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Ecological Risk Assessment and Metal Pollution in Water and Fish in a Mediterranean Lagoon: A Case Study of Edku Lake, Egypt.

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Abstract

In the current study, laser-induced breakdown spectroscopy (LIBS) was utilized to assess the presence of heavy metals (HMs) in the water of Edku Lake and their accumulation in the muscles of edible fish, primarily Nile tilapia. The results obtained from LIBS were validated using the inductively coupled plasma (ICP) technique, specifically on iron (Fe) and aluminum (Al). The average concentrations of various metals, including Fe, Al, manganese (Mn), zinc (Zn), chromium (Cr), and cadmium (Cd) as determined by ICP, during winter and summer were found to be in the following ranges (in µg/l): Fe (266.67-474.44), Al (333.33-1184.44), Mn (7.11-8.23), Zn (9.00-8.66), Cr (5.00–23.23), and Cd (2.49-1.20, 1.26-0.52). For the fish muscle samples, the average metal content (in µg/g) was ranked in the following order: Al (9.43-5.57) > Fe (8.37-6.51) > Zn (0.9) > Mn (0.5-0.57) > Cr (0.08-0.1) > Cd (0.01-0.007). The obtained analytical results demonstrated good consistency between the LIBS and ICP methods. However, for the very low-concentration metals, such as Mn, Cr, and Cd in water, as well as all metals in fish, this level of agreement was not observed. The results of the present work revealed that Edku Lake faces challenges with poor water quality due to heavy metal pollution; however, the levels of metals in Nile tilapia remain within safe limits for human consumption. The LIBS technique is promising for monitoring heavy metals in water samples, but its sensitivity needs further improvement to effectively detect low concentrations of elements in biological tissues.

Keywords: Lake Edku; Heavy metals; Water; Fish; LIBS; ICP

1. Introduction

Lakes play a crucial role in the water infrastructure of delta and coastal zone societies, as lake ecosystems are critical resources for aquatic life and human needs, and changes in their environmental quality and water renewal rates have a vast impact on the surrounding area's socio-economic activities and ecological implications. Lakes are the world's most vulnerable, productive ecosystems, but unfortunately, the lakes have reached a point of crisis due to industrialization and unplanned urbanization [1]. As the population increases, people are expected to live, work, and recreate around the lake environment, so optimizing and governing the management of lakes is essential.

The Egyptian Mediterranean coast has five brackish (northern delta lagoons): Mariout, Edku, El-Burullus, El-Manzallah, and El Bardawil. For a long time, the north Egyptian lakes have been the main source of fish [2]. In the last 50 years, the northern lagoons faced severe problems that retarded its environmental and fisheries development. The most serious one is that heavy metal pollution, climate change, and overfishing all put pressure on the water cycle [1]. The coastal lakes play an essential role in the Egyptian economy, as in 2021, more than 82 % of Egyptian production was harvested from them, representing 49.2 % of the total natural fish production [3, 4].

Due to anthropogenic activities and pollution, Lake Edku is one of Egypt's most threatened aquatic lagoons. An estimated 1.738 billion cubic meters of drain water reaches Lake Edku annually through drains in the eastern part of the lake and the Barsik Drain, which connects to the lake in the southern part. The lake's area now reaches 4,000 acres, representing the "only outlet" for the livelihoods of 10,000 fishermen. The lake also receives seawater from Abu Kir Bay on its northwestern part through Boughaz El-Maadia. Abu Kir Bay is a shallow basin that receives considerable amounts of raw industrial waste from many factories [5].

Pollution of the environment can be seen in the level of the HMs content in water bodies, like rivers and lakes, which is considered one of the most dangerous hazards affecting both developing and developed countries. HMs pollution can be adsorbed, precipitated, or dissolved in the environment when pollutants are discharged into water bodies without adequate treatment. HMs can cause significant damage to the environment and the health of humans and aquatic organisms [6]. Water quality measurements are essential for the biology and physiology of fish and should be kept within a specific limit to ensure their good performance. Many researchers have studied the hydrographic and chemical characteristics of Lake Edku water and sediments [1,7,8]. A study conducted in the winter of 2019 determined the concentrations of Fe, Cr, Cd, nickel (Ni), and lead (Pb) in Edku water, as well as the muscle of the edible fish [8]. They found that Fe had the highest mean concentrations in water and fish samples, while Cd had the lowest values. A study conducted between 2011 and 2012 examined whether the physical and chemical characteristics of Edku Lake water were favorable to fish health and quality [9]. The study found that drainage wastewater and environmental factors affect fish condition and quality.

A study conducted throughout all four seasons of 2019 investigated the concentrations of specific heavy metals in water

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and fish in Edku Lake for the HMs in water are as follows: Fe > Mn > Pb > Zn > Cd [10]. For the same heavy metals in fish: Fe > Zn > Mn > Pb > Cd. However, based on the pollution index (PI), heavy metal evaluation index (HEI), and Hazard index (HI), "Cd" was less than 1 for all heavy metals from all sites. The study concluded that Edku Lake is contaminated in several ways and recommended that effluents be treated before being discharged into the lake.

The LIBS technique has been proposed and tested across nearly every field of analytical chemistry, including industrial and environmental diagnostics, forensic analysis, biomedicine, cultural heritage studies, and more. LIBS is a spectrochemical technique that utilizes a low-energy, high-power laser pulse focused on the surface of a sample. When comparing LIBS to traditional elemental analysis methods like Flame Atomic Absorption Spectrometry (FAAS), X-ray fluorescence (XRF), and ICP, it's clear that LIBS offers several advantages compared to other spectrochemical analytical techniques. It allows for in situ detection and enables the determination of the elemental composition of samples with little to no preparation. Additionally, it is an environmentally friendly method that does not require reagents for basic sample preparations. LIBS is widely used for detecting and analyzing heavy metal contaminants in water, wastewater, and groundwater [11,12]. When analyzing liquid samples quantitatively, LIBS has several difficulties, such as splashing, a substantially shorter plasma lifetime, and a much weaker spectrum. Several studies have been published in recent years that addressed converting water to solid to solve these issues. Lee et al. (2012) used filter papers as substrates to convert aqueous solutions into solid samples for LIBS analysis of pre-concentrated dissolved heavy metal ions, specifically chromium and palladium [13]. By pre-concentrating the heavy metal ions, the limit of detections (LODs) significantly improved, and the resulting data compared to the outcomes of the ICP method showed potential as a quick, dependable method of evaluating water quality.

A study published in 2020 measured (Cd, Mn, Cr, and Cu) in aqueous solutions using LIBS and enhanced the results by combining filter paper with LIBS [14]. All results showed that the filter paper enrichment method was effective and accurate for rapid on-site detection of trace metals in aqueous solutions. The results aligned reasonably well with those obtained from ICP. In addition, they concluded that filter paper enrichment combined with LIBS is a feasible approach to wastewater quality monitoring.

Additionally, LIBS is used to identify heavy metals in fish as an essential environmental monitoring tool [15,16]. Ponce et al. (2016), for example, used LIBS to track the accumulation of heavy metals in edible fish and compared the results with those from atomic absorption spectrometry to conclude that LIBS could be used as a portable system for the control of contamination in edible fish [17].

The current study aims to evaluate the effectiveness of LIBS as an environmentally friendly and straightforward technique for determining HM concentrations in the water and fish of Edku Lake. Additionally, it seeks to validate the LIBS results by comparing them with data obtained using the ICP technique for the same samples. The study will also assess the aquatic environment of Edku Lake by examining water quality indices, HM levels in the water, and metal pollution indices. Furthermore, it will investigate HM levels in fish, evaluate the potential impact on human health, and assess the risk to consumers who consume these fish.

2. Materials and Methods

2.1. Study region

Lake Edku is one of the Egyptian lagoons that is connected to the Mediterranean Sea and situated in the western part of the Delta Nile, around 30 km east of Alexandria, between longitudes 30°8'30" and 30°23' E and latitudes 31°10' and 31° 018' N. It includes islands that divide the lake into three well-defined basins: western, central, and eastern. The western and the eastern districts are smaller compared to the central basin. The main drains, El-Khairy and Berzik, discharge the wastes into the southeastern part. El Khairy Drain collected the wastes from three drainage systems: Damanhour, Edku, and El-Bousely subdrains, which carry industrial, agricultural, and domestic wastes. Meanwhile, Barsik Drain mainly carries agricultural drainage water to the lake [1].

2.2. Sampling procedure

Subsurface water samples were collected seasonally from 9 selected sites in the Edku Lake during 2020. Figure 1 shows duplicate subsamples collected from each site. The samples were kept in clean, stoppered plastic bottles for the laboratory measurement of physicochemical parameters.

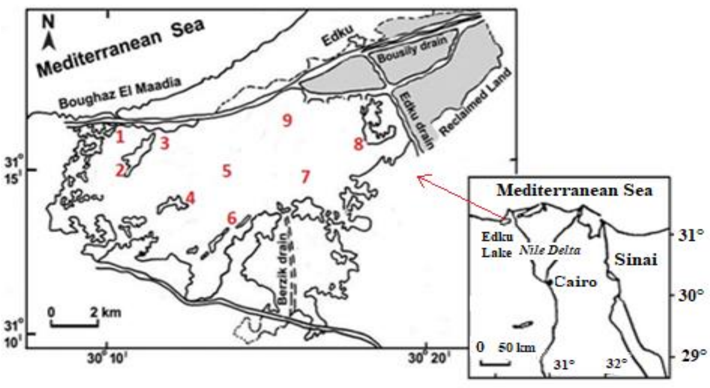

Figure 1. Locations of sampling sites of the study area

For heavy metal analyses using ICP, water samples were preserved with concentrated nitric acid (HNO_3) to reduce pH to below 2 to stop bacterial growth, block oxidation reactions, and prevent precipitation of the metals. The bottles were then stored in a refrigerator at 4°C to avoid change in volume due to evaporation. Water analysis using LIBS involves filtering 1000 ml of each collected sample with ashless filter paper, allowing it to dry, and then utilizing it as a target in the LIBS setup.

Thirty samples of Nile Tilapia, a well-known fish species in Egypt commonly referred to as Bolti, were collected during both winter and summer for heavy metal analysis using ICP and LIBS. The collected samples had a mean length of 17.3 ± 4.1 cm and a mean weight of 102.6 ± 19.7 g. For the ICP analysis, the fish muscle samples were carefully and quickly removed and then frozen at −20°C to determine the concentrations of heavy metals. On the other hand, dried muscle samples were used for the LIBS experiments.

2.3. Methodology

2.3.1. Physicochemical parameters in water

The analysis was done on 22 physical and chemical parameters using the American Public Health Association's standard procedures APHA (2005) [18]. Transparency was determined using a Secchi disc 30 cm in diameter, while the electrical conductivity (EC), temperature, and pH were recorded in situ using a multiparameter Thermo Orion Star A 329.

The dissolved oxygen (DO) and biochemical oxygen demand (BOD_5) were measured using the modified Winkler method, and the permanganate method was used to determine the chemical oxygen demand (COD). Total Dissolved Solids (TDS) were measured by filtering a known volume of a well-mixed sample through a glass microfiber filter (GF/C); the filtrate is evaporated to dryness in a weighed dish to constant weight at 90°C. The increase in weight represents the TDS. Ammonia (NH_4^+-N), Nitrate (NO_3^-–N), Nitrite (NO_2^-–N), ortho-phosphate (PO_4^{3-}-P), total nitrogen (TN), and total phosphorus (TP) were determined using a Jenway 6800 Double-Beam Spectrophotometer.

2.3.2. Heavy metals in water and fish using ICP

The ICP instrument was calibrated, and a 1000 mg/l multielement certified standard stock was used for the instrument standardization. The National Institute of Standards and Technology (NIST) standard reference materials were used to verify the analysis. By repeating measurements of the reference materials, the accuracy and precision of the analysis were verified. The recovery rates for metals ranged from 97.1 to 103.8%, within an acceptable recovery percentage range of 80–110 percent, as stated by Huber (2007) [19].

Water samples were digested using the nitric acid digestion method according to APHA (2005) [18]. Fish muscles were digested according to FAO/SIDA (1983) [20], using a mixture of nitric and perchloric acids in closed Teflon vessels heated to 160°C until organic matter decomposed. The digested solutions were cooled, transferred to volumetric flasks, diluted with deionized water, filtered, and stored in plastic bottles. Heavy metal concentrations were calculated using a specific formula and analyzed using Single Quadrupole Inductively Coupled Plasma Mass Spectrometry (SQ-ICP-MS). Results were expressed in µg/l for water and µg/g for fish.

2.3.3. LIBS setup

- *For Water*

As mentioned, water samples were collected from Edku Lake during different seasons. To prepare the samples for LIBS analysis, 1000 ml of the collected samples were filtered using ashless filter paper, left to dry, and then used as a target in the LIBS system. An Nd: YAG laser source (Brio Quantel, France) was used as the excitation source for LIBS, emitting a laser beam of wavelength 1064 nm with a pulse duration of 6 ns and laser pulse energy of 40 mJ. A quartz plano-convex lens of focal length 5 cm was used to focus the laser beam onto the sample surface. The samples were fixed vertically and stretched on a metallic plane substrate to ensure that the sample's surface was on the focal plane of the lens. The sample was then placed on the X-Y translational stage to allow changing the position of the laser spot during measurements. The samples were placed 1 mm before the focus to ensure no breakdown in the air and all the laser energy delivered to the samples.

The emission light produced from the laser-induced plasma plume was then collected via a quartz optic fiber of length 1.5 m and core diameter of 0.6 mm fixed at an angle of 45 degrees to the target and a distance of 1.5 cm. This fiber alignment allows the plasma emission to be within the collection cone of the fiber. The fiber delivers the emission to an echelle spectrometer (Mechell 7500, multichannel, Sweden) to be analyzed. The spectra were then recorded using an intensified charge-coupled device (ICCD) (DiCAM-PRO, PCO-computer optics, Germany). The echelle spectrometer is UV-enhanced, and its spectral range is between 200 and 700 nm. After an optimization procedure, the optimum ICCD delay time (the delay between the laser firing time and ICCD triggering) was adjusted to be 1500 ns, while the optimum time of the gate width was adjusted to be 2000 ns.

For each sample, five spectra were recorded. Each spectrum is the accumulation of 10 single spectra. Every spectrum was taken on a fresh surface position to ensure the filter paper was not penetrated. The five spectra recorded for each sample were then averaged and analyzed using LIBS++ software [21].

- *For Fish*

An adequate amount of fish muscle was dried in an oven at 60 ^{o} C to a constant weight. The LIBS setup is described above; the energy used was 40 mJ, the delay time was 1500 ns, and the gate time was set to 2500 ns. Five positions and fifty shots were taken at each location for every sample. The average spectrum of the five positions was obtained to obtain the spectrum.

2.4. Statistical analysis

A one-way ANOVA was used to check the significant variations between seasons and sampling sites for water analysis results. The Pearson correlation index was also used to compute the correlations between the many variables analyzed in Edku Lake's water.

2.5. Water quality indices (WQI)

Several WQI models were used, and the comparative results for those models are provided to facilitate the interpretation of the data of this study, as shown in Table 1. Three different WQI models were used for this purpose: the Canadian Water Quality Index (CWQI), the Oregon Water Quality Index (OWQI) by Cude (2001) [22], and the Aquatic Toxicity Index (ATI) by Wepener et al. (1992) [23]. In addition, three metal pollution indices were measured: heavy metal pollution index (HPI), metal index (MI), and pollution index (PI).

2.5.1. The Oregon Water Quality Index (OWQI)

A numerical score (0–100) assesses water quality for swimming and fishing activities. It is calculated using the equation:

$$\mathrm{OWQI} = \sqrt{\frac{\mathrm{n}}{\sum_{\mathrm{i}}^{\mathrm{n}} \frac{1}{\mathrm{S_i^2}}}}$$

where n is the number of sub-indices, and Si is the sub-index for each parameter. Details are provided in Cude (2001) [22].

2.5.2. Aquatic Toxicity Index (ATI):

Developed to assess water quality for aquatic life, particularly fish, with scores ranging from 0 (worst) to 100 (ideal). The index is calculated using:

$$\mathrm{ATI} = \frac{1}{100}\left(\frac{1}{\mathrm{n}}\sum_{\mathrm{i=1}}^{\mathrm{n}} \mathrm{q^i}\right)^2$$

where q^i is the quality of the i^{th} parameter (0–100), and n is the number of determinants. Details are in Wepener et al. (1992) [23].

2.5.3. CCME-WQI:

Developed by the Canadian Council of Ministers of the Environment, this index ranges from 0 (poor) to 100 (high quality) and is calculated using:

$$\mathrm{CWQI} = 100 - \frac{\sqrt{\mathrm{F_1^2} + \mathrm{F_2^2} + \mathrm{F_3^2}}}{1 \cdot 732}$$

where F1,F2,F1,F2, and F3F3 are factors scaled to 0–100. Details are provided in CCME (2017) [24].

Table 1. Categorization of water quality index models

CWQI		QWQI		ATI	
95-100	Excellent	90-100	Excellent	0-50	Unsuitable for normal fish life
80-94.9	Good	85-89	Good	51-59	Suitable only for hardy fish species
65-79.9	Fair	80-84	Fair/Medium	60-100	Suitable for all fish life
45-64.9	Marginal	60-79	Poor/Bad		
0-44.9	Poor	10-59	Very Poor		

-(CWQI): Canadian Water Quality Index; (OWQI): Oregon Water Quality Index; (ATI): Aquatic Toxicity Index.

2.6. Metal pollution indices

Three distinct quality indices, HPI, MI, and PI, were employed to assess metal contamination levels in Edku Lake water for aquatic life.

2.6.1. Heavy metal pollution index (HPI)

It is a classification model that assesses the overall quality of the water based on the combined effects of each heavy metal. HPI was determined in our work by using the following formula:

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} \mathrm{Q}_i\, \mathrm{W}_i}{\sum_{i=1}^{n} \mathrm{W}_i}$$

Q_i is the sub-index of the i^{th} metal, n is the number of measured heavy metals, and Wi is the weight unit of the i^{th} metal (between 0 and 1). Details of Q_I & W_I calculation are presented in El-Degwy et al. (2023) [25].

2.6.2. Pollution index (PI)

Since it is based on the concentration of each specific metal, each metal has a unique PI value. In addition, it is categorized into five classes, as illustrated in Table 2. PI was calculated using the following equation:

$$\mathrm{PI} = \frac{\sqrt{[\frac{\mathrm{C}_i}{\mathrm{S}_i}]^2_{\mathrm{max}} + [\frac{\mathrm{C}_i}{\mathrm{S}_i}]^2_{\mathrm{min}}}}{2}$$

Table 2. Categories of water pollution index

Class	PI value	Pollution grade
1	≤1	No effect
2	>1-2	Slightly affected
3	> 2-3	Moderately affected
4	> 3-5	Strongly affected
5	> 5	Seriously affected

2.7. Human Ecological Risk Assessment (HQ and HI)

The human health risk assessment related to fish consumption was determined using the Hazard Quotient (HQ) and Hazard Index (HI) created by the US Environmental Protection Agency and the following equation:

$$HI = \sum_{i=1}^{n} HQ_i,$$

where ***i*** indicates the individual heavy metal.

If HI < 1, it is assumed that the non-carcinogenic adverse effects due to fish consumption are negligible, while the potential for chronic effects may be a concern when HI > 1. Hence, HI < 1 means no hazard; 1 < HI < 10 means moderate hazard, while HI > 10 means high chronic hazard; when HQ_i< 1, the non-carcinogenic risk is negligible. Where HQ_i is the Hazard Quotient (HQ) for the ith metal.

$$HQ = \frac{C_i x\ IR\ x\ EFxED}{RFD_o\ x\ BW\ xAT}$$

Where HQ is the quotient of hazard via ingestion (unitless); C_i is the heavy metal concentration in water (mg/l); IR is the ingestion rate (day^{-1}); EF is the exposure frequency (days year^{-1}); ED is the exposure duration (years); BW is the body weight in (kg); AT is the average time (days), and RFD_0 is the oral reference dose (mg kg^{-1} day^{-1}). In the present study, EF = 365 days; ED = 70 years, BW = 70 kg, and AT = 25 550 days [26].

3. Results and Discussion

3.1. Environmental parameters

Table 3 illustrates the environmental parameters influencing water quality. Additionally, Pearson's correlation coefficient was used to describe a range of interrelated essential characteristics in brackish Lake Edku.

Table 3. Basic physical and chemical variables in Edku Lake,2020

Parameter		Season Winter	Spring	Summer	Autumn	Aquatic life CCME 2017
Temperature ^{ac} (°C)	Range	13.6-18.5	21.2-21.7	30.9-32.2	19.4-19.8	8-28 °C**
	Mean ±SD	16.07±1.47	21.44 ±0.16	31.37±0.42	19.71±0.14	
Transparency (cm)	Range	25-45	20-35	20-35	20-40	
	Mean ±SD	31.11±6.51	27.2±4.41	26.1±5.46	26.67±6.61	
EC (mS/ cm)	Range	2.64-18.05	3.1-6.44	2.52-4.29	2.36-3.79	
	Mean ±SD	6.17±4.93	4.15±1.16	3.04±0.53	2.94±0.44	
TDS (mg/ l)	Range	1.98-13.54	2.31-4.80	1.86-3.17	1.75-2.8	
	Mean ±SD	4.63±3.70	3.09±0.86	2.25±0.39	2.18±0.32	
TSS^{C}	Range	36.00-73.00	39.80-80.22	43.17-86.12	46.30-88.40	25**
	Mean±SD	57.60±12.17	64.2±14.87	70.54±14.06	81.22±13.73	
pH^{abc}	Range	8.16-8.68	8.34-9.18	8.15-8.96	8.12-8.67	6.5-9**
	Mean ±SD	8.34±0.15	8.99±0.26	8.7±0.25	8.31±0.18	
DO^{abc} (mg/ l)	Range	8.32-14.28	8.16-14.61	7.54-9.72	10.67-15.91	5.5-9.5**
	Mean ±SD	11.08±1.78	11.55±1.80	8.77±0.76	13.48±1.60	
COD^{ac} (mg/ l)	Range	16.86-51.90	21.76-42.97	43.10-62.70	17.10-41.10	
	Mean ±SD	32.81±10.60	30.92±7.1	54.12±7.18	28.43±8.29	
BOD_5^{ac} (mg /l)	Range	8.44-19.22	9.13-22.39	8.87-22.41	7.88-20.31	
	Mean ±SD	13.62±4.66	15.23±5.56	15.56±5.59	13.57±5.59	
NO^-_2-N(μg/l)^{c}	Range	27.64-259.41	54.01-325.67	18.58-82.57	137.72-371.62	60
	Mean ±SD	113.90±73.94	215.45±75.03	42.09±22.35	230.45±81.48	
NO^-_3-N(μg/l)^{ac}	Range	354.74-718.88	210.06-979.94	189.43-747.51	349.89-832.69	2900
	Mean ±SD	561.31-117.46	572.44-193.96	473.60-236.60	563.11-154.53	
NH_4^+-N (mg/l)^{abc}	Range	0.22-0.61	0.12-0.46	0.47-1.13	0.211-0.84	0.053-0.354 mg/l*
	Mean ±SD	0.39 ±0.12	0.25±0.102	0.84±0.19	0.45±0.23	
PO_4^{3-}-P^{abc} (μg/l)	Range	56.45-181.76	172.35-363.9987	44.64-448.610	59.52- 199.21	
	Mean ±SD	123.45±44.87	297.71±61.68	213.28±150.20	118.27±46.18	
TP^{a} (μg/l)	Range	124.71-463.15	327.1-529.3	98.78-665.94	127.4-288.7	
	Mean ±SD	276.764±107.05	420.25±74.23	331.81±211.42	187.99±56.84	
SiO_4^{-4} –Si (mg/l)	Range	5.86-14.53	6.96-11.90	1.76-6.90	7.30-13.85	
	Mean ±SD	9.60±3.35	10.75±1.55	3.06±1.72	9.82±1.90	

^{abc}The parameter used to calculate the ^{a}OWQI, ^{b}ATI, and ^{c}CWQI for aquatic life purposes.
*NH_4^+ concentration depends on pH value from 8 to 9 at 25 °C.
**According to CCME (2017) [24]

Correlation analysis is a preliminary descriptive technique to determine the degree of association among various variables measured in the study. Results of the correlation coefficient (r) were evaluated as follows: 0.0-0.32 (no); 0.33-0.42 (high); 0.43-1 (very high) for (n = 36). In addition, the water sample data for all variables were tested for significant differences among seasons and sites using a one-way ANOVA.

The seasonal distribution of the examined parameters and the CCME (2017) [24] aquatic life criteria were compared with the Edku water variables, as shown in Table 3. Temperature is an important water quality parameter, as the rate of chemical reactions increases at higher temperatures, and this could be proved by very high significant correlations between temperature and other parameters such as COD and NH_3 (r = 0.73 and 0.66, respectively; p = 0.01). The negative correlation between temperature and DO (r = -0.53; p = 0.01) could be attributed to the fact that the increase in temperature decreases the solubility of gases, especially the DO concentration. Aquatic organisms, including fish, become more sensitive to ammonia when their habitats have higher water body temperatures and low DO. Sharma et al. (2015) confirm that ammonia toxicity increases via aerobic metabolism (oxygen consumption) elevation as water temperature increases. In addition, ANOVA results for DO showed highly significant temporal differences (p>0.001) [27].

The transparency of Edku Lake water varied from 20 to 45 cm, giving rise to turbidity. Transparency was highly correlated with (EC& TDS) (r = 0.62, 0.62; P < 0.01). The highest transparency was recorded in the winter, and turbidity was maximum in the summer. One explanation could be that the lake becomes more transparent in the winter when seawater from Abu-Qir Bay enters through the Boughaz El-Maadia inlet. The High turbidity in summer may be caused by the influence of drainage water inflow through the lake, as turbidity increased during high flow events due to increased concentrations of suspended solids, making turbidity a known proxy for TSS concentration [28-29]. This is confirmed by the high negative correlation between transparency and TSS (r = -0.68; p = 0.01), as TSS causes light scattering and impacts water's optical properties [29].

ANOVA analysis showed a high difference between sites (spatial difference) regarding transparency (p > 0.001). The electrical conductivity (EC) showed a noticeable increase northward near El Boughaz and recorded the maximum value of 18.05 (mS/cm) with an average of 6.17±4.93 mS/cm in winter due to an increase in seawater intrusion into the lake [29]. This result agrees with that obtained by Elmorsi et al. (2017) [31]. The ANOVA results showed highly spatial and temporal significant differences for EC and TSS (p > 0.001).

pH was generally on the alkaline side, indicating well-buffered conditions, which was the proposed range (6.5–9.0) by the European Union (EU) for fisheries and aquatic life [9]. So, from our findings, a pH range of 8.26–9.04 with an average of 8.59 indicates suitable water quality for marine life. ANOVA data showed highly temporal significant differences (p > 0.001). DO is essential in determining whether water is suitable for aquatic life. Our DO results demonstrate that Lake Edku has adequate oxygenation for the entire year, as the average values of DO at all sampling sites were in the range of 5.5-9.5 mg/l, which represents the standard water quality criteria cited by CCME (2017) [24] for aquatic life suitability. ANOVA results showed highly significant temporal differences in DO (p > 0.001).

The BOD_5 and COD tests are good indicators of water pollution in the aquatic environment [32]. BOD_5 measures the amount of oxygen microorganisms use (e.g., aerobic bacteria) to oxidize organic matter [33]. According to our data, the summer has the greatest average BOD values (15.56±5.59 mg/l), which may be related to biological activity during the hotter months. ANOVA data showed a high difference between sites of BOD values. The maximum value of 22.41 mg/l was recorded at site Sw9 in front of the El-Khairy drain in summer, which was attributed to the discharge of heavily polluted effluent loaded with agricultural, industrial, and domestic wastes. On the other hand, COD measures the total amount of oxygen required to completely oxidize all organic matter in a site to CO_2 and H_2O [33]. In the same manner as BOD_5, the COD results increased in the eastern part, which was attributed to the effect of drains. ANOVA data of COD showed highly temporally significant differences (p > 0.001). BOD_5 levels directly increased with the increasing loads of TN (r = 0.65; P = 0.01). While COD is highly correlated with TN, NH_4^+ (r = 0.45; P = 0.01 & r = 0.62; P = 0.01).

The nutrient salts include compounds containing nitrogen and phosphorus; generally, the ammonia levels were inversely proportional to the DO and the pH levels. The ammonia concentration increases on the southeastern side, which may be attributed to major drains such as Barzik and El-Khairy. The value of ammonia ranged between 0.12 and 1.13 mg/l and exceeded the permissible limits for aquatic life of CCME (2017) [24] (0.053-0.354 mg/l), especially in the southeastern sector. The nitrite values ranged between 18.58 and 371.62 µg/l; nitrite levels generally exceeded the permitted maximum nitrite content of 60 µg/L CCME (2017) [24]. Nitrate is the prime plant nutrient, and raising its content might increase water eutrophication. This study's nitrate levels were significantly below the 2.93 µg/l (maximum permitted nitrate concentration)[24]. From the above, we can conclude that both ammonia and nitrite levels exceeded aquatic life guidelines in the eastern sector, reflecting the influx of anthropogenic effluents with high nitrogen species concentrations. ANOVA results showed highly temporally significant differences in NH_4^+ and NO_2^- (p > 0.001), and TN shows high spatially substantial differences (p > 0.001).

Phosphates (PO_4^{3-}) do not pose human or health risks except in very high concentrations. PO_4^{3-} is highly correlated with (NO_3^- and TN) (r=0.33 and 0.36; n=36, p<0.05), indicating the same origin of nutrient salts. It could be agricultural, industrial, or domestic waste, considered a different source of nitrogen and phosphorus input into the Edku Lake body. Reactive silicate (SiO_4^{4-} –Si) ranged from 1.76 to 13.85 mg/l. Despite the high silicate concentrations in the southeastern part of Edku Lake, lower silicate concentrations have been found in the western part. This may have been caused by the influence of seawater inflow through the lake-sea connection close to this area [34]. ANOVA results showed highly significant temporal results regarding SiO_4^{4-}.

3.2. Water quality indices

Water quality indices are categorized in our study by three models: OWQI, CCME -WQI, and ATI. OWQI and CCME-WQI are calculated multi-variable water quality data illustrated in Figure 2 to show the significance of different variables at different times and locations on overall water quality and to compare measured data against water quality benchmarks, respectively. At the same time, ATI assesses the health of aquatic ecosystems and shows the toxic effects of different water quality on fish.

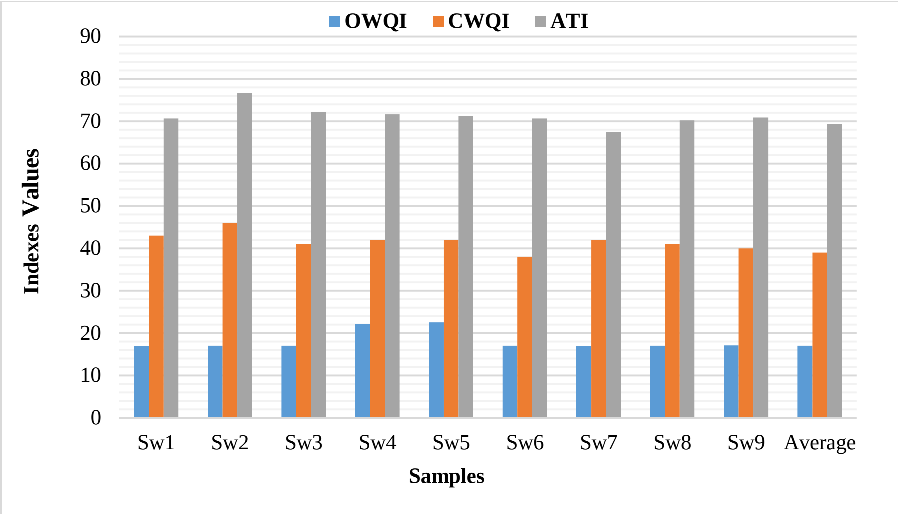

Figure 2. Water quality values of Edku Lake according to OWCI, CWQI, and ATI

The OWQI was calculated using nine water Table 3 characteristics, and the findings for Edku Lake ranged from 13.96 to 23.55 Figure 2. These results showed that the lake is "very poor" among all sites in different seasons and unfit for fishing. The CCEM-WQI values ranged from 36 to 46 Figure 2, using 10 water parameters chosen for computation Table 3. The CCEM-WQI indicated that the water quality categorization for all sampling stations was "poor", indicating that the lake is unfavorable for fish life.

On the other hand, the ATI was developed to evaluate the health of the marine ecosystem and determine the suitability of aquatic environments for different fish species. Seven water parameters in Table 3 were selected to compute the ATI. The values of ATI, the score of which ranged from 61.60 to 82.82 Figure 2. These results indicate the suitability of Edku's water for all fish species.

3.3. Metal analysis in Edku lake water

As heavy metals are mainly soluble in water, fish bioaccumulation occurs [35]; thus, evaluating their content in water and fish muscles is essential. For the present study, based on the findings summarized in Table 4, in winter and summer 2020, "Al" and "Fe" were the most abundant elements. Other heavy metals, such as Zn, Mn, Cr, and Cd, appear dissolved in water, and some of them are bound or absorbed by particulate matter, which eventually settles in the sediment bed [35].

Table 4. Heavy metals concentrations in (µg/l) measured by ICP

	Fe		Al		Mn[b]		Zn[b]		Cr[b]		Cd	
Samples	**Seasons**											
	W	**S**	**W**	**S**	**W**	**S**	**W**	**S**	**W**	**S**	**W**	**S**
Sw1	190.00	310.00	240.00	460.00	12.26	9.26	8.83	8.95	2.01	1.18	0.86	0.35
Sw2	270.00	210.00	370.00	330.00	1.81	7.61	9.88	8.20	2.01	1.08	1.15	0.32
Sw3	130.00	210.00	180.00	620.00	3.38	7.93	7.13	6.70	1.89	1.01	0.85	0.74
Sw4	450.00	810.00	550.00	1030.0	15.56	3.18	12.55	7.51	3.03	1.39	1.48	0.60
Sw5	220.00	470.00	200.00	1320.0	11.57	6.76	12.73	9.86	2.53	1.12	2.46	0.48
Sw6	100.00	670.00	130.00	1090.0	14.63	19.93	9.88	4.88	3.14	1.44	1.15	0.85
Sw7	320.00	310.00	350.00	600.00	1.51	11.76	5.26	4.88	2.99	1.24	1.23	0.45
Sw8	140.00	470.00	200.00	1240.0	1.88	1.06	9.86	14.26	2.25	1.26	1.15	0.37
Sw9	580.00	810.00	780.00	3970.0	1.39	6.58	4.86	12.74	2.53	1.08	1.03	0.49
Average	266.67	474.44	333.33	1184.44	7.11	8.23	9.00	8.66	2.49	1.20	1.26	0.52
STD	150.99	225.44	199.22	1039.6	5.85	5.08	2.66	3.05	0.45	0.14	0.46	0.170
USEPA	1000 µg/l*		0.1 µg/l*		100 µg/l*			120 µg/l *	11 µg/l*		0.72 µg/l*	

W: winter; S: summer *USEPA, 2024 [36]

The concentrations of the studied heavy metals in Edku Lake water were found in the ranges of 266.67-474.44, 333.33-1184.44, 7.11-8.23, 9.00-8.66, 5.00–23.23, 2.49- 1.20, 1.26-0.52, and 1.26-0.52 µg/l for Fe, Al, Mn, Zn, Cr and Cd, respectively. Generally, the metal contents were in the order of Al>Fe>Mn>Zn>Cr>Cd. Generally, the concentration of metal ions (Fe, Al, Mn) in Edku Lake is higher in summer than in winter, while winter concentrations of Cr and Cd are higher than in summer.

The maximum concentrations of all measured heavy metals in Edku Lake water were observed in the southeastern area in front of the Berzik and El-Khairy drains and site Sw4 in front of fish farms. These findings are consistent with what we found in the Edku sediments in a previous study [3]. Zn and Mn concentrations are significant at Site Sw1, located in front of El Boughaz and close to the international road. The high concentration of manganese could be attributed to the production of iron and steel and the burning of diesel fuel in automobiles, as these are the main sources of manganese and lead in the air and water [37]. According to Saeed and Shaker (2008), significant levels of zinc that have leached from boat protection plates containing active zinc may be the cause of the high quantity of zinc in lake water samples [36], in addition to the high concentration of zinc that could be found and enter the environment from several sources, including industrial and municipal wastes, urban runoff, and mainly from the erosion of Zn-containing soil particles [38]. However, the northwest section (sites Sw1, Sw2, and Sw3) had the lowest concentration values of Al, Fe, Cr, and Cd. In contrast, sites Sw2 and Sw3 had the lowest concentrations of Zn and Mn. In general, seasonal fluctuations in the concentration of heavy metals can be linked to changes in the quantity of untreated sewage, industrial waste, and agricultural drainage [25] that supply the water bodies of the lake with vast amounts of inorganic anions and heavy metals.

Table 4 shows that the Fe, Mn, Zn, and Cr concentrations in Edku Lake were below the International permissible limits. In both seasons, Cd levels in winter and Al concentrations exceed the USEPA limits at all sites. An increase of both Al and Cd may lead to a risk to aquatic organisms and poor water quality of Edku Lake, especially in the sites facing and closest to the drains. This may cause adverse human health effects. Aluminum can exist in various dissolved and precipitated forms that may harm living things, and cadmium is highly toxic to humans, even in very low concentrations [25].

The Spearman correlation was significant for Al with TSS, PO_4^{3-}, and BOD (r= 0.48, 0.35,0.32; n = 36, P<0.05), respectively. In addition, Fe vs. TSS (r=0.56; P<0.01), Cd vs DO (r=0.44; P<0.01), and Cd vs Ni (r=0.63; P<0.01). The high relation between TSS with Al and Fe indicates that TSS may include a significant fraction of mineral seston derived directly from terrigenous sources or indirectly by resuspension of already deposited materials [29]. Cd showed very high negative significant correlations with Temperature and pH (r= -0.73, -0.45; P=0.01), where it decreases with alkalinity increases. According to Zhang et al. (2018), Cd release increases in the acidic medium, which confirms the negative correlation between Cd and pH [39].

ANOVA results for Fe, Al, and Cd indicated that there were highly significant temporal differences (p < 0. 01), while Mn, Zn, and Cr show significant differences (P > 0.05) among sites and seasons. Generally, the temporal and spatial variations in metal concentration in water bodies depend on many factors, such as weathering, climate, soil type, pH, redox potential, and dilution capacity [40].

3.4. LIBS analysis

First, LIBS's optimum condition for the delay time was examined. Where the plasma emission signals were recorded at different delay times in the spectral range between 500 and 6000 ns. Then, a plot was drawn for the Al spectral line at 309.2 nm - the same spectral line used in our previous study when studying sediment samples [3] - to find the relation between the delay time and the LIBS signal intensity. In the early stages of the plasma lifetime, an intense continuum emission resulted, and after an appropriate delay, the plasma cooled to the point where atomic and ionic emissions could be observed.

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 best LIBS signals are recorded at around 1500 ns, where the continuum emission was avoided, and the maximum signal-to-background ratios were observed. Thus, all measurements have been performed at a delay time of 1500 nm and gate width/gate time of 2000 ns.

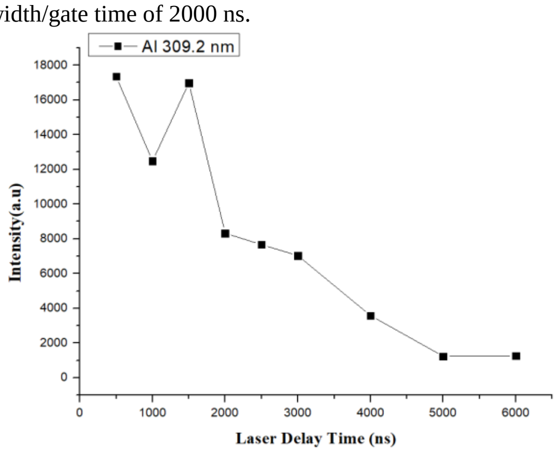

Figure 3. Dependence of LIBS signal intensity on delay time for Al 309.2 spectral line in water samples

Two elements, Al and Fe, were selected to compare the effectiveness of LIBS in analyzing the elemental composition of pollutants in Edku Lake with the ICP method. These elements were chosen because they exhibit the highest concentrations among the polluting elements, ensuring their concentration levels fall within the LIBS technique's detection limit. Figure 4 (a & b) shows this study's typical LIBS spectrum for HMs. It highlights the spectral lines used to analyze water and fish samples. Selecting the appropriate spectral lines is a crucial step in LIBS analysis. Several factors must be considered in this selection process, including choosing symmetric isolated lines to avoid overlaps and excluding resonant lines to prevent self-absorption.

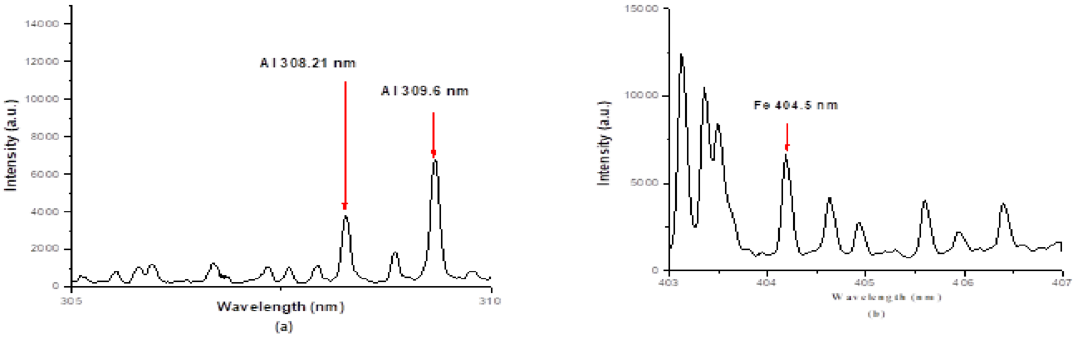

Figure 4. Two sections (a,b) of a typical LIBS spectrum for the collected water samples with assigned Al and Fe metal lines

Table 5 lists the spectral lines chosen to fulfill the LIBS spectral line conditions and their spectroscopic data. Spectral lines have been assigned by LIBS++ software and confirmed from the NIST database [41].

Table 5. The spectroscopic data of the transitions of spectral lines.

Elements	Wavelength (nm)	A ($10^8 S^{-1}$)	g Upper	g Lower	e Upper	e lower	Intensity (long)	Intensity (Short)
Fe (I)	404.58	0.862	9	9	4.549	1.485	4.217e-06	3.066e-06
Al(I)	308.21	0.63	4	2	4.021	0.000	1.360e-05	8.722e-06

For semi-quantitative analysis, LIBS spectral lines are normalized to follow up the change in concentration for different samples. The normalized intensities of Al and Fe, as determined by LIBS throughout the winter (W) and summer (S) seasons, are shown in Figure 5 (a,c) and (b,d), respectively. Figure 5 shows a comparison between the results of LIBS (red bars) and ICP (blue bars) for both Al and Fe. The two methods demonstrate a good agreement, indicating the potential of LIBS in performing measurements of the elements' relative concentrations.

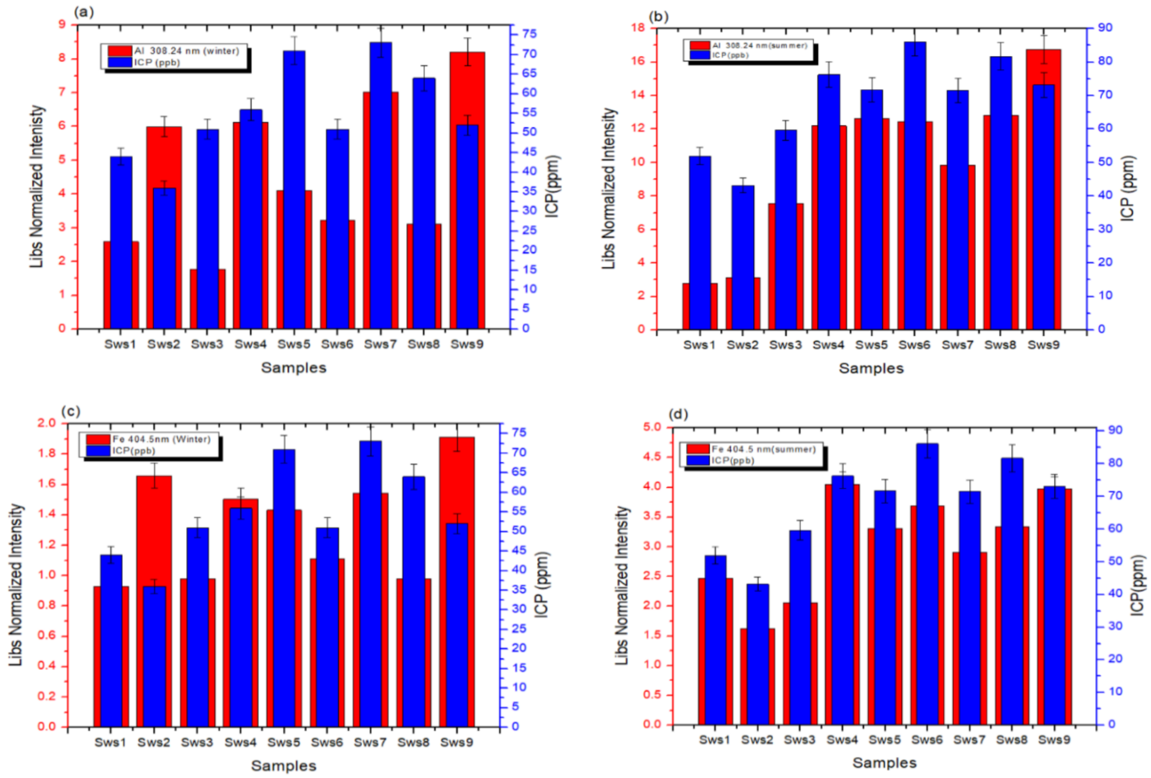

Figure 5. Bar graphs for LIBS and ICP results for Al (upper) and Fe (lower) in different water samples in winter (a,c) and summer (b,d)

3.5. Metal pollution indices in Edku Lake water

For metals in water, three pollution indices were calculated: PI, MI, and HPI, which are used to assess the heavy metal level in the water of Edku Lake.

3.5.1. Pollution Index (PI)

Six metals (Fe, Mn, Zn, Cr, Cd, and Al) are selected to assess the metal pollution of each element in Edku Lake water according to the pollution index. Fe, Mn, and Zn recorded no pollution effects at all stations, as shown in Table 6; Cr exhibits a slightly moderate pollution effect at various locations according to the aquatic life criteria, while Cd and Al have slight pollution at some locations.

Table 6. Pollution index (PI) of the measured metals in Edku Lake water according to guideline levels of aquatic life utilizations

	Fe		**Mn**		**Zn**		**Cr**		**Cd**		**Al**	
Samples	PI	Pollution effect	PI	Pollution effect	PI	Pollution effect	PI	Pollution effect	PI	Pollution effect	PI	Pollution effect
Sw1	0.37	No Effect	0.08	No Effect	0.07	No Effect	1.49	Slightly	0.80	No effect	1.03	Slightly
Sw2	0.29	No Effect	0.04	No Effect	0.05	No Effect	1.59	Slightly	0.83	No effect	0.46	No Effect
Sw3	0.18	No Effect	0.04	No Effect	0.06	No Effect	1.49	Slightly	0.92	No effect	0.31	No Effect
Sw4	0.87	No Effect	0.08	No Effect	0.07	No Effect	2.31	Moderately	1.11	Slightly affected	1.19	Slightly
Sw5	0.32	No Effect	0.07	No Effect	0.06	No Effect	2.06	Moderately	1.74	Slightly affected	0.66	No Effect
Sw6	0.66	No Effect	0.10	No Effect	0.05	No Effect	2.40	Moderately	1.18	Slightly affected	0.95	No Effect
Sw7	0.29	No Effect	0.06	No Effect	0.04	No Effect	4.51	Strongly	0.91	No effect	0.36	No Effect
Sw8	0.35	No Effect	0.01	No Effect	0.06	No Effect	1.66	Slightly	0.84	No effect	0.62	No Effect
SW9	0.77	No Effect	0.03	No Effect	0.06	No Effect	1.91	Slightly	0.95	No effect	1.99	Slightly
Lake	0.45	No Effect	0.05	No Effect	0.05	No Effect	1.92	Slightly	0.84	No effect	0.61	No Effect
<1 No effect, 1–2 Slightly affected, 2–3 Moderately affected, 3–5 Strongly affected, >5 Seriously affected												

3.5.2. High Pollution Metal Index (HPI)

HPI is used to assess the heavy metal pollution in each site value in Edku Lake water; Table 7 shows that the values ranged from 3.34 to 6.68. These results demonstrate that all the studied metals have no polluting effects on aquatic life usage, as the critical limit is an HPI of more than 100. According to the HPI index, aquatic organisms living in Edku Lake are not exposed to risks [42].

Table 7. High Pollution Metal Index (HPI) values

Samples	HPI value	Category
Sw1	4.06	Not polluted
Sw2	3.52	Not polluted
Sw3	3.34	Not polluted
Sw4	5.96	Not polluted
Sw5	4.99	Not polluted
Sw6	5.40	Not polluted
Sw7	3.48	Not polluted
Sw8	3.95	Not polluted
Sw9	6.68	Not polluted
Overall Edku Lake	4.88	Not polluted

3.6. Metals in Fish Samples

Heavy metals accumulate in fish muscles, making measurements of these metals in fish an essential indicator of historical exposure. Food, water, and sediment are widely understood to be the primary sources of heavy metal intake. Additionally, tissue concentrations of heavy metals can serve as reasonable indicators of both public health standards and animal health. Urbanization, untreated waste disposal, municipal sewage discharge, and industrial effluents are the leading causes of increased heavy metal concentrations in fish [43].

The concentration of metal ions in fish muscles is higher in winter than in summer. The order of metal ions in fish samples is as follows: Al > Fe > Zn > Mn > Cr > Cd. Fe, Mn, Zn, Cd, and Cr concentrations were below the international permissible limits. So, we can conclude that the fish muscles are safe and suitable for human consumption Table 8.

3.7. LIBS measurements for Fish samples

Although Fe and Al were qualitatively determined, achieving reliable semi-quantitative results using LIBS was impossible. This limitation arose because the concentrations of all other heavy metals were below 1 µg/g, below the LIBS detection limit. Ponce et al. (2016) reported that for copper (Cu) at concentrations lower than 100 parts per million (ppm) [17], the LIBS signal intensity falls below the threshold necessary for detection, indicating that the technique lacks sensitivity at these levels.

3.8. Human Risk Assessment Index

The health risks from consuming Blue Nile Tilapia Fish from Edku Lake have been estimated based on HQ. The HQ is a ratio of the determined dose of a pollutant to a reference dose level. The interpretation of the HQ value is binary: HQ is either ≥ 1 or < 1, where HQ > 1 indicates a reason for health concern. Figure 6 depicts the non-carcinogenic risks associated with heavy metals through exposure to edible tissues, using the eleven measured metals to calculate the HQ values. According to the USEPA guidelines from 2024 [36], there is no health risk from consuming fish if the HQ or HI is below one. Conversely, a higher HQ or HI indicates a more significant risk associated with fish consumption. Specifically, an HI of less than 1 signifies no hazard, an HI between 1 and 10 indicates a moderate hazard, while an HI greater than 10 represents a high level of danger or risk [44]. The HQ results indicate no potential risk to consumers from fish produced in Lake Edku. Additionally, the total non-carcinogenic HI for the analyzed heavy metals is 0.079 in winter and 0.064 in summer. These findings suggest that the risks associated with consuming the edible muscle of Nile Tilapia are significantly lower than the threshold value of 1 [44].

Table 8. Heavy metals concentrations (µg/g) in muscle muscles of Nile Tilapia Fish using ICP collected from Edku Lake in comparison with the international standard permissible limits

Organization/Country	References	Fe	Mn	Zn	Cd	Al	Cr
FAO	FAO (1983)			30		N	12
FAO/WHO	FAO/WHO (1989)			40	0.5	N	N
WHO	WHO (1989)	100	1	100		N	N
USFDA	USFDA (1993)					N	13
England	MAFF (2000)			50	0.2	N	N
EU	EU (2001)				0.1	N	N
Europe	EC (2005)				0.05	N	N
Turkey	Dural et al. (2007)		20			N	N
Present study	Winter 2020	8.37	0.5	0.9	0.01	9.43	0.08
	Summer 2020	6.51	0.57	0.9	0.007	5.57	0.1

N: Not available

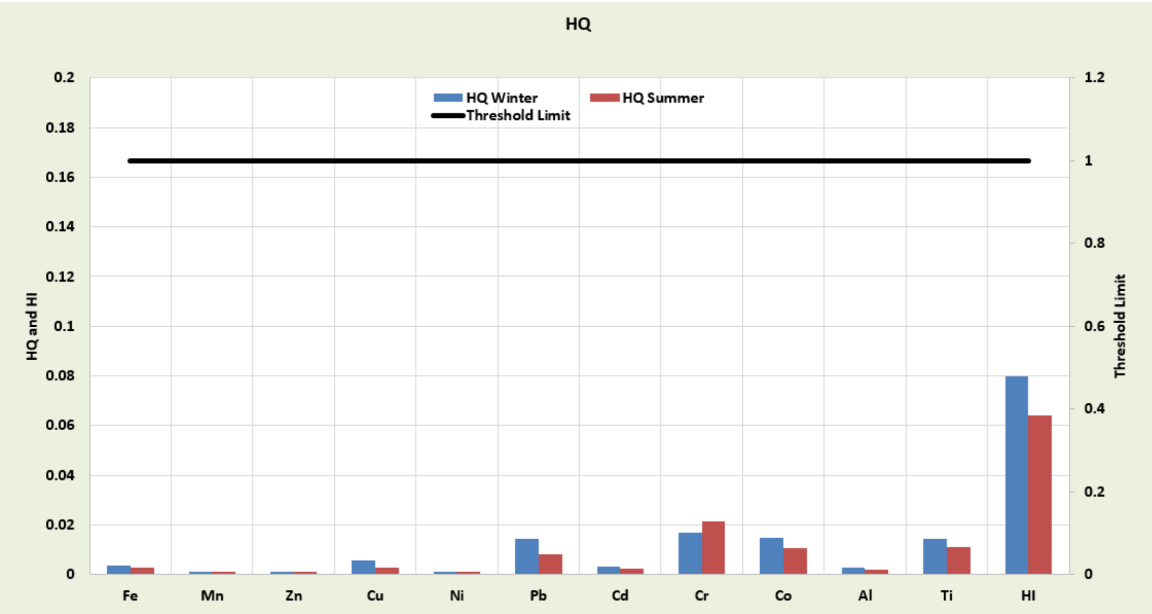

Figure 6. HQ and HI to the human population from metals through Nile Tilapia Fish from Edku Lake

4. Conclusion

Edku Lake, a vital Mediterranean lagoon in Egypt, faces significant pollution from wastewater discharges via drains like El-Khairy and Barzik, which carry domestic, agricultural, and industrial effluents. This study employed LIBS and ICP techniques to analyze heavy metal concentrations in the lake. Results revealed higher metal concentrations in the eastern part of the lake, influenced by pollutant inflows from nearby drains. "Cr" was identified as a significant pollutant, with PI values ranging from 2 to 3 near Barzik, indicating a notable impact on aquatic life. However, the HPI suggested that Edku Lake remains suitable for fish and other organisms, as overall metal concentrations do not severely threaten the ecosystem.

Spectrochemical analysis of Nile tilapia muscles showed that most heavy metal levels were within internationally permissible limits. The bioaccumulation order in fish tissues was Al > Fe > Zn > Mn > Cr > Cd. Despite the lake's poor water quality, the metal concentrations in fish do not significantly endanger consumers. LIBS successfully detected Fe and Al in water samples, with results consistent with ICP measurements. However, only qualitative detection of Al and Fe spectral lines was achieved in fish tissues, as other metals with concentrations below 1 µg/g fell below LIBS's detection limit.

In conclusion, while Edku Lake suffers from heavy metal pollution, the HM levels in Nile tilapia remain safe for human consumption. LIBS shows promise for monitoring heavy metals in water but requires improved sensitivity for trace metal detection in biological tissues. Regular monitoring and environmental impact assessments are essential for developing effective lake conservation strategies. Enhancing LIBS's sensitivity as an eco-friendly qualitative and semi-quantitative analysis technique in water and fish samples is also recommended.

5. Conflicts of interest

"No conflicts to declare", Funding: NA

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