

The present study aims to follow up the incorporation of both Na^+ and Fe^{++} ions into the gypsum crystals. Time of stirring as controlling factor for the variation of crystal lattice and morphology of the gypsum crystals has been also investigated.

MATERIALS AND METHODS

Analytical reagent grade chemicals, triply distilled water and graded glass were used. Solutions of calcium chloride, sodium sulphate, sodium chloride and ferrous chloride were prepared using reagent grade (J.I. Backer Co.), chemical solutions were filtered ($0.22 \mu\text{m}$, millipore filters) before used. Metal ion concentrations were determined by passing aliquots through a cation exchange resin (Dowex 50) in the hydrogen form and titrating the diluted acid against standardized sodium hydroxide.

Dehydrate calcium sulphate crystals were precipitated by drop-wise addition of 500 ml 0.2 M calcium chloride solution to 500 ml of 0.2 M sodium sulphate solution at 70°C . The crystals were washed repeatedly with triply distilled water. The solid material was subjected to X-ray powder diffraction studies and Scanning Electron Microscopy.

To determine the effect of stirring time on crystal-lattice and morphology, different time periods of stirring e.g. 1/2 h, 1 h, 2 h, 4 h, 8 h, 16 h, 24 h, 48 h have been suggested.

To examine the effect of metal ion incorporation on both crystal-lattice and - morphology, different concentrations of Na^+ and Fe^{++} were added during synthesise of gypsum crystals. The incorporated Na^+ was measured using "Corning 400 flame photometer" while incorporated Fe^{++} was determined using atomic absorption spectroscopy (Perkin Elmer 2380 A.A.S.). The solid phases were examined by X-ray diffraction (Philips 1840) and scanned using Scanning Electron Microscope SEM (Jeal SEM-25S II).

RESULTS AND DISCUSSIONS

Time of stirring as controlling factor for the variations in crystal-lattice - and morphology:

The variations in both crystal-lattice and morphology have been followed up by X-ray diffraction analysis and Scanning Electron Microscope, considering time of stirring as controlling factor for such variations. Figure (1) reveals that the gypsum crystals show their ideal form after 1 hour with d-spacing for (020), 7.5553\AA . The continuous stirring results in shifting of the d-spacing that reflects continuous deformation of the crystals. Figure (2) illustrates the uniformity of the crystal after 1 hour of stirring, while Figure (3)

**EFFECT OF SODIUM, IRON IONS AND TIME OF (STIRRING)
ON THE CRYSTAL-LATTICE AND MORPHOLOGY
OF THE GYPSUM CRYSTALS.**

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Key Words: Crystal lattice, Morphology, Sodium, Iron, Stirring time.

ABSTRACT

The influence of the presence of Na⁺ and Fe⁺⁺ ions on the crystal-lattice and - morphology of gypsum crystals has been investigated. Generally, the degree of crystallinity is affected by the replacement of Ca⁺⁺ by metal ions. The replacement and the partial deformation of crystal is more in case of incorporated Na⁺ than that of Fe⁺⁺ ions. The minimum allowed concentration of Na⁺ as impurities in the gypsum must not exceeds 4% to obtain ideal gypsum crystals. Also the effect of different stirring time was examined. The change in stirring time results in irregular crystal faces of gypsum crystals.

INTRODUCTION

The sequence of precipitation of salts from seawater during evaporation was originally worked out by Usiglio (1849). The growth of calcium sulphate crystals has important applications in areas such as desalination technology, geochemistry and petroleum technology (e.g.. Spriegler, 1962; Stumm and Morgan, 1970; Vitter and Philips, 1970). During crystallization processes of gypsum in industrial environments usually all kinds of impurities are present which influence on the crystallization processes in many aspects, not only the nucleation and kinetics of crystal growth, but also the crystal shape and morphology are subjected to drastic changes (Nancollas *et al.*, 1978). According to Weijnen *et al.* (1983); in processes where gypsum is formed as by-product, the ores being processed are important source for metal ions, particularly, heavy metal ions like Cd²⁺, Pb²⁺ and Cu²⁺ are often incorporated into the gypsum lattice; Weijnen *et al.* (1983).

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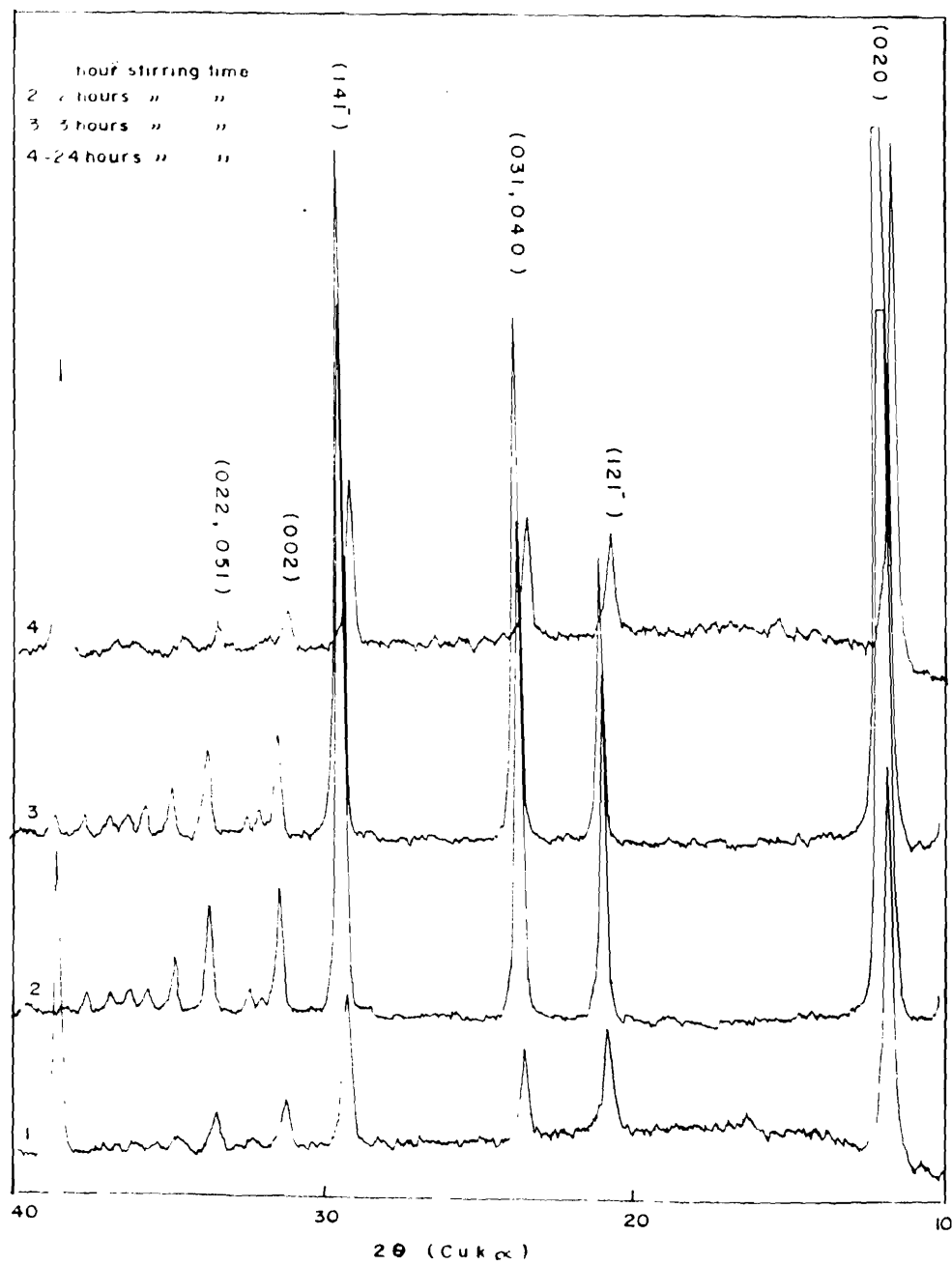


Figure 1. Effect of stirring time on the crystal lattice of gypsum.



Figure 2. Well crystallized gypsum crystal after 1 hour of stirring time (SEM X3000).



Figure 3. Deformed gypsum crystal after 48 hours of stirring time (SEM X1000).

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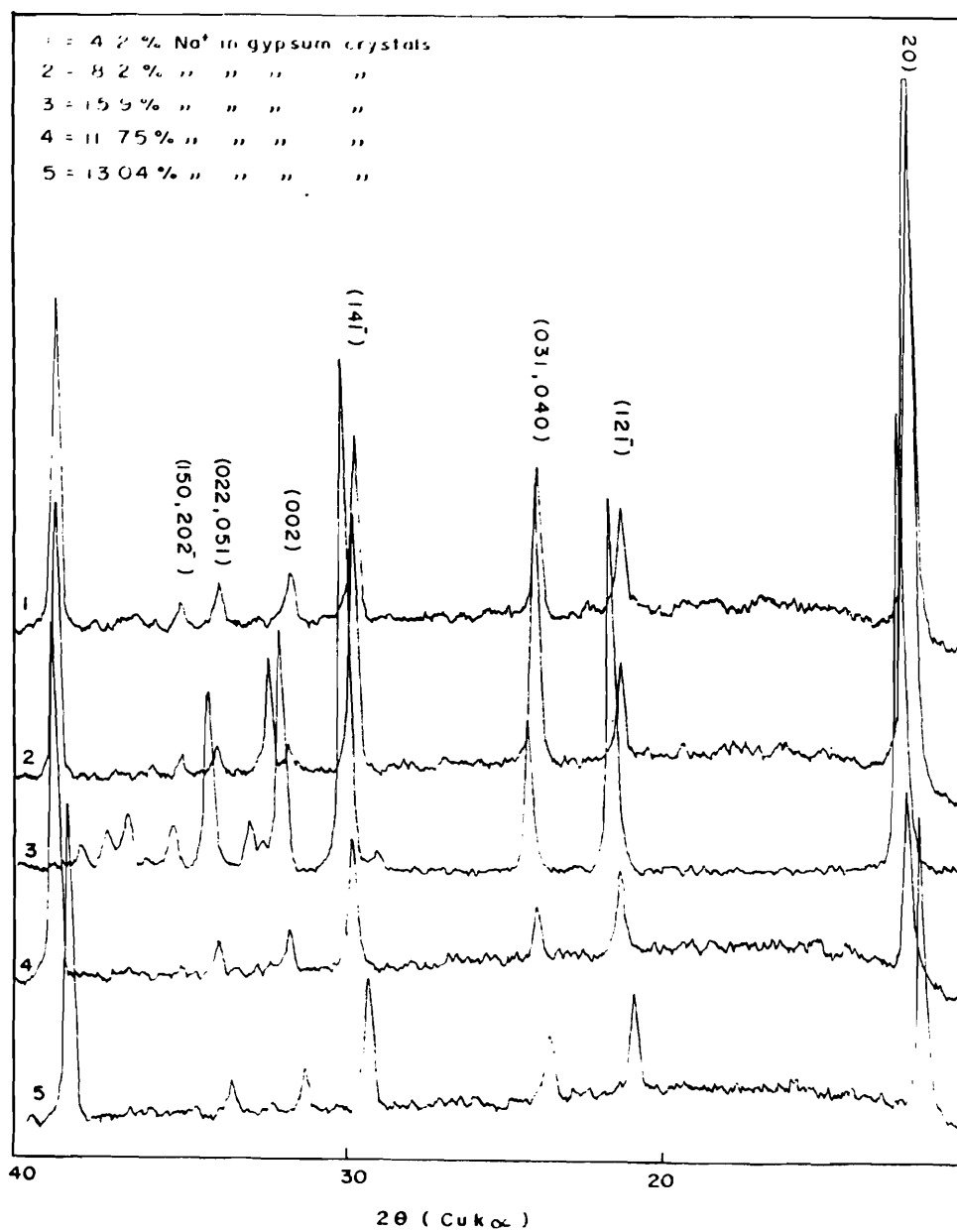


Figure 5. Effect of Na⁺ ion incorporation on the crystal lattice of gypsum.

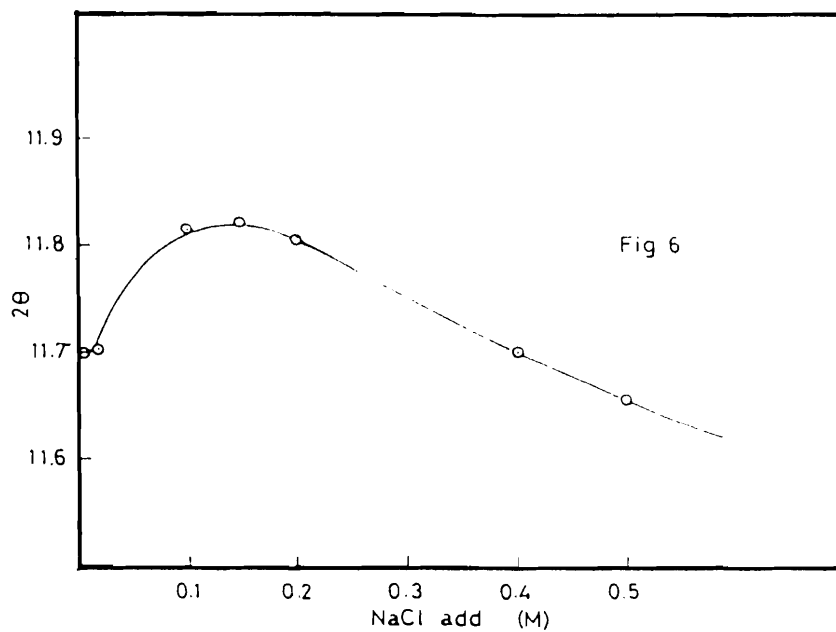


Figure 6. Effect of NaCl dissolved in the parent solution on Na/Cl molar ratio of the precipitate.

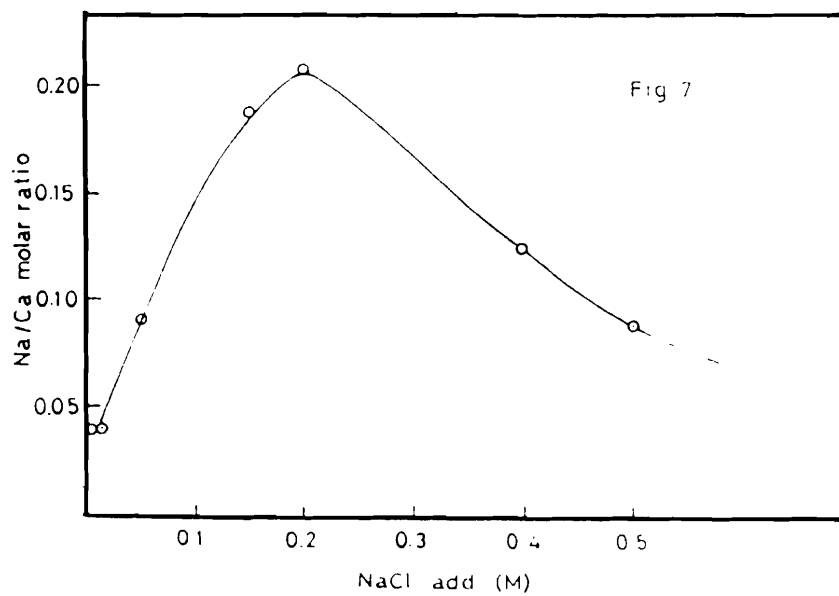


Figure 7. Effect of Na⁺ ion incorporation on the diffraction angle (2θ) of (020) in gypsum crystals.

Na/Ca ratio decreases suggesting that the ability of the found crystals to accept new incorporated Na⁺ ions decreases. The comparison between Figures 6 and 7 reflects the strong relation between the ionic exchange and the variation of d-spacing whereas the maximum shift in 2θ from the ideal form is accompanied with the highest value of Na/Ca molar ratio.

The degree of crystallization of the synthesized gypsum is also affected by the replacement processes. It can be measured as the area of mean peak (020). Figure (8) illustrates a negative correlation between the concentration of Na⁺ ions incorporated into the gypsum and the degree of crystallinity. This can be interpreted on the basis of partial deformation which result from the replacement processes.

Fe²⁺ incorporation into the crystal lattice of gypsum and its effect on crystal- lattice and - morphology of the gypsum:

Ferrous sulphate may occur in several hydrated forms e.g. Melanterite FeSO₄.7H₂O, Siderotil FeSO₄.5H₂O, Rozenite FeSO₄.4H₂O and Szomolnokite FeSO₄.H₂O. In the present study it was able to obtain intermediate series of solid phases between calcium and ferrous sulphates containing Fe²⁺ with concentrations ranging from 1.6 to 8.9% (Table 2).

Table (2): Effect of Fe⁺⁺ ion incorporated into gypsum crystals.

Sample No.	Conc. of FeCl ₂ add (M)	Percent of Na ⁺ incorporated in the gypsum crystal	Fe/Ca Molar %	2e d-spacing
8	0.1	1.664	0.170	11.70 7.4895
9	0.2	3.120	0.032	11.85 7.5189
10	0.3	8.920	0.097	11.75 7.5829
11	0.4	6.300	0.070	11.65 7.5102
12	0.5	4.500	0.050	- - - - -

Figure (9) reveals the effect of Fe⁺⁺ ions incorporated into gypsum on its crystal lattice. It is noted that the lower concentration of incorporated Fe⁺⁺ the crystal lattice of gypsum is not markedly affected. Figure (10) illustrates the shift in diffraction angle 2θ of (020) as a result of Fe⁺⁺ incorporation into gypsum crystals. Figure (11) reveals that the conversion point at which Fe/Ca molar ratio attains its maximum value corresponds about 0.3 M of added FeCl₂. However the comparison of both Na⁺ and Fe⁺⁺ incorporation reveals the susceptibility of gypsum crystals to take up Na⁺ is higher than Fe⁺⁺.

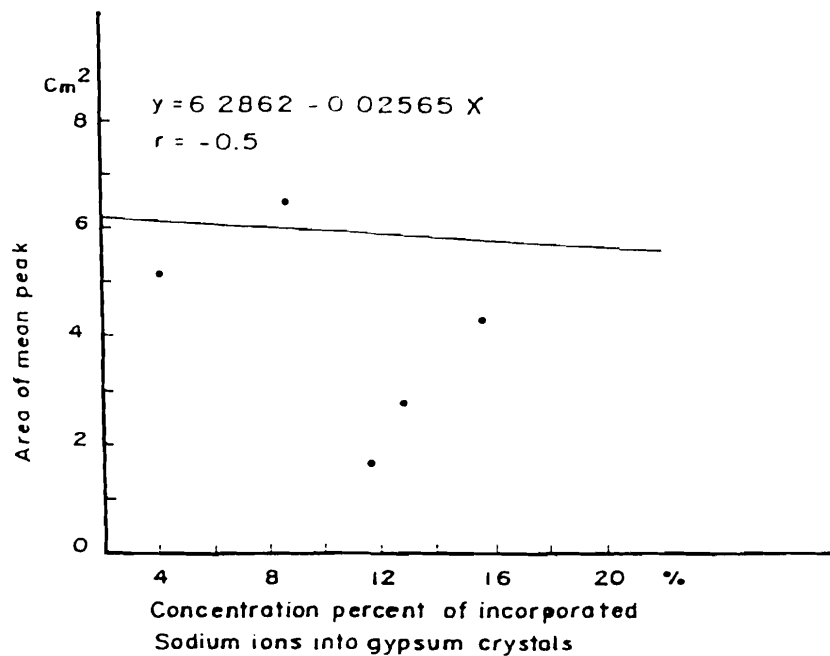


Figure 8. The degree of crystallinity versus Na^+ ion incorporated into the gypsum crystals.

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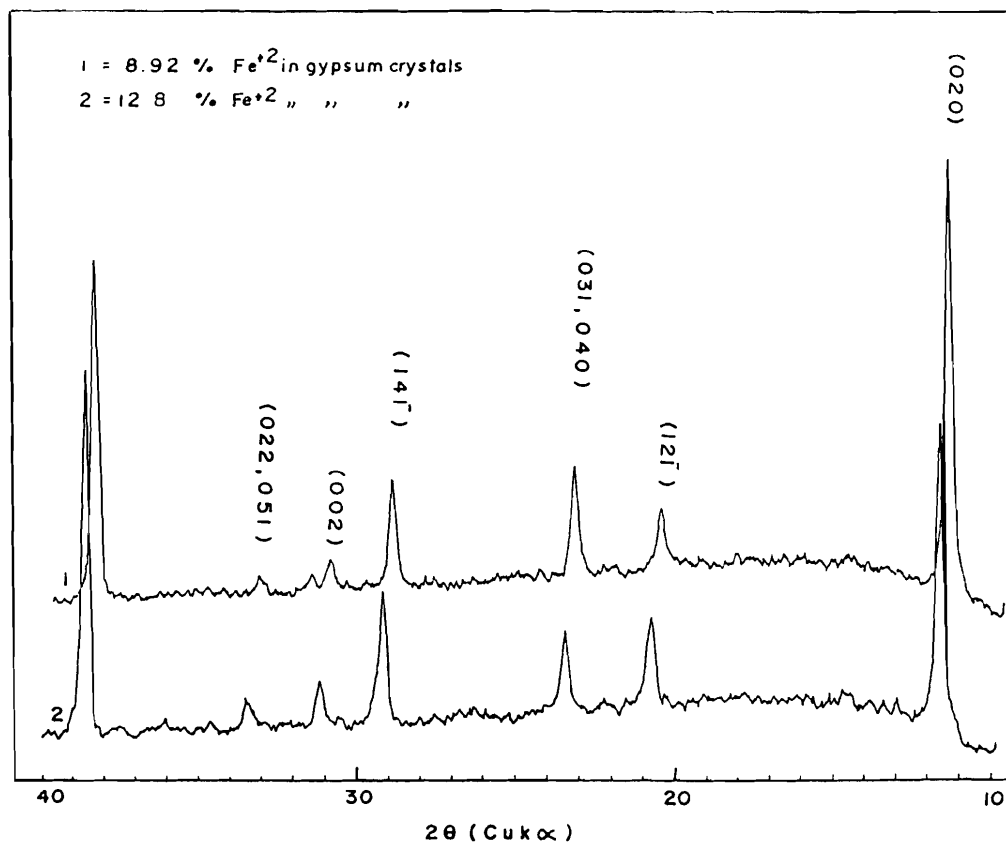


Figure 9. Effect of Fe^{2+} ions incorporated on the crystal lattice of gypsum.

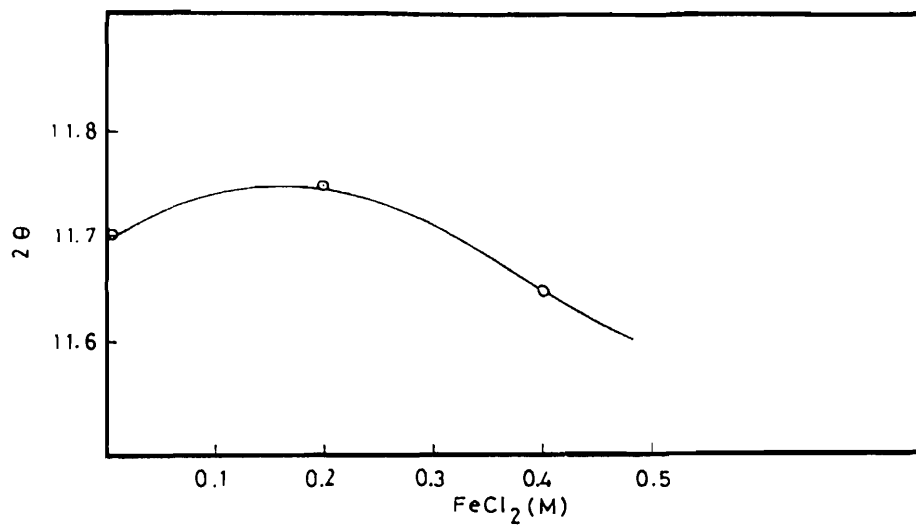


Figure 10. Effect of FeCl₂ dissolved in the parent solution on Fe/Ca molar ratio of the precipitate.

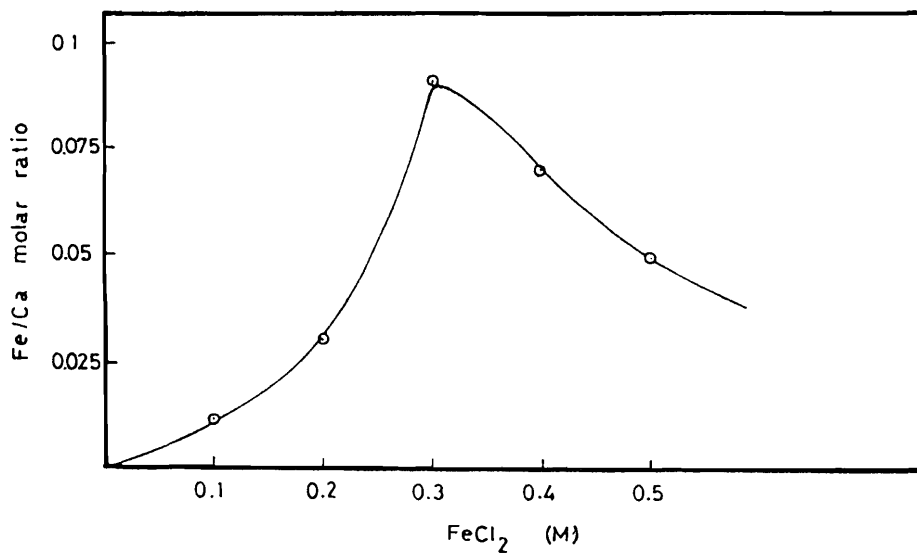


Figure 11. Effect of Fe²⁺ incorporated ions on the diffraction angle of (020) in the gypsum crystals.

CONCLUSION

The present investigation illustrates that with continuous stirring, both crystal - lattice and - morphology are partially affected. Also it can be concluded that the incorporation of Na^+ and Fe^{2+} into gypsum result in a shift of precipitated gypsum crystals from their ideal form. This phenomenon is strongly correlated with the ionic exchange capacity of the present solution. Finally it is observed that the replacement and the effective deformation in case of Na^+ is more than that of Fe^{2+} incorporation.

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stored in a desiccator, with silica gel as desiccant, for subsequent analyses. All weighings for chemical and biochemical analysis were performed at accuracy of 5×10^{-4} and sensitivity and readability of 0.1 ug.

The carbon and nitrogen concentrations were determined using Model 1104 Carlo Erba elemental analyzer located in the Department of Oceanography, Liverpool University, using Acetanilide as standard containing 10.73 % nitrogen and 71.09 % carbon. The mean relative errors for duplicate calculations of standard was + 3 % carbon and + 6 % nitrogen.

For phosphorus determination, 5 to 20 mg of dried adult *E. acutifrons* were fused with NaOH in a platinum crucible and then dissolved with concentrated HCl. In this solution, phosphorus was analyzed using the Molybdate method according to Murphy and Riley (1962).

Samples for nitrate, phosphorus, chlorophyll a were simultaneously collected and analyzed using the methods described by Strickland and Parsons (1972) while salinity was determined using the RSC-76 induction salinometer.

RESULTS AND DISCUSSION

Carbon content :

The carbon content (as percentage of dry weight) of *E. acutifrons* showed, not only variation between the different localities, but also within the different sampling sites of the same area (Figure 2). In Abu Qir, the lowest carbon of the copepod was generally observed during summer at the inshore sites opposite to El-Tabia pump station discharging the industrial waste of about 36 factories (st. 10). The same results was also recorded for Boughaz El-Maadia discharging brackish water from Lake Edku (St. 15). The dissolved oxygen content at this station was extremely low 1.31 ml/l. However, in the other seasons, the carbon content at this location was normally low varying from 30.9 % in spring to 36.1% in winter. The maximum carbon content observed for El-Tabia sector reached 48.4 % at the offshore location (st. 12) during winter.

On the other hand, the carbon content of *E. acutifrons* in the coastal st. 15 of Boughaz El-Maadia sector, affected by agricultural discharge, varied over the same magnitude like those of El-Tabia i.e. between 32.6 % in summer and 38.6 % in winter, but with a slightly higher range. Similarly, the carbon content in this sector increased gradually offshore at st. 13 (range 41.8 % - 52.8 %), far from the discharge point (Fig. 2). The carbon content in both sectors showed a peak in winter with a general average of 44.6 ± 7.4 % for El-Maadia sector and 41.4 ± 6.3 % for El-Tabia sector (Fig. 2).

The carbon content of *E. acutifrons* in the E.H. (sts 6-9) and W.H. (st. 4 and 5) (Fig. 2) are significantly ($p < 0.01$) higher than those recorded for Abu Qir Bay i.e. annual averages 48.3 ± 5.5 % and 46.6 ± 3.9 %, respectively

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(Table 1). Carbon was characteristically high at the central station of E.H. reaching 61.9 % during autumn (Fig. 2). Stations affected by sewage discharge (st. 6 and 8) showed characteristically the lowest carbon contents (annual av. 44.9 + 6.8 % and 43.7 + 3.9 %, respectively). The minimum value for carbon in the E.H. was recorded at st. 8 in spring, i.e., 38.3 %. The overall average calculated for the mid W.H. station, i.e. 42.4 + 4.4 % was significantly lower ($p < 0.05$) than that located opposite to the agricultural discharge i.e. 47.5 + 5.1 %.

Stations sampled at El-Mex Bay showed significantly considerable variations in their carbon content of Euterpina depending on their position relative to agricultural/industrial mixture discharge location. Opposite to the discharge point, the carbon content fluctuated between 30.8 % and 36.4 % in autumn and summer, respectively. On the other hand, despite of the relative oligotrophic nature of st. 1 sampled at the western coast, the average carbon content of Euterpina acutifrons was 51.2 + 2.6 % (Table 1). Generally, seasonal variations in sampling sites were related principally to the seasonal amplitude in the discharge from landbased sources as well as its reflection on the productivity and biomass of phytoplankton in the different localities.

Coastal stations that are highly affected by either industrial or agricultural discharge indicated by low salinity values reaching 16.41 ‰ at El-Maadia opening in Winter showed low carbon contents (Fig. 2). Industrial disposal seemed to have a higher impact on the carbon content (st. 3 and 10).

On the other hand, the chlorophyll a in the Eastern Harbour av. 7.67 mg chl. a/m³) corresponds to the maximum carbon content of the organisms for locations subjected to land discharge (av. 48.3 %, Table 1).

Correlation between the carbon content and chlorophyll a in this basin was statistically significant ($r = 0.9686$, $p < 0.001$) while for the whole coastal area was ($r = 0.7103$, $p < 0.01$) indicating the importance of food supply in building up the carbon content of the organism.

Hardsted-Romeo (1982) observed high carbon values (48 %) in plankton samples from the N. western Mediterranean. He concluded that phytoplankton are richer in mineral elements and carbohydrates than zooplankton which are characterized by low mineral content. Curl (1962 a & b) reported 29.8 % C (dry weight) in samples of mixed copepods and phytoplankton and an average of 38.3 % carbon in crustaceans. Beers (1966) observed 41.6 % C (dry weight) in copepods from Sargasso Sea off Bermuda. Among 4 copepod species from the N.W. Mediterranean, Champalbert and Kerambrun (1978) found carbon ranging from 32.4 % to 43.3 %.

For the inland sea of Japan, Hirota (1981) estimated the total carbon for different copepod species and observed concentrations varying from 45.85 % for Acartia erythraea and A. pacifica to 51.96 % for the harpacticoid Microsetella norvegica. The carbon content of Oithona berricornis, Oncea media and Corycaeus sp. was 49.51 % and 48.14 % respectively. For 128 organisms of Pontella mediterranea, Champalbert and Kerambrun (1979) recorded carbon concentrations between 40.6 and 46.0 %.

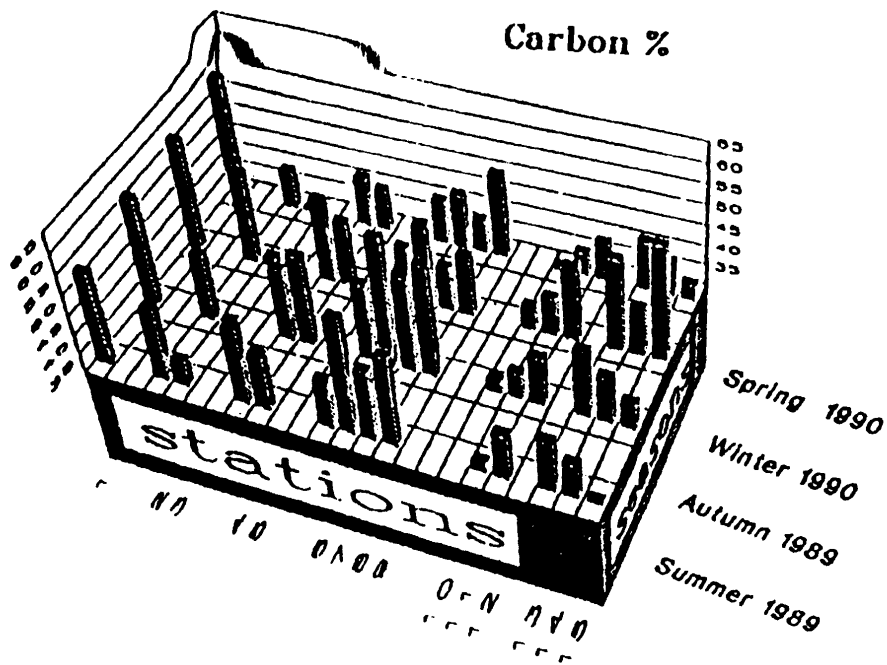


Figure 2: Carbon content (% of dry wt) of *E. acurifrons* in the coastal waters of Alexandria.

Table (1): Average carbon content (%) of *E. acurifrons* in the different regions of the coastal waters of Alexandria.

Location Season	AG	MX	WH	EH	AQ (TB)	AQ (MD)	Seasonal average
Summer, 1989	50.1	42.2	44.9	49.5	36.2	37.5	43.3 + 8.02
Autumn, 1989	48.6	38.7	48.2	55.6	37.0	41.1	44.9 + 9.45
Winter, 1990	51.1	42.5	46.5	44.7	41.4	44.6	45.1 + 6.90
Spring, 1990	54.8	35.5	40.3	43.4	35.4	38.2	41.3 + 7.73
Annual averag	51.2	39.8	45.0	48.3	37.5	40.4	43.7 + 1.80
S.D.	+ 2.6	+ 3.4	+ 3.4	+ 5.5	+ 2.7	+ 3.2	

* AG = AGAMI MX = MEX BAY WH = WESTERN HARBOUR
 EH = EASTERN HARBOUR AQ (TB) = ABU QIR/EL-TABIA SECTOR
 AQ(MD) = ABU QIR/EL-MAADIA SECTOR.

S.D. = Standard Deviation.

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The present investigation reveal an average carbon content for E. acutifrons of $43.7 \pm 1.80 \%$ (Table 1) of dry weight which is accepted for inshore tropical species and considered within the range recorded by most investigators.

Nitrogen content :

Available information on the nitrogen content of copepods, are scarce (Beers, 1966; Champalbert and Kerambrun, 1978; 1979; Hirota, 1981; Williams and Robins, 1982).

The present data revealed a nitrogen level (av. $5.6 \pm 0.97 \%$) which is at least one order magnitude lower than those recorded in other localities (Table 2). Comparatively, in this study, the nitrogen content of E. acutiforms covered the range between 2.0 % and 10.4 %. Such wide variation reflects the effects of LBS on decreasing of increasing the body contents of the organisms sampled opposite to the effluents. The lowest value i.e. 2.0 % was observed opposite of El-Tabia pumps in spring (Fig. 2). However, this season was characterized with a common low nitrogen contents in all sampled areas, leading to the lowest seasonal average i.e. 4.2 % (Table 2). Even the E.H. which normally showed the higher nitrogen levels during the study period (av. 6.2 ± 2.1), showed the lower average during the season i.e. 4.0 % (Table 2).

For the E.H., the mid harbour station generally recorded the highest values especially in summer and autumn (absolute maximum). Stations affected by the external sewage discharge from Kayet Bey pump station (st. 6) and that sampled in the ship anchorage (st. 9) normally showed high levels while st. 8 directly affected by sewage discharge inside the harbour recorded low values ranging between 3.2 % in spring and 8.7 % in autumn, respectively. Similar to Abu Qir Bay, the nitrogen levels of E. acutifrons increased seaward in Mex Bay, as the organism is apart from the direct discharge, reaching nearly half the value example: winter (Fig. 3).

It is interesting to note that the highest average recorded for the study area including the western station (Agam) ($6.4 \pm 0.89 \%$) are observed during winter 1990, except for the E.H. where the maximum average occurred during autumn i.e. $9.1 \pm 1.1 \%$. Williams and Robins (1982) measured nitrogen in Calanus helgolandicus collected from the Celtic Sea and observed levels around $10.89 \pm 0.73 \%$, $10.36 \pm 1.5 \%$ and $9.28 \pm 1.61 \%$ for fresh, frozen and fixed specimens. For Pontella mediterranea, Champalbert and Kerambrun (1979) reported an average nitrogen content of 11.4 %. Beers (1966) observed 9.62 % N (dry weight) in copepods and 7.83 % N in other crustaceans from samples collected from the Sargasso Sea. Among 4 species of copepods from The NW Mediterranean, Champalbert and Kerambrun (1978) found nitrogen concentrations ranging from 9.3 from 9.3 % N and 11.5 % N. For Inland Sea of Japan, Hirota (1981) reported nitrogen contents of different copepods varying between 9.78 % and 13.14 %.

Table (2): Average nitrogen content (%) of *E. acutifrons* in the different regions of the coastal waters of Alexandria.

Location Season	AG	MX	WH	EH	AQ (TB)	AQ (MD)	Seasonal average
Summer, 1989	6.5	5.0	5.3	6.3	5.2	5.6	5.7 + 0.91
Autumn, 1989	7.1	4.2	6.3	9.1	4.6	5.1	6.1 + 2.12
Winter, 1990	7.8	6.3	7.1	5.5	5.6	6.1	6.4 + 0.89
Spring, 1990	6.8	3.4	4.2	4.0	3.3	3.6	4.2 + 1.07
Annual average	7.1	4.7	5.7	6.2	4.7	5.1	5.6 + 0.97
S.D.	+ 0.6	+ 1.2	+ 1.3	+ 2.1	+ 1.0	+ 1.1	-

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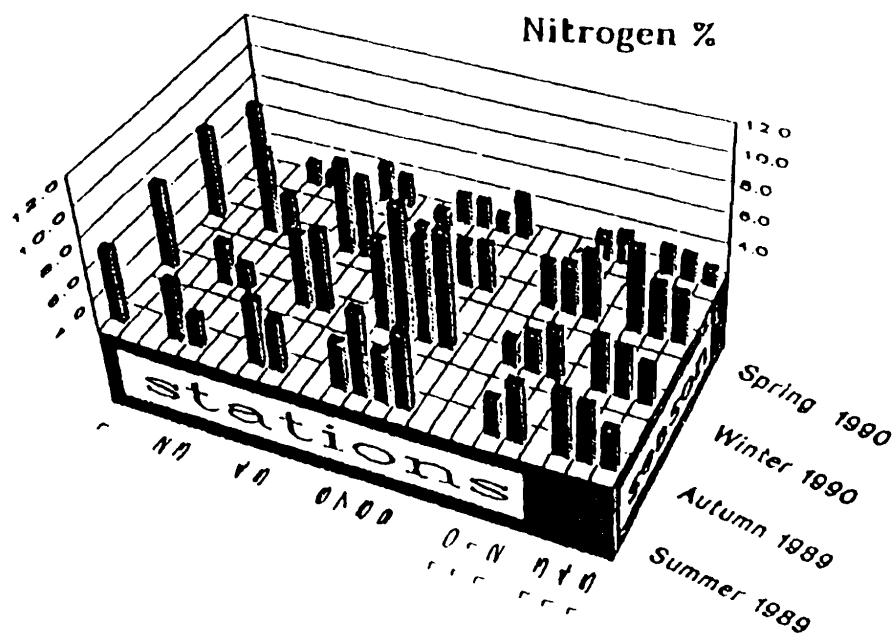


Figure 3: Nitrogen content % of dry wt. of *E. acutifrons* in the coastal waters of Alexandria

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The nitrogen content of the E.H. copepods is highly related to the chlorophyll a biomass of the harbour showing strong coincident peaks ($r = 0.9668, 9 < 0.001$). In other areas like W.H. (st. 4 and 5) and El-Maadia sector (station 13 to 15) a negative correlation was observed between chlorophyll a content and the nitrogen content of the copepod ($r = -0.5300, p < 0.1$ and $r = -0.1339$, insignificant) indicating that factors other than the available food regulates the nitrogen content of the organism.

Using the data for nitrogen content of the copepod in a relation with the nitrate content of water; it was clearly evident that a negative, not highly significant relationship exists. The general regression equation was:

$$N (\%) \text{ orgs.} = 6.145 + 1.00 + 0.0947 + 0.0467 \text{ NO}_3 (\mu\text{M})$$

with a regression coefficient of $-0.3985, p < 0.0153$. Regressions for different seasons showed insignificant differences, all showing an inverse relationship indicating the use of nitrate for Euterpina body nitrogen synthesis which appeared through a mediator i.e. Phytoplankton. The intercept in the equation indicates that the organism in addition to nitrate, depends on other sources in building up its body nitrogen. Ammonia, which was not measured by that time could be an additional and/or substitutional source. When nitrogen sufficient media prevails, indicated from the concentrations in water, the organism contained a consistent amount of nitrogen. However, the organism could suffer nitrogen starvation with a total decrease in cellular nitrogen, internal decrease of NO_3 and amino acids followed by a drastic reduction of protein and NO_3 normally used to sustain growth when nitrogen source is depleted, constituting the nitrogen store when N is plentiful (Dortch, 1982).

Phosphorus content :

The annual average concentration of content of Phosphorus *E. acutifrons* collected from the coastal waters of Alexandria was $0.34 + 0.06 \%$ (Table 3). A minimum value was recorded in spring at st. 10 (0.1%) opposite to the industrial outfall in Abu Qir Bay whereas the maximum value was observed at st.7 (E.H.) during autumn (0.64%) (Fig. 4). During summer and autumn the highest average values were recorded at the E.H. (0.38% and 0.57%), although in summer, nearly similar values were noticed at AG (0.37%) and Maadia sector of AQ (0.36%); (Table 3). Similar annual averages of phosphorus content (0.32%) were noticed at both Mex and W.H. stations (Table 4). The highest annual average of phosphorus $\%$ was recorded at AG ($0.46 + 0.09 \%$), whereas the two sectors of AQ Bay were represented by the lowest annual average values of phosphorus $\%$ which ranged from $0.27 + 0.07 \%$ to 0.29% + 0.09% (Table 3).

Generally, *E. acutifrons* collected from stations affected by direct discharge of industrial wastes showed remarkably low phosphorus contents especially at times of high discharge periods (st. 10, spring and st. 3, summer). However, the discharge of agricultural runoff from Lake Edku through Boughaz El-Maadia enriched with reactive phosphorus during Winter i.e. $2.767 \mu\text{M}$ and salinity 16.41% . Lead to a corresponding elevation in the phosphorus levels in *E. acutifrons* during this season. (0.34%) Sewage disposal to the E.H. seems

Table (3): Average phosphorus content (%) of *E. acutifrons* in the different regions of the coastal waters of Alexandria.

Location Season	AG	MX	WH	EH	AQ (TB)	AQ (MD)	Seasonal average
Summer, 1989	0.37	0.29	0.34	0.38	0.33	0.36	0.35 + 0.06
Autumn, 1989	0.40	0.36	0.28	0.57	0.26	0.28	0.36 + 0.13
Winter, 1990	0.51	0.43	0.42	0.31	0.31	0.34	0.39 + 0.08
Spring, 1990	0.55	0.19	0.23	0.22	0.17	0.16	0.75 + 0.11
Annual average	0.46	0.32	0.32	0.73	0.27	0.29	0.34 + 0.06
S.D.	+ 0.09	+ 0.10	+ 0.08	+ 0.15	+ 0.07	+ 0.09	

* AG = AGAMI MX = MEX BAY WH = WESTERN HARBOUR
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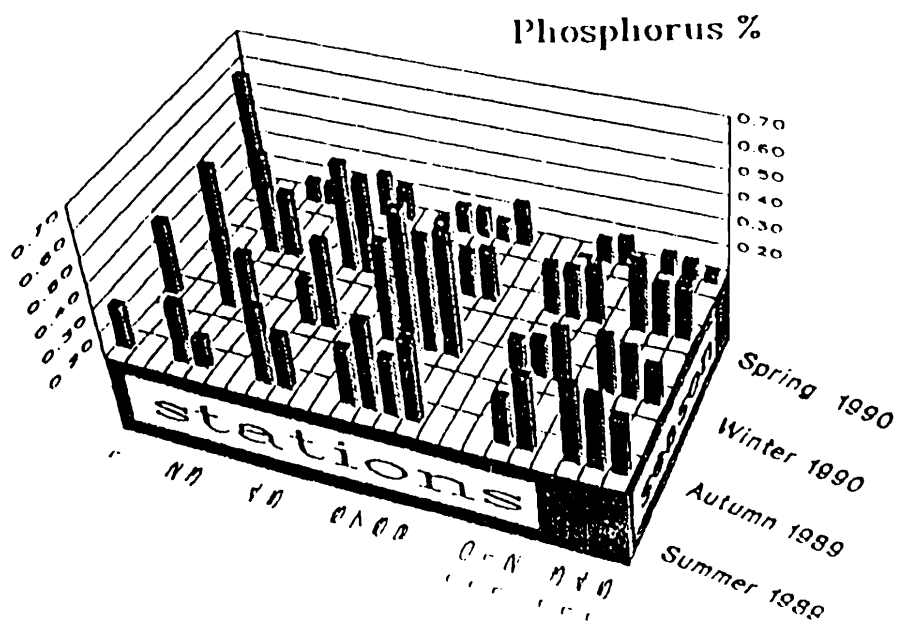


Figure 4: Phosphorus content (% of dry wt) of *E. acutifrons* in the coastal waters of Alexandria.

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generally to increase phosphorus levels in the organism as recognized from the highest annual average recorded at the harbour (0.37 %, Table 3), during the study period. In spite of this, maximum discharge periods are not accompanied by high P contents probably because most of the P is discharged in the organic form (Aboul-Kassim, 1987). It seems likely that the phosphorus content of the organism is slightly affected by reactive phosphorus concentration in water. A regression equation described such relationship. This relation though not highly significant was negative for both seasons. The general regression is :

$$P (\% \text{ dwt) orgs.} = 0.3467 + 0.094 - 0.0377 + 0.02 P \text{ water}(\mu\text{M})$$

$$(r = -0.1985, P < 0.063).$$

Similar to nitrogen, Euterpina use phosphorus in water through phytoplankton uptake to build body phosphorus, though still other sources like Dissolved Organic Phosphorus, (Dop) could be of considerable importance. DOP in the coastal waters of Alexandria constituted between 20 and 65 % (Aboui-Kassim, 1987). However, the phosphorus content of water is not only a factor of discharge but also of the amount of chlorophyll a (chosen as a phytoplankton biomass indicator) concentration.

Table (4): Average C/N ratio for *E. acutifrons* in the different regions of the coastal waters of Alexandria.

Location Season	AG	MX	WH	EH	AQ (TB)	AQ (MD)	Seasonal average
Summer, 1989	7.9	8.7	8.1	8.0	7.0	6.7	7.7 + 0.74
Autumn, 1989	7.4	7.0	7.0	6.1	8.1	8.1	7.3 + 0.80
Winter, 1990	6.9	6.7	6.3	8.2	7.4	7.3	7.1 + 0.70
Spring, 1990	8.6	10.6	9.3	11.0	11.6	10.7	10.3 + 1.10
Annual average	7.7 + 0.7	8.3 + 1.8	7.7 + 1.3	8.3 + 2.0	8.5 + 2.1	8.2 + 1.8	8.1 + 1.50

* AG = AGAMI MX = MEX BAY WH = WESTERN HARBOUR
 EH = EASTERN HARBOUR AQ (TB) = ABU QIR/EL-TABIA SECTOR
 AQ(MD) = ABU QIR/EL-MAADIA SECTOR.

S.D. = Standard Deviation.

Copepods sampled at st. 1 located at the Alexandria western coast, were characterized by high phosphorus content especially during winter and spring and to a lower extent in autumn (0.51 %, 0.55 % and 0.4 %, respectively).

Reactive phosphorus levels in this station were extremely low (range 0.08-0.32 μM), thus a negative relation between water phosphorus and organism phosphorus appeared ($r = -0.8802$, $P > 0.01$). On the other hand, a significantly positive relation ($r = 0.9525$, $P < 0.01$) appeared between the phosphorus content of the organisms and phytoplankton biomass in water. This condition indicates that despite the low phosphorus content of water, phytoplankton can assimilate these low concentrations, forming a phosphorus rich diet to copepods. Unavailable data on phytoplankton phosphorus content in the area make it impossible to reach a concise conclusion.

Hardstedt Romeo (1982) for the southern French coast, observed low phosphorus content in near shore planktonic samples which were mainly composed of phytoplankton and a relatively higher content for those were mainly composed of copepods and other crustaceans. However, Mayzaud and Martin (1975), for California current, noted a value of 0.59 % for phytoplankton whereas Beers (1966) in the Sargasso Sea, reported higher levels of phosphorus for copepods (0.79 %), for Euphausiacea (1.48 %) and for other crustacea (1.26 %). In the Liguro-Provencal basin Hardstedt-Romeo, (1982) recorded an average of 0.79 + 0.11 for the total zooplankton population for March 1980 samples.

As a general trend, apart from the low average recorded in spring, i.e. 0.25 % (Table 3), variations in the average values of the phosphorus content of *E. acutifrons* in the coastal waters are not significant (ranging from 0.35 to 0.39 %, Table 3). The low average in spring was mainly driven from low values located opposite to areas affected by industrial discharge (Abu Qir and Mex Bays). This decrease also corresponds with the decrease in P content of the copepod food. On the other hand, the N content of *Euterpina* also decreased during this time of the year (Fig. 4). Therefore it is possible that changes of the *Euterpina* N and P contents are caused by different grazed algae. Diatoms production was high as indicated from the high average chlorophyll a recorded during this season.

C/N, C/P and N/P ratios in *E. acutifrons* :

C/N ratio is frequently interpreted as a gross measure of condition because of its apparent connection with proportions of lipid and protein (Conover and Corner, 1968). C and N propionate levels reflect food quantity, production cycles and trophic level (Omori, 1970; Ikeda, 1974).

In general, in *E. acutifrons* the estimated C/N ratio in spring (av. 10.3 + 1.1) was higher than those estimated in other seasons which showed insignificant differences in between 7.7 + 0.74 (summer), 7.3 + 0.8 (autumn) and 7.1 + 0.7 (Winter), (Table 4).

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Seasonal trends of C/N does match the seasonal variations in chlorophyll a biomass ($r = -0.646$, $P < 0.01$). This could suggest that copepods could sustain themselves during periods of low phytoplankton production by feeding on detritus or microzooplankton. High C/N ratio followed to a some extent phytoplankton blooms while lower averages were observed before the bloom. In Sargasso, Sea, C/N ratio for copepods range from 5.0 to 3.8 (Beers, 1966). However, in contrast, Omori (1969) observed a fairly constant and low ratio throughout the year because of the uniformity of the environment.

Despite the variation in environmental impacts of different sampled areas, the annual average of C/N ration at the different localities showed insignificant variations (Table 4) ranging from 7.7 at both Agami and W.H. to 8.5 for El-Tabia sector. Highest averages of C/N ratio were recorded at El-Tabia sector (11.6) and E.H. (11.0) in spring.

Relative to Redfield et al., (1963), the C/N ratio observed in the present study, was remarkably higher than that expected for marine organisms. Omori (1969) found Calanus cristatus that when Copepodite V are healthy and large sized diatoms are abundant, they eat diatoms and store great reserves of fat in their bodies. As a result, the percentage of N decreases while the C/N ratio increases.

The high C/N values, which correspond to no measurable phytoplankton production, indicate that the energy requirements are met mainly from internal deposits (Tande and Hopkins, 1981).

The work of Gatten et al., (1979; 1980) and Tande (1982) supported the idea that despite the restricted external energy supply, mainly based on deficient particulate matter, copepods may to a large extent rely on internal lipid resources.

Recorded C/N ration for Acartia clausi collected from different areas near Marseille (Kerambrun, 1978) fluctuated from 3.22 to 3.80 with minimum values in summer and highest in winter. Carbon concentrations varied from 38.87 to 45.49% while nitrogen from 10.35 to 13.55 %. He calculated energy equivalents to range from 4.28 to 5.00 cal mg^{-1} DW, using carbon levels. Applying his conversion factor for E. acutifrons, the organism could have an average energy equivalents of 4.8 ± 0.2 cal mg^{-1} DW, (The same factor, i.e. 0.09 was recommended by Salonen et al., 1976; in case of negligible inorganic carbon).

Differences in the C/N ration reflects differences in the biochemical composition of the organism. Orr (1934) and Marshall et al., (1934) declared that different factors affect C/N ration of the organism. They classified these factors to internal (Like growth rate and reproduction condition) and external (Like geographic area and season). High C/N ration indicate that metabolism was oriented by lipid and/or carbohydrate synthesis rather than protein. This could be supported also by energy equivalent values which agreed with means reported in literature for non-lipidic species, but were far below those recorded for species which are able to store lipids. On the other hand, Calanus finmarchicus have equivalent energy values of 5.232 to 7.672 k cal g^{-1}

EFFECT OF SODIUM, IRON IONS ON MORPHOLOGY OF THE GYPSUM CRYSTALS.

illustrates the changes which occur in the crystal morphology after 48h of stirring. Figure (2) shows also the precipitation model by which the seeding of gypsum proceeds, whereas one crystal acts as nucleus for the following precipitated crystals. Figure (4) illustrates that the shift in diffraction angle attains its maximum value after 8 hours of continuous stirring after which a general tendency of decrease toward the ideal form of the gypsum. This can interpreted on basis of the crystal homogeneity after certain stirring time.

Na⁺ ion incorporation in the crystal-lattice of gypsum and its effect on crystal-lattice and - morphology:

The present study deals with the incorporation of Na⁺ ions into the crystal lattice of synthesized gypsum and the possibility of synthesis a series of intermediate solid phases between Thenardite Na₂ SO₄ and gypsum CaSO₄.2H₂O. Natural Thenardite forms under certain conditions of high temperature, high salinity, strong ionic exchange (Smykatz 1974), i.e. beginning with gypsum it is very difficult to attain complete replacement of Na⁺ ions in the sites of Ca⁺⁺ ions under normal conditions of laboratory. The ions of alkali metals are loosely hydrated, thus the full replacement of Na⁺ ions to replace Ca⁺⁺ ions completely in the crystal of gypsum is limited Luder et al. (1965).

In the present investigation it could be seen that one can obtain a series of solid phases of gypsum containing Na⁺ with different concentrations ranging from 4.2 to 19.04% Table (1).

Table (1): Effect of Na⁺ ion incorporated into gypsum crystals.

Sample No.	Conc. of NaCl add (M)	Percent of Na ⁺ incorporated in the gypsum crystal %	Na/Ca Molar	20 d-spacing
1	0.01	4.20	0.0438	11.7 7.5571
2	0.05	8.50	0.0924	--
3	0.10	15.81	0.1880	11.85 --
4	0.15	17.98	0.2190	11.7 7.4305
5	0.20	19.04	0.2350	11.8 7.4555
6	0.40	11.75	0.1300	11.7 7.4932
7	0.50	8.50	0.0920	11.66 7.4305

Figure (5) illustrates the shift in d-spacing as result of Na⁺ incorporation into the gypsum crystal lattice. It has been found that the allowed minimum concentration of Na⁺ as impurities in the synthesis of gypsum must not exceeds 4% to obtain ideal gypsum. Figure (6) reveals the shift in the diffraction angle as result of Na⁺ ion incorporation into crystal lattice of gypsum. Figure (7) shows the relation between NaCl added (M) and Na/Ca molar ratio, whereas this ratio attains its maximum (0.235) when NaCl added is 0.2 M, after which

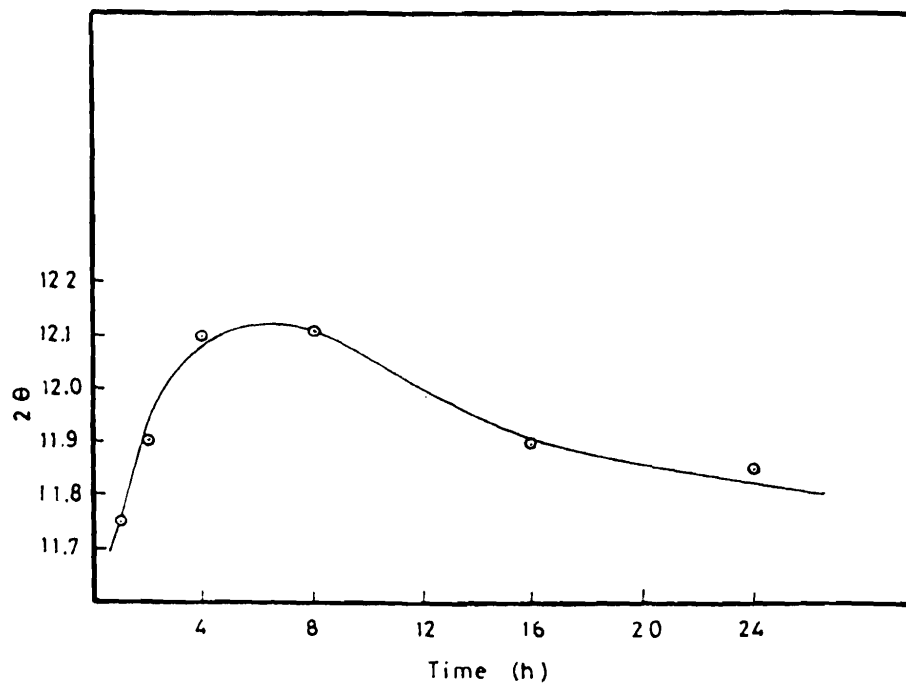


Figure 4. Effect of stirring time on the diffraction angle of (020) in gypsum crystals.

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Table (5): Average C/P ratio for E. acutifrons in the different regions of the coastal waters of Alexandria.

Location Season	AG	MX	WH	EH	AQ (TB)	AQ (MD)	Seasonal average
Summer, 1989	190.7	152.0	130.2	133.4	110.8	103.0	136.7 + 31.7
Autumn, 1989	145.4	106.3	143.9	97.7	141.2	145.4	130.0 + 21.9
Winter, 1990	140.5	97.5	96.0	144.0	134.5	132.0	124.1 + 21.6
Spring, 1990	102.2	186.0	159.5	200.6	228.5	234.6	185.3 + 49.2
Annual average	144.7	135.6	132.4	143.9	153.8	153.7	144.0 + 28.9
S.D.	+ 36.2	+ 41.6	+ 27.1	+ 42.7	+ 51.5	+ 56.8	

* AG = AGAMI MX = MEX BAY WH = WESTERN HARBOUR
 EH = EASTERN HARBOUR AQ (TB) = ABU QIR/EL-TABIA SECTOR
 AQ(MD) = ABU QIR/EL-MAADIA SECTOR.

S.D. = Standard Deviation.

Table (6): Average N/P ratio for E. acutifrons in the different regions of the coastal waters of Alexandria.

Location Season	AG	MX	WH	EH	AQ (TB)	AQ (MD)	Seasonal average
Summer, 1989	24.3	17.6	16.1	16.7	15.8	15.6	17.7 + 3.3
Autumn, 1989	19.7	11.6	20.4	16.0	17.5	18.0	17.2 + 3.2
Winter, 1990	20.2	14.5	15.5	17.6	18.2	18.0	17.3 + 2.0
Spring, 1990	11.9	17.6	17.2	18.3	19.7	21.9	17.8 + 3.3
Annual average	19.0	15.3	17.3	17.2	17.8	18.4	17.5 + 1.3
S.D.	+ 5.2	+ 2.9	+ 2.2	+ 1.0	+ 2.6	+ 2.6	

* AG = AGAMI MX = MEX BAY WH = WESTERN HARBOUR
 EH = EASTERN HARBOUR AQ (TB) = ABU QIR/EL-TABIA SECTOR
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In general, the changes of the copepod N/P ratio is mainly due to whether or not nutrients in certain area limits the phytoplankton growth, the main copepod food. In the present study, though N/P ratios in phytoplankton are not available, a statistical significant relationship appeared between N/P ratios in both water and organism ($r = 0.7655$, $P < 0.001$).

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PHYTOPLANKTON PRODUCTION, DIVERSITY AND CHLOROPHYLL-A
IN THE SUEZ CANAL, EGYPT.

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Key Words: Phytoplankton, Diversity, Biomass, Productivity, Suez Canal.

ABSTRACT

Qualitative and quantitative estimations of phytoplankton and its diversity, beside determination of chlorophyll-a, phytoplankton biomass, gross primary production and dissolved oxygen of the Suez Canal were carried out during the four seasons of 1991. The samples were taken from 15 stations along the Canal and they were further grouped into three regions, namely; Port-Said, Ismailia and El-Suez.

A total of 139 species and varieties were identified from the different samples, of them, 94 species and varieties representing 40 genera belong to diatoms and 36 species within 11 genera belong to dinoflagellates. The highest number of species (100) were recorded from El-Suez region, followed by Port-Said and Ismailia respectively (97 & 90 species). Most species and varieties were wide spread through the canal except of 13, 8 and 15 species which were confined to Port-Said, Ismailia and El-Suez respectively, where these species were recorded in Mediterranean, Red Sea and Lake Manzalah. It was found that at least 13 species of Red Sea origin have crossed the canal northward to Port-Said, while many species have immigrated south to El-Suez.

Quantitatively, the standing crop was numerically much higher at Ismailia region (average 25,380 units L^{-1}) than Port-Said and El-Suez regions (18,883 and 4,767 units L^{-1} respectively). The highest counts of phytoplankton were recorded at St.6 (39×10^3 Units L^{-1}) and it decreased towards both the south and north except of a remarkable increase noticed at St.1. The minimal value was recorded at St 13 (2.8×10^3 units L^{-1}). The annual average of the total phytoplankton counts amounted to 16,342 units L^{-1} . Also, the standing crop attained its highest density during winter (average 41,658 units L^{-1}) in all regions, with its maximum at Ismailia (59,584 units L^{-1}) and Port-Said

(50,372 units L⁻¹) while its minimum was recorded at El-Suez (15,034 units L⁻¹). In all regions, diatoms constituted more than 97% by number of the standing crop.

The concentration of chlorophyll-a, phytoplankton biomass, gross primary production and dissolved oxygen amounted with averages 1.95 mg m⁻³, 0.146 mgC L⁻¹, 2.936 ml O₂ L⁻¹ 8 hr⁻¹ and 4.1 ml O₂ L⁻¹ respectively in the Suez Canal and they showed the same regional and seasonal trend of the phytoplankton standing crop.

The relatively low numbers of species and low standing crop of phytoplankton numerically and its biomass after reopening the Suez Canal for navigation is attributed to the fact that the water is always turbid and slightly polluted as supported by the results of diversity (average 1.8) in the present investigation.

INTRODUCTION

The Suez Canal lies between longitudes 32° 20' and 32° 35' E, and between latitudes 29° 55' and 31° 15' N. It is a passage between the Mediterranean Sea at Port-Said and Red Sea at Port-Taufiq. The Canal was opened in 1869 with 162 Km length, recently increased to 195 Km including Lake Timsah, the Great Bitter Lake and Little Bitter Lake through which the canal passes. Also, the canal is connected at Port-Said with Lake Manzalah .

Little work has been done on the phytoplankton of the Suez Canal, and this was confined to the preliminary reports of Macdonald (1933) and Ghazzawi (1939), while Dowidar (1976) studied the phytoplankton community in the Canal during July, 1969 and February, 1970 when the canal was closed against navigation.

For the lack of any particular study on the Suez Canal plankton during the last 20 years and after its promotion and reopening in 1985 for navigation, the present investigation was necessary to deal with the phytoplankton community, chlorophyll-a Biomass, gross primary production and population diversity.

MATERIAL AND METHODS

Through the period from June to December, 1991 four trips were carried out in the Suez Canal, representing four seasons, namely; spring (June), summer (August), autumn (October) and winter (December).

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The samples were taken from 15 stations along the Canal. These stations were further grouped into three main regions as follows: I Port-Said region (stations 1-5) and it comprises stations (1) Deleceps, (2) 22- Hectometer, (3) Ras El-Esh, (4) El-Cap and (5) El-Ballah. II- Ismailia region (stations 6-10) which comprises stations (6) Lake Timsah, (7) East-Defersoir, (8) West-Defersoir, (9) East-Fayed, (10) West-Fayed. III- El-Suez region (Stations 11-15) and it includes stations (11) 1-Kabret, (12) 2-Kabret, (13) Genefa, (14) 2-Port Taufiq and (15) 1-Port Taufiq. (Fig. 1).

Samples used for determination of dissolved oxygen were fixed immediately after collection and analysed in the laboratory; according to the classical Winkler technique (Strickland and Parsons, 1965) and the results were given in ml O₂ L⁻¹. Gross primary production was determined as oxygen production according to the light and dark bottle method (Strickland and Parsons, 1968). In situ measurements were carried out by exposing the glass bottles containing the water samples just below the surface water in the canal for 8 hours (from 8 a.m to 4 p.m.). The data were expressed as ml O₂ L⁻¹ and ml O₂ L⁻¹ 8 hr⁻¹. Chlorophyll-a was determined spectrophotometrically after extraction of the studied samples with 90% acetone solution and expressed in mg m⁻³ according to the method described by Strickland and Parsons (1972). The phytoplankton biomass was tentatively calculated in ug C L⁻¹ by multiplying chlorophyll-a content by factor 75 as given by Holm-Hansen (1973). Estimation of the phytoplankton standing crop was carried out by using the sedimentation method and the different species were calculated as their total number per liter (units L⁻¹). Diversity index of the phytoplankton community was calculated on computer according to the equation of Shannon-Wiener (Shannon & Weaver, 1963), using primer program.

RESULTS

Community Composition of Phytoplankton:

The phytoplankton community in the Suez Canal was rich in the numbers of species but showed moderate density. Altogether, about 139 species and varieties were recorded, included 94 diatom species and varieties representing 40 genera, 36 dinoflagellates including 11 genera, one species of silicoflagellates, 3 species of chlorophytes belonging to 3 genera and 5 species within 4 genera of cyanophytes.

As shown in Table (1), the community composition appeared more or less similar in the three regions except of 13, 8 and 15 species which were confined to Port-Said, Ismailia and El-Suez regions respectively.

The phytoplankton population of Port-Said region comprised 97 species and varieties forming 69.8 % to the total number of species recorded in the Canal. The diatoms constituted 73.2 % of the total number of species. Most of them

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Table (1). Distribution of phytoplankton species recorded from the Suez Canal during 1991.

A: Species recorded along the Suez Canal.
 B: Species recorded from each region .
 C: Species only recorded at each region.

PS, SI, IP : Species recorded as share between two regions.

Phytoplankton	A			P			I			S		
	B	C	PI	B	C	IS	B	C	IS	B	C	SP
Diatoms	71	9	47	60	2	48	70	9	54			
Dinoflagellates	36	3	16	27	4	18	25	4	13			
Silicoflagellates	1	--	--	--	--	--	1	--	1			
Green Algae	3	1	--	--	--	--	2	1	1			
Blue Green algae	5	--	1	3	2	--	2	1	1			
Total No. of species	139	97	13	64	8	66	100	15	70			

P: Port-Said I: Ismailia S: El-Suez.

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belong to the Mediterranean flora, which have been previously recorded by Dowidar (1976) in the same area beside the two Indopacific species Coscinodiscus gigas and Ceratium egyptiacum which have been previously reported in Port-Said and/or off Alexandria (Dowidar, 1965; 1971 & Halim, 1970) and in the same region (Dowidar, 1976). These 2 species are immigrants into the Mediterranean through the Suez Canal.

Thirteen species were confined to Port-Said region, namely; Coscinodiscus radiatus, Surirella striatula, Gomphonema gracile, Mastogloia elliptica, Cosinodiscus gigas, Surirella gemma, Chaetoceros densum, Thalassiothrix longissima, Streptotheca thamenis, Ceratium pulchellum var euphcellum, C. pulchellum var. tripodioides, Dinophysis caudata and Coelastrum microporum. The first 4 species and the latter one were recorded in Lake Manzalah (El-Sherif et al., 1993) and the other species were recorded in the Mediterranean (Dowidar, 1974) except Streptotheca thamenis which appeared in Red Sea (Halim, 1969).

Other species of brackish affinities were also recorded in Port-Said region as Crucigenia tetrapedia, Spirulina laxissima, S. platensis, Cocconcis placentula, Pleurosigma elongatum, Chaetoceros affinis, Synedra ulna, Melosira granulata, Cyclotella meneghiniana, Amphiprora paludosa, Hyalodiscus laevis, Nitzschia spp and Navicula cryptocephala all of them were recorded in the adjacent brackish water Lake Manzalah (El-Sherif et al., 1993) and were transported to Port-Said region. A total of 66% of the species estimated in this region was also recorded in Ismailia sector (Table 1).

The community composition of phytoplankton at Ismailia region was relatively lower than that of the other two regions. A total of 90 species and varieties were enumerated forming 64.7 % of the total number of species recorded in the Canal. Of these, the diatoms were represented by 60 species [forming about 66.7 % of the total population]. A total of 73.3% of the species present in this region was also recorded in El-Suez (Table 1). Eight species were confined to this region, namely; Biddulphia alternans, Rhizosolenia styliiformis, Ceratium karsteni, Noctiluca milaris, Peridinium leosis, P. portus-orientalis, Oscillatoria limnetica and Gomphosphaeria aponiana, all of them were previously recorded in the Mediterranean (Dowidar, 1974) except the latter two species which are considered as fresh forms. While, the species from the second to the fifth were also recorded in the Red Sea (Halim, 1969).

At El-Suez region, 100 species and varieties were recorded, representing about 72% of the total species estimated in the Canal. Diatoms were represented by 70 species and varieties.

About 15 species were confined to this region, being absent from Port-Said and Ismailia regions (Table 1), namely; Bacillaria paradoxa, Cosinodiscus oculus-irdis, Nitzschia panduriformis, Biddulphia laevis, B. mobiliensis, B. aurita, Synedra undulata, Epithemia zebra, Rhopalodia gibba, Pediastrum tetras, Oscillatoria tenuis, Exuviella opora, Ceratium longirostrum, C. extensum and

Goniaulax spinifera. The first species and the latter two ones were recorded in both the Red Sea (Halim, 1969) and the Mediterranean (Dowidar, 1974). The rest of the recorded species were also observed in the Mediterranean Sea except

PHYTOPLANKTON IN THE SUEZ CANAL, EGYPT.

The samples were taken from 15 stations along the Canal. These stations were further grouped into three main regions as follows: I Port-Said region (stations 1-5) and it comprises stations (1) Deleceps, (2) 22- Hectometer, (3) Ras El-Esh, (4) El-Cap and (5) El-Ballah. II- Ismailia region (stations 6-10) which comprises stations (6) Lake Timsah, (7) East-Defersoir, (8) West-Defersoir, (9) East-Payed, (10) West-Payed. III- El-Suez region (Stations 11-15) and it includes stations (11) 1-Kabret, (12) 2-Kabret, (13) Genefa, (14) 2-Port Taufiq and (15) 1-Port Taufiq. (Fig. 1).

Samples used for determination of dissolved oxygen were fixed immediately after collection and analysed in the laboratory; according to the classical Winkler technique (Strickland and Parsons, 1965) and the results were given in $\text{ml O}_2 \text{ L}^{-1}$. Gross primary production was determined as oxygen production according to the light and dark bottle method (Strickland and Parsons, 1968). In situ measurements were carried out by exposing the glass bottles containing the water samples just below the surface water in the canal for 8 hours (from 8 a.m to 4 p.m.). The data were expressed as $\text{ml O}_2 \text{ L}^{-1}$ and $\text{ml O}_2 \text{ L}^{-1} \text{ hr}^{-1}$. Chlorophyll-a was determined spectrophotometrically after extraction of the studied samples with 90% acetone solution and expressed in mg m^{-3} according to the method described by Strickland and Parsons (1972). The phytoplankton biomass was tentatively calculated in ug C L^{-1} by multiplying chlorophyll-a content by factor 75 as given by Holm-Hansen (1973). Estimation of the phytoplankton standing crop was carried out by using the sedimentation method and the different species were calculated as their total number per liter (units L^{-1}). Diversity index of the phytoplankton community was calculated on computer according to the equation of Shannon-Wiener (Shannon & Weaver, 1963), using primer program.

RESULTS

Community Composition of Phytoplankton:

The phytoplankton community in the Suez Canal was rich in the numbers of species but showed moderate density. Altogether, about 139 species and varieties were recorded, included 94 diatom species and varieties representing 40 genera, 36 dinoflagellates including 11 genera, one species of silicoflagellates, 3 species of chlorophytes belonging to 3 genera and 5 species within 4 genera of cyanophytes.

As shown in Table (1), the community composition appeared more or less similar in the three regions except of 13, 8 and 15 species which were confined to Port-Said, Ismailia and El-Suez regions respectively.

The phytoplankton population of Port-Said region comprised 97 species and varieties forming 69.8 % to the total number of species recorded in the Canal. The diatoms constituted 73.2 % of the total number of species. Most of them

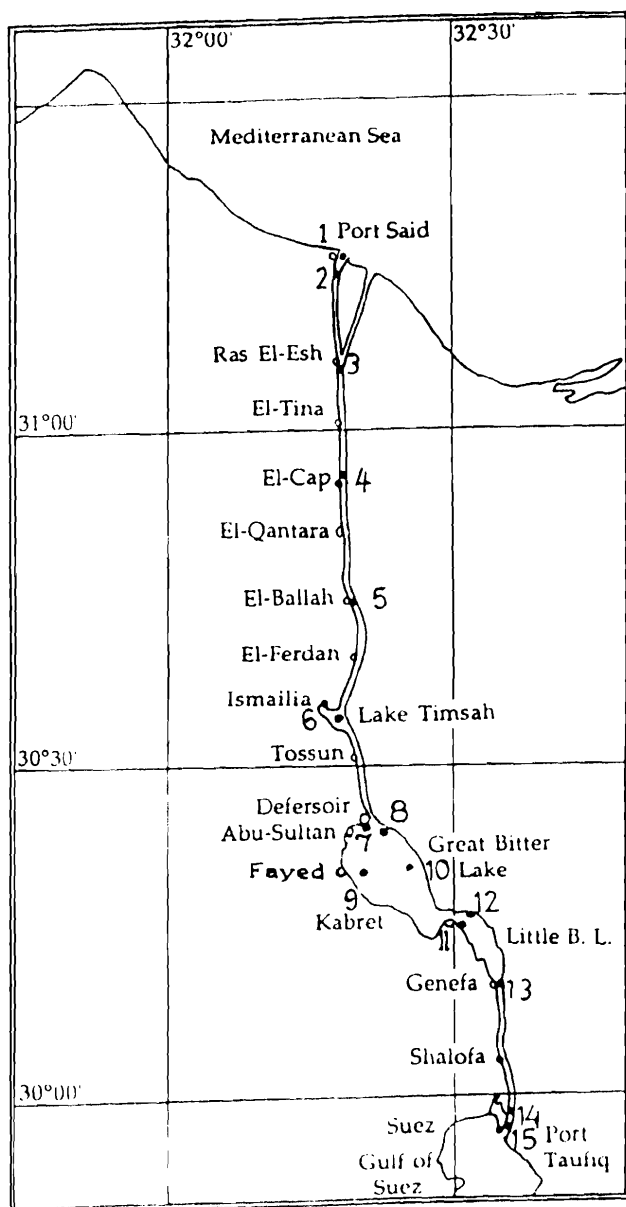


Figure 1 : Sampling stations along the Suez Canal.(•)