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Heavy Metal Analysis in Edku Lake Sediments Using Spectrochemical Analytical Techniques

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Abstract

Lake Edku is one of the essential northern Egyptian coastal lakes in the Nile Delta and is seriously influenced by man-made pollutants. It receives vast amounts of agricultural, domestic, and fishing waste, particularly from the El-Khairy and Barsik drains. The levels of heavy metals (HMs) in Lake Edku sediments were evaluated using laser-induced breakdown spectroscopy (LIBS) and inductively coupled plasma (ICP) spectrochemical analytical techniques. Also, environmental risk assessment and potential adverse effects on benthic organisms were carried out using different indices and Sediment Quality Guidelines (SGQ). The present study showed that the lake sediment is contaminated to various degrees according to the indices used. The eastern sector was found to be the most contaminated area, and the most polluting elements were Cd, Zn, Mn, and Ni. Cd recorded the highest enrichment factor (FF) values (31.1–36) and contamination factor (CF) values (4.8–5.4) at the eastern sites, indicating very high enrichment and significant contamination. In addition, many HMs, particularly Co, Ni, Mn, and Cd, exceeded the threshold effect concentration levels (TECs) and probable effect concentration levels (PECLs), recording potentially harmful effects on sediment-dwelling organisms. For example, the average content of Co (9.62 mg/kg) is much higher than its TECs and PECLs values. It was also found that LIBS's results agreed with the ICP results. These findings demonstrated the potential of using LIBS as a significant quantitative analytical method to assess the HMs in the sediments of water bodies. The study's outcomes will warn decision-makers, encouraging them to adopt more suitable policies and action plans toward sustainable development that reduce environmental risk and preserve the lake's natural ecosystem.

Keywords: Lake Edku; Heavy metals; Sediments; LIBS; ICP

1. Introduction

The Egyptian Mediterranean coast comprises deltaic and non-deltaic lakes. The coastal lakes play an essential role in the Egyptian economy, as in 2021, more than 82 % of Egyptian lake production was harvested from them, representing 49.2 % of total natural production [1]. Over the years, these lakes have faced multiple challenges due to their increasing vulnerability to climate change, especially sea level rise (SLR) due to the shallowness of these lakes [2]. In addition, deltaic lakes (like Edku Lake) are the most polluted lakes in Egypt because they receive large quantities of agricultural, industrial, and municipal waste through several drains and from factories around them. Lake Edku gets enormous amounts of freshwater from two main drains, namely El-Khairy and Barsik drains. The first drain carries wastewater from fish farms, industries, agricultural lands, and domestic sewage, while the second mainly carries agricultural drainage water into the lake [3]. Heavy metals can reach the sediment by many pathways; over 99 % of those that enter the aquatic system can be stored in the sediment in various ways [4]. They are identified by their high toxicity, extended retention periods, and resistance to degradation. The most important anthropogenic sources of HMs for soils include commercial fertilizers, sewage sludge, and atmospheric deposition from industrial, urban, and road emissions. Some metals, such as Pb, Co, and Cd, are exceptionally hazardous even, at minor concentrations. Metals like Cr, Cu, Ni, and Zn are vital trace nutrients required for various physiological and biochemical processes [5]. Lake sediments have two contradictory roles; they provide nutrients to living organisms and, at the same time, are considered sensitive indicators for monitoring pollutants, as they can act as a sink and carrier of contaminants in the aquatic environment [6]. Thus, lake sediment analysis is vital in evaluating the

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pollution status in a hydrous environment [4] and is a significant environmental indicator of water pollution [7]. Laser-Induced Breakdown Spectroscopy (LIBS) is a well-known atomic emission spectrochemical technique that has shown tremendous potential as an efficient technique for simple and fast multi-elemental detection [8]. LIBS is a spectrochemical analytical method that analyzes atomic and ionic emission lines generated at the sample's surface after focusing an intense laser pulse on such a surface. The obtained LIBS spectra can provide qualitative and quantitative information about the elemental composition of the sample [9]. While qualitative analysis with LIBS is a simple method, quantitative analysis may include some difficulties [10]. Several variables affect the accuracy of the quantitative analysis, such as the sample's overall composition, which has a downside known as the matrix effect [11]. That is why semi-quantitative analysis is done in the case of samples with unknown matrices [12].

The sensitivity of the LIBS system depends on many factors, including the characteristics of the laser pulse (wavelength, pulse duration, pulse energy, etc.), sample homogeneity, and sampling geometry (distance from focusing lens to sample, the focal length of collecting lens, optical fiber, etc.) [13]. LIBS has many advantages over other spectrochemical analytical techniques, such as detecting in situ, determining the elemental composition of samples with minimal or no sample preparation [14], and using an environmentally clean technique that does not require reagents for basic preparations. Due to these advantages, it has been widely used for elemental analysis in various fields, such as environmental monitoring [13,15-18], industrial analysis [19], and bio-medicine [20]. However, the relatively high limit of detection (LOD) of LIBS, compared to other well-established spectrochemical analytical techniques, limits its utilization in some fields. [21]. Compared to LIBS, the methods most usually used for elemental analysis purposes, such as Flame Atomic Absorption Spectrometry (FAAS), X-ray fluorescence (XRF), Inductively Coupled Plasma (ICP-MS, ICP-OES), usually provide better LODs but are time-consuming, expensive, limited by the complex detection process, which needs sample preparation, and environmentally unfriendly thus cannot meet the demands of real-time detection [18]. For instance, Mekonnen et al. (2013) [13] applied LIBS for the analysis of Cr, Mn, and Fe in sediments collected from a polluted river in Ethiopia, and some observed differences between LIBS and FAAS were found and were attributed to the occurrence of matrix effect. In another study, Senesi et al. (2009). [15] measured the contents of Zn, Cu, Cr, Pb, and V in soil and sludge samples, using LIBS after graining and pressing the samples into pellets with no further pretreatment, and then normalize the emission intensity to the spectral background, because no suitable standard was found in the analyzed set of samples, the results of such comparisons between LIBS performance with that of ICP-OES are reported and showed a good agreement between the two techniques.

The present work aims to evaluate the potential of LIBS as an environmentally clean technique for determining HMs contents in the sediment of Edku Lake and validate the LIBS data using the analytical data obtained via the ICP technique for the same samples. In addition, the environmental impact risk of Lake Edku will be evaluated using certain contamination indices such as the geoaccumulation index (Igeo), the contamination factor (CF), and the pollution load index (PLI).

2. Materials and Methods

2.1. Study area

Lake Edku is situated west of the River Nile delta between longitudes 30°8'30" and 30° 23' E and latitudes 31°10 ' and 31° 018 ' N. The lake is connected to the Mediterranean Sea through Boughaz El Maadiya inlet.

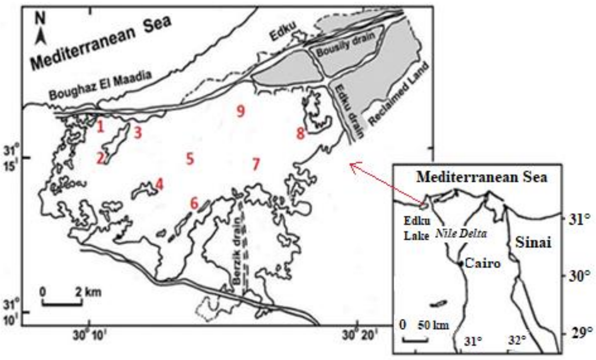

Figure 1. Locations of sampling sites of the study area

2.2 Sampling Program

The sampling program commenced in the winter and summer of 2020. Eighteen duplicate surface sediment samples were collected using a grab sampler (Ekman type) each season at nine selected sites (Figure 1), instantly packed in airtight polythene bags, placed in an ice box, and brought to the lab. Subsamples of the sediments were ground up using a pestle and mortar after oven drying at 60 °C to constant weight. The sediment type and composition at Edku Lake were taken from the Egyptian Environmental Affairs Agency (EEAA) 2021 [22].

The samples were divided into two groups. The first group was compressed into tablets to be used with LIBS. The second group was digested for ICP using a microwave digestion system (model, Multiwave PRO Anton Paar), where 2 ml of concentrated nitric acid, 2 ml of concentrated hydrofluoric acid, and 1 ml of hydrogen peroxide were added to 0.5g of sieved grounded and dried sediment samples in PFA (Perfluoroalkoxy-polymer) digestion vessel. After cooling, the vessels were opened carefully in a fume cupboard. The sample solutions were transferred to 25 ml calibrated flasks and diluted up to mark with deionized water. After filtration, all metals were analyzed by ICP spectroscopy [model, Single Quadrupole Inductively Coupled Plasma Mass Spectrometry (SQ-ICP-MS)]. Results are expressed as mg/kg dry weight. The blank solution, with Suprapur® grade (Merck) regents, subjected to the same treatment as the samples, was prepared as well.

2.3. LIBS setup

The LIBS setup utilized in this study is explained in detail elsewhere [10]. The experimental system was based on an Nd: YAG laser source (Brio Quantel, France), emitting a laser beam at a wavelength of 532 nm. The laser pulse energy was adjusted to be 25 mJ per pulse. A 5.5 cm plano-convex quartz lens focused the laser beam onto the sample surface. The sample was placed on an XYZ translational stage to change the position of the laser spot during measurement. The sample was placed 1 mm before the focus to ensure no breakdown in the air. The laser-induced plasma plume emission was collected via a quartz optic fiber (core diameter 0.6 mm, length 1.5 m). The free terminal was positioned approximately 15 mm above the plasma at a 45-degree angle to contain the plasma emission within the fiber's collection cone. The other end of the fiber was connected to an echelle spectrometer (Mechell 7500, multichannel, Sweden). An intensified charge-coupled device (ICCD) (DiCAM-PRO, PCO computer optics, Germany) was used to record the spectra. The ideal delay between the laser firing time and ICCD triggering was determined by monitoring the line intensities over different delay times.

2.4. Pollution indices

The sediment's environmental assessment was made by calculating four metal pollution indices. Three single indices were included in the set: the contamination factor (CF), the enrichment factor (EF), and the index of geo-accumulation (Igeo). On the other hand, the pollution load index (PLI) is an integrated index.

Enrichment factor (EF) is one often used indices to assess the level of anthropogenic contamination to determine enrichment ratios [23,24] using equation EF = (CM/CX) sample / (CM/CX) earth crust, where CM is the concentration of the metal under study. CX is the concentration of an immobile or reference element, which may be Al, Fe, or Mn[23]. In the present study, Fe was used as the reference element for determining EF values. According to Sutherland (2000) [25], five categories are mentioned in (Table 1) of the pollution degree of (EF). Pollution monitoring systems frequently use the Contamination Factor (Cf), an effective indicator for determining the degree of metal contamination.

It is calculated from the ratio of the metal concentration in the sediment to the background concentration of the metal CF= C metal / C background [26, 27], (Cf) is categorized into four levels as illustrated in (table 1). the pollution Load Index (PLI) is indicated by the heavy metal contamination in a particular area [28], PLI of the sampling site = $n^{th}\sqrt{CF1 \times CF2 \times \ldots CFnt}$, where CF = contamination factor and *n* = number of metals), (table1) shows the PLI and provides simple comparison methods. Geoaccumulation Index (Igeo) values are calculated for minerals, as presented by Muller (1981) [29] using Igeo = $\log_2$ (*Cn*/ 1.5×*bn*). Where *Cn* is the measured concentration of the metal under study (*n*) in the sediment sample and *bn* is the geochemical background of elements (*n*), measured directly in the pre-industrial reference deposits in the region or taken from the literature (the average value of shale described by Turekian and Wedepohl (1961) [27].

Table 1. Pollution classes indices

Single Indices							Integrated Indices	
EF classes		CF classes		Igeo classes			PLI	
Ef value	Pollution	Cf value	Pollution	Igeo	Igeo class	Pollution	value	Pollution
EF<2	Depletion to mineral	CF <1	Low	<0–0	0	Unpolluted	0	Perfection
2 ≤EF≤ 5	Moderate	1 ≤CF≤ P3	Moderated	0–1	1	Unpolluted to moderated	<1	Baseline levels
5 ≤ EF≤20	Significant	3 ≤ CF ≤6	Considerable	1–2	2	Moderated polluted	>1	Polluted
20 ≤ EF≤40	Very high	CF >6	Very high	2–3	3	Moderated to highly polluted		
EF>40	Extremely high			3–4	4	Highly polluted		
				4–5	5	Highly to extremely polluted		
				5–6	>5	Extremely polluted		

3. Results and Discussion

3.1. Grain size distribution

The sediment texture of Edku Lake was taken from EEAA 2021 [22]. Table 2 displays the study of sediment type, which is crucial in understanding metal distribution in sediment since the distribution of metals has always been affected by variations in lake sediment texture [23]. Hence, the concentrations of heavy metals in sediment increase as the amount of organic material increases. Also, sediment has a different capacity to absorb different metals from water seeping through it, as this capacity is the lowest for carbonate-sandy fractions of sediments (Lake-sea area) and highest for clayey organic matter-rich sediments [22].

Table 2. Sediment types and compositions at Edku Lake

Samples	Sediment type	Sediment composition (%)				
		Gravel	Sand	Mud	Silt	Clay
S1	Muddy Sand	0.1	57	42.9	30.4	11.2
S2	Sandy Mud	0.68	23.6	75.72	45.6	19.6
S3	Gravelly Sandy Mud	16.3	35.2	48.5	29.8	15.4
S4	Muddy Sand	0.16	51.6	48.24	38.5	13.1
S5	Muddy Sand	0.09	51.2	48.71	37.2	16.4
S6	Gravelly Sandy Mud	9.8	35.06	55.14	38.4	14.8
S7	Sandy Mud	6.9	41.1	52	38.9	10.6
S8	Muddy Sand	1.1	55.9	43	32.1	10.8
S9	Sandy Mud	0.02	26.8	73.18	43.9	29

The mechanical analysis illustrated in (Table 2) indicates that the sediments of Lake Edku close to the Boughaz inlet area have a high accumulation of sand, as sand is the predominant fraction with an average of 57%, and also in the middle of the lake with an average of 51%. In contrast, the mud fraction is most prevalent in the eastern part of the lake. This is in line with grain size investigations by Badr al-Din et al. (2023) [30], which showed that the sand fraction was dominating on average (56–60%) in the northwest regions close to Boughaz El-Maadi inlet with increasing muddy textures eastward accompanied by sand fraction decreasing of Lake Edku.

In addition, according to Khalil et al. (2013) [31], the Edku Lake sediments are made up of an admixture of sand silt and clay; the sand-rich sediments dominate in the lake sea area, mainly come from the Mediterranean Sea and marine sediments, while the eastern region, in front of EL- Khairy drain, is rich with silt and clay sediments transported by the drains.

3.2. Heavy metals' concentrations in sediment

All samples were collected as indicated in the methodology and assessed using ICP spectroscopy in winter (W) and summer (S) seasons. The results are shown in Table 3, together with the geochemical background concentrations (the reference earth crust) of studied metals provided by Turekian and Wedepohl (1961) [27] and Standard shell from the National Oceanic and Atmospheric Administration (NOAA) (2009) [32].

Table 3. Heavy metals concentrations in mg/kg measured by ICP

	Fe		Al		Mn		Cr		Ni		Zn		Cd		Ti		Co	
Samples	Seasons																	
	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S
S1	12164.00	12364.82	13621.00	11679.78	438.10	567.71	21.64	29.09	42.18	39.39	67.33	76.91	1.37	1.27	311.70	176.00	14.31	16.63
S2	11086.41	12014.40	10461.80	13635.39	401.66	296.20	24.76	26.19	30.22	53.91	74.05	84.73	1.02	1.32	228.50	372.00	10.74	15.37
S3	9876.50	13015.60	10081.50	10047.13	429.64	641.76	27.66	28.70	26.74	43.40	82.16	83.44	1.14	1.18	189.64	394.80	9.62	17.73
S4	13792.51	13015.60	13816.70	9867.71	689.31	543.03	23.17	24.91	43.91	52.33	88.15	84.93	1.53	1.15	294.20	367.60	13.65	20.91
S5	14883.20	14517.40	11971.50	10047.13	613.74	572.64	21.07	24.91	49.67	51.44	91.04	86.17	1.40	1.11	308.61	272.00	15.81	16.86
S6	15187.20	15418.00	12983.70	10226.54	678.20	674.33	23.76	30.12	30.17	41.24	92.16	90.88	1.62	1.10	267.40	282.80	16.74	18.55
S7	14682.70	16019.20	12951.60	11482.47	810.31	736.54	24.92	24.91	42.16	42.53	94.65	88.05	1.81	1.07	310.21	357.60	15.93	18.17
S8	15212.30	15192.70	12109.40	13455.97	842.18	592.39	22.16	23.05	43.12	48.77	95.27	91.62	1.86	1.39	271.65	324.00	17.42	19.82
S9	15762.43	14016.80	10162.30	12200.09	837.10	641.75	24.91	19.71	51.34	46.10	101.33	96.12	1.74	1.28	341.70	392.00	17.65	21.06
Average	13627.47	13952.72	12017.72	11404.69	637.80	585.15	23.78	25.73	39.95	46.57	87.35	86.98	1.49	1.21	280.40	326.50	14.70	18.35
STD	2088.32	1427.97	1467.78	1387.82	178.57	124.03	2.05	3.26	8.84	5.27	10.92	5.54	0.29	0.11	47.20	71.80	2.90	1.95
Shale Standard	47200		80000		850		90		68		95		0.3		4600		19	
Earth Crust	56300		82300		950		102		84		70		0.15		5650		25	

W: winter S: summer

The results showed that Fe and Al have the highest concentration while Cd has the lowest. The high concentrations of the most studied metals in Edku Lake and the most polluted sites were recorded at S6, S7, S8, and S9. Samples S6 and S7 are mainly affected by the agricultural land banks. Sample stations S8 and S9 face the Barsik and El-Khairy drains, respectively. Minimum concentrations of heavy metals are found at site S3, located south of the international road.

Accordingly, it can be concluded that drain water discharged into the lake caused an increase in the amounts of metals in the eastern part. Moreover, according to Shalaby et al. (2017) [33], sites closest to the drain contain the highest concentrations of heavy metals, which may be due to the area in front of the drains containing high concentrations of organic compounds and fine sediments, which affects the absorption of pollutants [34].

Water drainage contains a high percentage of organic and inorganic materials deposited at the bottom of the lake, and the deposition of these materials varies from region to region. Since the sedimentation process depends on water drainage, it can be concluded that our results differ from one site to another depending on the sedimentation process, as the sedimentation process not only depends on the water drainage but also the density of aquatic plants in different areas, and the type of sediment.

3.3. Ecological Risk Assessment

Table 4 displays the concentrations of heavy metals in Edku Lake sediments that were assessed against the development and evaluation of consensus-based Sediment-Quality Guidelines (SQGs) [35, 36]. The effects-based SQGs that met the selection criteria were then grouped to facilitate the derivation of consensus-based SQGs [37].

Specifically, the previously published SQGs for protecting sediment-dwelling organisms in aquatic ecosystems were grouped into two categories according to their original narrative intent: Threshold Effect Concentration levels (TECs) and Probable Effect Concentration Levels (PECs). TECs were intended to identify contaminant concentrations below which harmful effects on sediment-dwelling organisms were not expected. The PECs were intended to identify contaminant concentrations above, which were expected to have frequent harmful effects on sediment-dwelling organisms [38,39]. The concentration of metals in the sediment samples was compared with the consensus-based TEC and PEC values (Table 4).

Table 4. Comparison between HMs contents in Edku and SQGs

Metals		Al	Fe	Mn	Ni	Zn	Cr	Cd	Ti	Co
Present study Concentration range (mg/kg)	Min	9867.7	9876.50	296.20	26.74	67.33	19.71	1.02	176.0	9.62
	max	13816.7	16019.2	842.1	53.9	101.3	30.12	1.86	394.8	21.1
TEC			20000	673	22.70	121	43.40	0.99	not available	1
PEC		58030	40000	1081	48.60	459	111	4.98	not available	4

The results show that Al, Fe, Zn, and Cr content have no harmful effects on sediment-dwelling organisms.

The concentration of Mn in sediments for S6, S7, S8, and S9 exceeds the TEC value, adversely affecting the ecosystem. For Ni, concentrations show that 100% of sampling sites surpass the TEC value (22.7mg/kg) in both seasons. Furthermore, Ni concentrations at S2, S4, S5, S8, and S9 exceed the PEC value (48.6mg/kg). Thus, the harmful effect on sediment-dwelling organisms was expected. Therefore, it could be concluded that 44.4% of sampling sites in summer are toxic and dangerous, while a lower percentage 22.2% in winter. The Cd concentrations slightly exceeding the TEC value may moderately affect sediment-dwelling organisms. For Co, results show that all sampling sites exceed the PEC value, so 100% exhibits a high effect on sediment.

3.4. Contamination Assessment of Heavy Metals in Sediment

The assessment of the lakes' sediment pollution involved calculating EF, CF, and Igeo indices for each element. At the same time, PLI allowed for the integrated assessment of sediment pollution for all heavy metals in each sampling site. The definitions and calculations of the values of EF, CF, PLI, and Igeo were mentioned in the methodology.

As shown in (Figure 2 (a)), the measured ranges of EF of heavy metals in sediments revealed that all sediment samples had Al, Co, Cr, and Ti that typically less than 2 (EF < 2), indicating that all the heavy metals in the sample came from the crust and occurred naturally.

All sites had measured levels for Ni and Mn ($2 \leq EF \leq 5$), indicating moderate enrichment. Zn showed moderate enrichment from S1 to S6 and significant enrichment in S7, S8, and S9 as ($5 \leq EF \leq 20$). Most sample sites that exhibit extremely highly enriched values had Cd values ($20 \leq EF \leq 40$) content. However, the CF values in Fig. 2(b) supported this finding, showing that all sediment samples examined were categorized as highly contaminated with Cd.

All Cd values exceed 3 (3 ≥ CF < 6), while all other elements examined at all sites were characterized as low-contaminated (CF < 1), which is consistent with Shalaby et al. (2017) [33] research on Lake Edku. Our study showed that the CF of the sediments was typically increasing eastward, which is consistent with the findings of Badr al-Din et al. (2023) [30], who also documented a very high degree of Cd contamination in Edku Lake.

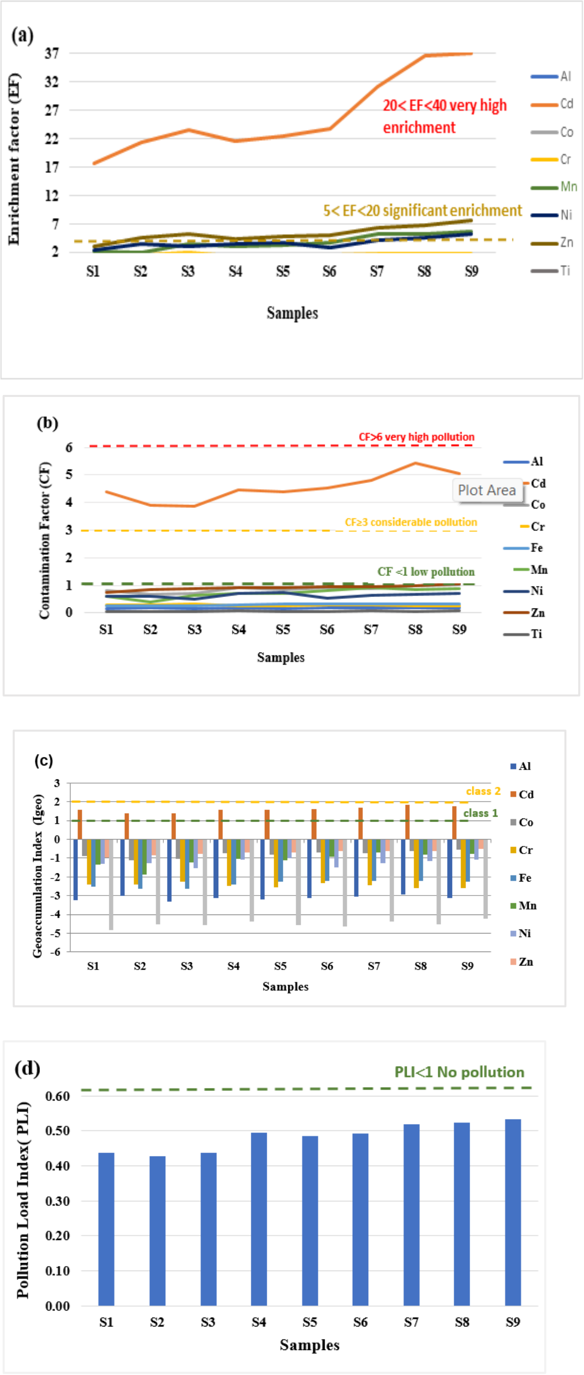

Figure 2. State of HMs pollution of the Edku Lake sediments based on (a) EF, (b) CF, (c) Igeo, and (d) PLI

In parallel with our findings, the Igeo values are consistent with the EF and CF results, as shown in Figure 2(c). The cadmium content in all sampling sites gives a moderate contamination value, consistent with the study conducted by Shalaby et al. (2017) [33]. In contrast to Cd, the other studied metals, based on Igeo data, showed no contamination effect. Somewhat different results were obtained by analyzing PLI index values for investigated samples, as PLI values permitted complex assessment of pollution of sediments and the recorded values were lower than one as shown in Fig.2(d), so it could be concluded that sampling sites are classified as unpolluted areas.

3.5. *LIBS analysis*

LIBS was used as an emerging technique for elemental analysis based on atomic emission spectroscopy. It is an environmentally clean technique to be used for the first time in the environmental analysis of Edku Lake, especially for detecting heavy metals in sediments. First, LIBS optimum conditions for the camera gate and delay time were determined. This was done by plotting a relation between the delay time and the LIBS signal intensity of the Al spectral line at 309.2 nm at different delay times from 500 to 6000 ns.

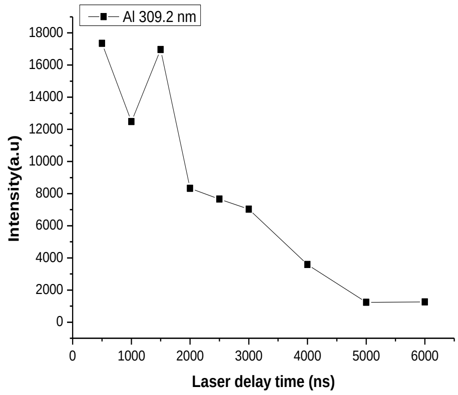

Figure 3. Dependence of LIBS signal intensity on delay time for Al 309.2 nm spectral line in sediment sample S1

A typical plot of the dependence of LIBS signal intensity on the delay times at the selected wavelength is presented in Figure 3. It is clear from the figure that the maximum LIBS signals are recorded at around 1500 ns, where the maximum signal intensity-to-background ratios were observed. Thus, all measurements have been performed at this delay time of 1500 nm and gate width of 2000 ns.

The typical LIBS spectrum of HMs in the present study was demonstrated in Figure 4 (a&b) of the sediment sample, in which many emission lines are produced for each element. The most essential heavy metals in sediment are located in the visible region at 400 – 700 nm. The lines of the elements under study were chosen to fulfill the LIBS spectrum conditions [40].

Table 5 illustrates the spectral lines chosen to fulfill the LIBS spectral line conditions. The emission lines used for semi-quantitative analysis were listed along with their spectroscopic data. Spectral lines have been assigned by LIBS++ software and confirmed from the NIST database [41].

The normalized intensities of Fe and Ti, as determined by LIBS throughout the winter (W) and summer (S) seasons, are shown in Figures 5 (a,c) and (b,d), respectively. The results were compared to the ICPs in mg/kg, and it can be seen that Fe and Ti exhibit almost identical findings. In addition, Figure 6 (a, b) shows the spectral lines of Fe and Ti in different sampling sites S3, S6, and S9, and the spectra are overlaid for comparison, showing the intensity change for both Fe and Ti from one sampling site to another in winter.

On repeating the same comparison on the other heavy metals under study, it was found that a good agreement was obtained between the LIBS intensities and ICP concentrations of Al, Ni, Mn, Zn, Cr, and Co in both seasons.

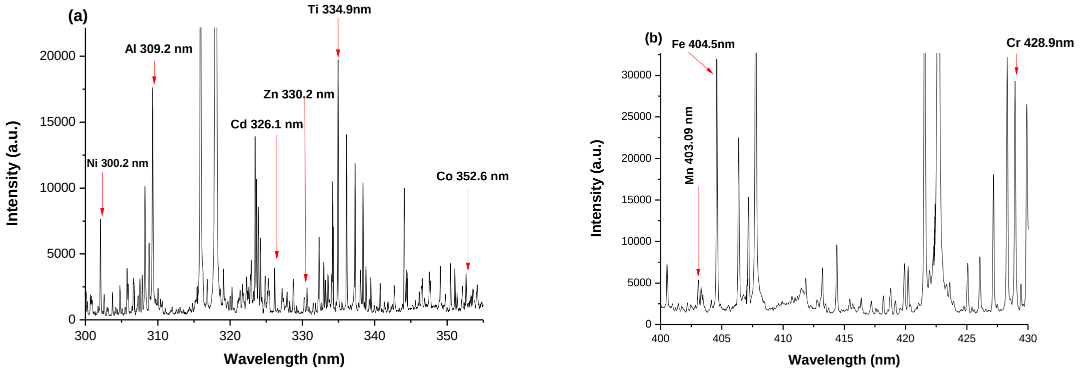

Figure 4. Two sections (a,b) of a typical LIBS spectrum for the collected sediment sample with assigned heavy metals spectral lines

Table 5. The spectroscopic data of the spectral lines transitions

Elements	Wavelength (nm)	Transition probability (A_{ki})	Energy upper (E_K)	g_k	g_i	*e* Upper	*e* Lower
Fe (I)	404.58	8.63E-01	3.67E+04	9.00	9.00	4.55	1.49
Al(I)	308.21	6.3E-01	3.2E04	4.00	2.00	4.021	0.000
Ti(II)	334.90	1.33E+00	3.02E+04	12.00	10.00	3.75	0.05
Ni (I)	338.05	1.3E00	3.3E04	3.00	5.00	4.089	0.423
Mn(I)	403.09	1.74E-01	2.48E+04	8.00	6.00	3.08	0.00
Cr(I)	428.93	3.16E-01	2.33E+04	5.00	7.00	2.89	0.00
Co(I)	352.68	1.30E-01	2.83E+04	10.00	10.00	3.51	0.00
Zn(I)	330.25	1.07E+00	6.28E+04	5.00	3.00	7.78	4.03
Cd(I)	326.13	7.08E-03	3.07E+04	3.00	1.00	3.80	0.00

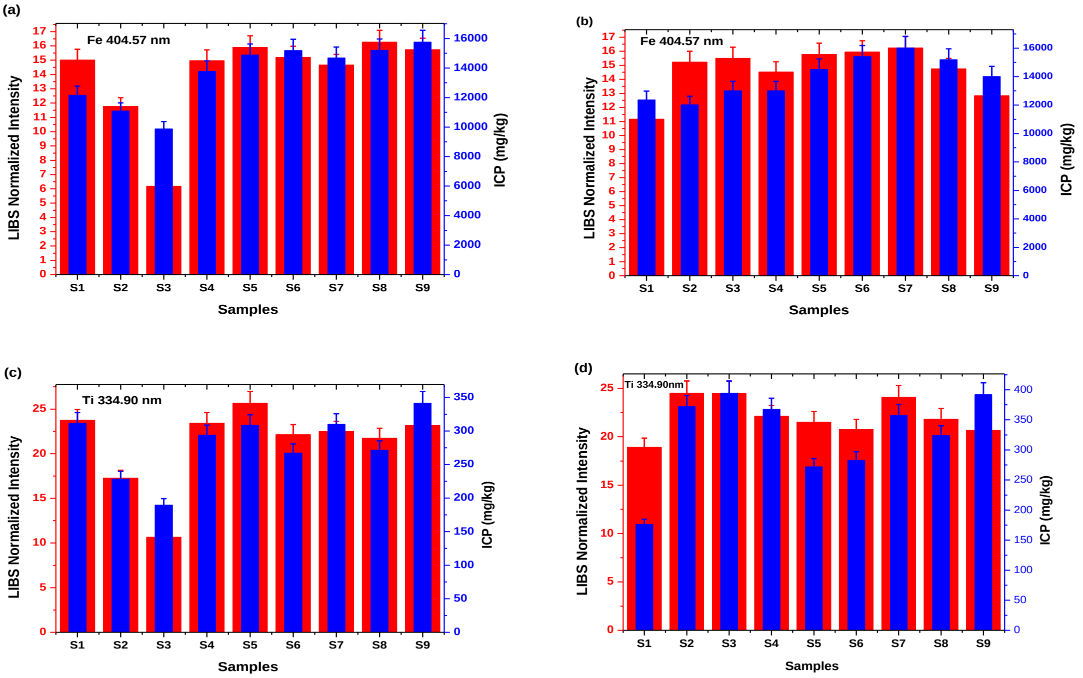

Figure 5. Bar graphs for the LIBS and ICP results for Fe and Ti in different samples, in winter (a,c) and summer (b,d).

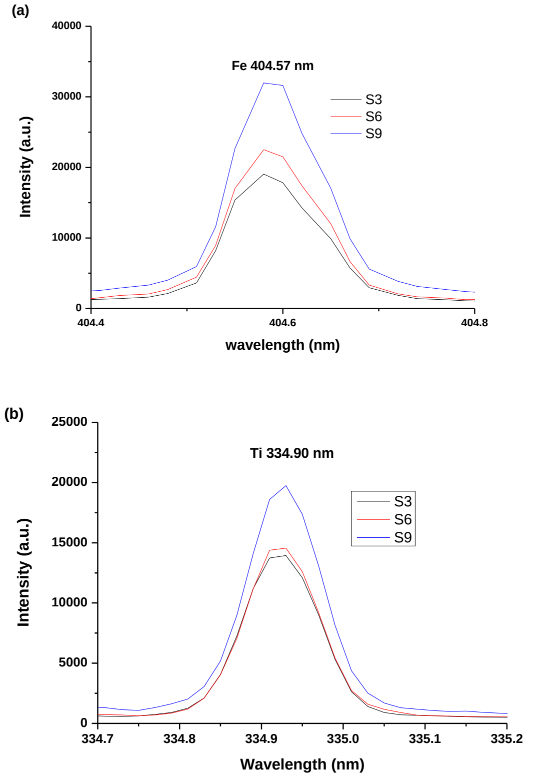

Figure 6. LIBS Intensity variation for (a): Fe (404.57 nm) and (b): Ti(334.90 nm) in three sediment samples

On the other hand, Cd LIBS results failed to validate the Cd results of the ICP as a fluctuation between both intensity and concentration was observed from site to site; maybe this was due to the low concentration of Cd, which is below the detection limit of LIBS.

According to the previous results, LIBS and ICP are in good agreement. However, slight differences arose in some elements, which can be attributed to the micro-heterogeneity of the samples as well as self-absorption. It was also reported that different types of constituents and sediment properties in the sample may cause changes in the plasma excitation [42]. This is the case with our samples, composed of a mixture of sand, silt, and clay, where the soil properties are different from one sample to another, as shown in Table 2. Han et al. (2018) [17] also reported complex samples, such as sediments, influenced by matrix effects augmented by the fact that they present different properties in terms of texture, grain size (sand, silt, and clay contents), and chemical composition.

3.6 Estimation method and Statistical analysis of LIBs and ICP results

In order to obtain quantitative LIBS analysis, the subsequent steps were used:

1. The winter results measured by both LIBS (relative intensity) and ICP (concentration by mg/kg) in all sampling sites were used to infer linear relationships with an equation represented by Y= aX+C, as shown in (Table 6).
2. The normalized intensities measured by LIBS (X) during summer were used to mathematically estimate their concentrations by using the inferred equations obtained in the previous step; these results will be referred to as (calculated LIBS=Y), as shown in (Table 7).

3. Concurrently, the concentrations of all summer samples were also measured by ICP, referred to as (measured ICP) as shown in (Table 7).
4. A normality test was conducted to evaluate the significant difference between the calculated LIBS concentrations and measured ICP concentrations to ensure that the data follows a normal distribution pattern where normality is assumed for all regression procedures. Normally distributed elements are required for the T-test, and non-normally distributed elements are needed for the Mann-Whitney Rank Sum Test, as shown in (Table 8).
5. If P >0.05, we can conclude that there is no significant difference, and calculated LIBS concentrations could be used to estimate quantitative measurements without ICP confirmation.

Different equations have been used to estimate the HMs' summer concentrations; Figure 7 (a,b) illustrates Fe and Ti as illustrative examples. Both normalized intensities and concentrations for winter sampling sites were used to obtain a regression equation (Y= 562.5 X + 5765) and (y = 9.3393x + 82.808) for Fe and Ti, respectively. Also, all elements have a high correlation (R2) except Cd (Table 6).

From Table 6 to Table 8, no significant difference exists between measured and calculated concentrations using estimated regression equations as P> 0.05 for most elements except for Cd. Cd gives a low correlation where R^2 equals 0.42, which explains their P values as P<0.05, meaning a significant difference is found. Low Cd content and/or the matrix effect in LIBS can justify this apparent lack of correlation.

From all of the results, one we suggest that LIBS is a direct method for quantitative analysis using statistical methods. So, the present estimated method used the simple LIBS analytical technique to estimate the concentration of HMs in sediment instead of traditional methods that consume time and require sophisticated sample preparations.

Thus, we can conclude that the proposed method is effective for indirect quantitative analysis using LIBS.

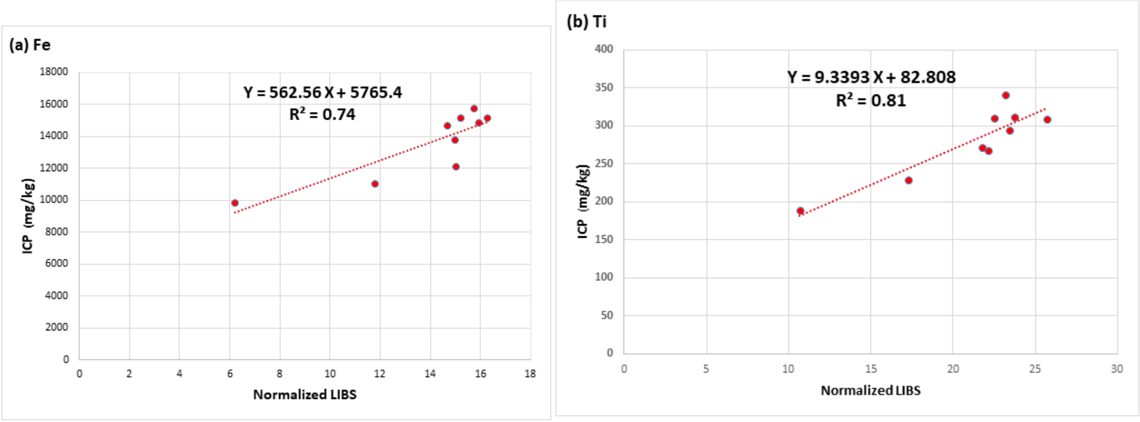

Figure 7. Estimated relationships between LIBS and ICP results for Fe (a) and Ti (b) in winter

Table 6. The LIBS Normalized intensity and the corresponding ICP (mg/kg) concentrations for different elements in different samples that are used in estimating regression equations in winter

	Fe		Al		Mn		Cr		Ni		Zn		Cd		Ti		Co	
Samples	LIBS	ICP	LIBS	ICP	LIBS	ICP	LIBS	ICP	LIBS	ICP	LIBS	ICP	LIBS	ICP	LIBS	ICP	LIBS	ICP
S1	15.0	12164.0	14.1	13621.0	4.4	438.1	5.7	21.6	4.6	42.2	1.6	67.3	8.7	1.4	23.8	311.7	2.1	14.3
S2	11.8	11086.4	12.1	10461.8	2.4	401.7	9.8	24.8	3.2	30.2	1.4	74.1	5.2	1.0	17.3	228.5	2.0	10.7
S3	6.2	9876.5	12.0	10081.5	3.1	429.6	10.6	27.7	2.7	26.7	1.7	82.2	3.7	1.1	10.7	189.6	1.5	9.6
S4	15.0	13792.5	16.5	13816.7	4.9	689.3	6.7	23.2	4.5	43.9	2.0	88.2	7.2	1.5	23.4	294.2	2.4	13.7
S5	15.9	14883.2	14.6	11971.5	4.6	613.7	4.1	21.1	5.2	49.7	2.1	91.0	9.2	1.5	25.7	308.6	2.3	15.8
S6	15.2	15187.2	17.5	12983.7	5.6	678.2	7.2	23.8	3.3	30.2	2.2	92.2	6.5	1.6	22.1	267.4	2.7	16.7
S7	14.7	14682.7	13.5	12951.6	5.3	810.3	7.3	24.9	4.1	42.2	2.5	94.7	8.2	1.8	22.5	310.2	2.3	15.9
S8	16.3	15212.3	13.1	12109.4	6.3	842.2	7.5	22.2	4.4	43.1	2.5	95.3	7.4	1.9	21.8	271.7	2.5	17.4
S9	15.7	15762.4	13.4	10162.3	4.6	837.1	6.0	24.9	4.9	51.3	2.8	101.3	8.4	1.7	23.2	341.7	2.4	17.7
R^2	0.74		0.9149		0.66		0.63		0.94		0.83		0.42		0.81		0.74	
Regression	y = 562.56x + 5765.4		y=1.5322x-6287		y = 119.68x + 88.429		y = 0.8039x + 17.992		y = 10.064x - 1.2439		y = 21.883x + 41.661		y = 0.105x + 0.7594		y = 9.3393x + 82.808		y = 7.1601x - 1.3539	

Table 7. P values for concentrations in group 1 (G1): measured by ICP, and in group 2 (G2): calculated LIBS

	Fe		Al		Mn		Cr		Ni		Zn		Cd		Ti		Co	
Samples	G1	G2	G1	G2	G1	G2	G1	G1	G1	G2	G1	G2	G1	G2	G1	G2	G1	G2
S1	12364.8	12046.7	11679.7	11968.2	567.7	639.3	29.1	26.8	39.3	35.8	76.9	72.1	1.3	1.6	176.0	259.5	16.6	19.5
S2	12014.4	14335.5	13635.4	13091.5	296.2	447.6	26.2	22.1	53.9	59.4	84.7	75.2	1.3	3.2	372.0	312.0	15.4	17.9
S3	13015.6	14490.9	10047.1	10733.5	641.7	675.5	28.7	23.3	43.4	48.9	83.4	77.9	1.2	2.2	394.8	311.5	17.7	22.1
S4	13015.6	13938.2	9867.7	10331.0	543.0	587.9	24.9	23.8	52.3	51.3	84.9	81.7	1.2	2.3	367.6	289.6	20.91	24.1
S5	14517.4	14643.1	10047.1	10743.0	572.6	615.5	24.9	23.0	51.4	48.5	86.2	84.5	1.1	2.1	272.0	283.9	16.8	18.6
S6	15418.0	14740.4	10226.5	11218.5	674.3	644.1	30.1	24.4	41.2	42.3	90.9	89.5	1.1	1.9	282.8	276.7	18.5	21.1
S7	16019.2	14901.3	11482.5	11228.2	736.5	651.9	24.9	24.3	42.5	43.5	88.1	97.9	1.1	1.4	357.6	307.9	182	21.1
S8	15192.7	14060.8	13455.9	12473.1	592.3	636.1	23.1	25.6	48.8	41.9	91.6	100.5	1.4	1.7	324.0	286.8	1981	23.3
S9	14016.8	12990.9	12200.1	12128.8	641.7	616.4	19.7	24.6	46.1	47.9	96.1	102.9	1.3	1.8	392.0	275.9	21.1	26.6
P	0.912		0.81		0.596		0.157		0.98		0.791		<0.001		0.133		0.325	

Table 8. Statistical analysis using Sigma plot 12.5

	(Shapiro-Wilk)			
HMs	Normality	Test	p	difference
Fe	Yes	T-test	0.92	No
Al	Yes	T-test	0.81	No
Mn	No	Mann-Whitney Rank Sum Test	0.6	No
Cr	Yes	T-test	0.2	No
Co	Yes	T-test	0.3	No
Ti	No	Mann-Whitney Rank Sum Test	0.13	No
Ni	Yes	T-test	0.98	No
Zn	Yes	T-test	0.791	No
Cd	Yes	T-test	<0.001	yes

4. Conclusions

Results obtained in this work show that the LIBS technique applied to the determination of several heavy metals in sediment is successful for the qualitative recognition of metal and semi-quantitative analysis but is still to be considered in quantitative analysis, especially when the metal concentration is low.

All studied elements show good agreement between LIBS and ICP. We were able to construct calibration curves through calculated equations. The T-test was found and proven to be in good agreement after comparing the estimated concentration of summer data with the ICP-measured concentration equations as P> 0.05. However, because of the low concentration of Cd, it did not show good concurrence and could not be predicted as P<0.05.

The most contaminated area was determined to be in the eastern part of the lake. Fe, Al, Cr, and Ti were determined to be at normal levels, while Ni, Mn, Cd, and Zn were the most polluting elements. Zn and Mn, in the eastern sites, exhibit enrichment values (EF) ranging from (6.2-7.6) and (5.1-5.7), respectively, indicating significant pollution, whereas the Ef values for Ni varied from 4 to 5.2, indicating moderate to significant pollution. Furthermore, Zn, Co, and Mn have contamination factors greater than 1, indicating moderate contamination.

Based on the SQGs, Co, Ni, Mn, and Cd surpassed the levels of both TECs and PECs. The average level of Co (9.62 mg/kg) is higher than its TECs (1) and PECLs (4) values. Moreover, Ni and Mn concentrations at several stations surpass their TEC values of 22.7 and 673, respectively, while the Cd concentration range (1.02-1.86) is more significant than its TEC value (0.99).

With this regard, LIBS can be considered an environmentally clean analytical technique, relatively simple, and can also be easily adapted for the in situ determination of metals in hostile environments, contrary to the ICP technique, which needs a lot of preparation, making it inappropriate for in situ environmental measurements.

5. Conflicts of interest

"No conflicts to declare", Funding: NA

6. Acknowledgments

"None"

7. References

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