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A Pilot Study on the Concentration of Heavy Metals in Sediments from the Lower Orange River, //Karas Region, Namibia

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Abstract

Global water shortage is caused not just by the physical scarcity of water, but also by gradual deterioration of the quality of water resources such as lakes, streams and rivers with heavy metals. This present study evaluated the status of Mn, Fe, Cr, Cu, Ni, As, Zn, Pb and Cd in sediments from the lower Orange River by Inductively Coupled Plasma Atomic Emission Spectrometry technique by collecting a total of eleven samples, each weighing 1 - 2 kg at the depth of 15 - 20 cm from two observations sites along the lower Orange River and applying pollution indicators such as contamination factor(CF), pollution load index(PLI), index of geo-accumulation(I_{geo}) and enrichment factor(EF) to assay the nature and extent of heavy metals contamination in sediments. The sequence of the total heavy metal content in descending order was Fe > Mn > Cr > As > Zn > Ni > Cu > Pb > Cd. The results of CF and I_{geo} showed Mn, Cd, Ni, Zn and Pb were minor sources of sediment contamination since most of the samples were unpolluted and moderately polluted by these metals. However, most sediments were moderate to considerably polluted with Cr, As and Fe suggesting that these were the major pollution sources. The value of PLI at one of the two observation sites was equivalent to the value of baseline level, while the next site indicted quality deterioration of the sediments. The EF revealed that Cr was moderately enriched and arsenic (As) significantly enriched in all the sediments, which suggested contamination due to anthropogenic intervention. Hence, it is recommended that sediment quality be evaluated on a regular basis to avoid further deterioration of the Orange River's health, which might have detrimental repercussions for both aquatic life and local communities along the river.

Keywords

Anthropogenic, Heavy Metal, Pollution, Sediment, Orange River

1. Introduction

Despite the fact that global emphasis has been focused on water capacity, efficiency, and distribution, incompetent wastewater management has resulted in major water-quality issues in many regions of the world, exacerbating the water crisis (water insecurity). Global water shortage is caused not just by physical scarcity, but also by the gradual degradation of water quality in many countries and hence the amount of water that is safe to use is of a limited amount [1]. Freshwater bodies such as lakes, reservoirs, ponds, rivers, streams, wetlands and groundwater which represent only 3% of all the water on earth are under threat from a myriad of anthropogenic forces [2]. These forces of anthropogenic origin exerting stress on the quality and quantity of the vital, yet finite freshwater resource include mining, agriculture, industrial activities and domestic waste [3]. A prime threat to water quality emanating from anthropogenic activities is the contamination of the water bodies with heavy metals (HMs), which are generally defined as metallic elements with a considerably higher density than water or at least 5 times that of water [4]. Examples of heavy metals include titanium, lead, vanadium, copper, iron, nickel and arsenic among others. Mining, despite its numerous social and economic benefits, is one of the most significant sources of HMs in the environment [5]. Large volumes of waste are produced and discharged in the environment in various paths including waste runoff as a result of mineral processing and metallurgical extraction to retrieve the needed elements [6]. Similarly, agricultural works such as the application of fertilizers, pesticides, waste water, biosolid and manure also contribute to the accumulation of heavy metals in the ecosystem [7]. In the same way, heavy metal pollution is also caused by industrial operations such as coal-fired power plants and nuclear power plants [4] [8]. Moreover, HMs are also contaminated in the environment as a result of the use of synthetic products such as paints and batteries [9]. Likewise, practices such as discharge of domestic effluents into water bodies and improper disposal of domestic waste by open dumping and poor management of landfills also introduce heavy metals in the natural environment [10] [11].

HMs, like other metals, are found in the earth's crust, however they can't be degraded or eliminated owing to their persistent and stable nature [12] [13]. It has been established that HMs are bioaccumulated, meaning they may progressively infiltrate plants, animals, and humans via air, water, and the food chain over time [14]. Certain HMs such as iron, copper, cobalt, zinc, magnesium and selenium are important elements for a variety of biochemical and physiological processes [15]. A lack of these micronutrients leads to a number of deficiency illnesses or syndromes [16]. Nonetheless, these elements can cause adverse effects depending on forms, degree, duration and routes of exposure [17]. Metalloids and metals such as arsenic, cadmium, chromium, lead, and mercury are very poisonous as they may cause numerous organ damage even at low doses. HMs toxicity can cause acute and chronic effects in different organ systems including immune system malfunction, renal dysfunction, neurological system abnormalities, vascu-

lar damage, skin lesions, birth defects, and cancer, to name a few [18] [19]. In Namibia, a semi-arid country, evaluation and monitoring of pollution of freshwater ecosystems are important to mitigate water shortage. This has been demonstrated by several local studies that aimed at assessing the levels of pollution due to heavy metals in marine environments (e.g [20]-[28]). However, the Orange river which extends from Lesotho through South Africa and Namibia into the Atlantic Ocean is poorly studied in Namibia, thus locally there exists limited literature on the status of metal pollution in this river. It has also been reported that the quality of water from this river has deteriorated, attributed to littering, domestic waste and chemicals [29], yet direct abstraction of water for consumption by local communities along the river is still reported [30] [31]. It is against this background that the present study's objective was formulated, which is to investigate the extent of heavy metals contamination, if any, associated with anthropogenic activities along the lower Orange river with emphasis on lead, iron, cadmium, zinc, copper, chromium, nickel, arsenic and manganese. The study analyses the accumulation of selected heavy metals and metalloids using physicochemical and pollution indices, in sediments, which are known to be the principal carriers and possible sources of pollutants in marine settings.

2. Methods and Materials

2.1. Study Area

The study was done at two locations along the Namibian portion of the lower Orange River shown in **Figure 1**, at about 10 km and 60 km downstream (northwest) of Noordoewer, which is a settlement about 800 km from the capital city Windhoek, situated in southern Namibia. The two sites of study are site A (28˚41'0"S 17˚34'0"E) and site B (28˚19'0"S 17˚22'0"E). The area which is a semi-arid desert experiences two seasonal climatic situations, winter and summer with an annual average temperature over 18˚C accompanied by sparse and erratic rainfall. The Orange River in its entirely is 2200 km long and flows westward, establishing a natural international boundary between Namibia and South Africa, emerging from the Drakensberg highlands in Lesotho at an altitude of more than 3000 meters [32] [33]. This river is a source of water for agricultural, mining, industrial, and municipal use, as well as hydroelectric generation along its route. Mixed woody vegetation, such as buffalo thorn, wild olive, indigenous wild tamarisk, sweet thorn, cape willow, karee trees, and reeds, dominate the riparian area of the Orange River, which stabilizes the bank and prevents erosion [34]. There also exists a small population of cactiform and succulent plants in the far-off river zones, which are adapted to dry climate by storing large amounts of water in their stems and enduring extended periods of dryness [35]. In Namibia, the lower Orange River incises through the Mesoproterozoic Namaqua Metamorphic Complex between Noordoewer and Oranjemund (the river's mouth) before cutting the Neoproterozoic Gariep Belt (the southern arm of the Damara Orogen) close to the river's mouth on the Atlantic Ocean seaside [36].

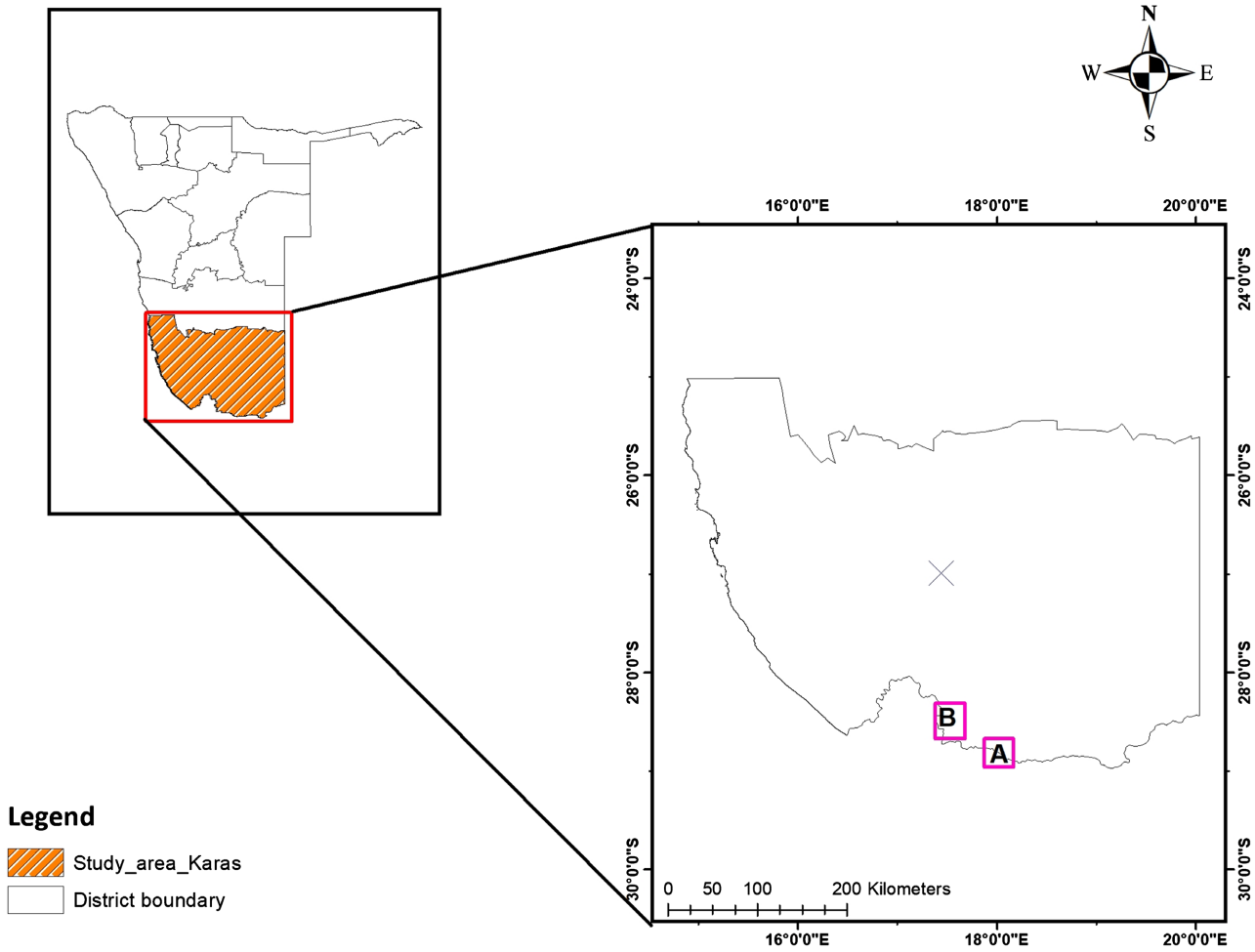

Figure 1. Map showing location of study area, Site A and Site B along the lower Orange River, //Karas region, Namibia.

2.2. Sample Collection and Pre-Treatment

Two sampling locations were established for the collection of a total of eleven samples in the month of September 2018. The first location, site A situated about 10 km from Noordoewer in the downstream of the river where eight samples were obtained at an interval of about 200 m. Second location, site B situated about 60 km from Noordoewer also in the downstream of the river where three samples were collected at the same spacing as in site A. For each sample, 1 - 2 kg was collected, at the depth of 15 - 20 cm using a shovel and stored in sealed polythene bags which were marked accordingly. The exact position of each sampling site was obtained using a handheld Global Positioning System (GPS). All samples were oven-dried at a temperature of about 95˚C and then crushed to about 2 mm after which pulverized to much more finer grains and passed through a sieve.

2.3. Sample Preparation and Measurements

For each, a mass of about 0.25 - 0.30 g was weighed using an analytical balance and transferred into the digestion tubes. Then 9 mL concentrated HCl, 3 mL of concentrated HNO_3 and 1 mL of hydrofluoric acid were added to the samples in

the digestion tubes. This was followed by heating the samples in the block digester to 95˚C and reflux for 15 min without boiling. To neutralize hydrofluoric acid and prevent its destructive impact on the glass components of the utilized analytical equipment, 6 mL of boric acid was added to the sample after it had cooled. Then, the samples were transferred into small vials and stored in a refrigerator prior to elemental analysis. The Inductively Coupled Plasma Atomic Emission Spectrometry (ICP AES) technique was utilized for the elemental analysis at the Namibia University of Science and Technology (NUST). For the physicochemical parameters, pH and conductivity, a portable PH/EC/TDS (HI 9811–5, Hanna instrument) probe was used to determine the pH and conductivity of each sediment (at 20˚C). The probe was inserted into a mud mixture composed of sediment and distilled water.

2.4. Metal Assessment in Sediments

It has long been established that it is feasible to measure the degree of contamination in sediments by heavy metals through computing parameters such as the contamination factor (CF), pollution load index (PLI), the enrichment factor (EF), and index of geo-accumulation (I_{geo}). In the present study, an integral approach used from [37] study was adopted for the computation of the four parameters highlighted above.

The contamination factor was calculated using the following equation:

$$CF = Cm/CB_n \tag{1}$$

where CF is the proportion between the measured content of each metal and its background value (world average shale values (WASV) in sediment.

The Pollution Load Index was determined using the following formula:

$$PLI = \left(CF1 \times CF2 \times CF3 \times \cdots \times CF_n\right)^{1/n} \tag{2}$$

where n is the number of metals assessed in the study.

An assessment degree of contamination by the toxic metals was also determined by calculating the geo-accumulation index by the following equation:

$$I_{geo} = \log_2\left[Cn/1.5Bn\right] \tag{3}$$

where Cn is the concentration of metal n, Bn is the metal n's background data (WASV), and 1.5 is a lithological change factor.

The enrichment factor is generally used to evaluate anthropogenic influences on trace metals in sediments [38]. The enrichment factor for each sample was calculated by using the element iron (Fe) as the normalization element in order to detect anomalous heavy metal influences. The EF was computed by using the following equation:

$$EF = \left\{C/Fe\left(Sample\right)\right\}/\left\{C/Fe\left(WASV\right)\right\} \tag{4}$$

where C/Fe (sample) represent the heavy metal-to-Fe ratio in our study and C/Fe (background) represent the heavy metal-to-Fe ratio in the background.

The interpretation of the concentration of heavy metals in sediments presented

in this study was based on the comparison against the Environmental Protection Agency (EPA) Sediment Quality Criteria shown in Table 1. The elucidation of the physicochemical parameters was based on the criteria of the World Health Organization (WHO). Multiple indices (CF, PLI, I_{geo} and EF) classification used in [20] [39] as presented in Table 2, was adopted in this work to categorize pollution level, nature of enrichment and sediment quality.

3. Results and Discussion

3.1. Physicochemical Parameters

The electrical conductivity (EC) and pH measured in the laboratory for each

Table 1. EPA sediment quality criteria (mg/kg), Note: ND = no data.

Heavy metals	Not polluted	Moderately polluted	Heavily polluted
Mn	<300	300 - 500	>500
Fe	ND	ND	ND
Cr	<25	25 - 75	>75
Cu	<25	25 - 50	>50
Ni	<20	20 - 50	>50
As	<3	3 - 8	>8
Zn	<300	300 - 600	>600
Pb	<40	40 - 60	>60
Cd	--	<6	>6

Table 2. Multiple indices (CF, PLI, I_{geo} and EF) classification of sediments [20] [39].

Geo-accumulation index (I_{geo})			Enrichment Factor (EF)		Contamination Factor (CF)		Pollution Load index (PLI)	
I_{geo}	I_{geo} class	Sediment quality	EF Value	Nature of enrichment	CF Value	Pollution level	PLI	Indication
0	0	Not polluted	EF<2	Deficiency to mineral enrichment	CF < 1	Low	0	Perfection
$0 \le I_{geo} < 1$	1	Not polluted to moderately polluted	EF = 2 - 5	Moderate enrichment	$1 \le CF < 3$	Moderate	=1	Baseline level
$1 \le I_{geo} < 2$	2	Moderately polluted	EF = 5 - 20	Significant enrichment	$3 \le CF < 6$	Considerable	>1	Polluted
$2 \le I_{geo} < 3$	3	Moderately to strongly polluted	EF = 20 - 40	Very high enrichment	$CF \ge 6$	Very high		
$3 \le I_{geo} < 4$	4	Strongly polluted	EF > 40	Extremely high enrichment				
$4 \le I_{geo} < 5$	5	Strongly to extremely polluted						
$I_{geo} \ge 5$	6	Extremely polluted						

sample are given in Table 3. The conductivity values of sediments in this study were found to be within the range 100 - 2210 μS/cm with eight samples with measured conductivity values within the WHO and EPA recommended limit (≤700 (μS·cm^{-1}) for domestic use and three samples (LOR-8, 10 and 11) with values above that same limit. For the pH values, it was found that all samples had values within the WHO and EPA accepted range (6.5 - 8.5) with a mean level of 7.2 which is also in fairly good agreement with that reported by authors [40] in the year 2014.

3.2. Heavy Metal Concentrations in the Sediments

The results of metal concentrations in sediments from the lower Orange river are presented in Table 4. According to Table 4, among the target metals, iron (Fe) recorded the highest metal content from all the sampling sites with a concentration range of 14,787 - 95,464 mg/kg. This may be attributed to the geochemical rock structure (Namaqua metamorphic complex) through which the river cuts. Manganese (Mn) recorded the second highest in concentration with a range of 478 - 2211 mg/kg with sampling sites under moderately to a heavily polluted category of United states-EPA guidelines for sediments. It was also found that chromium (Cr) and arsenic (As) were heavily polluted in the analyzed sediments with metal contents in the range of 99 - 290 mg/kg and 55 - 105 mg/kg, respectively. For copper (Cu), the assessed concentration fluctuated with sampling sites with some values under unpolluted, moderately to heavily polluted.

Table 3. pH and EC of the sediments from lower orange river.

Site	Sample code	pH	Electrical conductivity (μS/cm)
A	LOR-1	7.2	150
	LOR-2	7.0	130
	LOR-3	7.3	300
	LOR-4	7.5	440
	LOR-5	8.2	320
	LOR-6	7.2	160
	LOR-7	7.3	300
	LOR-8	7.7	2210
B	LOR-9	6.6	100
	LOR-10	7.3	1950
	LOR-11	6.4	1520
	Min	6.4	100
	Max	8.2	2210
	Mean	7.2	689
WHO/US-EPA (domestic use)		(6.5 - 8.5)	≤700 (μS·cm^{-1})

Table 4. EPA heavy metal guidelines for sediments (mg/kg), Note: BDL = below detection limit.

Heavy metals	Not polluted	Moderately polluted	Heavily polluted	Present study	Shell value	Continental crust value
Mn	<300	300 - 500	>500	478 - 2211	850	750
Fe	ND	ND	ND	14,787 - 95,464	47,200	35,900
Cr	<25	25 - 75	>75	99 - 290	90	71
Cu	<25	25 - 50	>50	23 - 133	45	32
Ni	<20	20 - 50	>50	23 - 65	68	49
As	<3	3 - 8	>8	55 - 105	13	10
Zn	<300	300 - 600	>600	44 - 205	95	129
Pb	<40	40 - 60	>60	4	20	0.3
Cd	-	<6	>6	BDL	0.3	16

According to the content of nickel (Ni), observation revealed that majority of sites were moderately polluted except sampling points LOR-7 and LOR-8 which were heavily polluted with concentrations of 48 mg/kg and 65 mg/kg respectively. However, the metal content with respect to Ni in all sediments was below the shell value (68 mg/kg). In all sites, sediments with respect to zinc (Zn) were found not polluted as their content was in the bounds of 44 - 205 mg/kg. Cadmium (Cd) on the hand could not be evaluated as its concentration was below detection limit (BDL). Similarly, lead (Pb) content could not be detected in most samples as it was also below the detection limit, except one sample from sampling point LOR-10 with a value of 4 mg/kg which is unpolluted and below the shell value (20 mg/kg). The trend of heavy metal mean concentrations in sediments from the lower Orange River were in decreasing order of Fe > Mn > Cr > As > Zn > Ni > Cu > Pb > Cd.

3.3. Heavy Metal Pollution in Sediments

Heavy metal pollution in the sediments of the lower Orange River was assessed using the contaminant factor (CF), pollution load index (PLI), geo-accumulation index (I_{geo}), and enrichment factor (EF). The results of the evaluated average contamination factor from the two studied locations are plotted in **Figure 2**. As presented in **Figure 2**, site A and B were both found with pollution of moderate level with respect to Cr. Moreover, considerable arsenic (As) pollution was found in both sites. However, site B recorded a low level of pollution with respect to Fe while site A was noted with a moderate level. Also, pollution from Cu in site A was moderate. Low pollution levels were noticed for Mn, Cd, Ni, Zn, and Pb in both sites. Thus, the general trend in decreasing order of pollution level based on contamination factor values is As > Cr > Fe > Cu > Mn > Zn > Ni > Pb > Cd. **Table 5** summarizes the computed pollution load index (PLI) values for metals in the sediments with site A classified as polluted (PLI > 1) and site B within the

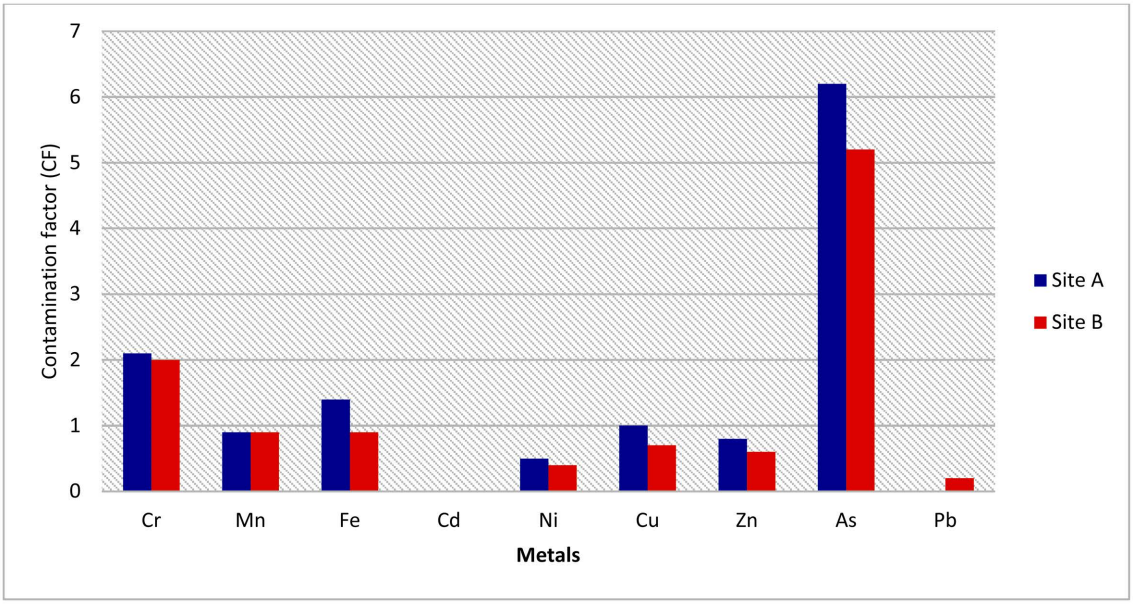

Figure 2. Contamination factor (CF) values for heavy metals in the sediments of the lower Orange River. Low degree, CF < 1; moderate degree, 1 ≤ CF < 3; considerable, 3 ≤ CF < 6; very high degree, CF ≥ 6 [20] [39].

Table 5. Average pollution load index of site A and B.

Site	Pollution load index
Site A	1.2
Site B	1.0

baseline level or unpolluted (PLI=1). The slightly elevated PLI value at site A shows that the sediments of the examined river are deteriorating in a gradual manner. This also suggested that As, Cr and Fe are the main sources of sediment contamination. Additionally, the fairly higher PLI values are more likely attributed to the region's geological make-up and agricultural practices along the riparian areas. The geo-accumulation index values for the metals examined are shown in Table 6. The index of geo-accumulation (I_{geo}) indicated the decreasing order of As > Cr > Fe > Cu > Mn > Zn > Ni > Pb > Cd. The sediments analyzed in this study showed uncontaminated to moderately contaminated status, while the I_{geo} values for arsenic (As) indicated that the sediments are moderately contaminated. The enrichment factor (EF) was also applied to assess the nature of metal enrichment and deduce the source in the examined sediments. The calculated values of the enrichment factor are summarized in Table 7, from which it is shown that the EF of Mn, Cd, Ni, Cu, Zn, Pb was below 2 at both site A and B. Thus, all the sampling points were deficient in enrichment of the above metals. However, Cr and As were observed to be moderately enriched (EF = 2 - 5) and significantly enriched (EF = 5 - 20), respectively at all examined sites. The relatively low EF values of Mn, Cd, Ni, Cu, Zn, and Pb could be due to natural sources, whereas the moderate enrichment of Cr and the significant enrichment of As are more likely due to anthropogenic intervention.

Table 6. Geo-Accumulation Index (I_{geo}).

Heavy Metal	Site A	Site B
Cr	0.4	0.4
Mn	−0.9	−0.8
Fe	−0.6	−0.9
Cd	ND	ND
Ni	−1.7	−2.0
Cu	−0.6	−1.1
Zn	−0.7	−1.5
As	1.9	1.8
Pb	ND	−3.0

Table 7. Enrichment factor (EF).

Heavy metal	Site A	Site B
Cr	3.7	2.5
Mn	1.3	1.1
Cd	ND	ND
Ni	0.6	0.4
Cu	1.4	0.8
Zn	1.0	0.7
As	9.2	6.8
Pb	ND	0.2

4. Conclusion

Based on the results obtained from the analysis of physicochemical parameters of sediments from the lower Orange River, it was found that the pH of all samples was within the WHO and EPA recommended range for domestic use. The electrical conductivity for most samples was also below the EPA maximum permissible value except for samples LOR-8 from site A and LOR-10 and LOR-11 from site B which recorded values above the limit. According to the obtained total metal content in sediments, Fe scored the highest in all samples with Cd being the least as it was below the detection limit. The comparison of obtained metal content with the EPA sediment quality guideline shows that studied sediments suffered a varying degree of pollution from unpolluted, moderately to heavily polluted. In particular, sediments suffered mostly from Cr and As which each recorded metal content range of 99 - 290 mg/kg and 55 - 105 mg/kg respectively. On the basis of pollution indices, it was shown that Mn, Cd, Ni, Zn and Pb were minor sources of sediment contamination, whereas As, Cr and Fe were major pollution sources. The observed general trend in decreasing order of pol-

lution level based on CF values was: As > Cr > Fe > Cu > Mn > Zn > Ni > Pb > Cd. For the PLI, site A was categorized as polluted (PLI = 1.2 > 1) and site B within baseline level (PLI = 1). The slight difference in PLI values of site A and B might be attributed to the region's geological make-up and agricultural practices along the riparian areas. The I_{geo} indicated the decreasing order of As > Cr > Fe > Cu > Mn > Zn > Ni > Pb > Cd with arsenic (As) moderately contaminated. The EF of all sediments was below 2 (EF < 2) for Mn, Cd, Ni, Cu, Zn and Pb which suggested a deficiency of enrichment of these elements. However, Cr and As were observed to be moderately enriched (EF = 2 - 5) and significantly enriched (EF = 5 - 20) respectively. The relatively low EF values of Mn, Cd, Ni, Cu, Zn, and Pb are due to natural sources, and the high values of Cr and As could be due to anthropogenic intervention. The current study found that human activities have a considerable impact on heavy metal buildup in the Orange River. As a result, it is advised that sediment quality be monitored on a regular basis in order to prevent further deterioration of the Orange River's health, which might have negative consequences for both aquatic life and local residents that depend on this river.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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