

The seasonal assessment of heavy metals pollution in the waters of the Mediterranean and Atlantic seas of Morocco

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Abstract

Heavy metal pollution is a topical problem that concerns all communities anxious to maintain their water assets to a certain degree of quality. Heavy metals are not metabolized, they can be transferred into the food chain and accumulate in living matter. Metals, which are normal constituents of the environment, are all toxic above a certain threshold. In order to evaluate the health risk for humans and preserve the environment, we studied the level of metallic pollution (Cd, Pb, Zn, Fe, Cu, Cr and Ni) in water samples from both Moroccan coasts; the Mediterranean Sea (Nador coast), and the Atlantic coast (Casablanca coastline), this samples for the autumn and spring seasons between 2023 and 2024. The results obtained show that the concentrations of the metallic elements studied exceed the standard set by the WHO for certain elements.

Keywords: Heavy metals ; Contamination ; Water sample ; Pollution ; Moroccan coasts

Introduction

Marine pollution has become a major global environmental challenge, mainly due to the discharge of various contaminants such as

industrial effluents, agricultural runoff, domestic wastewater, and heavy metals into aquatic ecosystems (Duce et al., 2009; Wang et al., 2022). Among these pollutants, heavy metals are particularly concerning due to their persistence, bioaccumulative nature, and toxicity, even at low concentrations (Ali & Khan, 2019; Luo et al., 2014). Once introduced into marine environments, these metals tend to accumulate in sediments and biota, posing serious ecological and human health risks (El Nemr, 2020; Rahman et al., 2021).

Moroccan coastal waters, located at the interface of the Mediterranean and Atlantic basins, are of high ecological and economic significance. These waters support diverse marine biodiversity and sustain key industries such as fisheries, aquaculture, tourism, and maritime trade (Bounoua et al., 1999; El Morhit et al., 2012). However, rapid industrialization, urbanization, and agricultural expansion in Morocco have led to growing concerns about heavy metal contamination in marine environments, which may threaten aquatic life and public health (El Moumni et al., 2015; Salghi et al., 2023).

Heavy metal contamination originates from various anthropogenic and natural sources. Industrial discharges, mining activities, shipping, and agricultural runoff contribute significantly to metal pollution, while natural processes such as rock weathering, volcanic activity, and atmospheric deposition also play a role (Pacyna et al., 2006; Amiard et al., 2021). These metals, including cadmium (Cd), lead (Pb), zinc (Zn), iron (Fe), copper (Cu), chromium (Cr), and nickel (Ni), are known for their toxic effects on marine ecosystems and humans, particularly through seafood consumption (USEPA, 2017; Ahmed et al., 2021). High levels of these elements have been associated with neurotoxicity, carcinogenicity, and organ damage in humans (Jaishankar et al., 2014; WHO, 2018).

Several studies have investigated heavy metal pollution in marine waters across different regions of the world, revealing significant contamination levels in highly industrialized and urbanized areas (Agah et al., 2009; Ganjavi et al., 2010; Malafaia et al., 2022). In the Mediterranean region, studies have reported alarming concentrations of metals such as lead and cadmium due to industrial discharges and untreated wastewater (Bessa et al., 2020; El Baz et al., 2022). Similarly, Atlantic coastal areas are facing increasing metal contamination due to urban wastewater, oil spills, and port activities (Anweting et al., 2024; Pereira et al., 2021). However, despite these global concerns, research on heavy metal contamination in Moroccan marine waters remains limited (Fahssi & Chafi, 2015; Baghdadi Mazini, 2012).

To address this gap, the present study aims to assess the seasonal variations in heavy metal concentrations in seawater samples collected from

two Moroccan coastal regions: the Mediterranean coast (Nador) and the Atlantic coast (Casablanca). These sites were chosen due to their high socio-economic importance and significant environmental pressures, including industrial discharges, port activities, and urban expansion (El Morhit et al., 2012; Salghi et al., 2023).

This study, conducted over a two-year period (2023–2024) during autumn and spring, aims to:

- Determine the concentrations of Cd, Pb, Zn, Fe, Cu, Cr, and Ni in seawater samples from both study sites.
- Compare the obtained results with WHO standards to evaluate potential environmental and health risks.
- Analyze seasonal variations in metal concentrations to identify patterns and influencing factors.
- Compare findings with previous studies in Morocco and other regions to provide a broader perspective on heavy metal pollution trends.

The results of this study will provide critical baseline data for Moroccan coastal waters, contributing to improved environmental management strategies and policies aimed at mitigating heavy metal contamination and its associated risks.

Methodology

Study Area

This study focuses on two distinct Moroccan coastal regions:

- **The Mediterranean coast (Nador)**



Fig. 1. Location of Nador by google earth

○ The Atlantic coast (Casablanca)



Fig. 2. Location of Casablanca by google earth

These sites were selected due to their high socio-economic importance and significant environmental pressures. The Nador coastline is influenced by industrial discharges, port activities, and agricultural runoff, whereas the Casablanca coastline is exposed to urban wastewater, industrial emissions, and maritime traffic (El Morhit et al., 2012; Baghdadi Mazini, 2012; Salghi et al., 2023). Both regions face increasing contamination risks from anthropogenic sources, necessitating a systematic assessment of heavy metal pollution in their marine waters (Fahssi & Chafi, 2015; Anweting et al., 2024).

Sample Collection and Preparation :

Water samples were collected seasonally (autumn and spring) over a two-year period (2023–2024) from both coastal sites. Triplicate samples were taken at each site to ensure data reliability. The sampling procedure followed the guidelines set by the United States Environmental Protection Agency (USEPA, 2017) and the World Health Organization (WHO, 2018) for marine water quality monitoring.

Sampling Protocol:

1. Sterilized glass bottles (pre-washed with acid and distilled water) were used for collection to prevent contamination (Rodier et al., 2009).
2. Samples were taken at a depth of 50 cm from the water surface to minimize the influence of surface contaminants (El Baz et al., 2022).
3. Filtration through Millipore membranes (0.45 μm pore size) was performed to remove suspended particles (Rahman et al., 2021).

4. Samples were acidified with ultra-pure nitric acid (HNO_3 , 5 mL per liter) to preserve dissolved metals and stored at 4°C in polypropylene bottles until analysis (Amiard et al., 2021).

Heavy Metal Analysis

The concentrations of seven heavy metals - cadmium (Cd), lead (Pb), zinc (Zn), iron (Fe), copper (Cu), chromium (Cr), and nickel (Ni) - were analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). This method is widely recognized for its high sensitivity and precision in detecting trace metals in environmental samples (El Nemr, 2020; Bessa et al., 2020).

Analytical Procedure

- Instrument: Thermo Fisher iCAP 6000 Series ICP-AES.
- Calibration: Standard solutions prepared using certified reference materials (CRM) from National Institute of Standards and Technology (NIST) (NIST, 2022).
- Detection Limits: Method detection limits (MDL) were determined for each metal following the protocol of USEPA (2017).

The accuracy of the ICP-AES analysis was validated through:

- Internal quality control (QC) samples, analyzed every 10 measurements.
- Certified reference material (CRM) spiked into seawater samples to check matrix effects (Rahman et al., 2021; Salghi et al., 2023).
- Triplicate analysis, with results expressed as mean \pm standard deviation (SD).

Statistical Analysis

All statistical analyses were performed using SPSS 17.0 software. **Descriptive statistics** (mean, standard deviation) were used to summarize data. **One-way ANOVA** was applied to evaluate seasonal variations in metal concentrations.

Data Quality Assurance and Control

To ensure reliability, the following quality control measures were implemented:

- Blanks and duplicates were analyzed to check for contamination and reproducibility.
- Recovery tests were conducted using spiked samples, achieving recoveries of 92–105% for all metals.

- Comparison with previous studies in Morocco and globally ensured validity (Baghdadi Mazini, 2012; El Mounni et al., 2015; Anweting et al., 2024).

Compliance with International Standards

The measured metal concentrations were compared with:

- World Health Organization (WHO) water quality standards (WHO, 2018).
- United States Environmental Protection Agency (USEPA) guidelines (USEPA, 2017).
- European Union (EU) water framework directive (EU, 2021).

Results and Discussion

Seasonal Variations in Heavy Metal Concentrations in the Mediterranean Coast (Nador) :

The concentrations of heavy metals (Cd, Pb, Zn, Fe, Cu, Cr, Ni) in seawater samples from the Nador coast (Mediterranean Sea) during the four seasonal samplings (2023–2024), analyzed according to the techniques described above are represented in the table and the figure below. They are expressed in milligrams per liter (mg/l). Each result is expressed as (mean \pm SD). summarised in (Table 1).

Table 1: Seasonal variations in heavy metal concentrations in seawater in mg/l

ML	S1 Autumn	S2 Spring	S3 Autumn	S4 Spring
C(Cd)	0.0047 \pm 0.001	0.004 \pm 0.002	0.005 \pm 0.002	0.014 \pm 0.01
C(Pb)	0.08 \pm 0.005	0.06 \pm 0.04	0.08 \pm 0.01	0.036 \pm 0.04
C(Zn)	0.255 \pm 0.09	0.179 \pm 0.08	0.238 \pm 0.1	0.176 \pm 0.08
C(Fe)	0.01 \pm 0.001	0.06 \pm 0.08	0.013 \pm 0.001	0.045 \pm 0.04
C(Cu)	0.006 \pm 0.0005	0.034 \pm 0.04	0.006 \pm 0.0005	0.007 \pm 0.001
C(Cr)	0.002 \pm 0.003	0.019 \pm 0.02	0.001 \pm 0.002	0.006 \pm 0.005
C(Ni)	0.015 \pm 0.001	0.036 \pm 0.02	0.015 \pm 0.001	0.025 \pm 0.01

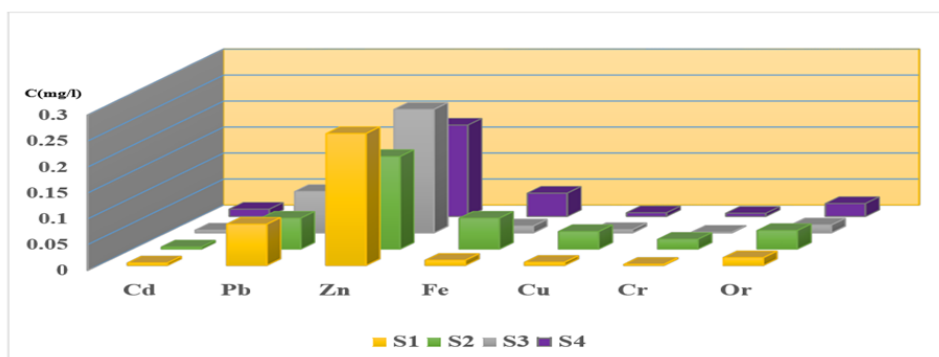


Figure 1. Seasonal variations in metal levels in seawater samples

Analysis of heavy metals in seawater samples shows that the highest concentrations are zinc, which ranges from a minimum of 0.176 mg/l obtained during in the fourth spring season, and a maximum level of 0.255 mg/l recorded during the first autumn season, these values do not exceed the WHO standard of 3 mg/l. For lead, a maximum level of 0.08 mg/l was recorded during the two fall seasons studied, and the lowest level was obtained during the fourth spring season at a value of 0.036 mg/l, the results found during all the seasons studied exceed the WHO standard of 0.01 mg/l for lead. Similarly, for cadmium, the WHO standard is 0.003 mg/l, while the concentrations obtained during the first three seasons exceed this standard, with the highest value being in the order of 0.005 mg/l. Iron concentrations range from 0.06 mg/l, which is the highest concentration, to 0.01 mg/l, which is the lowest concentration obtained during the first fall season. Nickel has non-negligible levels such that the highest level is 0,036 mg/l, and the lowest value is of the order of 0,015 mg/l. For copper and chromium the concentrations are low such that the highest concentrations are respectively (0.034 mg/l, 0.019 mg/l).

Heavy metal accumulation orders can be established for all four seasons and the result is presented in the following table 2:

Table 2. The order of accumulation of heavy metals during the four seasons

Heavy Metal	Order of Accumulation (from highest to lowest)
Cd	S4 > S3 > S1 > S2
Pb	S3 > S1 > S2 > S4
Zn	S1 > S3 > S2 > S4
Fe	S2 > S4 > S3 > S1
Cu, Cr, Ni	S2 > S4 > S3 > S1

Thus, we can establish an order of enrichment for the different metal elements during the four seasons studied and we obtain the result presented in the table 3 below:

Table 3. Heavy metal enrichment order for the four seasons

Heavy Metals Studied	The Order of Accumulation
S ₁ , S ₃	Zn > Pb > Ni > Fe > Cu > Cd > Cr
S ₂	Zn > Pb > Fe > Ni > Cu > Cr > Cd
S ₄	Zn > Fe > Pb > Ni > Cd > Cu > Cr

Analysis of the results for heavy metal levels in water samples from the Mediterranean Sea (the coastline of the city of Nador) shows that the highest levels during all seasons are zinc, but these values remain below the WHO standard. In addition, we noted a surprising contamination of cadmium and lead samples that exceeded the WHO standard. this may be due to the

existence of a strong industrial activity whose releases are the main cause of these values, as well as agricultural activities involving the intensive use of phosphate fertilizers, fungicides and insecticides, and which are responsible for a significant input of the metals used in these substances, such as zinc for fungicides, cadmium which is a residue of phosphate compounds, all these metals reach the aquatic environment by leaching which is closely related to the rainfall regime. For this reason, values in the fall season are highest. Seasonal variations in metal elements may be due to weather influences. As the bioaccumulation of heavy metals changes over time as a function of physical factors such as temperature, salinity, dissolved oxygen...

Comparison with Global Studies

Similarities with Other Mediterranean Regions

The observed high lead and cadmium concentrations align with studies from Turkey (Şimşek et al., 2021) and Italy (Bessa et al., 2020), where industrial and port activities have significantly contributed to heavy metal pollution. In the Turkish Aegean Sea, Pb concentrations reached 0.07 mg/L, close to our maximum of 0.08 mg/L, while cadmium levels were also above the WHO limit.

Contrasts with Other Regions

In contrast, Spanish Mediterranean waters have shown lower Pb and Cd levels, with concentrations below 0.02 mg/L due to stricter environmental regulations (Pereira et al., 2021, Şimşek et al., 2021)). This suggests that Moroccan waters may experience higher anthropogenic pressure, particularly from untreated industrial effluents.

Possible Sources of Contamination

Previous studies in Morocco (El Morhit et al., 2012; El Moumni et al., 2015) have linked high Cd and Pb levels to:

- Industrial discharges from metallurgy and phosphate industries (common in northeastern Morocco).
- Agricultural runoff containing fertilizers and pesticides rich in Zn and Cd.
- Shipping and port activities, which contribute Pb from fuel combustion and antifouling paints (Amiard et al., 2021).

Seasonal Variations in Heavy Metal Concentrations in the Atlantic Coast (Casablanca)

Heavy metal levels (Cd, Pb, Zn, Fe, Cu, Cr, and Ni) in samples of Atlantic coast water. (Case of the Casablanca coastline) in the four seasons studied between 2023 and 2024, analyzed according to the techniques

described above are represented in the table and the figure below. They are expressed in milligrams per liter (mg/l). Each result is expressed as (mean \pm SD). summarised in (Table 4).

Table 4. Seasonal variations in heavy metal concentrations in the seawater in mg/l

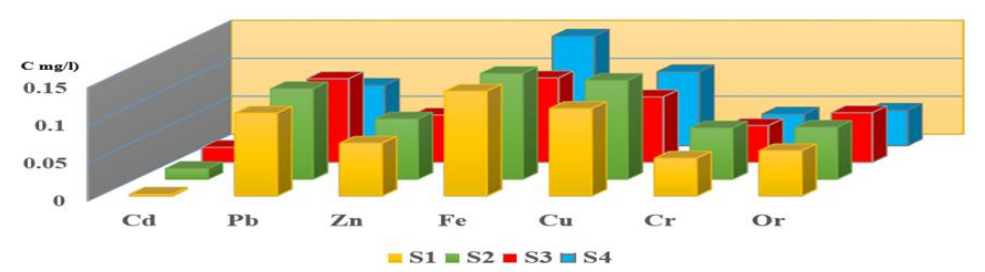


Figure 2. Seasonal variations in metal levels in seawater samples

The results of the analysis of heavy metals in the sea water samples of the Atlantic coast of Casablanca, show that all metal concentrations are high, and that there is not a very significant difference between the concentrations found, such that the iron contents are the highest and they vary between a minimum of 0.112 mg/l obtained during the third autumn season, and a maximum content of 0.145 mg/l recorded during the fourth spring season, moreover these values do not exceed the WHO standard of 0.3 mg/l. For lead, a maximum level of 0.120 mg/l was recorded during the second spring season, and the lowest level was obtained during the fourth spring season at a value of 0.08 mg/l, the results found during all the seasons studied far exceed the WHO standard of 0.01 mg/l for lead. Similarly, for cadmium, the standard is 0.003 mg/l, while concentrations over three seasons exceed this standard, with the highest value being in the order of 0.02 mg/l. Copper concentrations range from 0.131 mg/l, which is the highest concentration, to 0.087 mg/l, which is the lowest concentration in the third fall season. Zinc has non-negligible levels such that the highest level is 0.08 mg/l and the lowest value is in the order of 0.061 mg/l. For chromium, and nickel, concentrations are low relative to other levels found, such that the highest levels are respectively (0.068 mg/l, 0.069 mg/l).

Heavy metal accumulation orders can be established for all four seasons and the result is presented in the table 5 below.

Table 5. The order of accumulation of heavy metals during the four seasons

Heavy Metals Studied	Order of Accumulation
Cd	S3 > S4 > S2 > S1
Pb, Ni	S2 > S3 > S1 > S4
Zn, Cr	S2 > S1 > S3 > S4
Fe	S4 > S2 > S1 > S3
Cu	S2 > S1 > S4 > S3

Thus, we can establish an order of enrichment for the different metal elements during the four seasons studied and we obtain the result presented in the table 6 below:

Table 6. Heavy metal enrichment order for the four seasons

Heavy Metals Studied	The Order of Accumulation
S1, S4, S2	Fe > Cu > Pb > Zn > Ni > Cr > Cd
S3	Fe > Pb > Cu > Ni > Zn > Cr > Cd

Analysis of the results for heavy metal levels in water samples from the Atlantic coast (the coastline of the city of Casablanca) shows that the highest levels during all seasons are iron, but these values remain below the WHO standard. In addition, we noted a surprising contamination of cadmium and lead samples that exceeded the WHO standard. this may be due to the existence of a strong industrial activity such as the automotive industry; The seasonal variations in metal elements may be due to an influence of weather conditions. As the bioaccumulation of heavy metals changes over time as a function of physical factors such as temperature, salinity, dissolved oxygen...

Comparison with Global Studies

Similarities with Other Atlantic Coastal Areas

Our high Fe and Pb levels are comparable to findings from Brazil's Atlantic coastline, where industrial and urban activities have led to Pb concentrations of 0.11 mg/L, similar to our maximum of 0.12 mg/L (Malafaia et al., 2022). Similarly, Cd levels in Casablanca exceed WHO limits, mirroring observations in Nigerian coastal waters, where Cd reached 0.018 mg/L due to port activities (Anweting et al., 2024).

Contrasts with European Atlantic Waters

Conversely, France's Atlantic coastal waters reported Pb concentrations below 0.05 mg/L due to strict environmental policies and wastewater treatment plants (Pereira et al., 2021). The significantly higher Pb levels in Casablanca suggest inadequate pollution control and potentially high maritime emissions from shipping activities.

Possible Sources of Contamination

The elevated metal levels in Casablanca can be attributed to:

- Heavy industrialization, particularly in the automotive, chemical, and petroleum sectors (Salghi et al., 2023).
- Wastewater discharges, as Morocco still lacks comprehensive wastewater treatment infrastructure.
- Port activities, which contribute Cu and Pb from ship coatings and fuel emissions (Bouthir et al., 2006).

Seasonal Trends and Environmental Implications

Influence of Seasonal Changes

Autumn had higher metal concentrations compared to spring, likely due to: Increased rainfall and surface runoff, which mobilizes metals from industrial zones and agricultural lands. Higher tourism and maritime traffic, leading to greater waste disposal in coastal waters. Spring showed lower levels, possibly due to dilution effects from increased water circulation and lower industrial activity during this period.

Environmental and Health Risks

The presence of Pb and Cd above WHO limits poses serious risks to marine biodiversity and human health. Chronic exposure to these metals is associated with neurological, renal, and cardiovascular disorders (Jaishankar et al., 2014). Bioaccumulation of metals in fish species can threaten seafood safety, particularly for local populations dependent on fisheries (Ahmed et al., 2021). Iron and zinc levels were within safe limits, but long-term monitoring is needed to assess cumulative effects.

Comparison with Previous Moroccan Studies

Study	Location	Pb (mg/L)	Cd (mg/L)	Zn (mg/L)	Fe (mg/L)
This study	Casablanca	0.08–0.12	0.002–0.02	0.07–0.08	0.112–0.145
El Morhit et al. (2012)	Loukkos Estuary	0.06	0.004	0.11	0.09
Fahssi & Chafi (2015)	Saidia Coast	0.04	0.002	0.09	0.07
Baghdadi Mazini (2012)	Moroccan Atlantic	0.05	0.003	0.08	0.1

Compared to previous Moroccan studies, our results indicate a worsening trend in Pb and Cd pollution, especially in Casablanca, highlighting the urgent need for tighter regulations and pollution control measures.

Conclusion

This work has highlighted several interesting and original results, These results bring new knowledge that is important not only for understanding the contamination of the area on the Kingdom but also more generally on the risks associated with the consumption of certain fishery products. The results of analyzes of seasonal variations in heavy metal concentrations in the waters of the Mediterranean and Atlantic seas of Morocco showed a surprising contamination of cadmium and lead in certain samples that exceeded the WHO standard.

This study provides a comprehensive assessment of heavy metal contamination in Moroccan coastal waters. The findings suggest serious pollution concerns, particularly for Pb and Cd, and highlight the need for improved wastewater management and industrial regulations. Future studies should focus on biomonitoring in marine species to assess the long-term impact on food safety and public health.

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Data Availability: All data are included in the content of the paper.

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