African Journal of Advanced Pure and Applied Sciences (AJAPAS)
Online ISSN: 2957-644X
Volume 4, Issue 4, 2025
Page No: 630-635
Website: https://aaasjournals.com/index.php/ajapas/index

ISI 2025: 1.126 **SJIFactor 2024: 6.752** **معامل التأثير العربي: 1.62**

Estimation of Some Heavy Elements in Different Marine Samples Collected from the Beaches of Zawiya City

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تقدير بعض العناصر الثقيلة في عينات بحرية مختلفة جُمعت من شواطئ مدينة الزاوية

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Received: September 12, 2025	Accepted: November 22, 2025	Published: December 06, 2025

Abstract:
This study assessed heavy metal (cadmium, lead, and arsenic) contamination in fish, algae, and seawater samples from the coast of Zawiya, Libya. Concentrations were determined using **Atomic Absorption Spectrophotometry (AAS)** after appropriate sample digestion. Results showed that all metal concentrations in fish and seawater were below detection limits, indicating they are currently safe for human consumption and the environment. In contrast, certain marine organisms demonstrated a significant capacity for **bioaccumulation** of these metals. A sample of seaweed (*Posidonia oceanica*) showed a cadmium concentration of 9.6 mg/kg, which exceeded the internationally permissible limit of 5.5 mg/kg. Similarly, brown algae accumulated a high concentration of arsenic (26.6 mg/kg), highlighting its role as a biomonitor. These findings underscore the importance of using algae and seagrasses as **effective bioindicators** for monitoring heavy metal pollution in coastal ecosystems, even when contamination is not evident in fish or water.

Keywords: Heavy metals, Marine pollution, Atomic Absorption Spectrophotometry (AAS), Zawiya, Libya, Marine Samples.

الملخص
قيّمت هذه الدراسة تلوث الأسماك والطحالب ومياه البحر بالمعادن الثقيلة (الكادميوم والرصاص والزرنيخ) في عينات الأسماك والطحالب ومياه البحر المأخوذة من ساحل الزاوية، ليبيا. حُددت التركيزات باستخدام مطياف الامتصاص الذري (AAS) بعد هضم العينة بشكل مناسب. أظهرت النتائج أن جميع تركيزات المعادن في الأسماك ومياه البحر كانت أقل من حدود الكشف، مما يشير إلى أنها آمنة حاليًا للاستهلاك البشري والبيئة. في المقابل، أظهرت بعض الكائنات البحرية قدرة كبيرة على التراكم البيولوجي لهذه المعادن. أظهرت عينة من الأعشاب البحرية (Posidonia oceanica) تركيزًا للكادميوم بلغ 9.6 ملغم/كغم، متجاوزًا الحد المسموح به دوليًا البالغ 5.5 ملغم/كغم. وبالمثل، تراكمت لدى الطحالب البنية تركيز عالٍ من الزرنيخ (26.6 ملغم/كغم)، مما يُبرز دورها كأداة رصد بيولوجي. تُؤكد هذه النتائج أهمية استخدام الطحالب والأعشاب البحرية كمؤشرات بيولوجية فعّالة لرصد تلوث المعادن الثقيلة في النظم البيئية الساحلية، حتى عندما لا يكون التلوث واضحًا في الأسماك أو المياه.

الكلمات المفتاحية: المعادن الثقيلة، التلوث البحري، مطيافية الامتصاص الذري، الزاوية، ليبيا، عينات بحرية.

Introduction

Global environmental pollution is recognized as a complex challenge and a major concern for human and ecosystem health, where environmental degradation is often perceived as the disruption of normal ecological functions [16], [15]. The Mediterranean Sea, being a semi-enclosed basin with slow water renewal, is regarded as one of the most vulnerable marine ecosystems to anthropogenic stressors. Domestic and industrial discharges, food industry wastes [13], oil pollution, effluents from power stations, agricultural runoffs, livestock-derived toxins [14], volatile organic compounds [15], and heavy metals [4] are among the key contributors to contamination in this fragile system. These pollutants compromise marine biodiversity and pose direct and indirect threats to human health, particularly through seafood consumption. Heavy metals such as cadmium (Cd), lead (Pb), and arsenic (As) are of special concern due to their persistence, toxicity, and bioaccumulation potential. They can disrupt aquatic ecosystems by inducing structural and physiological damage in fish at cellular and molecular levels [11], [12], while also accumulating in human tissues through the food chain.

International organizations including FAO/WHO and WHO have established threshold guidelines for metals in water and seafood [10], [22]. These serve as critical benchmarks for monitoring marine contamination. Marine organisms respond differently to heavy metal exposure; macroalgae in particular are effective bioindicators due to their high uptake capacity and ability to accumulate metals over time [7], [8]. Comparative studies in Mediterranean and Red Sea ecosystems have shown that algae frequently contain higher levels of Cd and Pb than seawater and fish, highlighting their role as early-warning sentinels of environmental contamination.

In the Libyan and broader eastern Mediterranean context, evidence indicates that heavy metal distribution is site-specific, influenced by local hydrodynamic conditions and pollution sources. Recent studies along the Libyan coast demonstrate significant variability in Cd, Pb, and As levels, with algae consistently showing pronounced accumulation relative to fish and seawater [9], [1], [5]. Findings from Zwitina Harbor also confirm the presence of heavy metals in commercial fish species [6]. These results emphasize the importance of incorporating multiple matrices—fish, algae, and seawater—into monitoring frameworks to obtain a comprehensive picture of contamination and to identify suitable biomonitoring species.

Within this framework, the present study focuses on Zawiya Beach, Libya, where industrial activities, petroleum-related operations, and urban runoff may contribute to heavy metal pollution. The study aims to: (i) measure Cd, Pb, and As concentrations in fish (Scomber japonicus, Sardina pilchardus, Sarpa salpa, Mugil auratus*)*, marine algae (brown algae and other related groups), and seawater; (ii) compare the results against international safety guidelines (FAO/WHO and WHO); and (iii) evaluate the potential of algae as biomonitors of marine contamination in the Zawiya coastal environment. The outcomes are expected to inform risk assessment for seafood safety, support environmental management strategies, and contribute to the regional understanding of heavy metal dynamics along Libyan coasts.

Material and methods

2.1. Methodology and Study Site

The study was conducted in the city of Zawiya, located on the western coast of Libya, approximately 48 km west of the capital, Tripoli, at approximate geographical coordinates of 32.75∘ N latitude and 12.72∘ E longitude. The sampling sites were chosen for their rocky coastal nature, which contributes to the diversity of marine life. These sites included Juddaim, Dila, Al-Harsha, and Al-Muttered.

2.2. Chemicals and Equipment

In this study, several chemicals and pieces of equipment were utilized. The chemicals included 65% nitric acid (HNO_3), 36% hydrochloric acid (HCl), 60% Perchloric acid ($HClO_4$) and distilled water for all digestion and extraction procedures. The instrumentation and tools employed were an Atomic Absorption Spectrophotometer (AAS), specifically the Agilent Technologies 200 model, along with an electric furnace (Oven) for drying, a hot plate, an electric blender, a sensitive analytical balance, a water bath, and a reflux apparatus. Various laboratory glassware was also used throughout the processes.

2.3. Sample Collection

Three types of samples were collected: fish, algae, and seawater.

A. Fish Samples Fish samples, including the species Scomber japonicus, Sardina pilchardus, Sarpa salpa, and Mugil auratus, were collected and washed with distilled water. The samples were then dried at 105∘C for 24 hours. The dried samples were ground and homogenized using an agate mortar, then stored in polyethylene bottles. All samples were frozen at −20∘C until analysis.

B. Algae Samples Samples of Seaweed and Brown Algae were collected and washed with distilled water at 38∘C to remove small particles. The samples were then placed in a glass dish and dried in an oven at 70∘C. The dried samples were ground using an electric blender, and the resulting powder was stored in clean, tightly sealed plastic containers.

C. Seawater Samples Seawater samples were collected from the aforementioned sites for subsequent analysis.

2.4. Digestion and Analysis Procedures

Heavy metal concentrations in all samples were determined by an **Agilent Technologies 200 series Atomic Absorption Spectrophotometer (AAS)** after appropriate digestion procedures for each sample type.

- **Limits of Detection (LODs):**
  - The method-applied LODs for the heavy metals in the solid samples (fish and algae) were determined (likely from the analysis of "Blank Solutions") and found to be:
    - **Cadmium (Cd):** <0.0005 mg/kg
    - **Lead (Pb):** <0.006 mg/kg
    - **Arsenic (As):** <0.003 mg/kg

A. Fish Sample Digestion A **dry ashing method** was used for the preparation of fish samples [20], [21]. A five-gram portion from each dried and homogenized sample was placed into a porcelain crucible. The furnace temperature was slowly increased to 450∘C in one hour and maintained for approximately 14 hours until a white or grey ash residue was obtained. After cooling, 5 mL of 25%v/v HNO_3 was added to the residue, and the mixture was slowly heated to dissolve it. The solution was then transferred to a 25 mL volumetric flask and made up to volume with distilled water. The procedure was performed in triplicate for each sample.

B. Algae Sample Digestion The algae samples were digested using a **wet acid digestion method** [18]. A 0.5 g portion of the powdered sample was weighed and placed in a 100 mL conical flask. To this, 5 mL of 65% HNO_3 was added, and the samples were left for 16 hours at room temperature. The samples were then digested in a water bath at 100∘C for one hour. Following this step, 1 mL of 60% $HClO_4$ was added, and heating was continued for 30 minutes until a clear solution was obtained. The digest was then diluted to a final volume of 50 mL with distilled water and filtered through appropriate filter paper prior to analysis. This procedure was also repeated three times for each sample.

C. Seawater Sample Digestion The digestion procedure for seawater samples followed the method described in **Standard Methods for the Examination of Water and Wastewater** [3]. A 50 mL aliquot of the water sample was placed in a 100 mL volumetric flask, and 5 mL of 5% HNO_3 was added. The sample was heated on a hot plate until it evaporated to a white residue. Subsequently, 2 mL of HNO_3 and a few drops of HCl were added to dissolve the residue. The volume was brought up to 50 mL with distilled water, and the sample was filtered through a 0.45μm filter paper.

D. Blank Solutions Blank solutions were prepared for each sample type (fish, algae, and water) by following the same digestion procedures but without the sample. The concentrations measured in these blanks were subtracted from the concentrations of the original samples to account for potential contamination from reagents or laboratory conditions.
The obtained concentrations of Cd, Pb, and As were compared with the internationally permissible limits recommended by FAO/WHO (1983) and WHO/FAO (2003), as well as the Codex Alimentarius standards for contaminants in food (Codex STAN 193-1995).

Results and discussion

The concentrations of cadmium (Cd), lead (Pb), and arsenic (As) were measured in seven samples collected from the beach of Zawiya city. The results are presented graphically (Figure 1) and summarized in **Table 1**, which includes the mean values and standard deviations (±SD) of these elements in fish, algae, and seawater, compared with FAO/WHO permissible limits [10], [22].

Table 1: Concentrations of Cd, Pb , and As in the studied samples from the beach of Zawiya city

Sample Type	Sample Code	Scientific Name	Cadmium (Cd)	Lead (Pb)	Arsenic (As)
Fish	A	*Scomber japonicus*	0.0005<	0.006<	0.003<
	B	*Sardina pilchardus*	0.0005<	0.006<	0.003<
	C	*Sarpa salpa*	0.0005<	0.006<	0.003<
	D	*Mugil auratus*	0.0005<	0.006<	0.003<
Algae	E	Seaweed	9.6 ± 0.0432	0.06<	0.03<
	F	Brown algae	0. 5 ± 0.0029	0.06<	± 0.0319 26.6
Seawater	X	Seawate	< 0.00005	< 0.0006	< 0.0003
Permissible Limits	FAO/WHO (1983) mg/kg	Fish/Algae	0.05 – 5.5	0.05 – 6	86
	WHO/FAO (2003) mg/L	Water	0.05	0.05	5

Permissible limits according to FAO/WHO (1983), WHO/FAO (2003), and Codex Alimentarius (Codex STAN 193-1995).

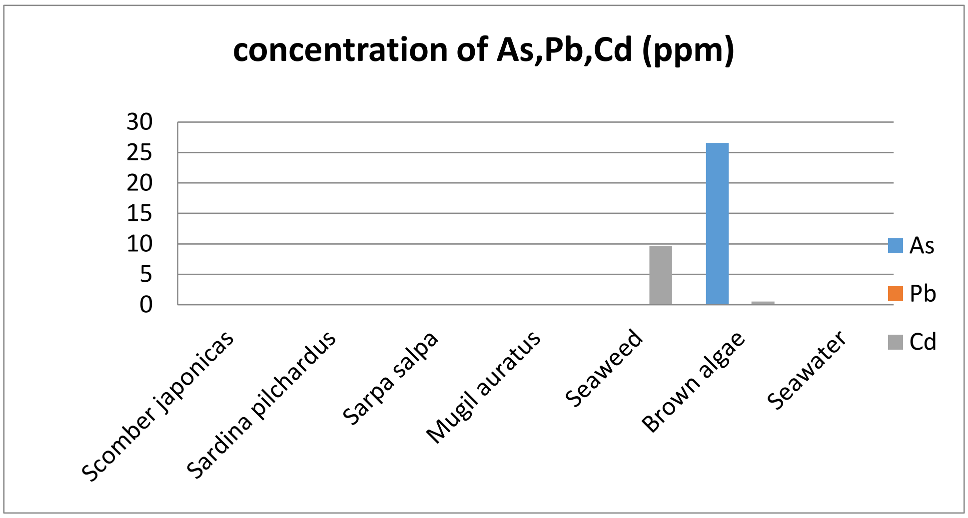

Figure 1: illustrates the differences in the concentration of cadmium, lead, and arsenic in the studied samples.

Fish Samples

Samples A–D (Scomber japonicus, Sardina pilchardus, Sarpa salpa, and Mugil auratus) revealed concentrations of Cd, Pb, and As below detectable limits (<0.0005 mg/kg for Cd, <0.006 mg/kg for Pb, and <0.003 mg/kg for As). These concentrations are far below the international permissible limits (Cd: 0.05–5.5 mg/kg; Pb: 0.05–6 mg/kg; As: 86 mg/kg) [10] . This indicates that fish from Zawiya beach are free from significant heavy metal contamination and are safe for human consumption. Similar findings were reported in Sabratha, Libya, where Cd concentrations in fish were within safe levels [5]. Comparable results were also documented in Yemen, where Cd, Pb, and As in marine organisms were below international standards [2].

Marine Algae Samples

Seaweed (Sample E): Cadmium concentration reached 9.6 ± 0.0432 mg/kg, exceeding the permissible limit of 5.5 mg/kg. In contrast, Pb (<0.06 mg/kg) and As (<0.03 mg/kg) remained at low levels (Figure 3). This suggests potential environmental Cd contamination and raises health concerns if seaweed is consumed or used in feed [10] [22],.

Brown algae (Sample F): Cd (0.5 ± 0.0029 mg/kg) and Pb (<0.06 mg/kg) remained within safe limits. However, As concentration (26.6 ± 0.0319 mg/kg), though below the maximum permissible value (86 mg/kg), was considerably higher compared to fish and seaweed (Figure 2)., indicating bioaccumulation potential. This agrees with studies in Al-Khoms, Libya [1], but differs from Bali, Indonesia, where metal concentrations in algae were lower than permissible limits [19].

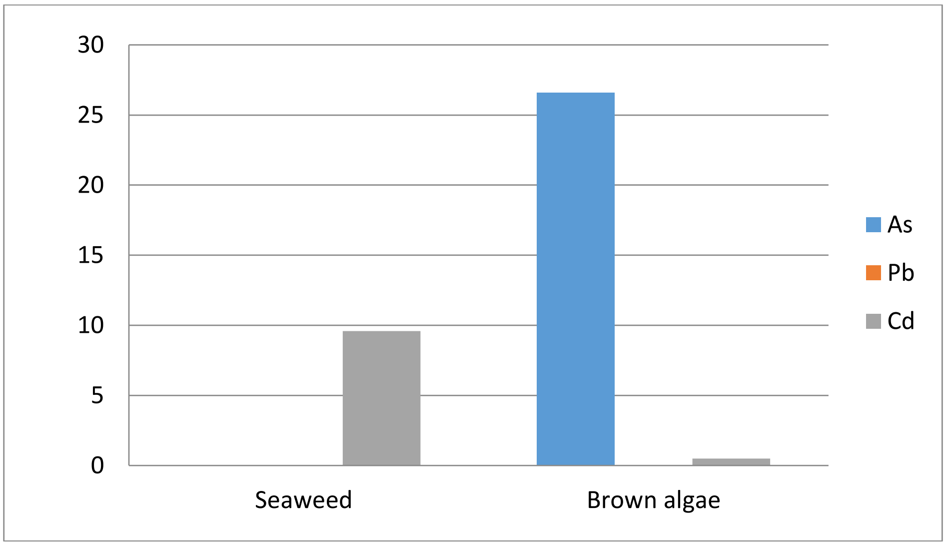

Figure 2: illustrates the differences in the concentration of cadmium, lead, and arsenic in the seagrass sample.

Seawater Sample

Sample X showed Cd (<0.00005 mg/L), Pb (<0.0006 mg/L), and As (<0.0003 mg/L), all well below the WHO/FAO permissible limits (Cd: 0.05 mg/L; Pb: 0.05 mg/L; As: 5 mg/L). This indicates that seawater in Zawiya beach is not significantly impacted by heavy metal pollution [22].

Comparative Context

These findings align with studies along the Libyan and Egyptian coasts. For example, El-Moselhy et al. (2014) [7] reported that macroalgae in Alexandria accumulated Cd and Pb more than seawater and sediments, highlighting their role as bioindicators. Similarly, El-Sherif & Ahmed (2015) [8] observed bioaccumulation of Cd and Pb in marine algae from Al-Khoms, Libya. More recently, El-Tantawi et al. (2023) [9] confirmed heavy metal contamination in seawater, algae, and fish along the eastern Libyan coast, while El-Barassi et al. (2025) [6] linked fish contamination in Zwitina Harbor to petroleum activities. These results collectively suggest that heavy metal distribution along the Libyan coast is site-specific, with algae serving as reliable biomonitors for Cd, Pb, and As.

Conclusion

The study results indicate that **fish from Zawiya beach are safe for human consumption** regarding heavy metal concentrations (Cadmium, Lead, and Arsenic). All levels in fish samples were below the detection limits and significantly lower than international permissible limits. Seawater also showed negligible concentrations, suggesting minimal pollutant input into the water column at the time of sampling.

However, the study revealed **significant heavy metal accumulation in primary marine organisms**, raising concerns and confirming the existence of persistent environmental pollution sources:

- **Cadmium (Cd) in Seaweed (Sample E):** The concentration exceeded the globally permissible limit (9.6 mg/kg versus the international limit of 5.5 mg/kg).
- **Arsenic (As) in Brown Algae (Sample F):** Relatively high concentrations were recorded (26.6 mg/kg), though still within the allowed limit (86 mg/kg).

These findings emphasize that **algae and primary marine organisms serve as reliable bioindicators** for heavy metal pollution, revealing biological accumulation even when metal levels in fish and the surrounding water are low.

Recommendations

Based on the noticeable accumulation of metals in the algae, the following is recommended to ensure the long-term sustainability of the marine environment and consumer health:

1. **Continuous Environmental Monitoring:**
   - **Mandate environmental bodies** to establish a **periodic and intensive monitoring program** to check the levels of heavy metals in **algae and seaweed** at Zawiya beach and adjacent coastal areas, at least semi-annually, to assess temporal trends in pollution.
2. **Identification and Control of Pollution Sources:**
   - **Conduct a comprehensive survey** of the coastal area and nearby discharge points to **identify potential sources** of Cadmium and Arsenic discharge (e.g., industrial waste, untreated sewage, agricultural activities using contaminated pesticides or fertilizers).
   - **Develop an urgent plan** to control these sources and enforce environmental regulations to minimize discharge.
3. **Study of Biological Transfer:**
   - **Support research** investigating the **transfer pathway of these metals** from algae into fish and other marine organisms consumed as food, to predict potential future impacts on fish safety.
4. **Awareness and Preventive Measures:**
   - **Launch awareness campaigns** targeting the local public about the role of algae as a pollution indicator.
   - **Implement preventive measures** to control human activities that could increase the deposition of these metals in the marine environment.

Compliance with ethical standards

This study does not involve any experiments on human participants or laboratory animals. Fish and algal samples were collected from natural marine environments following standard environmental sampling guidelines.

The authors declare that they have no conflict of interest.

All procedures related to sample collection and analysis comply with institutional, national, and international ethical standards for environmental and marine research.

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