

Chemical Studies of water Samples Collected from area extended between Ras Al –Halal and El Haniea

Abstract

The present study aimed to investigate chemical formulations of water Samples Collected from area extended between Ras Al –Halal and El Haniea, Libya. The geographic location of the Mediterranean governs the water temperature and salinity. The hot climate of the eastern basin raises the water temperature, causing increased evaporation and high salinities. The present study included visiting the study sites (8 stations on the eastern coast of Libya) during winter and summer seasons 2019. The concentration of different water quality parameters was analyzed and reported accordingly. The palnktonic composition was also evaluated.

Keywords: Chemical formulations, palnktonic composition, water quality, Mediterranean Sea

Introduction

The Mediterranean Sea: The Mediterranean Sea is an almost closed marine basin between Europe, Asia and Africa with an area of 2.96 million km². consists of two basins, western and eastern separated by the Strait between south Italy and Tunisia. Due to massive evaporation in the eastern basin, there is a constant flow of near surface waters that run in a counterclockwise direction from the shores of North Africa to the Levant, then north and west via Southern Turkey, Greece and back to Gibraltar (Islam and Tanaka, 2004).

The geographic location of the Mediterranean governs the water temperature and salinity. The hot climate of the eastern basin raises the water temperature, causing increased evaporation and high salinities. This produces a clear west-east gradient of both temperature and salinity. For example, the range of surface temperatures in the western basin is 8-24 C°. While in east it is 13-31 C°. Similarly, Salinity in the western basin is close to 30-35 ‰ reaching 39 ‰ in the phalastin and Lebanese coasts (Michael, 2010).

The Libyan coast: The Libyan State has a vast coastline of 1970 Kms of the Mediterranean Sea. Libyan coast has been divided into three sectors: west coast: extending from Ras Jadir on the Libyan-Tunisian border to the Port of Misurata iron and steel factor, The coast of the Gulf of Sirte: Extending between the Ras El borj in west and Tukarah in the east.

East coast: This extends coast of Tukarah in the west to Ramala head in the east on the Libya-Egyptian border (Fauzi *et al.*, 2001).

The Libyan coast in general has a few natural bumps, that is why there is no any natural harbors except a Port of Tobruk, which was held in a gap is coming inside a rocky coast for 4 Kms far, while the Port of Dernah-that was built in a slot that hurt for a valley of Dernah: has got its importance as apart from industrial barriers that set up to protect it from the waves as well as the new Port of Soussa that built in 1996. The coastal area in the north of Libya get a change in width from a region to other and that is depending on the approach of the plateau from the sea. In Benghazi the average for width of the coastal area is about 40 Kms while the edge of the green mountain has a narrow coastal is getting wide up several Kilometers (Almabrok, 2006).The aim of this study is evaluate of some water samples collected from coast locations at some Algabal Alkhder (Libya).

Materials and methods:

The present study included visiting the study sites (8 stations on the eastern coast of Libya) during winter and summer seasons 2019 and:

- ❖ Measuring main physical and chemical parameters of surface water of the near shore intertidal region in each site,
- ❖ Taking surface water samples from each site for establish their major and trace elements constituents

The study sites: The study sites including El-Hania, Twat AlGwarib, Alhamama, near the desalination plant of Susa, Susa harbor, between Susa and Ras Hilal (Two stations: St. 1 and St. 2) and Ras Al-Hilal on the eastern coast of Libya, Figure (1).

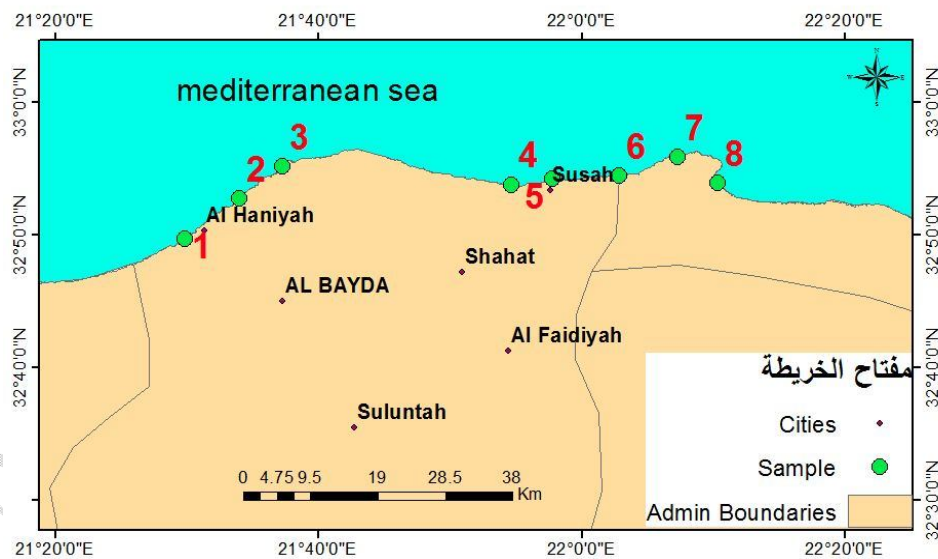


Figure (1): The study sites (8 subsites)

On site surface water parameters:

These are the physical-chemical parameters of the near shore surface water: salinity, temperature, pH and dissolved oxygen.

Major elements: The water samples are digested with 5ml of concentrate Nitric acid and placed on a preheated until near dehydration, then filtered to remove particulates and transferred to a 100 ml flask and complete until the mark distilled water. Take 1 ml of water sample in a 100 ml volumetric flask and add distilled water to the label and It is also measured(sodium , potassium and calcium) by Flam photometer (Hasan, 2006)

Estimated phosphorus and nitrogen in both sediment and water samples, added 5 ml of the sample + 5 ml vanadium in a 25 ml volumetric flask and add distilled water to estimate phosphorus on the Spectro photometer at 410 nm wavelength. Nitrogen Add 1 ml + 1 ml

Neslar in a 10 ml flask and supplement the distilled water with a wavelength 420 nm (Hasan, 2006).

Trace elements: The iron was estimated by Spectrophotometer. Where 4 ml of (KSCN), 0.2 ml (HCl) was added, the solution was left for 20 (min), than the absorbance was measured at 480 nm. The nickel, added 5 ml sample + 4 ml dimethyl glyoxime + 1 ml ammonia(NH₃) in a 25 ml volumetric flask and supplement the distilled water at a wavelength of 550nm. And to estimate the copper, add 2 ml sample+ 2 ml ammonia solution (NH₃) in a 25ml volumetric flask and supplement the distilled water at a wavelength of 745nm (Hasan, 2006).

Results & Discussion

Water analysis

Physico-chemical parameters:

The obtained results of the water analysis can be shown in the following Tables (1 - 2) and Figures (11 - 12) :

Table (1): Variation of Physico-chemical parameters values in the studied area during winter 2019.

Stations Parameters	Alhaneah	Twat AlGwarib	Alhamama	Desalination plant, Susa	Susa harbor	Susa- Ras Hilal 1	Susa- Ras Hilal 2	Ras Hilal	±SD	average
D.O	3.60	4.23	4.45	3.55	4.86	5.87	5.90	6.15	1.04	4.83
pH	7.20	7.15	7.55	7.45	7.22	7.45	7.70	7.80	0.24	7.44
T °C	18.1	18.70	18.20	19.15	18.50	18.30	18.55	18.12	0.35	18.45
S ‰	33.70	34.10	35.15	34.15	33.15	35.50	36.10	35.90	1.09	34.72

Table (2): Variation of Physico-chemical parameters values in the studied area during Summer 2019.

Stations Parameters	Alhaneah	Twat AlGwarib	Alhamama	Desalination plant, Susa	Susa harbor	Susa- Ras Hilal 1	Susa- Ras Hilal 2	Ras Hilal	±SD	average
D.O	3.15	4.12	4.18	3.10	3.45	5.65	5.80	5.78	1.18	4.40
pH	7.1	7.3	7.45	7.10	7.65	7.12	7.8	7.60	0.28	7.39
T °C	22.31	22.34	23.16	24.10	23.90	22.90	22.60	22.45	0.70	22.97
S ‰	34.20	34.30	36.20	35.15	33.70	35.70	35.90	36.10	0.97	35.16

Dissolved Oxygen:

Dissolved oxygen is an important environmental parameter for the survival of aquatic life. Dissolved oxygen affects the growth, survival, distribution, behavior and physiology of shrimps and other aquatic organisms (Solis, 1988). Oxygen distribution also strongly affects the solubility of inorganic nutrients since it helps to change the redox potential of the medium. It can also determine whether the environment is aerobic or anaerobic (Beadle, 1981). The principal source of oxygen that is dissolved in water is by direct absorption at the air-water interface which is greatly influenced

by temperature (Plimmer, 1978 and Kutty, 1978). Dissolved oxygen concentration of 5.0 mg/L and above are desirable for fish survival (Boyd, 1979).

The distribution pattern of D.O at the different stations varied from a minimum of (3.10 ppm) at Desalination plant, (Susa) in summer to a maximum of (5.90 ppm) at Susa-Ras Hilal 2 in winter. Low dissolved oxygen concentrations are known to be one of the major problems of faunal and floral survival in the aquatic environment.

The statistical analysis of correlation coefficient matrixe represents a positive trend between DO and salinity in the surface water ($r = 0.753$ and $r = 0.702$) during winter and summer, respectively.

Hydrogen ion concentration:

In water the hydrogen ion concentration is measured in terms of pH, which is defined as the negative logarithm of hydrogen ion concentration (Boyd, 1979). This concentration is the pH of neutrality and is equal to 7. When the pH is higher than 7 it indicates increasing salinity and basicity while values lower than 7 tend towards acidity i.e. increase in hydrogen ion concentration. The pH higher than 7, but lower than 8.5 is ideal for biological productivity, while pH lower than 4 is detrimental to aquatic life (Abowei, 2010). It was reported that the pH of natural waters is greatly influenced by the concentration of carbon dioxide which is an acidic gas. Phytoplankton and other aquatic vegetation remove carbon dioxide from the water during photosynthesis, so the pH of a water body rises during the day and decreases at night (Boyd and Lichtkoppler, 1979)

The pH-values ranged between a minimum value of (7.1) during summer and a maximum of (7.80) during winter Figures (2 & 3). The pH of an aquatic system is an important indicator of the water quality and the extent of pollution in the watershed areas. Low pH values or acidic waters are known to allow toxic elements and compounds such as heavy metals to become mobile thus producing conditions that are inimical to aquatic life (APHA, 1995).

However, the pH values showed a negative correlation with most chemical parameters. The positive correlation between pH and DO ($r = 0.671$ and $r = 0.453$) justified the important role of photosynthetic activity.

Temperature:

The water temperature ($^{\circ}\text{C}$) measured in situ exhibited wide variations, which attains its maximum value of 23.90°C during summer at Susa harbor area and its minimum value of 18.1°C during winter at Alhaneah, Figures (2 & 3).

High water temperature enhances the growth of microorganisms however the effect of changes in temperature on living organisms can be critical. Temperature controls the solubility of gases in water, and the reaction rate of chemicals, the toxicity of ammonia, and of chemotherapeutics to fish. Temperature is the most important physical variable affecting the metabolic rate of fish and is therefore one of the most important water quality attributes in aquaculture (IEPA, 2001).

The correlation coefficient matrixes of surface water temperature, showed a negative correlation with dissolved oxygen during winter and summer seasons ($r = -0.387$ and $r = -0.471$) respectively, Decreasing in water temperature leads increase of oxygen solubility and decrease in rate of bacterial decomposition of organic matter. Also, the pH values are negatively correlated with surface water temperature during winter and summer seasons ($r = -0.193$ and $r = -0.051$) respectively, as well as salinity ($r = -0.278$ and $r = -0.168$) respectively.

Salinity:

The Salinity values ranged between a minimum value of (33.15 ‰) during winter and a maximum value of (36.20 ‰) during summer (Figures 11 & 12). marine salinity water is usually higher than that of fresh water because the former contains more electrically charged ions than the latter. The total load of salts of water is in direct relation with its salinity (Golteman and Kouwe, 1980). It is an index of the total ionic content of water, and therefore indicates freshness or otherwise of the water (Egborge, 1994; Ogbeibu and Victor, 1995), which states that rain falling into a water body, or rain runoff flowing into it, will decrease conductivity/salinity because the salinity/conductivity of coastal waters is influenced by sea spray that can carry salts into the air, which then fall back into the waters with rainfall. Evaporation and loss of freshwater will increase the conductivity and salinity of a water body, also, warm weather can even increase ocean salinity (CWT, 2004). In general the salinity of surface waters depends on the drainage area, the nature of its rock, precipitation, human activity in the area and its proximity to marine water (McNeely *et al.*, 1979).

correlation coefficients were recorded between salinity and major cations especially Na^+ ($r = -0.126$ and $r = 0.178$), , during winter and summer seasons, respectively. Changing of salinity may affect on the variation of pH in the aquatic system, where positive correlation between salinity and pH was recorded ($r = 0.880$ and $r = 0.212$) during above mentioned seasons.

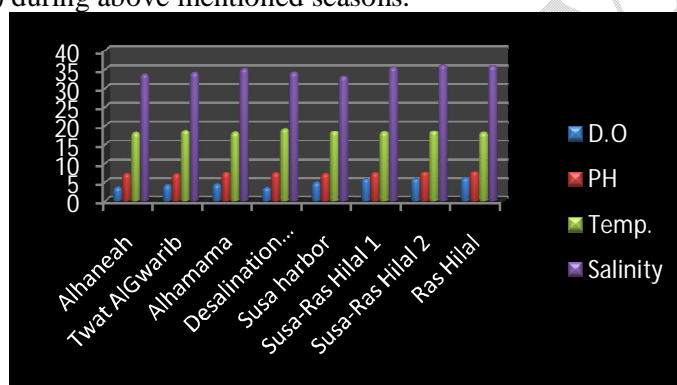


Figure (2): Parameters values in the studied area during winter 2019.

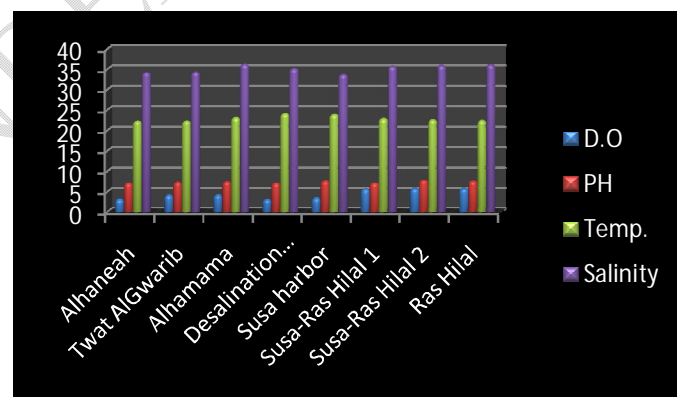


Figure (3): Parameters values in the studied area during summer 2019.

Major and Trace Elements of water samples:

The distribution of elements is controlled by biological cycling. Most of the marine “life” and certainly all the photosynthesizing organisms are confined to the upper 100 meters or so of the ocean (the photic zone), (Boyle *et al.*, 1976). These

phytoplankton uptake dissolved carbon and other nutrients in order to grow and produce organic matter and hard body parts. Therefore, such nutrients as phosphate, nitrate and trace metals that are either needed for metabolic pathways or taken “by mistake” are depleted from surface water. 90% of the organic matter produced is recycled in the photic zone but the remaining 10% (of dead organisms and fecal matter) sinks into the deeper ocean, gets remineralized (bacterial oxidation or dissolution) and returns to the water column as dissolved inorganic compounds. The result is depletion of the dissolved “recycled elements” in surface waters and enrichment at depth. Note the depth profiles for elements related to the organic (soft parts, e.g. phosphate and nitrate) and those concentrated in hard parts (shells, e.g. silica) are different. This depends on the depth of highest remineralization (shallower for organic matter and deeper for the skeletal remains) (Donat and Bruland, 1995).

The elements whose concentrations in surface waters drop down to zero are considered bio-limiting, as they have the potential to limit biological productivity. Others, like C and Ca are only partially depleted and are considered bio-intermediate. Many other elements follow these types of curves because they adsorb or react with the organic or skeletal particles are recycled with them. Several of the most important elements in living organisms (O, H, S and also C) are not limiting in the ocean (Libes, 2009).

The results obtained from analysis of water samples of the study sites are shown in Tables (3 & 4) and Figures (4 -11). The reported values refer to the mean value of water samples collected in two seasons at different areas along the stretch on the eastern coast of Libya.

Table (3): Major and trace elements of water samples during winter 2019.

Stations Element	Alha - neah	Twat AlGwa rib	Alham -ama	Desalina tion plant, Susa	Susa harb or	Susa- Ras Hilal 1	Susa- Ras Hilal 2	Ras Hilal	±SD	Avera ge
Na	4829	5162	5019	7686	5352	4733	5352	5686	943.9 3	5477.3 8
K	398	446	382	430	478	382	414	446	34.21	422.00
Ca	229	181	205	420	205	229	157	181	267.6 7	292.38
T.N	4.23	5.45	5.18	5.45	4.65	8.05	5.48	5.33	1.13	5.48
T.P	2.04	1.39	0.83	1.00	1.70	1.83	1.26	1.52	0.41	1.45
Fe	0.39	0.48	0.48	0.64	1.03	0.27	0.64	0.42	0.23	0.54
Ni	1.768	1.746	1.820	1.799	1.821	1.851	1.842	1.822	0.04	1.81
Cu	1.00	1.83	3.33	4.50	5.00	0.83	4.67	1.50	0.36	18.09

Table (4): Major and trace elements of water samples during summer 2019.

Stations Element	Alha n-eah	Twat AlGwa rib	Alham ama	Desalina tion plant, Susa	Susa harbor	Susa- Ras Hilal 1	Susa- Ras Hilal 2	Ras Hilal	±SD	Average
Na	6254	6411	6793	6838	7422	7760	6501	7220	527.18	6899.88
K	400	436	436	491	473	509	427	527	44.43	462.38

Ca	95.9	82.2	95.9	109.6	68.5	123.3	68.5	109.6	19.97	94.19
T.P	0.57	0.43	0.48	0.43	0.74	0.48	0.33	0.70	0.14	0.52
Fe	0.21	0.30	1.15	0.58	0.30	0.42	0.45	0.61	0.30	0.50
Ni	1.228	1.198	1.228	1.138	0.973	1.207	1.213	1.174	0.09	1.17
Cu	0.33	0.67	1.00	0.83	3.17	0.67	4.17	1.33	0.85	11.70

Major elements:

Materials that caused the water to be turbid are wastes originate from the ships or transported from the land, organic matters, microscopic microorganisms, planktons, inorganic matters or even sediment (Lawler, 2004).

Sodium:

Sodium are generally highly soluble in water and are leached from the terrestrial environment to groundwater and surface water. They are nonvolatile and will thus be found in the atmosphere only in association with particulate matter (WHO, 2015).

The maximum value of sodium was recorded in summer season comparing with their values during winter season, generally the sodium values were ranged between (7760 ppm) and (4733 ppm), during summer and winter seasons, respectively. The high concentrations might be due to higher evaporate transpiration in summer and extra unrecorded deposition of sea-salts. The results also showed that, there is small variations in sodium contents of the area under investigations. These variations are not expected to have impact on meiofauna because sodium is biologically none limiting.

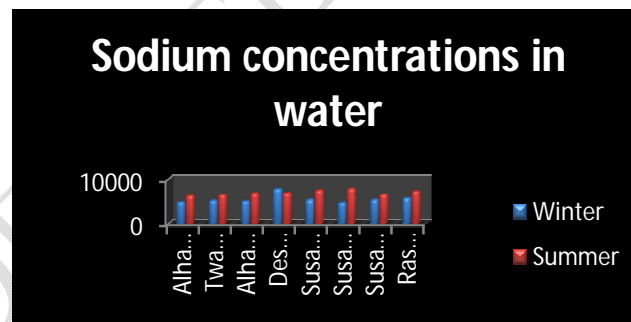


Figure (4): Concentrations of Sodium in water samples of the studied stations during winter and summer seasons.

Potassium:

Potassium does not occur in nature because of its high reactivity. It reacts violently with water (Holleman et al., 1985) and also reacts with oxygen. Orthoclase (potassium feldspar) is a common rock-forming mineral. Granite for example contains 5% potassium, which is well above the average in the Earth's crust. The deposits often show layers starting with the least soluble at the bottom and the most soluble on top (Prud'homme and Krukowski, 2006). The maximum values of Potassium was recorded (527 ppm) in summer season and minimum values was (382 ppm) during winter season, with small variations in potassium contents of the area. where high rates of evaporation, low precipitation and low run-off. Like sodium, potassium is also biologically none limiting and is not likely to affect meiofauna and other marine organisms. The correlation coefficient matrixes of K^+ with other parameters showed a

strong positive correlation with Na^+ ($r = 0.322$ and $r = 0.821$) during winter and summer, respectively.

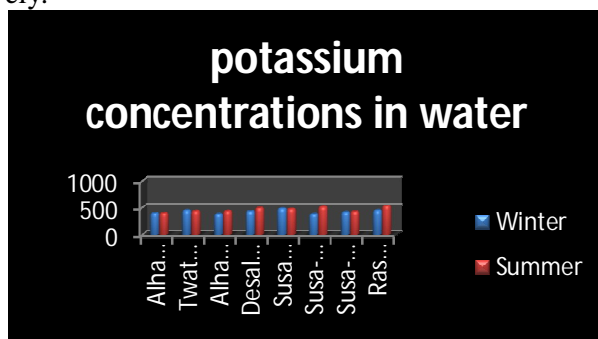


Figure (5): The concentrations of potassium of water samples during winter and summer seasons.

Calcium:

Calcium is most abundant ions in fresh water and is important in shell construction, bone building and plant precipitation of lime (Verma *et al.*, 2010).

Whereas the values of calcium concentrations were ranged between (420 ppm) in winter season by the addition of sewage waste along with rain water and responsible for the increase in amount of calcium (Verma *et al.*, 2010) and (68.5 ppm) in summer due to calcium absorbed by the large number of organisms for shell construction, bone building and plant precipitation of lime (Solanki, 2012). The results also showed that, there is large variations in Calcium. However, availability of calcium to aquatic organisms (including meiofauna) is also strongly dependent on temperature and pH of the water, which decide speciation between CO_2 , HCO_3^- and CO_3^{--} .

The correlation coefficients showed, a positive trend between calcium and pH ($r = -0.027$ and $r = -0.664$).

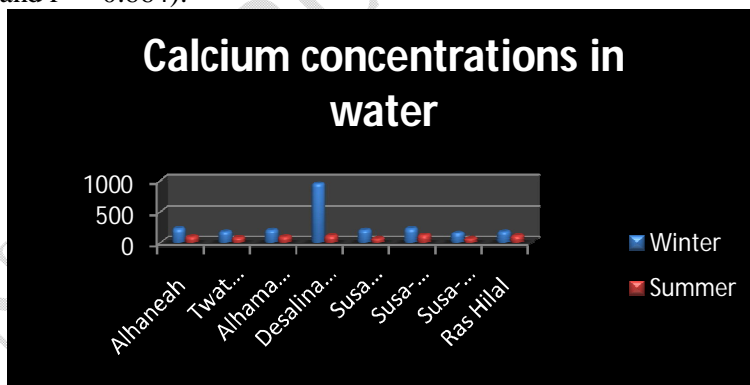


Figure (6): The concentrations of calcium of water samples during winter and summer seasons.

Total Nitrogen:

Concerning the water compartment, the nitrite and nitrate levels point to an absence of significant quantities of biodegradable organic material, and adequate oxygenation levels (Madson de G. Pereira *et al.*, 2012).

The values of Total Nitrogen concentrations assigned ranged between (4.23 ppm - 8.05 ppm) during winter season. The highest amount of nitrate concentration was known to support the formation of blooms because of high vegetation during winter which supported the growth of plankton (Uduma, 2014; Pandit and Solanki, 2004). The lowest amount of nitrate by the utilization by plankton and aquatic plants

(Verma *et al.*, 2010). The results also showed that , there is high variations in Total nitrogen contents of the area. showed an aquatic ecosystem preserved from eutrophication. It must be noted that this environmental panorama was observed, despite increasing human pressure promoted by real-estate development and tourism (Madson de G. Pereira *et al.*, 2012).

The correlation coefficient between TN and salinity shows, Positive trend ($r = 0.500$) during the period of study. This reflects the run-off enriched with nutrients.

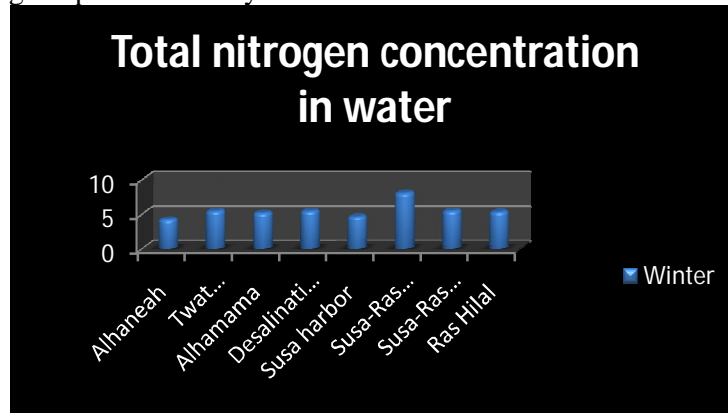


Figure (7): The concentrations of Total nitrogen of water samples during winter and seasons.

Total Phosphorus:

The phosphate comprises another anion of great importance for assessing the quality of an aquatic ecosystem, as it can be responsible for eutrophication, along with nitrate. In addition to the natural weathering process of rocks and anthropic inorganic fertilizers, phosphate is predominantly introduced into bodies of water through domestic and industrial discharges containing synthetic detergents (Manahan, 1994).

While Total phosphorus for the water samples, the values of maximum concentration were (2.04 ppm) found in winter season. The highest P concentration were possibly due to the atmospheric inputs such as dry (dust) and wet (rain) depositions (Faragallah *et al.*, 2009 and Schlosser *et al.*, 2014). and minimum concentration (0.33ppm) in summer season, where recorded small variations in Total phosphorus contents of the area. The normal levels of soluble phosphate indicate that there is no appreciable source of waste containing detergents (Madson de G. Pereira *et al.*, 2012).

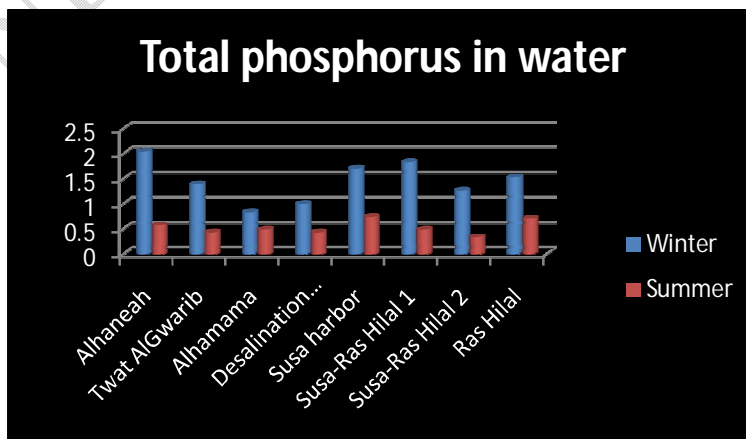


Figure (8): The concentrations of Total phosphorus of water samples during winter and summer seasons.

Heavy metals:

Metals become harmful to marine life by forming insoluble and/or soluble metal complexes with other naturally occurring ligands. Moreover, they can exist in the dissolved phase as three forms: 1) free hydrated metal ions; 2) organic complexes and; 3) inorganic complexes, the most toxic being free hydrated metal ions because of their high bioavailability in the marine environment, relative to the other two. This availability of the metal complexes for bioaccumulation (absorption, storage and excretion of substances by an organism due to exposure in water, food, sediment or air) is the basis for much of the concern about contamination and pollution in the marine environment (Velasquez, 2002).

Iron:

Iron is the most abundant metal in the earth's crust. It is an important trace element required for all biological life activities. At high concentration the iron II is toxic for most organisms (Dyrssen and wedborg, 1974).

The high levels of maximum iron (1.15 ppm) were recorded during winter. While, the minimum level (0.21 ppm) was recorded during summer season Figure (18), The results also showed that, there is small variations in iron contents of the area under investigation. The maximum concentration of iron in oceanic surface sea water is controlled by the solubility of inorganic forms and the availability of organic complexing ligands to promote higher solubility (Zhu *et al.*, 1997; Jickells and Spokes, 2001; Vink and Measures, 2001).

The correlation coefficients of iron with DO were ($r = -0.119$ and $r = 0.141$), Tables (5&6), during winter and summer seasons, respectively, indicating the tendency of iron to increase in the less oxygenated bottom water. This may indicate the release of heavy metals from bottom sediments in poorly oxygenated water that is characterized by the presence of HS^- ion and their adsorption in oxygenated water (Emara and shriadah, 1991).

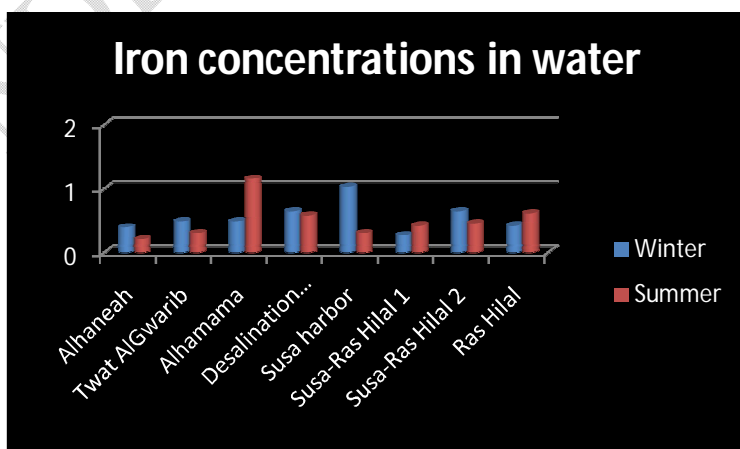


Figure (9): The concentrations of Iron of water samples during winter and summer seasons.

Nickel:

The maximum value of nickel was recorded during summer season comparing with their values during winter season, generally the Ni values were ranged between (1.851 ppm) and (0.973 ppm), during summer and winter seasons, respectively, Figuer (19). where recorded small variations in nickel contents of the studied area were recorded. Nickel in seawater exists in the form of free ion, the most toxic form to marine biota because of its ability to be sorbed (Chapman *et al.*, 1991).

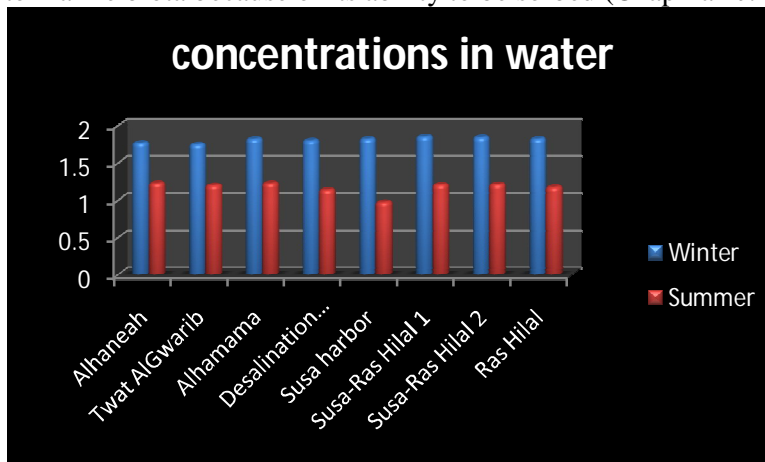


Figure (10): The concentrations of Nickel of water samples during winter and summer seasons.

Copper:

Copper is introduced in to the aquatic environment through a number of natural sources. The main sources of copper in the aquatic environment are:

- Minerals in soil and weathered rock that form the sediments and suspended particles in the water, (Lewis, 1995).
- Extraction of copper from rock into a dissolved state.
- Biological particles, including both living and dead organic material.
- Hydrothermal systems in which heated or chemically altered water are found. This includes volcanic action and thermal vents.
- Input from sediments.
- Anthropogenic inputs - either directly into the water or leached after deposition on land.
- Deposition from the atmosphere – a major source here is anthropogenic. Copper is introduced from all these sources into the marine aquatic environment but not equally in all areas. It exists in water, sediments and organisms (Neal Blossom, 1990).

The high levels of concentration of copper (5.00 ppm) was found in winter season and the minimum of (0.33 ppm) was recorded during summer season, Figure (20). the results also showed that, there is small variations in copper contents of the studied area. Copper is also removed over time from the oceans water via the formation of sediments. This can occur via biological or physiochemical processes or by particulate settling. Biological activity can remove copper when organisms utilize copper and excrete that copper in fecal material, or when organisms die or molt and these biogenic materials become sediment (Martin and Windom, 1991).

The statistical analysis of correlation coefficient of copper with other parameters showed a positive behavior with other heavy metals (Fe and Ni). A positive correlation was represented with pH ($r = 0.104$ and $r = 0.860$) and negative correlation with dissolved oxygen ($r = -0.100$ and $r = 0.312$) to point the latter is of minor importance to be involved in such behavior with the possible existence of $\text{Cu}(\text{OH})_2$ (Jakson *et al.*, 2003).

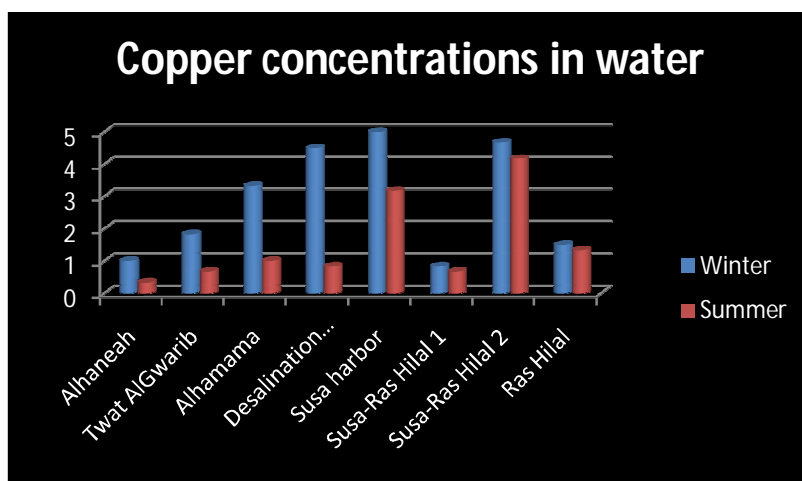


Figure (11): The concentrations of copper of water samples during winter and summer seasons.

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