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Level of Total Petroleum Hydrocarbons in the Water and Sediments of Abu- Zariq Marsh, Thi- Qar Governorate - Southern Iraq

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Abstract: The current study was conducted during the summer and winter of 2021 to study the concentrations of total hydrocarbons in the water and sediments of three stations in Abu- Zariq, Marsh one of the marshes of southern Iraq in Thi- Qar Governorate, Some environmental characteristics were also measured by estimating the organic carbon content in the sediments, air and water temperature, pH, salinity, dissolved oxygen, and biological oxygen requirement. The first station of the summer season recorded the lowest concentration of total petroleum hydrocarbons in relation to water and sediment, and their rates reached (2.73) µg/l for water and(3.87) µg/g dry weight for sediment. The highest concentration of total petroleum hydrocarbons in the water and sediments at the second station was in the winter, and it reached 6.01 µg/l for water and 7.03 m µg/g dry weight for sediments. It was noted from the results that there was a seasonal and locational variation in the concentrations of total petroleum hydrocarbons in the waters and sediments of Marsh Abu- Zariq. Clearly higher concentrations were recorded in the winter compared to the summer, and the studied area is somewhat unpolluted. As for other physical and chemical measurements of the water, they showed the highest rate of total organic carbon in sediments, 2.1%, in the second station during the winter, the lowest value was 0.41% in the first station during the summer, and the air temperature recorded the lowest value in the winter in the third station, reaching 18°C, and the highest value during the summer in the third station, reaching 49°C. While the water temperature recorded its lowest value in the winter in the third station, which reached 14°C, and the highest value in the summer in the third station, which reached 35°C. The highest pH rate was recorded at 8.55 in the second station during the winter, while its lowest value reached 7.13 in the first station during summer season The highest rate of salinity was 2.78 ppm in the second station during the winter, while the lowest rate was 0.56 ppm in the third station during the summer. The highest rate of Dissolved Oxygen(DO) was recorded at 9.1 mg/L in the first station during the winter, while its lowest rate was 6.85 mg /L in the second station during the summer, while the highest rate of Biological Oxygen Demand(BOD) reached 4.99 mg/L in the second station during the winter, while its lowest rate reached 2.59 mg/L in the third station during the summer.

Keywords: Abu- Zariq Marsh- Total petroleum hydrocarbons - Water - Sediments - Thi –Qar.

Introduction

The marshes of southern Iraq are among the oldest and largest marshes in the world, the Middle East, and Western Asia. By their nature, they are of economic importance first and environmental importance second and are expressed as (the Gardens of Eden on Earth). The marshes cover areas of Basra and Amara Governorate amounting to 8,635 km2 and are in the shape of a triangle with its vertex down at the city of Basra and its base to the north in the line passing between the city of Amara and Nasiriya. They are shallow bodies of water whose depth ranges between 1-3 m (Al-taie, 2013). The marshes suffered from drying operations through the implementation of many projects and cutting off the water of the Tigris and Euphrates rivers by constructing channels to drain the water out of the marshes, and earth dams were built to prevent the flow of water towards the marshes (Akbar *et al.*, 2005). The drying of 90% of the marshes during the 1980s led to the risk of drought, which exposed the marshes to the deterioration of their environmental, agricultural, fauna and population condition, the departure of rare birds and the creation of major changes in the geography of fish and animal wealth (UNEP, 2001). Iran worked to build a dam on the Karkheh River, which feeds the Aleazim River, in addition to the decline in the tributaries of the Iraqi rivers from the Al-Masharrah and Kahla area, east of Misan, due to preventing the flow of water feeding the Tigris and Euphrates Rivers from Turkish territory (Al- Haidary, 2009). It is not possible for the marshes to return to their previous state in 1973 due to agricultural and population growth and other activities (Al-Marsoumi, 2008), such as pumping oil. The future of these marshes remains dependent on the amount of water available, and this depends on how Iraq deals with dams, Reversed tide, and various other matters such as pollutants, competition for water, and drought (Almaarofi *et al*., 2012). The marshes have a major role in the process of environmental balance in the region, but the drying projects and the continuous decline in the water revenue available to the country have negatively affected their area, the decline in the hydrological characteristics of the marshes, and the high percentage of salts and some chemical elements in them (Safiya Shaker Maatouq, 2015). Pollution is considered one of the most prominent global problems in the modern era that threatens living organisms on the surface of the Earth because of its clear impact on the physical, chemical and biological characteristics. It occurs as a result of the transfer of pollutants from their sources in various quantities, causing health and economic harm to humans and other living organisms (UNEP, 1993), Water is constantly exposed to pollution from various sources, which reduces its suitability for various human uses and negatively affects the aquatic organisms that live in it. Man has realized the truth of this, but he continues with his various activities that cause pollution of water sources located near his population centers, agricultural projects, and industrial facilities, to begin slowly. By harming the planet on which it lives, to the extent that organisms become at high risk levels, sometimes leading them to the point of death (EPA, 1999). There are two types of water pollutants: The first type is point sources, which appear when harmful substances enter directly into the water body, such as pouring oil directly into the ocean water, to kill thousands of water birds, mammals, fish, and other organisms. As for the second type, nonpoint sources, its pollutants are derived from indirect environmental changes, such as pollutants that find their way directly into waterways, such as transferring fertilizers from agricultural lands to rivers through disposal processes (Crance & Masser, 2005). Oil pollution has occupied an important position among the sources of environmental pollution. This importance comes due to the increase in global oil production rates (Elias, 1989) and the study of water resources of all kinds is of interest to researchers because water is one of the strategic resources identified for economic development (Al-Khafaji, 2016) and its seriousness. And the toxicity of this type of pollutant. Therefore, this study was conducted to determine the distribution of total petroleum hydrocarbon concentrations in water and sediments and some physical and chemical characteristics in Abu- Zariq Marsh in the southeast of the city of Nasiriya.

Materials and methods

Description of the study area

The study was conducted on the Abu- Zariq marsh, south-east of the city of Nasiriya, which is located within the administrative boundaries of the districts of Islah, Al-Fahud and Al-Hammar, Figure (1). This marsh is one of the important marshes in the city in southern Iraq. It is located within a balanced environmental region in terms of its uniqueness in terms of its spread and distribution, its distinctive biological character, and the settlement of more than (500) year, It is submerged in water either permanently or seasonally, and is characterized by the growth of reeds, papyrus, grasses and aquatic weeds, as well as animal life represented by fish wealth. It is also distinguished by its low basin shape on the sides of the Tigris and Euphrates rivers, which are bodies of water fed by the Tigris and Euphrates rivers. Samples were collected from the three stations, as shown in Figure (1) and Table (1), and were collected on a monthly basis and expressed in a seasonally manner for the winter and summer of 2021. The sample collector used a Samper Grab Veen Van to collect sediment samples. They were collected in plastic bags to the laboratory, then dried and ground until they were ready for analysis. As for water samples, they were collected in clean, sterile glass bottles, and 50 ml of carbon tetrachloride was added to them per liter of water. Samples for measuring dissolved oxygen were collected in 250 ml Winkler bottles (APHA, 2003).

Table (1) Coordinates of the study site

station	Coordinates
St.1	31.147100 N-46.612474 E
St.2	31.133384 N-46.619875 E
St.3	31.121006 N - 46.625972 E

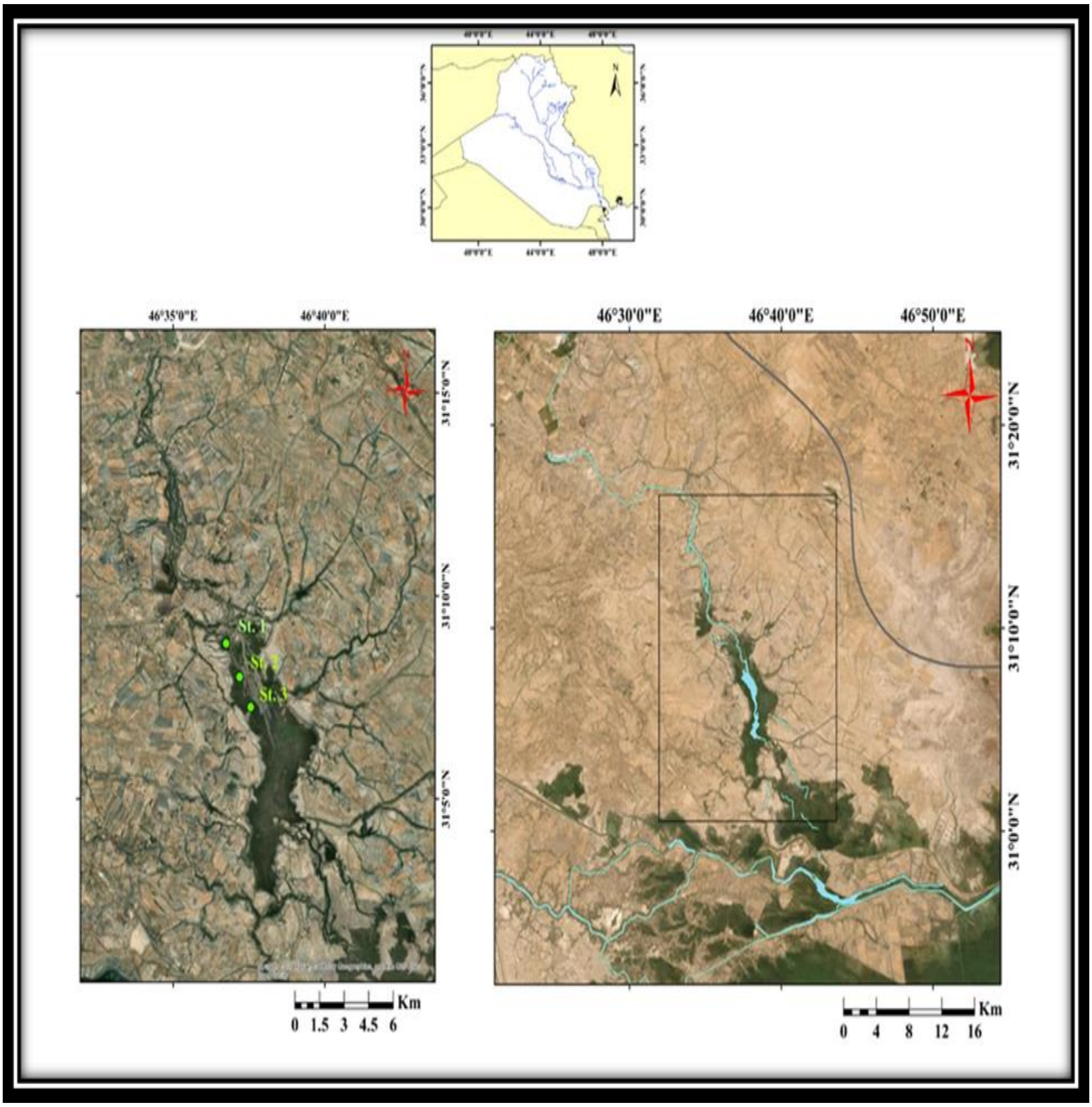

Figure (1) Map of study sites.

Extraction of total petroleum hydrocarbons from water.

The concentrations of total petroleum hydrocarbons in the water of the study stations were measured according to the method used by the United Nations Environment Program (UNEP, 1989), by shaking a 5 liter volumetric sample to which 50 ml of carbon tetrachloride (CCl_4) was added (shaking vigorously for 30 minutes so that the layer (CCl_4) (From mixing with all the water content of the sample, I took a layer (CCl_4) and added another 50 ml to the sample and shook it again. Then it was collected and added to the first part. Then it was passed over a column containing sodium sulphate SO_2Na_4. The extract was collected and carbon tetrachloride was evaporated using a rotary evaporator. 3 ml, then dried, re-dissolved in regular hexane, then measured in a Spectroflurometer.

Extraction of total petroleum hydrocarbons from sediments.

The UNEP (1993) method was followed, where 10 g of dried sediment sample was taken and extracted using a discontinuous soxhlet extraction device using a mixture of methanol and gasoline in a ratio of (1:1) for 24 hours, then the extract was transferred to a separating funnel containing a saturated acidic sodium chloride solution. Shake well, then take the lower layer and extract it three times in a column containing sodium sulphate. The extract was concentrated using a rotary evaporator device under low pressure and at a temperature not exceeding 40°C. The process of saponification was carried out with a solution of saturated sodium chloride and hexane. Then the hexane layer was taken, it was concentrated, and the petroleum hydrocarbons were measured. The kidney using a fluorescence device under the same previous conditions mentioned in the water part.

Estimating the total organic carbon content in sediments (TOC%).

The incineration method was used to measure the total carbon content in the sediments (Weaver & Clements, 1973). Samples were collected from each station, then air-dried and ground using a ceramic mortar. The solid parts were removed, then they were passed through a sieve with holes diameter of 63 micrometers. The samples were stored in marked bags, then weighed. 5 grams of the sample, three replicates for each station, then it was transferred to a ceramic bowl with a specific weight and placed in an electric oven at a temperature of 110°C for three hours and the weight was repeated accurately. The sample was then placed in an incineration oven at a temperature of 550°C for 12 hours and then repeated. Weigh again, and by finding the difference between the initial weight and the final weight, we obtain the amount of carbon in the sediment, and the result is expressed as a percentage relative to the dry weight.

Measure the temperature of air and water.

The air temperature was measured using a field thermometer graduated from 0-100°C. The water temperature was also measured by dipping the thermometer directly in the specified location to take the sample and measuring the temperature after it stabilized.

pH measurement.

The pH of the water was measured directly using a pH-meter after calibrating it with standard buffer solutions with a pH of 9,7,4 (APHA, 2003).

Measurement of salinity.

The salinity of the water was measured in the field using a Salino-meter by dipping the electrode of the device into the water, and the salinity reading was determined by measuring it(ppm).

Dissolved oxygen (DO) measurement.

Oxygen was measured in the field using a dissolved oxygen device (DO-meter) in units (mg/L), and the process was repeated several times to confirm the reading.

Measurement of biological oxygen demand (BOD_5).

Water samples were incubated for five days at a temperature of 20°C, then the amount of remaining dissolved oxygen was measured, and the BOD_5 value was calculated from the equation:

BOD_5 mg/L = DO1 – DO2

DO1 = dissolved oxygen concentration before incubation (mg/L).

DO2 = dissolved oxygen concentration after incubation for 5 days (mg/L). (APHA, 2003).

Statistical analysis.

Statistical analysis was conducted using the Completely Randomized Design (D.R.C.) (Al-Rawi and Khalf allah 1980) to analyze the results and find the least significant difference D.S.L.R., using the ready-made statistical program SPSS.

Results and Discussion.

Total petroleum hydrocarbons in water

The results of the current study showed that the concentrations of total petroleum hydrocarbons in water were highest in the winter and lowest during the summer at all stations, Figure (3-2). The reason for the increase in total concentrations of petroleum hydrocarbons in water during the winter is due to several reasons, the most prominent of which is due to lower temperatures, and thus the evaporation process of these compounds decreases (DouAbul *et al*., 2012). In addition, the effectiveness of microorganisms that break down hydrocarbon compounds decreases with decreasing temperatures (Shamshoom *et al.*, 1990). The decrease in temperature leads to a decrease in the numbers of oil-degrading bacteria (Ali,2012). Hydrocarbon compounds also reach the aquatic environment from the atmosphere with rain as products of the combustion of fuel, oil and its derivatives (Aceves and Grimalt, 1993). The first station recorded the lowest concentrations in the summer, which amounted to 4.02 (μg/L), and the highest concentration recorded in the winter, at the second station, which amounted to 6.01 (μg/L). This indicates the effect of temperature on removing petroleum hydrocarbons from water (Al-Saad, 1983), Most of the hydrocarbon compounds that reach the study area are of biological origin (human origin), and there are few or no oil pollutants resulting from the movement of ships, ships, refineries, and what reaches the waters of the regions from laboratories, factories, industrial facilities, and urban waste, as the high concentrations in the aquatic environments are associated with the presence of oil refineries, high population density, or major ports,(Al-saad *et al*., 2011), Concentrations of petroleum hydrocarbons in water recorded significant differences between seasons for all stations studied at the level of $p < 0.05$.

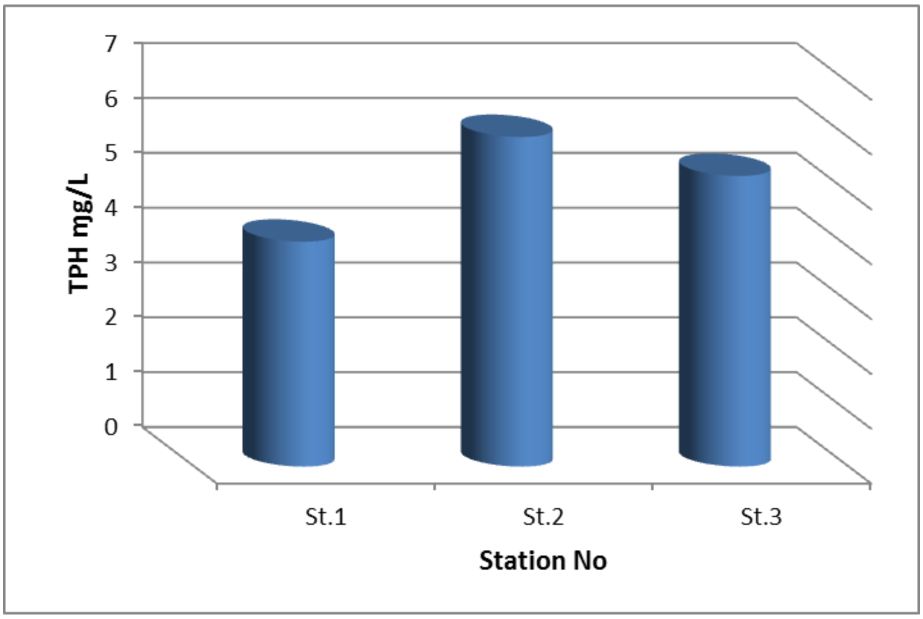

Figure (2) Concentration rates of total petroleum hydrocarbons in water samples (μg/l) during the winter season

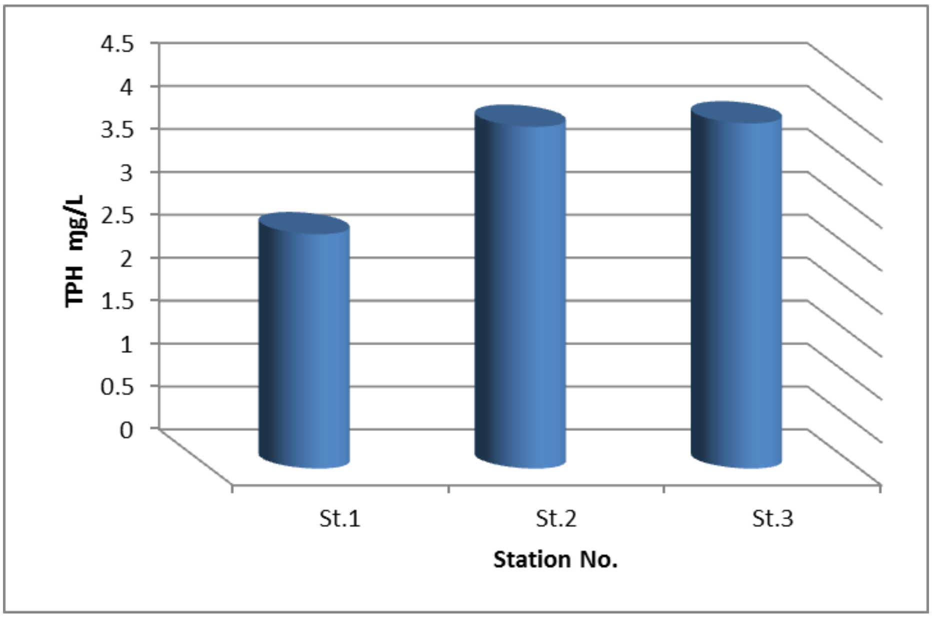

Figure (3) Concentration rates of total petroleum hydrocarbons in water samples (µg/l) during the summer season

Total petroleum hydrocarbons in sediments.

The upper layer of sediment, which is in direct contact with water, is considered the point of attachment of hydrocarbons with the sediment. The upper layer of sediment is exposed to varying degrees of analysis by bacteria. This process, which causes variation in the concentrations of hydrocarbons in the sediment, depends on the availability of oxygen and nutrients, in addition to the presence of some Trace minerals found in oil and needed by microscopic organism(GESAMP,1993), As the total carbon increased and the size of the sediment particles decreased, the area exposed to the deposition of hydrocarbons increased (Nishigima, 2011). The study recorded the highest concentrations in the second station during the winter season, reaching 7.03(µg/g dry weight) Figure (4-5) and the lowest in The first station in summer (3.35 µg/g dry weight), and this is confirmed by the positive significant correlation between the total carbon content and the size of sediment grains with the concentration of hydrocarbons. The study recorded significant differences between the seasons for all stations studied at the level of $p<0.05$.

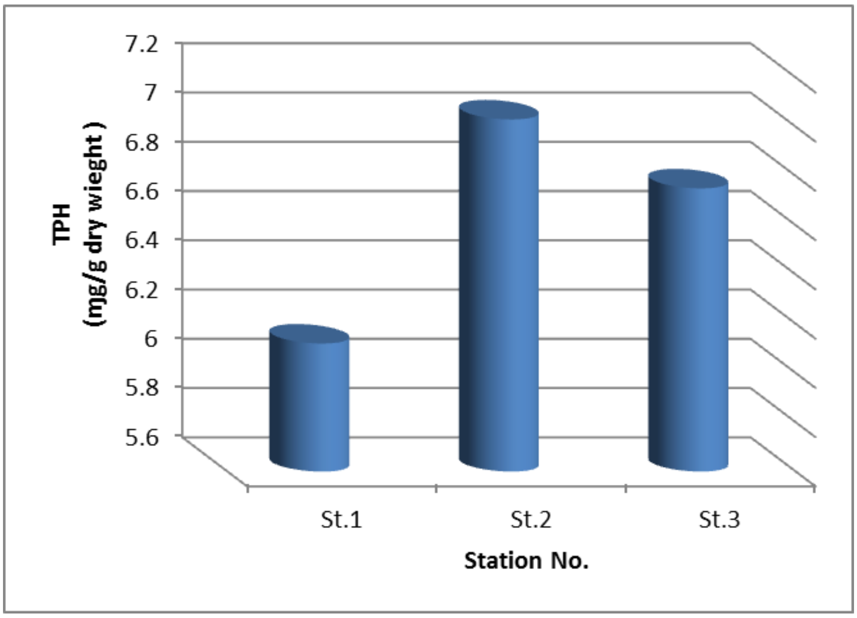

Figure (4) Concentration rates of total petroleum hydrocarbons in sediment samples (µg/g) dry weight during the winter season.

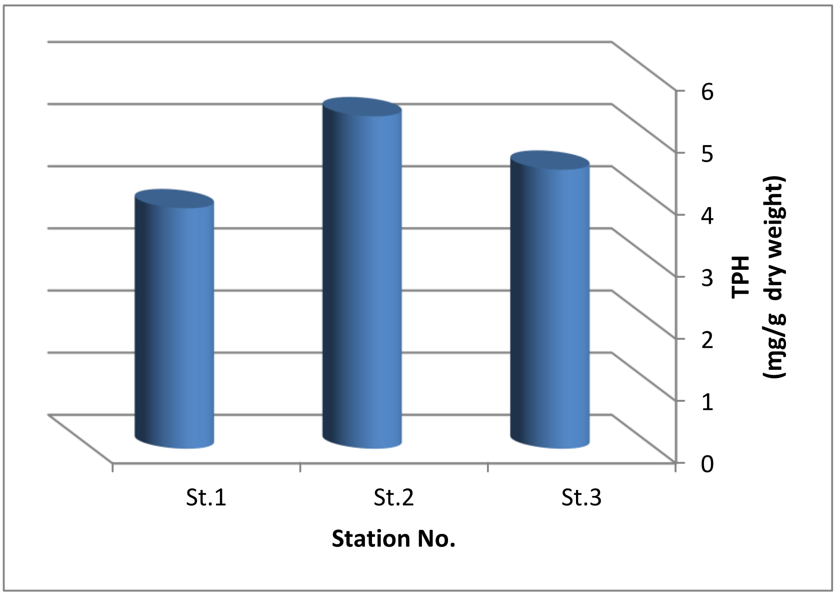

Figure (5) Concentration rates of total petroleum hydrocarbons in sediment samples (µg/g) dry weight during the summer season.

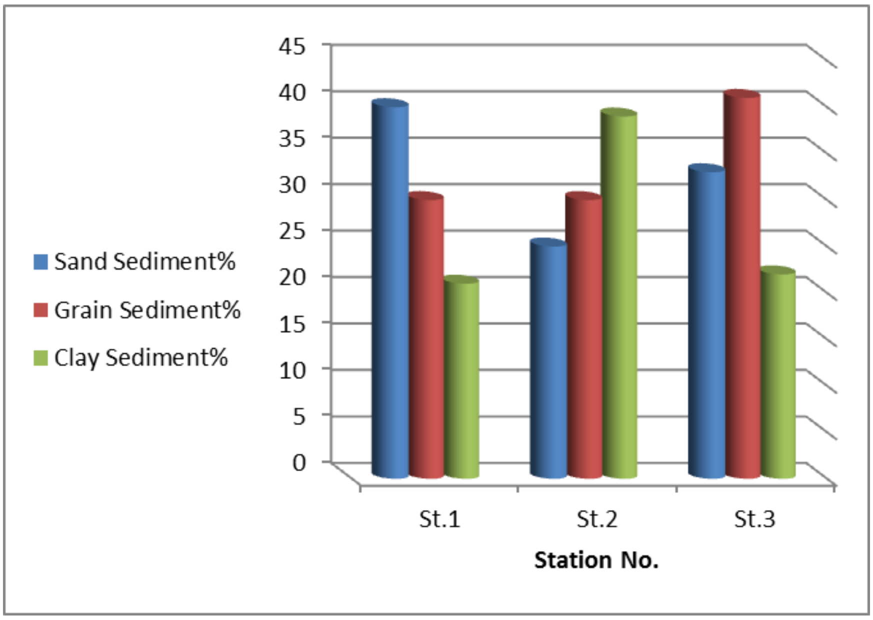

Figure (6) Percentage rates of sediment texture of the Abu- Zariq marsh during the study period

Total organic carbon content of sediments (TOC%)

The highest values of total carbon content were recorded in the second station during the winter, reaching (2.1%), while the lowest values were in the first station and during the summer, reaching (0.41%) (Figure 7-8). The results of the statistical analysis ($p = 0.05$) showed the presence of differences. Significant between stations and seasons, and a positive correlation was observed between total organic carbon and vital oxygen requirement ($r = 0.73$)

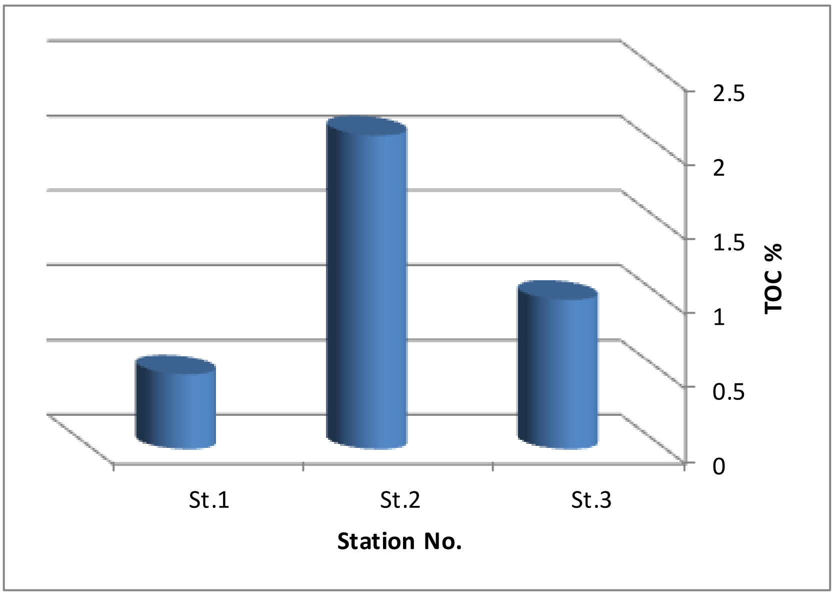

Figure (7) Total organic carbon percentage rates (TOC%) in sediment samples during the winter season

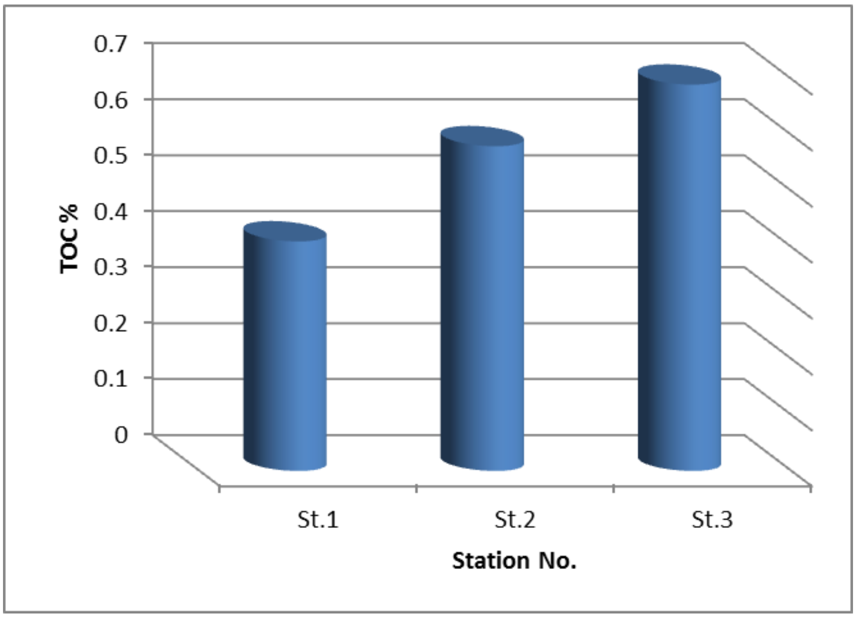

Figure (8) Total organic carbon percentage rates(TOC%) in sediment samples during the summer season

Air and water temperature

All physical and chemical processes and transformations are affected in one way or another by temperature, and all the characteristics studied here are directly affected by temperature change, while temperature, as is known, is affected by some climatic and geographical factors such as atmospheric pressure, winds, and distance from the equator Measuring temperature is one of the important measures required to give an idea about the self-purification of rivers and control of treatment, and it is one of the most influential environmental factors on the growth and survival of microorganisms in the water (Madigan *et al.*, 2000) Temperature affects the dissolution of oxygen and carbon dioxide in water, and affects the taste of water through its effect on organic components and organic pollutants (WHO, 2000). The results indicated that there is a direct relationship between the temperature of water and air, as the former tends to follow seasonal changes in Air temperature Which is due to the angle of incidence of sunlight on the Earth (Al-Saadi, 2006). In the current study, the highest air temperature was during the summer in the third station (49C°) and the lowest temperature was during the winter in the first station and reached (18C°), While the water temperature was its highest value during the summer in the third station and reached 35 °C, while the water temperature was its lowest value during the winter in both the first and second stations and reached 13.5 °C. Field measurements of air temperature and water temperature, which were measured at a depth of 30 cm from the water surface, showed clear seasonal changes, while these changes were slight between stations (Figure 9-10-11-12)The results of the statistical analysis (P<0.05) showed the presence Significant differences between the summer and winter seasons

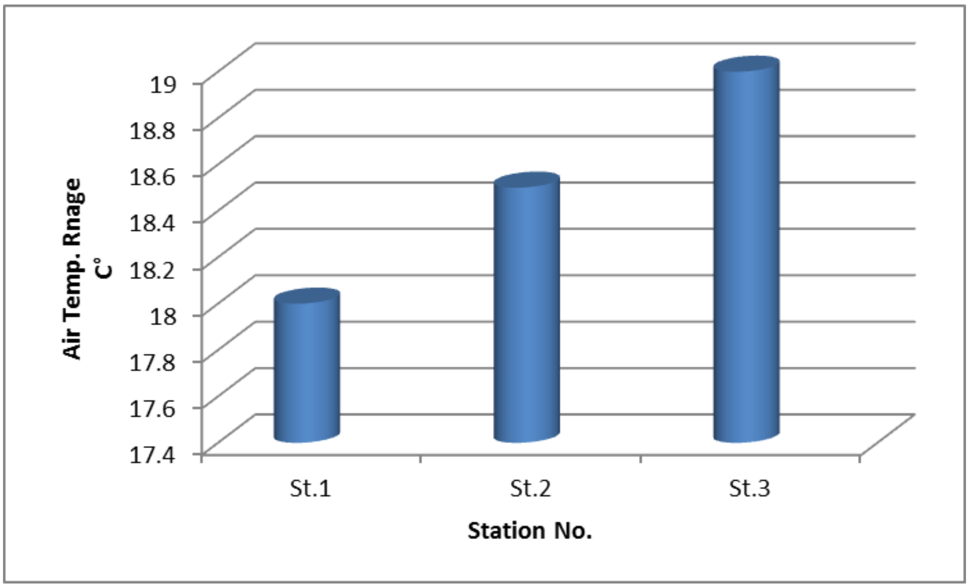

Figure (9) Air temperature rates (C°) between stations in winter

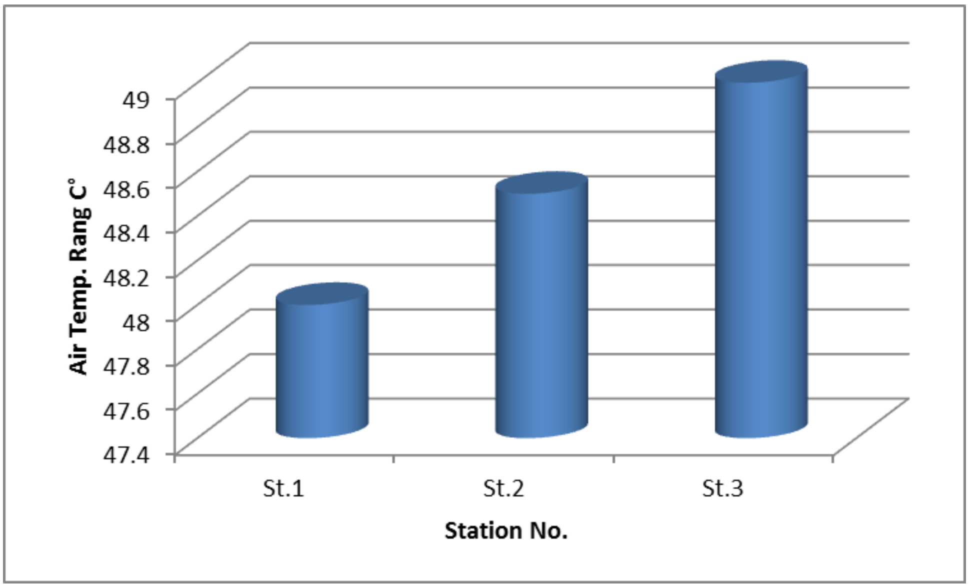

Figure (10) Air temperature rates (C°) between stations in summer.

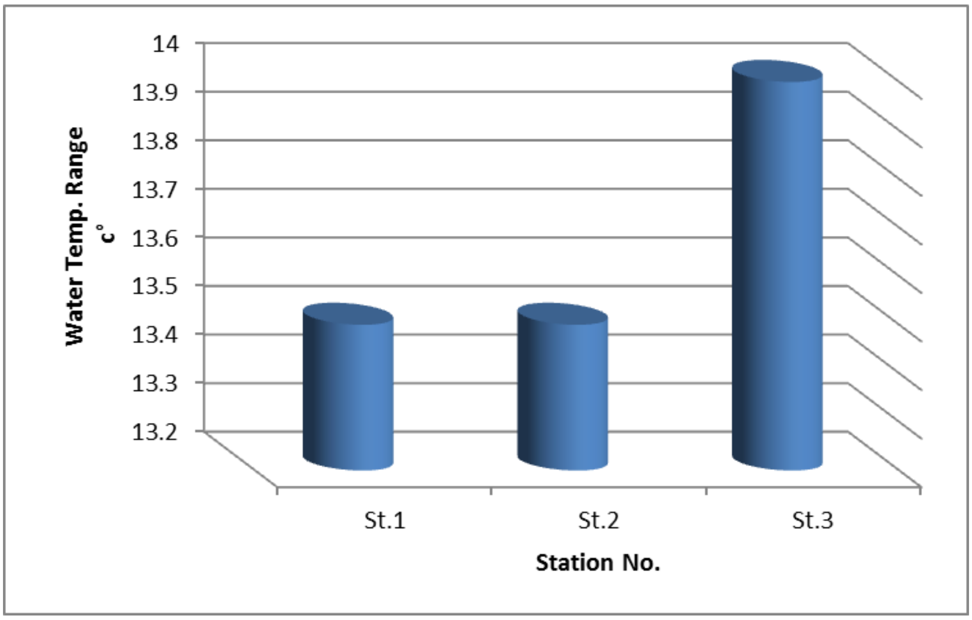

Figure (11) water temperatures rates (C°) between stations in the winter.

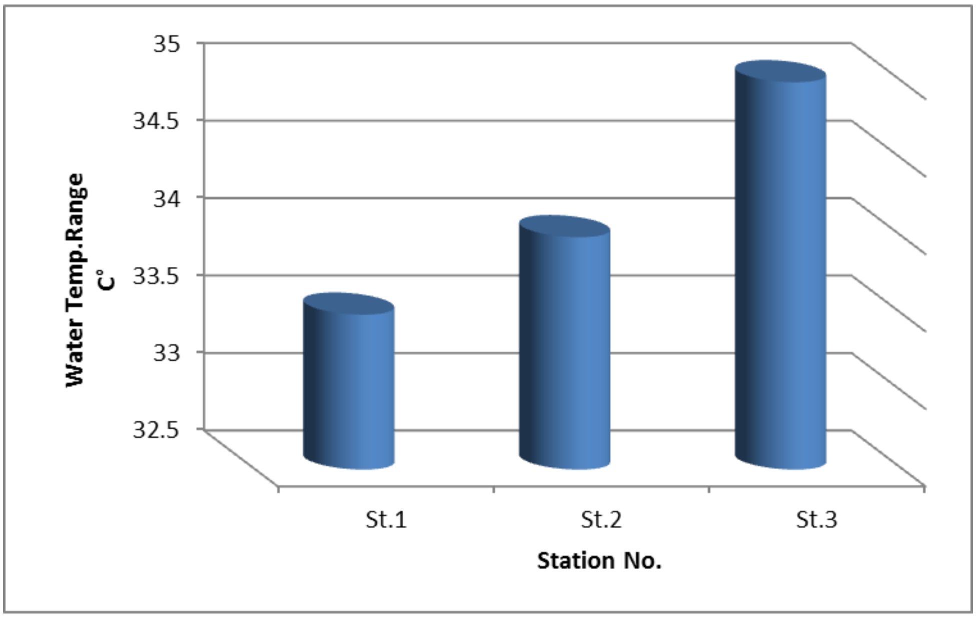

Figure (12) water temperatures rates (C°) between stations in the summer.

pH indicator

The pH values ranged between the highest value during the winter, reaching 8.55 in the second station, and the lowest value, 7.13, during the summer in the second station. It was noted from the results of this study (Figure 13-14) that most of the water samples studied are of Alkalinity nature, which is a general characteristic of Iraqi water (Hassan, 2004; Talling, 1980) The basicity of water indicates abundant primary productivity (Al-Moussawi and Hussein, 1994). The results of the current study agreed with previous studies regarding pH values in Iraqi internal waters, including studies of: (Tahir *et al*.,2008; Mahmood ,2008 ; Kazar ,2009). The pH value of water is nothing but the result of many chemical and biological reactions that take place in it, and it is one of the factors affecting the bacterial presence in water (Geldreich, 1996). The pH value plays a major role in the aquatic environment, and its amount depends on the activity of microorganisms and algae in a way. especially as algae consume carbon dioxide for the purpose of carrying out the process of photosynthesis, the pH value rises during the day, and the decomposer microorganisms and the rest of the organisms consume oxygen and release carbon dioxide in the process of respiration, so the pH value decreases, and therefore the pH value depends on the balance between the two processes.

(Photosynthesis and respiration), in addition to other chemical reactions that occur in the aquatic environment, such as oxidation and reduction reactions. (WHO, 2004).

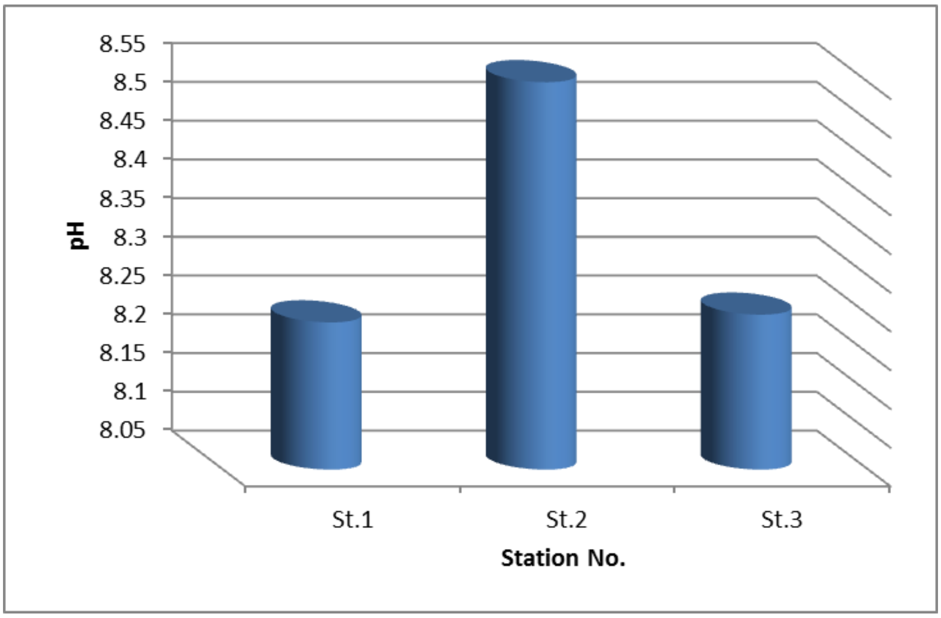

Figure (13) pH values for all stations during the winter season

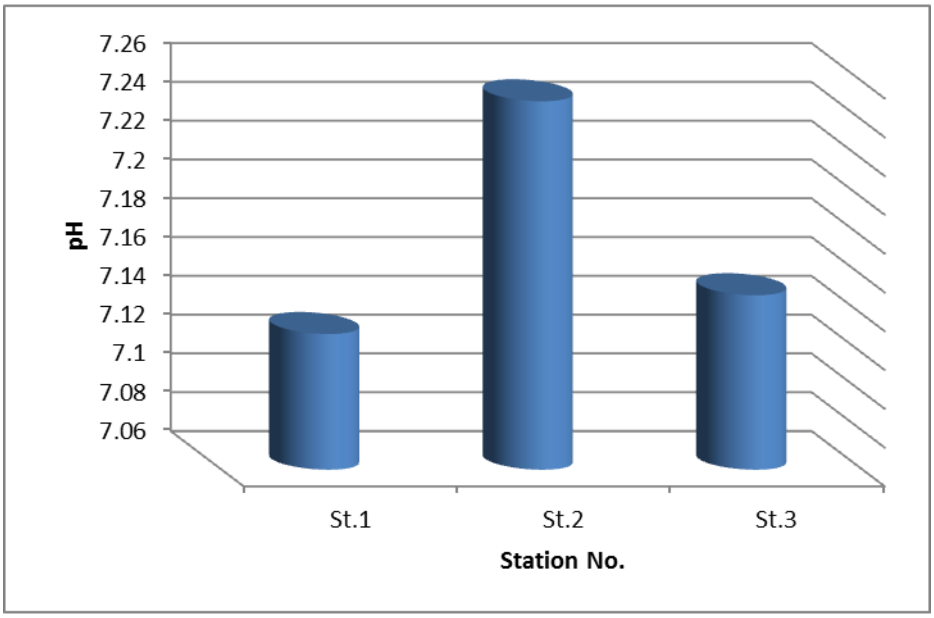

Figure (13) pH values for all stations during the summer season

Salinity

The results of the current study showed that salinity values ranged between (0.56- 2.78 ppm) at the third and second station, respectively, Figure (15-16). High salinity was observed in the winter due to low water levels, and due to rains that wash the soil and wash it into water. The marsh, while there was a decrease in its value during the summer due to the rise in marsh levels during this season due to the increase in water in the Tigris River. Dissolved salt values are usually determined by measuring electrical conductivity because it depends on the concentration of dissolved ions in the model, which in turn depends on temperature. Increases and decreases in salinity affect the physiological actions of aquatic organisms, regardless of the extent of their influence, and salinity is not considered a major polluting factor in inland rivers (Hawakes, 1982). Iraqi waters are generally considered oligohaline waters, as they fall between 0.5 and 5 ppm.

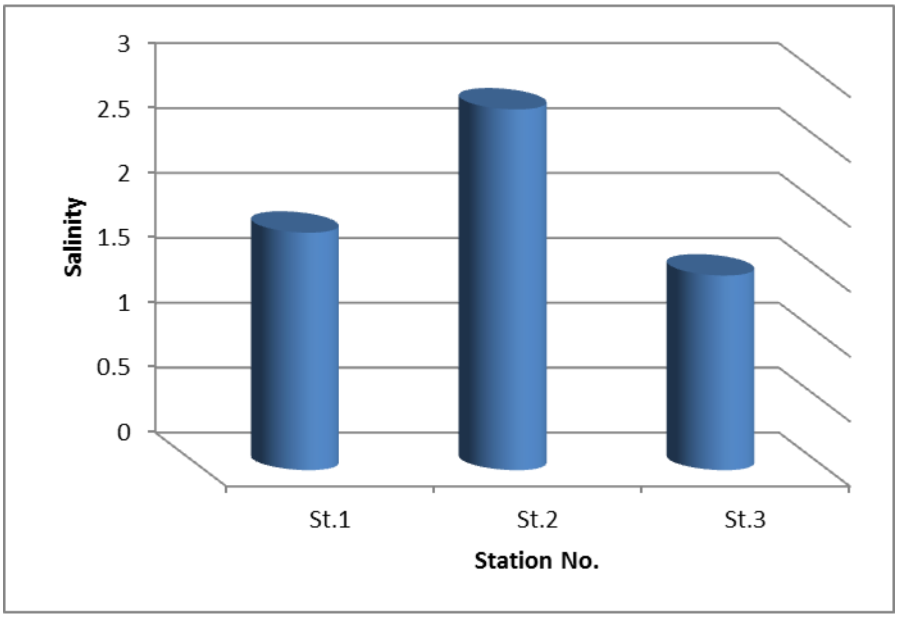

Figure (15): Water salinity rate (ppm) for all stations during the winter

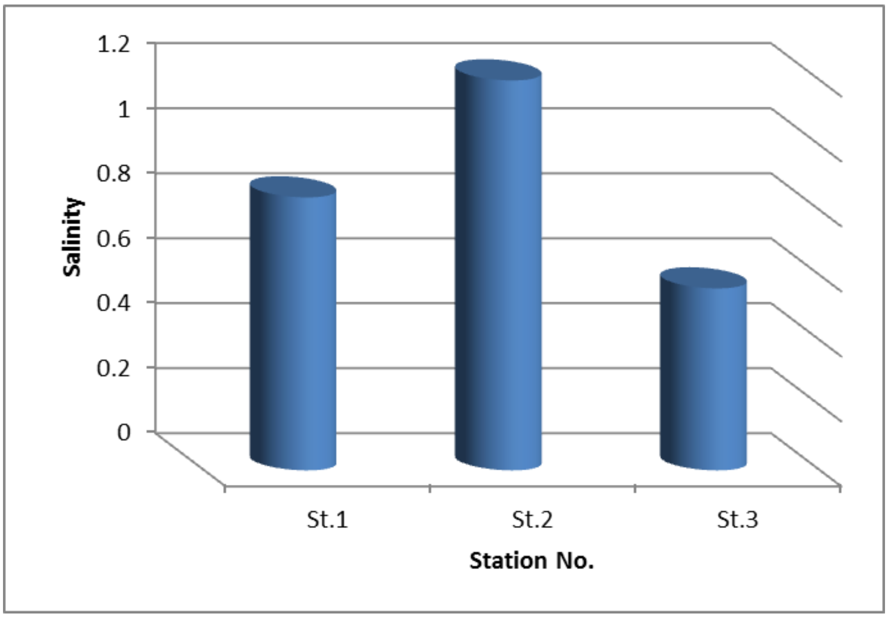

Figure (15): Water salinity rate (ppm) for all stations during the summer

Dissolved oxygen (DO)

Dissolved oxygen in water is one of the most important factors that affect water quality and its effect is essential in the natural balance. A significant deficiency of this factor has a harmful effect on living organisms and is considered an indicator of organic pollution. It is also essential for the respiration of aquatic organisms to release energy to support their growth and sustain their life. There are several Factors that affect the concentration of dissolved oxygen in water, including the process of photosynthesis and respiration of aquatic organisms(Al-Kinzawi, 2007; Mermillod-Blondin *et al.*, 2003) and high temperatures lead to a decrease in the solubility of oxygen in water (Mahmood, 2008)in addition, decomposer organisms use dissolved oxygen during the process of breaking down organic materials (Anber, 1984). The process of photosynthesis carried out by aquatic plants and plankton leads to the production of oxygen, and thus there is a continuous compensation for the deficiency in dissolved oxygen. When comparing the results of the concentrations of dissolved oxygen in the water for the three stations (Figure 17-18), which were the highest during the winter and amounted to 9.1 mg/l at the first station and the lowest during the summer and amounted to 6.85 mg/l at the second station with the parameters of the river maintenance system from pollution, which determined the concentration by more than 5 mg/l for dissolved oxygen in water. We find that the results of the current study are higher with these parameters, and this may be due to the continuous compensation of oxygen in abundance before Plant organisms that are characterized by their abundance in the study area, in addition to the good ventilation that occurs in the marshes as they are large areas that accommodate large amounts of oxygen, which fills the deficiency that occurs in the consumption of organisms.

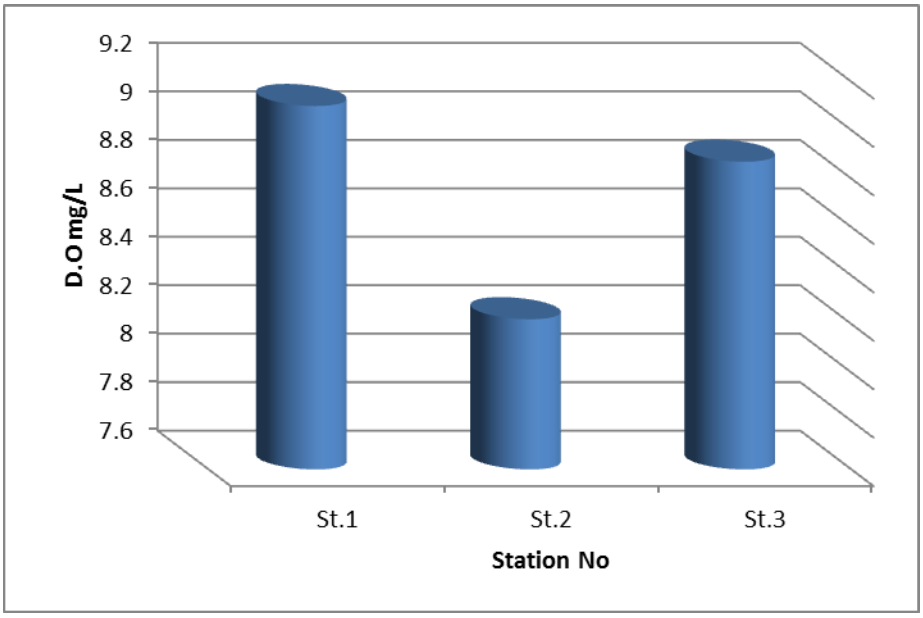

Figure (17) Dissolved oxygen values (mg/l) for all stations during the winter

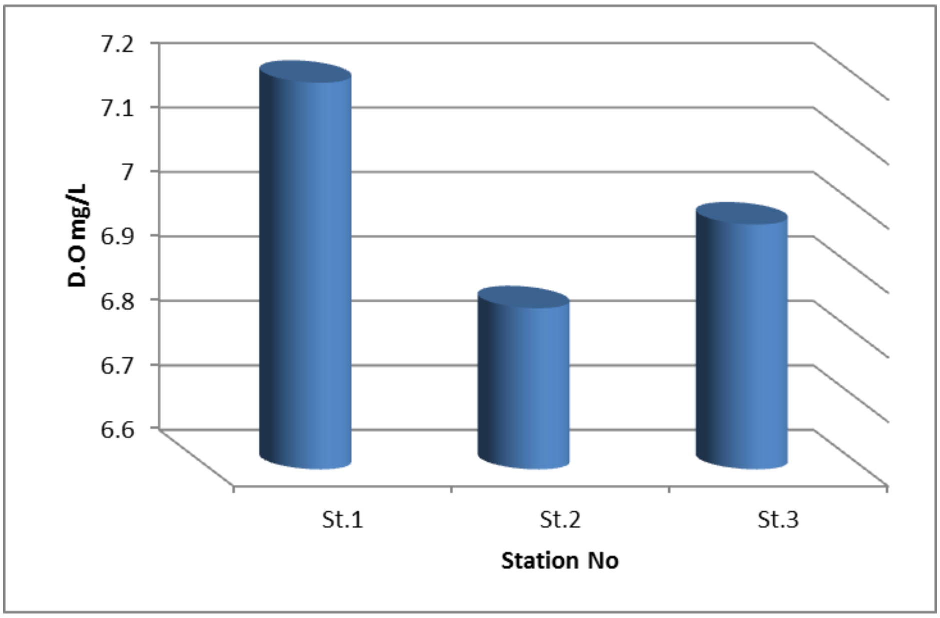

Figure (18)Dissolved oxygen values (mg/l) for all stations during the summer

Biological Oxygen Demand (BOD_5)

It was noted from the results (Figure 19-20) that the highest BOD_5 values were in the second station, which amounted to 4.99 mg/l during the winter. This means that the aforementioned station is more polluted with microscopic organisms that consume dissolved oxygen in the process of decomposing organic matter, while the lowest BOD_5 values were recorded in the third station, which amounted to 2.59 mg/l during the summer. This station is less polluted than the first and second stations. The values of the biological Oxygen Demand (BOD_5) express the amount of oxygen needed by microorganisms for the purpose of decomposing organic materials present in the water. If DO is the oxygen balance, then the BOD_5 is the demand for this balance. The lower the BOD_5 values, the better the water quality, and vice versa. Measuring the biological requirement for oxygen is a widespread means of determining water quality in terms of organic pollution, especially in rivers and streams. BOD_5 values depend on the proportions of oxygen available in the water, which are affected by contact with the air (aeration), the process of photosynthesis, respiration, and organic oxidation, and the process of photosynthesis of plankton. Vegetation increases the amount of dissolved oxygen if the river is poorly polluted, while the process of respiration and organic oxidation consumes oxygen and reduces its percentage in the water, especially if these two processes have high levels (Al-Rubaie, 2002).

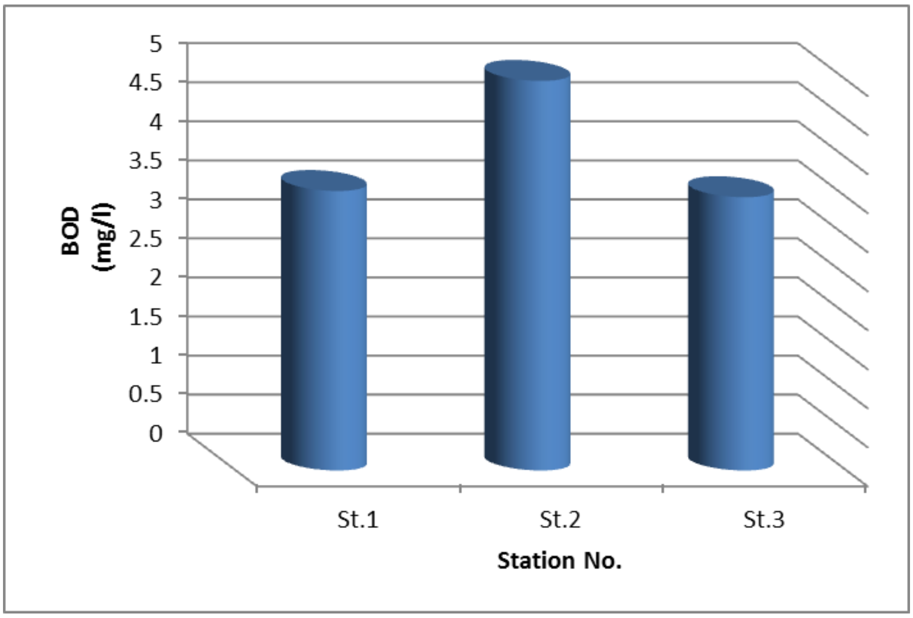

Figure (19) Biological oxygen demand rate (mg/l) for all stations during the winter

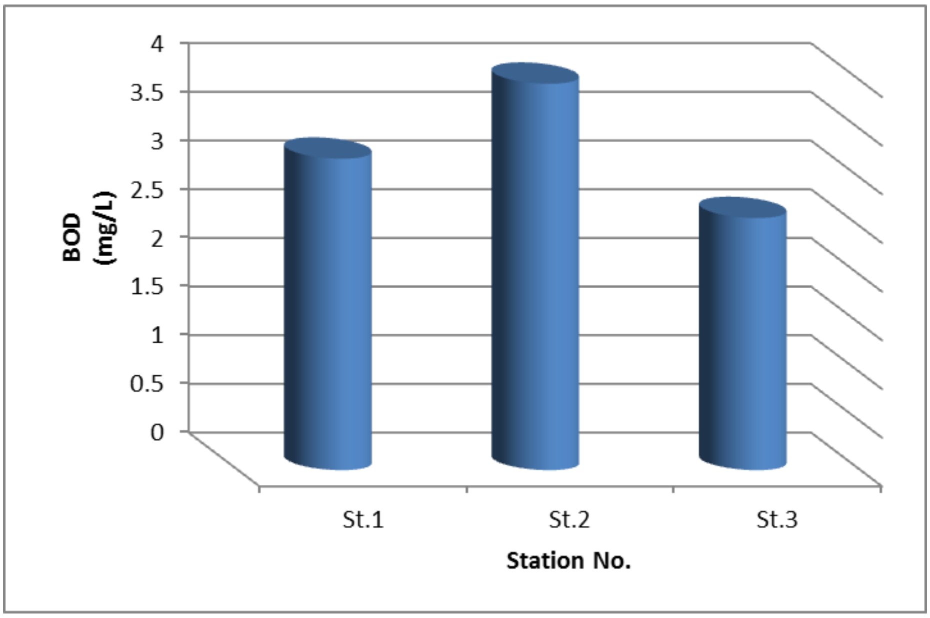

Figure (20) Biological oxygen demand rate (mg/l) for all stations during the summer

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