



Soil Heavy Metal Pollution and the Associated Toxicity Risk Assessment in Ajdabiya and Zueitina, Libya

Mohamed Hamid Bahnasawy¹, Mohammed Ali Zeyadah², Ahmed M. Deedah³, Hamad M. Adress Hasan⁴ and Doaa A. El-Emam²

¹Zoology Department, Faculty of Science, Damietta University, New Damietta, Egypt. ²Environmental Science Department, Faculty of Science, Damietta University, New Damietta, Egypt. ³Environmental and Natural resource Science, Omar Al-Mukhtar University, Libya.

⁴Chemistry Department, Omar Al-Mukhtar University, Libya.

Received: 18 November 2023 /Accepted: 01 January 2024

*Corresponding author's E-mail: doaa_elemam17@yahoo.com

Abstract

This study provides a comprehensive assessment of the potential adverse effects on the environment and human health arising from introducing chemicals from one of the principal petrochemical complexes in Libyan districts of Ajdabiya and Zueitina. Mathematical models utilized to assess heavy metal indices, such as the contamination factor (CF), enrichment factor (EF), degree of contamination (DC), pollution load index (PLI), and geo-accumulation index (I_{geo}). The study's conclusions showed that the concentrations of heavy metals in the sediment samples showed the following pattern: iron > lead > cobalt >cadmium> copper. Each heavy metal element's enrichment factor (EF) was calculated by contrasting it with the background values, which were normalised using the Fe element. Based on the mean values of enrichment factors (EFs), the heavy metals in the sediments exhibited the following descending order of enrichment: iron >lead >cadmium > copper >cobalt, arranged from highest to lowest. iron (Fe) was found to exhibit substantial to extremely high levels of contaminant across various stations within the study area. Furthermore, I_{geo} values were also seen in the below order: iron (Fe) > lead (Pb) > cobalt (Co) > copper (Cu) > cadmium (Cd). The research area's soil may include heavy metal pollution, which might have both carcinogenic and non-carcinogenic effects, according to the health risk assessment (HRA).

Keywords: Heavy Metals, Health Risk Assessment, Toxicity, Contamination Factor, Sediments, Petroleum Industry.

Introduction

The country of Libya covers an area of

approximately 1.7 million square kilometers. 90% of the people live mainly on less than 5% of the coastal land. Population density in the central and south of the country is less than 1 km² (Almaktar, and Shaaban, 2021). This low

population density in the central and southern regions of Libya is primarily due to the arid desert conditions and lack of infrastructure, making it difficult for people to settle in these areas. However, the coastal regions with higher population density benefit from access to resources such as water and transportation, which support human habitation and economic activities (Zurqani et al. (2019); Zeyadah et al., (2023)).

Libya contains several oil companies affiliated with the National Oil Corporation. The largest of these oil-producing companies is the Waha Company (WOC), followed by the Arabian Gulf Oil Company (Agoco), the Zueitina Oil Company (ZOC), and the Sirte Oil Company (SOC), which represents the oil sector. Libyan gas is more than 70% of GDP, more than 95% of exports, and about 90% of government revenue (Kalifa et al. 2020). The production of oil and gas has the potential to contaminate the soil. water, and air. Additionally, heavy metals are regarded as one of the most significant pollutants since the development of industry has increased pollution and the amount of pollutants released into the environment overall. Distribution networks may also contribute to pollution, particularly when underground storage tanks at petrol stations and other distribution locations, factories, and residential buildings leak (Ulakpa et al. 2022).

Heavy metals are naturally occurring metals with a large atomic weight and density five times greater than water. The heavy metals include lead (Pb), cadmium (Cd), arsenic (AS), chromium (Cr), thallium (Ti), and mercury (Hg). They are natural components of the Earth's crust, and the proportions of these minerals have increased during industrial waste, agricultural activity, and mining. Furthermore, the production of these hazardous compounds of heavy metals is thought to be mostly sourced from the petrochemical industry (Hasaballah et al. (2019); El-Emam, (2020); Hasaballah et al. (2023); El-Alfy, et al. (2024)).

Environmental assessment of the oil and gas industry is one of the most important contemporary environmental issues. It is well known that this business releases a substantial quantity of heavy metals into the environment throughout several procedures including drilling, extraction, and transportation. (Ji and Wang, 2021). These heavy metals can have detrimental effects on ecosystems and human

health, making it crucial to closely monitor and regulate the environmental impact of the oil and gas industry. Additionally, finding sustainable alternatives to reduce heavy metal emissions from this industry is a pressing concern for mitigating its environmental footprint (Hosseinzadeh-Bandbafha et al. 2024).

The present study focuses on the analysis of heavy metal variation in the soil and the subsequent ecological risk assessment during the year of 2022 in the regions of Ajdabiya and Zueitinain Libya. Soil heavy metal content and the associated toxicity risk assessment are crucial for understanding the potential environmental impacts on these regions. By analyzing the levels of heavy metals such as lead, cadmium, and mercury in the soil, researchers can evaluate the extent of contamination and assess the potential risks to human health and ecosystems. Additionally, this assessment can help identify potential sources of heavy metal pollution, enabling policymakers to implement effective mitigation strategies to safeguard the environment and public.

Materials and Methods

Study Area

The study was collected in the year 2022, and samples were collected from eight distinct sites. The spatial separation between the sea samples was around five kilometres, while the inside samples exhibited varied degrees of separation. The division of the samples was carried out as follows: Five samples in all were taken from the sandy beach located in the Zueitina area adjacent to the Zuetina Company. The remaining samples were obtained from locations south of the city of Ajdabiya. Figure (1) displays the geographical coordinates of the study samples, which were determined through the utilisation of GPS technology during the research process. Soil samples were collected at a deepness of 4 cm by a manual shovel. The specimens were gathered and thereafter placed within plastic containers. The samples underwent digestion in the laboratory.



Figure 1. An aerial map of the research region (Google earth 2023)

Mathematical Models using Heavy Metals Indices:

Factor of Contamination (CF):

CF is determined by applying the equation that follows to the soil samples in order to determine the level of contamination caused by heavy metals:

> Factor of Contamination C metal C background

The initial value refers to initial concentrations as documented by Turekian and Wedepohl (1961), which are derived from the relative abundance of the component in the sedimentary layers. The importance of the subject matter is delineated as follows: The contamination factor (CF) can be categorised into different levels. A CF value fewer than 1 indicates a low contamination factor, while a value between 1 and 3 suggests a moderate contamination factor. A large contamination factor is indicated by a CF value between 3 and 6, and a CF value equal to or greater than 6 signifies a very high CF (Hasaballah et al. 2021).

Pollution Load Index (PLI):

The pollution load index PLI provides data regarding the concentration of heavy metals in a particular geographical location. The PLI is calculated using the following equation:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times ... \times CF_n)1/n$$

The formula for calculating the Pollution Load Index (PLI) is derived as the geometric mean of the pollution factors (CF1, CF2, CF3, ..., CFn), where CF represents the pollution factor associated with each metal (Sallet et al. 2019). In the event that the Pollution Level Index (PLI) score is below 1, There would be no documented cases of contamination. Pollution. on the other hand, would be noticed and recorded if the PLI score exceeded 1. Conversely, a numerical value of zero signifies an optimal state, while a value of one represents the fundamental threshold of contaminants, and any value over one would signal a deterioration in the site's overall condition (El-Emam, 2020).

Enrichment Factor (EF):

To determine the degree of pollution and comprehend the distribution of materials resulting from human activity, enrichment factor (EF) was utilised, with the aim of determining the magnitude of contaminants in the environment (Agyeman et al. 2023). The element iron (Fe) was chosen as the dominant element for the purpose of identifying metals that possess unusual concentrations, as stated by Wu et al. (2021).

In the case where the EF values were below 2, it would be recommended that the metal be attributed to entirely natural processes or crustal materials. Conversely, if the EF values exceeded 2, it would indicate the metal's origin was anthropogenic.

EFM

CM(sediment) / CFe(sediment)

Cm(*earthcrust*) / *CFe* (*earthcrust*)

The notation "Cm (sediment)" indicates the amount of metal contained in the sediment sample, whereas "CFe (sediment)" shows how much of the reference metal (Fe) is contained in the sediment sample. The abbreviation "Cm" in the context of the earth's crust refers to the measurement of metal concentration inside this geological layer (Hasaballah et al. 2021).

The EF values can be categorised into six distinct groups: baseline concentration, depletion resulting in little enrichment, depletion resulting in moderate enrichment, moderate enrichment ranging from 2 to 5, considerable enrichment ranging from 5 to 20, very high enrichment ranging from 20 to 40, and extremely high enrichment above 40, (Baghaieet al. 2019).

Degree of contamination (DC)

$$DC = \sum_{i=1}^{N} CFi$$

Contamination degree (DC), as described by Hokanson (1980), is an additional metric derived from CF values. It quantifies the cumulative presence of pollution-related constituents at a specific location.

In this context, n represents the total count of components within a given system, while CF denotes the sole factor contributing to contamination. Values of DC below n would suggest low levels of contamination, while values between n and 2n would indicate moderate contamination levels. If the DC value falls between 2n and 4n, it would suggest considerable contamination levels. On the other hand, if the DC value exceeds 4n, it would indicate extremely high levels of contamination.

The aforementioned categories were employed for the purpose of classifying the extent of pollution observed at the designated study location.

The contamination levels can be classified as follows: a DC value less than 11 indicates a minimal levels of pollution, a DC value between 11 and 22 suggests a moderate degree of contamination, a DC value between 22 and 44 indicates a large degree of contamination, and a DC value greater than 28 signifies a extremely high level of pollution. Where n is the count of the heavy metals that were investigated, with a value of 11., (El-Emam, 2020).

Geo-accumulation Index

The index of geo-accumulation (Igeo), initially proposed by Muller in 1969, serves as a metric quantifying and characterising for the contamination of metals in sedimentary environments. This is achieved by comparing the current metal concentrations with those observed in sediments before to the industrial era, as expressed by the equation shown below:

Iaeo = Log2(Cn/1.5Bn)

The variable Bn represents the geochemical background value for element n in typical shale. On the other hand, Cn denotes the observed concentration of heavy metals in sediments. Additionally, the value 1.5 corresponds to the background matrix adjustment that arises from terrigenous effects. The utilisation of a factor of 1.5 is justified due to potential variations in baseline values of a specific metal in the environment and little anthropogenic influences.

According to the study conducted by Buccolieri et al. in 2006, the geo-accumulation index (Igeo) was categorised into seven distinct groups. The index of geoaccumulation (Igeo) is a measure used to classify the pollution levels of a given area. The Igeo values range from 0 to 6, with different classes representing varying degrees of pollution. Class 0 signifies an unpolluted environment. Class 1 indicates a pollution level ranging from unpolluted to moderately polluted. Class 2 denotes a moderate level of pollution. Class 3 signifies a strong level of pollution. Class 4 represents a high level of pollution. Class 5 indicates a pollution level ranging from strong to extremely polluted. Finally, class 6 is assigned to areas with an extremely high level of pollution, where Igeo exceeds 5 (Hasaballah et al 2021).

Potential Ecological Risk Index (RI)

The researchers introduced the potential ecological risk index (RI) as a tool for assessing the extent of heavy metal sediment pollution, utilising principles derived from sedimentary theory. The purpose of this index is to assess the ecological risk associated with the presence of heavy metals in sedimentary environments. The possible ecological risk index, first put out by Hakanson in 1980, has been used extensively in the assessment of sediment heavy metal pollution in subsequent studies. The subsequent equations can be utilised to ascertain the value of RI:

$$Eir = T^{i}_{r}x C^{i}f$$
$$RI = \sum E^{i}_{r}$$

Tir represents the toxicity response factor associated with a certain substance, with values assigned as follows: Zn = 1, Pb = Cu = 5, Cd =30, Cr = 2, Ni = 5, Mn = 1. On the other hand, Eir is a quantitative measure used to indicate the potential ecological hazard posed by a specific pollutant. The contamination factor, sometimes referred to as CIF, is a metric used to quantify the level of contamination. (Sojka et al., 2022).

Health Risk Assessment

a-Non cancer effect evaluation

Heavy metals can potentially come into contact with the human body through three distinct pathways, inclusive ingestion, inhalation, and skin contact. The mean intake per day (ADI) of metals in soil is computed by employing the following equations.:

ADDing = C * IRing * EF * ED*SAF / BW * ATADDdermal = C * SA * ABS * EF * ED* SAF / BW * AT ADDinhalation

$$= C * IRinh * EF * ED$$
$$* CF / PEF * BW * AT$$

where C is the concentricity of a certain metal in the soil (as determined in this research and expressed in milligrammes per kilogramme). The acronym IR_{ing} represents the ingestion rate, which is established at 100 mg per day for adult individuals. EF represents exposure frequency, which corresponds to a frequency of 180 days annually. ED denotes exposure duration, which spans a period of 24 years for adult individuals. IRinh signifies inhalation rate, which amounts to 14.7 m3 per day for people. The dust emission factor (PEF) is quantified as 1.36 * 109 m3 per kg. The skin exposure area (SA) for adults is measured at 5700 cm². The adherence factor (SAF) and dermal absorption factor (ABS) are also included, with a value of 0.001 for all elements. The acronym BW represents body weight, which is typically 57 kg for adult individuals. The average annual exposure time for non-carcinogens is denoted as AT. For a duration of 365 days, the exposure duration (ED) is considered. Additionally, the lifetime exposure to carcinogens such as arsenic (As), chromium (Cr), and cadmium (Cd) is multiplied by 70 and then further multiplied by 365 days. (Das et al. 2023).

Non-carcinogenic Risk Assessment

The evaluation of potential health risks connected with the non-carcinogenic impacts of metals on soils followed the suggested procedure of the US Environmental Protection Agency. The hazard quotient (HQ) was calculated by utilising the ratio between the reference dose (RFD) and the acceptable daily intake (ADI) for a certain metal.

HQ = ADI/RfD

The variable "RfD" is the reference dosage of the metal, expressed in milligrammes per The kilogramme per day. elemental composition is as follows: iron (Fe) with a concentration of 0.7, cobalt (Co) with a concentration of 0.02, copper (Cu) with a concentration of 0.04, cadmium (Cd) with a concentration of 0.001, and lead (Pb) with a concentration of 0.0035. The maximum permissible concentration of a metal that does not pose a risk to human health is reached at that specific dosage. The cumulative HQ values of the metals present in the soil, denoted as HI, were employed to assess the collective noncarcinogenic impacts that various metals may exert on human health. (Mlangeni et al., 2023).

$$HI = HQ_1 + HQ_2 + \dots + HQ_r$$

In the case that the Hazard Index (HI) attains a value of 1, there exists a potential for noncarcinogenic outcomes. Conversely, if the HI surpasses 1, it indicates a substantial probability of adverse health effects manifesting.

b- Cancer Effect Evaluation

The probable carcinogens are assessed in terms of the lifetime cumulative risk associated with each individual's likelihood of developing cancer due to exposure to these substances. The above equation may be employed to ascertain the surplus lifetime cancer risk:

$Cancer\,risk = \Sigma ADI * CSF$

The concept of risk plays a crucial role in determining an individual's lifetime susceptibility to acquiring cancer. The mean daily consumption (ADI) and cancer slope factor (CSF) for heavy metals are expressed in units of milligrammes per kilogramme per day (mg/kg/day). The user's text does not provide any information to rewrite in an academic manner (Mlangeni et al., 2023)

Based on the findings of the United States Environmental Protection Agency (USEPA) in 2012, the cancer slope factors (CSF) for cadmium (Cd), cobalt (Co), lead (Pb), and nickel (Ni) are reported as 6.3, 9.8, 0.0085, and 9E⁻⁵ mg/kg/day, respectively. The permissible range for the LCR (Likelihood of Cancer Risk) as mandated by regulatory standards falls between 1.0E-06 and 1.0E-04. It is worth noting that the threshold value for cancer risk, which is considered acceptable, is 1.0E-04. According to the study conducted by Peirovi-Minaee et al. (2023).

Results

Heavy Metals Indices:

Models for assessing pollution are employed to ascertain the magnitude and density of humaninduced pollutants that have been deposited onto soil (Nguyenet al. 2023).

Contamination Factor (CF):

Table 1 and Figure 2 show the pollution factors that were recorded during the study period. The highest value was recorded for the two elements cadmium and cobalt with an average of $0.3 \pm 0.182522 - 0.3 \pm 0.153757$, while the lowest value was recorded for the trio of elements iron (0.0009 ± 0.0009) , copper (0.001 ± 0.0004) , and lead (0.096±0.055).

Table (1): The average values per year of the total concentration of heavy metals in the sediments' contamination factor (CF), degree of contamination (DC)andpollution load index (PLI).

Station		CF	рі і	CD				
NO	Pb	Cu	Cd	Co	Fe	rLI	CD	
WS1	0.09	0.00084	0.082	ND	0.4	0.012	0.911	
WS2	0.097	0.0016	0.042	0.36	0.46	0.025	0.879	
ES1	0.075	0.001	0.035	0.53	0.44	0.036	0.956	
ES2	0.08	0.0008	0.034	0.4	0.44	0.02	0.821	
ES3	0.062	0.00046	0.028	0.4	0.4	0.016	0.742	
SS1	0.07	0.00086	0.03	0.29	0.68	0.02	0.661	
SS2	0.23	0.0014	0.031	0.35	0.22	0.037	0.893	
SS3	0.07	0.0017	0.026	0.4	0.27	0.031	0.734	
Mean	0.096	0.001	0.3	0.3	0.0009	0.024	0.82	
CD		0 0004	0 100	0 1 5 2	0 0000	0 0000	0 1 0 2	



Figure 2: Average Values of PLI and DC in the study area

Pollution Load Index (PLI):

The pollutant load index (PLI), which took into account the contribution of the five metals being studied, offered an appraisal of the sample's overall toxicity status. The pollutant load index average values for the five different heavy metals ranged from 0.012 in the WS1 region to 0.037 in the SS2 region, according to the results. The remaining regions recorded a range of values, which are as follows: WS2 0.025, ES1 0.036, ES2 0.02, ES3 0.016, SS1 0.02, and SS3 0.031.

Degree of contamination (DC)

According to the current DC value results, there is a slight level of pollution along the study area. The SS1 area recorded the lowest value, which was 0.661, and the ES1 area recorded the highest value, which was 0.95. The remaining areas recorded varying values, which were as follows: WS1 0.91, WS2 0.87, ES2 0.82, ES3 0.74, SS2 0.89, and SS3 0.73 (with an average of 0.82 ± 0.102) (Table 1).

Enrichment Factor (EF)

Utilising the enrichment factor (EF), one may ascertain the extent of metal contamination present in sediments. In Figure 3, the EF was determined for every heavy metal. With an average of 0.92 ± 0.90 , the element iron had the lowest value, while the element cobalt had the greatest value. averaging 376.48 + 149.1807267. The other elements' levels were as follows: lead (93.4±53.8), copper 1.13±0.43, and cadmium 370.3±166.0 (figure 3).



Figure 3: The heavy metal enrichment factors (EF) in the sediments of the study area.

Geo-accumulation Index

The Index of Geoaccumulation (Igeo) for average concentrations of heavy metals in sediments is displayed in Figure 4.

The research region was found to be free of cadmium pollution, as evidenced by the average value of 5.51±0.51, which fell between the range of values of -5.96 and -4.34. The copper element, on the other hand, showed different levels of contamination, from slightly to highly contaminated. with an average of 0.46±0.63 and a value of (0.11–1.22).

The average Igeo values for Fe revealed extremely high contamination levels (ranging from 6.95 to 9.71), while the Pb readings suggested moderate to strong contamination levels ranging from 2.55 to 4.46, with an average of 3.05 ± 0.60 . 7.75 ± 1.15 on average. The precise Igeo values were seen as follows: cadmium (Cd) > copper (Cu) > iron (Fe) > lead (Pb) > cobalt (Co).



Figure 4: Geo-accumulation index (I_{geo}) of the mean total heavy metal concentrations in sediment

otential Ecological Risk Index (RI)

Based on the analysis presented in Figure 5, it can be observed that the E values of Pb, Cu, Cd, and Co (WS1, WS2, ES2, and ES3) are all below the threshold of 40; in contrast, the potential ecological risk index for Fe and Co (namely ES1, SS1, and SS2) exceeded 80 but remained below 320, signifying a substantial ecological danger. The index was separately applied to each station within the study region for all five metals examined in this study. The research region had an average value of 57.12, suggesting a moderate level of possible ecological risk.



Figure 5: Monomial potential ecological risk (Eⁱ_r)

Health Risk Assessment (HRA)

Non-carcinogenic risk assessment

The evaluation of potential health risks

connected with the non-carcinogenic impacts of metals on soils followed the suggested procedure of the US Environmental Protection Agency. The computation of the hazard quotient (HQ) involved utilising the ratio between the reference dose (RFD) and the acceptable daily intake (ADI) for a certain metal. The reference dose (RfD) represents the recommended dosage of the metal in milligrammes per kilogramme per day.

Carcinogenic risk assessment

The assessment of carcinogenic hazards involves the use of the incremental probability of an individual acquiring cancer throughout their lifespan due to exposure to a potential carcinogen. The cancer slope factors (SF) for cadmium (Cd), lead (Pb), and cobalt (Co) are 6.3, 0.0085, and 9.8, respectively. The cumulative lifetime cancer risk (LCR) is quantified by aggregating the cancer risks associated with individual exposure pathways. The LCR (Lead and Copper Rule) value deemed acceptable or tolerable for regulatory purposes is 1×10^{-5} , as stated by the United States Environmental Protection Agency in 2012. To assess the non-cancer risk associated with each element (Pb, Cd, and Co) and exposure pathway, the corresponding reference dose (RfD) is utilised. This involves dividing each element and exposure pathway by their respective RfD values, resulting in the calculation of a hazard quotient (HQ). The cumulative hazards associated with non-cancer health effects, quantified as the hazard index (HI), are determined by summing the hazard quotients (HQs) as presented in Table 2. In cases where the Hazard Index (HI) surpasses a value of 1, there is a possibility of noncancerous adverse consequences occurring. This likelihood tends to escalate as the HI value grows.

Table 2 presents a comprehensive overview of the HRA, encompassing both cancer and noncancer risks. While certain heavy metals, such as lead (Pb) and iron (Fe), are necessary for proper nutrition, in the context of HRA interpretation, the assessment of overall cancer risk, also known as cancer hazard, and the cumulative hazard quotient (HQ) for noncancer risk involved the combination of the hazard index (HI) for the heavy metals investigated in the sediment of the designated area. The ingestion pathway was shown to have the highest contribution to both the total lifetime cancer risk (LCR) and hazard index (HI) values. This was followed by dermal contact, which was the second most significant pathway in terms of contribution to LCR and HI values. According to the obtained data, the average hazard index (HI) values for heavy metals were found to be less than 1, suggesting that there is no likelihood of non-cancerous harmful effects. The elements Pb, Cd, Co, and Fe exhibit a Hazard Index (HI) value more than 1 for all five elements, suggesting diverse pollution sources in the research area that are associated with heavy metal exposure and potential implications for human health.



Figure 6 Potential ecological risk index (RI) of heavy metals in the study area.

Disscution

Pollution assessment models are employed to ascertain the magnitude and density of humaninduced pollutants that have been deposited onto soil (Nguyenet et al., 2023). The study area's CF results were comparable to those of Kusin et al. (2018). Using the pollution factor, it was possible to determine how much pollution a specific material in the sediment had caused. Indeed, the contamination factor (CF) and the value of the pollutant load index are less than 4, which means sites are polluted from medium to high (Ibrahim et al., 2018).

When the PLI value is 0, the site quality is ideal; when it is one, there are just baseline levels of pollutants present; and when it is two or above, there is progressive site quality degradation. PLI values greater than 1 indicate pollution, while PLI values less than 1 show no pollution. Tokatlı et al. (2023), who examined the features of pollution and evaluated the health risks associated with possibly harmful substances in the sediments, concur that the PLI

in the study region did not indicate any pollution in the study area.

Table (2): Hazard quotient (HQ) and cumulative hazard index (HI) for non-carcinogenic risk.

Site	Pathway	Pb	Cu	Cd	Со	Fe
ws1	ADD _{ing}	0.111	0.00657	0.042	ND	0.68
	ADD_{dermal}	0.006	0.00374	0.00242	ND	0.039
	ADD _{inhalatio}	0.0003	1.86E-07	0.00117	ND	9.26E-06
	ADI average	0.0392	0.0034	0.0151	ND	0.239
	HI	33.628	0.257	45.59	ND	1.0271
ws2	ADD _{ing}	0.117	0.012	0.022	0.018	0.78
	ADD _{dermal}	0.0067	0.00072	0.00126	0.00106	0.044
	ADD _{inhalatior}	0.0003	6.81E-07	0.000313	0.000226	1.21E-05
	ADI average	0.061	0.0042	0.0078	0.0064	0.2746
	HI	35.342	0.3180	23.573	0.964	1.177
	ADD _{ing}	0.092	0.0084	0.018	0.027	0.74
	ADD _{dermal}	0.0052	0.0004	0.0013	0.0015	0.042
ES1	ADD _{inhalatior}	0.000235	2.85E-06	0.00021	0.00049	0.00001
	ADI average	0.0325	0.0029	0.0064	0.0096	0.2606
	HI	27.864	0.2241	19.24	1.45	1.117
ES2	ADD _{ing}	0.097	0.00622	0.017	0.02	0.74
	ADD _{dermal}	0.0055	0.00035	0.001	0.0011	0.042
	ADD nhalation	0.000261	1.68E-07	0.000204	0.0002	0.000011
	ADI average	0.0342	0.0021	0.0061	0.0071	0.260
	HI	29.368	0.1643	18.214	1.069	1.117
ES3	ADD _{ing}	0.076	0.00363	0.014	0.02	0.68
	ADD _{dermal}	0.0043	0.00021	0.00084	0.00118	0.038
	ADD _{inhalatior}	0.00015	5.63E-08	0.00014	0.000208	9.21E-06
	ADI average	0.02682	0.00127	0.00499	0.00712	0.2393
	HI	22.996	0.0959	14.988	1.0694	1.0257
SS1	ADD _{ing}	0.086	0.00674	0.015	0.015	1.16
	ADD _{dermal}	0.00492	0.000384	0.000897	0.000877	0.066
	ADD _{inhalatior}	0.000203	1.95E-07	0.000159	0.00015	2.68E-05
	ADI average	0.0303	0.0023	0.00535	0.0053	0.4086
	HI	26.035	0.1781	16.056	0.80135	1.7514
SS2	ADD _{ing}	0.28	0.011	0.048	0.018	3.89
	ADD _{dermal}	0.016	0.00066	0.000927	0.00104	0.22
	ADD _{inhalation}	0.00221	5.47E-07	0.00017	0.0002	0.00029
	ADI average	0.0994	0.0038	0.0163	0.0064	1.37009
	HI	0.29821	0.2915	49.097	0.9628	5.87184
-	ADDing	0.085	0.013	0.014	0.02	4.63
	ADD _{dermal}	0.00486	0.00076	0.000789	0.00119	0.26
SS3	ADD nhalation	0.000201	7.73E-07	0.000121	0.000282	0.000422
	ADI average	0.0301	0.0045	0.00497	0.0071	1.6301

HI 25.731 0.3442 14.91 1.0736 6.986 If the value of DC is lower than n, the contamination level can be classified as minor. For values of DC between n and 2n, the contamination level can be considered moderate. If DC falls between 2n and 4n, the contamination level can be classified as considerable. Finally, if DC exceeds 4n, the contamination level can be categorised as very high. DC 5 denotes a state of pollution characterised by modest levels. On the other hand, DC 10 signifies a state of contamination with moderate levels. When the value of DC exceeds 10 but is less than 20, it suggests a state of contamination with considerable levels. Finally, when the value of DC surpasses 20, it signifies an exceedingly high degree of contamination. The variable n, with a value of

5, represents the quantity of heavy metals that were subjected to examination. The DC findings in the research region showed that the area is mildly contaminated, with an average value of 0.824, according to the study done by Hasaballah et al. (2021), According to Ayyamperumal et al. (2019), pollution levels for some sections of this study came from the oil industry, ship discharge of anti-fouling paints, and other human-caused sources such sewage discharge and industrial effluents.

The utilisation of the enrichment factor has been extensively employed in evaluating the degree of enrichment factor and identifying the origins of pollution, as per the categorization proposed by Khan et al. (2023).

The enrichment factor (EF) may be used to determine the amount of metal contamination present in sediment. Nevertheless, the biological and chemical mechanisms underlying the activity of EF remain elusive. However, EF may have the potential to provide insights into the possible origin of metals and metalloids by indicating their source location (Figure 3). After normalising using the element Fe, the EF for each heavy metal was computed in relation to the background values. (Hasaballah et al., 2021).

When evaluating and characterising metal contamination in sediments, the geoaccumulation index (Igeo) is used to compare current concentrations with levels from before industrialization. The determination of the enrichment of metal concentration above the background or baseline concentration is accomplished through the utilisation of the geoaccumulation index (Igeo). When a hazardous heavy metal's concentration was more than 1.5 times that of the lithogenic background, the Igeo index was employed to assess the degree of metal deposition in the sediment. According to the study conducted by Kumar et al. (2023), the geo-accumulation index (Igeo) was categorised into seven distinct groups. The index of geoaccumulation (Igeo) is a numerical value that ranges from 0 to 6, with different classes assigned to specific ranges. Class 1 represents an environment that is unpolluted to moderately polluted, while class 2 indicates a moderately polluted environment. Class 3 signifies a strongly polluted environment, while class 4 also represents a strongly polluted environment. Class 5 indicates an environment that is strongly polluted to extremely polluted.

Finally, class 6 is assigned to environments with an Igeo value greater than 5, indicating an extremely polluted condition.

Using concepts from sedimentary theory, the potential ecological risk index (RI) was employed in this study to determine the degree of heavy metal sediment contamination. This score is meant to evaluate the ecological risk that comes with heavy metals in sediments. Since its creation by Hakanson in 1980, the potential ecological risk index has been extensively used to evaluate the level of heavy metal contamination in sediment. (Hasaballah et al., 2021).

Tri represents the toxicity response factor associated with a certain substance, where the values for different materials are as follows: Ni = 5, Cd = 30, Pb = Cu = 5, Cr = 2, Zn = 1, and Mn = 1. On the other hand, Eir acts as a quantitative measure to identify the potential ecological risk that a particular pollutant poses. The contamination factor, often known as CIF, is a parameter used to quantify the level of contamination. (Devanesan et al., 2017).

Due to the presence of diverse and physiological behavioural factors, individuals may encounter exposure to in environmentally chemicals present contaminated media. Health Risk Assessment is a systematic procedure employed to ascertain the nature and probability of unfavourable health outcomes in human beings (Yanget al., 2023).

The slope factor (SF) is a parameter that converts an individual's incremental risk of developing cancer based on their projected daily intake of a toxic substance across their lifetime of exposure. According to the study conducted by Fernández-Caliani et al. (2019),

In the context of cancer risks, the attributable dose (ADD) is multiplied by the matching slope factor (SF) in order to determine the magnitude of the cancer risk. The integrated risk information system (El-Emam, 2020) was used to figure out the slope factor (SF), the inhalation unit risk (IUR), the gastrointestinal absorption factor (ABSGI), and the dermal absorption factor (ABSd).

The primary cause of contamination with these elements can be attributed to the existence of petroleum industries. The presence of multiple factors exceeding a certain threshold may suggest that the observed toxicity could potentially be attributed to the presence of heavy metals.

Conclusion

Models of pollution assessment are utilised to ascertain the magnitude and density of humaninduced pollutants in soil. The contamination factor is used to assess the level of contamination resulting from a particular material inside sediment, with the highest values recorded for iron and lead. The pollutant load index (PLI) evaluates the sample's overall toxicity status, with values greater than 1 indicating pollution. The degree of contamination (DC) is calculated using the CF values, with values ranging from minor to very high.Based on the analysis presented in the input, it can be concluded that the study region exhibits a minor degree of pollution based on the degree of contamination (DC) and a low potential for ecological harm based on the potential ecological risk index (RI) and the potential ecological risk index (E_{r}^{i}) . The geoaccumulation index (Igeo) categorizes the level of metal pollution in sediments, ranging from unpolluted to extremely polluted. According to (HRA), there is a possibility of both carcinogenic and non-carcinogenic consequences resulting from soil with heavy metals. In general, the presence of heavy metals in the area under study poses concerns not only to the health of humans but also to the health of the ecosystem. The pollution of these elements can be located in back mostly to industries related to the petroleum industries.

Acknowledgments

The authors express their gratitude to the colleagues and staff of the Environmental Sciences and Zoology Departments at Damietta University, as well as the Chemistry and Environmental and Natural Resource Science Departments at Omar Al-Mukhtar University in Libya, for their amazing assistance in carrying out this research. The authors express their gratitude to everyone who played a significant role in overseeing this study. We also thank the anonymous reviewers for their insightful insights.

Conflicts of Interest:

All authors certify that they have no

affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

Reference:

- Agyeman, P. C., John, K., Kebonye, N. M., Borůvka, L., &Vašát, R. (2023). Combination of and positive enrichment factor matrix factorization in the estimation of potentially toxic element source distribution in agricultural Geochemistry soil. Environmental and Health, 45(5), 2359-2385.
- Alghamdi, M. A., Hassan, S. K., Al Sharif, M. Y., Khoder, M. I., & Harrison, R. M. (2023). Pollution characteristics and human health risk of potentially toxic elements associated with deposited dust of sporting walkways during physical activity. Atmospheric Pollution Research, 14(1), 101649.
- Almaktar, M., &Shaaban, M. (2021). Prospects of renewable energy as a non-rivalry energy alternative in Libya. Renewable and Sustainable Energy Reviews, 143, 110852.
- Alnash, A. S., Sharif, O. M., & Nassar, Y. F. (2022). Evaluation of the environmental impacts resulting from the spread of various industrial activities and fuel stations in the northwestern region of the coast extending from Tajoura in the east to Maya in the west and south to Qasr Bin-Ghashir and Al-Azeziez. Journal of Pure & Applied Sciences, 21(1), 62-71.
- Ayejoto, D. A., & Egbueri, J. C. (2023). Human health risk assessment of nitrate and heavy metals in urban groundwater in Southeast Nigeria. ActaEcologicaSinica.
- Ayyamperumal, R., Kumari, K., Gandhi, M. S., Huang, X., Chengjun, Z., Nazir, N., ... & Das, P. (2023). Environmental hazard assessment and metal contamination in coastal sediments. Chemosphere, 338, 139434.
- Baghaie, A. H., & Aghili, F. (2019). Investigation of heavy metals concentration in soil around a PbZn mine and ecological risk assessment. Environmental health engineering and management journal, 6(3), 151-156.
- Buccolieri, A.; Buccolieri, G. and Cardellicchio, N.; et al. (2006). Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, Southern Italy). Marine Chemistry., 99: 227-235.
- Das, A., Baig, N. A., Yawar, M., Kumar, A., Habib, G., &Perumal, V. (2023). Size fraction of hazardous particulate matter governing the

respiratory deposition and inhalation risk in the highly polluted city Delhi. Environmental Science and Pollution Research, 30(5), 11600-11616.

- Devanesan, E., Suresh, G. M., Selvapandiyan, M., Senthilkumar, G. and Ravisankar, R. (2017). Heavy metal and potential ecological risk sedimentscollected assessment in from Poombuhar to Karaikal Coast of Tamilnadu using Energy Dispersive X-ray fluorescence (EDXRF) technique. Beni-Suef University Journal of Basic and Applied Sciences., 6(3): 285-292
- El-Alfy, M.A., Elfanagily, B.A., Zyadah, M.A. et al. (2024) CA-Markov chain for simulation and prediction of LULC and assessing the status of water pollution in Manzala Lake after recent development. J Coast Conserv 28, 4 (2024). https://doi.org/10.1007/s11852-023-01005-2
- El-Emam D. A. (2020). Monitoring and assessment of water pollution in River Nile-Damietta Branch-Egypte. A Ph.D thesis in Science Environmental Science/Environmental Quality Monitoring. Environmental Sciences Department Faculty of Science, Damietta University, Egypte
- Fernández-Caliani, J. C.; Giráldez, M. I. and Barba-Brioso, C. (2019). Oral bioaccessibility and human health risk assessment of trace elements in agricultural soils impacted by acid mine drainage. Chemosphere., 237:124441
- Hasaballah FA., Hegazy AT., Ibrahim SM., Elemam AD. (2019). Assessment of water and sediment quality of the River Nile, Damietta Branch, Egypt. Egypt J AquatBiol Fish 23(5 (Special Issue)):55-

65. https://doi.org/10.21608/EJABF.2019.64835

- Hasaballah, A. F., Hegazy, T. A., & Elemam, D. A. (2023). Performance evaluation of Pistia stratiotes and Lemna minor for wastewater phytoremediation: optimum conditions for pilotscale. International Journal of Environmental and Technology, Science 1-14 https://doi.org/10.1007/s13762-023-05001-9
- Hasaballah, A.F.; Hegazy, T.A.; Ibrahim, M.S. and El-Emam, D.A. (2021). Health risk assessment of heavy metals contamination in sediments of the River Nile, Damietta Branch using mathematical models. Egypt. J. Aquat. Biol. 25(2):947-971. Fish., doi: 10.21608/ejabf.2021.170342
- Hosseinzadeh-Bandbafha, Н., Aghaei, S., Aghbashlo, M., Kiehbadroudinezhad, M., Gupta, V. K., Mohammadi, P., ... & Tabatabaei, M. (2024).Biodiesel plants: real-world sustainability analysis using environmental and social life cycle assessment. In Sustainable Biodiesel (pp. 301-332). Academic Press.

- Ibrahim, S. A., Abed, M. F., & Al-Tawash, B. S. (2018). Calculation of pollution indicators and health hazards of heavy elements in surface soils in Samarra City. Iraqi Journal of Science, 1419-1429.
- Ji, M., & Wang, J. (2021). Review and comparison of various hydrogen production methods based on costs and life cycle impact assessment indicators. International Journal of Hydrogen Energy, 46(78), 38612-38635.
- Kadhim, S., Zarraq, G. A., & F Abed, M. (2017). Calculating pollution indices and health risks of heavy metals in surface soil at Tikrit City. Kirkuk University Journal-Scientific Studies, 12(3), 391-413.
- Kalifa, A. M., Triyuwono, I., Irianto, G., &Prihatiningtias, Y. W. (2020). The use and benefit of management accounting practices in Libyan oil companies. Asian Journal of Accounting Research, 5(1), 91-102.
- Khan, Z. I., Haider, R., Ahmad, K., Alrefaei, A. F., Mehmood, N., Memona, H., ... &Ugulu, I. (2023). The Effects of Irrigation with Diverse Wastewater Sources on Heavy Metal Accumulation in Kinnow and Grapefruit Samples and Health Risks from Consumption. Water, 15(19), 3480.
- Kumar, V., Bhatti, R. C., Kaur, R., Singh, S., Nirmala, C., & Singh, A. N. (2023). Comparative Geo-Accumulation Index of Heavy Metal Concentration in the Urban Soils of Chandigarh and Baddi Areas under Industrial Activities in A Lower Shiwalik Region. India. Eur. Chem. Bull, 12, 937-953.
- Kusin, F. M.; Azani, N. N. M.; Hasan, S. N. M. and Sulong, N. A. (2018). Distribution of heavy metals and metalloid in surface sediments of heavily-mined area for bauxite ore in Pengerang, Malaysia and associated risk assessment. CATENA., 165: 454-464.
- Mlangeni, A. T., Raab, A., Chibaya, S. B., Namaumbo, S., &Feldmann, J. (2023). Health risk assessment of toxic metal (loids)(As, Cd, Pb, Cr, and Co) via consumption of medicinal herbs marketed in Malawi. Toxicology Reports, 11, 145-152.
- Nguyen, M. K., Rakib, M. R. J., Lin, C., Hung, N. T. Q., Le, V. G., Nguyen, H. L., ... & Idris, A. M. (2023). A comprehensive review on ecological effects of microplastic pollution: An interaction with pollutants in the ecosystems and future perspectives. TrAC Trends in Analytical Chemistry, 117294.
- Peirovi-Minaee, R., Alami, A., Moghaddam, A., &Zarei, A. (2023). Determination of concentration of metals in grapes grown in Gonabad Vineyards and assessment of associated health risks. Biological Trace

Element Research, 201(7), 3541-3552.

- Sallet, R.; Vital, H.; Price, J. D. and Moritz, R. (2019). The geochemical behavior of F and Cl during the weathering-diagenesismetamorphism-anatexis cycle. Insights from the clay fraction of fine sands from the Amazon River mouth and metapelititic rocks from the Seridó Belt, Brazil. Chemical Geology., 525: 260-267.
- Sojka, M., Jaskuła, J., Barabach, J., Ptak, M., & Zhu, S. (2022). Heavy metals in lake surface sediments in protected areas in Poland: concentration, pollution, ecological risk, sources and spatial distribution. Scientific Reports, 12(1), 15006.
- Tokatlı, C., Varol, M., Ustaoğlu, F., & Muhammad, S. (2023). Pollution characteristics, sources and health risks assessment of potentially hazardous elements in sediments of ten ponds in the saros (Türkiye). Chemosphere, 340, region bay 139977.
- Ulakpa, R. O. E., Ulakpa, W. C., & Eyankware, O. E. (2022). Petroleum filling stations and their impact on the environment in Nigeria. Journal of Environmental & Earth Sciences, 4(1), 1-14.

- Wu, C. Y., Chu, M. F., Huang, K. F., &Hseu, Z. Y. (2022). Rare earth elements associated with pedogenic iron oxides in humid and tropical soils from different parent materials. Geoderma, 423, 115966.
- Yang, S., Sun, L., Sun, Y., Song, K., Qin, Q., Zhu, Z., &Xue, Y. (2023). Towards an integrated health risk assessment framework of soil heavy metals pollution: Theoretical basis, conceptual perspectives. Environmental model. and Pollution, 316, 120596.
- Zurqani, H. A., Mikhailova, E. A., Post, C. J., Schlautman, M. A., & Elhawej, A. R. (2019). A review of Libyan soil databases for use within an ecosystem services framework. Land, 8(5), 82.
- Zeyadah M. Bahnasawy, M. H., Deedah A. M., El-Emam D. A. and Adress H. M. (2023). Evaluation of the Contents of Aliphatic and Aromatic Hydrocarbons in Sediment from Zwitina Harbor Coast (Libya), as Indicator of Petroleum Pollution. Egyptian Journal of Aquatic Biology and Fisheries, 27(6), 253-265. doi: 10.21608/ejabf.2023.328456.

الملخص العربي

عنوان البحث: تلوث التربة بالمعادن الثقيلة وتقييم مخاطر السمية المرتبطة به فى أجدابيا والزويتينة،

محمد حامد بهنساوي (، محمد على زيادة ، أحمد ديده ، حسن أدريس حسن ؛ ، دعاء حافظ الإمام ّ

اقسم الحيوان، كلية العلوم، جامعة دمياط، دمياط الجديدة، مصر.

^٢قسم العلوم البيئية، كلية العلوم، جامعة دمياط، دمياط الجديدة، مصر.

"قسم علوم البيئة والموارد الطبيعية، جامعة عمر المختار، ليبيا.

·قسم الكيمياء، كلية العلوم، جامعة عمر المختار، ليبيا.

تقدم هذه الدراسة تقييماً شاملاً للأثار الضارة المحتملة على البيئة وصحة الإنسان الناجمة عن إدخال المواد الكيميائية من أحد المجمعات البتروكيماوية الرئيسية في منطقتي أجدابيا والزويتينة الليبيتين. تم استخدام النماذج الرياضية المستخدمة لتقييم مؤشرات المعادن الثقيلة، مثل عامل التلوث (CF) ، وعامل الإثراء (EF)، ودرجة التلوث (DC) ، ومؤشر حمل التلوث (PLI) ، ومؤشر التراكم الجغرافي(Igeo).

فأشارت نتائج الدراسة إلى أن مستويات المعادن الثقيلة في عينات الرواسب أظهرت التسلسل التالي: الحديد > الرصاص > الكوبالت > الكادميوم > النحاس. كما تم تحديد عامل الإثراء (ĒF) لكل عنصر من عناصر المعادن الثقيل من خلال مقارنته بقيم الخلفية، والتي تم تطبيعها باستخدام عنصر الحديد. استناداً إلى القيم المتوسطة لعو امل التخصيب(EFs) ، أظهرت المعادن الثقيلة في الرواسب الترتّيب التنازلي التالي للتّحصيب: الحديد > الرصاص > الكادميوم > النحاس > الكوبالت، مرتبة من الأعلى إلى الأدني. وقد وجد ان عنصر الحديد يظهر مستويات عالية إلى عالية للغاية من الملوثات عبر محطات مختلفة داخل منطقة الدراسة. علاوة على ذلك، شوهدت قيم مؤشر التراكم الجغرافي أيضًا بالترتيب التالي: الحديد (Fe) > الرصاص (Pb) > الكوبالت (Co) > النحاس (Cu) > الكادميوم(Cd) . ووفقا لتقييم المخاطر الصحية، هناك احتمال حدوث عواقب مسرطنة وغير مسرطنة ناتُجة عن التلوث بالمعادن الثقيلة في ترُبة منطقة الدر اسة.