A Follow-up Assessment Of Heavy Metal Pollution Recorded In Scleractinian Corals In Southern Red Sea, Hodeidah, Yemen

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presented by

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Aims of the study

1. To assess the current levels of heavy metal pollution recorded in scleractinian corals in two harbors (Al-Luhaya and Al-Saleef), southern Red Sea, Hodeidah, Yemen.
2. To determine the potential effects of the current military activities in these areas, which was investigated eight years ago before the political conflict has been started.

Heavy metal pollution in marine ecosystem:

The effects of these heavy elements start once they have been released into the aquatic environment
They can incorporate, accumulate into the food chain and cause lethal effects.
Their riskiness comes from their toxicity, and they are non-biodegradable

Essential heavy metals [Fe, Mn, Zn, Cr, Cu, and S]

- They are vital components of enzymes, respiratory proteins, and certain structural elements of all living organisms.
- If their concentrations in living organisms reach above certain threshold concentrations, they are potentially toxic to both humans and aquatic biota

Non-essential heavy elements [Al, Ba, Cd, Co, Ni, Pb, V and Sr]

- They do not play physological role.
- They are often toxic even in small quantity (Nordberget al. 2007).

Scleractinian corals are good indicators of environmental pollution

1. They are sedentary, and good representive of the surrounding area.
2. Abundant, common , widespread in marine ecosystem.
3. Accumulate the pollutants to a certain level without being executed.
4. Sufficient long lived.
5. Having chronological bands make them a good pollution archive.

Our previous study

1. The pollution level in selected areas was studied eight years ago (April, 2015) and the heavy metal measurements accordingly with descriptive statistical analysis as well as the pollution loading index proved the areas were unpolluted.
2. **Now** a follow up research is an urge to be conducted in order to assess the pollution level in the selected areas, hence these areas are a hot political conflict and under military activities

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Status of the Coastal Marine Environment in the Southern Red Sea, Yemen, as Reflected by Elements Accumulated in the Skeletons of Scleractinian (Stony) Corals

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Abstract
The purpose of this study was to assess the level of anthropogenic contamination as well as to collect more data concerning the mineral composition of scleractinian corals from Southern Red Sea, Hodeidah Governorate, Yemen. The mass fractions of 31 elements were determined in the skeleton of nine coral colonies collected in the vicinity of the south-western coast of Yemen. All measurements were conducted by Instrumental Neutron Activation Analysis (INAA). The final results concerning the distribution of considered elements were comparable and, in some cases, inferior to those reported worldwide. The determined mass fractions of V, Cr, Mn, Fe, Ni, and Zn as Presumably Contaminating Elements (PCE) together with the mass fractions of the same elements previously reported in the literature regarding Red Sea Pleistocene corals permitted calculating the individual Contamination Factor (*CF*) and collective Pollution Load Index (*PLI*). In spite of high mass fraction values of Mn and Fe in only a few coral colonies, for all investigated places, the *PLI* values corresponding to studied areas were less than unit, suggesting the investigated areas could be considered as uncontaminated.

Marine ecosystems are under increased anthropogenic stress, especially in the vicinity of ports, nearshore mining industrial entities or chemical plants, along busy shipping lines, great human agglomeration, or as a result of local wars (Dicks, 1984; Fowler et al., 1993; Kennish, 1994; Saadoun, 2015; Fitt, 2021). These could be added steady increasing urbanization of its shores which represents an extra source of contamination (El Nemr and El-Said, 2014; Nour and Nouh, 2020).

Among marine organisms, corals showed the be one of the most sensitive organisms to environment alteration, and, due to their hard exoskeleton and low growth rate, good tracer of sea contamination (Dodge and Gilbert, 1984; Scott, 1990; Guzman and Jimnez, 1992; Ramos et al., 2004; Al-Rousan et al., 2007; Anu et al., 2007). Corals, as sedentary organisms, accumulate various pollutants from the marine environment, furnishing in this way, reliable information concerning the local contamination processes (Butler et al., 1970). For this reason, their exoskeleton could be regarded as a true historical archive of the marine environment, especially as their growth rate, driven by seawater temperature, presents a periodical variation of skeleton density with a one-year periodicity, similar to tree rings (Lough and Barnes, 2000). Therefore, a significant number of studies were devoted to this category of bio-indicators on short (Loya, 1975; Ramos et al., 2004; Sabdono, 2009; Gopinath et al., 2010; Kumar et al., 2010; Nour and Nouh, 2020) as well as on long term marine environment contamination (Hanna and Muir, 1990; Carilli et al., 2009; Kumar et al., 2010; Inoue et al., 2014). In what concerns the Red Sea, the majority of

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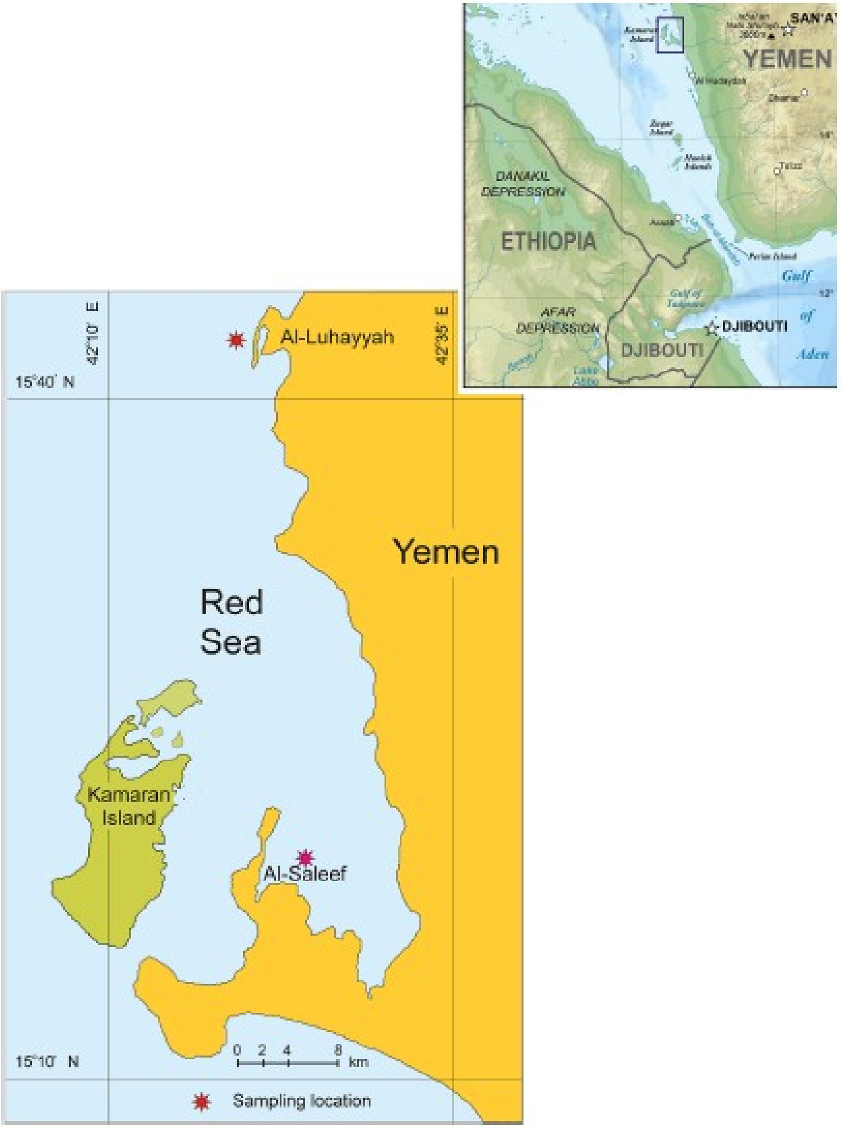
The study areas

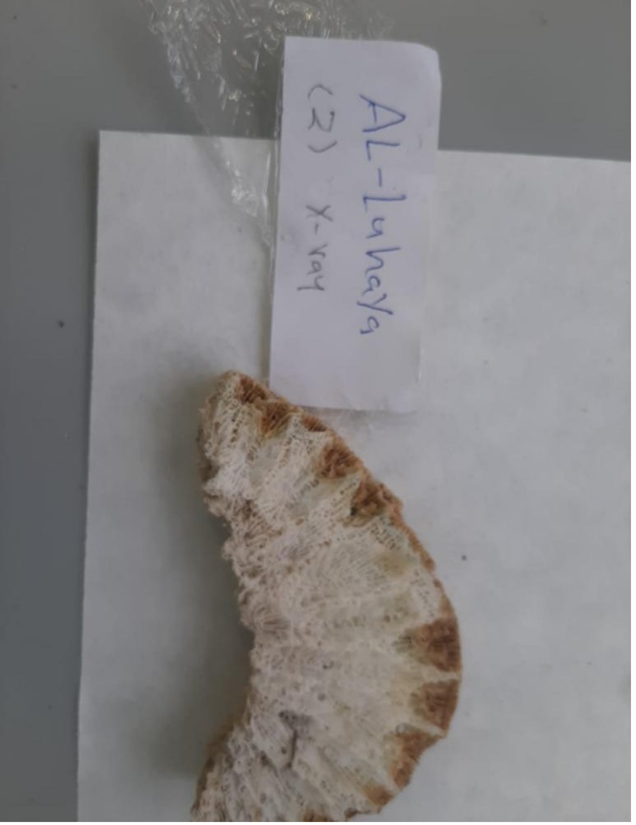
- We have chosen these areas, as they are two important harbors in the south of the Red Sea.

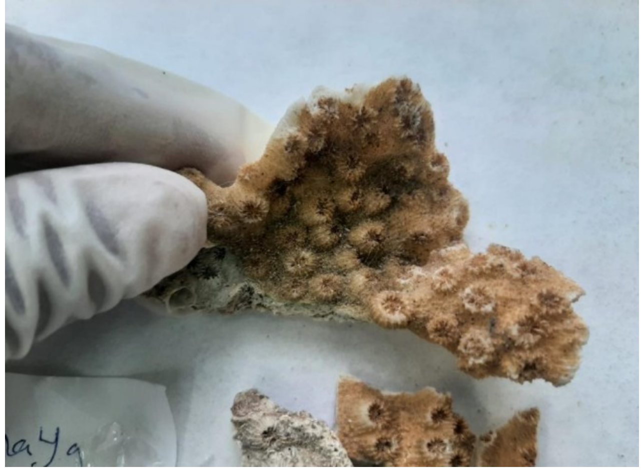
1. Al-Saleef harbor (15.3172197° N 42.6748505°E) specialized in the production and export of salt.
2. Al-Luhya harbor (15°42’ N, 42°41’ E), was previously specialized in exporting coffee, but now it is specialized only in some limited navigation operations.

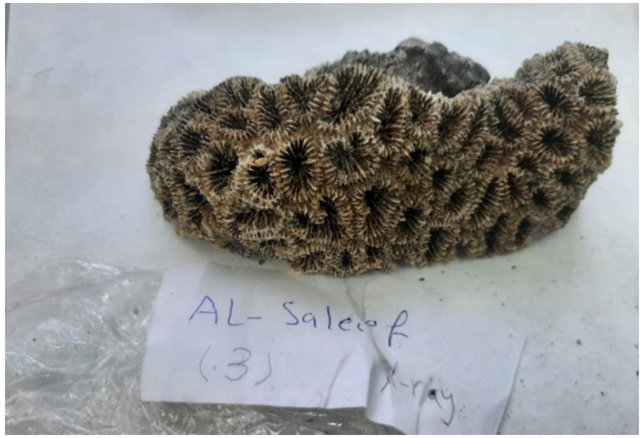


Al-Luhaya

Al-Saleef







Samples preparation

- Samples were collected by scuba diver manually at the depth between 5 and 10 m.
- The living part were cut using stain steel knife.
- All samples were washed by sea water, put into

  plastic bags, sun dried, and transferred to Cairo, Egypt.
- A slab was cut from each sample and a sub-samples were sent to Frank Laboratory, Joint Institute for Nuclear Research (INR), Dubna, (Russian Federation) for ICP-AOS analysis.

ICP-OES Measurements

Ten coral samples were measured using inductively coupled plasma optical emission spectroscopy at frank Laboratory

ICP-OES analysis

- Coral samples were dried and homogenized.
- 0.5 g of samples were placed in Teflon vessels and digested with 5 mL of trace pure HNO3 (Sigma-Aldrich, Germany) and 2 mL H2O2 p.a.
- The digestion was performed at 180 ºC in Mars 6 microwave digestion system (CEM, USA).
- After cooling, the digested samples were quantitatively transferred into 50 ml flasks.
- Content of Al, Ba, Co, Cd, Cr, Cu, Fe, Mn, P, Pb, Sr, S, V and Zn was determined using ICP-OES PlasmaQuant 9000 Elite (Analytik Jena, Germany.
- The calibration solutions were prepared from IV-STOCK-27 (Inorganic Ventures, USA) standard solution.
- All control standards were analyzed after every 10 samples.
- The recovery of the majority of elements from the reference material ranged from 90% to 105%.
- Quality control of the measurement was ensured by analysis of reference material Oriental Basma Tobacco Leaves (INCT-OBTL-5).

➤ Al-Luhaya harbor

The Preliminary observations in (µg/g) showed the order of the trace elements in the samples from Al-Luhaya harbor is Al> Fe > Ba> Mn> Zn> V> Cu> Ni> Cr> Cd> Pb> Co

Species	Al	Ba	**Cd**	Co	Cr	Cu	Fe	Mn	Ni	**Pb**	S	Sr	V	Zn
pirobranchus kraussii	224.25	24.34	0.27	0.17	0.51	0.92	173.14	8.01	0.70	0.12	2374.18	1187.58	0.67	1.26
Favites abdita	177.92	37.09	0.12	0.12	0.38	0.67	150.68	2.66	0.53	0.19	2915.55	1193.15	0.61	0.91
Porites pukoensis	927.94	18.47	1.18	0.11	1.67	0.50	**614.04**	7.76	0.69	0.33	4696.62	1333.19	4.77	2.75
Porites lobata	37.78	24.19	0.94	0.16	0.19	0.60	28.75	7.00	0.74	0.21	2816.84	1567.32	0.37	2.95
Echinopora lamellosa	17.07	24.68	0.15	0.15	0.10	0.82	7.84	8.37	0.56	0.22	2215.10	1317.65	0.11	1.38

➢ Al-Saleef harbor

The Preliminary observations showed the order of the trace elements in the samples from Al-Luhaya harbor is Al> Fe> Ba> Mn> Zn> V> Ni> Cu> Cr> Pb> Co> Cd.

Species	Al.	Ba.	Cd	Co.	Cr	Cu	Fe.	Mn	Ni	Pb	S	Sr	V	Zn
Favites abdita	443.05	42.97	0.69	0.92	0.87	1.63	312.33	17.72	3.54	0.36	2754.83	1567.32	1.25	5.61
Acropora Spp	406.53	9.97	0.12	0.17	1.20	0.59	277.94	5.92	0.50	0.85	2380.52	1574.13	0.91	3.55
Pocillopora damicornis	810.87	10.48	0.02	0.12	1.49	0.52	513.26	8.15	0.50	0.49	3044.15	1520.99	1.41	1.86
Porites fontanesii	50.45	285.90	0.10	0.20	0.24	1.03	28.86	12.97	0.80	0.34	3047.10	1495.89	0.20	8.23
Echinopora gemmacea	8.68	13.14	0.11	0.43	0.11	0.88	33.19	11.78	1.10	0.20	2065.96	1054.09	0.58	5.40

Comparisons between the current mean concentrations of heavy elements and the mean concentrations in the previous study in both sites.
Table (1) Al-Luhaya
Table(2) Al-Saleef

Year	Al	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	S	Sr	V	Zn
2021	276.99±374.5	25.75±6.84	0.533 ± 0.49	0.14±0.03	0.57±0.63	0.70±0.17	194.89±245.31	6.760±2.35	0.64±0.09	0.22±0.08	3003.66±990.8	1319.78±154.09	1.31±1.75	1.85±0.93
2015	143±25	61.60±71.89		0.045±0.01	1.50±0.70		51±29	1.2±0.20	0.31±0.08			5460±785.81	0.735±0.17	2.7±1.76
	Al=2Pre.	Ba=3Pre.		Co=2Pre.	Cr=1/2Pre.		Fe=4Pre.	Mn=6Pre.	Ni=2Pre.			Sr=2Pre.	V=2Pre.	Zn=2/3Pre.

Year	Al	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	S	Sr	V	Zn
2021	343.92±327.99	72.49±120.09	0.21±0.27	0.368±0.33	0.78±0.60	0.93±0.44	233.116±205.22	11.31±4.56	1.289±1.28	0.45±0.25	2658.511±429.4	1442.48±219.53	0.87±0.49	4.93±2.39
2015	277±65	6.6±5.28		0.188±0.12	1.09±0.50		103±32.00	6.8±9.20	0.66±0.13			4460±1021.22	0.458±0.28	1.6±0.80
	Al=Pre.	Ba=14Pre.		Co=2Pre.	Cr=Pre.		Fe=2Pre.	Mn=Pre.	Ni=2Pre.			Sr=2Pre.	V=Pre.	Zn=3Pre.

Possible heavy elements anthropogenic pollution sources:

Oil fuel → Co, Pb, Ni, V, (Amani Badawi, et.al, 2021, Abdo, et.al, 2022, WHO,1996)

Marine pigments → Cd, Co, Cr, Ni, (Amani Badawi, et.al, 2021, Jaishankar M,2014)

Anti-fouling paint for boat hulls → Cu, Ni (Frances Solomon, 2009)

Detergents → Cd (Gautam et al. 2014)

Detritus from man coastal activities and old sunken bouts, Pipeline, and solid wastes → Fe, Ba, Mn (Abdo, et.al, 2022, Amani Badawi, et.al, 2021)

Sewage → Zn ,Ni , (Cempel M, 2006).

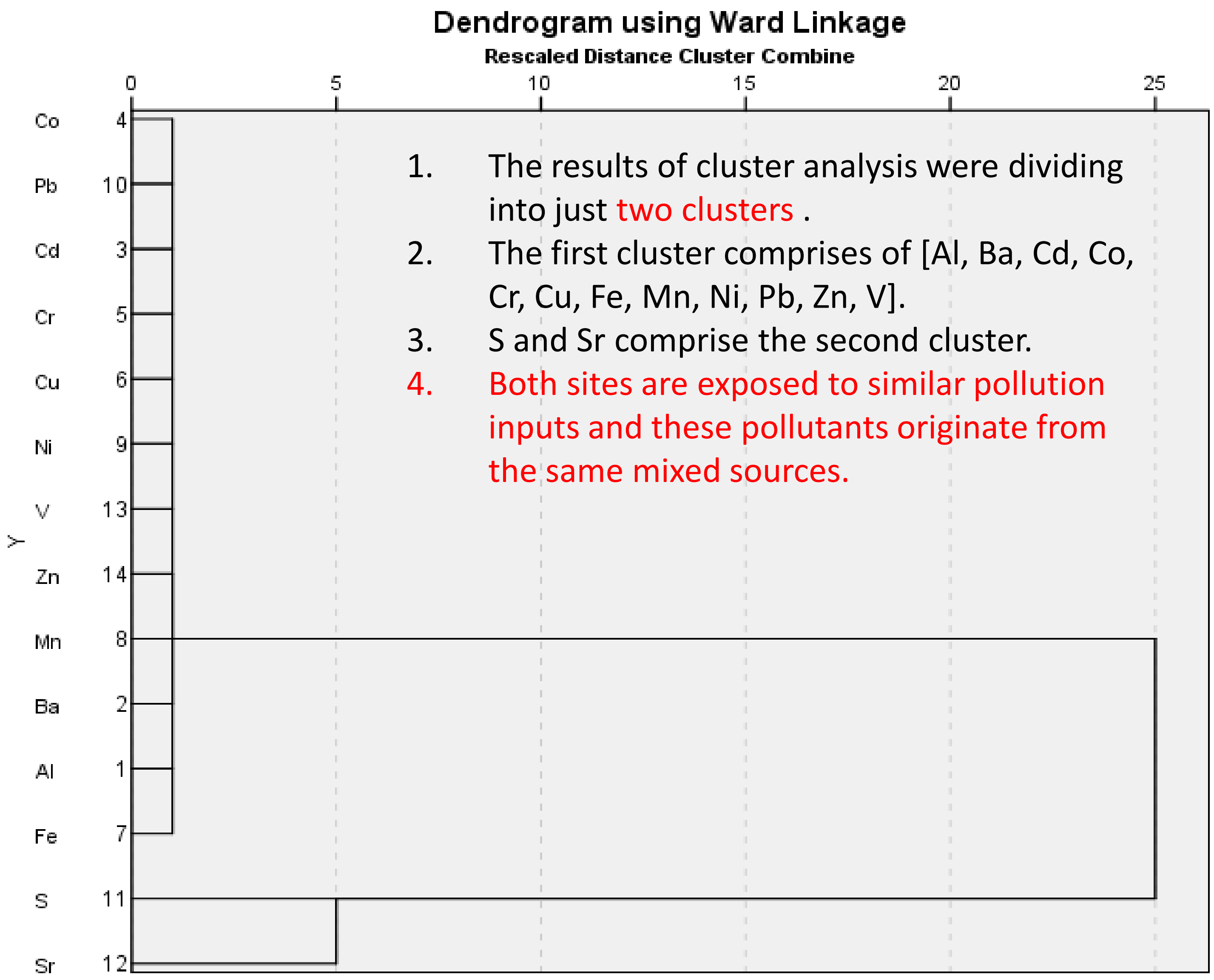
Correlation analysis

		Al	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	S	Sr	V	Zn
Al	Pearson Correlation	1													
	Sig. (2-tailed)														
Ba	Pearson Correlation	-.301	1												
	Sig. (2-tailed)	.398													
Cd	Pearson Correlation	.358	-.197	1											
	Sig. (2-tailed)	.310	.585												
Co	Pearson Correlation	-.045	-.009	.155	1										
	Sig. (2-tailed)	.903	.980	.669											
Cr	Pearson Correlation	.976**	-.297	.299	-.063	1									
	Sig. (2-tailed)	.000	.405	.402	.863										
Cu	Pearson Correlation	-.260	.305	-.006	.885**	-.286	1								
	Sig. (2-tailed)	.469	.392	.987	.001	.422									
Fe	Pearson Correlation	.997**	-.327	.367	-.018	.973**	-.240	1							
	Sig. (2-tailed)	.000	.357	.297	.961	.000	.504								
Mn	Pearson Correlation	-.044	.363	.112	.829**	-.080	.843**	-.048	1						
	Sig. (2-tailed)	.905	.303	.757	.003	.827	.002	.895							
Ni	Pearson Correlation	.057	.017	.288	.975**	.023	.884**	.081	.810**	1					
	Sig. (2-tailed)	.876	.962	.420	.000	.949	.001	.824	.005						
Pb	Pearson Correlation	.428	-.044	-.170	-.020	.598	-.190	.412	-.049	-.040	1				
	Sig. (2-tailed)	.217	.903	.639	.957	.068	.599	.237	.892	.913					
S	Pearson Correlation	.714*	.102	.660*	-.217	.639*	-.299	.709*	-.097	-.065	.037	1			
	Sig. (2-tailed)	.020	.780	.038	.547	.047	.402	.022	.790	.858	.919				
Sr	Pearson Correlation	.284	.211	.233	.146	.367	.090	.245	.219	.248	.617	.176	1		
	Sig. (2-tailed)	.427	.559	.518	.687	.296	.804	.496	.543	.489	.058	.627			
V	Pearson Correlation	.834**	-.247	.655*	-.073	.781**	-.273	.844**	-.045	.026	.142	.877**	.012	1	
	Sig. (2-tailed)	.003	.492	.040	.842	.008	.445	.002	.901	.943	.695	.001	.974		
Zn	Pearson Correlation	-.211	.716*	-.013	.491	-.171	.532	-.221	.742*	.437	.169	-.016	.268	-.121	1
	Sig. (2-tailed)	.559	.020	.971	.150	.636	.114	.540	.014	.207	.641	.966	.454	.740	

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

1. The table shows heavy elements pairs significantly correlated with each other examples: [Al,Cr],[Al,Fe] [Cr,Fe] which may signify that each paired elements has identical source or common sink in the marine sediments.
2. The rest of elemental pairs show no significant correlation with each other, which indicate that they might have different anthropogenic and natural sources.



1. The results of cluster analysis were dividing into just two clusters .
2. The first cluster comprises of [Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, V].
3. S and Sr comprise the second cluster.
4. Both sites are exposed to similar pollution inputs and these pollutants originate from the same mixed sources.

Pollution Load Index

- Pollution load index (PLI) helps determining the magnitude of heavy metal contamination in given samples, according to Tomilson et al. (1980),
- Pollution load Index =(CF1*CF2 *.....* CFn) ^1/n Where, n is the number of metals (eight in the present study, which are Zn, Pb, Mn, Fe, Cr, Co, Ni, Cu, and CF is the contamination factor.
- if PLI value < 1 indicates unpolluted area, where as PLI >1 indicates polluted area.

Results:

- PLI= 0.12 for Al-Luhaya harbor and 0.22 for Al-Saleef harbor.
- Both PLI values < 1, consequently both harbors are found to be unpolluted

❑ Conclusion

1. The final outcomes of this study proved that there is a remarkable increase in the studied heavy elements concentrations during the past eight years especially for Fe, Mn, Co,Ni.
2. However, pollution loading index is still within the normal range for all elements.
3. Descriptive statistical methods we used, clustering, correlations show mixed different pollution sources.

Recommendations

Very recent studies, literatures reviews and conferences, all demand for toxicity thresholds of chemical pollutants for corals (Eileen M. Nalley et.al 2021), and (Dakis-Yaoba Ouedraogo et.al 2023) .

A need for standardized guidelines (cut-off level) for coral pollution similar to the regulations established for freshwater sediments (David Batts and Jim Cubbage,1995).

A Continued tracking of the anthropogenic sources of these heavy elements since there is an elevation in their concentrations in the aquatic ecosystem.

Regular monitoring and clearing of the solid pollutants on the beach.

Thank you