NIHAL G. SHAMS EL-DIN; ADEL M. AMER AND MAHA. A. ABDALLAH

National Institute of Oceanography and Fisheries Nihalshamseldin@yahoo.com

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ABSTRACT

The two species Ulva lactuca (Linnaeus) and Enteromorpha compressa (Linnaeus) Nees belonging to Chlorophyceae, Jania rubens (Linnaeus) Lamouroux (Rhodophyceae) and Petalonia fascia (Müller; O.Kuntze) (Phaeophyceae) were collected from five stations along the Alexandrial coast subjected to different ecological conditions. Natural components of macroalgae (total protein, total carbohydrates and total lipid content) iodine and pigments (chlorophylls and β -carotene) were measured seasonally in these four algal species from September 2004 to July 2005. In addition, nutrient salts (Nitrate, nitrite, ammonia, and reactive phosphate) were determined. However, the results indicated that Abu-Qir Bay recorded the highest concentration of nitrate (18.16 μ g at/L), ammonia (19.1 µg at/L), total organic nitrogen (114 µg at/L), total nitrogen (152.6 µg at/L), reactive phosphate (6.8µg at/L) and total phosphate (13.28 µg at/L), while El-Maadiya recorded the highest concentration of nitrite (4.06 µg at/L). On the other hand, there were great variations in the level and the pattern of distribution of the measured natural components in the four algal species, with a general decrease in their concentrations than the previous records. The correlation coefficient between the natural components in the four algal species was calculated (n= 26 at p < 0.05). In addition, the correlation coefficient between nutrients and the natural components in the two species Ulva lactuca and Enteromorpha compressa was calculated (n= 17, n= 5), respectively, at a confidence limit 95% and revealed that nutrients were not limiting factors for total protein content (TPr) and total carbohydrates content (TCH) while total lipid content (TL) was negatively correlated with total nitrogen and total organic nitrogen in Ulva lactuca whereas nutrients were not significantly correlated with natural components in Enteromorpha compressa. Thus, further studies are still needed to search for other environmental conditions affecting the level and pattern of distribution of these components and for the factors responsible for the decrease in their concentrations since there is a worldwide interest for their production.

1. INTRODUCTION

However, there is a worldwide interest for macroalgal components, since they are used in medicine and in pharmacology for their antimicrobial, antiviral, antitumor, anticoagulant and fibrinolytic properties (Parker, 1993; Honya *et al.*, 1994; Fleurence, 1999, Fleurence *et al.*, 1999). As they are rich in carbohydrates, fats, amino acids, trace elements and vitamins (Waaland, 1981 & Hamdy, 1982) and because of their high protein content, protein concentrates (PCs) they have become more important for the food industry, especially in developed countries (Wong & Cheung 2001). Their recent utilization as an animal feed is on increase. The use of macroalgae as food for fish larvae has been initiated as an alternative to microalgal cultures. In consequence, the nutritional content of macroalgae is being

investigated with a view to their being utilized as animal feed (Mustafa & Nakgawa, 1995; Wahbeh, 1997; Foster & Hodgson 1998, Lindsey Zmeke-White & Clements 1999; Wassef *et al.*, 2001 and Wassef *et al.*, 2005).

In comparison with vegetables, algae are more rich with vitamins (Lee, 1975) especially vitamin A (Hamdy, 1982). Deficiency of vitamin A is considered as a serious world health problem. Three provitamins are known from the algae, β , α and γ carotenes. These types differ in their chemical structure and biological activity. Of these forms, the most widespread and active carotene in algae is the β -carotene. In algae, the carotenoids are synthesized de novo and are reported to have several important functions. In addition to carotenoides, chlorophylls play the major role in photosynthesis and their occurrence varied in the different classes of algae.

On the other hand, seaweeds are a promising source of iodine (Dave *et al.*, 1967). It occurs mostly as iodide (Lunde and Closs, 1930) and many types of seaweed have the capacity to concentrate iodide to levels far above that of their environment (Shaw, 1962). Iodine and its compounds are widely used in medicine, especially in treatment of goiter (Saenko *et al.*, 1978).

Marine algae are dependent on and influenced by different environmental factors, substratum, nutrients, temperature and light (Heinz *et al.*, 1979, Amer *et al.*, 2004 and Shams El-Din *et al.*, 2004).

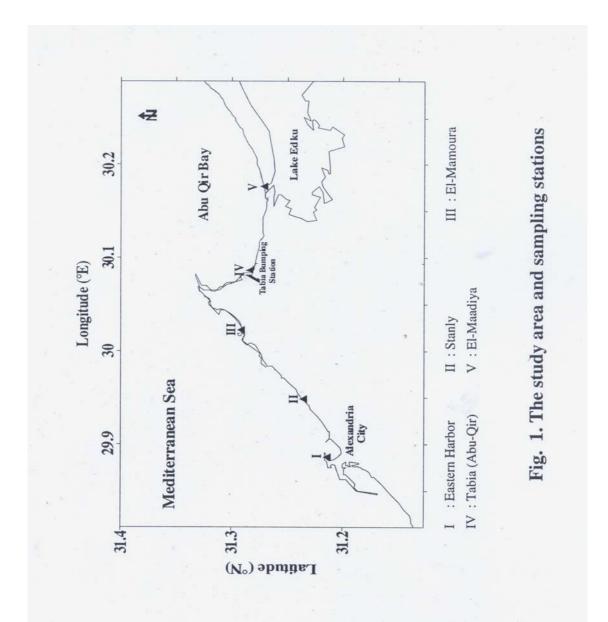
Although a wide varieties of seaweeds spreading along the Egyptian waters, many marine algae are usually collected and thrown away without any exploitation. However brown, red and green algae along the Alexandrial coast have been studied only in a limited number of articles (Nasr and Aleem, 1948; Aleem, 1993; El Tawil and Khalil, 1983; Wassef *et al.*, 2001; Wassef *et al.*, 2005 and Ibrahim *et al.*, 2005). The present study deals with determination of some natural components in different algal species in relation to its space time variations and aimed to emphasize the role of the nutrients and their effect on the production of these constituents.

2. MATERIALS AND METHODS

2.1. Study area

Samples collected were carried out seasonally during Autumn (September); 2004, Winter (January), Spring (April) and Summer (July); 2005 covering the polluted sites along the Alexandrial coast from Eastern Harbor to Abu-Qir Bay (Fig. 1).

The stations are: Eastern Harbor (St. I) is a shallow semi-enclosed basin receiving sewage effluents coming from several minor sewers as Hunting club and Yacht club in addition to shipping activities and fisheries. Stanley beach (St. II) where the construction of the new bridge (2001) and the filling by sand resulting in the development of a new small bay which may affect the distribution and occurrence of algae. El-Mamoura beach (St. III) lies relatively far away of the pollution sources, while Abu-Oir Bay at the area of El-Tabia pumping station (St. IV) is the most industrialized area in Alexandria and especially susceptible to pollution and is usually considered to be a heavily stressed ecosystem. Finally, El-Maadiya (St. V) is subjected to freshwater discharge at sometime from Lake Edku through Bougaz El-Maadiya connecting the lake with Abu-Qir Bay.



2.2. Sample collection

All the surface water samples, from all studied areas, were collected directly into 5 liters capacity plastic Jerry cans, just opening at the desired depth (usually at depth >50 cm) for measurements of chemical parameters.

Four algal species were collected from the five sites at the sublittoral zone at depth about 1 m. Representing three algal groups. Two members of Chlorophyta: Ulva lactuca (Linnaeus) and Enteromorpha compressa (Linnaeus) Nees. One member of Rhodophyta: Jania rubens (Linnaeus) and of Phaeophyta: Lamouroux one Petalonia fascia (Müller; O. Kuntze). Throughout the study period 28 algal samples were collected; 18 samples of Ulva lactuca were from Eastern Harbor, Stanly, El-Mamoura, Abu-Qir, and El-Maadiya, 7 samples of Enteromorpha compressa were from Stanly, El-Mamoura, Abu-Qir, and El-Maadiya, while two samples of Jania rubens were from Eastern Harbor and one sample of Petalonia fascia was collected from El-Mamoura. Algal samples were collected and separated in the field then kept in ice-box. Quick rinsing of the algae for removing of epiphytes, salts and most impurities with tap water was carried out in laboratory throughout the same day of sampling. Herberium sheets with a preliminary identification of separated species were done and/ or preserved in 4% formalin. Microscopic identification of the investigated algae was carried out according to Riedel (1970) and Aleem (1993).

2.3. Measurements of chemical parameters

Nutrient salts (Nitrate, nitrite, ammonia and reactive phosphate) were determined according to APHA (1995). The determination of total nitrogen (TN) and total phosphorus (TP) was carried out according to Valderama (1981). These parameters were measured using a Shimazdu double beam Spectrophotometer UV-150-02.

2.4. Measurements of natural products

Total protein (TPr), total carbohydrates (TCH) and total lipids (TL) measurements: 1 g dry weight of the different algal samples was taken. Total protein content was estimated spectrophotometrically at 650 nm by the method described by Lowery *et al.* (1951). Total carbohydrates content were estimated according to Dubois *et al.* (1959), while total lipids were estimated according to Bligh and Dyer (1959). The results were expressed as mg/ gm dry weight.

Iodine measurement: the method of iodine measurements depend on alkali fusion and ashing of dry seaweed powder using Sodium Carbonate, Sodium Hydroxide and dilute Nitric Acid (Hamdy, 1982), the diluted solution was measured spectrophotometry at 540 nm according to Rogin and Dubravcic (1953). The results were expressed as g/100 gm dry weight.

Pigment analysis: 0.5 g of the dried seaweed powder was taken for pigment extraction of β -carotene. The method was given by Evans (1988) based on successive extractions using Acetone (90%), Methanol (80%) and Hexane. Another 0.5 g of the dried seaweed powder was taken for pigment extraction of chlorophyll-a in the four algal species, chlorophyll-b in green algae (Ulva lactuca and Enteromorpha compressa) and chlorophyll-c in the brown alga (Petalonia fascia). The method was given by Jeffrey and Humphrey (1975) based on extraction using acetone (90%). The extinction of the Acetone-Hexane extract for β-carotene was measured at 480 and 661 nm and Methanol extract for chlorophyll-a and chlorophyll-b and chlorophyll-c was measured at 664, 647 and 630 nm using of DU-6 Beckman Spectrophotometer. The results were expressed as mg/100 g dry weight.

2.5. Statistical analysis

The correlation coefficient between natural products (n = 26, p<0.05) was calculated, in addition to the correlation coefficient between natural products and nutrients for *Ulva lactuca* (n = 17, p<0.05) and *Enteromorpha compressa* (n = 5, p<0.05) was done.

3. RESULTS AND DISCUSSION

3.1. Nutrient salts

The seasonal distributions of the different nitrogenous and phosphorus compounds are illustrated in Table (1) and Figures (2 and 3).

3.1.1. Eastern Harbor E.H (station I)

In the Alexandria E.H, the NO₃-N concentration is ranging from 0.56 μ g at/L in summer to 3.15 μ g at/L in spring with average 1.39±1.19 μ g at/L. While NO₂-N that considers the intermediate state between oxidation of NH₄ to NO₃ in nitrification and reduction of the NO₃ (Santschi *et al.*, 1990), ranging between 0.71 μ g at/L in winter to

3.77µg at/L in autumn with average 2.34 ± 1.65 µg at/L. The seasonal distribution of ammonia (NH₄-N) content in the E.H waters fluctuated between the minimum value of 0.67 µg at/L in winter to the maximum one 6.69 µg at/L in spring, with average value 3.20±2.56 µg at/L. NO3 forming about 20% of TIN and NO₂ forming 34% of TIN, while NH₄ representing about 46% of the TIN this may refer to occurrence of denitrification processes in this harbour (Abdelmoneim et al., 1997). Total Nitrogen (TN) fluctuated between 8.75 µg at/L in winter and 78.58 µg at/L in summer, with average value of 29.02±33.3 µg at/L. The Total Organic Nitrogen (TON) is the dominant form of nitrogenous compounds in this Harbour, whereas it represent >84% of the TN. This is mostly due to proteinated nitrogenic compounds accompanying the domestic sewage (Metcalf and Eddy, 1991) since the E.H receives considerable amount of untreated domestic sewage effluents disposal from the central part of Alexandria (Abdallah and Abdallah, 2007, El-Rayis et al., 1996).

Table (1): Range and concentration average \pm SD of nutrients (µg at/L) at the different stations of the study area during autumn 2004-summer 2005.

Stations	NO ₃	NO ₂	NH ₄	TIN	TON	TN	PO ₄	TP
E.H	0.56-3.15	0.71-3.77	0.67-6.69	2.17-13.85	4.9-74.7	8.75-78.58	0.81-5.25	2.53-5.36
	1.39 <u>+</u> 1.2	2.34 <u>+</u> 1.6	3.20 <u>+</u> 2.5	6.99 <u>+</u> 5.2	24.53±3.58	29.02 <u>+</u> 33.3	2.29±2.0	3.4 <u>+</u> 1.3
Stanly	1.9-4.41	0.42-2.78	0.66-4.07	3.61-7.25	2.45-85.85	8.93-89.46	0.50-1.45	0.98-4.22
	2.87±1.1	1.18±1.1	1.96 <u>+</u> 1.5	6.0±1.6	46.24±14.1	52.24±41.4	1.06±0.4	2.33±1.4
El-Mamoura	3.72-8.07	0.24-0.50	N.D-7.94	4.96-16.25	15.37-37.6	27.93-55.33	0.36-3.89	1.59-3.91
	5.03±2.1	0.39±0.1	5.35 <u>+</u> 2.7	9.67±5.0	29.69±13.7	39.36±12.3	2.3±1.6	2.93±1.2
Abu-Qir	10.3-18.16	1.23-2.54	0.73-19.1	16.24-38.52	68.52-114.0	84.76-152.6	N.D-6.8	1.92-13.28
	13.81±4.0	2.07±0.7	10.17 <u>+</u> 9.2	26.06±11.4	88.2±23.4	114.23±34.7	5.94±1.2	7.02 <u>+</u> 5.7
El-Maadiya	N.D-5.63	0.92-4.06	0.94-3.67	4.37-12.52	7.01-32.9	19.53-37.57	1.72-7.53	2.42-7.63
	2.97±2.4	2.48±1.7	2.57±1.2	8.04±4.1	18.16±10.7	26.20±8.2	3.68±2.7	4.78±2.1

* Note: ND = not detected

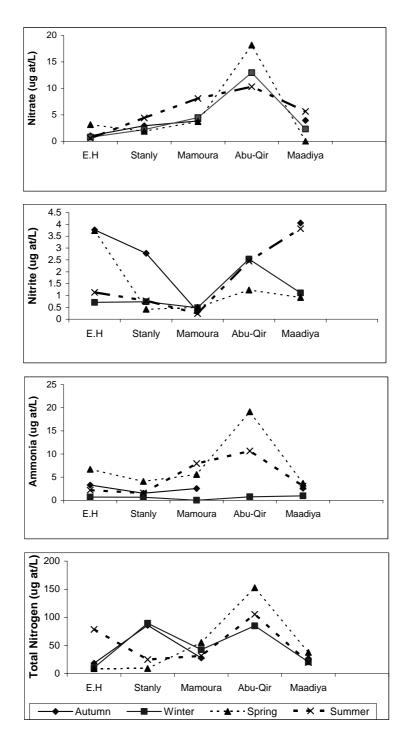


Fig 2. Seasonal variations of nitrate, nitrite, ammonia and total nitrogen in Alexandria coastal water during 2004-2005

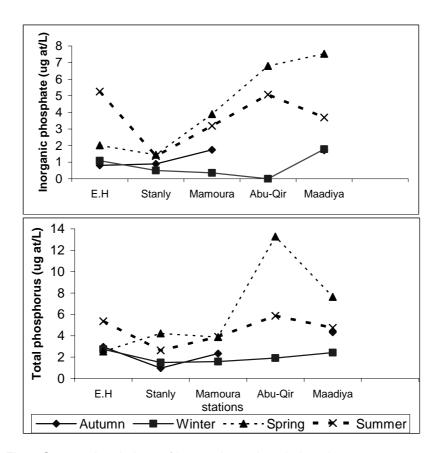


Fig 3. Seasonal variations of inorganic and total phosphorus in Alexandria coastal water during 2004-2005

Similar to nitrogenous compounds dissolved phosphorus (PO₄-P) is very important for growth and reproduction of marine algae (Riley and Chester, 1971), in the E.H fluctuated between 0.081 µg at/L in autumn to 5.25 μ g at/L in summer with average 2.29 ± 0.2 µg at/L, it is higher than that recorded by Abdelmoneim et al. (1997). Also the TP was fluctuated between 2.53 μg at/L in spring to 5.36 µg at/L in summer with seasonal average 3.4 ± 1.3 µg at/L. As the PO₄-P not like N (has no limited source), its main source is mostly from the land. Undoubtedly, degradation of auto and allochthonous organic matter including detergents present in sewage effluents is most probably the important source of PO₄-P in the E.H.

3.1.2. Stanley Beach (station II)

The values of NO₃-N in waters of Stanley area are ranging from 1.9 µg at/L in spring to 4.41µg at/L in summer with seasonal average 2.87 ± 1.12 µg at/L forming >47% of TIN. The seasonal distribution of nitrite (NO2-N) in Stanley area ranged between 0.42 µg at/L during spring to 2.78 µg at/L in autumn with seasonal average of 1.18±1.08 µg at/L forming about 20% of TIN. While (NH₄-N) content in Stanley waters was fluctuated between the minimum value of 0.66 µg at/L in winter to the maximum one 4.04 μ g at/L in spring, with average value 1.96±1.5 µg at/L, forming about 32% of TIN i.e. it comes as second order after NO₃. Total Nitrogen (TN) fluctuated between 8.93 µg at/L in spring and 89.46 µg at/L in winter, with average value of 52.24±41.4 µg at/L. The Total Organic Nitrogen (TON) is the dominant form of nitrogenous compounds at this station, whereas it represent >88% of the TN. However, these results reflect that the TIN in Stanley water is less dominant than TON.

On the Other hand, according to the phosphorus compounds concentrations in

Stanley area, the average concentration of reactive phosphorus (PO₄-P) are fluctuated between 0.50 µg at/L in winter and 1.45 µg at/L in spring with seasonal average $1.06\pm0.4\mu g$ at/L. Also the TP was fluctuated between 0.98 μ g at/L in winter to 4.22 μ g at/L in spring with seasonal average 2.33 ± 1.43 µg at/L. As mentioned before the construction of the new bridge and the environmental change may affect the ecosystem in this area, the hence concentration of nutrient salts.

3.1.3. El-Mamoura beach (station III)

The concentration values of NO₃-N in waters of El-Mamoura beach are ranging from 3.72 μ g at/L in spring to 8.07 μ g at/L in summer with seasonal average 5.03 ± 2.1 µg at/L forming >46% of TIN. The seasonal distribution of nitrite (NO₂-N) in El-Mamoura beach ranged between 0.24 μ g at/L during summer to 0.50 μ g at/L in winter with seasonal average of 0.39±0.1 µg at/L forming about 3% of TIN. While (NH₄-N) content in this waters was fluctuated between the minimum value of 2.53 μ g at/L in autumn to the maximum one 7.94 µg at/L in summer, with average value $5.35\pm2.7 \ \mu g \ at/L$, forming about 50% of TIN i.e. it comes as first order then NO₃ The higher oxidant state of nitrogen forms (NO_3+NO_2) are 50% of TIN, i.e. the oxidant state of nitrogen forms is equal with that of NH₄ in this water.

Total Nitrogen (TN) fluctuated between 27.93 μ g at/L in autumn and 55.33 μ g at/L in spring, with average value of 39.36±12.3 μ g at/L. The Total Organic Nitrogen (TON) is the dominant form of nitrogenous compounds in this Bay, whereas it represent > 75% of the TN.

According to the phosphorus compounds in El-Mamoura beach, the average concentration of reactive phosphorus (PO₄-P) and TP are 2.3 ± 1.6 and 2.93 ± 1.2 µg at/L respectively. From the results it is noticed that, the relatively low concentration of phosphorus compounds in that area may due to no land based source or sewage outfall.

3.1.4. Abu-Qir Bay (station IV)

According to the nitrogenous compounds, nitrate content (NO3-N) in the investigated area ranged from 10.3 µg at/L during summer to its maximum one (18.16 μ g at/L) in spring, with seasonal average of $13.81\pm4.0 \ \mu g \ at/L$. The seasonal distribution of nitrite (NO₂-N) in Abu-Qir Bay ranged between 1.23 µg at/L during spring to 2.54µg at/L in winter with seasonal average of 2.07±0.7 µg at/L. While the seasonal distribution of ammonia (NH₄-N) content in the investigated Bay waters fluctuated between the minimum value of $0.73 \ \mu g \ at/L$ in winter to the maximum one 19.1µg at/L in spring, with average value 10.17 ± 9.2 µg at/L. The higher oxidant state of nitrogen forms (NO₃+NO₂) are >60% of TIN, ammonia constitutes <40% of the TIN i.e. the oxidant state of nitrogen forms is the dominant form in this Bay.

Total Nitrogen (TN) fluctuated between 84.76 µg at/L in winter and 152.57 µg at/L in spring, with average value of 114.23±34.7 µg at/L. The Total Organic Nitrogen (TON) is the dominant form of nitrogenous compounds in this Bay, whereas it represented about 77% of the TN. Accordingly, Abu-Qir Bay reveals high concentrations of nitrogenous compounds, Since this Bay receives various types of land discharges through three main point sources; Tabia outlet (agricultural and industrial wastewater), Maadiya opening (agricultural drainage waters) and Rosetta mouth (agricultural drainage waters with pulses of proper Nile water).

The relatively high concentration of NO_3 in Abu-Qir especially during spring and the low concentration in summer could be interpreted on the basis of the decomposition of organic matter as well as the drainage water since nitrate mainly came from riverine input (Liu *et al*, 2005). Presence of TON in high concentrations (77% of TN) in the Bay waters is mostly due to the direct discharge of wastewater from Ammonia/Urea Plant (fertilizer) about 1800 m³/day (Badr, 1993).

On the Other hand, according to the phosphorus compounds in Abu-Qir Bay, the average concentration of reactive phosphorus (PO₄-P) and TP are 5.94 ± 1.2 and 7.02 ± 5.7 µg at/L respectively. The high phosphorus concentration in the Bay is undoubtedly due more to the rich supply of nutrient salts discharged with the untreated non-saline waters disposed to the Bay rather than due to the benthic flux from the bottom sediments (Faragallah, 2004).

3.1.5. El-Maadiya area (station V)

Maadiya opening is the Lake Edku outlet on Abu-Qir Bay where surplus water from the Lake is freely flowing into the Bay. Nitrate (NO₃-N) concentrations in this water ranged between 2.32 µg at/L in winter to 5.63µg at/L in summer with seasonally average 2.97±2.4 µg at/L. While nitrite (NO₂-N) values were fluctuated from 0.92 μ g at/L in spring to 4.06µg at/L in autumn with average value of 2.48±1.7 µg at/L, and ammonia (NH₄-N) content in this waters was fluctuated between the minimum value of 0.94 µg at/L in winter to the maximum one 3.67 μ g at/L in spring, with average value 2.57±1.2 µg at/L, forming about 32% of TIN i.e. it comes as second order after NO₃ (37%) of TIN) The higher oxidant state of nitrogen forms (NO_3+NO_2) are 68%, i.e. the oxidant state of nitrogen forms is the dominant form in this water.

Total Nitrogen (TN) concentrations were fluctuated between 19.35 μ g at/L in summer and 37.57 μ g at/L in spring, with average value of 26.20 \pm 8.2 μ g at/L. The Total Organic Nitrogen (TON) is the dominant form of nitrogenous compounds in this Bay, whereas it represents about 69% of the TN.

On the Other hand, the phosphorus compounds concentrations in E-Maadiya area, the concentration of reactive phosphorus (PO₄-P) are fluctuated between

the absolute minimum value of 1.72 μ g at/L in autumn to the maximum one 7.53 μ g at/L in spring with seasonal average 3.68±2.71 μ g at/L. Also the TP was fluctuated between 2.42 μ g at/L in winter to 7.63 μ g at/L in spring with seasonal average 4.78±2.1 μ g at/L. The observations for that region reflect the role of the land-based non-saline waters loaded with PO₄-P discharged from Boughaz El-Maadiya.

Generally, in all areas the higher oxidant state of nitrogen forms (NO₃+NO₂) are ranged between 50-68% of TIN, ammonia constitutes 32-50% of the TIN i.e. the oxidant state of nitrogen forms is the dominant form. On the other hand, the dominance of TON (69-88.55% of TN) than TIN, containing the preferable N-forms (NH₄-N and NO₃-N) by plants, in all study areas, is mostly due to the consumption rate of TIN by aquatic organisms in these waters is more than its production rate from the degradation of the organic matter containing-N or supplemented from the land-based sources. (Metcalf and Eddy, 1972 and Mahida, 1981). Some organic matter containing nitrogen usually resists bacterial attack and remains in the water or sink to the sediment as bottom humus (Riley and Chester, 1971), in addition the rate of ammonification is less than the rate of nitrification in these areas, this may interpret the relatively high concentration of both NO₃ and TON.

The relatively high concentration of NH_{4} , NO_3 and NO_2 in stations collected from Abu-Qir Bay, El-Maadiya and Eastern Harbour (E.H) probably due to the effect of the huge amounts of drainage wastes discharged into these areas. Accordingly Abu-Qir Bay receives mixed wastes through El-Tabia Pumping station in addition to agricultural wastes and sewage via Boughaz El-Maadiya and the E.H receives sewage wastes through many sewers along the Harbor coast in addition to the waste dumping from ships and shipping activities. There was a noticeable variation in ammonia and nitrite levels along the investigated areas, the lowest value of ammonia $(1.96\pm1.5 \text{ µg at/L})$ was recorded in El-Mamoura while the lowest value of nitrite $(0.39\pm0.1 \text{ µg at/L})$ was recorded in Stanley beach as there is no discharges from the land-based sources.

The abundance of TN in the investigated areas is generally in the following order: Abu Qir > Stanley > Mamoura > E.H > Maadiya. While the abundance of TP in the investigated areas is generally in the following order: Abu Qir > Maadiya > Mamoura \geq E.H > Stanley, since Abu Qir Bay considered the mostly high nutrients concentration in this study.

3.2. Natural components:

3.2.1. Total protein, total carbohydrates and total lipids

The results showed that TPr, TCH and TL contents differed interspecifically, spatially and temporally. For Ulva lactuca the TPr fluctuated from 49 mg/gm (St. V) during summer to 159 mg/gm (St. I) during spring (Table 2). The same pattern was followed for TCH ranging from 53 mg/gm (St. V) during summer to 102 mg/gm during spring (St. I), whereas TL fluctuated from 105 mg/gm (St. IV) during winter to 194 mg/gm (St. I) during spring. The results showed that St. I was the most productive station for the three nutritional contents in Ulva lactuca (Table 2) coinciding with the lowest value of nitrate $(1.39 \ \mu g \ at/L)$ (Table 1), while spring was the most productive season (Fig.4a). Mathers & Montogomery (1997) found that TPr in Ulva lactuca lie between 18.22% and 19.29%, Total soluble carbohydrates (TSCH) ranged between 3.22% and 2.26%. Fleurence et al.(1999) found that TPr contents of Ulva spp vary between 18% and 26% whereas Dere et al.(2003) foud the highest average values of TPr in U. rigida (28.1%) and U. lactuca (27.75%). In this study, TPr contents in Ulva lactuca lied between 4.9% to 15.9% with an average 8.6% and TCH contents between 5.3% and 10.2% with an average

6.8% (Table 6). The decrease in concentration of the two components than the previous records may be due to the difference in the environmental conditions.

The green alga Enteromorpha compressa was completely absent at Eastern Harbor, while at the other four sites it was not represented during the four seasons. The values of TPr fluctuated from 46 mg/gm (St. V) during summer to 72 mg/gm (St. IV) during spring (Table 3), coinciding with high values of nitrate, nitrite, ammonia and inorganic phosphate (18.16, 1.23, 19.13, 6.8µg at/L, respectively) (Fig.2 & Fig.3). The pattern of variation of carbohydrates and lipids contents differed from TPr. TCH contents ranged from 60 mg/g (St. II & IV) during autumn and spring, respectively, to 74 mg/g (St. V) during summer. While, TL contents varied from 130 mg/g (St. III, spring) to 177 mg/g (St. V, winter) (Table 3). The station V was the most productive for carbohydrates and lipids with averages of 68 mg/g and 165 mg/g, respectively, (Table 3), while winter and summer were the most productive seasons for the two components (Fig. 4b). In this study TPr contents in Enteromorpha compressa lied between 4.6% to 7.2% with an average of 6.2%, while Dere et al. (2003) found that TPr in Enteromorpha compressa recorded 8.2% (Table 6).

The red alga *Jania rubens* was represented only at St. I & II during winter and autumn, respectively, (Table 4).The station I was the most productive for TPr and TCH (61 & 63 mg/g), respectively, coinciding with the lowest values of nitrogenous compounds recorded at station I during the winter season (Fig. 2). Whereas St.II recorded highest value for TL contents (113 mg/g) (Table 4). The concentration of the two components (TPr and TCH) was very low compared with the results of Khalil and El-Tawil (1982) (Table 6).

The brown alga *Petalonia fascia* was represented only at St.III during spring. TPr contents recorded 59 mg/g while TCH and TL attained 61 and 138 mg/g, respectively, (Table 5). These values coincided with the concentrations of nitrate, nitrite, ammonia and inorganic phosphate recorded as following: (3.72, 0.5, 5.57, 3.89 μ g at/L, respectively) (Fig. 2 & 3). Compared with Çetingül (2001) the concentration of TPr was lower than the previous study, while for TL the highest concentration was recorded in this study (Table 6).

Comparing the four species, the green alga Ulva lactuca recorded the highest values for the two constituents (TPr& TCH), followed by Enteromorpha compressa, Jania rubens and Petalonia fascia. Thus the distribution of TPr & TCH was as following: Rhodophyceae Chlorophyceae > >Phaeophyceae. While for TL the highest value was recorded in Ulva lactuca followed by Enteromorpha compressa, Petalonia fascia and Jania rubens. Thus the distribution of the three constituents was as followed: Chlorophyceae Phaeophyceae > >Rhodophyceae.

Khalil and El-Tawil (1982) and El-Tawil and Khalil (1983) found that the order of concentration of TPr content was as follows: Chlorophyceae > Rhodophyceae >Phaeophyceae. Whereas, Heiba et al. (1990) recorded the highest level in Rhodophyceae > Chlorophyceae > Phaeophyceae, while Dere et al. (2003) found the inverse pattern. The order of concentration of TCH content recorded by Khalil and El-Tawil (1982) and El-Tawil and Khalil (1983) and Heiba et al. (1990) was as following: Phaeophyceae > Rhodophyceae > Chlorophyceae. On the other hand, the order of concentration of TL content recorded by Khalil and El-Tawil (1982) was as follows: Phaeophyceae, > Rhodophyceae > Chlorophyceae, while Heiba et al. (1990) found the inverse pattern. However, there a high decrease in concentration values of TPr & TCH than the previous records. In contrast, TL recorded higher concentration values during this study (Table 6). The great variations in the level and the pattern of distribution of the three constituents (TPr, TCH, TL) in the different

algal groups may be attributed to the ecological differences. In this trend many researchers found that nutritional contents of macroalgae depend not only on season and geography (Fleurence 1999, Fleurence *et al.*,

1999, Haroon *et al.*, 2000 and Dere *et al.*, 2003) but also on the nutrient content of the environment (Marin *et al*, 1998 and Shams El-Din *et al.*, 2004).

Stations	Natural products	Autumn 2004	Winter	Spring	Summer 2005
Eastern harbor	Protein	94	100	159	81
	Carbohydrate	68	64	102	62
(I)	Lipids	130	148	194	126
	Chlorophyll- a	13.09	13.1	4.67	4.78
	Chlorophyll- b	7.64	12.39	4.0	4.32
	B-Carotene	0.0013	0.0009	0.0024	0.0024
	Iodine	0.0136	0.017	0.0752	0.0062
Stanly	Protein	122	87	100	58
5	Carbohydrate	86	63	70	55
(II)	Lipids	124	138	134	162
	Chlorophyll- a	9.66	9.48	8.45	24.32
	Chlorophyll- b	8.63	9.37	8.00	23.30
	B-Carotene	0.0007	0.0011	0.001	0.0011
	Iodine	0.0434	0.002	0.0713	0.0083
El-Mamoura	Protein	*	73	87	61
	Carbohydrate	*	62	74	66
(III)	Lipids	*	127	153	171
	Chlorophyll- a	*	10.68	11.73	21.53
	Chlorophyll- b	*	9.82	7.42	20.79
	B-Carotene	*	0.0031	0.0034	0.001
	Iodine	*	0.085	0.0794	0.0163
Abu-Qir	Protein	*	77	92	56
-	Carbohydrate	*	72	73	57
(IV)	Lipids	*	105	124	114
	Chlorophyll- a	*	13.67	10	6.36
	Chlorophyll- b	*	11.72	8.92	6.23
	B-Carotene	*	0.0026	0.0032	0.0011
	Iodine	*	0.0845	0.068	0.0236
El-Maadiya	Protein	78	83	103	49
	Carbohydrate	64	60	82	53
(V)	Lipids	132	130	142	137
	Chlorophyll- a	ND	9.57	5.56	12.09
	Chlorophyll- b	ND	7.56	4.58	11.06
	B-Carotene	ND	0.0014	0.0024	0.0012
	Iodine	ND	0.014	0.0004	0.0337

 Table (2): Natural components in Ulva lactuca at the different stations of the study area during autumn 2004-summer 2005.

Note: Total protein and total carbohydrate are expressed as mg/gm dry weight. Pigments are expressed as mg/ 100 g.

Iodine is expressed as g/100 g

* Algae are not found.

Stations	Natural products	Autumn 2004	Winter	Spring	Summer 2005
EasternHarbor	Protein	2004	*	*	2005
Lasicilinatuoi	Carbohydrate	*	*	*	*
	Lipids	*	*	*	*
(I)		*	*	*	*
	Chlorophyll- <i>a</i>	*	*	*	*
	Chlorophyll- <i>b</i>	*	*	*	*
	B-Carotene	*	*	*	*
0, 1	Iodine	-	*	*	
Stanly	Protein	48			61
	Carbohydrate	60	*	*	70
(II)	Lipids	150	*	*	146
	Chlorophyll-a	4.33	*	*	14.09
	Chlorophyll- b	4.18	*	*	12.16
	B-Carotene	0.0017	*	*	0.0007
	Iodine	0.00018	*	*	0.0035
El-Mamoura	Protein	*	*	67	*
	Carbohydrate	*	*	61	*
(III)	Lipids	*	*	130	*
	Chlorophyll-a	*	*	ND	*
	Chlorophyll-b	*	*	ND	*
	B-Carotene	*	*	ND	*
	Iodine	*	*	ND	*
Abu-Qir	Protein	*	*	72	*
~	Carbohydrate	*	*	60	*
(IV)	Lipids	*	*	138	*
	Chlorophyll-a	*	*	5.92	*
	Chlorophyll- b	*	*	3.91	*
	B-Carotene	*	*	0.0027	*
	Iodine	*	*	0.0763	*
El-Maadiya	Protein	70	50	*	46
5	Carbohydrate	64	66	*	74
(V)	Lipids	143	177	*	174
× /	Chlorophyll-a	15.73	9.67	*	17.17
	Chlorophyll- b	15.59	8.19	*	16.14
	B-Carotene	0.0016	0.0035	*	0.0017
	Iodine	0.012	0.0797	*	0.014

Table (3): Natural components in *Enteromorpha compressa* at the different stations of the study area during autumn 2004 summer 2005.

Note: Total protein and total carbohydrate are expressed as mg/gm dry weight. Pigments are expressed as mg/ 100 g. Iodine is expressed as g/100 g.

* Algae are not found.

Stations	Natural products	Autumn 2004	Winter	Spring	Summer 2005
Eastern Harbor (I)	Protein Carbohydrate Lipids Chlorophyll- <i>a</i> B-Carotene Iodine	* * * * *	61 63 104 4.55 0.0016 0.0218	* * * * *	* * * * *
Stanly (II)	Protein Carbohydrate Lipids Chlorophyll- <i>a</i> B-Carotene Iodine	50 57 113 12.67 0.0031 0.0758	* * * * *	* * * *	* * * * *
El-Mamoura (III)	Protein Carbohydrate Lipids Chlorophyll- <i>a</i> B-Carotene Iodine	* * * * * *	* * * * *	* * * * *	* * * * *
Abu-Qir (IV)	Protein Carbohydrate Lipids Chlorophyll- <i>a</i> B-Carotene Iodine	* * * * * *	* * * * *	* * * * *	* * * * *
El-Maadiya (V)	Protein Carbohydrate Lipids Chlorophyll- <i>a</i> B-Carotene Iodine	* * * * * *	* * * * *	* * * * *	* * * * *

Table (4): Natural components in Jania	a rubens in the different	stations of the study area
during autumn 2004- summe	r 2005.	

Note: Total protein and total carbohydrates are expressed as mg/gm dry weight. Pigments are expressed as mg/ 100 g. Iodine is expressed as g/100 g. * Algae are not found.

Stations	Natural products	Autumn 2004	Winter	Spring	Summer 2005
	Protein	*	*	*	*
	Carbohydrate	*	*	*	*
Eastern harbor	Lipids	*	*	*	*
	Chlorophyll-a	*	*	*	*
(I)	Chlorophyll-c	*	*	*	*
	B-Carotene	*	*	*	*
	Iodine	*	*	*	*
	Protein	*	*	*	*
Ct 1	Carbohydrate	*	*	*	*
Stanly	Lipids	*	*	*	*
	Chlorophyll-a	*	*	*	*
(II)	Chlorophyll-c	*	*	*	*
	B-Carotene	*	*	*	*
	Iodine	*	*	*	*
	Protein	*	*	59	*
	Carbohydrate	*	*	61	*
El-Mamoura	Lipids	*	*	138	*
	Chlorophyll-a	*	*	11.34	*
(III)	Chlorophyll-c	*	*	9.34	*
	B-Carotene	*	*	0.0021	*
	Iodine	*	*	0.022	*
	Protein	*	*	*	*
	Carbohydrate	*	*	*	*
Abu-Qir	Lipids	*	*	*	*
	Chlorophyll-a	*	*	*	*
(IV)	Chlorophyll-c	*	*	*	*
× /	B-Carotene	*	*	*	*
	Iodine	*	*	*	*
	Protein	*	*	*	*
	Carbohydrate	*	*	*	*
El-Maadiya	Lipids	*	*	*	*
2	Chlorophyll-a	*	*	*	*
(V)	Chlorophyll-c	*	*	*	*
× ,	B-Carotene	*	*	*	*
	Iodine	*	*	*	*

Table (5): Natural components in *Petalonia fascia* at the different stations of the study area during autumn 2004-summer 2005.

Note: Total protein and total carbohydrates are expressed as mg/gm dry weight. Pigments are expressed as mg/ 100 g. Iodine is expressed as g/100 g.

* Algae are not found.

Groups	Total protein		Total Carbohydrates		Total	lipids	
	Present Study	Previous study	Present Study	Previous Study	Present study	Previous Study	References
Ulva lacuca	8.6%	38.20%	6.80%	50.44%	13.8%	11.36%	EL Tawil and Khalil,
		27.75%					1983 Dere <i>et al.</i> 2003
							2003
Enteromorpha Compressa	6.2%	8.2%	6.3%		14.5%		Dere <i>et</i> <i>al</i> .2003
Jania rubens	5.5%	25.34%	6%	68.66%	10.8%	6%	Khalil and El Tawil,1982
Petalonia fascia	5.9%	12- 23.87%	6.1%		13.8%	1.21%- 3.25%	Çetingül, 2001

Table 6: The percentages of Total protein, total carbohydrates and total lipid contents in the present study and the previous studies.

3.2.2. Iodine in algae

The amounts of iodine were ranged from 0.00018 g/100 g in Enteromorpha compressa at St. II during Autumn to about 0.085 g/100gm in Ulva lactuca at St.III and St.IV during winter. Iodine contents in Ulva lactuca were ranged from 0.0004 g/100 g (St. V) during spring to about 0.085 g/100 g (St. III & St. IV) during winter (Table 2), which represent the maximum value of iodine, coinciding with relatively low values of ammonia and inorganic phosphate at the first station while with high values of nitrate and nitrite at the second one (Fig. 2&3) and with an average of 0.037 g/100g. The station III was the most productive for iodine content while spring was the most productive season (Fig. 4a). Amer (1999) recorded a maximum value of iodine in Ulva lactuca (0.106 g/100 g) at Faied in Suez Canal during winter. The iodine values in Enteromorpha compressa fluctuated from 0.00018 g/100 g (St. II) during autumn which represent the minimum concentrations of iodine to 0.0797 g/100gm (St. V) during winter (Table 3), with an average of 0.030 g/100 g. This coincided with low values of nitrate, nitrite, ammonia (2.32, 1.11, 0.94 µg at/L, respectively) (Fig.2). Amer (1999) recorded the highest value of iodine content in Enteromorpha compressa (0.94 g/100gm) at Devresoir in Suez Canal during Spring and Summer. Jania rubens had only two values of iodine, the lowest was 0.0218 g/100 g (St. I) during winter while the highest was 0.0758 g/100 g (St. II) during autumn (Table 4), with the highest average of iodine 0.048 g/100 g. The maximum concentration of iodine coincided with low values of ammonia and inorganic phosphate (1.53, 0.9 ug at/L, respectively) (Fig. 2 & 3). Khalil and El-Tawil (1982) recorded in Jania rubens much lower iodine content (0.004 g/100 g) in the Red Sea coast, North Jeddah. The only sample of Petalonia fascia had iodine concentration of 0.022 g/100 g (St. III) during spring (Table 5). Thus, the order of concentration of iodine content was as followed: Chlorophyceae > Rhodophyceae > Phaeophyceae. Saenko et al. (1978), El-Tawil and Khalil (1983) and Amer (1999) found a different pattern as followed: Rhodophyceae Phaeophyceae > Chlorophyceae. Seasonally the lowest iodine content (0.0018 g/100gm) was recorded during Autumn and the highest value (0.085 g/100 g) during winter. Amer (1999) recorded the lowest value of iodine content (0.009 g/100 g) during Autumn and the highest (0.110 g/100 g) during Spring in Suez Canal (Table 7). On the other hand, the investigated algae at Alexandria coast showed relatively lower iodine concentrations than that recorded in algal species collected from Suez Canal at greater depth. Saenko et al., (1978) found that seaweed growing at greater depth showed increased iodine content. The previous results indicate that, the major reason for these studied variations was the fluctuation of iodine accumulation in the investigated species during seasons, (El-Tawil and Khalil, 1983 and Amer, 1999).

3.2.3. Pigments in algae

In Ulva lactuca chlorophyll-a and bvaried from minimum values 4.67 and 4.0 mg/100 g (St. I) during spring to their maximum values 24.32 and 23.3 mg/100 g (St. II) during summer, respectively (Table 2), coinciding with the lowest concentrations of ammonia and inorganic phosphate (1.57, 1.37 µg at/L, respectively) (Fig. 2&3). Amer (1999) found that chlorophyll-a in Ulva lactuca attained a maximum of (11.0 mg/100 during Winter at Devresoir and **g**) chlorophyll-b (10.5 mg/100gm) during winter at Faied in Suez Canal. While Amer et al. (2004) recorded maximum values of chlorophyll-a and b(65.86 & 11.60 mg/100g), respectively, at the intertidal zone of National Institute of Oceanography and Fisheries during Spring in the Suez Bay. The chlorophyll-a in Enteromorpha

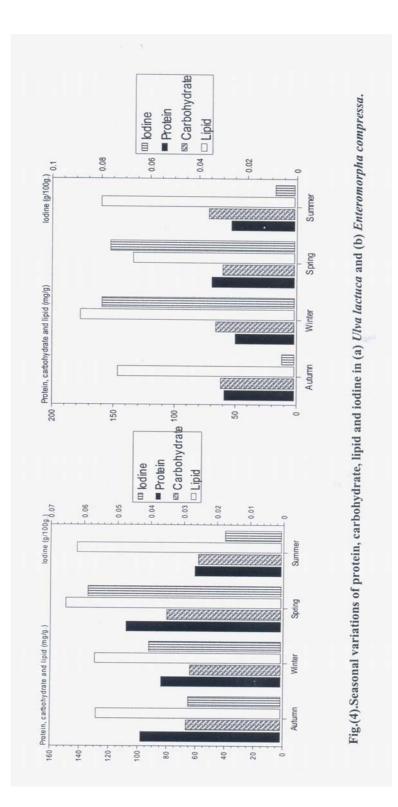
compressa showed its minimum 4.33 mg/100 g (St. II) during autumn while the minimum of chlorophyll-b 3.91 mg/100 g was recorded (St. IV) during spring, the maximums of chlorophyll-a 17.17 mg/100 g and chlorophyll-b 16.14 mg/100 g were noticed at station V during summer (Table 3). Thus, the Summer season was the most productive for the two green algae (Fig. 5a & b). Amer (1999) recorded lower values for chlorophylla and b in Enteromorpha compressa (14.0 and 5.2 mg/100gm, respectively) during Spring at Devresoir in Suez Canal. While Amer et al. (2004) recorded higher value for chlorophyll-a (61.44 mg/100 g) during winter at the intertidal zone of National Institute of Oceanography and Fisheries in the Suez Bay and lower value for chlorophyll-b (3.33 mg/100 g) during Spring at the intertidal zone of Power station in Suez Bay. In Jania rubens the lowest value of chlorophyll-a (4.55 mg/100 g)) was found at station I during winter, while its highest value (12.67 mg/100 g) was recorded at station II during autumn (Table 4), coinciding with the highest total nitrogen (85.74 µg at/L) and the lowest total phosphorus (0.98 μ g at/L) (Fig. 2&3). Petalonia fascia had one value during spring for each of chlorophyll-a (11.34 mg/100 g), chlorophyll-c (9.34 mg/100 g) and β -carotene (0.0021 mg/100 g) (Table 5). Thus Ulva lactuca recrded the highest value of Chlorophyll-a followed by Enteromorpha compressa, Jania rubens and Petalonia fascia as followed: (24.32, 17.17, 12.67 and 11.34 mg/100 g), respectively. While Ulva *lactuca* recorded higher value for chlorophyll-*b* than *Enteromorpha compressa* (23.30 and 16.14 mg/100 g, respectively).

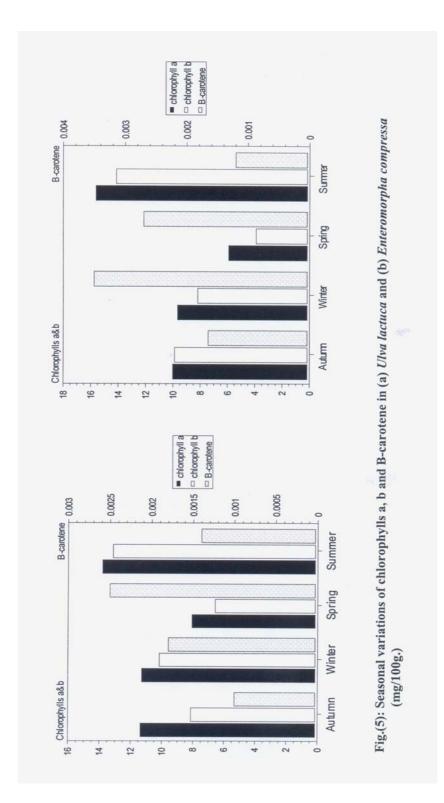
The highest value of chlorophyll-*a* in the four algal species in this study (24.32 mg/100gm) was lower than that found by Amer at al. (2004) (65.86 mg/100 g) in Suez Bay and relatively higher than that recorded by Amer (1999) (23.6 mg/100 g) in Suez Canal at greater depth. On the other hand, the maximum value of chlorophyll-b in the two green algal species (Ulva lactuca and Enteromorpha compressa) was higher than that found by both Amer (1999) and Amer et al. (2004) (10.5 and 9.82 mg/100gm, respectively). USEPA (2003) found that the high clarity of water had increased the irradiance which was expressed in increase in the rate of pigment biosynthesis.

The concentrations of β -carotene ranged from 0.0007 mg/100 g in Ulva lactuca collected from station II during autumn (Table 2) to 0.0035 mg/100 g in Enteromorpha compressa collected from Station V during winter (Table 3). The highest values of β -carotene in the four algal species was as followed: Enteromorpha compressa (0.0035 mg/100 g), Ulva lactuca (0.0034 mg/100 g), Jania rubens (0.0031 mg/100 g) and Petalonia fascia (0.0021 mg/100 g). The maximum value of β carotene in this study was much lower than that found by Amer (1999) (2.7 mg/100 g) in Suez Canal and by Amer et al. (2004) (0.095 mg/100 g) in Suez Bay.

Table (7): Comparison between minimum, maximum and average of iodine concentration (gm/100 g) in Alexandria region (2004-2005) and previous study in Suez Canal area (1999).

		Autumn	Winter	Spring	Summer
Present study	Min.	0.00018	0.002	0.0004	0.0035
	Max.	0.0758	0.085	0.0794	0.0337
Previous	Min.	0.009	0.086	0.094	0.059
study (Amer, 1999)	Max.	0.101	0.108	0.11	0.101





4. STATISTICAL ANALYSIS

The correlation coefficient between natural products (Table 8) revealed that there was a negative correlation between the TCH and TPr content (r = -0.64, n = 26 and p< 0.05). Our results agree with Morgan and Simpson (1981) where they found that carbohydrates content was inversely related to total nitrogen content. This result was previously confirmed by several observations made with other algal species (Butler 1931, Dawes et al., 1974, Mathieson and Tveter (1975 and 1976). However, the same findings were reported by Khalil and El-Tawil (1982), El-Tawil and Khalil (1983) and Dere et al. (2003). The positive or negative interactions between natural components (Table 8), depend on several factors which affect the synthesis process of these products, such as light density and quality, photoperiod and temperature (Zucchi & Necchi, 2001) and also nutrient content (Marin et al., 1998)

A correlation coefficient between nutrients and natural components in *Ulva lactuca* and *Enteromorpha compressa* was calculated while it was difficult for the other

two species (Jania rubens and Petalonia fascia) since the first appeared twice and the later appeared once during the study period. For Ulva lactuca there was no correlation between nutrients and natural components except the TL which was negatively correlated with both total nitrogen and total organic nitrogen (n = 17, r = -0.52 and r = -0.56, respectively, at p < 0.05) (Table 9). As these two parameters are of the essential elements for protein synthesis, our results agree with Khalil and El-Tawil (1982) and El-Tawil and Khalil (1983) who recorded that the protein content inversely related to lipid content. Whereas, there was no correlation between natural components and nutrients for Enteromorpha compressa which may be attributed to that they were not limiting factors for the synthetic process of these components in the green alga. On the other hand, chlorophyll-a was positively correlated with chlorophyll-b (r = 0.97, n =23 at p< 0.05) in the two green algae (Ulva lactuca and Enteromorpha compressa). Significant positive correlations between chlorophyll-a and accessory pigments were reported by Dere et al. (2003).

	Iodine	Chlorophyll-a	B-Carotene	Total Protein	Total Carboh ydrate	Total Lipids
Iodine	1.00	-0.15	0.67*	-0.38	0.43*	-0.06
Chlorophyll-a		1.00	-0.26	0.46*	-0.29	0.28
B-Carotene			1.00	-0.42*	0.25	0.01
Total Protein				1.00	-0.64*	0.15
Total Carbohydrate					1.00	-0.10

 Table (8): The correlation coefficient between the natural products in the study area during 2004-2005.

Marked correlations are significant at p < 0.05 N=26

	NO3	NO2	NH4	TIN	TN	TON	PO4	TP
Iodine	-0.37	-0.08	0.35	-0.31	-0.43	-0.42	-0.20	-0.22
Chl-a	-0.12	-0.30	-0.08	-0.25	-0.47	-0.47	-0.10	-0.31
Chl-b	-0.08	-0.37	-0.05	-0.24	-0.42	-0.42	-0.13	-0.29
β-Ca.	-0.06	-0.18	0.40	0.01	0.03	0.03	-0.08	0.30
TPr	-0.30	0.24	-0.14	-0.11	-0.09	-0.08	-0.11	-0.09
TCH	-0.07	0.27	-0.11	0.10	0.03	0.01	0.07	0.01
TL	-0.30	-0.06	-0.13	-0.14	-0.52*	-0.56*	-0.41	-0.15

 Table (9): The correlation coefficient between the natural products and nutrients in Ulva lactuca during 2004-2005.

Marked correlations are significant at p < 0.05N=17 (Casewise deletion of missing data)

5. CONCLUSION

Macroalgae are important sources of natural components extraction, further studies are still needed to search for other environmental conditions affecting the level and pattern of distribution of these components. However, there is a general decrease in concentrations of natural components in the collected four algal species than the previous records and this is a good reason for searching for the factors responsible for this decrease since there is a worldwide interest for these components.

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