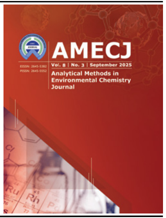
Anal. Methods Environ. Chem. J. 8 (3) (2025) 119-132

AMECJ

Research Article, Issue 3
Analytical Methods in Environmental Chemistry Journal
Journal home page: www.amecj.com/ir



Analysis and evaluation of toxic heavy metals in sediments of seabed cores using inductively coupled plasma optical emission spectroscopy

Muhand K. AL-Tememi [a], **Ahmed Y. Hammood**[a], **Zuhair A. Abdulnabi**[a], **and Ahmed Abdalhadi Majed** [b,c,*]
[a] *Marine Science Center, University of Basrah, zip code is 61004, Basrah, Iraq*
[b] *College of Education for Pure Science, University of Basrah, Iraq*
[c] *Scientific Research Center, Al-Ayen University, Thi-Qar, Iraq*

ARTICLE INFO:
Received 3 May 2025
Revised form 23 Jul 2025
Accepted 19 Aug 2025
Available online 30 Sep 2025

Keywords:
Heavy metals,
Analysis of sediments
Inductively coupled plasma optical emission spectroscopy,
Seabed,
Geoaccumulation Index

ABSTRACT

Soil sediments were studied in three areas in the northern Gulf within Iraqi territorial waters, where sediments were collected to cover all depths from 0 to 40 meters below the sea floor. The concentrations of the elements lead (Pb), cadmium (Cd), nickel (Ni), chromium (Cr), and vanadium (V) were measured using the inductively coupled plasma optical emission spectroscopy (ICP-OES), and arsenic (As) was determined by the graphite furnace atomic absorption spectrometry (GF-AAS) (%RSD < 5). The detection limits of Pb, As, Cd, Ni, Cr, and V were obtained at 0.511, 0.554, 0.525, 0.528, 0.501, and 1.221 μg L^{-1}, respectively. The Geoaccumulation Index (I-geo) compares the concentration of heavy metals in six classes in a sediment sample to its background value. The results were compared using I-geo calculations, which indicated high levels of contamination for arsenic and cadmium, with I-geo values ranging from 2.5 to 6.7 for arsenic, with moderately to significantly contaminated (Class 3 and 6), and from 2.4 to 3.9 for cadmium, with moderately to heavily contaminated (Class 3 and 4). There were lower contamination rates for nickel, as the I-geo values ranged from 0.23 to 2.09, while the concentrations of lead, chromium, and vanadium remained within safe levels. So, no dangerous concentrations for Pb, Ni, Cr, and V were found in any areas or depths from 0 to 40 meters below the seafloor.

1. Introduction

Heavy metals are among the key components of the Earth's crust. The level of heavy metals in soil varies widely depending on geological formation, depth, and location [1]. These elements can have a significant impact on the environment, economy, and human health when present in soil. Therefore, it is essential to understand the levels and concentrations of these minerals in sediment, especially in areas where human activities, such as commercial, industrial, agricultural, and marine fishing, are closely linked to the sediment [2]. The Earth's crust contains about 15 μg g^{-1} of lead. Lead levels in global soils vary from 2 to 200 μg g^{-1} on average. Lead is also present in many rocks, including argillaceous and magmatic types, where it can be found in significant amounts (10–40 μg g^{-1}), as well as in ultramafic rocks (0.1–10 μg g^{-1}) [3]. Cadmium is regarded as a rare element. Although its approximate abundance in the earth's crust is 0.1 μg g^{-1}, it is not found in nature as a

---

*Corresponding Author: Ahmed Abdalhadi Majed
Email: eduppg.ahmed.majed@uobasrah.edu.iq
https://doi.org/10.24200/amecj.v8.i03.1047

free metal [4]. The cadmium is present in sediment and volcanic rocks, such as Ultramafic 0.12 µg g^{-1}, Mafic 0.13-0.2 µg g^{-1}, Granite 0.09-0.2 µg g^{-1}, Limestone 0.028-0.1 µg g^{-1}, and Sandstone 0.05 µg g^{-1} [5]. The most common combinations of Nickel are found in iron-nickel sulfide minerals, such as pentlandite and millerite as a nickel-sulfur compound (NiS), limonite (iron oxide-hydroxides), nickel oxyhydroxide, where iron (Fe) is doped into the structure (Fe, Ni)-OOH, nickel-rich silicate minerals (garnierite), and arsenic with nickel in Nickeline [6]. In nature, nickel is typically found in small amounts, with concentrations of 100 µg g^{-1} in soil and 1.0 µg L^{-1} in seawater [7]. Chromium, with an average concentration of 100 parts per million, is the 21st most abundant element in Earth's crust [8]. The amounts of chromium are around 10 µg L^{-1} in the ocean, less than 1.0 µg L^{-1} in sediment, and less than 500 µg g^{-1} [9]. Ore, known as chromite ($FeCr_2O_4$), is mined for chromium [10]. Vanadium is present at 0.01% in the Earth's crust [11]. In terms of the natural abundance of chemical elements in the crust of Earth, vanadium is ranked twenty-first. Vanadium occurs naturally as chemical compounds in about 65 different minerals [12,13]. Carnotite [14], diclosite [15], and vanadinite as a red or orange hexagonal crystal [16] are the three most significant minerals, apart from Patronite as a black mixture of vanadium minerals [17]. Several techniques used for measuring heavy metals, such as ultrasound-assisted-dispersive solid-liquid multiple phase microextraction (USA-DSL-MPME) [18-21], atomic absorption spectrophotometer [22,23], electrothermal atomic absorption spectrometry (ET-AAS) [24-26], cloud point-assisted dispersive ionic liquid –liquid microextraction (CP-DILLME) [27-29], and inductively coupled plasma mass spectrometry analysis (ICP-MS) [30,31]. The northern Gulf region is of particular interest for studying heavy metal contamination in marine sediments due to its proximity to industrial and urban centers [32]. This region plays a crucial role in global hydrocarbon production, particularly oil and gas [33]. Research has consistently shown that extracting crude oil near deep reserves can lead to increased levels of heavy metal pollutants being released from underground sources. These pollutants are then transported during the extraction process [34]. While studies have examined the concentrations of heavy metals in the bottom sediments of the northern Gulf over various time periods, most have focused on shallow depths of less than one meter with a horizontal distribution [35]. Arsenic is one of the toxic elements, and it does not play a vital role for humans; It has minor natural effects in the body. Increased concentration of this element in non-arsenic organs can lead to poisoning; however, it plays a crucial and detailed role in chromosomes throughout the body [36, 37]. Arsenic is commonly used in industry, especially in semiconductor manufacturing in the electronic industry. Arsenic also enters alloys during their installation with lead. However, the recent applications are decreasing due to the toxicity of arsenic and its compounds, as well as the risk of contamination in underlying groundwater [38, 39]. There is a lack of information regarding the presence of heavy metals in deeper sediment layers. It has become evident that analysing deep, vertical core samples taken tens of meters below the seabed is essential for understanding the distribution of heavy metals in sediments at greater depths.

2. Materials and Methods

2.1. *Chemicals*

Several chemical materials were used, including nitric acid (65%) and hydrochloric acid (37%) from Sigma, Germany (CAS number: 7697-37-2 and 7647-01-0, respectively). Perchloric (70%) and Hydrofluoric acid (40%) from Sigma company with CAS number: 7601-90-3 and 7664-39-3, respectively. Multi-element (Pb, As, Cd, Ni, Cr, and V) standards were used and supplied by Merck. Heavy metals such as Lead (Pb, CAS number:7439-92-1), Arsenic (As, CAS number: 7440-38-2), Cadmium (Cd, CAS number: 7440-43-9), Nickel (Ni, CAS number: 7440-02-0), Chromium (Cr, CAS number: 7440-47-3, and Vanadium (V, CAS number: 7440-62-1) were prepared from Sigma, Germany.

2.2. *Instrumentation*

The instruments used for drying, weighing, digesting collected samples, and ovens were purchased from Baird and Tatiock, England. The Citizen CY-204 is an analytical balance designed for measurements with a maximum capacity of 220g and a readability of 0.1mg. The balance-instrument model Citizen Cy-204 and the hot plate magnetic stirrer from the Velp company. The metals were measured using ICP-OES from Thermo Fisher Scientific, Germany. The details of the ICP-OES are explained in Table 1.

2.3. *Sampling*

Three sediment cores from the seabed of the northwest Gulf were used, as shown in Figure 1. Each core covered a 40-meter depth column. The sediment cores were stacked in a five-meter-long polyethylene box with a depth-based meter number on each meter of sediment. As a result, we have 24 boxes, each containing eight boxes of sediments from a 40-meter-long continuous core, arranged and numbered sequentially, as shown in Figure 2.

Table 1. Conditions of ICP-OES for metal analysis

Parameters	Ranges
Dimensions (D x W x H)	690 x 615 x 933 mm
Purge Gas Flow	3.4 $\mathrm{Lmin^{-1}}$
Spectral Bandpass	7 pm at 200 nm
Standard Sampling Kit	Glass cyclonic spray chamber with EMT Duo torch
Warm Up Time	1 hour from off, 15 minutes from standby
Wavelength Range	167 to 852 nm
Auxiliary Gas Flow	MFC stabilized, fixed at 0.5 L $\mathrm{min^{-1}}$
Nebulizer Gas Flow	MFC tunable, 0.3-0.8 $\mathrm{Lmin^{-1}}$
Peristaltic Pump	3-channel (0 or 45 rpm)
Plasma Gas Flow	MFC stabilized, fixed at 12.5

Fig. 1a. Map showing the study area and sampling areas

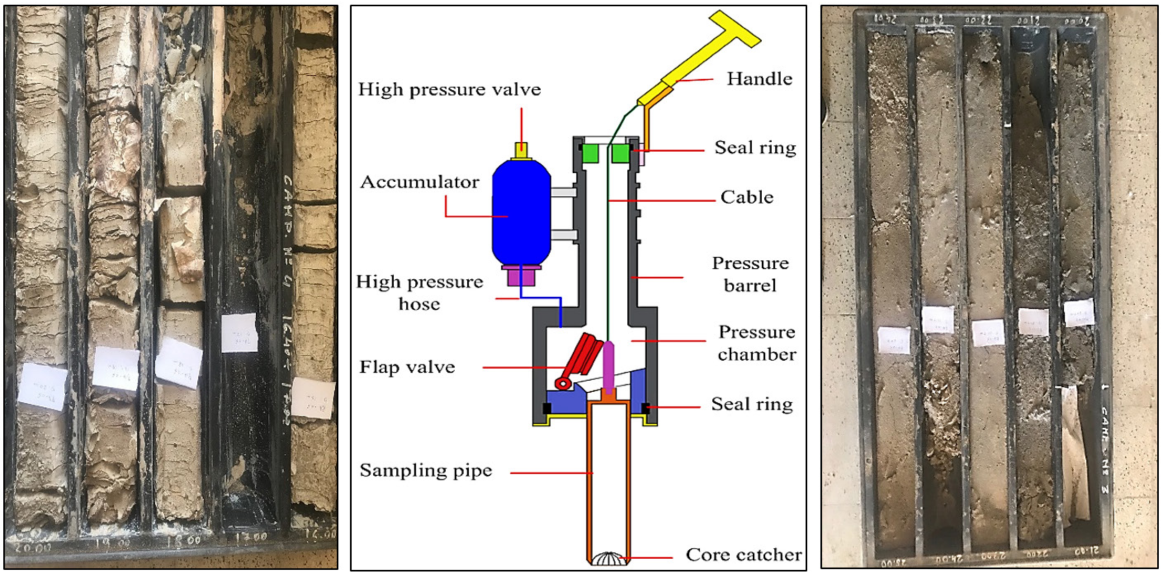


Fig. 1b. Two boxes containing core sediment samples and a sampler

2.4. Procedure

1.0 g of dry sediment sample was taken and placed in a Teflon flask. 6.0 mL of a 1:1 mixture of concentrated nitric and hydrochloric acids was added to the sample. The Teflon flask with the contents was heated on a hot plate at 80°C until the sample reached near dryness. (The temperature limitations of PTFE are 260°C or 500°F). After that, 4 mL of a 1:1 mixture of concentrated hydrofluoric and perchloric acids was added to the sample. The Teflon flask with the contents was reheated on the hot plate at a temperature of 70°C until the sample reached near dryness. To the precipitate formed, 20 mL of 0.5M hydrochloric acid was added. The solution was left for 10 minutes, after which it was transferred to special test tubes and placed in a centrifuge at 3000 rpm for 20 minutes. Transfer the clear solution containing the element ions to a 25 mL volumetric flask and fill the volume to the mark with ion-free water. The complete sample information, including the sample number, sediment column number, and depth, was recorded on the volumetric vial [40]. All prior steps were carried out on all sediment samples from the three columns, with 16 samples in each column. Finally, the samples were analyzed using multielement standards by ICP-OES and GF-AAS. Additionally, the Anton Paar Multiwave 3000 microwave system (model 3000) is used for validating the digestion process which was shown in Schema 1.

2.5. I-geo index calculation

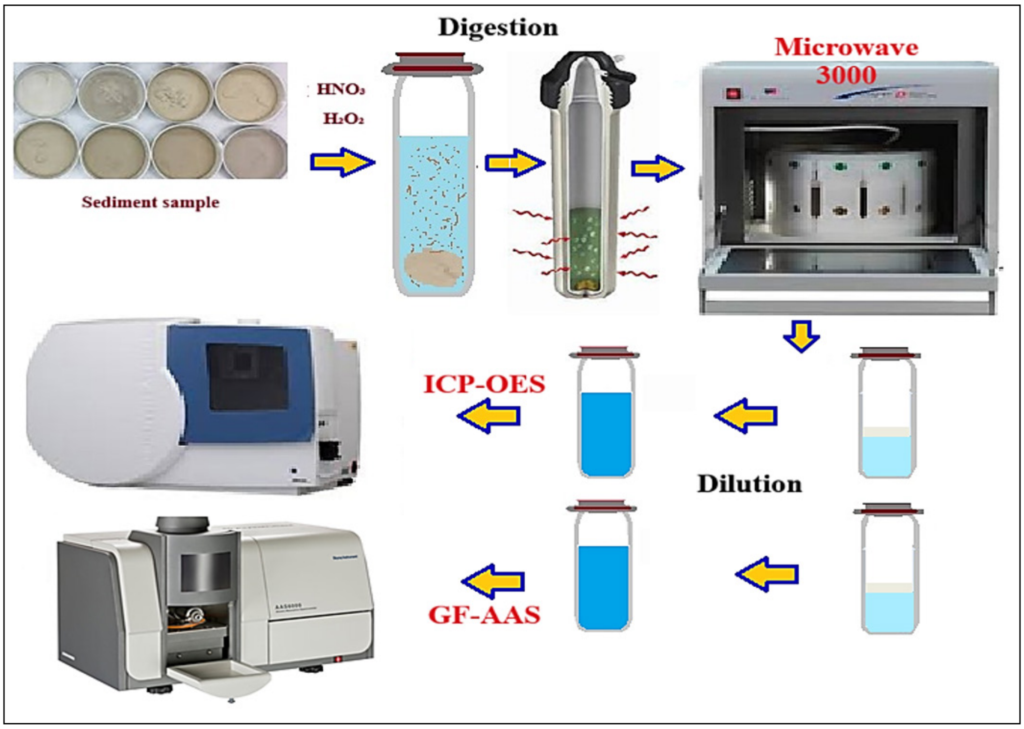
Using Muller's equation [29] for various metals, the geoaccumulation index was determined as shown in Equation 1. The I-geo accumulation index is shown in Table 1.

$$\text{I-geo} = \log_2 (C / 1.5\,B) \qquad \text{(Eq.1)}$$

Where C is the measured value for the metal concentration in the sediment, while B is the background value for the metal content in the soil (V 60 μg g^{-1}, As 0.25 μg g^{-1}, Cd 0.1 μg g^{-1}, Cr 100 μg g^{-1}, Ni 20 μg g^{-1}, and Pb 15 μg g^{-1}) [4], I-geo values were categorized using Muller classification [35].

3. Results and Discussion

Heavy metals, including lead, mercury, cadmium, chromium, and nickel, are often associated with oil contamination. When these metals are released into the ecosystem through oil pollution, they can have detrimental impacts on both living things and the environment [41]. The results showed convergence in the heavy metal concentration in surface samples, attributed to the proximity of the locations from which the samples were taken. In contrast, models with a vertical distribution showed variation in the measured heavy metal concentration. This is due to the difference in depositional periods, as surface sediments are mostly considered modern deposits,



Schema 1. Determination of heavy metals in sediments by ICP-OES and GF-AAS

Table 1. Geoaccumulation index (Igeo) for sediment pollution

Class type	I- geo value	Case of sediment pollution
Class one	less than zero	Background sample
Class two	1-2	Unpolluted to moderately polluted
Class three	2-3	Moderately polluted to polluted
Class four	3-4	Strongly polluted
Class five	4-5	Strongly to extremely polluted
Class six	> 5	Extremely polluted

I- geo: Geo accumulation index

approximately 100 years old, while sediments with depths of up to 35-40 meters date back to the recent Holocene era (approximately 10,000 years ago). The results showed that the lead concentrations of the three core samples under study are high at depths near the sea floor (from 0 to 1) metres. After a depth of 1 meter, lead concentrations begin to decrease with increasing depth, as the lowest value was recorded at a depth of 18 meters below the bottom. However, lead concentrations increased again in sediment samples taken from a depth of 22 to 40 meters, as shown in Figure 2. The difference in lead concentration in the sediments under study may be due to the difference in sedimentation time. These results are consistent with the results of soil texture examination, which clearly indicated that sediments from a depth of (0 to 22 metres) are similar and often date back to the same period of deposition in the Holocene era. Although the soil texture at depths of 35 to 40 meters differed, it was deposited within sediments of the ice age. The index of I-geo results was calculated for three cores and revealed a value within class 1 according to the Müller classification. The concentration of lead and arsenic in the sediments from a depth of 0 to one meter in Core No. 3 is the highest compared to the same depths in Core No. 2 and Core No. 1, and from observing the geographical location of Core No. 3, which appears to be farther away than the location of Core No. 3 from the coastline compared to the area of Cores 1 and 2. (Figures 2 and 3). Therefore, the surface sediments of Core No. 3 are in greater contact with marine water, which increases the period and ability of the sediments to absorb lead and arsenic. Especially since these marine waters are an area of petroleum and hydrocarbon activity, as increasing concentrations of lead and arsenic are often accompanied by increased hydrocarbon pollution, since their source is underground.

When comparing the I-geo values of lead given in Table 2 with the reference I-geo values shown in Table 1, we notice that all values for all depths in the three sites under study are less than zero. This indicates a practically unpolluted Background sample.

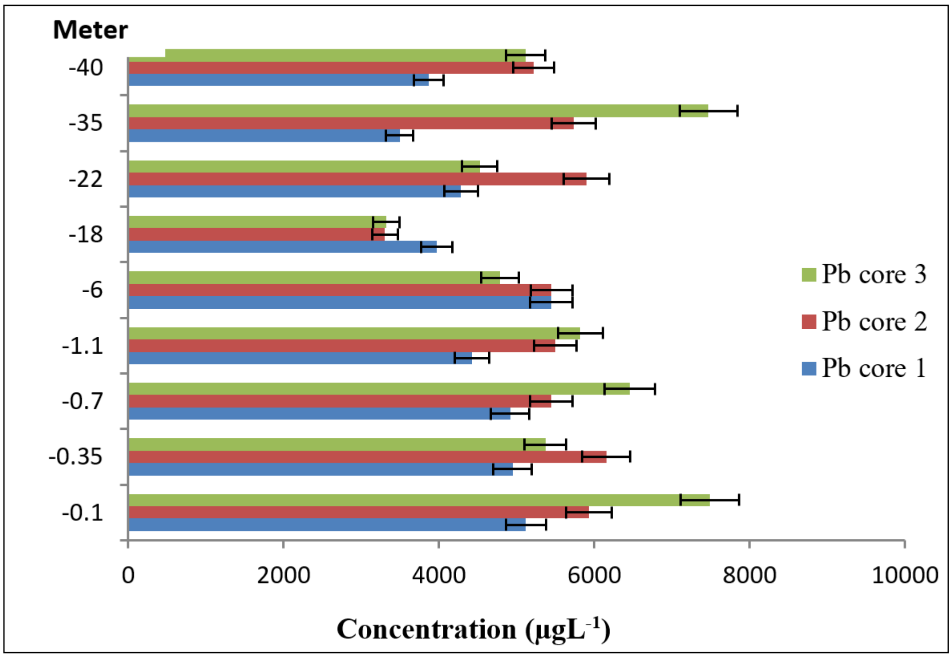


Fig. 2. Concentration of lead (Pb) in sediments at depths from 0 to 40 meters below the seafloor in three locations by ICP-OES and GF-AAS

Table 2. The measurements of the geo-accumulation index for lead at all depths based on core concentration (ng g^{-1})

Depth, m	Conc. Core 1	I-geo	Conc. Core 2	I-geo	Conc. Core 3	I-geo
-0.1	5117.49	-2.136	5927.88	-1.924	7488.75	-1.587
-0.35	4950.24	-2.184	6151.59	-1.871	5370.99	-2.067
-0.7	4915.482	-2.195	5448.84	-2.046	6454.86	-1.801
-1.1	4425.15	-2.346	5493.54	-2.034	5821.1	-1.951
-6	5444.94	-2.047	5449.8	-2.046	4787.4	-2.233
-18	3969.78	-2.503	3301.92	-2.769	3320.6	-2.760
-22	4284.81	-2.393	5895.45	-1.932	4525.1	-2.314
-35	3495.438	-2.686	5733.7	-1.972	7469.88	-1.591
-40	3868.86	-2.540	5221.53	-2.107	5113.74	-2.137

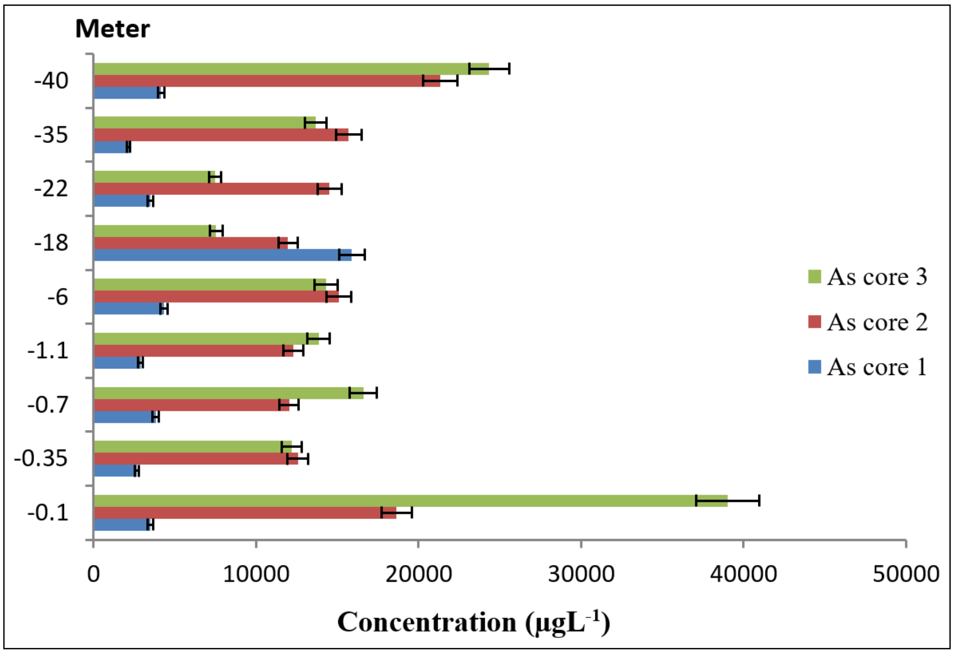


Fig. 3. Concentration of arsenic in sediments at depths from 0 to 40 meters below the seafloor in three locations

While the I-geo values for the Arsenic element, given in Table 3, indicate that most of the samples and for all depths in the three studied sites have I-geo values ranging from 2 to 6, depending on the location and depth of the sample, as the soil samples were in Core column number one has I-geo values from 2-4 which indicate moderately polluted to polluted -strongly polluted, With the exception of the soil sample taken at a depth of 18 meters, which showed I-geo values of more than 5, which is considered the highest classification of pollutants As for the sediment samples in core column No. 2 and 3, most of them showed very high I-geo values from (5 to 6), which indicate the classification strongly to extremely polluted-extremely polluted. In general, the surface samples taken from the three sites had higher I-geo values when compared to sediment samples taken from greater depths in the same core column. Therefore, surface samples are more contaminated with arsenic. This may be because surface sediments, being in direct contact with marine waters, are more likely to absorb

Table 3. The measurements of the geo-accumulation index for arsenic (As) at all depths based on core concentration (ng g^{-1})

Depth, m	Conc. Core 1	I-geo	Conc. Core 2	I-geo	Conc. Core 3	I-geo
-0.1	3478.68	3.214	18653.94	5.636	39027.39	6.701
-0.35	2650.41	2.821	12569.76	5.067	12196.02	5.023
-0.7	3828.60	3.352	12025.14	5.003	16593.93	5.468
-1.1	2883.84	2.943	12288.33	5.034	13853.16	5.207
-6	4340.40	3.533	15087.06	5.330	14323.83	5.255
-18	15899.37	5.406	11966.10	4.996	7545.43	4.331
-22	3490.95	3.219	14520.00	5.275	7492.21	4.320
-35	2149.11	2.519	15691.08	5.387	13669.98	5.188
-40	4151.03	3.469	21328.83	5.830	24351.48	6.021

pollutants associated with petroleum activities in the aquatic environment.

Figures 4, 5, 6, and 7 indicate that the three cores of sediment under study all show an increase in the concentrations of cadmium, nickel, chromium, and vanadium with increasing sediment depth, reaching their highest concentrations at depths of 18 to 22 meters. Then the concentrations of these elements begin to decrease in sediments at depths of 35 to 40 metres. The results also showed that comparing the concentrations of these elements at the same depth for the sediments of the three cores indicates that the concentrations of cadmium, nickel and chromium are often high in the sediments of Core No. 1. The lowest value in the sediments of Core No. 3. Thus, the vertical and horizontal distribution and spread of these three elements in the sediments is opposite to the pattern of distribution and spread of lead and arsenic in those same sediments.

The I-geo values for cadmium in Table 4 showed relatively high values, ranging from 2 to 4 in all sediment samples under study. By comparing these values to Table 1, we note that the sediments studied in the three regions and at all depths are

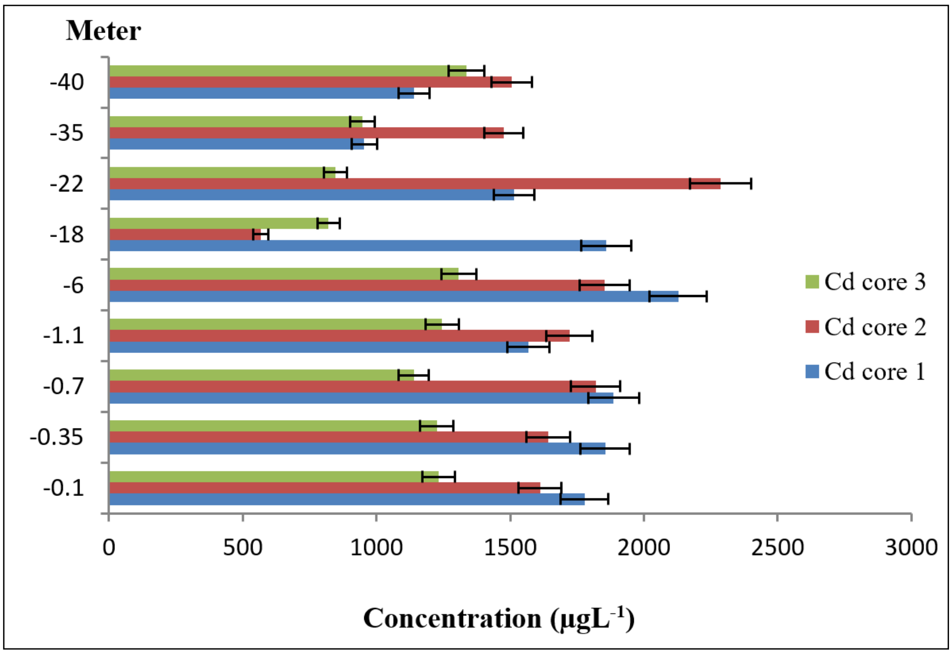


Fig. 4. Concentration of cadmium in sediments at depths from 0 to 40 meters below the seafloor in three locations

Table 4. The measurements of the geo-accumulation index for cadmium (Cd) at all depths based on core concentration (ng g^{-1})

Depth, m	Conc. Core 1	I-geo	Conc. Core 2	I-geo	Conc. Core 3	I-geo
-0.1	1778.04	3.567	1612.26	3.426	1232.97	3.039
-0.35	1855.41	3.629	1641.66	3.452	1225.68	3.031
-0.7	1887.238	3.653	1819.56	3.601	1140.06	2.926
-1.1	1567.92	3.386	1721.37	3.521	1245.70	3.054
-6	2128.98	3.827	1852.95	3.627	1308.27	3.125
-18	1859.43	3.632	566.55	1.917	821.20	2.453
-22	1515.84	3.337	2286.06	3.930	846.80	2.497
-35	954.788	2.670	1476.6	3.299	947.79	2.660
-40	1140.19	2.926	1506.72	3.328	1336.20	3.155

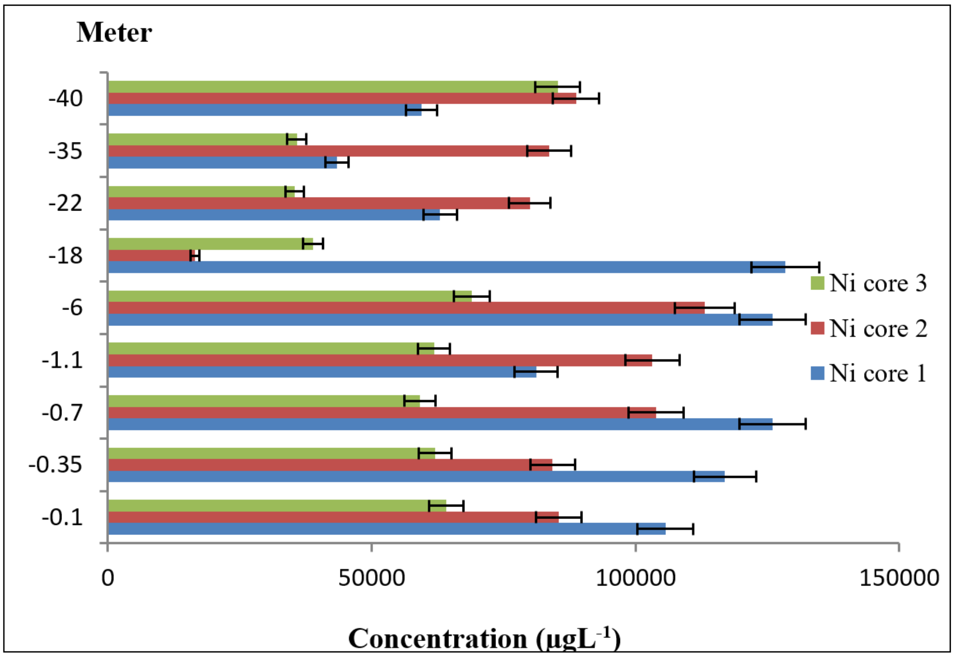


Fig. 5. Concentration of nickel in sediments at depths from 0 to 40 meters below the seafloor in three locations

Table 5. The measurements of the geo-accumulation index for Nickel (Ni) at all depths based on core concentration (ng g^{-1})

Depth, m	Conc. Core 1	I-geo	Conc. Core 2	I-geo	Conc. Core 3	I-geo
-0.1	105708.1	1.817	85,483.77	1.511	64,131.63	1.096
-0.35	116971.7	1.963	84,291.93	1.490	62,079.84	1.049
-0.7	125964.4	2.070	103,916.04	1.792	59,108.25	0.978
-1.1	81178.71	1.436	103,204.38	1.782	61,796.34	1.043
-6	125964.4	2.070	113,189.61	1.916	68,953.14	1.201
-18	128412.2	2.098	16,430.70	-0.869	38,853.71	0.373
-22	62991.36	1.070	79,936.17	1.414	35,409.42	0.239
-35	43450.4	0.534	83,622.30	1.479	35,828.46	0.256
-40	59388.92	0.985	88,715.55	1.564	85,254.60	1.507

within the moderately polluted to polluted or strongly polluted level.

From observing the I-geo values for nickel in Table 5, we find that most of the values ranged from 0 to 2 in all sediment samples under study. By comparing these values to Table 1, we note that the sediments studied in the three regions and at all depths are unpolluted to moderately polluted.

The (I-geo) values for both elements, chromium and vanadium, in Tables 6 and 7 indicate that most of the values are less than 0 for all sediment samples under study. By comparing these values to those in Table 1, we notice that the sediments studied in the three regions and at all depths are classified as number one (practically unpolluted, background samples).

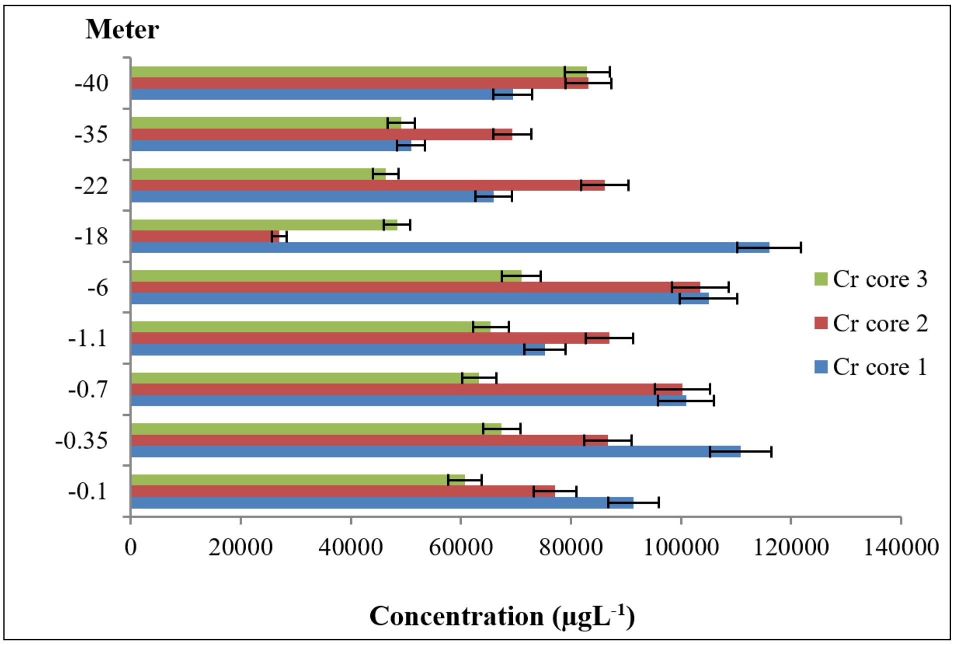


Fig. 6. Concentration of chromium in sediments at depths from 0 to 40 meters below the seafloor in three locations.

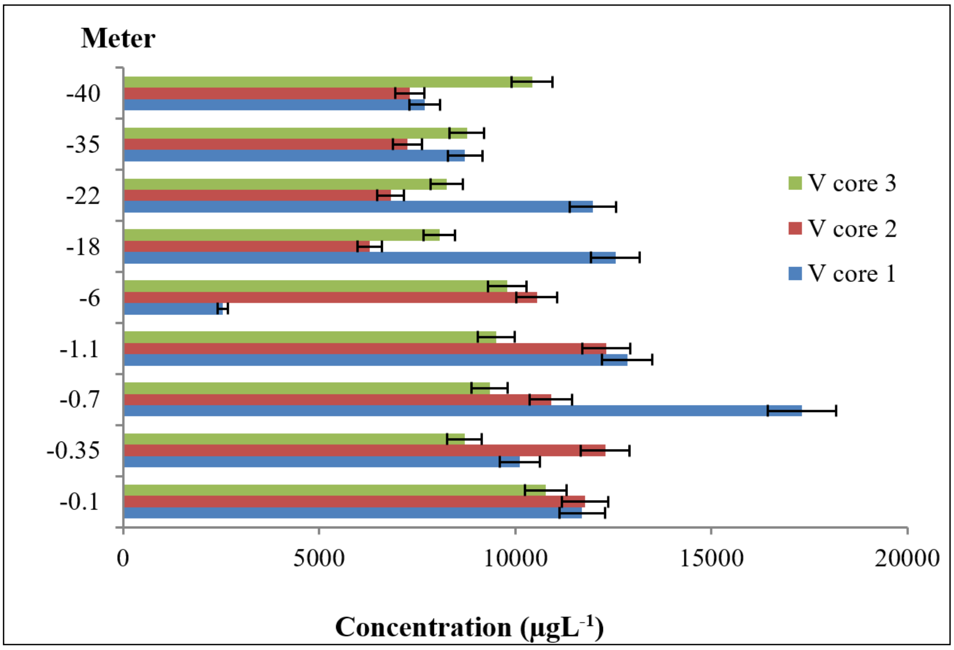


Fig. 7. Concentration of vanadium in sediments at depths from 0 to 40 meters below the seafloor in three locations

Table 6. The measurements of the geo-accumulation index for chromium (Cr) at all depths based on core concentration (ng g^{-1})

Depth, m	Conc. Core 1	I-geo	Conc. Core 2	I-geo	Conc. Core 3	I-geo
-0.1	91365.39	-0.71524	77,094.54	-0.96026	60,743.13	-1.30417
-0.35	110815.8	-0.4368	86,690.88	-0.79101	67,428.51	-1.15353
-0.7	100910.70	-0.57188	100,269.42	-0.58108	63,340.59	-1.24376
-1.1	75316.35	-0.99393	87,007.14	-0.78576	65,462.72	-1.19622
-6	105016.10	-0.51435	103,548.03	-0.53466	70,999.68	-1.07908
-18	116018.70	-0.37061	27,022.77	-2.47272	48,385.67	-1.63231
-22	65929.98	-1.18596	86,112.06	-0.80068	46,335.05	-1.69479
-35	50927.61	-1.55844	69,356.18	-1.11287	49,116.99	-1.61067
-40	69422.63	-1.11148	83,152.32	-0.85113	82,963.80	-0.85441

Table 7. The measurements of the geo-accumulation index for vanadium (V) at all depths based on core concentration (ng g^{-1})

Depth, m	Conc. Core 1	I-geo	Conc. Core 2	I-geo	Conc. Core 3	I-geo
-0.1	11706.81	-2.943	11786.79	-2.933	10780.47	-3.062
-0.35	10116.36	-3.153	12294.54	-2.872	8707.08	-3.370
-0.7	17314.33	-2.378	10910.88	-3.044	9348.6	-3.267
-1.1	12857.61	-2.807	12317.34	-2.869	9511.61	-3.242
-6	2551.08	-5.141	10550.22	-3.093	9792.81	-3.200
-18	12554.07	-2.842	6288.03	-3.839	8066.82	-3.480
-22	11980.23	-2.909	6828.72	-3.720	8248.15	-3.448
-35	8724.23	-3.367	7251.7	-3.634	8771.91	-3.359
-40	7694.608	-3.548	7311.34	-3.622	10434.93	-3.109

4. Conclusions

The concentrations of the elements lead (Pb), cadmium (Cd), nickel (Ni), chromium (Cr), vanadium (V), and arsenic (As) were determined using the inductively coupled plasma optical emission spectroscopy (ICP-OES) and graphite furnace atomic absorption spectrometry (GF-AAS) after microwave digestion (MWD) of sediments. Lead and arsenic concentrations are higher in the samples of Core No. 3 compared to Cores 1 and 2, but lead concentrations remain within normal concentrations, and the (I-geo) values did not show any level of lead contamination for all samples under study whereas the concentrations of arsenic have emerged with high pollution indicators in all samples of sediments and for all depths, according to I-geo values of arsenic the highest indicators of pollution in shallow samples were from 0-1 meter, which may be attributed to petroleum and industrial activity and the ability of surface deposits to adsorb arsenic from marine water. Cadmium and nickel concentrations differed according to the depth of the samples and their locations, but they showed noticeable differences, with high concentrations. The I-geo values for cadmium showed relatively high values, ranging from 2-4 in all sediment samples under study. We note that the sediments studied in the three regions and at all depths are within the moderately polluted to polluted or strongly polluted level. In contrast, the values of the

I-geo for nickel showed values ranging from 0.2 to 2.1, which indicate that not all sediments studied are moderately polluted. All studied sediment samples had natural concentrations of chromium and vanadium, and the I-geo values were low, indicating that they did not have any level of pollution.

5. References

[1] R. M. Al-Sheraefy, A. K. Hussien, A. Y. Al-Mallah, Spatial distribution of heavy metals in the soil of different areas at left bank in Mosul City, Iraq: Part 1, Iraqi Geol. J., 56 (2023) 40-61. https://doi.org/10.46717/igj.56.1C.4ms-2023-3-15

[2] S. M. Sharifuzzaman, H. Rahman, S. M. Ashekuzzaman, M. M. Islam, S. R. Chowdhury, M. S. Hossain, Heavy metals accumulation in coastal sediments, Environmental Remediation Technologies for Metal-Contaminated Soils, Springer, Tokyo, pp 21–42, 2016. https://doi.org/10.1007/978-4-431-55759-3_2

[3] C. Reimann, B. Flem, K. Fabian, M. Birke, A. Ladenberger, P. Négrel, A. Demetriades, J. Hoogewerff, Lead and lead isotopes in agricultural soils of Europe: The continental perspective, Appl. Geochem., 27 (2012) 532-542. https://doi.org/10.1016/j.apgeochem.2011.12.012

[4] P. M. Smith, The history and use of our earth's chemical elements: A reference guide, 2nd Edition (Robert E. Krebs), J. Chem. Educ., 84 (2007) 1767. https://doi.org/10.1021/ed084p1767

[5] M. Linde, Trace metals in urban soils–Stockholm as a Case Study, PhD. Thesis, Uppsala: Swedish University of Agricultural Sciences, 2005. https://pub.epsilon.slu.se/973/1/Avhandling_nr_111.2005_Kappanl.pdf

[6] G. M. Mudd, Global trends and environmental issues in nickel mining: Sulfides versus laterites, Ore Geol. Rev., 38 (2010) 9-26. https://doi.org/10.1016/j.oregeorev.2010.05.003

[7] J. Rieuwerts, The elements of environmental pollution. London: Routledge, Taylor & Francis, 2015. https://doi.org/ 10.4324/ 9780203798690

[8] J. Emsley, Chromium nature's building blocks: An A–Z guide to the elements, Oxford University Press, 538 pages, 2001. ISBN 978-0-19-850340-8

[9] J. Rieuwerts, The elements of environmental pollution, Taylor & Francis publisher, 352 pages, 2017. https:// doi.org/ 10. 4324/9780203798690

[10] National Research Council (U.S.), Committee on biologic effects of atmospheric pollutants chromium, Washington, DC: National Academies Press, 1974. https://doi.org/10.17226/20099

[11] S.C. Gad, T. Pham, Vanadium, Encyclopedia of Toxicology (Third Edition), Reference module in Biomed. Sci., (2014) 909-911. https://doi.org/10.1016/B978-0-12-386454-3.00960-X

[12] M. Ostrooumov, Y. Taran, Discovery of native vanadium, a new mineral from the Colima Volcano, state of Colima (Mexico), J. Spanish Mineral. Soc., 20, (2015) 109-110. https://www.semineral.es/websem/PdfServlet?mod=archivos&subMod= publicaciones&archivo=Macla20_109-110.pdf

[13] E. D. Carpio. L. Hernández, C. Ciangherotti, V. V. Coa, L. Jiménez, V. Lubes, G. Lubesa, Vanadium: History, chemistry, interactions with α-amino acids and potential therapeutic applications, Coord. Chem. Rev., 372 (2018) 117-140. https://doi.org/10.1016/j.ccr.2018.06.002

[14] A.V. Arakel, Carnotite mineralization in inland drainage areas of Australia, Ore Geol. Rev., 3 (1988) 289-311. https://doi.org/10.1016/0169-1368(88)90023-6

[15] W. F. Hillebran, The vanadium sulphide, patronite, and its mineral associates from Minasragra, Peru, J. Am. Chem. Soc., 29 (1907) 1019–1029. https://doi.org/10.1021/ja01961a006

[16] H. Okudera, Relationships among channel topology and atomic displacements in the structures of $Pb_5(BO_4)_3Cl$ with B=P (pyromorphite), V (vanadinite), and As (mimetite), Am. Mineral., 98 (2013) 1573–1579. https://doi.org/10.2138/am.2013.4417

[17] W.S. Steinberg, W. Geyser, J. Nell, The history and development of the pyrometallurgical processes at Evraz Highveld Steel and vanadium, S. Afr. Inst. Min. Metall., 111 (2011) 705-710. https://api.semanticscholar.org/CorpusID:55401705

[18] A. Rashidi, A. Vahid, Arsenic speciation based on amine-functionalized bimodal mesoporous silica nanoparticles by ultrasound assisted-dispersive solid-liquid multiple phase microextraction, Microchem. J., 130 (2017) 137-146. https://doi.org/10.1016/j.microc.2016.08.013

[19] N. Esmaeili, J. Rakhtshah, Ultrasound assisted-dispersive-modification solid-phase extraction using task-specific ionic liquid immobilized on multiwall carbon nanotubes for speciation and determination mercury in water samples, Microchem. J., 154 (2020) 104632. https://doi.org/10.1016/j.microc.2020.104632

[20] N. Esmaeili, J. Rakhtshah, E. Kolvari, A. Rashidi, Rapid Speciation of Lead in Human Blood and Urine Samples Based on MWCNTs@DMP by Dispersive Ionic Liquid-Suspension-Micro-Solid Phase Extraction, Biol. Trace Elem. Res., 199 (2021) 2496–2507. https://doi.org/10.1007/s12011-020-02382-7

[21] J. Rakhtshah, M. Dehghani Mobarake, Simultaneously speciation and determination of manganese (II) and (VII) ions in water, food, and vegetable samples based on immobilization of N-acetylcysteine on multi-walled carbon nanotubes, Food Chem., 389 (2022) 133124. https://doi.org/10.1016/j.food chem.2022.133124

[22] M.Aliomrani,M.A.Sahraian,H.Shirkhanloo,M.Sharifzadeh,M. R. Khoshayand,M. H. Ghahremani, Blood concentrations of cadmium and lead in multiple sclerosis patients from Iran, Iran. J. Pharm. Res., 15 (2016) 825-833. https:// doi.org/ 10.22037/ ijpr.2016.1941

[23] A. Y. Hammood, M. K. AL- Tememi, Z.A. Abdulnabi, A. A. Majed, Synthesis of magnetic spinal ferrite $CrFe_2O_4$nanoparticles and uses them to remove leadand cadmium ions from aqueous solutions, Adv. Nat. Sci.: Nanosci. Nanotechnol., 15 (2024) 045015. https://doi.org/10.1088/2043-6262/ad7c1c

[24] Z. Karamzadeh, J. Rakhtshah, N.M. Kazemi, A novel biostructure sorbent based on CysSB/MetSB@ MWCNTs for separation of nickel and cobalt in biological samples by ultrasound assisted-dispersive ionic liquid-suspension solid phase microextraction, J. Pharm. Biomed. Anal., 172 (2019) 285-294. https://doi.org/10.1016/j.jpba.2019.05.003

[25] M. K.Abbasabadi, Speciation of cadmium in human blood samples based on Fe_3O_4-supported naphthalene-1-thiol- functionalized graphene oxide nanocomposite by ultrasound-assisted dispersive magnetic micro solid phase extraction, J. Pharm. Biomed. Anal., 189 (2020) 113455. https://doi.org/10.1016/j.jpba.2020.113455

[26] S. D. Ahranjani, A lead analysis based on amine-functionalized bimodal mesoporous silica nanoparticles in human biological samples by ultrasound assisted-ionic liquid trap-micro solid phase extraction, J. Pharm. Biomed. Anal., 157 (2018) 1-9. https:// doi.org/ 10.1016/ j.jpba. 2018.05.004

[27] H. Shirkhanloo, M. Ghazaghi, M.M. Eskandari, Cloud point assisted dispersive ionic liquid- liquid microextraction for chromium speciation in human blood samples based on isopropyl 2 - [(isopropoxycarbothiolyl) disulfanyl] ethane thioate, Anal. Chem. Res., 10 (2016) 18-27. https://doi.org/10.1016/j.ancr.2016.10.002

[28] A. A. M. Beigi, M.M. Eskandari, Dispersive liquid-liquid microextraction based on task-specific ionic liquids for determination and

speciation of chromium in human blood, J. Anal. Chem., 70 (2015) 1448-1455. https://doi.org/10.1134/S1061934815120072

[29] A. F. Zarandi, An immobilization of 2-(Aminomethyl) thiazole on MWCNTs used for rapid extraction of manganese ions in hepatic patients, J. Pharm. Biomed. Anal., 240 (2024) 115941. https://doi.org/10.1016/j.jpba.2023.115941

[30] M. K.Abbasabadi, F. Hosseini, Nanographene oxide modified phenyl methanethiol nanomagnetic composite for rapid separation of aluminum in wastewaters, foods, and vegetable samples by microwave dispersive, Food Chem., 347 (2021) 129042. https://doi.org/ 10.1016/j.foodchem.2021.129042

[31] M. Arjomandi, H. Shirkhanloo, A review: analytical methods for heavy metals determination in environment and human samples, Anal. Methods Environ. Chem. J., 2 (2019) 97-126. https://doi.org/10.24200/amecj.v2.i03.73

[32] S. Mahboob, Z. Ahmed, M. F. Khan, P. Virik, N. Al-Mulhm, A.A. Baabbad, Assessment of heavy metals pollution in seawater and sediments, Saudi Arabia, J. King Saud. Univ. Sci., 34 (2022) 101677. https://doi.org/10.1016/j.jksus.2021.101677

[33] S. Tagliapietr, The impact of the global energy transition on MENA oil and gas producers, Energy Strat. Rev., 26 (2019) 100397. https://doi.org/10.1016/j.esr.2019.100397

[34] A. D. Mustafa, H. Juahir, K. Yunus, M. A. Amran, C. Che Hasnam, F. Azaman, I. Z. Abidin, S. H. Azmee1, N. H. Sulaiman1, Oil spill-related heavy metal: A review, Malay. J. Anal. Sci., 19 (2015) 1348 – 1360. http://mjas.analis.com.my/wp-content/uploads/2018/11/AhmadDasuki_19_6_25.pdf

[35] Z. A. Abdulnabi, M. K. Altememi, W. F. Hassan, D. K. Al-Khuzaie, S. M.Saleh, Assessing of some toxic heavy metals levels and using geoaccumulation index in sediment of Shatt Al-Arab and the Iraqi marine region, Baghdad Sci. J.,16 (2019) 323-331. https://doi.org/10.21123/bsj.2019.16.2.0323

[36] P. Kamiński, J. Baszyński, I. Jerzak, B. P. Kavanagh, E. Nowacka-Chiari, M. Polanin, M. Szymański, A. Woźniak, W. Kozera, External and genetic conditions determining male infertility, Int. J. Mol. Sci., 21 (2020) 5274. https://doi.org/10.3390/ijms21155274

[37] O. A. Odunola, A. Muhammad, A. D. Farooq, K. Dalvandi, H. Rasheed, M. I. Choudhary, O.L. Erukainure, Comparative assessment of redox-sensitive biomarkers due to acacia honey and sodium arsenite administration in vivo, Med. J. Nutrition Metab., 6 (2013) 119–126. https://doi.org/10.1007/s12349-013-0127-1

[38] S. C. Grund, H. Kuniber, H. U. Wolf, Arsenic and arsenic compounds, In: Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2005. http://dx.doi.org/10.1002/14356007.a03_113.pub2

[39] J. Maeki-Paakkanen, P. Kurttio, A. Paldy, J. Pekkanen, Association between the clastogenic effect in peripheral lymphocytes and human exposure to arsenic through drinking water, Environ. Mol. Mutagen., 32 (1998) 301–313. https://doi.org/10.1002/(sici)1098-2280(1998)32:4<301::aid-em3>3.0.co;2-i

[40] R. E. Sturgeon, J. A. Desaulincrs, S. S. Berman, D. S. Russell, Determination of trace metals in estuarine sediments by graphite-furnace atomic absorption spectrometry, Anal. Chem. Acta., 134 (1982) 288-291. https://doi.org/10.1016/S0003-2670(01)84198-2

[41] J. J. Peirce, P. A. Vesilind, R. F. Weiner, Environmental Pollution and Control Measures, 1998. https://www.bbau.ac.in/dept/UIET/TCE-033%20%20epdf.pub_environmental-pollution-and-control.pdf