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Ecological-Health Hazards and Multivariate Assessment of Contamination Sources of Potentially Toxic Elements from Al-Lith Coastal Sediments, Saudi Arabia

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Abstract: To assess contamination levels, sources, and ecological health risks of potentially toxic elements (PTEs) in the sediments of Al Lith on the Saudi Red Sea coast, 25 samples were collected and analyzed for Zn, V, Cr, Cu, Ni, As, Pb, and Fe using ICP-AES. The average concentrations of PTEs ($\mu g/g$) were found in the following order: Fe (14259) > V (28.30) > Zn (22.74) > Cr (16.81) > Cu (12.41) > Ni (10.63) > As (2.66) > Pb (2.46). Contamination indices indicated that Al Lith sediments exhibited either no or minimal enrichment of PTEs, with concentrations below the low effects range. This suggests that the primary source of these PTEs is the minerals associated to basement rocks of the Arabian Shield (sphalerite, vanadiferous magnetite, chromite, pentlandite, arsenopyrite, galena) and that they are unlikely to pose a substantial risk to benthic communities. The hazard index (HI) values for PTEs in both adults and children were below 1.0, indicating no significant non-carcinogenic risk. Lifetime cancer risk (LCR) values for Pb, As, and Cr in both adults and children were within acceptable or tolerable levels, posing no significant health threats. However, a few samples showed LCR values exceeding 1×10^{-4}, indicating potential risks.

Keywords: potentially toxic elements; hazard index; lead; arsenic; chromium; lifetime cancer risk

1. Introduction

Coastal ecosystems provide ideal settings for a variety of activities, including recreational tourism and numerous economic pursuits. However, these ecosystems are highly fragile and extremely vulnerable to human activities, as well as sea-level rise and climate change [1, 3]. Rapid economic expansion in coastal areas, including construction operations and industrial development, releases millions of tons of pollutants, including potentially toxic elements (PTEs), which become significant environmental stressors affecting water quality and marine organisms [4-7]. Potentially toxic elements can enter aquatic environments through weathering of nearby rocks via flooding and atmospheric deposition; industrial effluents; accidental oil spills; the use of fertilizers and pesticides in agriculture; and mining operations [8-11]. PTEs can accumulate in marine sediments or be released directly into the water column, where they can be absorbed by marine organisms. This absorption creates a pathway for PTEs to move up the food chain, posing potential threats to marine life and human health [12-15].

Potentially toxic elements are known for their persistence in the environment and their strong potential to bioaccumulate in aquatic organisms and human tissues. Consuming contaminated seafood, such as fish, crustaceans, and mollusks, is the main pathway for PTE exposure in human populations. Elements like Hg, Pb, As, Cd, and Cu can cause various health issues, including mental disorders, effects on blood constituents, brain and nerve disorders, dermal lesions, reproductive and endocrine system defects, and damage to the lungs, liver, kidneys, and other vital organs [15, 17-19]. Several studies have monitored PTEs in sediments, seawater, and marine organisms along the Red

Sea coast [e.g., 20-26]. These studies have identified significant enrichments of As, Cu, Cd, and Cr. However, no previous studies have addressed PTEs in the coastal sediments of Al Lith. Thus, the objectives of this study are to: (i) measure the concentrations of Fe, As, Ni, V, Zn, Cr, Pb, and Cu in the sediments of Al Lith on the Red Sea coast, Saudi Arabia; (ii) compare these PTE levels to those in coastal sediments worldwide and across various environmental contexts; and (iii) assess the potential ecological-health risks associated with these PTEs in the sampled sediments.

2. Materials and Methods

2.1. Study Area and PTEs Analysis

Al Lith City is located 180-200 kilometers south of Jeddah along the Red Sea coast. Geologically, the eastern part of the Al Lith area is covered by the basement rocks of the Arabian Shield, running parallel to the Red Sea [27, 28]. The western part consists of a coastal plain covered by Quaternary sand, gravel, and silt deposits. The beach sediments comprise fine to very coarse sands mixed with shallow marine biogenic materials, such as corals, mollusks, echinoids, and seagrass, transported by waves and currents [26, 29].

Twenty-five sediment samples were collected from the top 10 cm of the intertidal zone along the Al Lith shoreline (Fig. 1). Sample coordinates were recorded using a GPS device and stored in plastic bags. All samples were rinsed with distilled water to remove soluble salts, dried at 100°C, and grain size was assessed using a set of sieves. Fe, As, Ni, V, Zn, Cr, Pb, and Cu were analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES) at the ALS Geochemistry Lab in Jeddah, Saudi Arabia. A 0.50 g portion of the 63 μm fraction was digested with aqua regia (a mixture of one-part nitric acid and three parts hydrochloric acid) for 45 minutes on a hot plate with sand, at temperatures ranging from 60 to 120°C [5, 30]. The ICP-AES analysis covered a range of 0.01-50% for Fe, 2.00-10,000 μg/g for As, Zn, and Pb, and 1.00-10,000 μg/g for Ni, V, Cr, and Cu, encompassing both lower and upper limits. Validation of the ICP-AES technique included assessments of linearity, limits of detection (LODs), and limits of quantification (LOQs). Precision was confirmed by analyzing three samples in duplicate, demonstrating excellent precision with relative standard deviations (RSD%) consistently below 13.5% [31].
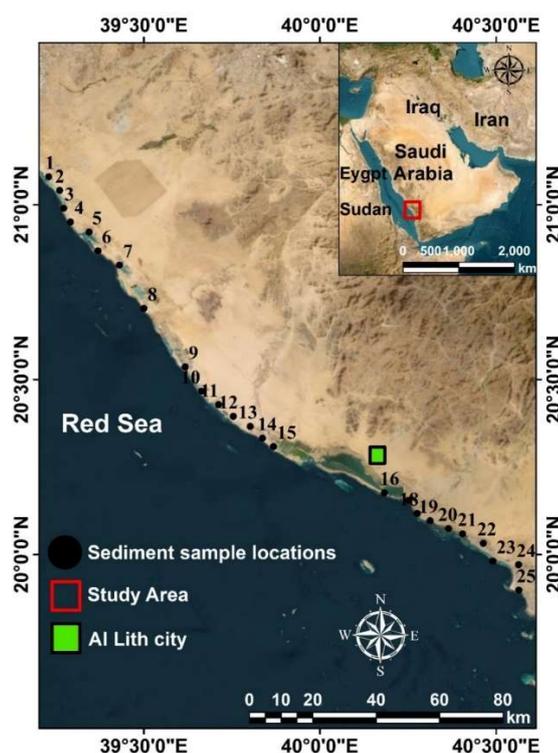

Figure 1. Sampling sites along Al Lith coastline.

2.2. Assessment of the PTEs

Various single and integrated contamination indices were employed in this study to evaluate the contamination levels and ecological risks of PTEs. These indices include the enrichment factor (EF), geoaccumulation index (Igeo), contamination factor (CF), potential ecological risk index (RI), and pollution load index (PLI). Equations (1) to (6) and Tables S.1 and S.2 detail the calculation procedures and classification of these contamination indices, as well as the parameters used in this research [32-34].

$$EF = (M/X)_{sample} / (M/X)_{background} \tag{1}$$

$$I\text{-geo} = Log_2 (Cn/ (1.5 \times Bn)) \tag{2}$$

$$CF = C_o / C_b \tag{3}$$

$$PLI = (CF_1 \times CF_2 \times CF_3 \times CF_4 \dots \times CF_n)^{1/n} \tag{4}$$

$$Er^i = Tr^i \times Cf^i \tag{5}$$

$$RI = \Sigma (Tr^i \times Cf^i) \tag{6}$$

To evaluate health risks for both adults and children through ingestion and dermal contact, various indices were utilized. These indices include chronic daily intake (CDI), hazard quotients (HQ), hazard index (HI), cancer risk (CR), and total lifetime cancer risk (LCR). Formulas (7) to (12) and Tables S.3 and S.4 describe the calculation methods for these indices and the exposure factors used to estimate CDI for non-carcinogenic risk [35-39].

$$CDI_{ing} = (Csediment \times IngR \times EF \times ED)/ (BW \times AT) \times CF \tag{7}$$

$$CDI_{derm} = (Csediment \times SA \times AFsediment \times ABS \times EF \times ED)/ (BW \times AT) \times CF \tag{8}$$

$$HQ = CDI/RfD \tag{9}$$

$$HI = \Sigma HQ = HQ_{ing} + HQ_{derm} \tag{10}$$

$$Cancer\ risk = CDI \times CSF \tag{11}$$

$$LCR = \Sigma Cancer\ Risk = Cancer\ risk_{ing} + Cancer\ risk_{derm} \tag{12}$$

The absence of an RfDderm value for Fe in Table S.4 may be due to inconsistencies among published data or a lack of reliable traceability to the original study for the reference value. Additionally, the impact of Pb on humans through dermal contact remains uncertain; therefore, CSF values for dermal contact with Pb are rarely referenced [38].

3. Results

3.1. Concentration and Ecological Assessment of PTEs

The grain size analysis of the studied coastline sediments showed a dominance of fine to very coarse sands (87.92%), along with mud (9.05%) and gravels (3.03%). The average concentrations of the investigated potentially toxic elements (PTEs) in the 25 surface sediment samples (dry weight) were as follows: Fe (14259 μg/g), V (28.30 μg/g), Zn (22.74 μg/g), Cr (16.81 μg/g), Cu (12.41 μg/g), Ni (10.63 μg/g), As (2.66 μg/g), and Pb (2.46 μg/g). Table S.5 presents the PTE concentrations across the study area, indicating that the highest levels were found in sample S21 (for Fe, As, Ni, V, Zn, Cr, Pb, and Cu), while the lowest levels were in sample S8 (for the same elements). Overall, PTE concentrations varied throughout the study area without a clear pattern. However, Figure 2 shows a significant increase in PTE levels in samples 16-21, collected at the mouth of Wadi Al-Lith. This

suggests that the coastal sediments and associated PTEs might have originated from the igneous and metamorphic rocks of the Arabian Shield.
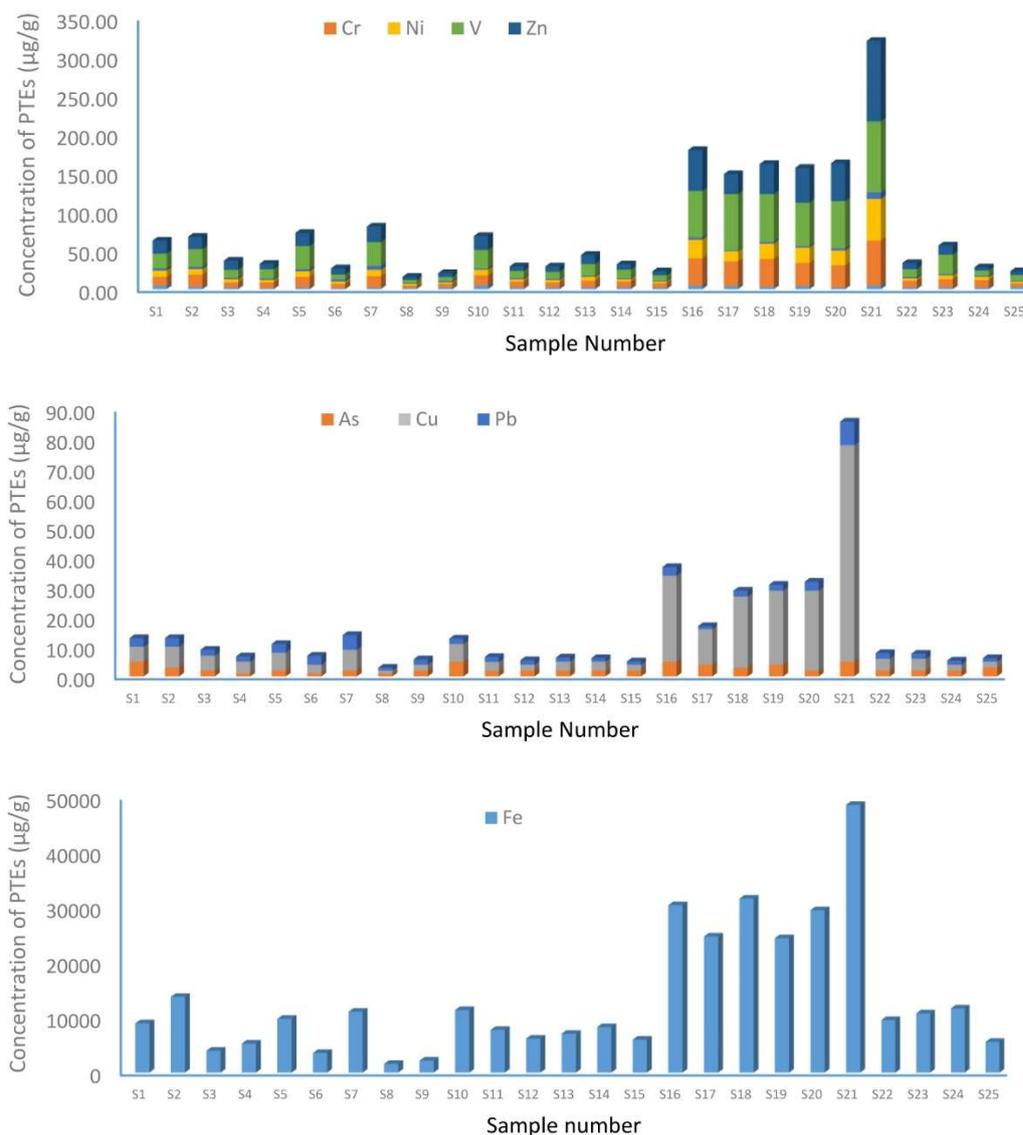

Figure 2. Distribution of PTEs in Al Lith coastal sediments.

The average Fe value was higher than those listed in Table 1, except for the background references [40, 41]. The average Cr value exceeded those reported for Ras Abu Ali, Aqeer, and Al-Jubail - Al-Khafji coastlines along the Arabian Gulf [5, 42, 43]. Furthermore, the average As value was greater than those from Al-Khobar, Saudi Arabia [44], and the background continental crust [41]. On the other hand, the average levels of Zn and Cu were generally lower than the reported values in the table, except for those found along the Red Sea coast in Egypt [45], Ras Abu Ali, Arabian Gulf [42], Aqeer coastline, Arabian Gulf [43], and Al-Jubail - Al-Khafji, Arabian Gulf [5].

Table 1. Comparison between PTEs in the study area and other coastal sediments, background references, and sediment quality guidelines.

References	V	Fe	As	Zn	Cu	Pb	Ni	Cr
present study	28.30	14259	2.66	22.74	12.41	2.46	10.63	16.81
[5]	7.22	5197	2.38	6.18	2.44	2.57	11.76	8.68
[21]	-	5895	6.83	80.4	35.87	7.72	23.5	27.11
[40]	130	47200	13	95	45	20	68	90

[41]		135	56300	1.8	70	55	12.5	75	100
[42]		6.67	4808	14.99	6.89	4.14	3.50	13.00	7.86
[43]		-	8092	14.99	7.62	11.27	3.88	0.57	3.67
[44]		268	7552	1.61	52.7	183	5.4	75	51.03
[45]		-	3022	-	5.66	0.38	2.10	1.50	-
[46]		-	3374	133	24	30	6.60	14	39
[47]		-	2432	-	28.5	31.6	2.3	20	32.9
[48]	ERL	-	-	8.2	150	34	46.7	20.9	81
	ERM	-	-	70	410	270	218	51.6	370

The enrichment factor (EF) is a valuable tool for determining the origin of heavy metals [49]. The average EF values for potentially toxic elements (PTEs) in descending order are: As (1.12) > Zn (0.75) > V (0.70) > Cr (0.69) > Cu (0.69) > Pb (0.67) > Ni (0.46). This suggests that the Al-Lith coastal sediments exhibit deficiency to minimal enrichment with PTEs (Table 2). However, moderate enrichment of As was observed in samples S1 and S9 (8% of the studied samples) [34]. The contamination factor (CF) results indicated low contamination for all PTEs, with average CF values less than 1. The pollution load index (PLI), used to assess contamination at specific sediment sites [50], ranged from 0.06 to 0.68, with an average of 0.21, indicating unpolluted sediment [5]. The risk index (RI), which helps understand and control heavy metal pollution at a site [43], ranged from 1.61 to 25.80, with an average of 6.84, suggesting low risk from heavy metals in the present sediments (Table S.5). All PTE levels were below the effects range-low (ERL), indicating that the Al-Lith coastal sediments do not pose a risk to benthic communities due to these PTEs [48].

Table 2. Minimum, maximum and average values of EF and CF in Al Lith coastal sediment.

PTEs	Indices	Min.	Max.	Aver.
Pb	EF	0.095	1.967	0.671
	Igeo	-2.708	-0.629	-1.988
	CF	0.050	0.400	0.123
Zn	EF	0.170	1.491	0.753
	Igeo	-2.880	0.378	-1.658
	CF	0.042	1.095	0.239
Cr	EF	0.448	1.311	0.688
	Igeo	-2.826	-0.152	-1.717
	CF	0.044	0.644	0.187
Ni	EF	0.217	0.868	0.458
	Igeo	-3.239	0.057	-2.128
	CF	0.029	0.794	0.156
Cu	EF	0.179	1.572	0.685
	Igeo	-6.077	0.113	-3.574
	CF	0.022	1.622	0.276
Fe	Igeo	-5.468	-0.540	-2.885
	CF	0.034	1.032	0.302
As	EF	0.245	3.301	1.123
	Igeo	-4.285	-1.963	-3.052
	CF	0.077	0.385	0.205
V	EF	0.217	1.111	0.701
	Igeo	-5.607	-1.084	-3.461
	CF	0.031	0.708	0.218

A significant positive correlation was found between Zn and As, Zn and Cr, Zn and Cu, Zn and Fe, Zn and Ni, Zn and Pb, and Zn and V (Table 3), indicating a common source for these elements [11]. Iron also showed strong positive correlations with other elements, suggesting natural sources,

primarily from the chemical weathering of the basement rocks in the nearby Arabian Shield mountains located to the east of the study area [51, 52]. In contrast, there was a weak correlation between As and Pb, indicating a different source for Pb in the investigated sediments. Principal Component Analysis (PCA) identified two principal components (PCs) that largely supported the correlation matrix (Table 4). PC1 had high loadings for As, Cr, Cu, Fe, Ni, Pb, V, and Zn (0.666, 0.981, 0.975, 0.988, 0.710, 0.935, and 0.988), while PC2 had high loading for Pb (0.597). Samples S16 to S21, located at the mouth of Wadi Al-Lith, showed high concentrations of Cr, Ni, As, V, Cu, Pb, Zn, and Fe. This suggests that the coastal sediments and associated PTEs originated from the igneous and metamorphic rocks of the Arabian Shield, which were weathered by rainwater and subsequently eroded and transported through Wadi Al-Lith. The lower EF values for these PTEs confirm their geogenic origin [53].

The basement rocks of the Arabian Shield in Saudi Arabia are rich in various metallic minerals, including PTEs. These include sphalerite (ZnS) found in hydrothermal vein systems, vanadiferous magnetite $(Fe,V)_3O_4$ associated with mafic to ultramafic rocks, chromite ($FeCr_2O_4$) within peridotite units, and chalcopyrite ($CuFeS_2$) linked to volcanic rocks and intrusive bodies. Additionally, pentlandite $((Fe,Ni)_9S_8)$ occurs in mafic-ultramafic complexes, arsenopyrite ($FeAsS$) is found with sulfide mineralization in hydrothermal systems, galena (PbS) is associated with hydrothermal veins, and both magnetite (Fe_3O_4) and hematite (Fe_2O_3) are found in volcanic and sedimentary rocks [54, 55].

Table 3. The correlation matrix of the analyzed PTEs.

	As	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**V**	**Zn**
As	1							
Cr	.638**	1						
Cu	.563**	.936**	1					
Fe	.625**	.988**	.927**	1				
Ni	.621**	.956**	.993**	.942**	1			
Pb	.340	.627**	.761**	.590**	.760**	1		
V	.624**	.973**	.860**	.956**	.888**	.545**	1	
Zn	.620**	.955**	.988**	.944**	.992**	.753**	.904**	1

Table 4. Principal component for the investigated PTEs.

	PC1	**PC2**
As	**.666**	-.182
Cr	**.981**	-.064
Cu	**.975**	.145
Fe	**.974**	-.129
Ni	**.988**	.118
Pb	**.710**	**.597**
V	**.935**	-.151
Zn	**.988**	.103
% of Variance	80.59	9.66
Cumulative %	80.59	90.25

3.2. Health Risk Assessment

Various essential potentially toxic elements (PTEs), such as Co, Cr, Fe, Zn, Ni, and Mn, play crucial roles in nutrition at trace levels. However, excessive exposure to these PTEs can lead to severe health issues in humans [15, 45, 56]. In the investigated area, the average chronic daily intake (CDI) values (mg/kg/day) for non-carcinogenic risk in adults ranged from 3.37392E-06 (Pb) to 0.01953 (Fe) through ingestion and from 1.34619E-08 (Pb) to 1.54661E-07 (V) through dermal pathways (Table 5). In children, the average CDI values varied from 3.14899E-05 (Pb) to 0.182310164 (Fe) through

ingestion and from 6.28224E-08 (Pb) to 3.16474E-07 (Cu) through dermal pathways. These findings indicate that children are at a heightened risk of non-carcinogenic exposure compared to adults.

The average hazard index (HI) values for potentially toxic elements (PTEs) in both adults and children, in descending order, were Fe, As, Cr, V, Pb, Cu, Ni, and Zn (Table 5). The distribution of HI values across sample locations revealed that the highest HI values for Cr, Pb, V, Zn, and Fe were found in sample S21, while the highest value for As was in sample S16 (Table S.6). This trend is likely due to elevated levels of PTEs in these specific samples. In adults, HI values ranged from 0.00010 (Zn) to 0.0280 (Fe), while in children, they ranged from 0.00097 (Zn) to 0.260 (Fe), indicating that children have a higher hazard index compared to adults for non-carcinogenic risk. Despite this, all HI values for PTEs were below 1.0, suggesting no significant non-carcinogenic risk for residents along the Al-Lith coastline [57, 58]. However, it is important to note that the HI value for iron exceeded 0.2 in children, highlighting the need to protect their health.

Table 5. The average CDI, HQ, and HI values for non-carcinogenic risk in adults and children.

PTEs	Adults				
	CDI_{Ing}	CDI_{Derm}	HQ_{Ing}	HQ_{Derm}	HI
As	3.65E-06	1.46E-08	0.0122	4.85E-05	0.0122
Cr	2.30E-05	9.19E-08	0.0077	3.06E-05	0.0077
V	3.88E-05	1.55E-07	0.0043	1.72E-05	0.0043
Ni	4.008E-06	1.60E-08	0.00019	7.99E-07	0.00019
Zn	3.12E-05	1.24E-07	0.00010	4.14E-07	0.00010
Pb	3.37E-06	1.35E-08	0.00096	3.85E-06	0.00097
Cu	1.70E-05	6.78E-08	0.00046	1.72E-05	0.00048
Fe	0.020	-	0.0279	-	0.0279
PTEs	Children				
	CDI_{Ing}	CDI_{Derm}	HQ_{Ing}	HQ_{Derm}	Hi
As	3.40E-05	6.79E-08	0.113	0.00023	0.114
Cr	0.00021	4.29E-07	0.072	0.00014	0.072
V	0.00036	7.22E-07	0.040	8.02E-05	0.040
Ni	3.74E-05	7.46E-08	0.0019	3.73E-06	0.0019
Zn	0.00029	5.80E-07	0.00097	1.93E-06	0.00097
Pb	3.15E-05	6.28E-08	0.0090	1.79E-05	0.0090
Cu	0.00016	3.16E-07	0.0043	8.02E-05	0.0044
Fe	0.182	-	0.260	-	0.260

The accumulation of potentially toxic elements (PTEs) such as As, Cr, and Pb in the human body can result in serious health complications, including an increased risk of lung, stomach, and skin cancers, as well as potential effects on the nervous system [59, 60]. Carcinogenic risks (CRs) associated with Cr, Pb, and As were evaluated in the examined samples (Table 6, Table S.7). In adults, the average CR values ranged from 2.87E-08 (Pb) to 1.15E-05 (Cr) through ingestion and from 2.18E-08 (As) to 4.60E-08 (Cr) through dermal exposure. In children, the average CR values ranged from 2.68E-07 (Pb) to 0.000107 (Cr) through ingestion and from 5.11E-05 (As) to 2.14E-07 (Cr) through dermal exposure. Lifetime cancer risk (LCR) values for adults varied from 2.87E-08 (Pb) to 1.16E-05 (Cr), while for children, they ranged from 2.68E-07 (Pb) to 1.08E-04 (Cr).

Table 6. Average CRs and LCR values for heavy metal(loid)s in the study area.

PTEs	Adults			Children		
	CR_{Ing}	CR_{Derm}	LCR	CR_{Ing}	CR_{Derm}	LCR
As	5.47E-06	2.18E-08	5.49E-06	5.11E-05	1.02E-07	5.12E-05
Cr	1.15E-05	4.60E-08	1.16E-05	0.000107	2.14E-07	1.08E-04
Pb	2.87E-08	-	2.87E-08	2.68E-07	-	2.68E-07

The distribution of lifetime cancer risk (LCR) values across sample locations revealed hot spots in S1, S10, S16, and S21 for As; S2, S7, and S16-S21 for Cr; and S21 for Pb (Table S.7 and Fig. 4). All LCR values for Pb, As, and Cr in both adults and children were within acceptable or tolerable carcinogenic risk levels, posing no significant health threats (ranging from 1×10^{-5} to less than 1×10^{-6}). However, six samples (S2 and S16-S21) showed LCR values exceeding 1×10^{-4} for Cr in children, indicating potential carcinogenic risks [19, 38, 61]. These elevated values were mainly found in samples collected at the mouth of Wadi Al-Lith and were associated with higher levels of PTEs, suggesting an origin from the basement rocks of the Arabian Shield.
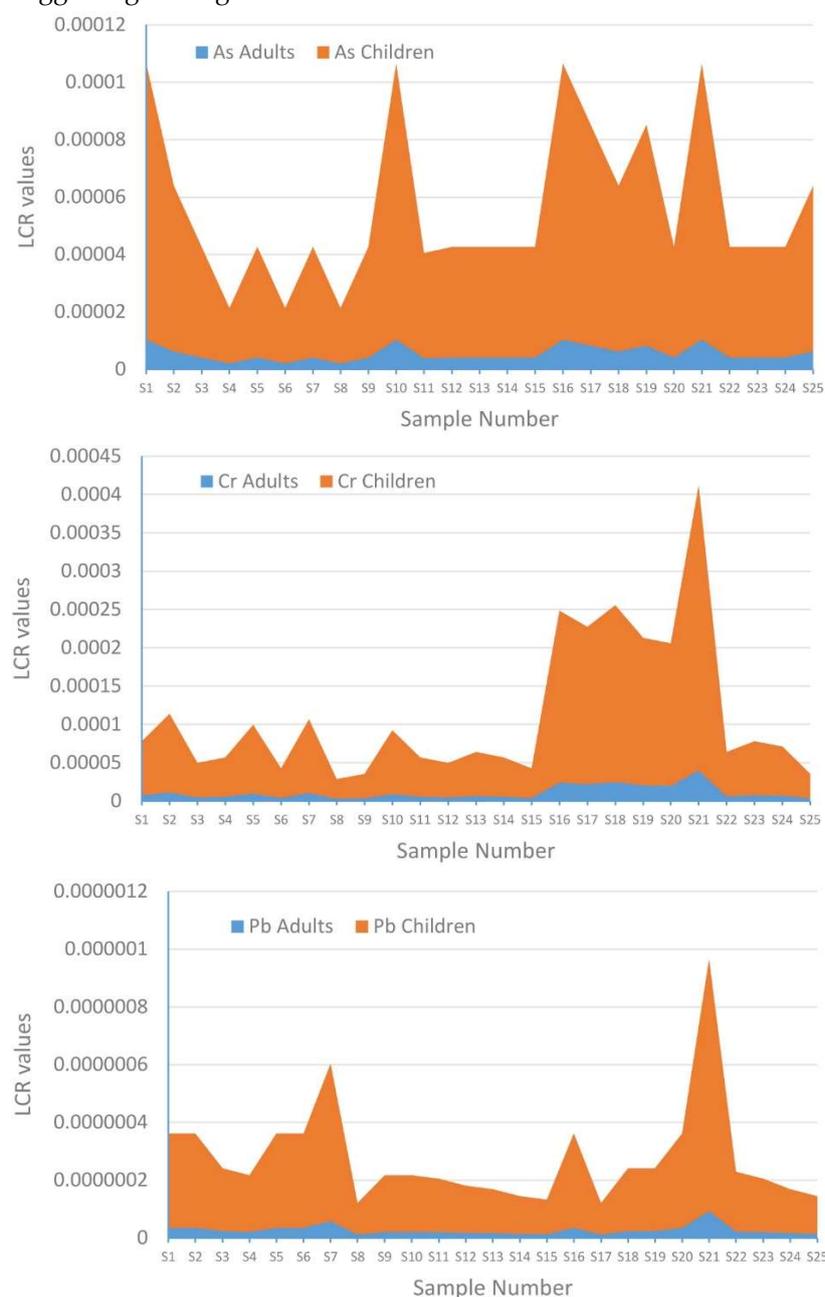
Figure 4. Spatial distribution of LCR for As, Cr, and Pb per sample locations in the study area.

4. Conclusions

This study examined the presence of potentially toxic elements (PTEs) in the surface sediment of the Al Lith region along the Saudi Red Sea coast. The findings indicated that the coastal sediments exhibited low to minimal enrichment of PTEs. However, samples from the mouth of Wadi Al-Lith showed higher concentrations of several PTEs, suggesting a natural source from the Arabian Shield. All hazard index (HI) values for PTEs were below 1.0, indicating no significant non-carcinogenic risk. Lifetime cancer risk (LCR) values for Pb, As, and Cr in both adults and children were within acceptable or tolerable levels, posing no significant health threats. Nonetheless, six samples showed LCR values exceeding 1×10^{-4} for Cr in children, indicating potential risks.

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