Evaluation and risk assessment of heavy metals in surface water collected along the Isipingo River, KwaZulu-Natal, South Africa

Gbadebo Clement Adeyinka [iD][a], Babatunde Femi Bakare [iD][a] and Samuel Ayodele Iwarere [iD][b]

[a]Department of Chemical Engineering, Mangosuthu University of Technology, Umlazi, South Africa; [b]Department of Chemical Engineering, University of Pretoria, Pretoria, South Africa

ABSTRACT

In this study, the pollution levels, sources, and ecological risks associated with five selected heavy metals (chromium, copper, iron, lead, and zinc)were evaluated in surface water, soil, and sediment systems along the Isipingo River, KwaZulu-Natal, South Africa. The surface water, soil and sediment samples collected along the river, were preserved, transported, and stored followed the standard procedures. Soil and sediment samples were digested for heavy metal determination using a microwave digestion system. The digested samples were quantitatively analysed using an inductively coupled plasma optical emission spectrometer (ICP-OES). The results demonstrate that majority of the targeted heavy metals were found below the detection limits in surface water except for iron (Fe), which was found within the concentration range of 9.54 to 46.76 µg/L. Lead was found below the detection limit in water, soil, and sediment samples, while other heavy metals were within the range not detected(ND)to 0.222 µg/kg dry weight and 0.212 µg/kg dry weight in soil and sediment respectively. The ecological risk assessment of the studied metals in soil and sediment systems from this riversignified that water from this river had less probable potential adverse effects on both animals and humans as well as benthic organisms.

1. Introduction

The continual existence of humans is largely dependent on the quality of its environment. Accessibility to adequate, clean, and safe water is critical for the survival of animals and humans. The quality of water could be altered due to the pollution load it receives from the surrounding environment resulting from human activities and climatic conditions; these activities could lead to water stress in developing countries across the world in the coming decades [1,2]. In recent times, the pollution of the water bodies resulting from anthropogenic activities has witnessed an exponential rise, due to population growth, with a preponderance in rapid industrialisation and urbanisation [3,4]. Some of these activities that encourage environmental pollution are landfills leaching, unregulated

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CONTACT Samuel Ayodele Iwarere ✉ adeyinkagbadebo78.ga@gmail.com

industrial and municipal contaminated waste discharge into the surface soil and water, underground water, improper management of raptured underground pipes and storage tanks, excessive usage of chemicals and solid waste seepage.

A significant amount of contaminated environmental media (water, soil, and sediment systems) globally contain complex mixtures of pollutants, such as, petroleum hydrocarbons, inorganic compounds (heavy metals, organic contaminants (pesticides, herbicides, or fertiliser), and solvents, which have high toxicity potential [5,6]. The degree of pollutions associated with heavy metals and organic contaminants is greatly dependent on different activities within a given catchment area of the environment. For instance, Gao et al. [7] suggested that the geohydrological conditions and the indiscriminate discharge of pollutants into river streams were primary factors responsible for the degree of surface sediment pollution along the coastal Bohai Bay. The authors noted that these anthropogenic influences were the main factors responsible for the spatial distribution of heavy metals contamination within the coastal sediments. This was attributed to the metal contamination resulting from land-based point source discharges.Chetty and Pillay [8] highlighted a similar study conducted on the effect of different human activities on water health in some selected rivers across KwaZulu-Natal, South Africa. The calculated sediment enrichment factors employed in the study indicated that anthropogenic activities were suspected to be the likely sources of metal pollution along the selected river course.

The significance of safe and quality drinking water standards for some health reasons and others for the aesthetic value in humans necessitated different regulated organisations such as World Health Organisation (WHO) to give specific limits of physicochemical and bacteriological parameters in drinking water [9]. The potential human health effect, and ecological imbalance to the aquatic lives resulting from the complex mixtures of contaminants such as heavy metals and organic pollutants have been well noted [10,11].

As reported by eThekwini Municipality, there is a high level of pollution of the Isipingo River with a significant impact on the people and aquatic lives (Coastal, Stormwater and Catchment Management, eThekwini Municipality, 2011) [12]. Therefore, it is important to understand and further investigate scientifically, any activities responsible to the current pollution status of the Isipingo estuarine system as reported by eThekwini municipality.

The current situation of Isipingo River has been characterised by various anthropogenic activities, such as, upstream activities from various industrial and community actions like Prospecton industrial area and Umlazi Wastewater Treatment Works which discharged their waste into this river, therefore these activities have subjected this river to excessive levels of pollution. Other significant pollution sources into this river are the rapid and continuous expansion of informal settlements within the Isipingo catchment. These settlements have no known significant sources of water supply or no proper form of sanitation, hence proliferating illegal dumping of human and aquatic wastes into the river, while depending on the river for their domestic use. In addition, runoff from leachates from the Umlazi landfill site, and the agricultural farmlands contribute to the degradative state of this river. The pollution load associated with these sources has caused serious concern because this river serves as a major source of water for the larger population (both domestic and agricultural purposes) around the Umlazi and Isipingo catchment area of KwaZulu-Natal, South Africa. This river was chosen because the selected areas are faced with serious threats arisen from various anthropogenic activities

along its course. There is therefore an urgent need to know the current state of this river in terms of pollution loads associated with heavy metals and organic pollutants.

This study is aimed at determining the concentration levels of the five selected heavy metals (, Cr, Cu, Fe,Pb, and Zn), which are known to be a potential risk and used as environmental quality criteria in environmental media. The influence of anthropogenic activities in relation to the pollution status associated with heavy metal pollution using pollution index, concentration factor, and pollution load index as an indicator within the river catchment would be estimated in this study. The river was chosen because the selected areas face serious threats from various anthropogenic activities along its course. To the best of the authors' knowledge, there are no significant scientific reports on this river's current state in terms of pollution status associated with critical contaminants such as heavy metals which this current study aimed to address. The selected pollutants are also important due to their suspected wide usage in various forms along the river course within this area. The selected pollutants are known as priority pollutants [13]. Their potential bioaccumulative, low biodegradative and recalcitrant natures in the environment are some of the properties of these pollutants, which places an important need to monitor the pollutants in the environment. More importantly, these pollutants have the potential to pose serious health threat to human and animal life therefore, there is a need to mitigate their effects in surface water systems.

2. Materials and method

2.1. Site description

The Isipingo catchment is located within the Prospecton industrial area South Durban in the Province of KwaZulu-Natal, South Africa. The Isipingo River is one of the major rivers within this catchment, with an estimated area of 50 km^2 and a river length of approximately 27 km, originating near the Iwabi area [14–16]. The flow of Isipingo River along the Prospecton industrial area presents a critical challenge concerning high pollution loads due to various industrial activities and other environmental factors such as frequent stream diversion and low river flow and along its course. The Isipingo estuary covers approximately 6.8 ha, comprising a northern arm and a southern `blind'' lagoon. The primary land use within the Isipingo catchment area is; residential, industrial, agricultural and domestic. Domestic activities include washing, recreation, swimming and fishing along the river bank. In addition, Isipingo River frequently receives untreated sewages from both domestic and industrial as its main pollution point sources. These anthropogenic activities could be thought to have caused a complete deterioration to this river ecosystem in the paste decades. The Prospecton industry within this catchment is home to some major industries, few among them are; South African Breweries, Sapref refinery and Shell Chemicals. The presence and operations of these industries could contribute significantly to the pollution load into this river, thereby compromising the health safety of animals and people who depend on this river.

2.2. Sample collection and preparation

In this study, the aquatic environment category considered is a freshwater system with input from wastewater treatment works. The sample locations were selected according to

the anthropogenic activities along the river course with appropriate site coordinates using google earth to identify potential and hot spots within the river catchment. The site coordinates are presented in Table 1.

Samples were collected from six stations, as indicated in Table 1, between October 21–23rd, 2019. Surface water was collected using the grab sampling method, soil samples were collected along the riverbank at the depths of 0 to 20 cm, and sediment samples were taken on the riverbed at a depth of 0 to 5 cm using a soil auger according to the standard protocol [17]. A separate sample for heavy metal determination was taken using a standard procedure as reported by Ahlers et al. [18] to avoid any contamination. Samples meant for metal analysis were collected into airtight polyethylene bags and plastic bottles, while aluminium foil was used. The collected water samples were acidified with 2 mL of analytical grade nitric acid; this was done to preserve metals and avoid precipitation [19] as well as adsorption onto the walls of the sampling bottles [20]. Samples were stored at moderately low temperatures and transported to the laboratory. All the samples were kept within 4°C upon being taken to the laboratory. Sample digestion and extractions were done within two weeks after collection to keep the integrity of the samples.

Soil and sediment samples were air-dried in the fume hood. The air-dried samples were gently crushed using pestle and mortar. The ground solid was thereafter sieved using < 200 µm mesh size [21], collected and homogenised afterwards.

2.3. Metal digestion

Sample digestion was done using the microwave acid digestion method as reported by Turek et al. 2019; Hseu, 2004 [22,23] with little modifications. About 6 mL concentrated HNO_3 and 2 mL concentrated HCl acids were added to 0.5 g of the air-dried sample in the Polytetrafluoroethylene (PTFE) vessels. The PTFE vessel was enclosed and placed in the Microwave Digestion System (Microwave Reaction System SOLV, Multiwave PRO, Anton Paar) for digestion. The three-stage protocol was followed as indicated: (a)temperature and power were maintained at 210°C and 1105 W respectively, for 5 min; (b) temperature was kept steady at 240°C for 35 min together with maximum pressure (40.0 bar), and (c)

Table 1. Sites coordinates and samples physicochemical parameters.

| Sample code | Coordinates | | Temp (°C) | pH | EC (µS) | TDS (ppm) | DO (ppm) | OC (%) | SOM (%) |
	Latitude	Longitude							
ISR 1	−29.987704	30.904849	23.6	7.56	665.6	332.7	3.48	0.588	3.183
WWTP	−29.991453	30.908166	21.4	6.96	636.6	318.2	3.45	0.945	4.485
ISR 3	−29.991662	30.908477	23.1	7.42	660.5	321.3	3.48	0.735	3.719
ISR 4	−29.995269	30.922097	25.4	7.02	701.7	349.5	1.47	0.777	3.872
ISR 5	−30.004198	30.006873	24.3	7.27	1350	676.5	1.64	1.26	5.634
ISR 6	−30.009079	30.935815	24.7	7.31	1700	860	2.49	0.42	2.570
WHO			*	7.0–8.5	*	*	*		
EPA			*	6.5–8.5	*	500	*		
DWAF			*	5.0–9.5	400–900	450–900	*		

WHO = World Health Organization, EPA = US Environmental Protection Agency, DWAF = Department of Water Affair and Forestry, TDS = Total Dissolve Solids, EC = Electrical Conductivity, DO = Dissolved Oxygen, OC = Organic carbon, SOM = Soil organic matter, * = Not available.

reduced temperature (70°C) and power (40%) were used for 0 min to cool down the Teflon vessels (maximum microwave power is 1,300 W when power is 100%). The digested samples were filtered into a 50 mL volumetric flask, filled up to mark with Milli-Q water and stored at low temperature in the refrigerator prior to further analysis. Surface water samples were prepared using Method 3005 [24] prior to the quantification of heavy metal. The heavy metals were quantitatively analysed using inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer) at a selected wavelength.

Analytical grade HNO_3 was used in this study to achieve, compatibility of the isolation of metals in the sample, which could aid the effective and direct determination after dilution, and minimize the risk of environmental contamination. All sample containers were prewashed with detergents, acids, and water. Blank determinations were carried out for each set of analysis using the same reagents. All the sample preparations were done within two weeks, analyses were performed in duplicates and data were corrected for the dry weight of the sample.

2.4. Ecological risk assessment of heavy metals in soil and sediments from the Isipingo River

It is important to evaluate the amount of pollution in the environment, most especially in freshwater systems, due to the significant impacts on human and animal life. As human activities increase, the overbearing effects of pollutants seem to increase exponentially, thereby affecting the natural ecosystems.In this study, four pollution indicators and Sediment Qualities Guidelines(SQGs) associated with heavy metal concentrations were considered. These are; pollution index, Enrichment factor, concentration factor, and pollution load index. The SQGs used in this study are; threshold effect level (TEL), effects range level (ERL), lowest effect level (LEL), minimal effect threshold (MET), Consensus Based (CB), threshold effect concentration (TEC).

2.4.1. Pollution index
The degree of heavy metal contamination along the Isipingo River was assessed in the soil samples using pollution index (PI) as proposed by [25–27]. The PI was evaluated by averaging the ratios of total concentrations of the heavy metals investigated to tolerable levels. The PI value for each location in this study was calculated for the selected heavy metals using Equation 1

$$PI = \frac{\left[+ {C_r}/{100} + {C_u}/{20} + {F_e}/{38000} + {P_b}/{100} + {Z_n}/{50}\right]}{6} \tag{1}$$

Pollution index values above 1 indicated that the soils are possibly polluted by anthropogenic input [28].

2.4.2. Enrichment factor
Enrichment factor (EF) has been widely used in different studies to measure the possible impact or the magnitude of contamination of heavy metals concentrations resulting from either anthropogenic activity or lithogenic origin in the environment [29–31]. In order to assess the level of ecological impact of heavy metal due to the anthropogenic

contribution, EF could be evaluated using Equation 2 as suggested by [32]. The choice of Fe as the normalising metal in this study is due to its natural abundance (about 32.1%), worldwide application, relatively low pollution potential in the environment, and as a reference concentration in uncontaminated areas [31,33]

$$EF = \frac{(Metal/F_e)sample}{(Metal/F_e)background} \tag{2}$$

where, (Metal/Fe)sample is the ratio of Fe in the sample of interest and (*Metal/Fe*) background is the natural background value of the metal to Fe ratio.

The EF value in the range of 0.5 to 1.5 could indicate that natural process is the main source of heavy metal in the soil, but if the EF value is greater than 1.5, the main source of heavy metal contamination could be attributed to the anthropogenic source or extremely high enrichment. When the values are less or equal to 1, it indicates there is no enrichment; 1–3 indicate minor; 3–5 indicate moderate; 5–10 is considered moderately severe; 10–25 is severe; 25–50 is considered very severe; and >40 is extremely high enrichment [30,34,35].

2.4.3. Concentration factor

The simple and effective factor in evaluating and monitoring the heavy metal contamination in sediment is the quotient obtained by dividing the concentration of each metal as proposed by Hakanson [36]. This can be evaluated using the ratio of the measured concentration of the heavy metals in the sediment samples to the background value of metals as indicated in Equation 3, and the degree of contamination (Cd) was defined as the sum of all contamination factors.

$$CF_i = \frac{C_i}{B_i} \tag{3}$$

Where CF_i, C_i and B_i are the contamination factor of heavy metal in sediment, measured concentration, and background value of metals i, respectively.

The value of CF as indicated could be used to evaluate the extent of heavy metal contamination in a given site. The following indicators suggest the level of contamination factor: CF < 1 (low contamination); 1 ≤ CF < 3 (moderate contamination); 3 ≤ CF < 6 (high contamination factor); CF ≥ 6 (considered very high contamination).

2.4.4. Pollution load index

The pollution load index (PLI) is an effective tool for assessing sediment environmental quality. This tool is an integrated pollution load index of selected heavy metals in a sediment site that is been calculated according to Tomlinson et al. [37]. The PLI is defined as the nth root of the multiplications of the CF for all the heavy metal in individual sediment samples. The PLI values reflects the status of comprehensive pollution caused by all the heavy metals. The PLI value of the site is calculated by obtaining the nth root of the multiplications of the CF of the total number of heavy metals assessed using Equation 4.

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots\ldots\ldots CF_n)^{1/n} \tag{4}$$

Where, CF = contamination factor, n = number of metals.

PLI > 1 indicates metal pollution, and PLI < 1 means there is no metal pollution [37,38].

The average concentration of Cu (5.5 µg/g), Pb (18 µg/g), and Cr (10 µg/g), Zn (26 µg/g) and Fe (3000 µg/g) reported for Durban Bay 1978 [39] was considered as the background value in this study as there are no background concentrations for this study site.

3. Results and discussion

3.1. *Water and soil physicochemical parameters*

Table 1 presents the physicochemical parameters of water and soil samples at different sampling sites. The temperature of the collected water samples ranged between 21.4 to 25.4°C. Although, water temperature was not identified as a parameter of interest in this study, since seasonal experiments were not conducted, reported as an influence for chemical reactions in water bodies.Properties such as odours and corrosion taste and the oxidation of some metal ions within the water system could occur due to water temperature changes [40]. The electrical conductivity (EC) is a key parameter in estimating soluble solid matter in water [41]. The cleaner the water, the lower the conductivity (the higher the resistivity). The water EC is crucial due to its direct impact in measuring the water quality as it indicates the amount of dissolved salts in the water. The EC values in this study were comparable to the maximum tolerable standards from the Department of Water Affairs and Forestry (DWAF) of South Africa. The EC values of water samples collected fromISR 1, WWTP, and ISR 3ranged between 636.5 to 1700 µS across the sites are, within the permissible limit of international standard values as presented in Table 1, indicating good water quality (low-nutrient waters). Samples collected from, sites 4 to 6 were however out of range, which could suggest the influence of anthropogenic activities and other factors along the river. The most notable things along the sites with higher EC values are the presence of industrial areas Sites ISR 4 and 5 which are located close to the Prospecton industrial area, and site ISR 6 was taken close to the Isipingo beach. The pH values of surface water obtained in this study were all within the recommended standard for drinking water as noted by regulatory agencies such as World Health Organization (WHO), Environmental Protection Agency (EPA) and DWAF. A low water pH could be indicative of acidic water which could originate from acid mine drainage and an elevated pH value suggest that there is a possibility of high nutrients associated with fertiliser seepage into the water body [42]. Another important parameter for measuring water quality is the total dissolved solids (TDS), which gives an indication of the degree of amount of dissolved salts (salinity) in water. This is normally associated with the amount of excessive use of fertilisers resulting from agricultural runoff or industrial wastes being discharged into the surface water [43]. The values obtained in this study (318.2–860 mg/L) were within the permissible levels as recommended by EPA and DWAF except for ISR 5 and 6 which are higher than the value provided by EPA of 500 mg/L. The high values recorded at sites 6 could be attributed to the influence of Isipingo beach introducing high salt concentration from seawater, thereby resulting in increased TDS concentration.consequently, the elevated level at site 5 could be attributed to the industrial runoff from the

nearby industries. The dissolved oxygen (DO) value obtained in this study ranged between 1.47 to 3.48 mg/L demonstrating that the level of DO indicate a relative increase in organic load. Our DO values are lower compared to reported data from Sezela and Palmiet River (3.640–11.26 and 7.600–13.14 mg/L) by Chetty and Pillay [8]. The soil organic carbon (OC) and organic matter (SOM) was evaluated using the standard wet digestion Walkley Black Method [44]. This method is used to describe the enrichment factor of the soil and an important indicator of soil productivity. SOM plays an important role in crop system sustainability most especially by improving soil texture, structure, water-holding capacity, nutrient availability, cation exchange capacity, and microbial biomass proper-ties. Soil with high organic matter contents can absorb heavy metals and inhibit herbi-cides leaching, thereby reducing the soil toxicity and contamination of surface and groundwater. Sites 2 and 5 were found with the highest OC and SOM values as presented in Table 1. This could be attributed to the influence of mineral contents and possible untreated effluents been discharged into the surface water due to the proximity to the industries and Isipingo wastewater treatment plant. The values of OC content obtained in the river soil system in this study (0.588 to 1.260%) is lower compared to the values (3.61 to 12.20%) reported by Saha and Hossain [44] in the sediment collected from the Buriganga River, Bangladesh.

3.2. Heavy metal concentration and distribution in surface water, soil and sediment

The levels of the selected heavy metals in surface water, soil and sediment samples across the sites are presented in Table 2. Except for iron (Fe) the targeted heavy metals were found below the detection limits in surface water. The concentration of Fe in surface water ranged between 9.54 to 46.76 μg/L across the sites. The levels of Fe in surface water across the sites were compared with the allowable standards as stipulated by EPA, EU and DWAF as indicated in Table 4 (EPA 300 μg/L, EU 200 μg/L and DWAF 100 μg/L respec-tively). However, the observed experimental value of Fe was below the stipulated stan-dards, indicating that the pollution of surface water resulting from Fe in this study is not significant and considered safe for aquatic organisms.Hence, the river might not posea serious aesthetic challenge when used for domestic purposes such as drinking and washing. The presence of Fein water is required at a moderate level as it is an essential element in human nutrition, which is required for the synthesis of haemoglobin in the red blood corpuscles, supports growth and metabolic processes in humans and animals [42,45–47]. Despite its importance for both animals and humans, the presence at high concentrations in water for domestic usage, such as drinking and washing could result into bad taste, and when consumed in large quantities could pose a serious health risks like haemochromatosis and a genetic disorder in humans [48]. Among other heavy metals investigated in surface water zinc (Zn) was found at traceable levels (1.66 and 28.00 μg/L) in surface water along with the two sites, in lower levels compared to the maximum permissible limit in drinking water (5000 μg/L) as provided by EPA. Similarly, our results showed lower concentrations compared to a recent study by Titilawo et al. (2018), who reported the concentration of Zn within 403 μg/L and 150 μg/L in ten major rivers of Osun State Nigeria. In addition, Nde and Mathuthu [49] investigated the concentration of potentially toxic elements such as Cu, Pb, Zn, Cr and Fe in the upper Crocodile River

Table 2. The concentrations of selected heavy metals in surface water (µg/L), soil and sediment (µg/kg dry weight) across the sites.

Sampling Site	Water (µg/L)					Soil (µg/kg dry weight)					Sediment (µg/kg dry weight)				
	Cr 267.716	Cu 324.754	Fe 259.940	Pb 220.353	Zn 213.857	Cr 267.716	Cu 324.754	Fe 259.940	Pb 220.353	Zn 213.857	Cr 267.716	Cu 324.754	Fe 259.940	Pb 220.353	Zn 213.857
ISR 1	‡	‡	46.70	‡	‡	0.00550	‡	92.80	‡	0.0797	‡	0.0620	83.30	‡	0.0538
WWTP	‡	‡	9.54	‡	28.00	0.0136	‡	104	‡	0.2011	0.143	0.0244	154	‡	0.212
ISR 3	‡	‡	33.4	‡	1.66	‡	0.0659	73.90	‡	0.222	‡	0.0691	78.40	‡	0.0443
ISR 4	‡	‡	41.6	‡	‡	‡	‡	51.50	‡	0.0181	‡	0.0128	68.30	‡	0.115
ISR 5	‡	‡	37.3	‡	‡	‡	‡	50.40	‡	0.0517	‡	0.0261	53.30	‡	0.155
ISR 6	‡	‡	15.8	‡	‡	‡	0.0456	44.90	‡	‡	‡	‡	47.50	‡	0.0208

‡ = not detected, the selected heavy metals were measured at the following wavelength Cr, Cu, Fe, Pb and Zn.

catchment area in North-west Province, South Africa. The concentrations range of the heavy metals recorded were, 30–80 µg/L for Cu, n/d – 20 µg/L for Pb, 40–100 µg/L for Zn, n/d – 10 µg/L for Cr, and 60–280 µg/L for Fe, respectively. Generally, the levels of heavy metals found in the Upper Crocodile River were far higher compared to what was obtained in this study. The concentrations of Pb and Fe for Upper Crocodile River were at an elevated level compared to stipulated guidelines for aquatic environments by DWAF (100 µg/L). These values were far higher than what was detected in this present study, although these values were considered below the USEPA and WHO target value of 5000 µg/L. The level of Zn obtained in surface water in this study could be considered safe with no possible adverse effect on both human and aquatic organisms which depend on this river. The levels of heavy metals found in sediment soil and water samples in this study were compared to other studies across the world as presented in Table 3. Generally, the concentrations of heavy metals investigated were lower compared to what was obtainable somewhere else.

Soil and sediment systems are considered as the reservoirs for heavy metal in the environmental media. The levels of the metals (Cr, Cu, Fe, Pb and Zn) evaluated in soil and sediment in this study are presented in Table 2. The results indicate that Pb was not detected in both soil and sediment across the sites;this could be attributed to possibly absence of anthropogenic activities, resulting in the enrichment of Pb into the river system along the course of this river. However, Cr was detected at sites 1 and 2 in soil but detected only at site 2 in the sediment (n/d – 0.0136 and n/d – 0.143 µg/kg dry weight) for soil and sediment respectively. The values of Cr recorded at these sites were below DWAF guidelines for the aquatic marine environment and EPA guideline for sediments for the not polluted value of < 25 mg/kg, therefore suggesting that the river is less toxic. In contrast to the non-detection of Pb across the sites, Zn was detected in both soil and sediment at the concentration levels which ranged between n/d – 0.222 and 0.0208–0.212 µg/kg dry weight in soil and sediments respectively. The concentration of Cu ranged between n/d – 0.0659 µg/kg in soil and n/d – 0.0691 µg/kg (dry weight bases) in sediment samples. The concentrations recorded across the site were found below < 90 mg/kg (Zn) and < 25 mg/kg (Cu) as stipulated by EPA guideline for sediments (Table 4) indicating that the sites were not polluted by Zn and Cu as the current state of the river suggest. The values of Cu recorded in this study were lower than the values (0.07–6.30 mg/L) reported by Gupta et al. [50] in the vegetables grown in wastewater-irrigated areas of Titagarh, West Bengal, India. Compared with the reports of other heavy metals from other surface sediments collected from other coastal areas such as Izmit Bay, Turkey. It was reported that the coastal sediment in this area has some average metal concentrations for Cr (74.3 mg/kg), Cu (67.6 mg/kg), and Pb (102 mg/kg and Zn (930 mg/kg) respectively [51]. Hyun et al. [52] also reported high values for the heavy metals investigated in Masan Bay, Korea as 67.1, 43.4, 44.0 and 206.3 mg/kg for Cr, Cu, Pb and Zn respectively. The concentrations of these heavy metals recorded in these river Bays were exponentially higher compared to what was found in this study as well. Cu is important when present at reasonable values for the development of the embryo, reproductive organs and performance of normal body metabolic activities [47]. Cu at a moderate level is required for the production of red blood cells and strengthening of

11

Table 3. The concentrations of selected heavy metals found in surface water (µg/L), soil and sediment (µg/kg dry weight) across the World.

Location	Heavy Metals					References
	Cr	Cu	Fe	Pb	Zn	
Isipingo River, South Africa	n/d[1], n/d – 0.0136[2], n/d – 0.143[3]	n/d[1], n/d – 0.0659[2], n/d – 0.0691[3]	9.54–46.70[1], 44.90–104[2], 47.50–154[3]	n/d[1], n/d[2], n/d[3]	n/d – 28.00[1], n/d – 0.222[2], 0.0208–0.212[3]	This study
Crocodile River, South Africa	n/d – 10[1]	30–80[1]	70–0.28[1]	n/d – 20[1]	40–100[1]	[49]
Mahanadi Basin, India	350–86080[1]	770–76050[1]	10–94550[1]	860 – 80210[1]	760–72860[1]	[54]
Daya Bay, China	n/d[3]	2080[3]	-	4570[3]	113000[3]	[55]
Coastal Bohai Bay, China	60.1–22450[3]	2010–6290[3]	-	2090–6640[3]	5530–45730[3]	[7]
Soil of Amhara Region, Ethiopia	-	5210–7730[2]	23,866-32,262[2]	1380–2320[2]	13,710–21340[2]	[56]
Fresh Water Environments, Osun State Nigeria	0 – 2100[1]	0–1350[1]	60–960[1]	-	10–650[1]	[57]
Buriganga River, Bangladesh	5280–13960[3]	70,000–346000[3]	-	6030–10560[3]	245,000–98490[3]	[58]
Atoyac River, Mexico	181830[3]	1470[3]	-	12170[3]	62170[3]	[59]
Groundwater Resources of TorbatHeydariyeh, South-eastern of Iran	2.2–173.7[1]	-	-	0.5–8[1]	-	[60]

n/d = Not detected, [1] = water sample, [2] = soil sample [3] = sediment sample

Table 4. International tolerable standards for the selected heavy metals.

Metal	EPA guideline for sediments (mg/kg)				Threshold effect sediment quality guidelines for metals (mg/kg) [61,62]					Maximum permissible limit in drinking water (µg/L)				
	Not polluted	Moderately polluted	Heavily polluted	This study (µg/kg)	TEL	ERL	LEL	MET	CB TEC	EPA 2008	WHO 2008	EU 1998	DWAF	This study (µg/L)
Cr	< 25	25–75	>75	n/d – 0.143	37.3	80	26	55	43.4	100	50	50	5	n/d
Cu	< 25	25–50	>50	n/d – 0.0691	35.7	70	16	28	31.6	1300	2000	200	2000	n/d
Fe	*	*	*	47.50–154						300	***	200	100	9.54–46.76
Pb	< 40	– 60	>60	n/d	35	35	31	42	35.8	15	10	10	10	n/d
Zn	< 90	90–200	>200	0.0208–0.212	123	120	120	150	121	5000	*	**	5000	n/d – 28.00

immunity in the body while its absence in the body could lead to nutritional anaemia in the human body [46]. Zinc is an essential trace element for plants, animals and humans, which exist in form of salts as a major component in many foods and potable waters [53]. Also, this current study evaluated the ecological significance of heavy metals in sediment systems of Isipingo River using the SQGs, parameters such as TEL, ERL, LEL, MET and CB TEC as indicated in Table 4. The heavy metal concentrations in sediments from the Isipingo River were found to be lower than the comparable SQGs values, which signifies that the water from this river has less probable potential adverse effects on both animals and humans as well as benthic organisms.

n/d = Not detected, * = Not available, ** = No guideline, because it occurs in drinking-water at concentrations well below those at which toxic effects may occur, *** No guide-line, because it is not of health concern at concentrations normally observed in drinking water, but may affect the acceptability of water at a concentration above 300 μg/L,

3.3. *Contamination intensity assessment associated with heavy metals*

In order to comprehensively understand the level of heavy metals contamination in soil and sediment systems of the Isipingo River, four major pollution indices were evaluated in this study. The results of these indices i.e. soil pollution index, enrich-ment factor, sediment contamination factor and pollution load index are presented in Table 5.

The results obtained from the evaluation of pollution index (PI) and enrichment factor (EF), was used to ascertain the extent and measure the possible impact or the magnitude of contamination of heavy metals concentrations resulting either from the natural or anthropogenic origin. The PI and EF values obtained in this study were less than 1. This indicates that the soil pollution possibly originates from a lithogenic source and the concentrations of Cr, Cu, Pb and Zn shown no enrichment.

The CF and PLI values of all investigated heavy metals in the sediment systems of Isipingo River were found to be generally low (<1) (Table 5). This demonstrates that the Isipingo River could face less probable environmental pollution resulting from most dangerous heavy metals such as Cr, Pb and Cu. Rabee et al. [63] reported a similar trend for PLI values in Tigris River sediment collected in Baghdad Region, however, the CF values for Pb and Cd were reported to be higher (>1). This was attributed to the influence of external discrete sources such as industrial activities, agricultural runoff, and other anthropogenic inputs. In a similar trend, Shen et al. [64] reported that average CF values of 0.86 for Cr, 0.84 for Cu, 0.97 for Zn, and 1.35 for Pb, respectively in the sediment samples collected from the Lishui River Watershed, Southern China. These results indicated that, the surface sediments in the Lishui River was only polluted by Pb and Cr, Cu, and Zn exhibited by low concentration and pose less of a threat to the aquatic lives. In contrary, Chetty and Pilay [8] have reported low-to-moderate contamination and minor-to-moderate enrichment of the selected heavy metals (Cu, Pb, and Zn) in Palmiet and Sezela River in KwaZulu-Natal, South Africa. The high values of PLI were said to be indicative of the deterioration of the Palmiet River system which had undergone deterioration due to the industrial

Table 5. Contamination factor, pollution load index, soil enrichment factor and pollution index values for the sediment and soil sample of the Isipingo River.

Sample	Concentration factor					Degree of Contamination	Pollution load index	Enrichment factor					Pollution index
	Cr	Cu	Fe	Pb	Zn			Cr	Cu	Fe	Pb	Zn	
Sed 1	*	0.0113	0.0513	*	0.00207	0.0647	0.0106	0.0178	*	1.0000	*	0.0991	0.0957
Sed 2	0.0143	0.0044	0.0261	*	0.00815	0.0530	0.00012	0.0392	*	1.0000	*	0.223	0.233
Sed 3	*	0.0126	0.0228	*	0.00170	0.0370	0.00787	*	0.486	1.0000	*	0.347	0.0097
Sed 4	*	0.0023	0.0178	*	0.00442	0.0245	0.00568	*	*	1.0000	*	0.041	0.0017
Sed 5	*	0.0047	0.0158	*	0.00596	0.0265	0.00765	*	*	1.0000	*	0.118	0.0024
Sed 6	*	*	0.0309	*	0.00080	0.0317	0.00497	*	0.554	1.0000	*	*	0.0035

activities in the area and extremely severe enrichment of Pb resulting from the high vehicular movements around the sampling sites.

4. Conclusions

This current study provided useful scientific insight into the current state of the Isipingo River, KwaZulu-Natal, South Africa associated with the selected heavy metals (Cr, Cu, Fe, Pb, and Zn) concentration levels, possible sources, and ecological risks. The results of this study indicated that all the heavy metals evaluated were not detected in surface water samples except for the Fe (9.54–46.70 µg/L), which was found below the tolerable standards as stipulated by EPA, EU and DWAF (EPA 300 µg/L, EU 200 µg/L and DWAF 100 µg/L respectively). The selected heavy metals were also found between not detected to 0.222 µg/kg dry weight and 0.212 µg/kg dry weight in soil and sediment samples. The levels of heavy metals found in sediment samples in this study (n/d – 0.143, n/d – 0.0691, 47.50–154, n/d and 0.0208–0.212 µg/kg) were compared to EPA guideline for sediments; the levels were below the minimum polluted values for Cr < 25, Cu < 25, Pb < 40 and Zn < 90.

The ecological risk assessment of heavy metals in soil and sediment systems from the Isipingo River was evaluated using various pollution indicators such as pollution load index, concentration factor, and Sediment Qualities Guidelines associated with heavy metal concentrations. The outcome of this investigation indicated that, the values of PI < 1 and EF < 1, suggested that the soil pollution possibly originated from a lithogenic source rather than the anthropogenic origin, and the concentrations of Cr, Cu, Pb and Zn showed no enrichment. The threshold effect sediment quality guidelines for metals in this were found below the comparable SQGs (TEL, ERL, LEL, MET, CB, and TEC). Other pollution indicator values found in this study signifies that the water has less probable potential adverse effects on both animals and humans as well as benthic organisms.

Compliance with ethical standards

Ethical compliance is not applicable for this study

Disclosure statement

No potential conflict of interest was reported by the author(s).

ORCID

Gbadebo Clement Adeyinka http://orcid.org/0000-0002-8655-3110
Babatunde Femi Bakare http://orcid.org/0000-0002-1521-682X
Samuel Ayodele Iwarere http://orcid.org/0000-0001-8566-6773

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