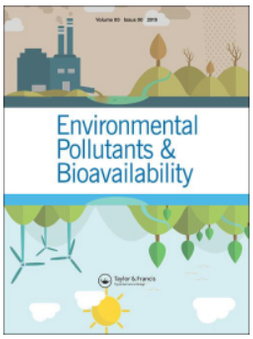

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RESEARCH ARTICLE

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Algoa Bay sediment metal distribution and potential ecological risk assessment

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ABSTRACT

The study assessed the heavy metal distribution and ecological risk in marine sediments across three depths (10, 20 and 30 m) in Algoa Bay, South Africa. The concentration of heavy metals varied between depths, ranging from 0.8 to 124.5 mg/kg at 10 m depth contour, 0.5–96.7 mg/kg at 20 m depth contour and 0.7–113.3 mg/kg at 30 m depth contour determined using X-ray fluorescence (XRF). Higher concentrations were reported both at 10 and 30 m depths. The sediment quality was evaluated against the threshold effect concentration (TEC), probable effect concentration (PEC), effect range low (ERL) and effect range medium (ERM) guidelines. Pollution indices, including geoaccumulation (I_{geo}), the enrichment factor (EF), the pollution load index (PLI) and the potential risk index (PERI), consistently demonstrated anthropogenic accumulation of As, Ag, Cd and Hg. The PERI demonstrated the ecological risk from low to significantly high across all depths; 10, 20 and 30 m had PERI of 4013, 5391 and 5051, respectively.

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Ecological risks; pollution indices; sediment; metal concentration; XRF; Algoa Bay

1. Introduction

Marine life plays a fundamental role in the global economy and in supporting the livelihood of coastal societies. Without a healthy, balanced marine environment, many essential marine ecosystem services would collapse, resulting in a knock-on effect for humans and animals [1]. Our oceans face several environmental challenges such as pollution, biodiversity loss, acidification and damaging fishing activities, alongside climate change resulting from global warming and resulting in sea level rise [2]. Anthropogenic activities such as oil spills, wastewater discharge, agricultural runoff, construction activities and marine traffic are some of the primary sources of heavy metal pollution in coastal marine sediments [3].

Heavy metals are naturally occurring in the Earth's crust, and some are essential for various biochemical and physiological functions of living organisms [4]. These heavy metals are universally investigated because of their ubiquitous distribution, mobility, potential toxicity in the marine environment and adverse effects on marine organisms [5]. To ensure that the economic and nutritional values derived from marine resources are sustained, assessing and controlling these metals in marine ecosystems becomes imperative [6]. Approximately 85% of heavy metals are known to accumulate in the sediments of the aquatic environment [7]. Hence, sediments act as source of heavy metals released into the water [8]. Heavy metals have a stronger affinity for binding to sediments through adsorption. However, this process depends on several factors, which include grain size, organic matter content and cation exchange capacity [9].

The amount of negative charge on the sediment-particles' surface influences the cation exchange of the heavy metals [10] and this varies according to sediment granulometry. Grain size is vital in sediment entrainment, transport and deposition. Fine-grained sediments such as silt and clay act as a sink for heavy metals since they are negatively charged, thus facilitating the adsorption process. On the other hand,

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coarse-grained sediments adsorb fewer heavy metals [11]. Furthermore, sediment organic matter such as plant residues and living and dead microorganisms, allows for more heavy metals to be adsorbed onto the sediment [12].

Sediment structure (e.g. granulometry, organic matter content), transportation and deposition are thus critical in aquatic ecosystems as they influence the distribution and concentration of heavy metals. Generally, finer particles are transported as a suspended load, with larger particles transported as a bed load [13]. Sediment grain size characterises different kinds of marine habitats, with coarser sediment grain sizes dominating high-energy zones along the shore. Finer sediment grain sizes generally increase with increasing bathymetry [11]. In addition to influencing contamination and/or pollution levels, sediment dynamics can also negatively affect aquatic life. For example, excessive levels of suspended sediment can reduce light penetration and affect the productivity of submerged aquatic plants and can also clog fish gills [14].

Although sediments can be a source of heavy metal pollution, they also provide various services to aquatic organisms, as they are a source of nutrients and minerals [15]. Many studies use the sediment compartments in aquatic ecosystems to assess heavy metal pollution [16–18], since sediments serve as both sinks and potential secondary sources of contaminants. Heavy metals can be remobilised from the sediments if the water column's pH, redox state, or salinity fluctuates, which can increase their concentrations in overlying waters and affect ecosystem health and potentially affect human health if these concentrations biomagnify along the food web [19]. To safeguard the integrity of the ecosystem's health, it is therefore important to understand the distribution and concentration of heavy metals in any ecosystem [20].

Natural sources and anthropogenic activities influence the distribution of heavy metals in coastal marine sediments. In 1978–1979, Watling and Watling [21] conducted a study along the coast of Algoa Bay to investigate the presence of heavy metals in water, sediments and molluscs. The study revealed that estuaries and sewer outfalls contribute considerably to the metal concentrations in Algoa Bay. The findings of Watling and Watling [21] serve as a baseline for future monitoring of this marine system if subjected to further urbanization and industrialization [21].

More research is necessary to enhance the understanding of pollution sources and the impact of heavy metals on marine ecosystems and to develop monitoring strategies to mitigate their release into the environment. This study aimed to determine the distribution of sediment heavy metals in the nearshore environment (10–30 m depth) of Algoa Bay and to determine the contamination and/or pollution status of this habitat using various single and integrated indices. The identification of heavy metals in Algoa Bay is a major concern to be addressed urgently, since Algoa Bay is considered the best monitored coastal area in Africa because of the availability of information, including biophysical, socioeconomic and socioecological data types [22].

A large portion of the bay was declared a marine protected area in 2019 to increase the protection of the bay [23]. Although there is a wealth of information in Algoa Bay, there is a little information regarding the distribution and concentration of heavy metals, and there is no information on the ecological risk of these metals. South African studies on coastal marine sediments, particularly along the Indian Ocean Coast, have commonly used reference upper continental values UCC as background concentrations, as no-region specific UCC values are currently available for South Africa [6,24,25].

This study uses two single-chemical-element indices [i.e. geo-accumulation (I_{geo}) and enrichment factor (EF)], one multiple-chemical-index or integrated index [i.e. pollution load index (PLI)], and one ecological risk index [i.e. potential ecological risk index (PERI) to describe the degree of contamination and/or pollution in Algoa Bay] and to define the ecological risk associated with these heavy metals. The particle size distribution and organic matter were considered as they play an important role in contamination and/or pollution.

This study employed X-ray fluorescence (XRF) for the quantification of heavy metals, which has been rarely used on marine sediments compared with frequently used spectroscopy methods (e.g. ICP-OES/ICP-MS and AAS) [26,27]. XRF is nondestructive, requires minimal sample preparation and eliminates the need for acid digestion. Therefore, this method is more environmental friendly, reducing the use of hazardous reagents and also more cost effective for routine analysis. Furthermore, XRF provides rapid analytical output, allowing for efficient quantification for both major and trace elements across a wide range of

sample matrices, which is useful for monitoring programmes [28]. Unlike other methods, X-ray fluorescence (XRF) does not require daily calibration, and once samples are prepared, they can be consistently re-analysed with reproducible results over time [29]. As such, XRF is therefore recommended for preliminary surveys and large-scale monitoring programs where time and resource efficient are crucial. Algoa Bay is South Africa's long-term monitoring site, where sediment health (focusing on metals) has not yet been included in the monitoring programme.

2. Materials and methods

2.1 Study area and sample collection

Algoa Bay is situated along the coast of South Africa's Eastern Cape Province (Figure 1). The region is influenced by the south-flowing Agulhas current. In the western corner of Algoa Bay lies the Nelson Mandela Metropole, incorporating the large industrial city of Gqeberha (formerly Port Elizabeth), where a multipurpose port is located. This port accommodates recreational and commercial fishing, cruise liners and merchant vessels. The Algoa Bay seafloor mostly comprises sand with several reef-out crops [23]. Sand mobility is high in the region, and substantial amounts of sand can cover low-relief reefs depending on wave and ocean conditions [30]. Considering these factors, eight sampling transects (i.e. A3–A10) were selected across the bay at which sediment samples were collected at three different depths (10, 20 and 30 m) (Figure 2). The sampling transects were located approximately 10 km (±2 km) from each other and placed perpendicular to the shoreline. Transect A3 was located between Papenkuils outfall and Swartkops Estuary mouth. Transect A4 was located approximately 3 km south of the Port of Ngqura entrance, while A5 was approximately 5 km north of the harbour. Transect 6 was located across the Sundays Estuary mouth. Transects A7–A10 were located equidistant from each other and spanned the length of the Alexandria Dunefield. Transect A10 is located across Woody Cape.

2.2 Sample preparation and analytical methods

A total of 22 marine sediment samples were collected in April 2023 using a Vaan Veen grab sampler (sampling area: 0.025 m^2). A collected sample from each sampling depth (approx. 1 kg each) was composited from triplicate samples and stored in an aluminium foil at 4 °C pending the analyses. A sediment sample was only acceptable if there was overlying water on top of the sediment inside the Van Veen grab and if the sediment depth was ≥5 cm. The SeaBird 19plusV2 CTD was used for the *in situ* measurement of physicochemical properties (i.e. temperature, pH and salinity). These parameters were measured 1 m from the sea floor.

In the laboratory, sediment samples were air-dried overnight and sieved to remove larger fractions using a 2000 µm stainless steel mesh sieve. Following, oven drying at 105 °C overnight to a constant weight and then re-sieved through a 63 µm mesh sieve, since heavy metals are generally associated with small grain sizes [28,31]. The samples were then ground to a fine powder using an agate mortar. All the pulverized samples were stored in a desiccator until they were analysed for major and trace elements.

2.2.1 Major elements analysis

The pulverised sediment sample was mixed with flux (66% lithium tetraborate and 34% lithium metaborate) and releasing agent (0.65% ammonium iodide) at a ratio (1:9) for fuse bead preparation. The homogenized sample (10 g) in a platinum crucible was fused at 1100 °C for 15 min in a furnace, cooled and stored in a desiccator until XRF analysis for the chemical composition of major elements [32].

2.2.2 Trace element analysis

The pulverised sediment sample (10 g) was mixed with a binder solution (5% Mowiol) for trace metal analysis. The homogenized mixture was well-ground and then compressed with a hydraulic press (20 tons) into a 34 mm diameter pellet and stored in a desiccator until analysed [33–35].

The concentrations of major and trace elements (Cr, Mn, Fe, Ni, Cu, Zn, Mo, Co, As, Se, Cd, Hg, Ag and Pb) were determined using a non-destructive Axios Max 4 KW wavelength-dispersion X-ray fluorescence

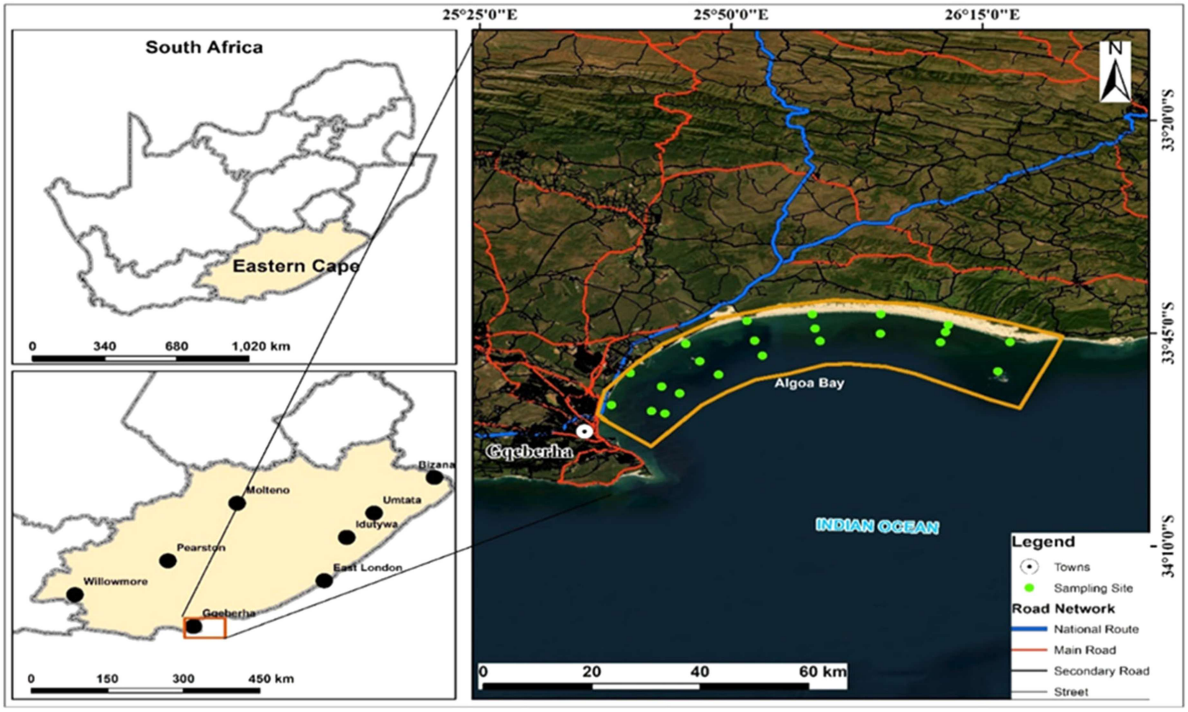

Figure 1. Map of the study area of Algoa Bay showing eight transects from which sediment samples were collected.

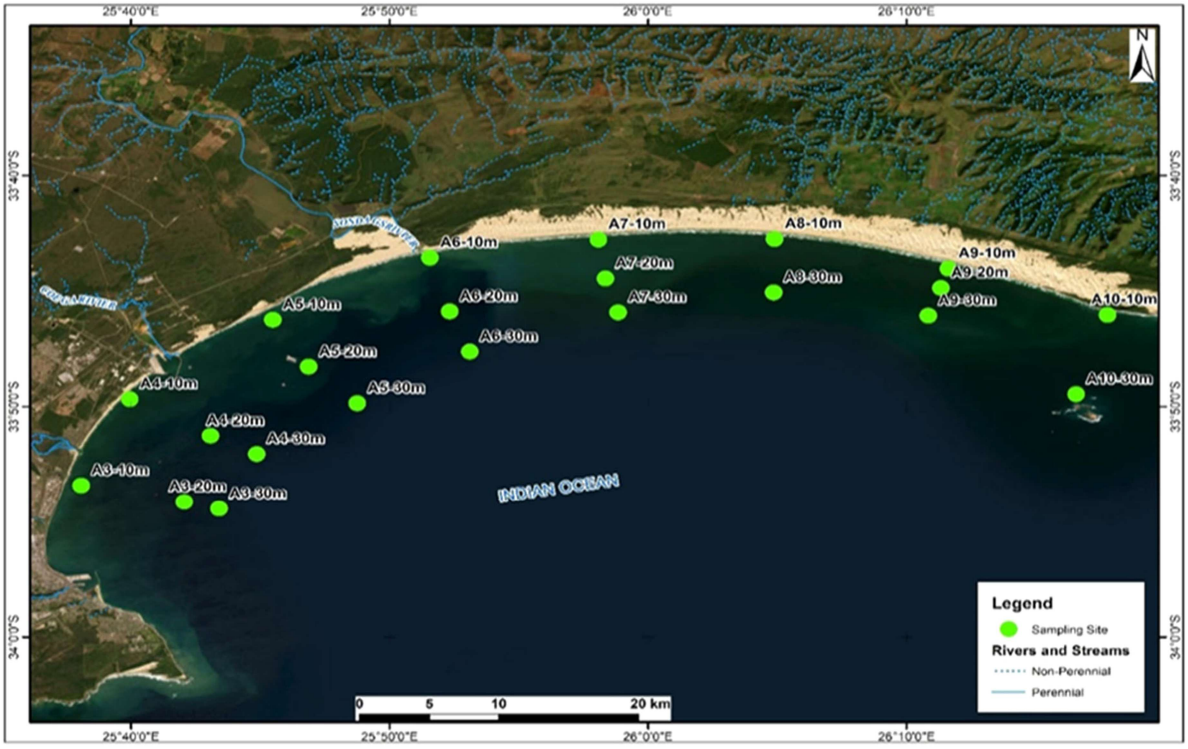

Figure 2. Algoa Bay sampling transects (A3–A10) and three sampling depths per transect. Sediment samples from 20 m at transects A8 and A10 could not be collected because of the presence of reefs.

(WDXRF) spectrometer (Panalytical, South Africa) on fused beads and pressed pellets, following the matrix correction method proposed by Franzini et al. [36] and Leoni and Saitta [37]. This spectrometer is equipped with a Rhodium tube as anode and a selection of filters, tube voltage and sample positions. Quantitative analysis was conducted with the help of an inbuilt SuperQ software. The international certified reference

Table 1. Calibration of major and trace elements including *k*-values, RMS and LLD.

Major/traces (standards)	*k*-Value	RMS value	LLD (mg/kg/%)
SiO_2 (Wroxi-05)	0.973	0.5933	26.59
TiO_2 (Wroxi-14)	0.3687	0.1825	12.58
Al_2O_3 (Wroxi-01)	0.6387	0.2950	13.17
Fe_2O_3 (Wroxi-16)	0.0280	0.1565	15.33
Mn_3O_4 (Wroxi-17)	0.0136	0.0672	12.92
MgO (Wroxi-02)	0.0348	0.2011	29.53
CaO (Wroxi-04)	0.036	0.2164	15.75
Na_2O (Wroxi-3 + 1)	0.1026	0.2011	29.39
K_2O (Wroxi-13)	0.0178	0.2164	11.43
P_2O_5 (Wroxi-20)	0.0061	0.0192	7.64
Cr (Trace-011)	0.0027	0.0009	1.61
Mn (Trace-012)	0.0043	0.0043	2.56
Ni (Trace-009)	0.0012	0.0012	1.81
Zn (RMG-1)	0.0017	0.0021	1.62
Ag (Trace-014)	0.0005	0.0017	2.14
Se (W-1)	0.0003	0.0003	0.55
As (RMG-1)	0.0017	0.0017	2.67
Cd (NIM-1)	0.0005	0.0005	2.06
Pb (RMG-1)	0.0006	0.0006	1.16
Hg (Trace-016)	0.0045	0.0045	3.28
Mo (Trace-009)	0.0014	0.0014	0.42
Co (RMG-1)	0.0009	0.0009	2.64

material (BCR-2, Columbia River Basalt) obtained from the USGS was used as a certified reference material (CRM) for the accuracy, calibration and standardization of the XRF instrument.

The calibration method utilized synthetic calibration standards and CRMs for the analysis of major and trace elements. The WROXI application employed 10 WROXI standards to calibrate major oxides using fused bead samples, while Pro-Trace application used 8 trace element standards for the calibration of pressed pellet samples. Calibration curves were established by plotting element concentrations against X-ray count rates. The calibration performance for each major oxide and trace element was evaluated using k-values, root mean square error (RMS) and the lower detection limits (LDL) summarised in Table 1. RMS assesses the overall accuracy of the calibration, whereas *k*-value provides more comprehensive evaluation by incorporating both the calibration quality and the reliability of the standards. Generally, lower RMS values and *k*-values below 0.05 indicate a well-optimised calibration, supporting accurate and reliable XRF measurements [29,38].

2.3 Quality assurance and quality control

Comprehensive quality control and assurance procedures were adopted for this study. Apart from analysing standards for calibration, the XRF instrument was routinely checked using two monitor samples for major elements (BGSMON and FLXS-3) and two for trace elements (AUSMON and BGSMON), ensuring across a wide intensity range. The metal calibration curves were monitored by coefficient correlation and standard deviation to maintain analytical integrity. The CRM (BCR-2-basalt) was analysed ten times to ensure the accuracy and precision of the data obtained. The recoveries for the certified reference material are presented in Table 2, and the findings were in agreement with the reference values. All analyses were conducted in triplicate, and the findings are presented as the mean concentrations. All reagents used in the experiment were of analytical grade or higher.

The recoveries from the analysis of a CRM were in agreement with the reference values. The recoveries ranged between 98.8%–107.8% (major elements) and 97.9%–105.6% (trace elements).

2.4 Sediment quality guidelines (SQGs)

The risk of contamination in this study was evaluated according to the United States Environmental Protection Agency (USEPA), sediment quality guidelines (SQGs), ecotoxicological values, which includes threshold effect concentration (TEC), probable effect concentration (PEC), effect range low (ERL) and effect range medium (ERM), since there are no South African sediment quality guidelines [15]. An element concentration lower than the TEC indicates a minimum range of effects to predict conditions under

Table 2. Analysis of CRM (BCR-2) for major (%) and trace elements (mg/kg) [39].

Majors	Certified	Measured (%)	Recoveries (%)	Traces	Certified	Measured (mg/kg)	Recoveries (%)
SiO_2	54.16	53.5	98.8	Cr	18 ± 2	19.0	105.6
TiO_2	2.34	2.5	107.8	Co	37.33	37.0	99.1
Al_2O_3	13.37	13.3	99.4	Ni	12.57	12.3	97.9
Fe_2O_3	13.82	14.0	101.4	Cu	19 ± 2	19.0	100.1
Mn_3O_4	0.20	0.2	105.5	Zn	127 ± 9	133.0	104.7
MgO	3.56	3.6	102.2	Mn	1520	1497	98.5
CaO	7.14	7.5	104.6	As	0.86	0.9	104.6
Na_2O	3.16	3.2	100.9	Pb	10.59	10.2	96.8
K_2O	1.75	1.8	105.4	Cd	0.69	0.7	102.9
P_2O_5	0.35	0.4	103.7	Mo	250.6	249.7	99.6

which biological impacts are rare. The higher concentration than TEC but lower than the PEC indicates the occasional occurrence of biological impacts [15]. Concentrations higher than PEC indicate negative biological impacts. The concentration values below ERL signify no biological effects, whereas the values above ERM indicate a harmful threat to the biological community [40].

2.5 Organic matter determination in sediment samples

The organic matter amount in sediments was determined using the Walkley–Black method of acid-base titration. This process is based on oxidising of all organic carbon content in the sediment samples using potassium dichromate ($K_2Cr_2O_7$) solution and concentrated sulphuric acid (98%) at appropriate concentrations during the heating treatment of the samples. Following was the addition of ortho-phosphoric acid (85%) and back titrated with ferrous ammonium sulphate base employing the diphenylamine indicator. To determine the organic matter content, approximately 0.2–0.5 g of the sediment was used in each sample and placed in a 25 mL volumetric flask thoroughly cleaned with nitric acid (10%) [41].

2.6 Particle size distribution analysis in sediment core samples

The wet sieving method was used for categorising sediments into sand, silt and clay percentage determination in marine sediment samples. The sediment samples were first soaked in 10% hydrogen peroxide (H_2O_2) to remove organic matter and 100 mL calgon (1%) solution dispersing agent to segregate the grain sizes in samples. The prepared sample was mixed with distilled water and then an aliquot was extracted at various times after monitoring the settling time required for sand, silt and clay-sized particles to determine the quantity of particles of a specific size that had settled. A description of the sediment was carried out using Folk's classification. According to the classification system, clay and silt are less than 63 µm, and sand particles range from 63 to 2000 µm, and when the sand grain size percentage increases, silt and clay decreases [42].

2.7 Assessing the contamination status of the sediment

To assess the source and status of the heavy metal contamination in sediments, five indices were used and are defined below.

2.7.1 Geo-accumulation (I)geo

The geo-accumulation index (I_{geo}) has been widely used to assess the pollution of heavy metals in sediments and soil. It was first proposed by Müller [43]. The I_{geo} values were calculated using the following equation:

$$\text{Igeo} = log_2\left[\frac{\text{Cs}}{1.5 \times \text{Bn}}\right] \quad (1)$$

where C_s represents the measured concentration of the heavy metals in the sample. B_n represents the background reference concentration. Owing to a lack of data on the background values of the study area,

Table 3. Range of pollution determined in the I_{geo} index proposed by Müller [42,46].

I_{geo} range	Interpretation
$I_{geo} < 0$	Uncontaminated
$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated
$1 < I_{geo} < 2$	Moderately contaminated
$2 < I_{geo} < 3$	Moderately to heavily contaminated
$3 < I_{geo} < 4$	Heavily contaminated
$4 < I_{geo} < 5$	Heavily to extremely contaminated
$5 < I_{geo}$	Extremely contaminated

Table 4. Enrichment factor (EF) contamination classes [46,47].

Enrichment factor (EF)	Classes
EF ≤ 2	Deficiency to minimal enrichment
2 < EF ≤ 5	Moderate enrichment
5 < EF ≤ 20	Significant enrichment
20 < EF ≤ 40	Very high enrichment
EF ≥ 40	Extremely high enrichment

Table 5. Pollution load index categories [46].

Pollution load index (PLI)	Categories
PLI < 1	Not polluted
PLI = 1	Baseline levels of pollution
PLI > 1	Polluted

the element concentrations of the upper continental crust (UCC values) were used as background references (Taylor and McLennan) [44,45]. The constant of 1.5 accommodates possible background value variations due to the sediment's lithologic variation. Geo-accumulation can be interpreted as indicated in Table 3.

2.7.1.1 Enrichment factor (EF)

The enrichment factor (EF) is a helpful indicator that reflects the status of the environmental contaminants, particularly heavy metals in the marine environment. It is used to assess whether heavy metal contamination in each sediment is of natural (EF < 2) or anthropogenic origin (EF > 2) [41]. The following equation expresses the enrichment factor:

$$EF = \frac{(Cs/Cn)\,sample}{(Cb/Cn)\,background} \tag{2}$$

where (C_s/C_n) refers to the ratio between the metal concentration in the sample (Cs) and the concentration of the reference metal (C_n) in the sediment sample. The (C_b/C_n) background is the ratio between the background concentration of the element (C_b) and the reference metal (C_n) of the normalizing element. Iron and aluminium are typically used as normalising elements because of their low variability in the environment [8]. In this study, iron was used as a normalising element because of its relative abundance in crustal materials [24]. EF is interpreted according to 5 classes (Table 4).

2.7.1.2 Pollution load index (PLI)

The pollution load index (PLI) is used to assess the toxicity status of each site. It evaluates the extent of the contamination by metals in the marine ecosystem [48]. The PLI was obtained as a function of the CF (contamination factor) of each metal by using the following equation:

$$PLI = (CF1 \times CF2 \times CF3 \times CFn)\,1/n \tag{3}$$

where *n* represents the number of heavy metals and CF represents the contamination factor. PLI is classified into 3 categories (Table 5). The contamination factor is calculated as a ratio between the heavy metal concentration and the background value using the following equation:

$$CF = Cs/Cn \tag{4}$$

Table 6. Relationship among E_r^i, PERI and pollution levels [52].

Ecological risk (E_r^i)	Grade of ecological risk of a single metal	Potential ecological risk index (PERI)	Grade of potential ecological risk of the environment
$E_r^i < 40$	Low ecological risk	PERI < 150	Low ecological risk
$40 \le E_r^i < 80$	Moderate ecological risk	150 < PERI < 300	Moderate ecological risk
$80 \le E_r^i < 160$	Considerable ecological risk	300 < PERI < 600	High ecological risk
$160 \le E_r^i < 320$	High ecological risk	PERI ≥ 600	Significantly high ecological risk
$E_r^i \ge 320$	Serious ecological risk		

where C_s represents the measured value of the element and where C_n represents the corresponding upper continental crust (UCC) background value (Taylor and McLennan) [44,45].

2.8 Assessing the potential ecological risk index (PERI) of sediment

The ecological risk index (E_r^i) represents a factor that comprehensively evaluates the potential ecological risk that heavy metals pose in marine sediment. It not only assesses the pollution status in the sediment but also combines ecological and environmental toxicology [15]. The index can reveal potential relationships (toxicity level, ecological sensitivity and synergy) between all assessed heavy metals [49]. E_r^i is calculated as follows, as proposed by Hakanson [50]:

$$Eri = TriXCF \tag{5}$$

where $T_r{}^i$ is the toxicity response of the single metal of interest, CF is the contamination factor calculated for each metal, and E_r^i is the ecological risk coefficient for the heavy meal of interest [51]. The following toxic response factors were used: Cu = Pb = Co = Mo = Ni = 5, Zn = 1, Cr = 2, Mn = 1, As = 10, Cd = 30, Hg = 40 [8,50]. The E_r^i and PERI categories are presented in Table 6. The potential ecological risk index (PERI) assesses the ecological risk related to all chemical elements present in the study area and is determined by the sum of the individual ecological risk factors of these elements. The PERI is calculated using the following equation:

$$PERI = \sum Eri \tag{6}$$

2.9 Statistical analysis

Pearson correlation was applied to assess the relationships among various heavy metals across Algoa Bay, using a bivariate approach to reveal the associations [53–55]. Statistical significance was assessed at 0.05 level in all cases. PCA was used to extract key components of the data responsible for explaining the variation in heavy metals concentration and to infer whether they had a common source [8]. All the statistical analysis were conducted using SPSS statistics software, version 29.0.

3. Results and discussion

3.1 Physio-chemical properties, organic matter and grain size

The temperature varied from 11 °C at A4 (30 m) to 18 °C at A5 (10 m) (Figure 3). Higher temperatures were generally recorded at a 10 m depth contour (shallow waters), which was generally closer to the shoreline, while lower temperatures were generally recorded in deeper waters at 30 m. Lower temperatures were also recorded at A4 and A6 at all water depths, indicating the potential influence of port activities from the Port of Ngqura at A4 and the influence of Sundays Estuary at A6. The temperature recorded in this study is within the temperature range recorded previously in Algoa Bay [56,57].

Furthermore, Figure 3 reported that the pH ranged between 7.69 at A6 (10 m) and 8.24 at A3 (10 m), with an average of 8.0. The results concur with Edworthy et al. [57], who recorded an average pH of 8.10 ± 0.06 (range: 8.02–8.32) at their offshore sites, which were located at 30 m depth contour while they recorded an average of 8.10 ± 0.13 (range: 7.98–8.44) at their inshore sites located at a surf zone (<1 m) [57]. The pH

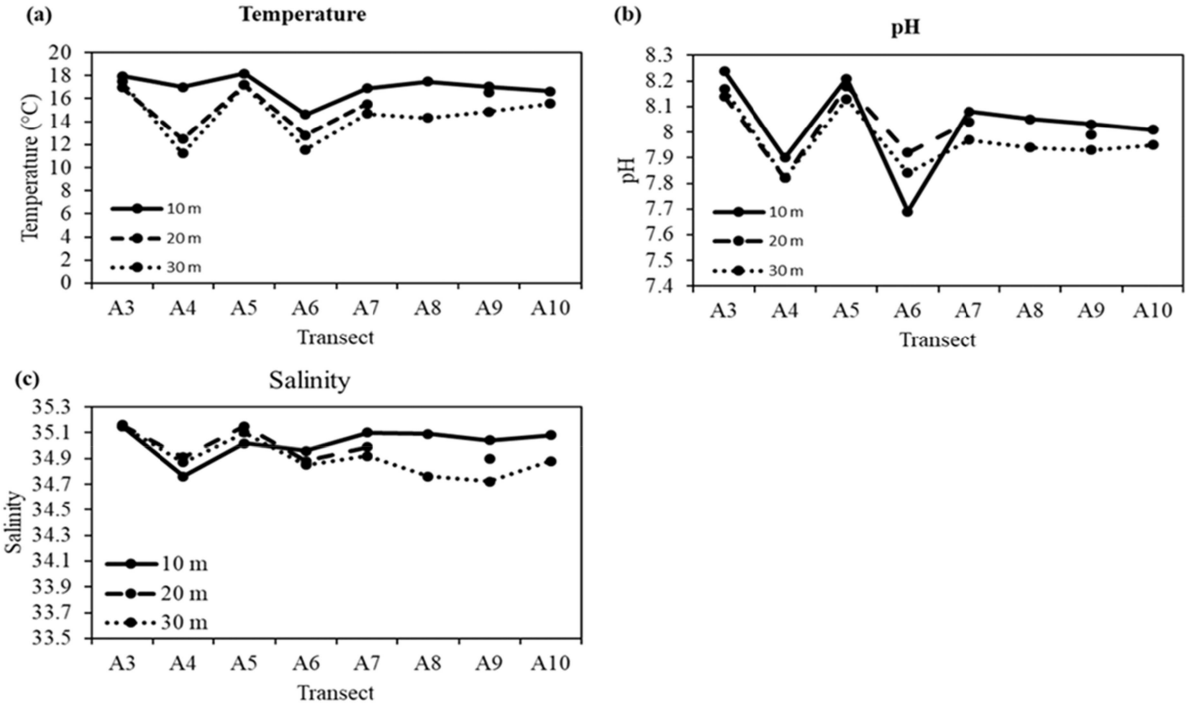

Figure 3. Representation of the variation in physicochemical properties across transects of different depths in Algoa Bay. i.e. (a) Temperature, (b) pH and (c) salinity.

generally decreased towards A10 (Woody Cape) with a considerably low pH recorded at A6 at all depths, followed by A4 at all depths. Variation in pH tends to increase the toxicity of heavy metals and that can damage the coastal marine ecosystem.

Salinity is a measure of dissolved salts in water and is an important parameter that affects the survival of aquatic plants and animals. Salinity ranged from 34.72 at A9 (30 m) to 35.16 at A3 (20 m) (Figure 3). Salinities of shallower waters at A3–A5 were generally lower, but higher from A6 to A10. An average salinity of 34.9 across the whole study area is in agreement with the findings of Edworthy et al. [57].

The organic carbon content in sediments and soils is highly associated with pollutants; hence, it can be used for estimating pollution levels. The sediment organic content (TOC %) ranged from 0.6% at A10 (30 m) to 4.04% at A4 (30 m), with an average of 2.2% (Figure 4). In most sampling sites, particularly in the western sector (i.e. A3–A6), the sediment organic content generally increased with increasing depth, whereas the organic content in the eastern corner generally decreased with depth, with the lowest organic content recorded at A10. The highest sediment organic content (>3%) was measured at A4–A6 at 30 m. The results for the organic carbon content are consistent with those obtained from the previous studies of the same area [58–60].

The sediment texture was generally sandy, with 91.5% sand recorded at A4 (30 m) to 100.0% sand recorded at A5 (10–20 m) (Figure 5). The mud fraction (i.e. silt + clay) was highly negatively correlated with the sand fraction, as expected. No mud was recorded in the shallower waters of A5, with a low percentage of 0.8% recorded in the shallow water of A6 and a high percentage of 8.5% recorded at deeper waters of A4.

3.2 Chemical composition

The results for the geochemical composition of the three laboratory replicates of marine coastal sediments (10 g of each sample) with their statistical percentages are presented in Table 7. They were ranked in descending order: SiO_2 > CaO >TiO_2 > NaO_2 > Fe_2O_3 > MgO > K_2O > Al_2O_3 > P_2O_5 > Mn_3O_4. SiO_2 was the most abundant ranging from 63.2% to 77.5% with an average of 71.2%, indicating that the sediments of Algoa Bay are rich in quartz [61]. Al_2O_3 concentration ranged from 0.2% to 0.9%, Fe_2O_3 from 0.7% to 1.9%,

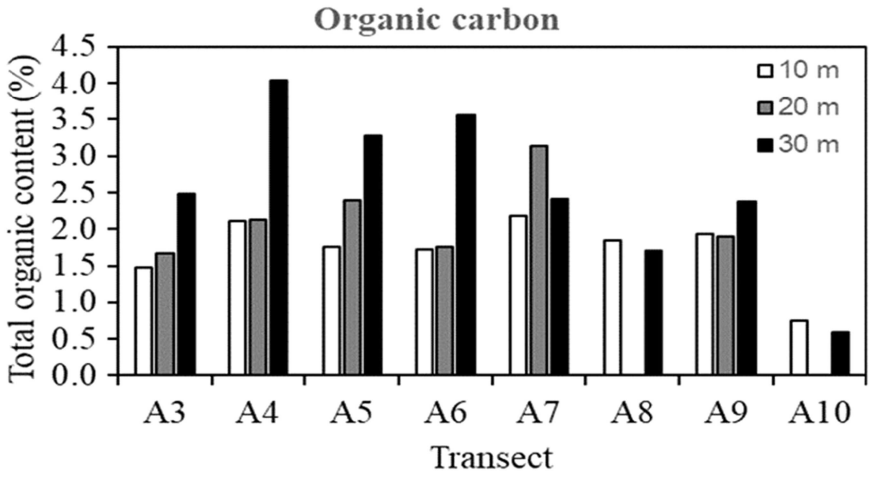

Figure 4. Representation of the organic carbon content variation across transects of Algoa Bay.

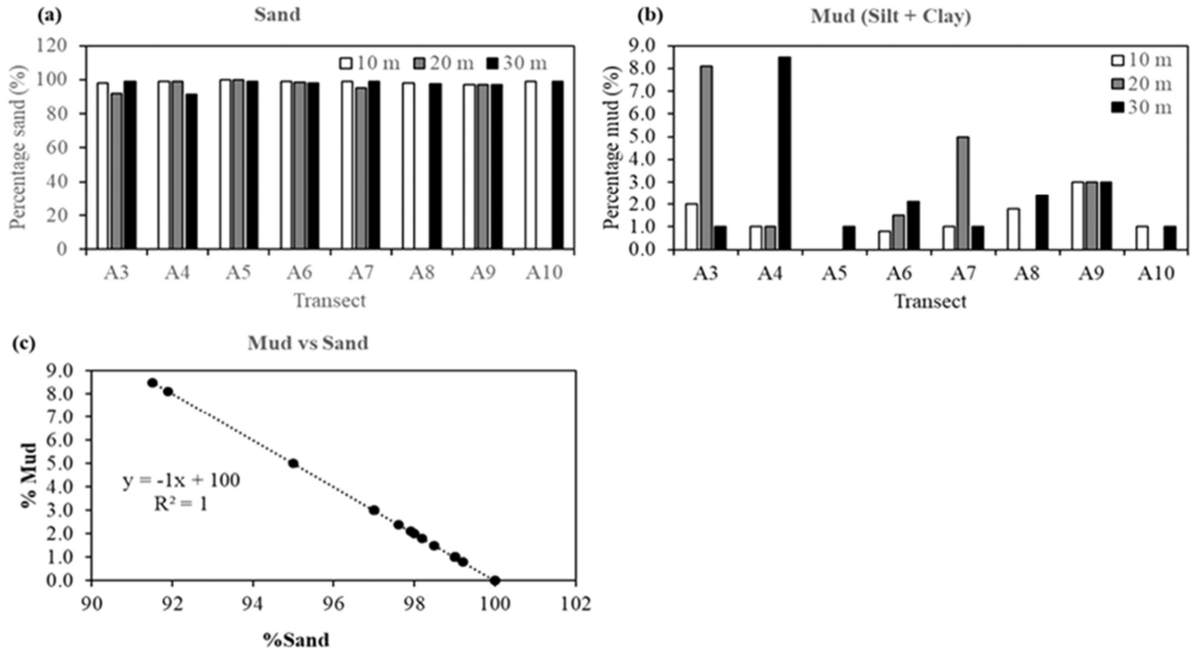

Figure 5. Representation of the granulomery correlation of sand against mud (silt + clay) of Algoa Bay. i.e. (a) Sand percentage, (b) mud (silt + clay) percentage and (c) mud vs sand correlation.

Table 7. Descriptive statistics and major oxides (%) of marine sediments of Algoa Bay: UCC – upper continental crust [63–65].

Parameters	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	Mn_3O_4	MgO	CaO	Na_2O	K_2O	P_2O_5
Min	63.2	0.2	1.1	0.7	0.1	0.7	21.6	0.7	0.3	0.1
Max	77.5	0.9	3.9	1.9	0.1	1.4	30.9	1.8	1.1	0.9
Mean (%)	71.2	0.5	2.5	1.2	0.1	1.0	26.2	1.3	0.7	0.2
SD	3.7	0.2	0.9	0.3	0.1	0.2	2.9	0.3	0.2	0.2
UCC values	66.00	15.20	0.50	4.50	0.1	2.48	4.20	3.90	3.40	0.17

Na_2O from 0.7% to 1.8%, K_2O from 0.3% to 1.8%, MgO from 0.7% to 1.4% and Mn_3O_4 remained relatively constant at 0.1%. Maliwa [62] conducted a study on seafloor sediments and grain size analysis in Algoa Bay, which revealed that lithological composition of the bay includes minerals such as quartz and hematite [62].

The oxide concentrations observed in this study were compared to average UCC values. Most major oxides were found at lower concentration than UCC values, except for SiO_2, CaO, P_2O_5 and TiO_2. P_2O_5 ranged from 0.1% to 0.9%. The elevated levels of CaO ranging from 21.6% to 30.9% in the sediments reflect

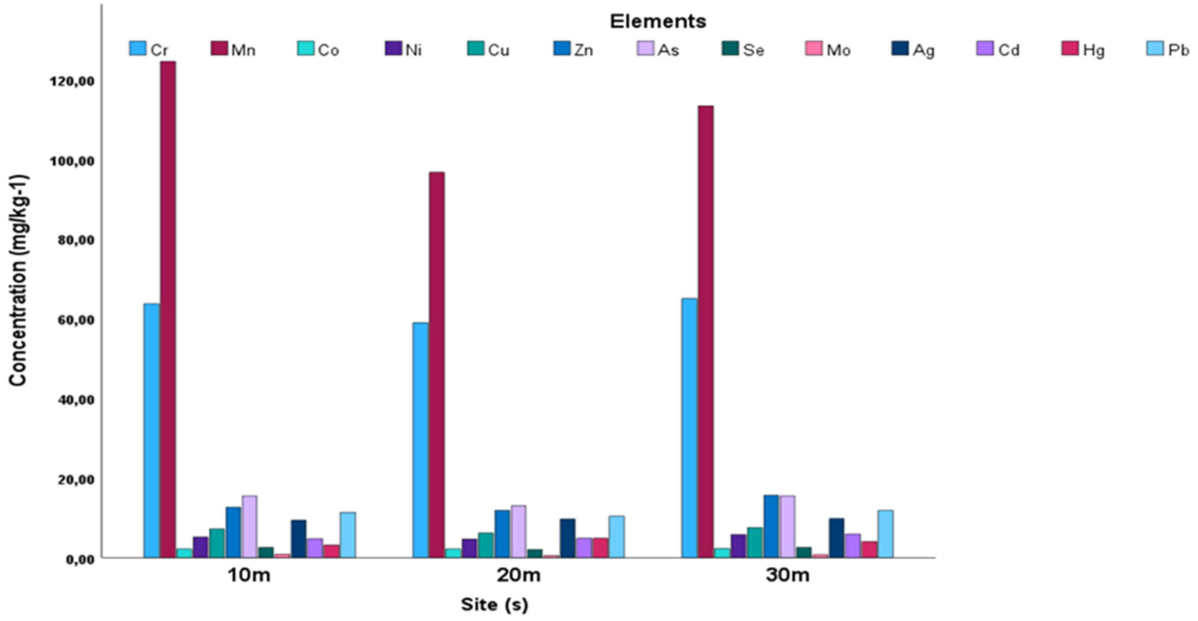

Figure 6. Heavy metal concentrations at different depths of Algoa Bay (10, 20 and 30 m).

the presence of calcium carbonate derived from biogenic sources such as shell fragments, which are common in Algoa Bay [62]. The elevated TiO_2 ranging from 1.1% to 3.9% may be attributed to the presence of accessory heavy minerals such as zircon and rutile [62].

3.3 Heavy metals concentration

The mean concentration of heavy metals measured at different depths (10, 20 and 30 m) for Algoa Bay in the marine coastal sediments are shown in Figure 6. The reported metal concentrations were generally greater than historically reported by Watling and Walting [21], whose data partially serves as baseline conditions, since it is not clear if subtidal sediments were collected at 30 m depth [21]. The concentration ranged from 0.8 to 124.5 mg/kg at 10 m depth contour, 0.5–96.7 mg/kg at 20 m depth contour and 0.7 mg/kg – Mn 113.3 mg/kg at 30 m depth contour. Higher concentrations were reported for Mn (124.5 mg/kg), As (15.5 mg/kg) and Mo (0.8 mg/kg) closer to shoreline at 10 m depth contour, while higher concentrations for Cr (65.0 mg/kg), Co (2.2 mg/kg), Ni (5.7 mg/kg), Cu (7.5 mg/kg), Zn (15.6 mg/kg), Se (2.5 mg/kg), Ag (9.7 mg/kg), Hg (4.0 mg/kg) and Pb (11.8 mg/kg) were reported in the deeper waters at 30 m depth contour. Lower concentrations were observed at 20 m depth contour.

High concentrations reported at A3, A4, A5 and A6 indicated the potential influence of Papenkuils River and Swartkops Estuary at A3, the influence of Port of Ngqura at A4, and the influence of Sunday Estuary mouth at A6. Based on the average concentrations, heavy metals in the 10 m contour were ranked in a descending order: Mn (124.5 mg/kg) > Cr (63.6 mg/kg) > As (15.5 mg/kg) > Zn (12.6 mg/kg) > Pb (11.4 mg/kg) > Ag (9.4 mg/kg) > Cu (7.1 mg/kg) > Ni (5.1 mg/kg) > Cd (4.8 mg/kg) > Hg (3.1 mg/kg) > Se (2.5 mg/kg) > Co (2.1 mg/kg) > Mo (0.8 mg/kg). Furthermore, the mean concentration of heavy metals in the 30 m depth contour were ranked in the descending order as follows: Mn (113.3 mg/kg) > Cr (65.0 mg/kg) > Zn (15.6 mg/kg) > As (15.5 mg/kg) > Pb (11.8 mg/kg) > Ag (9.7 mg/kg) > Cu (9.5 mg/kg) > Cd (5.8 mg/kg) > Ni (5.7 mg/kg) > Hg (4.0 mg/kg) > Se (2.5 mg/kg) > Co (2.2 mg/kg) > Mo (0.7 mg/kg).

Fe concentration analysed in this study was used as a normalising element for enrichment factor calculation. However, Fe concentration reported was greater at all depths as compared with other metals [i.e. 7616.48 mg/kg (10 m), 7818.32 mg/kg (20 m), 10011.43 mg/kg (30 m)]. Masikane [60] measured metals in sediments at 10 m depth contour in the western sector of Algoa Bay (King Beach to the mouth of Sundays River Estuary) in 2008 and found metals to be within the baseline concentrations except for a slight elevation of copper across the Papenkuils River [60]. The heavy metal concentrations reported for this study were higher than those reported by Masikane [60].

Table 8. Descriptive mean heavy metal concentrations, UCC values and sediment quality guidelines.

Country	Location	Method		Metal concentrations (mg/kg)													Reference
				Cr	Mn	Co	Ni	Cu	Zn	As	Se	Mo	Ag	Cd	Hg	Pb	
South Africa	Algoa Bay	XRF	10 m	63.8	124.5	2.1	5.1	7.1	12.6	15.5	2.5	0.8	9.4	4.8	3.1	11.4	Present study
			20 m	59.0	96.7	2.2	4.8	6.2	11.8	13.00	2.00	0.5	9.8	4.8	4.8	10.4	Present study
			30 m	65.0	113.3	2.2	5.7	7.5	15.6	15.5	2.5	0.7	9.7	5.8	4.0	11.8	Present study
Upper continental values (UCC-values) (mg/kg)				83.0	600.0	17.0	44.0	25.0	71.0	2.0	50.0	1.5	0.05	0.10	0.05	17.0	[44,45]
				Sediment quality guidelines (mg/kg)													
				Cr	Mn	Co	Ni	Cu	Zn	As	Se	Mo	Ag	Cd	Hg	Pb	
Threshold concentration (TEC)				43.4	–	–	22.7	31.6	121.0	9.79	–	–	–	0.99	0.18	35.80	[66]
Probable concentration (PEC)				111.0	–	–	48.6	149.0	459.0	33.0	–	–	–	4.98	1.06	128.0	[66]
Effect range low (ERL)				81.0	–	–	20.9	34.0	150.0	8.2	–	–	–	1.2	0.15	46.7	[40]
Effect range median (ERM)				370.0	–	–	51.6	270.0	410.0	70.0	–	–	–	9.6	0.71	218.0	[40]

The current study results indicated that at all depths, heavy metals, including Cr and As, were above the TEC (threshold concentration) but below the PEC (probable concentration), suggesting that biological impacts may occur in different organisms with varying sensitivity to heavy metals (Table 8). Hg (10, 20 and 30 m) and Cd (30 m) were above the PEC, indicating a possible negative biological impact on the marine system. The concentration of heavy metals such as Cr, Cu, Ni, Pb and Zn was below the ERL (effect range low) values in all depths, suggesting no harmful effect to aquatic biota due to the presence of these metals, whereas heavy metals such as Hg, As and Ag were above the ERM (effect range medium) in all depths, indicating harmful effects on the biological community. Cd at all depths was above ERL but below ERM indicating that biological impacts may occasionally occur.

The pollution of marine coastal sediments by heavy metals is due to anthropogenic activities [15,67,68]. When the mean values of the heavy metals were compared with the background reference values, the findings showed that As, Ag, Cd and Hg levels were higher than the UCC background values at all depths, suggesting the influence of anthropogenic activities. Walting and Walting [21] reported the elevation of cadmium (Cd) and mercury (Hg) concentration near the harbour in Algoa Bay. The elevated heavy metals (Cd and Hg) levels were detected in sediments collected from the mouth of Papenkuils River and Fish water flats sewer outfalls [21].

3.4 Pollution indices

3.4.1 Geo-accumulation (I_{geo})

The coastal sediments of Algoa Bay were assessed for contamination using the geo-accumulation index. The I_{geo} values were calculated for each heavy metal and were presented according to depths (10, 20 and 30 m) (Figure 7). Based on the classification system by Muller [43], sediments are uncontaminated by Cr, Mn, Co, Ni, Cu, Zn, Se, Mo and Pb ($I_{geo} < 0$) at all depths. However, the sediments were extremely contaminated by Ag, Hg and Cd ($I_{geo} > 5$) at all depths. The sediments were moderately to heavily contaminated by As ($2 \leq I_{geo} < 3$) at all depths. These results are consistent with some of the previous studies conducted on the South African coastline, particularly at the beaches, since there are very few published studies that have reported on subtidal marine sediment metals. For example, beach sediments of St. Lucia and Sodwana were heavily contaminated by Cr and Hg [24], meanwhile, beach sediments in the Richards Bay area were moderately to extremely contaminated by Cd [69]. Beach sediments south of Durban were moderately to extremely contaminated by Cr and Hg [25]. In False Bay, sediments were heavily to extremely contaminated by Hg ($4 \leq I_{geo} < 5$) and heavily contaminated by As and Cd ($3 \leq I_{geo} < 4$) [6].

3.4.2 Enrichment factor (EF)

Algoa Bay sediments showed very high enrichment ($20 < EF \leq 40$) by As, with closer to the shoreline sites (i.e. 10 m) at A4 and A5 showing extremely high enrichment ($EF \geq 40$) (Figure 8). Mo was significantly enriched ($5 < EF \leq 20$) in sites A6 (30 m), A8 (30 m), A9 (10 m) and A10 (10 m), and demonstrated very high enrichment ($20 < EF \leq 40$) to extremely high enrichment ($EF \geq 40$) at nearshore sites A4 and A5 (10 m). Ag was deficient in minimal enrichment ($EF \leq 2$) in closer to the shoreline sites (10 m) at A7 and A10, while showed significantly enriched ($5 < EF \leq 20$) in sites A3 (20 m), A4 (10 m), A6 (20 m) and A10 (10 m) and

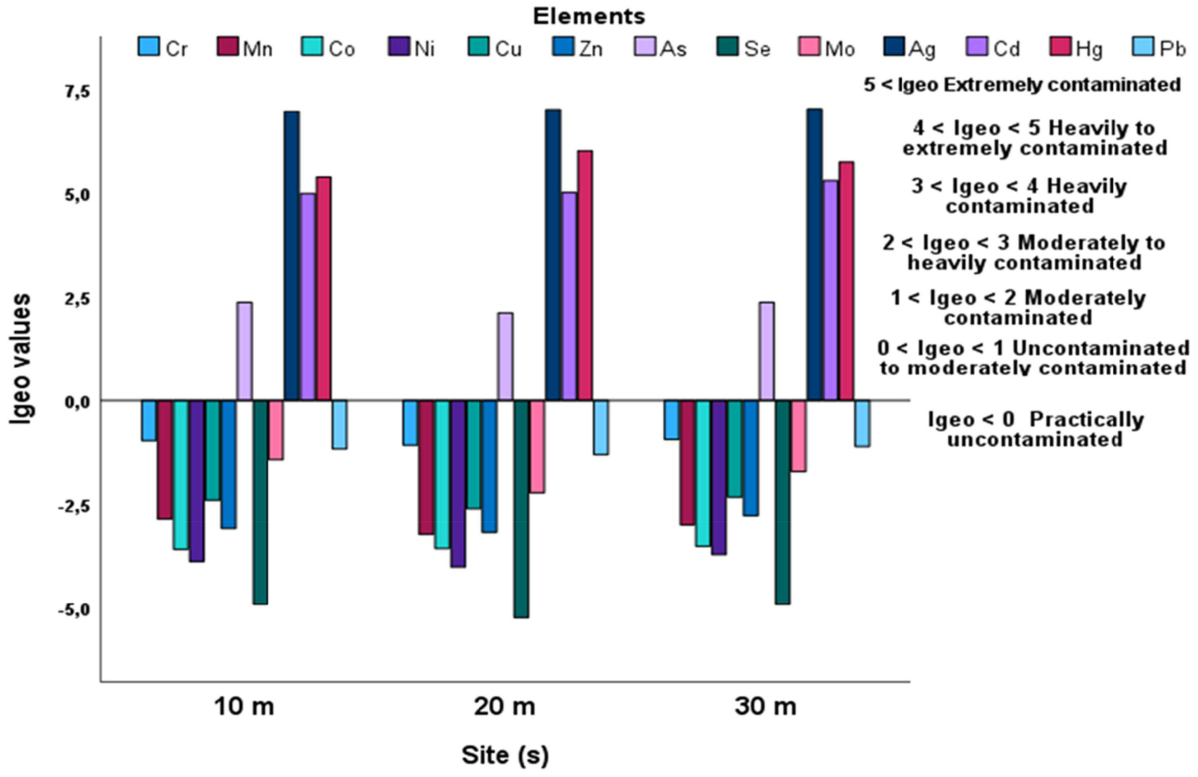

Figure 7. I_{geo} values at different depths of Algoa Bay (10, 20 and 30 m).

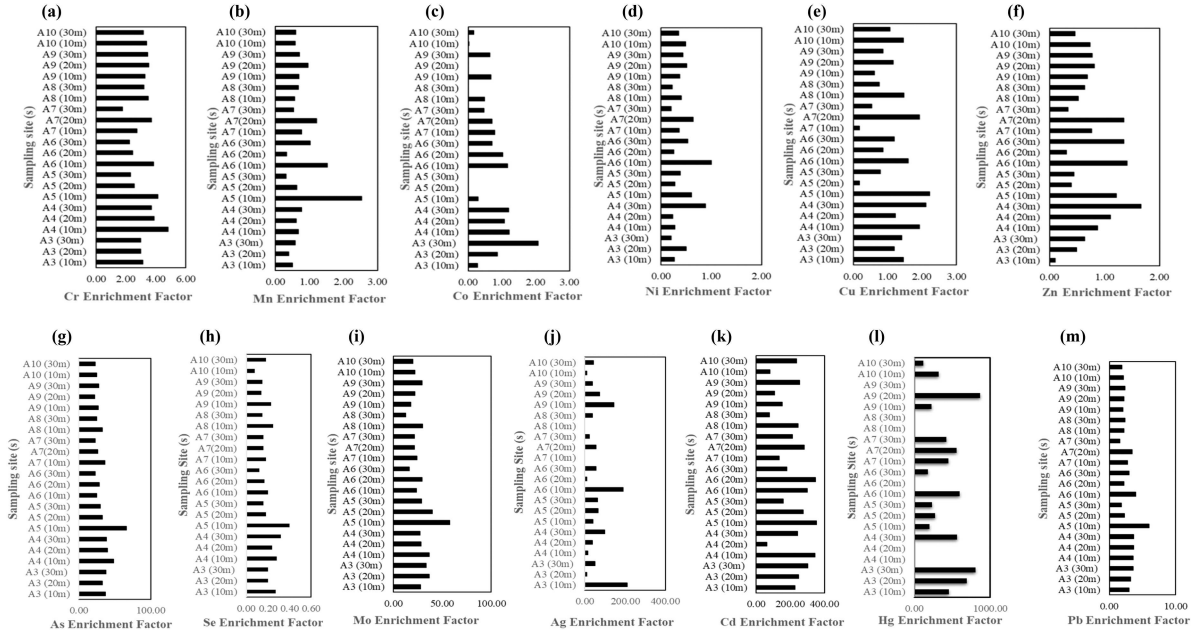

Figure 8. Enrichment factor heavy metals across Algoa Bay transects (a) Cr, (b) Mn, (c) Co, (d) Ni, (e) Cu, (f) Zn, (g) As, (h) Se, (i) Mo, (j) Ag, (k), Cd, (l) Hg and (m) Pb.

exhibited extremely high enrichment (EF ≥ 40) at A3, A4, A5, A6 and A10 deeper sites (i.e. 30 m). On the other hand, Cd was generally extremely high enriched (EF ≥ 40) across all sites, and Hg was also extremely high enriched (EF ≥ 40), except in A4 (10 and 20 m), A6 (20 m), A8 (10 and 30 m) and A9 (30 m). These results contrast with other previous studies conducted in the KwaZulu-Natal coastline (i.e. beach sediments of Durban North and Ballito were extremely severe enriched by Hg and Cd) [25].

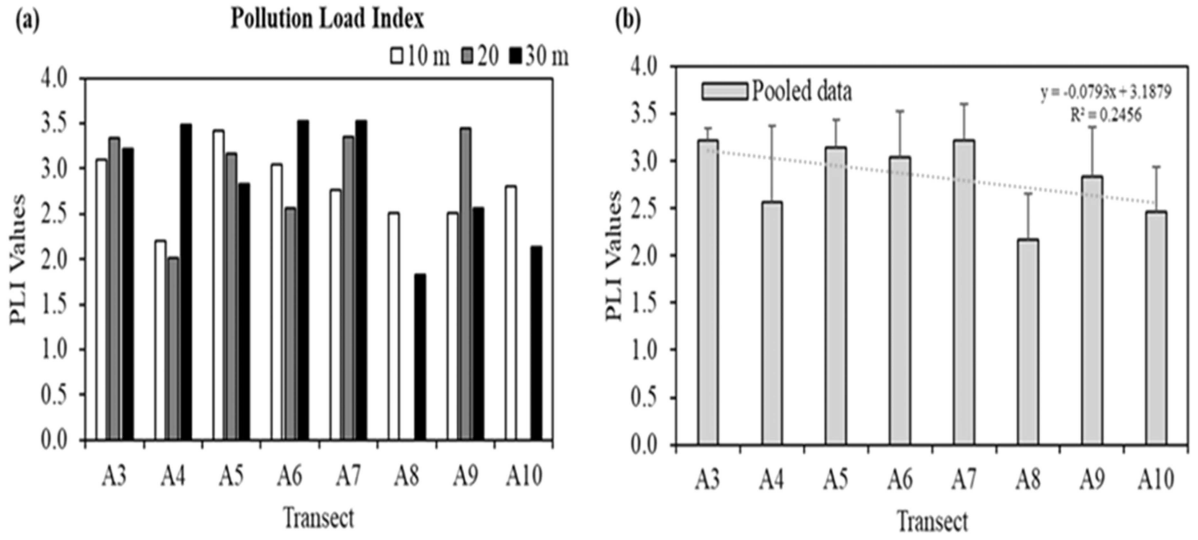

Figure 9. Pollution load across Algoa Bay shows no discernible pattern across transects and between depth contours. Data were pooled across depth for each transect, i.e. (a) PLI and (b) pooled data.

Sediments presented moderate (across sampling sites) to significant enrichment ($5 < EF \leq 20$) in Pb at site A5 (10 m), Cu at site A4 (30 m) and A5 (10 m), while Cr was moderately enriched ($2 < EF \leq 5$) across all the sampling sites. Mn, Se, Zn, Cu, Ni and Co were the only heavy metals that were generally deficiency to minimally enriched ($EF \leq 2$) across all the sampling sites, suggesting that these metals may be entirely from crustal materials or weathering processes. Newman and Watling [70] constructed a baseline metal concentration model in coastal sediments and the concentrations reported in their research were below the concentrations for this study. The cadmium baseline concentration was 0.322 µg/g [70].

3.4.3 Pollution load index (PLI)

Figure 9 shows the variation in the pollution load of each heavy metal across transects and between depth contours (10, 20 and 30 m). The sediments across the Algoa Bay sites were polluted by Ag, Hg, Cd, Mo and As, with pollution load ranging from 1.88 (A8, 30 m) to 3.52 (A6 and A7, 30 m). PLI showed no discernible pattern across transects except at A7 (i.e. PLI increased from 10 m to 30 m depth contour (i.e. PLI = 2.77 (10 m), PLI = 3.35 (20 m) and PLI = 3.52 (30 m)). In A5, the PLI decreases from closer to the shoreline (10 m) to deeper waters (30 m) (i.e. PLI = 3.42 (10 m), PLI = 3.16 (20 m) and PLI = 2.83 (30 m)) (Figure 10).

PLI is a valuable tool for identifying and managing sites with significant degradation, providing a perspective on pollution levels, and identifying areas of concern requiring management strategies [71]. Pooled PLI data revealed that the pollution load (PLI = 3.22) was greater at transect A3, which is located in the western corner of Algoa Bay, incorporating the large industrial city of Gqeberha (formerly Port Elizabeth), where the multipurpose port is located. However, the pollution load PLI (PLI = 2.17) was lower in transect A8, which is located across the eastern sector of Algoa Bay (Alexandria Dunefield). The general decrease in the pollution load from the western sector to the eastern corner corresponds with the longshore drift, which generally flows from south–west to north–east. Sediment transport from the western corner to the eastern corner also decreased drastically, decreasing from 400 $m^2 \times 10^3$ per annum from Cape Recife to 160 $m^3 \times 10^3$ per annum at A3 [61]. The higher PLI observed in transect A3 was likely due to the influence of the Papenkuils and Swatkops river estuary, which contribute a significant amount of heavy metals to the bay [72,73].

3.4.4 Potential ecological risk assessment (PERI)

The potential ecological risk assessment index (PERI) of the coastal sediments in Algoa Bay was assessed based on the potential toxic elements in all transects across three depths (10, 20 and 30 m). PERI may act as a tool to understand and control pollution [15]. The comprehensive PERI represents the sum of all potential ecological risk factors (E_r^i) of the heavy metals examined in this study. According to Hakanson (1980), the

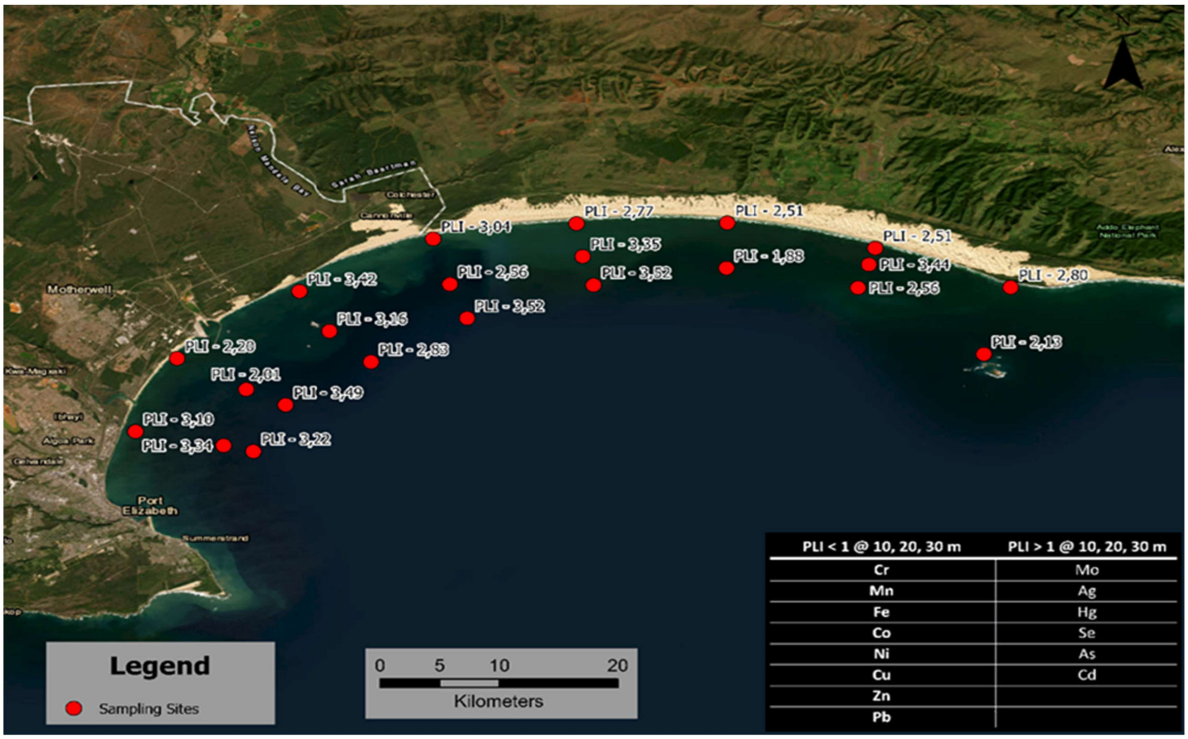

Figure 10. Evaluation of sediments contamination at different sampling sites of Algoa Bay with respect to the pollution load index (PLI).

ecological risk was low (E_r^i < 40) for heavy metals (i.e. Cr, Mn, Co, Ni, Cu, Zn and Pb), except for As with moderate ecological risk (40 ≤ E_r^i < 80). Cd and Hg exhibited significantly high ecological risk (E_r^i > 320). The potential ecological risk (E_r^i) in Algoa Bay decreased in the following order for all the sampling sites: Hg > Cd > As > Pb > Mo > Cr > Cu > Co > Ni > Mn > Zn.

The sum of PERI was calculated for each depth (10, 20 and 30 m) in Algoa Bay based on potential ecological risk factors associated with each heavy metal (Figure 11). PERI results suggested a significantly high risk (PERI > 600) at all depths (i.e. PERI = 4013 at 10 m, 5391 at 20 m and 5051 at 30 m depth). Cd and Hg were the main contributors to the significantly high ecological risk (PERI > 600). Similar findings align with results recorded for KwaZulu-Natal beach sediments [25,53,74]. For example, Cd and Hg contributed to the significantly high ecological risk of beach sediments in St. Lucia and Sodwana Bay [24]. However, the PERI obtained in Algoa Bay was lower than that recorded along the KwaZulu-Natal coastline. The difference attribute from industries activities along the KZN coast, which discharges directly or indirectly into nearby areas. In addition, fine particulate matter from these activities can be transported through wind-driven processes over time, further contributing to contamination [69]. The KZN coast is also characterised by several large rivers such as Tugela and Umngeni, which drain extensive agriculture, industrial zone and densely populated catchments [24].

The ecological risk factor for Hg was greater in St. Lucia and Sodwana Bay (South Africa) as compared to Algoa Bay, while Cd value had a lower ecological risk factor. In False Bay, Simon's town (South Africa), Cu contributed to a significantly high ecological risk (PERI > 600), while Cd contributed to a moderate ecological risk (150 ≤ PERI < 300), and Hg contributed to a low ecological risk (PERI < 150) [6].

3.5 Pearson correlation and principal component analysis

The results of the Pearson correlation analysis and their significance level are presented in Table 9. Mo was significantly (p < 0.05) correlated with Cr (r = 0.771), Mn (r = 0.921), Ni (r = 0.944) and Zn (r = 0.739). Zn was also positively correlated with Mn (r = 0.653), Ni (r = 0.826) and Cu (r = 0.650). Pb exhibited strong positively correlations with Mn (r = 0.912), Ni (r = 0.502), Cu (r = 0.838), Zn (r = 0.666), As (r = 0.807) and Ag (r = 0.657),

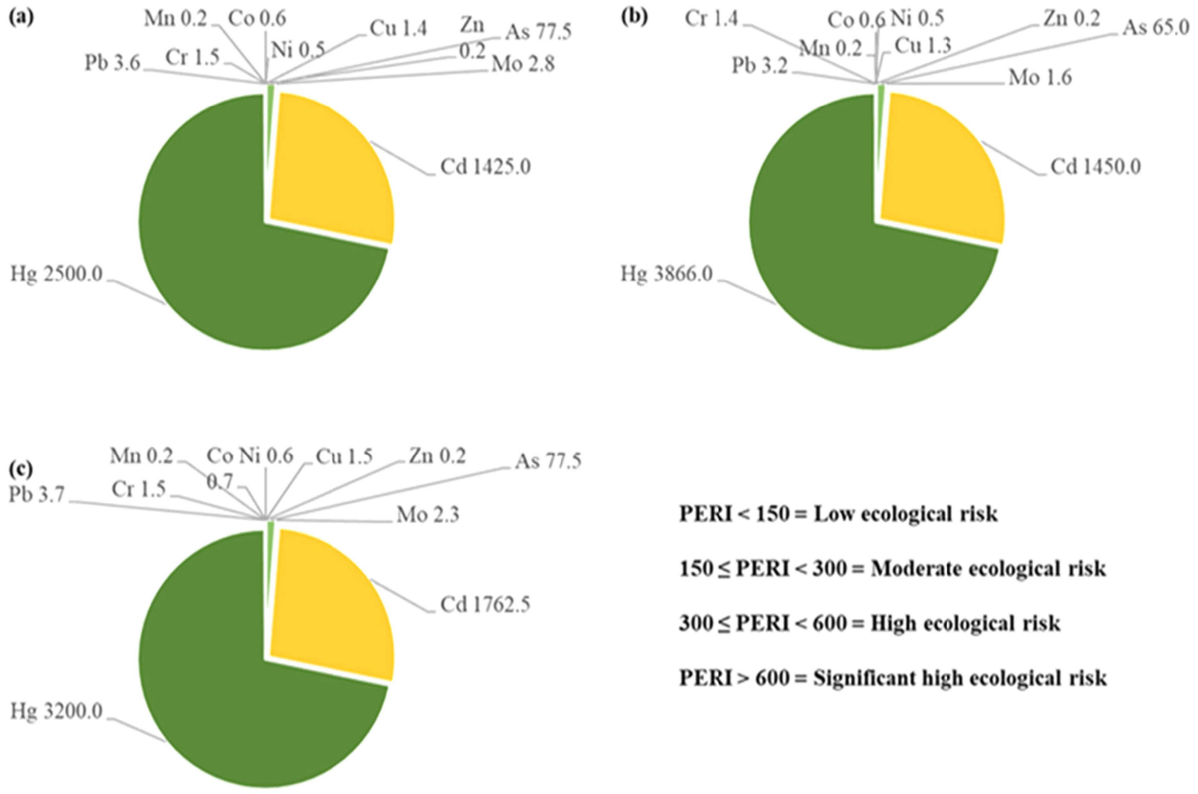

Figure 11. Potential ecological risk index (PERI) of sediments in Algoa Bay at (a) 10 m, (b) 20 m and (c) 30 m.

Table 9. Pearson correlation concentration of heavy metals.

Metals	Cr	Mn	Co	Ni	Cu	Zn	As	Se	Mo	Ag	Cd	Hg	Pb
Cr	1												
Mn	0.471*	1											
Co	−0.104	0.024	1										
Ni	0.493*	0.586**	0.387	1									
Cu	0.532*	0.498*	0.245	0.650**	1								
Zn	0.413	0.653**	0.456*	0.826**	0.650**	1							
As	0.020	0.465*	−0.070	0.058	0.290	0.141	1						
Se	0.222	0.365	0.069	0.235	0.378	0.192	0.777**	1					
Mo	0.771	0.921	−0.944	0.944	0.482	0.739	−0.896	−0.171	1				
Ag	−0.106	0.275	−0.214	−0.007	0.089	0.184	0.711**	0.465*	0.077	1			
Cd	0.072	0.253	0.255	0.213	0.258	0.033	0.357	.440*	0.027	0.584**	1		
Hg	0.048	0.182	−0.004	0.365	0.206	0.221	−0.092	0.034	0.012	0.724	0.024	1	
Pb	0.004	0.912**	−0.051	0.502	0.838*	0.666	0.807*	0.358	.[b]	0.657	0.462	0.464	1

The correlation is significant at the 0.05 level (2-tailed).
The correlation is significant at the 0.01 level (2-tailed).
[b] Cannot be computed because at least one of the variables is constant.

suggesting that these heavy metals originated from a common source and may have identical behaviour [70]. As was positively correlated with Se ($r = 0.777$). In contrast, Ag showed a weak negative correlation with Cr ($r = -0.106$), Ni ($r = -0.007$), Zn ($r = -0.184$) and Mo ($r = -0.077$), indicated these metals are likely originated from different sources. PCA extracted three components that accounted for 100% of the total variance in the relationship between the potential ecological risk and enrichment of each heavy metal at three depths (10, 20 and 30 m) (Figure 12). The findings of the Pearson correlation and PCA cluster analysis were consistence.

Cluster 1, located closer to the shoreline at the 10 m depth contour, showed a strong positive loading on Component 1 for several metals, including As (0.845), Se (0.813), Cr (0.774), Mn (0.819), Cu (0.782), Zn (0.645), Cd (0.901), Pb (0.935) and Mo (0.913). This pattern suggests a mixed inputs from both natural and anthropogenic sources. However, negative loadings were observed for PERI (−0.127), Ag (−0.073) and Hg (−0.271) indicating contamination of these metals and suggesting a likely common anthropogenic origin (most likely industrial sources or urban runoffs), as supported by enrichment factor analysis.

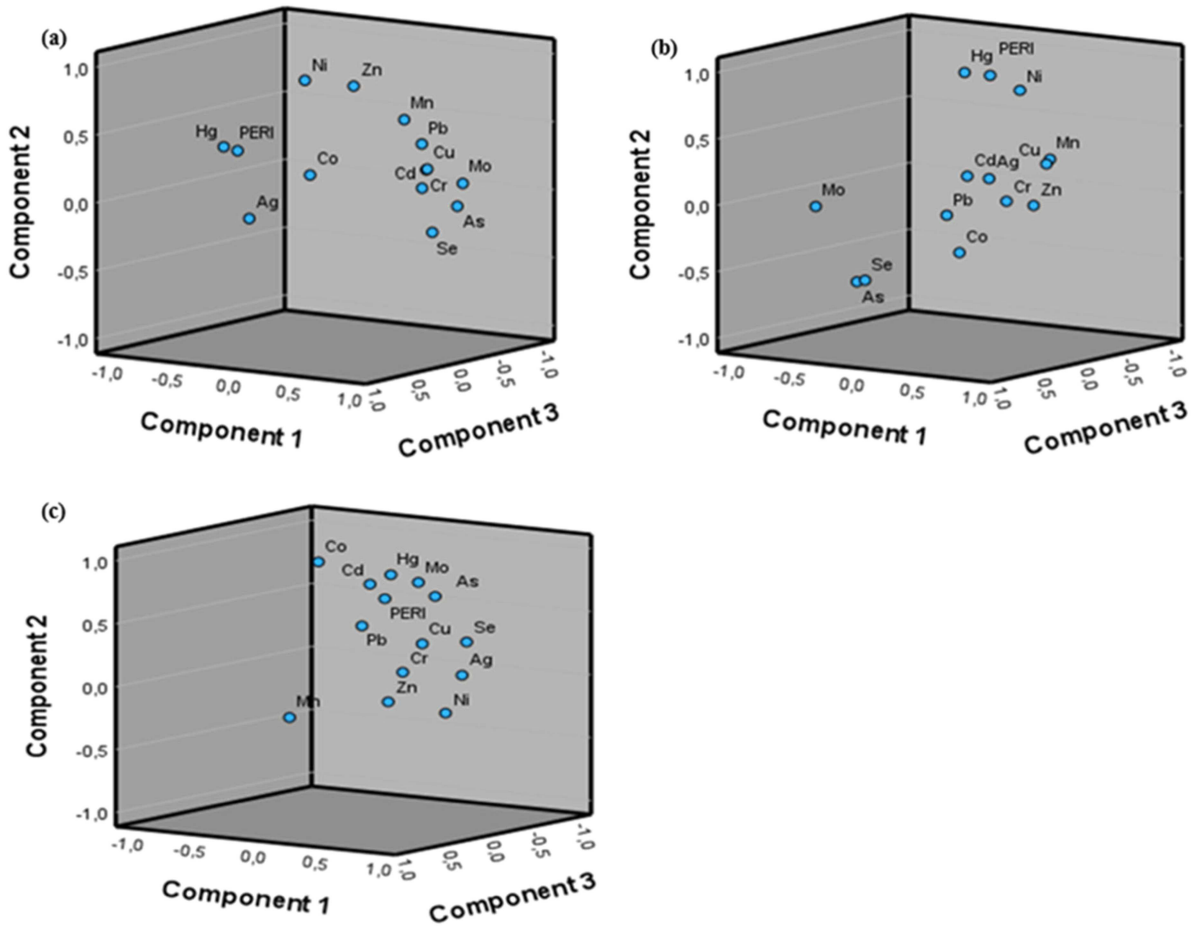

Figure 12. Representation of the principal component analysis (PCA) for PERI and heavy metals enrichment at (a) 10 m, (b) 20 m and (c) 30 m.

Component 3 presented strong negative loadings for PER (−0.265), Hg (−0.211), Ag (−0.031), Se (−0.260) and As (−0.323), suggesting that their presence is primary driven from anthropogenic activities, particularly industrial and urban effluents. Additionally, negative loadings of Mo (−0.307) and Mn (−0.257) in this component suggest mixed from both natural and human-related sources, such as manganese ore export, sewage effluents and catchment mineralization. Cr, Cd, Co, Zn, Cu and Ni displayed a positive loading, likely associated with road dust, vehicular emissions and runoffs.

Cluster 2 (20 m) and Cluster 3 (30 m) exhibited the same trend for PERI and observed metals, indicating comparable sources and transport pathways of metal enrichment. Overall, the PCA analysis results indicate that heavy metal distributions in the Algoa Bay are influenced by a combination of natural processes and anthropogenic activities, including industrial emissions and urban development.

3.6 Global comparison

The potential ecological risks index (PERI) for heavy metals in the marine coastal sediments of Algoa Bay (South Africa) were compared with other potential ecological risk assessments reported in the literature (Table 10). The sum of PERI in Algoa Bay was calculated in three depths, with Cd and Hg being the main contributors with significantly high ecological risk (PERI ≥ 600). This study is in agreement with the potential ecological risk in the sediments of the Red Sea (Egypt) with a significantly high ecological risk (PERI ≥ 600), with Cd being the main pollutant [68]. In contrast, the potential ecological risk in Limbe coastal ridges (Cameroon) was low (PERI < 150) for all pollutants [46]. In the Bay of Bengal Coast (Bangladesh), the

Table 10. Global comparison of potential ecological risk assessment index (PERI) and pollution load index (PLI) for marine sediments.

Location	Country	Method	Heavy metals	Ecological Risk Indices (PLI,PERI)	References
Sodwana Bay & St. Lucia	South Africa	ICPMS/OES	Fe, Mg, Cr, Mn, Co, Ni, Cu, Zn, Mo, Cd, Hg and Pb	PERI ≥ 600, significantly high ecological risk (Hg and Cd), 150 ≤ PERI < 300, moderate ecological risk (Cr).	[24]
Simons Town	South Africa	ICPMS/OES	Cr, Mn, Co, Ni, Zn, Cu, As, Se, Mo, Cd, Hg and Pb	PLI > 1, pollution(Co, Ni, Zn, Cu, As, Se, Mo, Cd, Hg, Pb), PERI ≥ 600, significantly high ecological risk (Cu),150 ≤ PERI < 300, moderate ecological risk (Cd), PERI < 150, low ecological risk (Hg)	[6]
Limbe Coastal Fringes	Cameroon	ICPMS/OES	Cr, Mn, Co, Ni, Cu, Zn and Cd	PERI < 150, low ecological risk	[76]
Red Sea	Egypt	ICPMS/OES	Mn, Co, Ni, Cu, Cd, Pb, Fe and Sr	PERI ≥ 600, significantly high ecological risk (Cd), PERI < 150, low ecological risk (Pb)	[68]
Black Sea Coast	Turkey	ICPMS/OES	Cr, Mn, Ni, Cu, As, Cd, Hg and Pb	150 ≤ PERI < 300, moderate ecological risk all metals	[15]
Bay of Bengal coast	Bangladesh	ICPMS/OES	As, Cr, Cd and Pb	PLI < 1 (geological origin) PLI > 1, pollution (As, Cr, Cd, Pb), PERI ≥ 600, significant high risk (Pb and Cr). 300 ≤ PERI > 600, high ecological risk (Cd).	[75]
Algoa Bay	South Africa	XRF	Cr,Mn,Co,Ni, Cu,Zn, As, Se, Ag, Mo Cd, Hg and Pb	PLI > 1, pollution (Hg, As, Se, Cd and Ag) PERI ≥ 600, significantly high ecological risk (Hg and Cd) (10, 20 and 30 m depth).	**Present study**

potential ecological risk was significantly high (PERI ≥ 600), with Cr and Pb being the main contributors [75]. The potential ecological risk in Black Sea Coast sediments (Turkey) was moderate (150 ≤ PERI < 300) [15].

Sediments across Algoa Bay sampling sites were anthropogenically polluted by Ag, Hg, Cd, Mo and As (PLI > 1), while False Bay sediments were polluted by Cr, Mn, Co, Ni, Zn, Cu, As, Se, Mo, Cd, Hg and Pb (PLI > 1) [6]. Bangladesh sediments were polluted by As, Cr, Cd and Pb through anthropogenic activities (PLI > 1) [75], while Black Sea Coast sediments were unpolluted by heavy metals [15].

4. Conclusion

Coastal heavy metal pollution, driven by increasing population and industrial activities, poses a significant environment and social challenges. This study assessed the spatial distribution and ecological risk of heavy metals in the nearshore sediments of Algoa Bay (i.e., depths ranging from 10 m to 30 m). Higher concentrations (i.e. Mn, As and Mo) were generally observed in both at shallow waters (10 m) and deeper waters (30 m), suggesting the potential for land drainage (e.g. estuarine and/or riverine discharges and port activities).

Certain metals particularly, As, Ag, Cd and Hg, exceeded background levels UCC suggesting the direct impact of anthropogenic activities. Hg (at all depths) and Cd (at 30 m depth) exceeded the probable effect concentration (PEC), indicating the potential ecological harm. As and Cr exceeded threshold effect concentration (TEC), suggesting biological effects, while other metals (e.g. Zn, Pb, Ag, Cu, Ni, Se, Co and Mo) remained below ecological risk thresholds, suggesting no harmful effects to aquatic biota.

This study further assessed contamination and/or pollution levels using various chemical-based indices. The evaluation of contamination assessments using geo-accumulation (I_{geo}) and EF (enrichment factor) revealed that the sediments were heavily to extremely contaminated and enriched, particularly with Hg, Cd and As. The accumulation of Hg and Cd, which is similar to other studies, suggests that their sources are anthropogenic. The pollution load index (PLI) suggested that pollution in the bay is widespread but has no discernible across-shore pattern. However, pooled data analysis revealed a general decrease in pollution from the western sector to the eastern sector.

The PERI demonstrated that the potential ecological risk ranged from low to significantly high, and this finding needs to be verified using faunal data, which are currently limited to the bay. Overall, the findings of this study highlighted the presence of heavy metals in Algoa Bay, with statistical analysis Pearson correlation and PCA showing correlation between metals and their potential sources. These results are valuable baseline data from which future studies (including long-term monitoring) can be based.

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Disclosure statement

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Sample availability

Marine sediment samples are available from the author.

References

[1] Truter HJ. Epibenthic biodiversity, habitat characterisation and anthropogenic pressure mapping of unconsolidated sediment habitats in Algoa Bay, South Africa. South Africa: University of Cape Town, South Africa; 2018.
[2] Ward D, Melbourne-Thomas J, Pecl GT, et al. Safeguarding marine life: conservation of biodiversity and ecosystems. Rev Fish Biol Fisheries. 2022;32(1):65–100. doi: 10.1007/s11160-022-09700-3
[3] Alkan N, Alkan A, Demirak A, et al. Metals/metalloid in marine sediments, bioaccumulating in macroalgae and a mussel. Soil Sedim Contam: Int J. 2020;29(5):569–594. doi: 10.1080/15320383.2020.1751061
[4] Yedjou CG, Patlolla AK, Sutton DJ. Heavy metals toxicity and the environment Paul B Tchounwou. Published in final edited form as: EXS. 2012;101:133–164. doi: 10.1007/978-3-7643-8340-4_6
[5] Kodat M, Tepe Y. A holistic approach to the assessment of heavy metal levels and associated risks in the coastal sediment of Giresun, southeast black sea. Heliyon. 2023;9(6):e16424. doi: 10.1016/j.heliyon.2023.e16424
[6] Sparks C, Awe A. Concentrations and risk assessment of metals and microplastics from antifouling paint particles in the coastal sediment of a marina in Simon's Town, South Africa. Environ Sci Pollut Res. 2022;29(40):59996–60011. doi: 10.1007/s11356-022-18890-z
[7] Xiao H, Shahab A, Li J, et al. Distribution, ecological risk assessment and source identification of heavy metals in surface sediments of Huixian Karst Wetland, China. Ecotoxicol Environ Safety. 2019;185:109700. doi: 10.1016/j.ecoenv.2019.109700
[8] Mohajane C, Manjoro M. Sediment-associated heavy metal contamination and potential ecological risk along an urban river in South Africa. Heliyon. 2022;8(12):e12499. doi: 10.1016/j.heliyon.2022.e12499
[9] Ramcharan, S. An assessment of the heavy metal concentrations in the water and sediment of the umgeni estuary, using visible and near-infrared reflectance spectroscopy, 2021.
[10] De Matos A, Fontes MPF, Da Costa L, et al. Mobility of heavy metals as related to soil chemical and mineralogical characteristics of Brazilian soils. Environ Pollut. 2001;111(3):429–435. doi: 10.1016/S0269-7491(00)00088-9
[11] Romano E, Magno MC, Bergamin L. Grain size data analysis of marine sediments, from sampling to measuring and classifying. A critical review. 2017;7(2):10–15. doi: 10.21014/acta_imeko.v7i2.537
[12] Magdoff F, Van Es H. Building soils for better crops. Sustain Agricult Network Beltsville. 2000; 4:24–25.
[13] Sukdeo P. A study of the natural and anthropogenic impacts on the sediment and water quality of the middle and lower Mvoti River System. South Africa: KwaZulu-Natal; 2010.
[14] Environmental F. Sediment transport and deposition. Fundam Environ Measure. 2014 Retrieved from http://www.fondriest.com/environmental-measurements/parameters/ hydrology/sediment-transport-deposition/
[15] Böke Özkoç H, Arıman S. Contamination and risk assessment of heavy metals in coastal sediments from the Mid-Black Sea, Turkey. Stochastic Environ Res Risk Assess. 2023;37(1):375–394. doi: 10.1007/s00477-022-02300-4
[16] El Zokm GM, Al-Mur BA, Okbah MA. Ecological risk indices for heavy metal pollution assessment in marine sediments of Jeddah Coast in the Red Sea. Int J Environ Anal Chem. 2022;102(16):4496–4517. doi: 10.1080/03067319.2020.1784888
[17] Tavakoly Sany SB, Hashim R, Rezayi M, et al. A review of strategies to monitor water and sediment quality for a sustainability assessment of marine environment. Environ Sci Pollut Res. 2014;21:813–833. doi: 10.1007/s11356-013-2217-5
[18] Khan M, Hasan M, Khan M, et al. Distribution of heavy metals in surface sediments of the Bay of Bengal Coast. J Toxicol. 2017;2017:1–7. doi: 10.1155/2017/9235764

[19] Ndhlovu A, Human LR, Adams JB, et al. Ecological risk assessment of metal pollutants in two agriculturally impacted estuaries. Mar Pollut Bull. 2023;195:115572. doi: 10.1016/j.marpolbul.2023.115572
[20] Cao Y, Wang R, Liu Y, et al. Improved calculations of heavy metal toxicity coefficients for evaluating potential ecological risk in sediments based on seven major Chinese water systems. Toxics. 2023;11(8):650. doi: 10.3390/toxics11080650
[21] Watling R, Watling H. Trace metal surveys in Mossel Bay, St Francis Bay and Algoa Bay South Africa. Water SA. 1983;9:57–65.
[22] Dorrington RA, Lombard AT, Bornman TG, et al. Working together for our oceans: a marine spatial plan for Algoa Bay, South Africa. SAJSc. 2018;114(3-4):1–6. doi: 10.17159/sajs.2018/a0247
[23] Truter H, Atkinson L, von der Meden C, et al. Characterising epibenthic diversity and physical drivers in unconsolidated marine habitats of Algoa Bay, South Africa. Afr J Mar Sci. 2022;44(1):69–81. doi: 10.2989/1814232X.2022.2036234
[24] Vetrimurugan E, Shruti V, Jonathan M, et al. Metals and their ecological impact on beach sediments near the marine protected sites of Sodwana Bay and St. Lucia, South Africa. Mar Pollut Bull. 2018;127:568–575. doi: 10.1016/j.marpolbul.2017.12.044
[25] Vetrimurugan E, Shruti V, Jonathan M, et al. Comprehensive study on metal contents and their ecological risks in beach sediments of KwaZulu-Natal province, South Africa. Mar Pollut Bull. 2019;149:110555. doi: 10.1016/j.marpolbul.2019.110555
[26] Varol M, Ustaoğlu F, Tokatlı C. Ecological risk assessment of metals in sediments from three stagnant water bodies in Northern Turkey. Curr Pollut Rep. 2022;8(4):409–421. doi: 10.1007/s40726-022-00239-2
[27] Krampah F, Nyarko SY, Danlogo K, et al. Application of pollution indices in the assessment of heavy metal contamination of surface sediments of river Bonsa, Ghana. J Geosci Environ Protect. 2019;7(02):176–189. doi: 10.4236/gep.2019.72012
[28] Harikrishnan N, Ravisankar R, Chandrasekaran A, et al. Assessment of heavy metal contamination in marine sediments of east coast of Tamil Nadu affected by different pollution sources. Mar Pollut Bull. 2017;121(1-2):418–424. doi: 10.1016/j.marpolbul.2017.05.047
[29] Ogasawara M, Mikoshiba M, Geshi N, et al. Optimization of analytical conditions for major element analysis of geological samples with XRF using glass beads. Bull Geol Surv Jpn. 2018;69(2):91–103. doi: 10.9795/bullgsj.69.91
[30] Schoeman RP, Erbe C., Plön S. Underwater chatter for the win: a first assessment of underwater soundscapes in two bays along the Eastern Cape Coast of South Africa. J Mar Sci Eng. 2022;10(6):746. doi: 10.3390/jmse10060746
[31] Sverchkov I, Gembitskaya I, Povarov V, et al. Method of reference samples preparation for X-ray fluorescence analysis. Talanta. 2023;252:123820. doi: 10.1016/j.talanta.2022.123820
[32] Qiu Z, Tao C, Ma W, et al. Material source of sediments from west Clarion–Clipperton zone (Pacific): evidence from Rare earth element geochemistry and clay minerals compositions. J Mar Sci Eng. 2022;10(8):1052. doi: 10.3390/jmse10081052
[33] Bamanga, A. An investigation of heavy metal sediments geochemistry in lagos harbour. Nigeria: University of Portsmouth; 2019.
[34] Zhang D-P, Xue D-S, Liu Y-H, et al. Comparative study of three mixing methods in fusion technique for determining major and minor elements using wavelength dispersive X-ray fluorescence spectroscopy. Sensors. 2020;20(18):5325. doi: 10.3390/s20185325
[35] Buscaroli A, Zannoni D, Dinelli E. Spatial distribution of elements in near surface sediments as a consequence of sediment origin and anthropogenic activities in a coastal area in northern Italy. Catena. 2021;196:104842. doi: 10.1016/j.catena.2020.104842
[36] Franzini M, Leoni L, Saitta M. A simple method to evaluate the matrix effects in X-ray fluorescence analysis. X-ray Spectrom. 1972;1(4):151–154. doi: 10.1002/xrs.1300010406
[37] Leoni L. X-ray fluorescence analysis of 29 trace elements in rock and mineral standards. Rend Soc It Mineral Petrol. 1976;32:497–510.
[38] Zambello FR, Enzweiler J. Multi-element analysis of soils and sediments by wavelength-dispersive X-ray fluorescence spectrometry. J Soils Sediments. 2002;2:29–36. doi: 10.1007/BF02991248
[39] Jochum KP, Weis U, Schwager B, et al. Reference values following ISO guidelines for frequently requested rock reference materials. Geostand Geoanal Res. 2016;40(3):333–350. doi: 10.1111/j.1751-908X.2015.00392.x
[40] Long ER, Macdonald DD, Smith SL, et al. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ Manage. 1995;19:81–97. doi: 10.1007/BF02472006
[41] Yozukmaz A, Yabanlı M. Heavy metal contamination and potential ecological risk assessment in sediments of Lake Bafa (Turkey). Sustainability. 2023;15(13):9969. doi: 10.3390/su15139969
[42] Vaezi A, Lak R. Sediment texture, geochemical variation, and ecological risk assessment of major elements and trace metals in the sediments of the Northeast Persian Gulf. Mine. 2023;13(7):850. doi: 10.3390/min13070850
[43] Müller L. Fundamentals of rock mechanics (Vol. 8), Vienna: Springer; 1969.
[44] Taylor SR, & McLennan SM. The continental crust: its composition and evolution. 1985.
[45] McLennan SM. Relationships between the trace element composition of sedimentary rocks and upper continental crust. Geochem Geophys Geosyst. 2001;2(4). doi: 10.1029/2000GC000109

[46] Ferreira SL, da Silva Jr. JB, dos Santos IF, et al. Use of pollution indices and ecological risk in the assessment of contamination from chemical elements in soils and sediments – Practical aspects. Trends in Environmental Analytical Chemistry. 2022;35:e00169. doi: 10.1016/j.teac.2022.e00169
[47] Adeyinka GC, Bakare BF, Iwarere SA. Evaluation and risk assessment of heavy metals in surface water collected along the Isipingo River, KwaZulu-Natal, South Africa. Int J Environ Anal Chem. 2023;103(17):6045–6061. doi: 10.1080/03067319.2021.1947265
[48] Vaezi A, Karbassi A, Fakhraee M. Assessing the trace metal pollution in the sediments of Mahshahr Bay, Persian Gulf, via a novel pollution index. Environ Monit Assess. 2015;187:1–12. doi: 10.1007/s10661-015-4833-7
[49] Kumar V, Pandita S, Setia R. A meta-analysis of potential ecological risk evaluation of heavy metals in sediments and soils. Gondwana Res. 2022;103:487–501. doi: 10.1016/j.gr.2021.10.028
[50] Hakanson L. An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res. 1980;14(8):975–1001. doi: 10.1016/0043-1354(80)90143-8
[51] Addo-Bediako A, Nukeri S, Kekana M. Heavy metal and metalloid contamination in the sediments of the Spekboom River, South Africa. ApWS. 2021;11(7):133. doi: 10.1007/s13201-021-01464-8
[52] Al-Mutairi KA, Yap CK. A review of heavy metals in coastal surface sediments from the Red Sea: health-ecological risk assessments. Int J Environ Res Public Health. 2021;18(6):2798. doi: 10.3390/ijerph18062798
[53] Yang G, Song Z, Sun X, et al. Heavy metals of sediment cores in Dachan Bay and their responses to human activities. Mar Pollut Bull. 2020;150:110764. doi: 10.1016/j.marpolbul.2019.110764
[54] Tholkappian M, Ravisankar R, Chandrasekaran A, et al. Assessing heavy metal toxicity in sediments of Chennai Coast of Tamil Nadu using energy dispersive x-ray fluorescence spectroscopy (EDXRF) with statistical approach. Toxicol Rep. 2018;5:173–182. doi: 10.1016/j.toxrep.2017.12.020
[55] Zhuang W, Zhou F. Distribution, source and pollution assessment of heavy metals in the surface sediments of the Yangtze River Estuary and its adjacent East China Sea. Mar Pollut Bull. 2021;164:112002. doi: 10.1016/j.marpolbul.2021.112002
[56] Schumann E, Churchill J, Zaayman H. Oceanic variability in the western sector of Algoa Bay, South Africa. Afr J Mar Sci. 2005;27(1):65–80. doi: 10.2989/18142320509504069
[57] Edworthy C, Potts W, Dupont S, et al. A baseline assessment of coastal pH variability in a temperate South African embayment: implications for biological ocean acidification research. Afr J Mar Sci. 2022;44(4):367–381. doi: 10.2989/1814232X.2022.2147999
[58] McLachlan A, Cockcroft A, Malan D. Benthic faunal response to a high energy gradient. Mar Ecol Prog Ser. Oldendorf. 1984;16(1):51–63. doi: 10.3354/meps016051
[59] Truter, H. Epibenthic biodiversity, habitat characterisation and anthropogenic pressure mapping of unconsolidated sediment habitats in Algoa Bay. South Africa: University of Cape Town; 2018.
[60] Masikane, NF. Nearshore subtidal soft-bottom macrozoobenthic community structure in the western sector of Algoa Bay. South Africa; 2011.
[61] Goschen WS, Schumann EH. The physical oceanographic processes of Algoa Bay, with emphasis on the western coastal region. South African Environmental Observation Network (SAEON) and the Institute of Maritime Technology (IMT). IMT Document Number PO106-10000-730002. 2011;1–84.
[62] Maliwa, X. Seafloor sediments and grain size analysis of the Algoa Bay and St Francis Bay in the Eastern Cape Province of South Africa. University of Fort Hare; 2016.
[63] Ali AR, Ali AM. Geochemistry of major and trace elements in stream sediments as a conservative mixture of source regions, observations from the Balakian River, Northern Iraq. Iraqi Geol J. 2023;1–12. doi: 10.46717/igj.56.1C.1ms-2023-3-12
[64] Temgo Sopie F, Ngueutchoua G, Armstrong-Altrin JS, et al. Provenance, weathering, and tectonic setting of the Yoyo, Kribi, and Campo beach sediments in the southern Gulf of Guinea, SW Cameroon. J Earth Syst Sci. 2023;132(2):92. doi: 10.1007/s12040-023-02101-5
[65] Turekian KK, Wedepohl KH. Distribution of the elements in some major units of the earth's crust. Geol Soc Am Bull. 1961;72(2):175–192. doi: 10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2
[66] MacDonald DD, Ingersoll C, Berger T. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch Environ Contam Toxicol. 2000;39(1):20–31. doi: 10.1007/s002440010075
[67] Al-Hashim MH, El-Sorogy AS, Qaisi SAl, et al. Contamination and ecological risk of heavy metals in Al-Uqair coastal sediments, Saudi Arabia. Mar Pollut Bull. 2021;171:112748. doi: 10.1016/j.marpolbul.2021.112748
[68] Al-Kahtany K, Nour HE, El-Sorogy AS, et al. Ecological and health risk assessment of heavy metals contamination in mangrove sediments, Red Sea coast. Mar Pollut Bull. 2023;192:115000. doi: 10.1016/j.marpolbul.2023.115000
[69] Vetrimurugan E, Jonathan M, Roy PD, et al. Bioavailable metals in tourist beaches of Richards Bay, Kwazulu-Natal, South Africa. Mar Pollut Bull. 2016;105(1):430–436. doi: 10.1016/j.marpolbul.2016.01.045
[70] Newman BK, Watling RJ. Definition of baseline metal concentrations for assessing metal enrichment of sediment from the south-eastern Cape coastline of South Africa. Water SA. 2007;33(5). doi: 10.4314/wsa.v33i5.184089
[71] Hasan MR, Anisuzzaman M, Choudhury TR, et al. Vertical distribution, contamination status and ecological risk assessment of heavy metals in core sediments from a mangrove-dominated tropical river. Mar Pollut Bull. 2023;189:114804. doi: 10.1016/j.marpolbul.2023.114804

[72] Watling R, Emmerson W. A preliminary pollution survey of the Papenkuils River, Port Elizabeth. Water SA. 1981;7(4):211–215.
[73] Ndhlovu A, Adams JB, Nel M, et al. A review of metal pollution in a transformed, urban South African Estuary. Region Stud Mar Sci. 2024;76:103588. doi: 10.1016/j.rsma.2024.103588
[74] Tian K, Wu Q, Liu P, et al. Ecological risk assessment of heavy metals in sediments and water from the coastal areas of the Bohai Sea and the Yellow Sea. Environ Int. 2020;136:105512. doi: 10.1016/j.envint.2020.105512
[75] Ali MM, Islam MS, Islam ARMT, et al. Toxic metal pollution and ecological risk assessment in water and sediment at ship breaking sites in the Bay of Bengal Coast, Bangladesh. Mar Pollut Bull. 2022;175:113274. doi: 10.1016/j.marpolbul.2021.113274
[76] Ekoa Bessa, AZ, Ngueutchoua, G, Kwewouo Janpou A, et al. Heavy metal contamination and its ecological risks in the beach sediments along the Atlantic Ocean (Limbe coastal fringes, Cameroon). ESE. 2021;5:433–444. doi: 10.1007/s41748-020-00167-5