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Original article

Physicochemical Characteristics and Heavy Metal Concentrations in Marine Waters Between Tolmitha and Tukra, Libya

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A B S T R A C T

This study aims to investigate the impact of pollution on some marine water samples collected from an area extending between Tolmitha and Tukra town along the eastern north side of the Libyan coast. The area under investigation was selected due to the presence of some human activities, such as fishers, a water plant for desalting seawater, and a presence area beside Benghazi city, which is considered the second largest city in Libya. The samples were collected during two seasons (winter and summer). Different physicochemical parameters, such as Temperature, Salinity, Dissolved Oxygen, and PH values, were estimated at the sites of the studied locations. Many different heavy metals were determined, including Iron, manganese, zinc, cadmium, cobalt, lead, copper, and chromium. These heavy metals were estimated using an atomic absorption instrument. The results of this study recorded that the water temperature values, salinity, and PH were ranged between: The temperature values were ranged as 18.20–18.40 °C in winter to 23.6–24.50 °C in summer, The salinity was as (33.50 – 35.14) and (34.10 – 35.90 ‰) during winter and summer season, respectively. Also, the DO concentrations ranged from 5.70–8.90 mg/L during the winter season and 3.67–6.15 mg/L during summer, while the PH during winter water samples exhibited values ranging from 7.13 to 8.10, while summer samples ranged from 7.34 to 8.28. Fe concentrations in seawater samples ranged from 0.021 to 0.28 ppm during winter and from 0.09 to 0.540 ppm during summer. Manganese. In this study, Mn concentrations in seawater ranged from 11.172 to 25.213 ppm during winter and from 9.12 to 22.15 ppm during summer. Zinc In this study, seasonal variations of Zn concentrations in seawater ranged from 0.017–0.76 ppm during winter and 0.065–0.920 ppm during summer. The seasonal variations of Cu concentrations in seawater ranged from 0.01–0.27 ppm in winter and 11.71–25.09 ppm in summer. In this study, seasonal variations of Pb concentrations in seawater ranged from 0.02–0.69 ppm in winter and 0.052–0.94 ppm in summer. Meanwhile, the seasonal variations of Cd concentrations in seawater ranged from 0.023–0.254 ppm in winter and 0.042–0.532 ppm in summer. In this study, seasonal variations of Co concentrations in seawater ranged from 0.106–0.227 ppm in winter and 11.71–25.09 ppm in summer. Seasonal variations of Cr concentrations in seawater ranged from 0.018–0.187 ppm in winter and 0.039–0.315 ppm in summer.

Introduction

Libya, located on the northern edge of Africa, stretches along the Mediterranean Sea with a coastline measuring about 1,810 kilometers. Much of this shoreline is still considered to be in relatively good natural condition, although it is increasingly exposed to human activity. Oil exploration and extraction, marine fisheries, and urban development dominate economic uses of the coast, yet many other activities also influence the fragile coastal system [1]. The Mediterranean region, while exceptionally rich in biodiversity and cultural heritage, is simultaneously one of the most environmentally vulnerable marine systems in the world. It is estimated that approximately 80% of marine pollution in the Mediterranean originates from land-based sources, particularly urban runoff and untreated sewage. Rapid coastal urbanization, combined with unregulated or poorly planned tourism infrastructure, has accelerated environmental degradation. In many cities across the region, wastewater treatment facilities are either insufficient or completely absent, meaning that large volumes of untreated wastewater are discharged directly into coastal waters. This practice not only damages marine habitats but also creates significant

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risks to public health [2]. One of the most concerning effects of coastal pollution is its impact on aquaculture and fisheries. Bivalves, such as mussels and clams, are commonly cultivated in densely populated areas because of their commercial value. However, these organisms are particularly sensitive to contamination and can easily accumulate pathogens present in sewage-polluted waters. Microorganisms originating from human and animal waste represent the primary source of bacterial contamination. Since bivalves filter and store these microbes in their tissues, they can act as a direct vector for human disease when consumed. This situation is especially critical given that large portions of coastal populations not only depend on nearshore waters for seafood but also use them for sewage disposal. As a result, water pollution is now recognized as both a pressing public health issue and an urgent environmental challenge, requiring effective management and regulatory practices to mitigate its effects. The present study has been developed in this context, with the aim of assessing water quality and providing scientifically accurate data that can guide future management strategies [3]. The concept of marine pollution has been formally defined by the United Nations' Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP). According to this definition, marine pollution occurs when substances or energy introduced by human activities either directly or indirectly cause harmful effects within the marine environment, including estuaries. These effects may include damage to marine life, risks to human health, disruption of marine-based activities such as fishing, degradation of seawater quality, and the overall reduction of environmental and social amenities [4]. The sources of marine pollution are diverse and interconnected. Natural processes such as erosion and river discharge contribute, but human activities account for the majority of inputs. These include agricultural runoff rich in fertilizers and pesticides, livestock waste, untreated or partially treated sewage, industrial effluents, stormwater discharges, vehicle emissions, and solid waste from urban areas. Pollution may occur as point-source pollution, which originates from a single, identifiable outlet such as a sewage pipeline or a factory outfall. In such cases, the concentration of contaminants is usually highest near the source and decreases with distance, depending on the pollutant type, water currents, sediment characteristics, and rate of discharge. In contrast, non-point source pollution arises from diffuse sources spread over wide areas, such as agricultural fields, urban landscapes, or road networks, making it more difficult to identify, monitor, and regulate. Both types of pollution contribute significantly to the degradation of coastal ecosystems and pose challenges for long-term management [5].

Marine pollutants can broadly be divided into two categories: biodegradable and non-biodegradable. Biodegradable pollutants, such as oil and organic matter in sewage, generally break down through natural chemical reactions or microbial activity and therefore do not persist for long. In contrast, non-biodegradable substances—including heavy metals, plastics, and radioactive waste—are highly resistant to degradation and remain in the environment for extended periods, causing long-term harm. Many of these compounds are xenobiotic, meaning they are foreign to natural biological systems and often toxic[6]. Heavy metals such as lead, copper, cadmium, chromium, manganese, zinc, and cobalt also threaten marine life. These elements are toxic even at low concentrations and accumulate in sediments and organisms, persisting in food chains [7]. Similarly, pesticides used in agriculture—whether insecticides, herbicides, or fungicides often reach the sea through runoff, where they poison marine organisms and destabilize ecosystems. Radioactive waste, discharged into oceans since the 1940s through nuclear activities, remains another long-lasting and hazardous form of pollution [8]. Nutrients such as nitrogen, phosphorus, and silicates are vital for the growth of phytoplankton, kelp, and seagrasses. However, when introduced in excess through sewage or agricultural runoff, they cause eutrophication and harmful algal blooms, reducing oxygen levels and threatening marine biodiversity. Other pollutants include thermal discharges, which raise water temperature and reduce dissolved oxygen, and plastics, which persist for centuries and accumulate as microplastics, entering marine food webs and posing long-term ecological risks [9]. Although pollutants are diluted once they enter the sea, marine organisms absorb and accumulate them through processes such as ingestion and assimilation. These contaminants then magnify up the food chain, reaching higher concentrations at successive trophic levels. This phenomenon, known as bioconcentration, bioaccumulation, and bio magnification, not only endangers marine species but also poses health risks to humans who consume seafood [10]. The Libyan coast, where about 85% of the national population resides, faces particular challenges. The absence of permanent rivers means pollutants from inland reach the sea mainly during storms, yet in coastal cities untreated municipal and industrial wastewater is directly discharged into the Mediterranean due to inadequate sanitation systems many of studies were carried out on the coastal, sediment, plants [11-56], soils and air samples along Libyan coast during the last years [57-90]. Oil spills near refineries and offshore platforms further intensify environmental degradation. Together, these pressures highlight the urgent need for better wastewater treatment, industrial regulation, and sustainable coastal management in Libya [91-102]. Tolmitha and Tukra are small towns located on the eastern side of Libya. They lie on the Mediterranean Sea beside one of the biggest cities in Libya (Benghazi). They are considered as fishers center besides the

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presence of different human activities inside these areas. This study aims to investigate the pollution impact on some marine water samples collected from different Libyan coastal regions.

Methods

Description of the studied area

The study area extends along the coastline between Tolmitha and Tukra, covering approximately 40 km. Tolmitha, historically known as Ptolemais, lies in a scenic location between the Green Mountain and the Mediterranean Sea, about 30 km west of Al Marj city. Originally established as a port to serve Al Marj, it grew into a thriving commercial hub by the 6th century BC. At that time, goods arrived from nearby ports such as Alexandria in Egypt, while local products, including silphium, honey, butter, and grains, were exported from the region. Tukra, historically referred to as Taucheira or later Arsinoë, is another coastal town in the Marj region, located roughly 60 km east of Benghazi. Founded by the Greeks in the late 7th century BC, it represents one of Libya's important ancient archaeological sites. The town still preserves a number of significant monuments, though many remain neglected and poorly maintained by local authorities. The areas of this study region are displayed in (Figure 1).

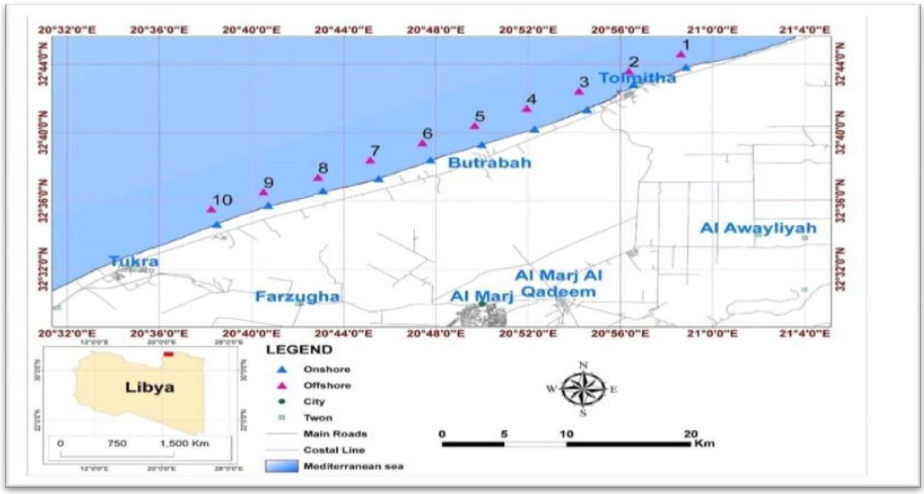

Figure 1. The stations of the studied area

Water Samples

Ten surface water samples were collected from each station during two seasons: winter (Season 1) and summer (Season 2) of 2018. Samples were taken in 2 L polyethylene bottles, pre-rinsed with distilled water, stored in a refrigerator, and transported to the laboratory for analysis.

Temperature (°C)

Water temperature was measured in situ using a digital thermometer.

pH Value

Hydrogen-ion concentration (pH) was determined directly at the sampling sites using a bench-type pH meter (JENWAY 3410 Electrochemistry Analyzer).

Dissolved Oxygen (DO)

DO concentrations were measured in the field with a portable DO meter.

Salinity (‰)

Salinity was estimated by measuring electrical conductivity with an inductive salinometer (Beckman model RS–10).

Heavy Metals

Iron, manganese, zinc, cadmium, cobalt, lead, copper, and chromium were analyzed. Water samples were filtered through 0.45 µm membrane filters to separate the dissolved phase, digested with HNO_3 and HCl, and analyzed by an atomic absorption spectrophotometer (AAS, Perkin-Elmer Model 2380). Results were expressed in µg/L.

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Statistical Analysis

Descriptive statistics, including mean, standard deviation (±SD), and correlation coefficients, were calculated using Microsoft Excel and R software.

Results

Sea Surface Temperature: (°C):

In the present study, results indicated normal seasonal variation in water temperature during the sampling periods. Surface temperatures ranged from 18.20–18.40 °C in winter to 23.6–24.50 °C in summer (Figure 1). As expected, the lowest values were observed in winter and the highest in summer. These fluctuations reflected climatic conditions, time of sampling, latitude, altitude, and average daily sunlight exposure. Additional factors such as turbidity, wind strength, vegetation cover, and humidity also influenced temperature variation. It is noteworthy that the study area showed no evidence of subsurface thermal inputs, confirming the natural stability of the region, where maximum recorded temperatures did not exceed 24.50 °C. Nevertheless, sudden increases in water temperature can elevate toxicity to fish, lower oxygen content, slow growth, and heighten vulnerability to disease, all of which have harmful consequences for fish populations. Correlation matrix analysis further revealed positive relationships between temperature, pH, and salinity, with correlation coefficients of 0.35 and 0.49, respectively. Conversely, decreasing water temperature enhanced oxygen solubility and slowed the bacterial decomposition of organic matter.

Salinity (S‰)

The percentage values of water salinity in the studied am were fluctuated in the ranges of (33.50 – 35.14) and (34.10 – 35.90 ‰) during winter and summer seasons, respectively. The most likely because of roundabout impact of temperature on the adjustment of the thickness and consistency of water, which in turn influences the rate of sinking of suspended particles, either tiny fish life forms or earth suspension. Salinity values are mainly affected by temperature and pH values; therefore, the correlation matrix analysis showed positive values with (PH, Temperature), (r 0.28 and 0.49), respectively. Changing of salinity may affect the variation of pH in the aquatic system.

Dissolved Oxygen (DO)

In the present study, DO concentrations ranged from 5.70–8.90 mg/L during the winter season and 3.67–6.15 mg/L during summer. The higher DO values in winter are likely related to the lower air and water temperatures, which increase oxygen solubility. Enhanced photosynthetic activity due to phytoplankton blooms may also contribute to elevated DO levels. Conversely, lower DO values in summer are probably due to higher water temperatures, which reduce oxygen solubility.

pH Values

In this study, winter water samples exhibited pH values ranging from 7.13 to 8.10, while summer samples ranged from 7.34 to 8.28. The increase in pH during summer may be associated with enhanced photosynthetic activity, which reduces CO_2 concentrations in water, or with higher evaporation rates during this season, which raises CO_3^{2-} content. pH levels are also influenced by the photosynthetic uptake of dissolved inorganic carbon. Conversely, lower pH values in winter may result from greater CO_2 solubility in colder water, leading to increased HCO_3^- formation and a reduction in CO_3^{2-} content and pH. Correlation matrix analysis showed positive relationships with temperature and salinity, with correlation coefficients of r = 0.35 and 0.28, respectively.

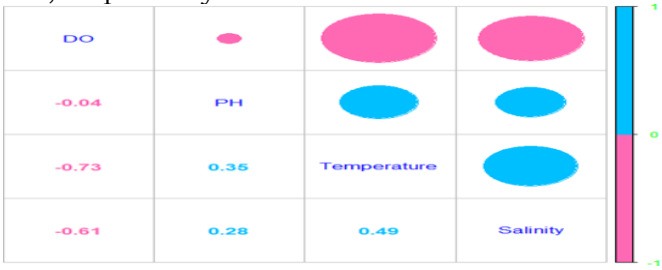

Figure 2. Correlation Coefficient matrix plot of the physical properties of seawater during winter and summer

Heavy Metals

Iron

In this study, Fe concentrations in seawater samples ranged from 0.021 to 0.28 ppm during winter and from 0.09 to 0.540 ppm during summer. The lower values in winter and summer may be attributed to the

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oxidation of Fe^{2+} to Fe^{3+}, followed by precipitation as hydroxides at pH > 7 in the presence of high dissolved oxygen (Kuma et al., 1998). The Correlation coefficient matrix is Fe in the seawater positively correlated with (Zn, Cu, Cd, Cr, and Co) (r = 0.18, 0.31, 0.29, 0.27, and 0.38) (Figure 3).

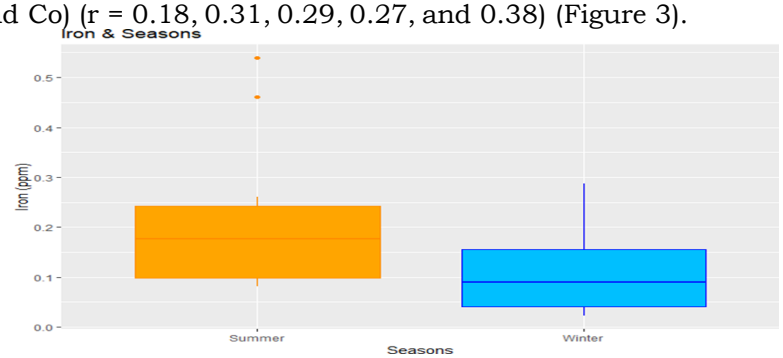

Figure 3. The grouped box plot illustrates the Fe content in the seawater during the winter and summer seasons

Manganese

In this study, Mn concentrations in seawater ranged from 11.172 to 25.213 ppm during winter and from 9.12 to 22.15 ppm during summer. The lower values and relative decrease of manganese in both seasons may be attributed to the removal of Mn from the dissolved phase to the solid phase during precipitation as MnO_2 or adsorption onto suspended particles. The correlation coefficient matrix showed that the Mn in the seawater samples is positively correlated with (Zn, Cu, Cd, Cr, and Co) (r=0.18, 0.31, 0.29, 0.27, and 0.38). (Figure 4).

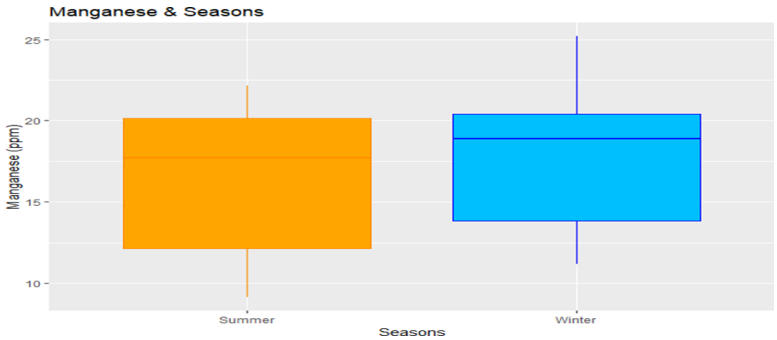

Figure 4. The grouped box plot illustrates the Mn content in the seawater during winter and summer seasons.

Zinc

In this study, seasonal variations of Zn concentrations in seawater ranged from 0.017–0.76 ppm during winter and 0.065–0.920 ppm during summer. The general decrease in zinc content in seawater during both seasons may be linked to uptake by phytoplankton and zooplankton, and/or precipitation at higher temperatures and pH. The Correlation coefficient matrix is the Zn in the seawater positively correlated with (Mn, Cu, Cd, Cr, Co, and Fe) (r= 0.45, 0.08, 0.25, 0.05, 0.25and 0.18) ,(Figure 5).

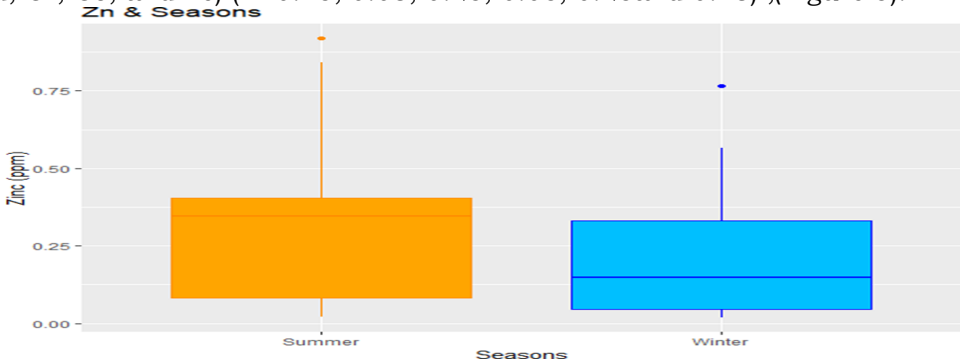

Figure 5. The grouped box plot illustrates the Zn content in the seawater during the winter and summer seasons

Copper

In this study, seasonal variations of Cu concentrations in seawater ranged from 0.01–0.27 ppm in winter and 11.71–25.09 ppm in summer. Higher values during summer may result from increased evaporation, higher water and air temperatures, and the release of Cu from sediments into overlying water. Conversely, lower winter values may be attributed to chelation of copper by marine organisms, adsorption onto humic

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substances, or retention in bottom sediments. The Correlation coefficient matrix is the Cu in the seawater, positively correlated with (Zn, Cd, Cr, Co, and Fe) (r=0.08, 0.8, 0.17, 0.24, and 0.31)(Figure 6).

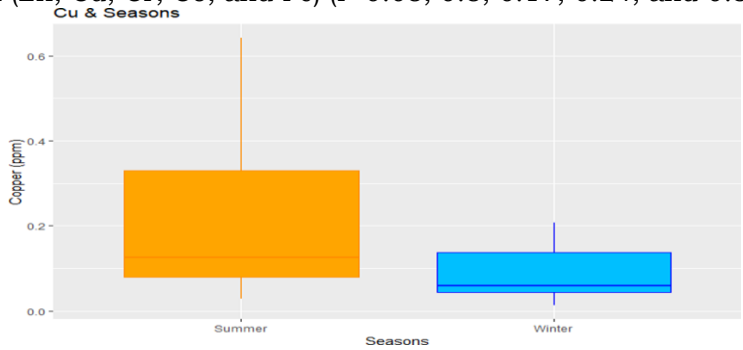

Figure 6. The grouped box plot illustrates the Cu content in the seawater during the winter and summer seasons

Lead

In this study, seasonal variations of Pb concentrations in seawater ranged from 0.02–0.69 ppm in winter and 0.052–0.94 ppm in summer. The increase in lead concentrations during summer may be attributed to mobilization from sediments into overlying water due to microbial activity and decomposition of organic matter under higher temperatures. The Correlation coefficient matrix is the lead in the seawater, positively correlated with (Co) (r=0.19) ,(Figure 7).

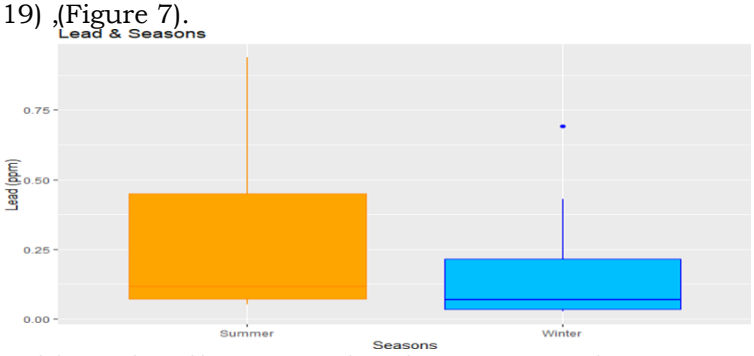

Figure 7. The grouped box plot illustrates the Pb content in the seawater during winter and summer seasons

Cadmium

In this study, seasonal variations of Cd concentrations in seawater ranged from 0.023–0.254 ppm in winter and 0.042–0.532 ppm in summer. The lower Cd levels observed during winter and summer may be attributed to the release of Cd from sediments into overlying water. Additionally, Cd uptake by phytoplankton plays a role in reducing its dissolved concentration. The observed increases in Cd concentrations are generally associated with sediment-to-water transfer processes, particularly in surface layers overlying the sediment. The Correlation coefficient matrix is the Cd in the seawater positively correlated with (Zn, Cu, Cr, Co, and Fe) (r=0.25, 0.8, 0.38, 0.3, and 0.29), (Figure 8).

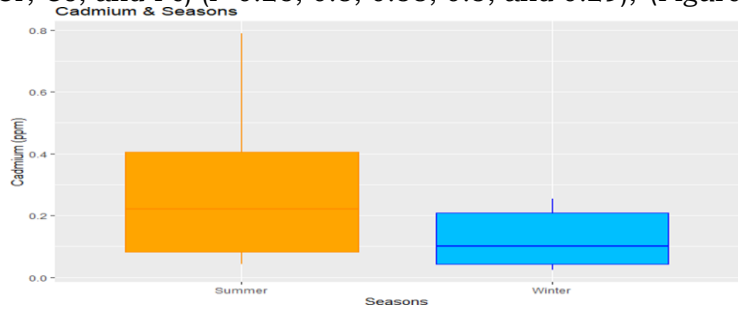

Figure 8. The grouped box plot illustrates the Cd content in the seawater during the winter and summer seasons

Cobalt

In this study, seasonal variations of Co concentrations in seawater ranged from 0.106–0.227 ppm in winter and 11.71–25.09 ppm in summer. The observed increase in Co during summer is likely associated with the growth of phytoplankton populations during this season. The Correlation coefficient matrix is the Coin, the seawater positively correlated with (Zn, Pb, Cu, Cd, Cr, and Fe) (r=0.25, 0.19, 0.24, 0.3, 0.25, and 0.38) (Figure 9).

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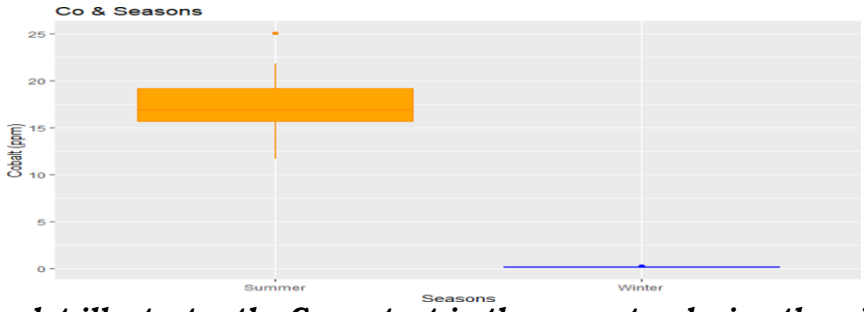

Figure 9. The box plot illustrates the Co content in the seawater during the winter and summer seasons

Chromium

Seasonal variations of Cr concentrations in seawater ranged from 0.018–0.187 ppm in winter and 0.039–0.315 ppm in summer. The higher Cr levels observed in summer may be attributed to increased phytoplankton uptake and/or the release of Cr from sediments to the overlying water. Major sources of chromium in the study area include domestic wastewater, industrial processes (especially metal-related), and sewage sludge disposal. The Correlation coefficient matrix showed positive correlation with (Zn, Cu, Cd, Co, and Fe) (r=0.05, 0.17, 0.38, 0.25, and 0.38), Figures (10 &11).

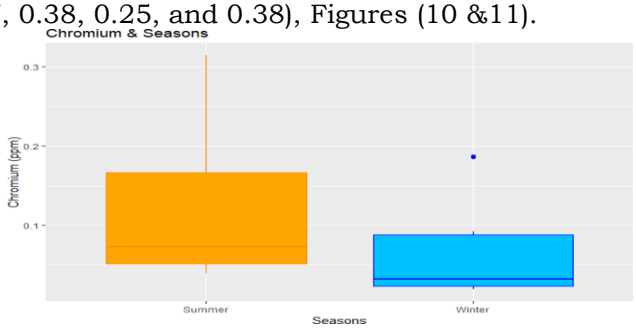

Figure 10. The grouped box plot illustrates the Cr content in the seawater during the winter and summer seasons

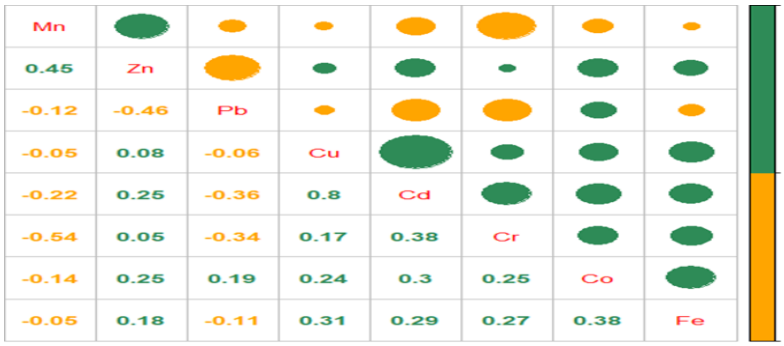

Figure 11. The Correlation Coefficient matrix plots the relationship between the heavy metals of seawater during summer and winter

Discussion

Sea surface temperature is one of the most important physical characteristics of the world's oceans. It varies mainly with latitude, with the warmest waters found near the equator and the coldest in the Arctic and Antarctic regions. As the oceans absorb more heat, surface temperatures rise, altering global circulation patterns that move warm and cold water around the planet. Shifts in sea surface temperature affect marine ecosystems in multiple ways. Temperature changes influence the distribution of plants, animals, and microorganisms, alter migration and breeding cycles, and place stress on sensitive organisms such as corals. Warmer conditions can also increase the frequency and intensity of harmful algal blooms such as "red tides" [10]. Over time, warming may weaken the upwelling of nutrients from deep waters to the surface, leading to changes in reef habitats, reduced nutrient availability, and declines in fish populations. These ecological disruptions ultimately threaten coastal communities that depend on fisheries for food and livelihoods. Additionally, warmer water holds less oxygen, reducing metabolic efficiency and overall fitness in marine organisms. Such effects are particularly pronounced near thermal

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discharges from power plants or industrial facilities, where water is often returned to the environment at higher temperatures than ecosystems can tolerate [4].

Saltiness is a seawater property connected with how much matter, essentially comprising of salts, is dissolved in the water. The first meaning of saltiness was as far as grams of disintegrated salts per kilogram of seawater. Saltiness is presently characterized by seawater conductivity, and is currently adjusted using a standard arrangement arranged at a research facility in the UK. The number of disintegrated salts, thus the saltiness, influences seawater thickness, which additionally relies upon temperature and pressure. Measuring these disintegrated constituents as the single boundary saltiness is conceivable in light of the fact that the source of solids is enduring, which happens on land time scales [103]. Consequently, saltiness contrasts are made exclusively by weakening or focusing as new water is added or taken out, or as pungent water is removed from ocean ice as it freezes. Other broken down non-salt constituents, for example, carbon, calcium, and silica, which are impacted by organic cycles, have sufficient spatial changeability to influence seawater thickness. This little variety isn't typically remembered for saltiness and thickness studies. Dissolved oxygen (DO) refers to the amount of oxygen that a specific volume of water can hold. Its concentration is influenced by atmospheric pressure, water temperature, and the presence of other dissolved substances. At sea level, freshwater can retain more oxygen due to higher atmospheric pressure, while cold water holds more oxygen than warm water.

Water with high concentrations of dissolved salts or minerals typically has a lower DO concentration compared to freshwater at the same temperature. When water reaches its maximum oxygen-holding capacity under a given temperature, pressure, and dissolved solids content, it is considered saturated with DO, or 100% saturation. Unlike air, which contains approximately 21% oxygen, water generally holds only a small fraction of this as dissolved oxygen. DO is commonly expressed in milligrams per liter (mg/L), parts per million (ppm), or as a percentage of saturation. The ocean plays a crucial role in regulating atmospheric carbon dioxide. As atmospheric CO_2 levels rise, the ocean absorbs more CO_2. Due to the slow mixing between surface waters and deeper layers, it can take hundreds to thousands of years to reach equilibrium.

Over recent decades, oceans have absorbed approximately 28% of the CO_2 generated by human activities such as fossil fuel combustion. While the ocean's CO_2 uptake slows the increase of atmospheric levels, elevated CO_2 concentrations in seawater can negatively impact marine organisms. CO_2 reacts with seawater to form carbonic acid, increasing acidity (reflected by lower pH values) and altering mineral balance. This makes it more difficult for corals, certain planktonic species, and other organisms to produce calcium carbonate, the primary component of their skeletons or shells. Consequently, declining pH can hinder the growth and survival of these species, potentially causing broader changes in coastal and marine ecosystems and affecting fish populations and communities dependent on them. Early signs of such impacts are already appearing in some areas [103-105].

Conclusion

This study showed natural variations of temperature, PH, and salinity values during two different seasons. These variations were due to the effect of temperature changes during the two seasons; also, the study recorded lower dissolved oxygen values during winter compared to the summer season. The results of this study also indicated different values of some heavy metals present in all the studied samples as Iron, manganese, zinc, cadmium, cobalt, lead, copper, and chromium. There are high values of these metals in the area under investigation. This study concluded that most of the heavy metal sources are mainly due to human activities.

Acknowledgment

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Conflict. The results recorded in this study have not been published in other studies, and there are no problems in publishing them in this journal

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