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Major Factors Controlling the Elemental Composition of Al-Kharrar Lagoon Bottom Sediments, Rabigh, Saudi Arabia

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Abstract: Bottom sediments of Al-Kharrar Lagoon, Rabigh area, Saudi Arabia were analyzed for mineralogical (26 samples) and major oxides, minor, and trace elements (46 samples). The prime objective is to document the controlling factors of the mineralogical and chemical composition of the lagoon bottom sediments. Hierarchical cluster (HCA) and the principal component (PCA) analyses are used to disclose the degree of similarities among elements to distinguish them into statistically significant groups. Results clarified the interplay of terrestrial sediment influx through the temporarily active Wadi Rabigh, hydrological regime and the autochthonous biogenic sedimentation, and to a lesser extent rare anthropogenic influence that impacted the lagoon sediments. The spatial distribution of minerals shows a southward increase in the siliciclastic-related minerals (quartz, clay minerals, k-feldspars, and plagioclase along with traces of amphiboles), whereas carbonate minerals (high Mg-calcite and aragonite) dominate the northern sector of the lagoon in areas far from the influence of detrital influx. The concentrations levels of oxides, minor, and trace elements display spatial variability. Three main distinctive elemental groups were delineated appraising the analysis of the elemental interrelationships and associated statistical analysis. The first group includes the positively correlated SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, K_2O, Na_2O, V, Cr, Ni, Zn, Rb, and Ba, which are concentrated in the southern sector of the lagoon. The second group is the carbonate-related elements (CaO and Sr) that dominate the northern sector. The distribution patterns of P_2O_5 and Cu varied highly across the lagoon. Enrichment factors revealed moderate levels of Cu in some sites supporting the anthropogenic source. The results showed the hospitable bottom ecological status of the lagoon despite local anthropogenic stressors such as an influx of flood water that contain a mixture of lithogenic and dissolved Cu from local farming.

Keywords: Al-Kharrar Lagoon; sediment geochemistry; lithogenic elements; anthropogenic effect; Red Sea coastal lagoons; carbonate-related elements; mineralogical composition

1. Introduction

Coastal lagoons are environmentally and socio-economically significant. They are highly productive and important sites for the ecological preservation of biodiversity, spawning, and nursery of many habitats as well as important fisheries and aquaculture sites [1–3]. In addition, they are the most desirable human living and recreation areas. Coastal lagoons are dynamic and environmentally complex affected by the interplay of terrestrial and marine influences and display rapid fluctuation in physical, chemical, and biological properties [4,5]. On the other hand, they are a highly sensitive and vulnerable ecosystem, and are negatively impacted by increased urbanization and anthropogenic activities such as fisheries, tourism, demographic expansion, and massive discharge of untreated domestic

and industrial wastewaters as well as urban drainage [6]. Monitoring of the environmental quality of these ecosystems is rather difficult because of the simultaneous interaction of several parameters such as hydrodynamics, grain size, mineralogical and chemical composition, and the contribution from anthropogenic activities. The study of the chemical composition of lagoon bottom sediments is one of the most applicable strategies that have been used to evaluate the environmental changes in response to coastal zone development and to monitor the quality of these highly fluctuating environments [6–10].

The economic plan of the Saudi Arabian Vision 2030 has paid great attention to the development of the Red Sea coastal zone. Intensive urbanization, recreation, and industrial projects have significantly increased in the last decade along the Red Sea coast of major cities such as Jazan, Jeddah, Rabigh, Yanbu, Umluj, Al-Wajh, and Duba. Recent interest in Red Sea coastal development has motivated geochemical research on the sediments of coastal lagoon ecosystems. Numerous coastal lagoons of different morphologies, surface areas, habitats, and depths extend along the Saudi Red Sea coast and connect to the Red Sea through single or multiple inlets [11]. The composition of their bottom sediments is largely dominated by autochthonous biogenic sediments with very rare lithogenous constituents of limited spatial distribution reflecting the extreme arid climate and the absence of perennial riverine input [12]. These lagoons are important fishing sites holding important living resources of commercial and ecological interest. Several geochemical studies have been conducted on the Red Sea lagoon sediments to determine the controlling factors on elemental distribution [12–14], to establish a geochemical background for the Red Sea coastal sediments [15], and to assess the pollution with heavy metals [16–18].

Al-Kharrar Lagoon, which is located about 10 km to the north of Rabigh City, receives allochthonous sediments from the drainage of some temporarily active wadis such as Wadi Rabigh to the south and W. Al-Habbak to the east, and autochthonous sediments from reef debris as well as indogenic skeletal remains either from the Red Sea or that inhabit the lagoon. Little is known about the compositional heterogeneity of lagoon bottom sediments. The discharge of untreated industrial and domestic wastewaters is absent or very negligible. It is expected to be impacted by rapid urbanization and increased industrial activities in the Rabigh area in the coming years. With the increase of human activities along the Red Sea coast, geochemical studies of lagoon bottom sediments are important in evaluating environmental degradation related to coastal zone development. The study of the chemical composition of bottom sediments in the Al-Kharrar Lagoon is important not only from the geochemical point of view but also from an environmental perspective. Several studies on the recent sediments of Al-Kharrar Lagoon have been conducted, but with dissimilar subjects including hydrographic, sedimentological, mineralogical, micropaleontological, and geochemical [13,15,19–24].

Characterizing the mineralogical and chemical composition of surface sediments in the Al-Kharrar Lagoon is important not only from the geochemical point of view but also from an environmental perspective. It is essential to determine the quality and to quantify the environmental stress that may arise with future development and urbanization. The aim of the present work is to identify the sources of sediments in the lagoon and the controlling factors of the minerals and elemental spatial distribution. The study provides a database for future biogeochemical and environmental research in the area of study and similar ecosystems along the Red Sea. It provides furthermore a monitoring tool needed to detect changes and to help in early warning regarding qualitative and quantitative risks.

2. Area of Study

Al-Kharrar Lagoon is a relatively shallow (5 ± 2.8 m deep) and elongated (20 km long and 5 km maximum width) coastal basin that connects to the Red Sea through a shallow and narrow inlet through which the water of the lagoon and Red Sea exchange. It extends between latitudes 22°50′ to 22°59′ N and longitudes 38°55′ to 38°57′ E, about 10 km north of Rabigh City (Figure 1a). The southern and eastern shorelines of the lagoon are bounded by extensive tidal flat (sabkha), whereas the western shoreline is separated from the Red

Sea by carbonate terraces trending parallel to the Red Sea shoreline. It includes two small islands; Al-Ultah and Um Dinar [13,20]. Al-Kharrar Lagoon is characterized by diverse ecosystems including coral reefs, mangroves, sea grasses, and macro-algae. The climate in the region is hot and arid with a very low precipitation rate (6 cm/y) and a relatively high evaporation rate (205 cm/y). The high evaporation and low precipitation rates promote a relatively high salinity of the water body varying between 38.8 and 41.5‰ (average 40.5‰). The surface water temperature varies between 23 °C and 34 °C in winter, and from 29.8 °C to 31.5 °C in summer. Like the other Red Sea lagoons, Al-Kharrar Lagoon is the terminal wetland of some inactive wadis that drain the Arabian-Nubian Shield (ANS) to the east. These wadis include Rabigh, Rehab, Murayykh, and Al-Khariq, which are intermittently and sporadically active during major flood seasons and supply the lagoon with freshwater and terrigenous sediments. The freshwater and sediment supply from land are very rare because wadis draining into the lagoons are almost inactive and dry most of the year. Wind stress and tidal currents are the major controls on water circulation in the lagoon [22,25]. The speed of tidal currents varies from 50 cm/s at the entrance to 5 and 20 cm/s inside the lagoon depending on the spring-neap cycle and sea level variations [22,25]. The tide is semi-diurnal with a small range varying from 0.20 to 0.30 m during a spring-neap cycle [22,26].
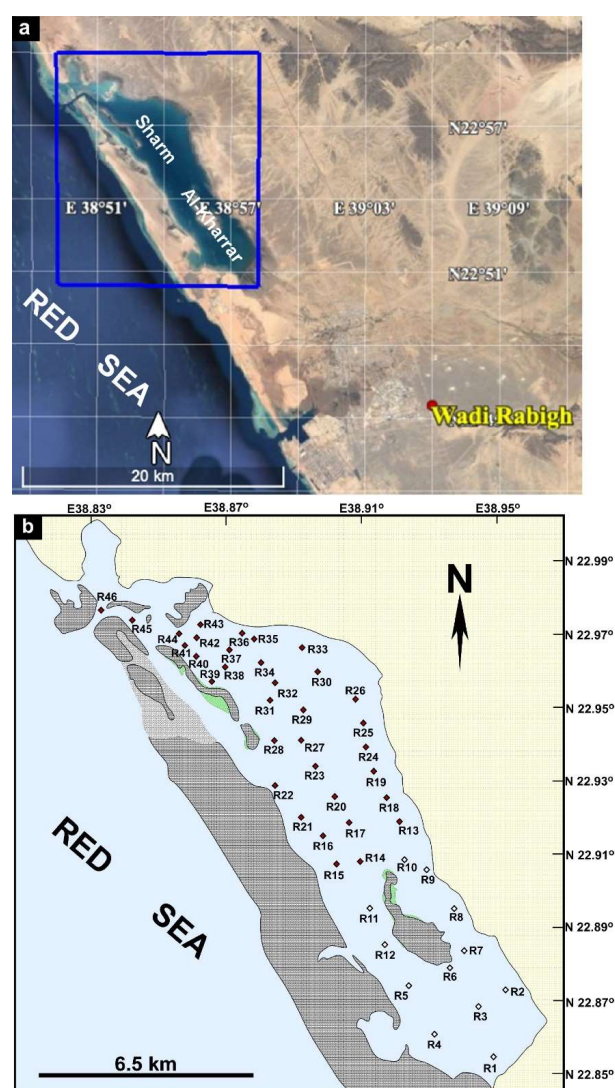

Figure 1. Google Earth map showing the location map of the Sharm Al-Kharrar (**a**) and a map showing sampling sites (**b**).

Based on grain size and mineralogical variations, Al-Washmi [20] differentiated the bottom sediments of Al-Kharrar Lagoon into two sedimentary facies; siliciclastic sediments to the south and calcareous dominated facies with abundant biogenic remains to the north and near the inlet. The chemical composition of Al-Kharrar Lagoon bottom sediments was a focus for many geochemical investigations in order to display the lateral variations within different grain size fractions [13] and to elucidate possible anthropogenic contaminations [17]. Basaham et al. [15] tried to establish a geochemical background for the Red Sea coastal sediments by selecting three pristine lagoons; Al-Kharrar Lagoon was an example of the lagoons at the terminal of Wadi. The modern environmental conditions in the Al-Kharrar Lagoon including pH, salinity, temperature, dissolved oxygen, and bathymetry have recently been the focus of some studies [11,24,27].

3. Materials and Methods

A total of 46 surface sediment samples were collected by the Van Veen Grab sampler to cover Al-Kharrar Lagoon (Figure 1b). The upper 2 cm was sampled and stored refrigerated. Samples were washed with deionized water to remove salts and subsequently wet sieved by 0.5 mm sieve and a fraction less than medium sands were used in this study. Samples were dried, finely ground with an agate pestle and mortar, and then analyzed for their mineralogical and chemical composition. The mineralogical composition of 26 samples was determined by Shimadzu X-ray diffraction equipped with Ni-filtered Cu Kα radiation at 15 kV to 40 mA at the Faculty of Marine Science, King Abdulaziz University. A gram of dry sediments was finely powdered in an agate mortar and packed into a cavity-bearing slide that was scanned from 2° to 60° 2θ at a speed of 1°/min. The relative abundances of minerals were estimated based on the height of the major peaks [28,29]. The concentrations of major oxides, and minor (1% > conc. > 0.1%) and trace (conc. < 0.1%) elements in 46 sediments samples were determined by a RIGAKU RIX 2100 X-ray fluorescence spectrometer (XRF), equipped with a Rh/W dual-anode X-ray tube at the Department of Geosciences, Osaka City University, Japan. The analysis was carried out under 50 kV and 50 mA accelerating voltage and tube current, respectively. About 1.8 g of dry powdered sediments were mixed with 3.6 g of Spectroflux ($Li_2B_4O_7$ 20 %, $LiBO_2$ 80 %, dried at 450 °C for 4 h), 0.54 g of oxidant $LiNO_3$ (dried at 110 °C for 4 h) and traces of LiI to form fused glass discs [30].

The degree of elemental enrichment was determined for the environmentally significant trace elements (V, Cr, Cu, and Zn) using the enrichment factor (EF). The EF of element X was determined by comparing the ratios of elemental concentrations to Al (X/Al) in sediments and the average chemical composition in shallow subsurface lagoon facies [31] as a background. The EF f is computed following the method described by Covelli and Fontolan [32] as:

$$EF_x = \text{Conc. } (X/Al)_{sample} / \text{Conc. } (X/Al)_{Back} \tag{1}$$

EF values less than 2 suggest a depletion with no or minimal pollution, while values in the range level of 2–5 suggest moderate enrichment/pollution, range level of 5–20 indicates significant enrichment/pollution, level of 20–40 clarifies very high enrichment/pollution, and EF values greater than 40 disclose extreme enrichment/pollution [33].

Data distribution and correlation among the variables were analyzed appraising the use of the SPSS Statistical package for Windows version 20. Pearson's correlation analysis was conducted to describe the strength and direction of the linear relationship between the studied elements at a significance level of 95%. Hierarchical cluster (HCA) and the principal component (PCA) analyses were applied to clarify the degree of similarity between elements. Variogram modeling using krigging implemented in ArcGIS 9.3 was appraised for rendering the spatial distribution of the variables where the spherical model was of major use. Surfaces produced were evaluated from the original sampling point data values applying cross-validations in a trial and error step, where maps with the least errors were further interpreted.

4. Results

The results of mineralogical and chemical analyses of the bottom sediments of Al-Kharrar Lagoon are summarized in Tables 1 and 2. Mineralogical and geochemical mapping showing the spatial distribution of the most common minerals (Figure 2), major oxides, minor, and trace elements (Figures 3 and 4, respectively) were used to evaluate the sediment quality in the lagoon.

Table 1. The mineral content in the bottom sediments of the Sharm Al-Kharrar as revealed by XRD.

Sample	Clay Minerals	Mica	Amphiboles	Quartz	K-Feldspars	Plagioclase	Aragonite	HMC	LMC	Dolom.
R1	10	-	7	44	20	-	4	4	11	2
R2	18	4	3	38	-	13	6	7	7	3
R3	9	-	5	42	5	18	6	7	5	2
R4	13	3	3	32	-	11	18	6	12	2
R5	12	-	4	36	-	13	14	7	11	2
R6	9	-	4	31	-	10	18	9	17	2
R8	14	-	4	35	4	13	10	8	10	3
R9	7	-	9	29	23	-	-	9	21	2
R10	11	-	3	31	-	11	17	9	17	2
R11	12	-	3	29	3	11	18	8	15	2
R12	11	-	5	33	4	10	14	7	13	2
R15	7	2	2	20	-	6	33	8	20	-
R17	10	-	2	23	4	9	23	10	16	3
R18	8	-	5	21	3	15	23	8	15	1
R19	6	-	2	19	3	13	30	8	19	-
R20	11	-	1	23	-	9	28	9	18	-
R22	5	-	2	16	-	5	38	9	22	2
R23	12	-	3	26	-	9	25	9	17	-
R24	5	-	5	22	-	24	22	7	14	1
R28	5	-	2	15	-	7	26	15	28	2
R29	5	3	3	23	-	8	25	11	22	-
R35	2	-	2	17	-	5	39	14	20	2
R36	10	3	-	17	-	7	34	12	21	-
R38	7	-	-	19	-	6	29	15	23	1
R39	5	-	2	14	-	9	37	11	20	2
R43	4	-	3	12	-	7	44	11	19	1

HMC; high Mg-calcite, LMC; low Mg-calcite, (-) undetected.

Table 2. Summary statistics showing the concentration ranges and average of oxides (%) and minor and trace elements (µg/g), elemental ratios, and enrichment factor (EF) of the environmentally significant trace elements in the bottom sediments of Sharm Al-Kharrar.

Oxides/elements	Minimum	Maximum	Mean
SiO_2	12.85	51.62	31.25
TiO_2	0.26	1.12	0.62
Al_2O_3	4.23	16.33	10.32
$T\text{-}Fe_2O_3$	2.06	9.12	5.35
MnO	0.04	0.15	0.09
MgO	3.39	6.26	5.16
CaO	8.12	61.27	35.20
Na_2O	0.69	2.8	1.65
K_2O	0.22	1.62	0.67
P_2O_5	0.13	0.51	0.24
V	48	168	104.74
Cr	34	155	82.26

Table 2. *Cont.*

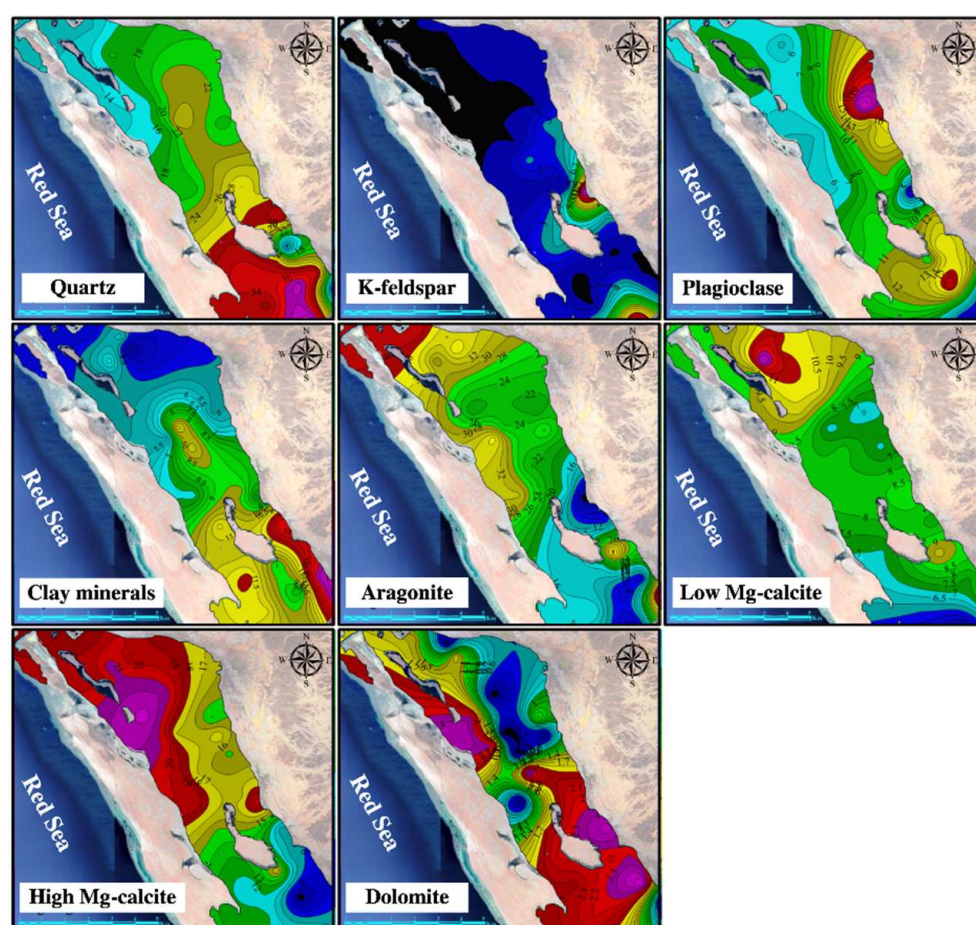| Oxides/elements	Minimum	Maximum	Mean
Ni	14	93	51.24
Cu	30	64	47.72
Zn	25	99	61.57
Rb	3	45	15.50
Sr	624	7932	4155
Ba	46	232	134
Mg/Ca	0.05	0.59	0.17
Sr/Ca	107	185	160
EF_V	0.55	0.68	0.61
EF_{Cr}	0.65	0.91	0.73
EF_{Cu}	0.64	3.63	1.52
EF_{Zn}	0.88	1.77	1.42

Figure 2. Contour maps showing the spatial distribution of the most common minerals in the bottom sediments of the Sharm Al-Kharrar. Light blue scale bar on maps equals 6 km.
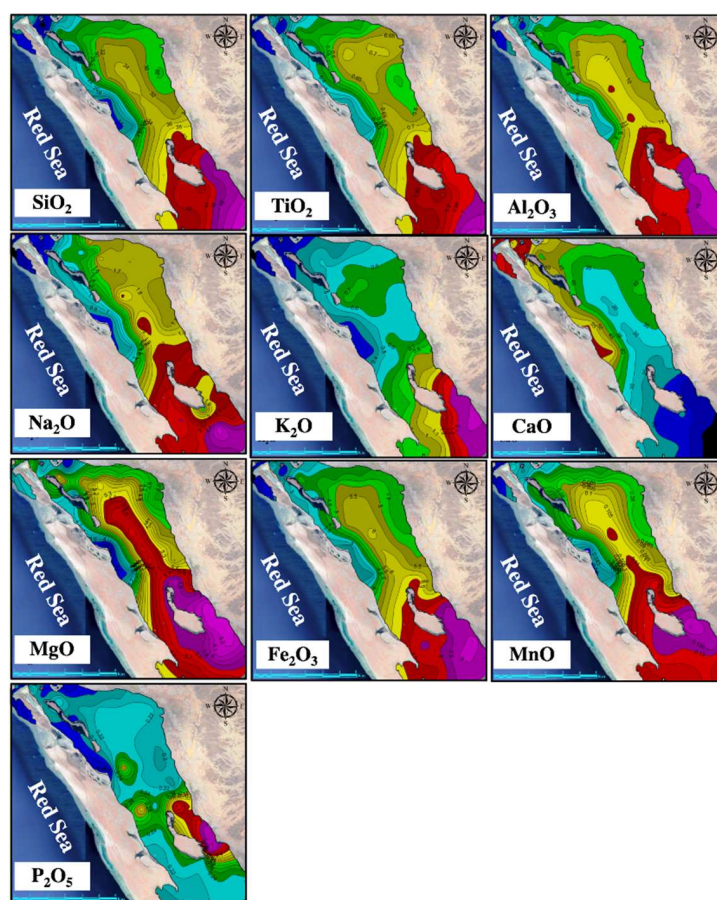
Figure 3. Contour maps showing the spatial distribution of the concentrations of oxides (%) in the bottom sediments of the Sharm Al-Kharrar. Light blue scale bar on maps equals 6 km.
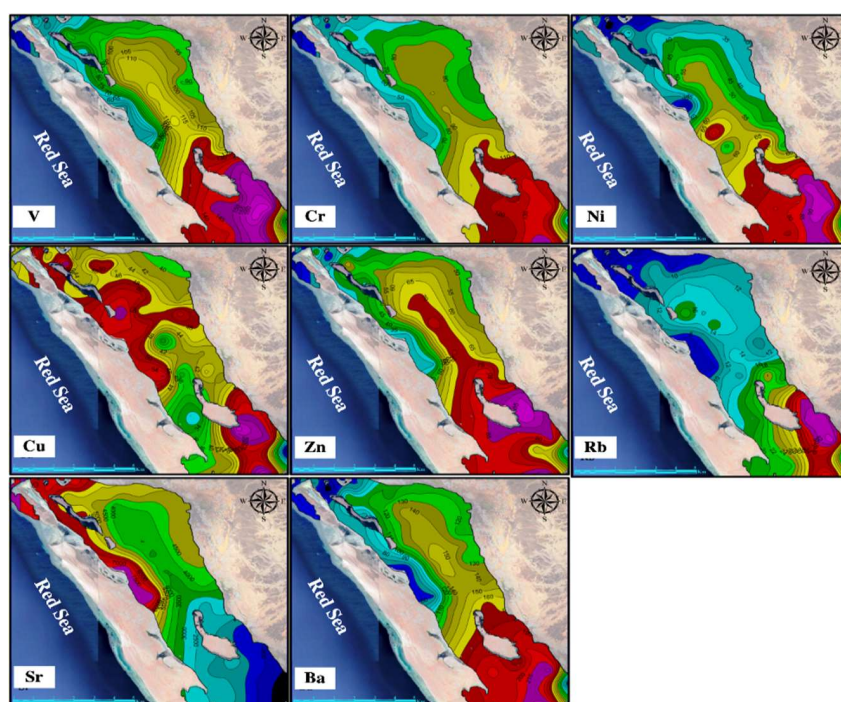

Figure 4. Contour maps showing the spatial distribution of the concentrations of trace elements (µg/g) in the bottom sediments of the Sharm Al-Kharrar. Light blue scale bar on maps equals 6 km.

4.1. Mineralogical Composition

XRD analysis of the sediment from the entire lagoon system revealed the presence of the two mineral groups for all sediments (Figure 2). The first group (clays, quartz, k-feldspars, plagioclase, and traces of mica and amphiboles) probably of detrital origin, derived from the hinterland. On the other hand, the second group (including aragonite, high and low Mg-calcite, and traces of dolomite) probably precipitated within the lagoon mainly as biogenous constituents. The distribution and abundance of the two groups are opposite. The minerals of the first group are more abundant in the southern sector of the lagoon than in the northern part.

4.2. Oxides

Descriptive statistics of oxides and minor and trace element concentrations in the bottom sediments of Al-Kharrar Lagoon are shown in Table 2. The concentrations of oxides in the analyzed sediments are consistent with the mineralogical composition. The chemical data showed a heterogeneous distribution throughout the lagoon. SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, Na_2O, and K_2O display a similar spatial distribution in that they are highly enriched towards the head of the lagoon near the southern coast. SiO_2 is the most abundant major oxide, ranging from 12.85 to 51.62 %; total concentrations of Al_2O_3 and TiO_2 vary from 4.23 to 16.33% and from 0.26 to 1.12%, respectively. On average, the concentrations of iron oxide (Fe_2O_3) (2.06–9.12%) and MnO (0.04–0.15%) decrease northward. Similarly, the concentrations of MgO, Na_2O, and K_2O decrease northward. The concentrations of Na_2O and K_2O display a similar spatial distribution. They vary between 0.69 and 2.8%, and 0.22 and 1.62%, respectively. The concentration of CaO displays an opposite distribution to other oxides and it is enriched towards the mouth of the lagoon (Figure 3). It varies from 8.12 and 61.27% (mean; 35.2%). Total phosphorus (P_2O_5: 0.13–0.51%) shows a relatively even distribution with a slight enrichment east of the Al-Ultah Island (Figure 3).

4.3. Minor and Trace Elements

The most abundant minor and trace elements are Sr > Ba > V > Cr > Zn> Ni > Cu > Rb. Vanadium (V), Cr, Ni, Zn, and Rb, display a similar spatial distribution to Al_2O_3. They show a southward increase in concentrations, ranging from 48 to 168 µg/g, 34 to 155 µg/g, from 14 to 93 µg/g, from 25 to 99 µg/g, 3 to 45 µg/g, from 3 to 11 µg/g, and from 8 to 30 µg/g, respectively. Copper (Cu) shows a fairly homogeneous spatial distribution over the study area with values ranging between 30 and 47.7 µg/g. The higher concentrations of Cu are recorded from areas near the mangrove. Similar to CaO, the highest Sr values (7932 µg/g) were obtained from the northern sector of the lagoon (Figure 4) coinciding with samples that are enriched in aragonite. Such high Sr levels are common in calcareous sediments containing abundant aragonite [34].

The ratio of Mg/Ca decreases more northward. It varied between 0.05 and 0.59 (mean; 0.17). On the other hand, the Sr/Ca ratio does not change remarkably from north to south. It ranges from 107×10^{-4} to 185×10^{-4} (mean; 160×10^{-4}).

4.4. Elemental Interrelationships

Pearson's correlation coefficients of elements in Al-Kharrar Lagoon are summarized in Table 3, showing various degrees of relationship among elements. The correlation matrix shows that most oxides and trace elements have a strong positive correlation with Al_2O_3 (r > 0.8) except for CaO and Sr, which show a strong negative correlation. Barium (Ba) displays a strong positive correlation with K_2O and Rb (R > 0.9). Iron oxide (Fe_2O_3) shows a strong positive correlation with other transitional elements (MnO, V, Cr, Co, Ni, and Zn). P_2O_5 and Cu show poor correlation with Al_2O_3 and CaO (Table 3).

Table 3. Correlation matrix of oxides and minor and trace element concentrations in the bottom sediments (n = 46 samples) of Sharm Al-Kharrar.

Oxides/Elements	SiO_2	TiO_2	Al_2O_3	$T\text{-}Fe_2O_3$	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	V	Cr	Ni	Cu	Zn	Rb	Sr	Ba
SiO_2	1																	
TiO_2	0.99	1																
Al_2O_3	0.99	0.97	1															
$T\text{-}Fe_2O_3$	0.98	0.97	0.99	1														
MnO	0.95	0.93	0.98	0.97	1													
MgO	0.89	0.86	0.93	0.90	0.92	1												
CaO	−0.99	−0.98	−0.99	−0.99	−0.96	−0.91	1											
Na_2O	0.88	0.87	0.86	0.83	0.82	0.75	−0.88	1										
K_2O	0.92	0.93	0.91	0.93	0.84	0.76	−0.92	0.73	1									
P_2O_5	0.50	0.48	0.50	0.50	0.47	0.54	−0.47	0.29	0.53	1								
V	0.98	0.97	0.99	0.99	0.97	0.90	−0.99	0.85	0.92	0.48	1							
Cr	0.98	0.98	0.98	0.99	0.95	0.87	−0.98	0.84	0.93	0.49	0.98	1						
Ni	0.84	0.83	0.87	0.88	0.83	0.78	−0.84	0.69	0.84	0.50	0.87	0.88	1					
Cu	0.07	0.08	0.09	0.12	0.03	0.07	−0.07	−0.29	0.26	0.23	0.09	0.13	0.20	1				
Zn	0.93	0.91	0.95	0.94	0.95	0.92	−0.93	0.74	0.81	0.54	0.93	0.92	0.82	0.02	1			
Rb	0.89	0.89	0.89	0.91	0.82	0.75	−0.88	0.64	0.98	0.56	0.90	0.91	0.84	0.35	0.82	1		
Sr	−0.99	−0.98	−0.99	−0.98	−0.96	−0.92	0.99	−0.87	−0.91	−0.48	−0.98	−0.98	−0.83	−0.06	−0.94	−0.88	1	
Ba	0.99	0.97	0.98	0.97	0.94	0.88	−0.99	0.90	0.90	0.44	0.97	0.97	0.83	0.05	0.91	0.86	−0.98	1

4.5. Enrichment Factor (EF)

The enrichment factors of V, Cr, Cu, and Zn were calculated (Table 2) and according to the classification of Southerland (2000), the bottom sediments of Al-Kharrar Lagoon are significantly depleted in V (0.55–0.68), Cr (0.65–0.91) and Zn (0.88–1.7). On the other hand, 8 sites out of 46 show moderate enrichment in Cu (2–3.6), whereas other sites are significantly depleted (EF < 2).

4.6. Statistical Analysis

Cluster analysis using correlation coefficient between all pairs of samples enabled discrimination of two groups of samples; A and B, representing samples of the southern and northern portions, respectively (Figure 5a). The samples within the two groups display a relatively similar geochemical composition. In addition, cluster analysis enabled classifying variables (oxides, minor, and trace elements) into two geochemical associations; C and D (Figure 5b). The association C displays a great similarity among lithogenic silicate and heavy mineral-related (SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MnO, V, Cr, Ni, Zn, Rb, and Ba), and feldspars-related (K_2O and Rb) elements. These elements display a similar spatial distribution in the lagoon, with higher concentrations recognized from the southern portion of the lagoon. On the other hand, association D represents carbonate-related elements (CaO and Sr) that display a dissimilar distribution pattern to the elements of group C. Copper (Cu) and P_2O_5 are not associated with the two geochemical associations.

Factor analysis allowed the identification of two factors (eigenvalues > 1) that explain 91.52% of the total variance (Table 4). Each factor represents compositional variables that identify a distinct group of elements. Factor 1 accounts for 84.85% of the total variance with a marked bipartition: on one hand, elements with significant positive factor loadings (SiO_2, Al_2O_3, Fe_2O_3, MgO, K_2O, TiO_2, Ni, Rb, V, and Ba) are related to silicates and clay minerals; on the other hand, elements with negative factor loadings (CaO and Sr) can be related to carbonates. Factor 2 accounts for 6.672% of the total variance. This factor is characterized by high positive loadings of Cu and P_2O_5. The source and spatial distribution of Cu and P_2O_5 are different from other elements. They display poor correlation either with Al_2O_3 or CaO suggesting a different source, possibly anthropogenesis.

Table 4. Factor loadings of geochemical variables in the bottom sediments of Sharm Al-Kharrar.

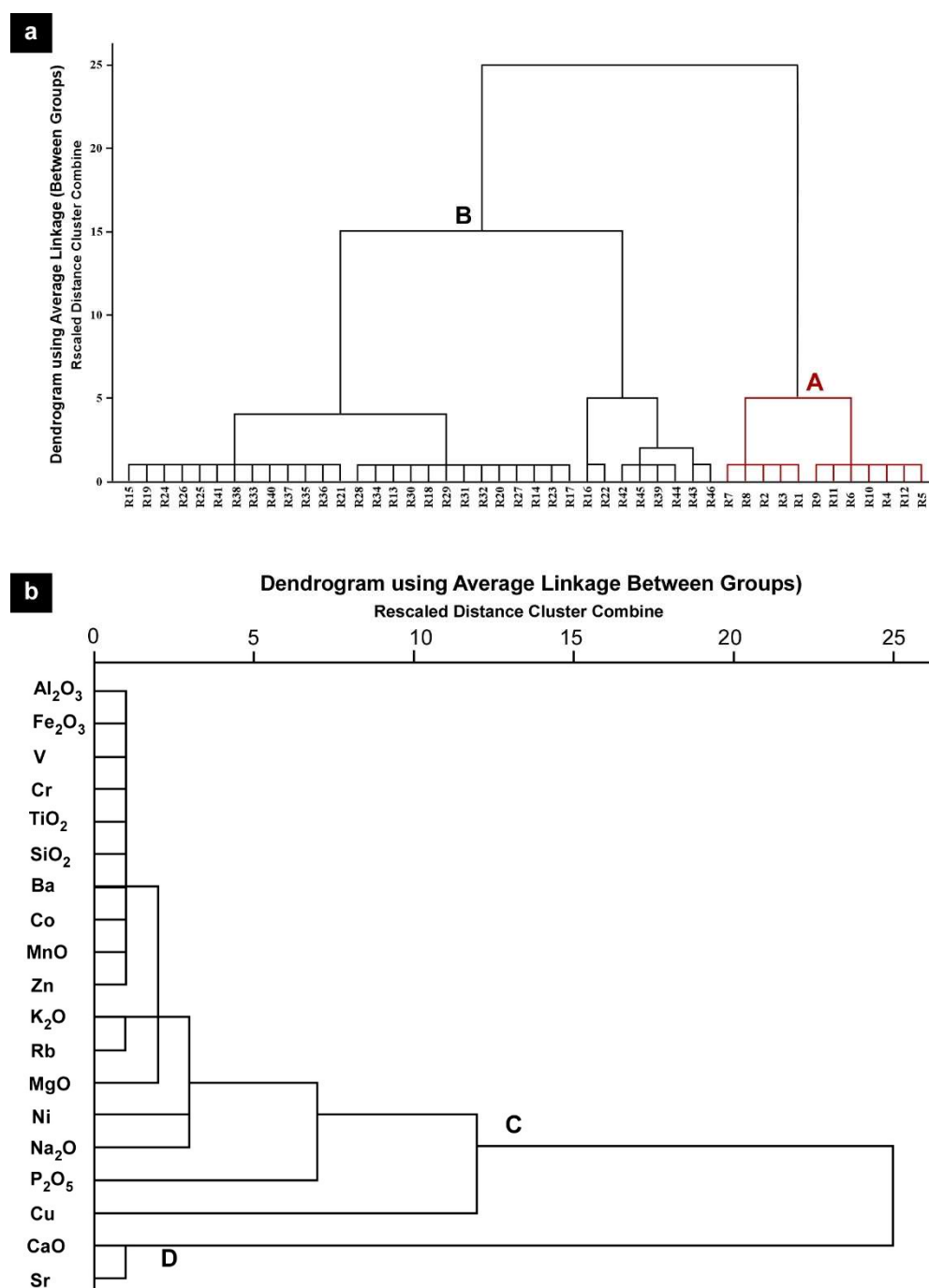| Variable	F1	F2
SiO_2	0.99	−0.055
TiO_2	0.98	−0.038
Al_2O_3	0.99	−0.032
Fe_2O_3	0.99	0.003
MnO	0.97	−0.087
MgO	0.91	−0.029
CaO	-0.99	0.062
Na_2O	0.85	−0.438
K_2O	0.93	0.195
P_2O_5	0.53	0.414
V	0.99	−0.027
Cr	0.99	0.007
Ni	0.88	0.138
Cu	0.11	0.925
Zn	0.94	0.002
Rb	0.91	0.3
Sr	−0.99	0.068
Ba	0.98	−0.10
Eigen value	17.18	1.4
% of variance	84.85	6.67

Figure 5. Dendrogram showing the clustering of samples (**a**) into two groups; A and B, representing the southern and northern sectors of the lagoon, respectively. (**b**) Clustering of elements into lithogenous-related (C) and carbonate-related elements (D).

5. Discussion

The spatial variation in the mineralogical and chemical composition of Al-Kharrar Lagoon bottom sediments reflects multiple sources. Statistical analysis and elemental interrelationships allowed the discrimination of three geochemical associations of dissimilar sources. The correlation of elements with Al_2O_3 (an indicator of the terrigenous influx; [35]) provides a useful tool in determining the source and behavior of elements. Oxides (SiO_2, TiO_2, Fe_2O_3, K_2O_3, MgO, and Na_2O) and trace elements (V, Cr, Co, Ni, Zn, Rb, and Ba) of the first geochemical association displayed significant positive correlations with

Al_2O_3 suggesting their association with the insoluble terrigenous aluminosilicates. The distribution patterns of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, V, Cr, Co, Ni, Zn, Rb, and Ba mirror each other, suggesting a similar detrital source. A considerable part of these geogenic elements is preferentially contributed from the igneous and metamorphic rocks of the Arabian Shield which are abundant in the Wadi Rabigh catchment basins. The elevated concentrations of Cr and Ni are mostly related to the occurrence of heavy minerals such as pyroxenes and amphiboles [36]. The positive correlation of K_2O, Na_2O, and MgO with Al_2O_3, suggests their detrital origin, mainly associated with K- and plagioclase feldspar, as well as clay minerals [37]. Barium (Ba) displayed a strong positive correlation with K_2O and Rb ($r > 0.9$) imposing a possible similar terrestrial source; possibly feldspars and mica. Transitional elements (MnO, V, Cr, Ni, and Zn) displayed a strong positive correlation with Fe_2O_3 suggesting their association with Fe-oxyhydroxides [38]. The second geochemical association (CaO and Sr) displayed a negative correlation with Al_2O_3 a group that relates to autochthonous biogenic carbonates. Carbonate content exhibits great variability, with the highest values observed in the northern sector of the lagoon, which is far from the dilution effect of terrigenous influx and dominated by calcareous skeletal remains. The absence of perennial riverine discharge and the low flow conditions are responsible for the short distance of terrigenous influx into the lagoon and therefore, the decrease in the concentration of lithogenic elements basin-ward.

The northward decrease in the Mg/Ca ratio suggests that the two elements have different origins, where a larger portion of Mg is of lithogenic origin, whereas Ca is mostly related to biogenic carbonate origin. Slight Mg enrichment in the sediment of the northern sector is attributed to the abundant high Mg-calcite. On the other hand, the Sr/Ca ratio notably does not change from north to south suggesting that Sr appears to be mainly controlled by the carbonate content particularly the presence of biogenic calcite and aragonite that constitute the tests of foraminifera, calcareous algae and coral remains and to a less and negligible contribution from feldspars [37]. The carbonate fraction is mainly of biogenic origin including shells and shell fragments of foraminifera, mollusks, coral remains, and echinoids.

The source of the Red Sea coastal lagoon bottom sediments includes the allochthonous detritus derived from the weathered parent rocks in the hinterland, the autochthonous biogenic calcareous remains, and the authigenic (hydrogenous) material precipitated at or near the sediment-water interface [12,18]. The content of detrital minerals (quartz, feldspars, and clay minerals) and lithogenic elements decrease from the shallow nearshore sites in the lagoon, whereas the abundance of carbonate minerals and carbonate-related elements (CaO and Sr) increases in the deeper sites and areas adjacent to the mouth of many Red Sea coastal lagoons [12,16]. This is attributed to the reduction of terrigenous materials mouth-ward and/or the dilution effect by biogenic carbonates [12]. Youssef and El-Sorogy [17] attributed the elevated concentrations of metals in the bottom sediments of Al-Kharrar Lagoon to the discharge of siliciclastic sediments by Wadi Rabigh during major floods and to a lesser extent the urbanization in the nearby areas such as King Abdullah Economic City.

Similar to cluster analysis, a ternary plot of major constituents of sediments; silica (SiO_2) vs. iron and aluminum oxides ($Al_2O_3 + Fe_2O_3$) vs. ($CaO + Na_2O + K_2O + MgO$) differentiates the bottom sediments of Al-Kharrar Lagoon into two groups; A and B displaying spatial variability based on their chemical composition he ternary diagram (Figure 6). The sediments near the head (group A; southern sector) are dominated by terrigenous minerals and elements supplied mainly by Wadi Rabigh during major flood seasons in addition to the contribution from the aeolian supply. Towards the mouth of the lagoon (group B; northern sector), the carbonate-related minerals and elements dominate (Figure 6).

The spatial distribution of Cu and P_2O_5 (third geochemical association) does not follow any of the two geochemical associations. Copper (Cu) and P_2O_5 are poorly correlated with Al_2O_3 and CaO suggesting a non-lithogenic and non-carbonate origin of the two elements.

Elevated concentrations and the local moderate enrichment of Cu indicate that a part of Cu in lagoon bottom sediments may be of an anthropogenic origin possibly anti-fouling boat paints and influxes from agrochemicals in farms bordering Wadi Rabigh, and may produce toxic and irreversible effects on living organisms in the future [39]. Copper (Cu) has been historically used as seed disinfectants, fungicides, herbicides, and added to fertilizers to meet the demand of plant growth [40,41]. Therefore, it may be contributed by the agricultural activities surrounding Wadi Rabigh. The source of Cu pollution in the bottom sediments of the Aetoliko (Etoliko) Lagoon Western Greece, resulted from the use of olive orchards Cu-based fungicide [42]. The elevated concentration of P_2O_5 adjacent to the Al-Ulta Island may reflect an increase of P input from the bird and mammal guano.

The quality of the sediments of Al-Kharrar Lagoon was assessed using enrichment factor (EF) of the environmentally significant trace elements (V, Cr, Cu, and Zn). The bottom sediments are depleted in V, Cr, and Zn (EF < 2), and depleted to moderately enriched for Cu (EF; 0.63–3.63). The EF values for V and Cr are below the regional geochemical background level and these elements are considered to be of a geogenic origin. The slight local enrichment of Cu may be attributed to urban pollution such as chemical fertilizers.

The chemical composition of the sediments in this study shows that the lagoon is not under anthropogenic stresses. However, it is important to take into account the negative impact and the potential accumulation of heavy metals in sediments even if they are trapped in minerals. With future changes in the pH, redox potential, salinity, and dissolved organic carbon of the lagoon, heavy metals trapped in sediments can be released into the water column and become bioavailable and posing a negative effect on biota. If the pH of bottom water drops to 5 and 5.5, Cu, and Zn can be rapidly bio-available in the aquatic environment, respectively [43,44]. In addition, the warm and dry climate and the construction of dams reduced the freshwater supply to the lagoon allowing increasing water salinity. The increase in salinity can indirectly increase metal bioavailability through the reduction of SO_4^{2-} and the decomposition of organic matter in sediment [45–47].

The local enrichment of Zn and Cu near the edges of the lagoon may be related to the presence of macrophytes (mangroves, seagrasses, and macro-algae) which provide the organic matter on which the two metals scavenge [48,49]. The elevated concentrations of Zn and Cu in the northern sector were attributed to biosorption by mucus algae that proliferate on the coarse shell fragments with the inlet channel [23].
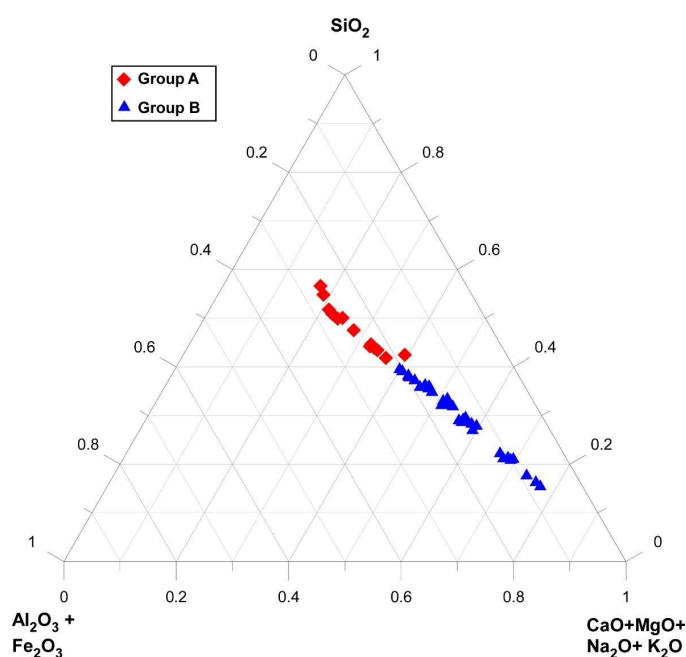

Figure 6. Ternary diagram of the oxide in the bottom sediments of Sharm Al-Kharrar.

6. Conclusions

Mineralogical and chemical analyses of Al-Kharrar bottom sediments provided the base for better understanding the factors interplayed to govern their variability summarized as follows:

1. The mineralogical and chemical composition of Al-Kharrar Lagoon bottom sediments reflects the interplay of terrestrial sediment influx through the temporarily active Wadi Rabigh, hydrological regime, and the autochthonous biogenic sedimentation, and to a lesser extent rare anthropogenic influence.
2. Minerals of detrital origin (quartz, k-feldspars, plagioclase, and amphiboles) and highly enriched in the nearshore shallow areas of the southern sector of the lagoon at the mouth of Wadi Rabigh, whereas carbonate minerals (aragonite, high and low Mg-calcite) dominate the marine-influenced northern sector.
3. Factor analysis distinguished two factors and allowed the subdivision of Al-Kharrar Lagoon bottom sediments geochemically into three geochemical groups. The first factor is characterized by positive loadings of lithogenic elements and negative values of variables linked to carbonate minerals. This factor records high concentrations of siliciclastic-related oxides and trace elements as well as high concentrations of carbonate-related elements. The second factor is characterized by positive loadings of Cu and P_2O_5 which have no relationship with the groups of the first factor. Statistical analysis has allowed the identification of two main groups of sediments.
4. The lithogenic-related oxides (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O, and K_2O) and trace elements (V, Cr, Ni, Zn, Rb, and Ba) are enriched in the southern sector near the head of the lagoon. The spatial distribution patterns reveal that lithogenous sediments settled rapidly mostly near the Wadi mouth, and the sediments are restricted to the shallow area and not transported far into the deeper parts of the lagoon due to the low flow conditions.
5. The carbonate-related oxides (CaO) and trace element (Sr) are significantly enriched in the northern sector where autochthonous shell fragments are the main source of carbonates.
6. The levels of heavy metals are generally below the recommended allowable limits and the lagoon is in good ecological condition. The EF values of Cu show a local slight enrichment supporting a possible anthropogenic source. However, there has currently no clear evidence of heavy metal contamination by anthropogenic sources in the Al-Kharrar Lagoon.
7. The obtained data are of particular significance providing a base to monitor any future environmental deterioration associated with development and urbanization.

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References

1. Morton, R.A.; Ward, G.H.; White, W.A. Rates of sediment supply and sea-level rise in a large coastal lagoon. *Mar. Geol.* **2000**, *167*, 261–284. [CrossRef]
2. Forrest, B.M.; Creese, R.G. Benthic impacts of intertidal oyster culture, with consideration of taxonomic sufficiency. *Environ. Monit. Assess.* **2006**, *112*, 159–176. [CrossRef]
3. Abidi, M.; Amor, R.; Gueddari, M. Assessment of the Trophic Status of the South Lagoon of Tunis (Tunisia, Mediterranean Sea): Geochemical and Statistical Approaches. *J. Chem.* **2018**, *2018*, 1–17. [CrossRef]
4. Benoit, J.M.; Gilmour, C.C.; Mason, R.P.; Heyes, A. Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. *Environ. Sci. Techol.* **1999**, *33*, 1780. [CrossRef]
5. Pérez-Ruzafa, A.; Marcos, C.; Pérez-Ruzafa, I.M.; Pérez-Marcos, M. Are coastal lagoons physically or biologically controlled ecosystems? Revisiting r vs. K strategies in coastal lagoons and estuaries. *Estua. Coast. Shelf Sci.* **2013**, *132*, 17–33. [CrossRef]
6. Arcega-Cabrera, F.; Garza-Pérez, R.; Noreña-Barroso, E.; Oceguera-Vargas, I. Impacts of geochemical and environmental factors on seasonal variation of heavy metals in a coastal lagoon Yucatan, Mexico. *Bull. Environ. Contam. Toxico.* **2015**, *94*, 58–65. [CrossRef]
7. Förstner, U.; Ahlf, W.; Calmano, W. Studies on the transfer of heavy metals between sedimentary phases with a multi-chamber device: Combined effects of salinity and redox variation. *Mar. Chem.* **1989**, *28*, 145–158. [CrossRef]
8. Yu, K.C.; Tsai, L.J.; Chen, S.H.; Ho, S.T. Correlation analyses on binding behavior of heavy metals with sediment matrices. *Water Res.* **2001**, *35*, 2417–2428. [CrossRef]
9. Karageorgis, A.P.; Anagnostou, C.L.; Kaberi, H. Geochemistry and mineralogy of the NW Aegean Sea surface sediments: Implications for river runoff and anthropogenic impact. *Appl. Geochem.* **2005**, *20*, 69–88. [CrossRef]
10. Ahmed, F.; Bibi, M.H.; Seto, K.; Ishiga, H.; Fukushima, T.; Roser, B.P. Abundances, distribution, and sources of trace metals in Nakaumi–Honjo coastal lagoon sediments, Japan. *Environ. Monit. Assess.* **2010**, *167*, 473–491. [CrossRef]
11. Rasul, N.M. Lagoon sediments of the Eastern Red Sea: Distribution processes, pathways and patterns. In *The Red Sea*; Springer: Berlin/Heidelberg, Germany, 2015; pp. 281–316.
12. Basaham, A.S.; Ghandour, I.M.; Haredy, R. Controlling factors on the geochemistry of Al-Shuaiba and Al-Mejarma coastal lagoons, Red Sea, Saudi Arabia. *Open Geosci.* **2019**, *11*, 426–439. [CrossRef]
13. Basaham, A.S. Mineralogical and chemical composition of the mud fraction from the surface sediments of Al-Kharrar, a Red Sea coastal lagoon. *Oceanologia* **2008**, *50*, 557–575.
14. Abu-Zied, R.H.; Al-Mur, B.A.; Orif, M.I.; Al Otaibi, A.; Ghandourah, M.A. Concentration distribution, enrichment and controlling factors of metals in Al-Shuaiba Lagoon sediments, Eastern Red Sea, Saudi Arabia. *Environ. Earth Sci.* **2021**, *80*, 1–20. [CrossRef]
15. Basaham, A.S.; El Sayed, M.A.; Ghandour, I.M.; Masuda, H. Geochemical background for the Saudi Red Sea coastal systems and its implication for future environmental monitoring and assessment. *Environ. Earth Sci.* **2015**, *74*, 4561–4570. [CrossRef]
16. Ghandour, I.M.; Basaham, S.; Al-Washmi, A.; Masuda, H. Natural and anthropogenic controls on sediment composition of an arid coastal environment: Sharm Obhur, Red Sea, Saudi Arabia. *Environ. Monit. Assess.* **2014**, *3*, 1465–1484. [CrossRef]
17. Youssef, M.; El-Sorogy, A. Environmental assessment of heavy metal contamination in bottom sediments of Al-Kharrar lagoon, Rabigh, Red Sea, Saudi Arabia. *Arab. J. Geosci.* **2016**, *9*, 474. [CrossRef]
18. Ghandour, I.M.; Aljahdali, M.H. Elemental Enrichment in Shallow Subsurface Red Sea Coastal Sediments, Al-Shuaiba, Saudi Arabia: Natural vs. anthropogenic Controls. *Minerals* **2021**, *11*, 898. [CrossRef]
19. Abou-Ouf, M.A. Variation of benthic foraminiferal assemblages in different microenvironments along the shore zone north of the Rabigh Coast, eastern Red Sea, Saudi Arabia. *Neues Jahrbuch für Geologie und Paläontologie-Monatshefte* **1996**, *9*, 129–139. [CrossRef]
20. Al-Washmi, H.A. Sedimentological aspects and environmental conditions recognized from the bottom sediments of Al-Kharrar Lagoon, eastern Red Sea coastal plain, Saudi Arabia. *J. King Abdulaziz Univ. Mar. Sci.* **1999**, *10*, 71–87. [CrossRef]
21. Hariri, M.S. Effect of hydrographic conditions on the ecology of benthic foraminifera in two different hypersaline lagoons, eastern Red Sea coast, Kingdom of Saudi Arabia. *J. King Abdulaziz Univ. Mar. Sci.* **2008**, *19*, 3–13. [CrossRef]
22. Al-Barakati, A.M.A. Application of 2-D tidal model, Shuaiba Lagoon, eastern Red Sea coast. *Can. J. Comput. Math. Nat. Sci. Med.* **2010**, *1*, 9–20.
23. Hariri, M.S.; Abu-Zied, R.H. Factors influencing heavy metal concentrations in the bottom sediments of the Al-Kharrar Lagoon and Salman Bay, eastern Red Sea coast, Saudi Arabia. *Arab. J. Geosci.* **2018**, *11*, 1–20. [CrossRef]
24. Al-Dubai, T.A.; Bantan, R.A.; Abu-Zied, R.H.; Al-Zubieri, A.G.; Jones, B.G. Distribution of Benthic Foraminifera in Intertidal Sabkha of Al-Kharrar Lagoon, Saudi Arabia: Tools to Study Past Sea-Level Changes. *Front. Mar. Sci.* **2022**, *351*. [CrossRef]
25. Al-Barakati, A.M.; Ahmad, F. Water column conditions in a coastal lagoon near Jeddah, Red Sea. *Oceanologia* **2012**, *54*, 675–685. [CrossRef]
26. Lisitzin, E. *Sea-Level Changes*; Elsevier Sci. Publ. Co.: Amsterdam, The Netherlands; Oxford, UK; New York, NY, USA, 1974.
27. Al-Dubai, T.A.; Abu-Zied, R.H.; Basaham, A.S. Present environmental status of Al-Kharrar Lagoon, central of the eastern Red Sea coast, Saudi Arabia. *Arab. J. Geosci.* **2017**, *10*, 305. [CrossRef]
28. Hardy, R.; Tucker, M.E. *Techniques in Sedimentology*; Blackwell Scientific Publications: Hoboken, NJ, USA, 1988; pp. 191–228.
29. Moore, D.M.; Reynolds, R.C., Jr. *X-ray Diffraction and the Identification and Analysis of Clay Minerals*; Oxford University Press: New York, NY, USA, 1989.

30. Tawfik, H.A.; Ghandour, I.M.; Maejima, W.; Armstrong-Altrin, J.S.; Abdel-Hameed, A.M. Petrography and geochemistry of the siliciclastic Araba Formation (Cambrian), east Sinai, Egypt: Implications for provenance, tectonic setting and source weathering. *Geol. Magaz.* **2017**, *154*, 1–23. [CrossRef]

31. Haredy, R.; Ghandour, I.M. Geochemistry and mineralogy of the shallow subsurface Red Sea coastal sediments, Rabigh, Saudi Arabia: Provenance and paleoenvironmental implications. *Turk. J. Earth Sci.* **2020**, *29*, 257–279. [CrossRef]

32. Covelli, S.; Fontolan, G. Application of a normalization procedure in determining regional geochemical baseline. *Environ. Geol.* **1997**, *30*, 34–35. [CrossRef]

33. Sutherland, R.A. Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environ. Geol.* **2000**, *39*, 611–627. [CrossRef]

34. Calvert, S.E. The mineralogy and geochemistry of nearshore sediments. In *Chemical Oceanography*; Riley, J.P., Chester, R., Eds.; Academic Press: London, UK, 1976; Volume 6, pp. 187–280.

35. Loring, D.H.; Rantala, R.T. Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth-Sci. Rev.* **1992**, *32*, 235–283. [CrossRef]

36. Mil-Homens, M.; Vale, C.; Raimundo, J.; Pereira, P.; Brito, P.; Caetano, M. Major factors influencing the elemental composition of surface estuarine sediments: The case of 15 estuaries in Portugal. *Mar. Poll. Bull.* **2014**, *84*, 135–146. [CrossRef]

37. Calvert, S.E.; Pedersen, T.F.; Thunell, R.C. Geochemistry of the surface sediments of the Sulu and South China Seas. *Mar. Geol.* **1993**, *114*, 207–231. [CrossRef]

38. Taylor, G.; Eggleton, R.A. *Regolith Geology and Geomorphology*, 1st ed.; John Wiley and Sons: Hoboken, NJ, USA, 2001.

39. Lejon, D.P.; Martins, J.M.; Lévêque, J.; Spadini, L.; Pascault, N.; Landry, D.; Milloux, M.J.; Nowak, V.; Chaussod, R.; Ranjard, L. Copper dynamics and impact on microbial communities in soils of variable organic status. *Environ. Sci. Technol.* **2008**, *42*, 2819–2825. [CrossRef]

40. He, Z.L.; Yang, X.E.; Stoffella, P.J. Trace elements in agroecosystems and impacts on the environment. *J. Trace Elements Medic. Biol.* **2005**, *19*, 125–140. [CrossRef]

41. Ruiz-Fernández, A.C.; Frignani, M.; Hillaire-Marcel, C.; Ghaleb, B.; Arvizu, M.D.; Raygoza-Viera, J.R.; Páez-Osuna, F. Trace metals (Cd, Cu, Hg, and Pb) accumulation recorded in the intertidal mudflat sediments of three coastal lagoons in the Gulf of California, Mexico. *Estu.Coast.* **2009**, *32*, 551–564. [CrossRef]

42. Avramidis, P.; Barouchas, P.; Dünwald, T.; Unkel, I.; Panagiotaras, D. The influence of olive orchards copper-based fungicide use, in soils and sediments-The case of Aetoliko (Etoliko) Lagoon Western Greece. *Geosciences* **2019**, *9*, 267. [CrossRef]

43. Adriano, D.C.; Wenzel, W.W.; Vangronsveld, J.; Bolan, N.S. Role of assisted natural remediation in environmental cleanup. *Geoderma* **2004**, *122*, 121–142. [CrossRef]

44. Badassan, T.E.; Avumadi, A.M.; Ouro-Sama, K.; Gnandi, K.; Jean-Dupuy, S.; Probst, J.L. Geochemical Composition of the Lomé Lagoon Sediments, Togo: Seasonal and Spatial Variations of Major, Trace and Rare Earth Element Concentrations. *Water* **2020**, *11*, 3026. [CrossRef]

45. Huo, S.; Xi, B.; Yu, X.; Su, J.; Zan, F.; Zhao, G. Application of equilibrium partitioning approach to drive sediment quality criteria for heavy metals in a shallow eutrophic lake, Lake Chaohu, China. *Environ. Earth Sci.* **2013**, *69*, 2275–2285. [CrossRef]

46. Nizoli, E.C.; Luiz-Silva, W. Seasonal AVS–SEM relationship in sediments and potential bioavailability of metals in industrialized estuary, southeastern Brazil. *Environ. Geochem. Health* **2012**, *34*, 263–272. [CrossRef]

47. Zhang, C.; Yu, Z.G.; Zeng, G.M.; Jiang, M.; Yang, Z.Z.; Cui, F.; Zhu, M.Y.; Shen, L.Q.; Hu, L. Effects of sediment geochemical properties on heavy metal bioavailability. *Environ. Int.* **2014**, *73*, 270–281. [CrossRef]

48. Guigue, J.; Mathieu, O.; Lévêque, J.; Denimal, S.; Steinmann, M.; Milloux, M.J.; Grisey, H. Dynamics of copper and zinc sedimentation in a lagooning system receiving landfill leachate. *Waste Manag.* **2013**, *33*, 2287–2295. [CrossRef]

49. Almahasheer, H.; Serrano, O.; Duarte, C.M.; Irigoien, X. Remobilization of heavy metals by mangrove leaves. *Front. Mar. Sci.* **2018**, *13*, 484. [CrossRef]