



## Seasonal Variation of Phytoplankton Biomass as Chlorophyll *a* and its Relation to Iron and Manganese in Ibn-Najem Marsh, Iraq

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### ABSTRACT

*Ibn-Najem marsh is one of the Iraqi Marshlands that occupies around 90 Km<sup>2</sup> distributed in three provinces. However, the majority of the marsh (75%) belongs to An-Najaf province, the rest of which is shared by Babylon and Al-Qadisiyah provinces'. The concentration of iron, manganese and phytoplankton biomass as chlorophyll were measured in winter, spring, summer, and autumn in 2009 in water and sediments of Ibn-Najem marsh. Phytoplankton were collected from seven sampling stations including Al-Haidarey, Abu Garab, Um Oyon, Al-Tail, Al-Gazali, Abu-Hallan and Al-Hamam respectively. Iron and Manganese ions were measured in water and sediments. The average rates of phytoplankton biomass were high in station 3 in spring with a value of 0.49 µg/l as the results indicated. The minimum value was found in station 1 in winter with a value of 0.03 µg/l. The concentration of manganese was extremely high in the sediments, while the concentration of iron was low in winter and autumn. Iron decreased in the sediments in winter, while in water, it recorded minimum values for iron which was measured in summer. The maximum values of iron and manganese were noticed in autumn. The minimum concentration of manganese was in spring. The concentration of iron and manganese elements exceeded than Iraqi limitations for freshwater quality.*

**Key word:** Chlorophyll, phytoplankton, Ibn-Najem, Marsh, Biomass.

### INTRODUCTION

The Iraqi marshes are freshwater wetlands of unique ecosystem in the Middle East and Western Asia (UNEP,2001). A major haven of regional and global biodiversity, the marshes provide habitat for significant populations of wildlife species (ITAP,2003).

Ibn-Najem Marsh is one of the middle Iraqi Marshlands, in which little research has been done. This is because of the extensive studies by scientists compared with the southern marshes. However a study on parasite attached to fish was done by (Al-Azebawe,2010), (Al-Haidarey *et al* 2012), and (Al-Zurfi,2010) regarding the aquatic plants environment. Phytoplankton is among the most significant organisms in the aquatic ecosystem. Its primary producer, is of a significant task in the circulation of material and flow of energy in the aquatic ecosystem (Ariyadejet *et al.*, 2008). Phytoplankton provides a invertebrates nutrition source and tiny fish in wetlands (Browder *et al.*,1994).

Investigation of phytoplankton biomass can be performed in many ways; one of them is by measuring chlorophyll *a* which is the fastest measuring method in chemistry (Vonshak, 1986). In an aquatic environment chlorophyll *a* is an index that is accepted for phytoplankton plenty and main producer's population (Camdevy'ren *et al.*,2005). Estimation for algal weight and volume is estimated by chlorophyll, and performs as an experiential connection between other biological phenomena and nutrient concentration in aquatic ecosystems (Julie and Michael, 2007).

Iron is a catalyst to chlorophyll biosynthesis and acts as an oxygen carrier that aids in respiratory enzyme systems, where manganese activates several important metabolic reactions, aids in chlorophyll synthesis, photosynthesis, accelerates germination and maturity and increases the availability of P and Ca (Monreal *et al.*, 2015). High dissolved concentrations of iron and manganese do not have any serious harm to human or animal health (Ebermann *et al.*, 2010), but these can cause aesthetic problems (Tredoux *et al.*, 2004).

Iron is considered the most factor of limitation to the growth of phytoplankton and acts as the biggest effect on the diversity of algal species. It also acts as a limiting ( $N_2$ ) fixation rates, and so is significant in scheming fixed nitrogen in ocean inventories (Sunda, 2012). Many other heavy metal nutrients (manganese, cobalt, copper, and zinc) may have an impact on organizing the species formation in communities of phytoplankton due to vast dissimilarities in cellular heavy metal concentrations and requirements of growth among species (Brand *et al.*, 1983; Crawford *et al.*, 2003; Ho *et al.*, 2003).

Manganese often exists in seawater in three states of oxidation namely  $Mn(II)$ ,  $Mn(III)$ , and  $Mn(IV)$ . Oxides of insoluble  $Mn(III)$  and  $Mn(IV)$  are the stable redox forms of this metal in oxygenated seawater, although  $Mn(III)$  occurs as soluble chelates with organic ligands in some environments (e.g., hypoxic waters; Trouwborst *et al.*, 2006). Enzymes are within the outer polysaccharide sheath of particular bacteria, catalyze  $Mn(II)$  oxidation to  $Mn(IV)$  oxides (Tebo *et al.*, 2004; Anderson *et al.*, 2009)

Recently a few papers on phytoplankton and primary production in Iraq marshes were published. Many environmental factors were affected by the distribution, diversity and abundance of phytoplankton algae on the hydrophytes in marshes, such as light, temperature, type and growth phase of host plant, depth, nutrients, etc. (Limpens *et al.*, 2003; Michael *et al.*, 2008).

The main purposes of this research are:

1. To evaluate phytoplankton biomass as chlorophyll a in Ibn-Najem Marsh.
2. To estimate the concentration of iron and manganese in water (dissolved) and sediments in Ibn-Najem Marsh.
3. To examine the relations between chlorophyll (a), iron and manganese in the Ibn-Najem Marsh.

## EXPERIMENTAL SECTION

Seven sites were chosen for investigation in this study :

- 1- Station one ( $A_1$ ), beside Al-Jomhory village that represents the area with water iterance from Al-Haidarey.
- 2- Station two ( $A_2$ ) in AbuGarab Village located at about 4km south of  $A_1$ .
- 3- Station three ( $A_3$ ) in Um Oyon Village (5 km from  $A_2$ ).
- 4- Station four ( $A_4$ ) in Al-Tail Village (2 km from  $A_3$ ).
- 5- Station five ( $A_5$ ) in Al-Gazali Village (2km from  $A_4$ ).
- 6- Station six ( $A_6$ ) in Abu-Hallan Village (4 km from  $A_5$ ).
- 7- Station seven ( $A_7$ ) in Al-Hamam Village (6km from  $A_6$ ). (figure 1)

The samples (water and sediment) were collected monthly for the period starting from January to December 2009 from the studied area in IbnNajem marsh. Water samples from each station were collected using polyethylene bottles with 1 liter capacity. The sediment samples were collected using grab sampler, and then placed in plastic bags, then all samples (water and sediment) preserved in a cooling box until reaching the laboratory. In the laboratory, 1 liter of water from each station was filtered using filter paper type (0.45) $\mu m$  in size. Heavy metals in the dissolved phase were extracted according to the procedure described by (Riley and Taylor, 1968; WASC, 2002). Sediment samples extracted were executed according to the method described by (ICARDA, 1996) and measured using an atomic absorption spectrophotometer. Concentrations of chlorophyll a were evaluated and then employed as an assessment of the phytoplanktonbiomass. The researcher took specimens with water rater sampler of 1 liter that were collected from water surface of 15-25 cm depth and filtered by a glass fiber filter (GF/C) with pump. The papers that were filtered were foil wrapped and sent to the laboratory in a cold container. Then the researcher measured chlorophyll a concentrations after extraction with 90% acetone using spectrophotometric method according to (Parson *et al.*, 1984).

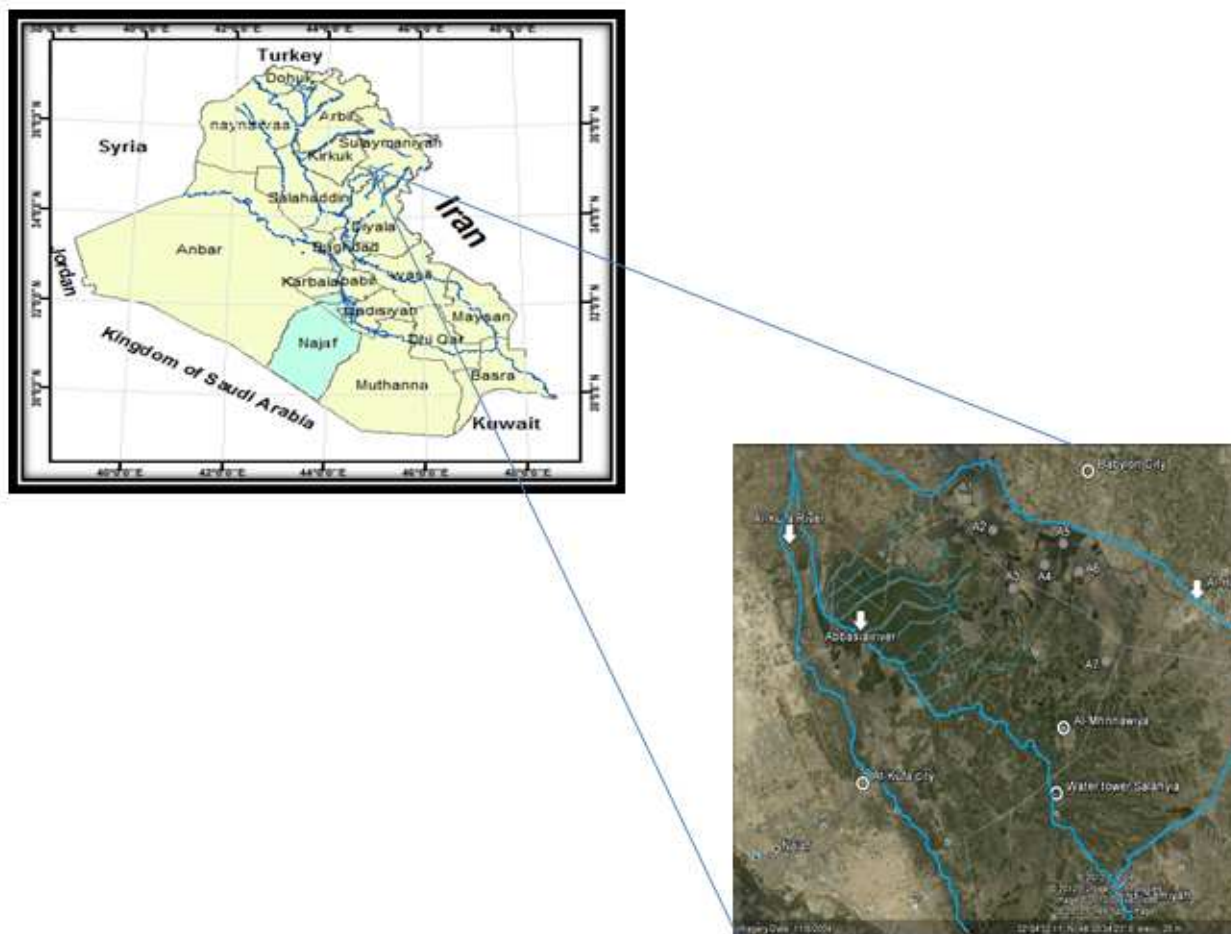


Fig 1 : The study stations as shown by Google earth (A1: N 32° 11' 34.5" E 44° 29' 40.7" , A2: N 32° 10' 25.9" E 44° 30' 47.9" , A3: N 32° 08' 21.2" E 44° 31' 32.1" , A4: N 32° 09' 05.0" E 44° 33' 05.7" , A5: N 32° 09' 45.8" E 44° 34' 01.4" , A6: N 32° 08' 44.9" E 44° 34' 39.8" , A7: N 32° 05' 33.6" E 44° 35' 38.9")

#### Statistical Analysis:

To identify the difference of the phytoplankton biomass level in every station, ANOVA statistical analysis was used. Correlation analysis was conducted by Microsoft Excel to identify the level of correlation between phytoplankton biomass as chlorophyll a and iron and manganese ions (Al- Rawi and Khalaf Allah1980).

## RESULTS AND DISCUSSION

### 4:1 Iron

In the present study the mean of iron concentration in water was ranged between 70 to 640  $\mu\text{g/L}$  (Table 1). It is clear that the concentration of the total iron increased gradually in December to a level that exceeding 640  $\mu\text{g/L}$ . These values were decreased in August. Minimum values were measured in the summer and maximum values were measured in autumn (figure 2). The results demonstrated that there were significant differences in the concentration of iron among seasons and this may be due to the heterogeneity of climatic factors, the physical and chemical properties of water, and water levels fluctuation. The oxidation of iron was slow in the when the organic matter is there which creates complexes. Chelation can take place inhibiting the oxidation of iron and manganese severely. (Filtronics, 1993). The maximum concentration of the Fe was in station (5), while the minimum values of the Fe were in the station (1) (figure 3). The mean concentrations of the iron elements in the dried stations were more than that in the wet stations. Heavy metals in Mesopotamian Marshes are readily affected by the environment issues such as runoff of surface, groundwater, dissolution from sediment, deposition from the atmosphere and anthropogenic pollutants (Al-Saad *et al.*, 2008).

The total iron of the sediments ranged from 190 to 720  $\mu\text{g.kg}^{-1}$ . The latter values were decreased in December. The minimum values were measured in the winter and maximum values were measured in the summer (figure 4). Rapid reductive dissolution of Fe-oxides was localized in these sediments, as well as the associated release of P might still enable precipitation of reduced Fe phosphates (Jilbert, 2013). This resulted in an increase in the concentration of iron in the sediment in summer and a decrease in winter after the fall turnover. The minimum value of Fe was in

station (4) , while the maximum values of Fe was in station (7) (figure 5). One of the complex phenomena is the circulation of metals in the sediment. Pollutants from the water column are removed by the metals adsorption suspended matter and subsequent sedimentation,. Sediment metals enrichment may cause their transport to the ground water release of compiled metals to water column and consequent accumulation by aquatic organisms (Abdelmoneim *et al.*, 1994).

The statistical analysis (ANOVA at F: 0.05) showed that there was a significant difference among stations for Fe metal during the period of study that was corresponded with Hassan (2007) in Shatt Al-Arab River and Al-Haidarey(2009)in Mesopotamian Marshes .

#### 4:2 Manganese:

The range of Mn values was found to be between 90 and 430  $\mu\text{g l}^{-1}$  (Table 1). The Mn value increased in December and decreased in March. The maximum concentration of manganese was recorded in autumn whereas the minimum concentration was measured in spring (figure 2).The uptake of dissolved chemicals and nutrients occurs during the growth season (spring) leading to decreased concentrations of manganese ( Al-Kinzawi, 2009). By contrast, in the Autumn the concentrations of manganese were increased due to the decrease in the productivity (living uptake) processes, and the majority of the manganese were increased in the Autumn possibly due to its reduction level under anoxic condition (Park *et al.*, 2008),these results agreed with the previous published studies (Al-Tae, 1999;Vymazal, 2008 ; and Mahmood, 2008).Figure 3 showed that the minimum value of Mn was seen in station 4 (115  $\mu\text{g L}^{-1}$ )and maximum value was in station 7 ( 279  $\mu\text{g L}^{-1}$ ). This is could be attributed to the lack of water level and an increase of the evaporation rate in Autumn, which led to this concentration level of salts in the seventh station.

Manganese concentrations in sediments were relatively high and exhibited a slight seasonal fluctuation, ranging between 120 to 2000  $\mu\text{g g}^{-1}$ (Table 1). The minimum values were measured in winter while maximum values were measured in summer (figure 4). The statistical analysis (ANOVA at F: 0.05) showed that there were significant differences among stations (figure 5). The sedimentations (traps by an aquatic macrophytes or physically sedimentation) and consumptions (by aquatic plants, phytoplankton, and other aquatic organisms) of heavy metals lead to sinking of some amounts of elements while the others will transform out of the Marsh. Ibn Najem Marsh may be the key source of some elements (i.e.Fe, Mn), whose forms depend on other elements which can be a storage for organic or inorganic forms and source of the same elements, anthropogenic activity (agriculture and industrial wastes), and weather. This finding agreed with Spieles and Mitsch (2000), and Franc, *et al.*(2005).

The number of interaction between manganese and iron was verified in these studies. It was noted that the increasing of manganese or iron in the growth media creates a decline of iron or manganese content of the plant, respectively. The alteration is noted mostly in the roots, possibly showing that these elements are racing for absorption sites(Tanaka and Navasero,1966). When O<sub>2</sub> was maintained at the ambient level in the water of the chambers in experiments, there was no release iron of manganese and from the sediment. Otherwise, the metals have been absorbed by the sediment from the overlying water during such circumstances (Sundby *et al.*, 1986; Skoog *et al.*, 1996).

#### 4.3Chlorophyll:

Chlorophyll (a ) concentrations of the surface samples are presented in table 1. It shows that the highest concentration was observed in spring (2.411  $\mu\text{g/l}$ ) while the lowest concentration was observed in December (0.026  $\mu\text{g/l}$ ). The biomass of algae often rises with existence of resource and becomes less with many sediment and toxic stressors by humans. The relation between nutrient inputs and algal biomass is one of the frequently used indicators of eutrophication in aquatic ecosystems (Doddset *al.*,1998). Mn was positively affected by the increased primary algal production as chlorophyll a in station 3 may cause high organic material by buffalo grazing in this station and resulting from increased element loads. It was caused by the intensive influence from inland activities, and maximum algal growth during spring, in case of penetration of light is highest, while phytoplankton loads in other wetland stations may gets top in the warm months (figure 6,7). The vacillation occurring in chlorophyll value indicates that the vacillation occurs in primary productivity among different seasons (Bellinger and Sige, 2010). There were several factors which influence the diversity of phytoplankton. To clarify these internal effects such as physiological varieties among phytoplankton species lead to a given form of phytoplankton growth (Akbayet *al.*,1999). The chlorophyll decreased in station 1 (Figure 7) resulting from metal deficiency leading to decreasing photosynthesis and probably the metal deficiency was due to increasing in some compounds formation such as fat and carbohydrate which come from proteins increase lyses rate then chlorophyll pigment damage (Syrett, 1981).

Chlorophyll a was correlated well with Fe and Mn metals as indicated in table 2. Correlation coefficient analysis between chlorophyll a, manganese and iron ions for seasons is presented in table 2. Generally, there are positive important ( $P < 0.05$ ) correlations of chlorophyll a between iron and manganese in water about ( $r = 0.52$  and  $0.79$ ) respectively and positively in sediments are ( $r = 0.38$  and  $0.26$ ) respectively.

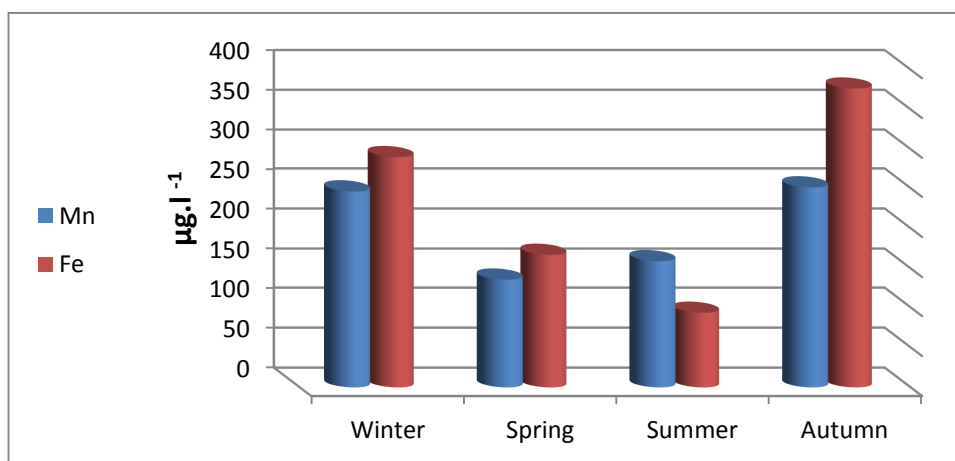
**Table 1. Concentration of Chlorophyll a, Iron and Manganese in the water and sediments in Ibn-Najim marsh**

Metal	Compartment	Jan.	Feb.	Mar.	Apr.	May	Jun	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
Iron	Water <sup>a</sup>	130	110	150	210	490	170	80	70	70	520	550	640
	Sediments <sup>b</sup>	310	230	270	330	640	660	610	720	590	340	240	190
Manganese	Water <sup>a</sup>	190	110	100	90	380	190	180	130	140	310	320	430
	Sediments <sup>b</sup>	720	120	730	410	2000	790	390	610	340	690	540	340
Chlorophyll a	$\mu\text{g L}^{-1}$	0.03	0.04	0.06	0.74	0.61	0.47	0.17	0.11	0.09	0.28	0.04	0.03

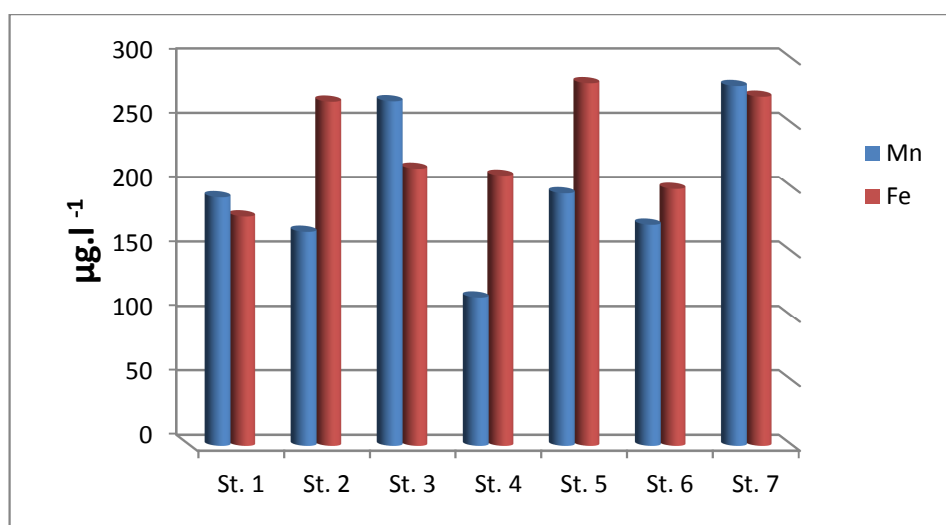
<sup>a</sup>  $\mu\text{g L}^{-1}$   
<sup>b</sup>  $\mu\text{g g}^{-1}$

**Table 2. Correlation coefficients between chlorophyll a and iron and manganese ions in Study stations**

	Mn water	Mn sediment	Fe water	Fe sediment	Chlorophyll a
Chlorophyll a	0.79	0.26	0.52	0.38	0.00
Mn water	0.00	0.48	0.40	0.64	0.79
Mn sediment	0.48	0.00	0.22	0.80	0.26
Fe water	0.40	0.22	0.00	0.59	0.52
Fe sediment	0.64	0.80	0.59	0.00	0.38



**Figure 2: Seasonal variation of Iron and manganese metals in the water Ibn-Najem marsh**



**Figure 3: Mean concentration of Iron and manganese metals in the water Ibn-Najem marsh in study stations**

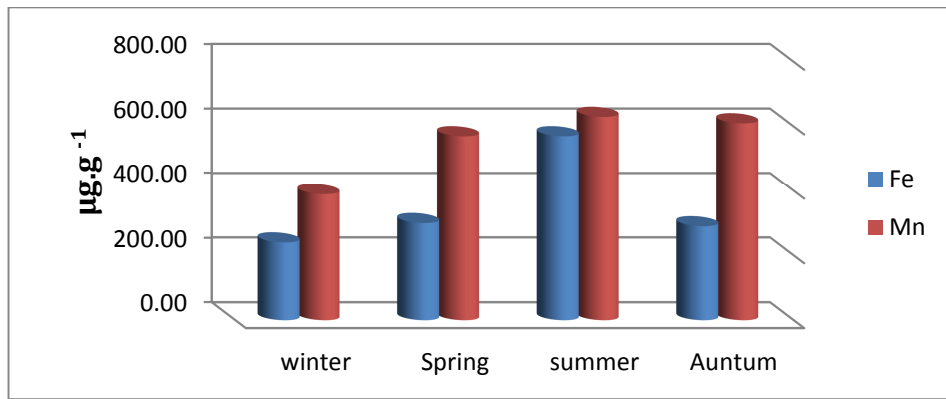


Figure 4: Seasonal variation of Iron and manganese metals in the sediments Ibn-Najem marsh

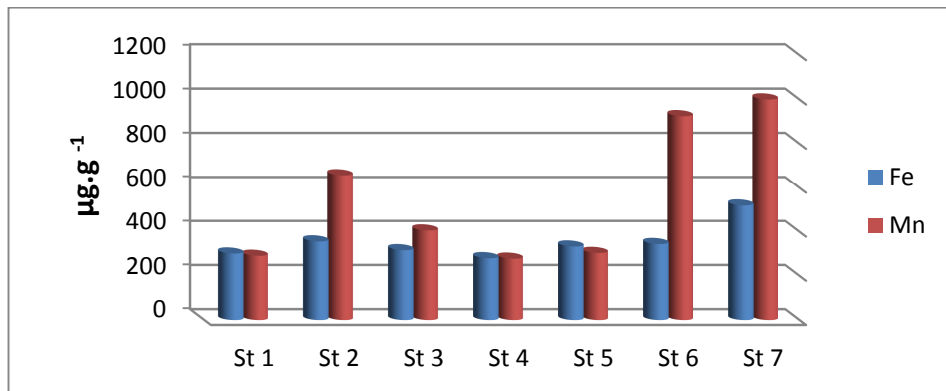


Figure 5: Mean concentration of Iron and manganese metals in the sediment Ibn-Najem marsh in study stations

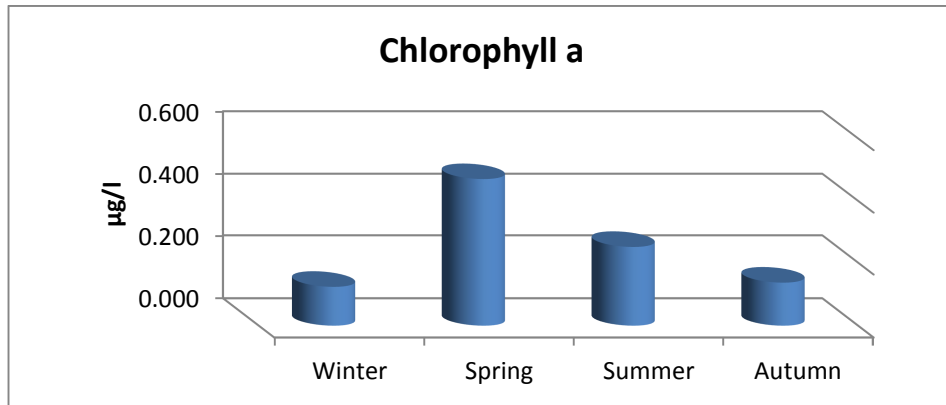


Figure 6. Seasonal variation of Chlorophyll a (µg/l) in surface samples for Ibn-Najem marsh at collected during study period

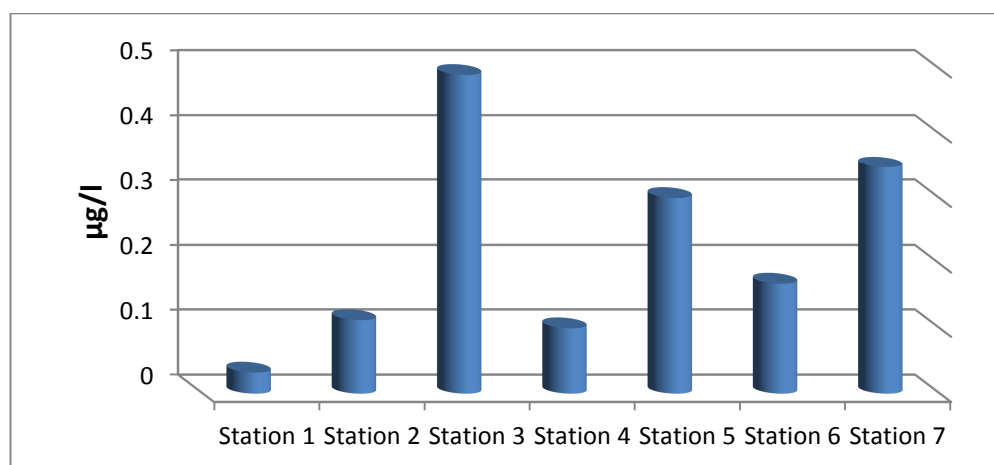


Figure 7: Mean concentration of Chlorophyll a (µg/l) in surface samples for Ibn-Najem marsh at study stations

### CONCLUSION

The present study concludes that the mean concentrations of manganese and iron were extremely high in the sediments in the summer. While the maximum values in the water were in autumn. The maximum concentration of the Fe in water was in station (5) while maximum values of Mn was in station (7). The concentration of iron and manganese elements exceeded the Iraqi limitations for freshwater quality.

It was observed that the highest biomass values of phytoplankton were recorded in the spring and the lowest values were recorded in the winter. The measured factors influenced biomass variations of phytoplankton in Ibn Najim Marsh including iron and manganese had positively significant correlations between chlorophyll a, and iron and manganese in water. It was also concluded that the high concentration of chlorophyll a is directly related to the concentration of manganese.

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