pm 0.4	1.45 \pm 0.25	0.8 \pm 0.25	1.36 \pm 0.3	1.3 \pm 0.3	1.75 \pm 0.45	1.5 \pm 0.25	1.51 \pm 0.33
Mn (μgg^{-1})	2.95 \pm 1.3	1.75 \pm 0.65	2.20 \pm 1.1	2.3 \pm 1.01	3.05 \pm 1.2	2.7 \pm 0.8	2.65 \pm 1.8	2.8 \pm 1.26

Speciation of Metals in Water and Sediments

Speciation of Metals in Water

The speciation results of metals in the surface water of river Sasa are presented in Figure 2. In a bid to understand the behaviour of metals in aquatic systems, an understanding of the different forms and/or species of metals in water is necessary. Speciation of toxic metals is an indicator of the bioavailability of metals to aquatic organisms (Korfali and Jurdi 2010; Huang et al. 2013). The distribution pattern for the metals in water samples of river Sasa is presented in Figure 2. Similar fractionation patterns were observed for the metals in both seasons. Preferential adsorption of Fe (72% and 82% respectively) and Mn (72.8% and 69.3% respectively) to suspended particles in both seasons was significantly high while notable preferential adsorption of Cr, Cu, and Zn to free metal form was observed. It is generally believed that dominant forms of Mn and Fe are usually co-precipitated or adsorbed as hydroxides of basic salts (Benes and Steinnes 1975). The suspended particulate metals are those that are bound by fulvic and humic acids present in natural organic matter in waters and have very low toxicity. Metals in suspended fractions are usually part of the crystalline structure of minerals, thus they remain relatively stable and inert, and they are difficult to release into the mobile and bioavailable phases (López-González *et al.* 2006; Wong *et al.* 2007). The high levels of Zn, Cu, and Cr occurring in the free metal ion fraction suggest that the metals are readily available for uptake by aquatic plants and animals at that level, and can subsequently lead to bioaccumulation and biomagnification. The high lability of Cu might be due to influential factors of dissolved oxygen and nitrate level of the water samples (Namieśnik and Rabajczyk 2010). Similarly, at pH values close to 8, the hexavalent form of chromium becomes dominant and available. The pH values obtained in this study might be responsible for the presence of Cr in the free metal ion fraction. The physicochemical forms of these metals significantly control their toxicity. However, the free metal ions represent the most toxic forms. The predominant association of Zn in river Sasa with the free metal fraction is consistent with an earlier report by Nemati et al. (2011).

Speciation of Metals in Sediments

Relevant information on the mobility and bioavailability of metals in sediments is provided by speciation analysis (Huang et al. 2013). The distribution pattern of the metals among the operationally-defined fractions in the river sediments is presented in Figure 3. Exchangeable and carbonate fraction metals represent the weakest bound metals in sediments due to their tendency

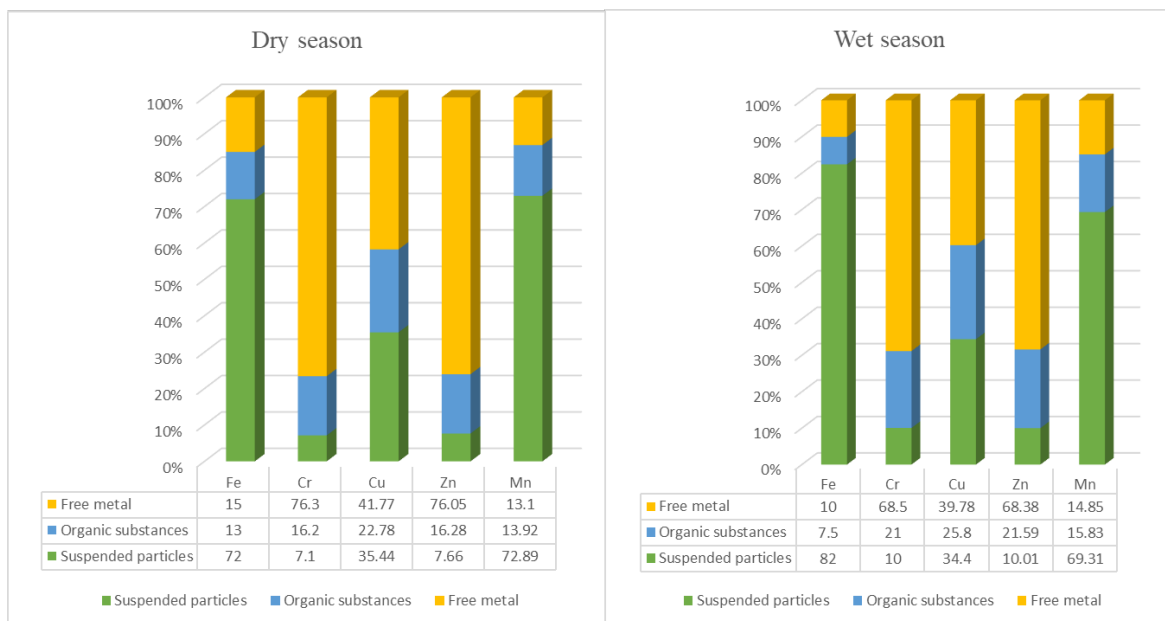


Fig. 2. Geochemical Phases (%) of Metals in Water Samples of River Sasa during Dry and Wet Seasons

to equilibrate with the aqueous phase, becoming available in the process (Huang et al. 2013). In both the wet and dry seasons, none of the metals was preferentially adsorbed to the exchangeable and carbonate fractions. The distribution of zinc in the five phases of the sediment fractions showed that in both the dry and wet seasons, Fe – Mn oxides adsorbed the highest concentration of zinc while the exchangeable fraction had the least concentration. 45.2% of total Zn content was adsorbed on Fe-Mn oxide in the dry season while 47.8% was adsorbed during the wet season. Fe-Mn oxides are natural accumulators of metals in sediments because of their large surface area because of the tendency of oxides to form chelates with other metals. The relative upsurge in Zn levels as opposed to other metals in Fe-Mn oxides might imply more mobility for Zn when environmental conditions change with seasonal changes (Zhang et al. 2015; Wojtkowska et al. 2016). Fe, Cr, Cu, and Mn were preferentially associated with residual fraction during the wet season while Fe, Cr, and Mn were preferentially associated with residual fraction during the dry season. This indicated that under natural conditions, these metals are inert. The strong affinity of these metals with silicates is an indication that they are insensitive to changes in environmental conditions (Ji et al. 2017). The contents of Mn associated with carbonates during the dry and wet seasons were 37.9% and 36.8% respectively. This is probably due to the relative abundance of Mn in the earth's crust (Fytianos and Lourantou 2004), and these are high enough to pose probable risks to aquatic organisms (Jain et al. 2010). During the dry season, 43.9% of the total Cu content had a strong affinity for the organic phase, and this was observed to decrease during the wet season to 39.1%. This could be due to the availability of more oxygen to the system which would lead to the organic phase undergoing oxidation and releasing some of the metal into the water. The association of Cu with the organic fraction during the dry season occurs by the mechanism of binding to specific functional groups such as -OH, -COOH, etc. present in the organic matter (Chen et al. 2007). This is consistent with the report of Vouve et al. (2014).

Risk Assessment of Metals in Sediments and Water Water Quality Index

The water quality index is a reflection of the composite influence of water quality parameters such as metals (Meng et al. 2016) and this was used in a bid to provide a comprehensive picture

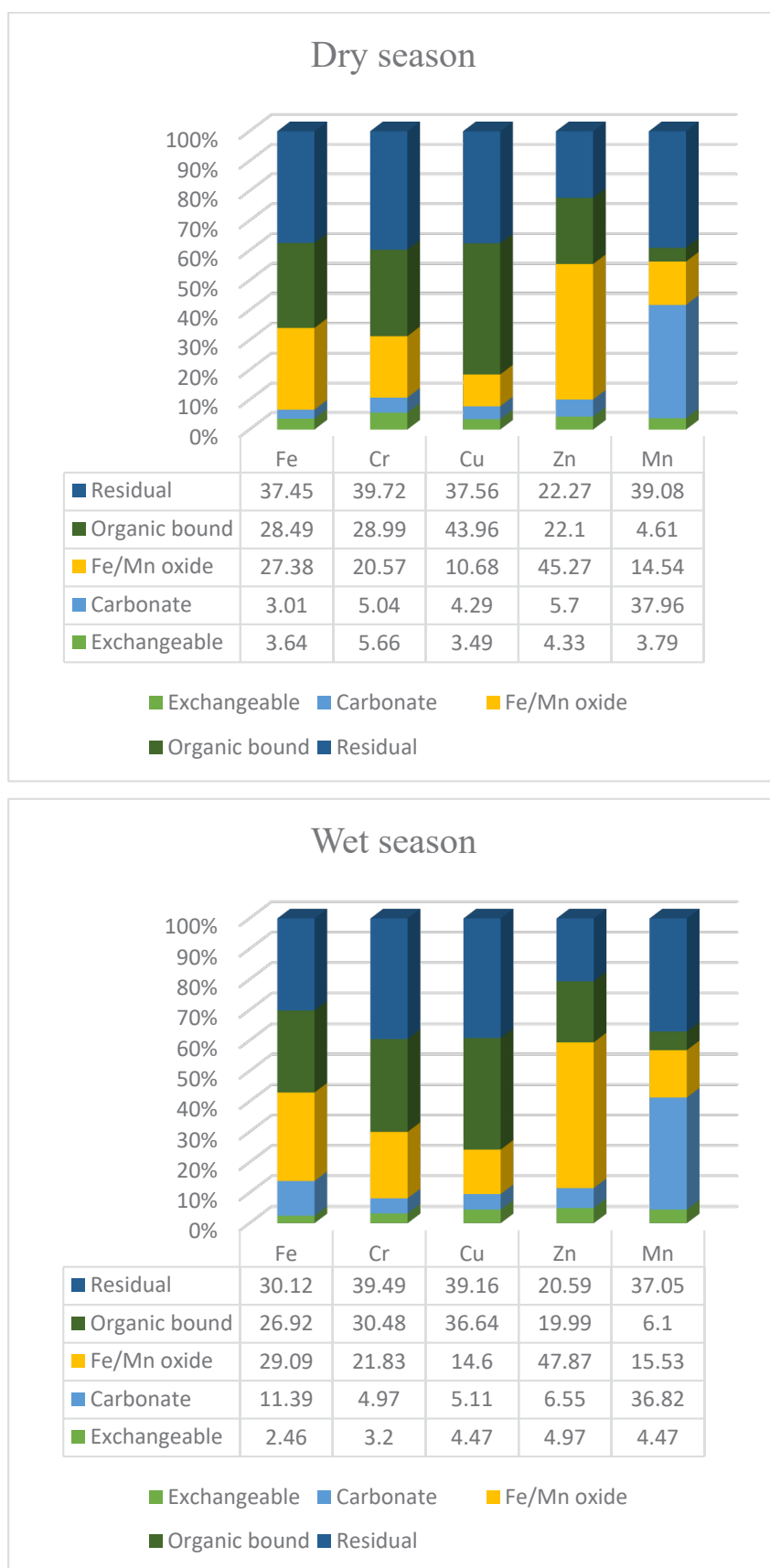


Fig. 3. Geochemical Phases (%) of Metals in Sediment Samples of River Sasa during Dry and Wet Season

Table 5. Water Quality Index of River Sasa during Dry and Wet Season

Metals	w_i	W_i	C_i/S_i (dry)	C_i/S_i (wet)	$W_i \times \frac{C_i}{S_i}$ (dry)	$W_i \times \frac{C_i}{S_i}$ (wet)
Fe	4	0.25	18.96	17.23	4.74	4.3075
Cr	5	0.3125	36.4	68.8	11.375	21.5
Zn	1	0.0625	0.58	0.43	0.03625	0.026875
Cu	2	0.125	0.13	0.155	0.01625	0.019375
Mn	4	0.25	1.525	2.525	0.38125	0.63125
WQI					1654.875	2648.5

Table 6. Sediment Pollution Indices of River Sasa during Dry and Wet Seasons

Indices	Dry season								Wet season							
	Fe	Cr	Zn	Cu	Mn	mCd	PLI	RI	Fe	Cr	Zn	Cu	Mn	mCd	PLI	RI
CF	0.08	22.2	13.2	71.5	0.64	18.9	4.10		0.07	27.4	14.3	71.4	0.77	19.9	4.40	
I_{geo}	-4.12	3.89	3.13	5.57	-1.20				-4.31	4.19	3.26	5.57	-0.94			
EF	-	7604.90	4513.95	24446.77	221.73				-	10676.99	5600.42	27794.65	303.13			
T_r	-	2	1	5	1				-	2	1	5	1			
E_r	-	44.5	13.2	357.62	0.64			415.98	-	54.8	14.3	357.25	0.77			427.31

*CF = contamination factor, I_{geo} = geoaccumulation index, EF = enrichment factor, T_r = toxicological response factor, E_r = ecological risk factor, mCd = modified degree of contamination, PLI = pollution load index, RI = potential ecological risk index

of water quality. The sum of weights was 16 and all the other parameters are shown in Table 5. The water quality index (WQI) values obtained for the dry and wet seasons are 1654.87 and 2648.5 respectively. These indicated that in both seasons, the water quality of river Sasa was “unsuitable for drinking” according to the WQI index. This is in contrast with the water quality reported in earlier reports by some authors (Xiao et al. 2014; Meng et al. 2016; Tripathi et al. 2016).

Sediment Pollution Indices

The extent of the threat posed by the measured levels of Fe, Cr, Zn, Cu, and Mn to the surrounding ecological system was assessed by computing several pollution indices and potential ecological risk assessment. The results of the sediment pollution indices are presented in Table 6. Little or no variation existed in the threats posed by the metals in the sediment samples for seasons. During both seasons, contamination factor (CF) results indicated that the river sediments exhibited low contamination by Fe and Mn. This suggested that the levels of Fe and Mn in the river sediments might be as a result of lithogenic sources. The river sediments were however observed to exhibit very high contamination by Cr, Zn, and Cu ($CF > 6$). The modified degree of contamination (mCd) result showed that the analyzed metals exhibited an extremely high degree of contamination in the river sediments. Geo-accumulation index (I_{geo}) results showed that the river sediments were unpolluted by Fe and Mn, in consonance with the CF result. The sediments were strongly polluted by Cr during the dry season and strongly to extremely polluted during the wet season. The sediments were strongly polluted by Zn and extremely polluted by Cu during both seasons, this could be due to the low flow of water in this area or the discharge of untreated anthropogenic/industrial effluent from neighbouring areas. Decreased water volume, lower flow rate that could lead to higher rate of sedimentation, and decayed organic matters that could furnish chelating agents, such as humic and fulvic acids in the sediment might have contributed to higher levels of some of the metals in the sediments. The pollution load index (PLI) result indicated a deterioration in the quality of the river sediments. The enrichment factor (EF) results indicated that the river sediments were severely enriched with all the studied metals. For both dry and wet seasons, Zn and Mn exhibited low potential

Table 7. Health Risk Assessment of potentially toxic elements in Sediments of River Sasa from Ingestion, Inhalation and Dermal Exposure during Dry and Wet Seasons

Metals	Seasons	CDI _(ing)	CDI _(inh)	CDI _(derm)	RfD _(ing)	RfD _(inh)	RfD _(derm)	HQ _(ing)	HQ _(inh)	HQ _(derm)	HI	RR (%)
Fe	Dry	8.07E-04	7.60E-09	3.22E-05	0.3	NA	1.40E-01	2.69E-03	NA	2.30E-04	2.92E-03	1.87
	Wet	7.09E-04	6.68E-09	2.83E-05				2.36E-03	NA	2.02E-04	2.56E-03	
Cr	Dry	3.92E-04	3.69E-09	1.56E-05	0.003	3.00E-05	7.50E-05	1.30E-01	1.23E-04	2.08E-01	3.39E-01	90.97
	Wet	4.83E-04	4.55E-09	1.93E-05				1.61E-01	1.52E-04	2.57E-01	4.18E-01	
Zn	Dry	2.33E-04	2.19E-09	9.28E-06	0.3	3.00E-01	7.50E-02	7.75E-04	7.30E-09	1.24E-04	8.99E-04	0.54
	Wet	2.54E-04	2.39E-09	1.01E-05				8.45E-04	7.95E-09	1.35E-04	9.80E-04	
Cu	Dry	3.36E-04	3.16E-09	1.34E-05	0.04	4.02E-02	2.40E-02	8.39E-03	7.86E-08	5.58E-04	8.95E-03	5.84
	Wet	3.36E-04	3.16E-09	1.34E-05				8.38E-03	7.86E-08	5.58E-04	8.94E-03	
Mn	Dry	1.52E-04	1.43E-09	6.08E-06	0.14	5.00E-05	1.84E-03	1.08E-03	2.87E-05	3.30E-03	4.42E-03	0.75
	Wet	1.83E-04	1.72E-09	7.30E-06				1.30E-03	3.44E-05	3.96E-03	5.31E-03	

*CDI = chronic daily intake, ing = ingestion, inh = inhalation, derm = dermal, RfD = oral reference dose, HQ = hazard quotient, HI = risk index, RR = relative risk, NA = Not available

Table 8. Health Risk Assessment of potentially toxic elements in Water of River Sasa from Ingestion and Dermal Exposure during Dry and Wet Seasons

Metals	Seasons	CDI _(ing)	CDI _(derm)	RfD _(ing)	RfD _(inh)	RfD _(derm)	HQ _(ing)	HQ _(derm)	HI	RR (%)
Fe	Dry	3.34E-04	1.33E-06	0.3	NA	1.40E-01	1.11E-03	9.52E-06	1.12E-03	2.95
	Wet	3.04E-04	1.21E-06				1.01E-03	8.65E-06	1.02E-03	
Cr	Dry	1.07E-04	4.26E-07	0.003	3.00E-05	7.50E-05	3.56E-02	5.68E-03	4.13E-02	94.45
	Wet	2.02E-04	8.06E-07				6.73E-02	1.07E-02	7.80E-02	
Zn	Dry	1.02E-04	4.08E-07	0.3	3.00E-01	7.50E-02	3.41E-04	5.43E-06	3.46E-04	0.90
	Wet	7.57E-05	3.02E-07				2.52E-04	4.03E-06	2.56E-04	
Cu	Dry	1.53E-05	6.09E-08	0.04	4.02E-02	2.40E-02	3.82E-04	2.54E-06	3.84E-04	1.01
	Wet	1.82E-05	7.26E-08				4.55E-04	3.03E-06	4.58E-04	
Mn	Dry	3.58E-05	1.43E-07	0.14	5.00E-05	1.84E-03	2.56E-04	7.77E-05	3.33E-04	0.67
	Wet	5.93E-05	2.37E-07				4.24E-04	1.29E-04	5.52E-04	

*CDI = chronic daily intake, ing = ingestion, inh = inhalation, derm = dermal, RfD = oral reference dose, HQ = hazard quotient, HI = risk index, RR = relative risk, NA = Not available

ecological risk ($E_r < 40$), Cr exhibited moderate potential ecological risk, while Cu exhibited severe ecological risk ($E_r > 320$). The cumulative risk posed by these metals on the ecological system is high.

Health Risk Assessment of Metals in Water and Sediments

The risk assessment models for potentially toxic elements developed by USEPA were used in assessing the non-carcinogenic health risks associated with exposure to water and sediments of river Sasa (Iqbal and Shah 2013). The results of the health risk assessment of metals in water and sediments of river Sasa are shown in Tables 7 and 8 respectively. Potential adverse health effects could arise if the hazard quotient (HQ) of metal exceeds unity. In contrast, minimal hazards are associated with exposure to a metal contaminant if its hazard quotient is below unity. However, the results indicated that during the dry and wet seasons, no non-carcinogenic health risks emanate from inhalation, dermal exposure, and ingestion of the studied metals in the sediment and water of river Sasa. Nevertheless, Cr exhibited a 90.9% and 94.4% risk contribution in the river sediment and water respectively. The ingestion of Cr, particularly its hexavalent form, has been reported to induce oxidative reactions, damaging blood cells in the process (Dayan and Paine 2001). In a bid to improve the aquatic ecosystem, this should be factored in. The ingestion route represented the principal exposure pathway for the studied metals due to its relatively high HQ values.

CONCLUSION

The extent of contamination of sediments and water of River Sasa in terms of their heavy metal levels and physicochemical properties was determined in this study. The results of the physio-chemical parameters suggested that the water was good for aquatic life. However, the metal levels of the river water suggested that it was unsuitable for drinking as revealed by the water quality index. Differences existed in the bioavailability of the studied metals. Chromium, Cu, and Zn were associated with the free metal fraction in water, thus suggesting high availability for uptake and hence potential toxicity. The metals in the river sediments had relatively low bioavailability, nevertheless, their total metal levels exhibited varying degrees of contamination and pollution. Generally, a minimal hazard potential emanating from dermal exposure, ingestion, and inhalation routes, was observed, but chromium posed the most significant contribution to potential adverse health risks.

COMPLIANCE WITH ETHICAL STANDARDS

This study was not funded. There are no conflicts of interest that are relevant to the content of this article that the authors must disclose.

DATA AVAILABILITY

This published article contains all of the data generated.

AUTHORS' CONTRIBUTIONS

All the authors Abolanle Saheed Adekunle, John Adekunle Oyedele Oyekunle, Solomon Sunday Durodola, Ayotomi Samson Oladele, Oluwaseyi Samson Ojo, Nobanathi Wendy Maxakato, John Paul Kaisam, and Odunayo Timothy Ore contributed equally to the manuscript.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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