

**NITROGEN AND PHOSPHORUS FORMS IN ALEXANDRIA
WESTERN HARBOUR**

By

R. B. NESSIM

National Institute of Oceanography and Fisheries, Alexandria, Egypt.

Key words :Nitrogen and Phosphorus ratio. Alexandria, Mediterranean Sea.

ABSTRACT

The present paper reports the variations of five forms of Nitrogen and Phosphorus in Alexandria western harbour water. These nutrient fractions include dissolved organic as well as inorganic and particulate compounds in addition to total dissolved and non dissolved forms.

The mean annual ratios for the different N-Forms to the total N-content are more or less identical to those corresponding P. The dissolved inorganic/total average ratio is nearly 1:5; while that of organic/total element is 1:2.

The most abundant fraction of total N or P is the total dissolved form, being about 2/3 of the total average content. The particulate part/total ratio did not exceed 1/3.

The N/P mean ratios for the different forms are around 50: 1; indicating that P was the potentially most limiting nutrient for phytoplankton biomass production in the harbour water.

INTRODUCTION

Inspite of the low concentrations of inorganic and organic Nitrogen forms in sea water when compared with the dissolved molecular gas (10 %), still these forms are extremely important (Martin, 1970). With respect to dissolved inorganic forms (DIN); Nitrate, Nitrite and Ammonia are the most important N-compounds in the sea water in addition to very small amounts of DIN constituents such as nitrous oxide, hydroxylamine and hyponitrite ions may be found.

A great number of nitrogenous organic compounds either dissolved or non dissolved, (particulate), could also be present. According to Eppley *et al.*, 1973, nearly half of the Nitrogen excreted by zooplankton was in the form of urea. Uptake of urea by natural phytoplankton population is well established by McCarthy (1971, 1972) and Carpentar *et al.* (1972 a,b).

Phosphorus is one of the most important nutrients. This element is taken up by phytoplankton and enters the food chain in the sea. After death and decomposition of organisms and plants a portion of this P is returned to the water.

Inorganic phosphate exists in the sea as ions, orthophosphoric acid. About 10% is present as $(PO)_4^{-3}$ ions and practically all remaining phosphate as $(HPQ)^{-2}$ ions. Diphosphoric acid $H_4P_2O_7$ and all polyphosphoric acid are due to pollution of detergents in the coastal waters.

Organic Phosphorus such as phospholipids, sugar phosphate and aminophosphoric acid are produced in the surface water from excretion or decomposition of organisms (Kittredge *et al.*, 1969).

The present work is an attempt to compute the temporary and spatial variations of the different forms of both Nitrogen and Phosphorus in Alexandria western harbour water, their interrelationships, ratios deviation and limitation when compared with oceanic condition.

MATERIAL AND METHODS

The most important harbour of Egypt is the Alexandria western harbour (WH). The harbour has an area of 31 Km² with a maximum depth of 16 m and connected to the sea through El-Boughaz opening. Its basin receives about 6×10^6 m³ d⁻¹ of untreated industrial, agricultural and domestic effluents. It is divided to two parts; inner and outer Harbour (Fig. 1).

Water samples were taken at eight stations representing the different regions of the harbour using a plastic Ruttner water sampler. Samples were collected monthly at surface, 5m depth and near bottom during the year 1989.

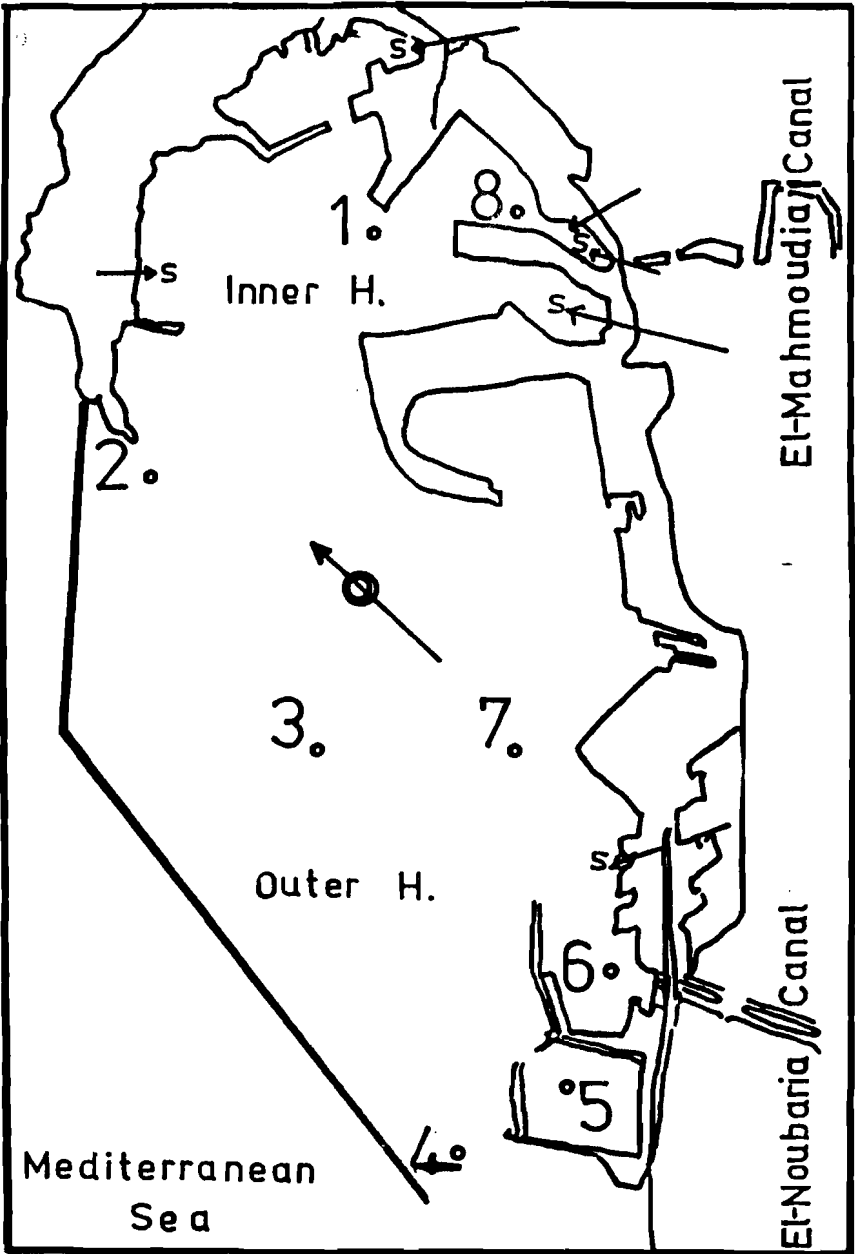


Fig.1. Alexandria Western Harbour; Sampling Locations & Sewers (s).

Nessim, R. B.

For the nutrient determinations, samples were immediately filtered after collection using GF/C Whatman Filter paper (4,7 cm). Filtered and non filtered water samples were analyzed spectrophotometrically according to the oceanographical recent methods described by Strickland & Parsons (1972) and Grasshoff (1976) using a Shimadzu double beam Spectrophotometer UV - 150-02 as follows:

a) Nitrogen forms

Dissolved inorganic Nitrogen (DIN) was calculated by the summation of the different inorganic Nitrogen forms according to Grasshoff (1976):

$$\text{DIN - N} = \text{NO}_3\text{-N} + \text{NO}_2\text{-N} + \text{NH}_3\text{-N}$$

Total Nitrogen (TN) was determined according to the method described by Koroleff (1977), modified by Valderrama (1981). The samples were oxidized by ($\text{K}_2\text{S}_2\text{O}_8$ + Boric acid + Na OH) solution for 30 minutes at 110 - 115°C in a pressure cooker. Thus all Nitrogen compounds become oxidized to nitrate and determined according to Grasshoff (1976).

Total dissolved Nitrogen (TDN) was determined using the same method described for TN but on filtered samples.

Dissolved organic Nitrogen (DON) was calculated by subtraction where :

$$\text{DON-N} = \text{TDN-N} - \text{DIN-N}$$

While particulate Nitrogen was calculated by subtraction

where :

$$\text{PN-N} = \text{TN-N} - \text{TDN-N}$$

b) Phosphorus forms :

Dissolved, reactive, inorganic Phosphorus (DIP) was determined by the molybdate method. Total Phosphorus (TP) was analyzed on unfiltered samples. Digestion was performed using the persulphate procedure (ICES, 1972). The reactive Phosphorus thus resulted was determined by molybdate method. Total dissolved Phosphorus was determined on filtered samples. Digestion and measurement were the same as those used for TP.

Dissolved organic Phosphorus (DOP) was calculated by subtraction where:

$$\text{DOP-P} = \text{TDP-P} - \text{DIP-P}$$

Particulate Phosphorus (PP) was calculated as follows :

$$\text{PP-P} = \text{TP-P} - \text{TDP-P}$$

RESULTS AND DISCUSSION

Nitrogen forms:

1) Dissolved inorganic Nitrogen (DIN)

The DIN content in the harbour water is relatively high (0.26 - 61.62 μM) with an annual average of 10.61 μM which represents 30 % of TDN or 1/5 of T/N. With respect to annual means most of the studied localities gave moderate values with a narrow range (5.31 - 9.02 μM), stations 7 & 8, on the other hand, showed high averages (> 20 μM).

The surface water, in general, was enriched with DIN most of the year when compared with the bottom one. This situation was reversed in June and to a less extent in August as a result of nutrient exhaustion by phytoplankton bloom occurred in the upper surface water.

i) NO_2 - N

It is the minor form of DIN; comprising 8.5 % of TDN and 1.4 % of TN. The mean value of NO_2 -N in the harbour water amounted to 0.73 μM . Maximum concentration of 5.60 μM , detected in the surface water at st. 8 during February associated with low salinity (< 37 ‰), low dissolved oxygen, low chlorophyll-a, low transparency and high ammonia content suggesting the input of nitrite in sewage (Zaghloul and Nessim, 1991).

A significant correlation between nitrite and nitrate ($r = 0.4591$, $p < 0.001$) was detected, more significant correlation coefficient was found during spring-summer period ($r = 0.6489$, $p < 0.001$). A less significant correlation, on the other hand, was found between nitrite and ammonia ($r = 0.2566$, $p < 0.001$) indicating that nitrate reduction rather than ammonia oxidation is the main source of nitrite in the harbour water. Similar condition was recorded in the Alexandria eastern harbour (Aboul-Kassim, 1987).

ii) NH₃-N

Ammonia is the most abundant form of DIN, comprises 50.7 %, 15.2 % of TDN or 10 % of TN. The ammonia/DIN ratio showed wide fluctuations (1.9 - 88.5 %); March represents the lowest while August the highest. High averages were found at st. 8 (14-18 uM), away from outfalls the averages were relatively low (< 5uM). The overall mean of 5.38 uM is higher than that recorded in the eastern harbour (Aboul-Kassim, 1987).

It seems that only the surface water layer near the outfalls was markedly subjected to the effect of effluents, a sudden drop in the ammonia content downwards at st. 8 was observed during October starting from 48.63 uM at the surface, decreasing to 8.81 at 5m. depth, with undetectable amounts of ammonia found at the bottom water.

An inverse significant correlation between ammonia and salinity ($r = - 0.2753$, $p < 0.001$) confirms the allochthonous origin of ammonia in the harbour water.

According to Wafar *et al.*, 1986, ammonia has been realized as important alternative N source for aquatic plants and may be assimilated in preference to nitrate. Complete exhaustion of ions by phytoplankton during the blooming spring months was observed at several localities.

iii) NO₃ -N

Nitrate comprises 42.6 % of DIN, 12.8 % of TDN or 8.7 % of TN. Contrary to ammonia condition, NO₃/DIN average ratio reached its maximum in March and minimum in August, being 86.8 and 9.8 % respectively. The relative low NO₃-N content noticed in the surface water during warm months may be attributed to the increase in ions uptake by phytoplankton (Zentara & Kamykowski, 1977). The nitrate reduction process may also affect its amount in the bottom water (Calvert & Price, 1971). Further more the accumulation of high organic matter in the vicinity of sewers decomposes utilizing nitrate oxygen (Dugdale *et al.*, 1977).

2) Dissolved organic Nitrogen (DON)

DON is the most abundant form of TDN in the harbour water comprising nearly 70 %. It is evident that most of dissolved Nitrogen or nearly half of the total Nitrogen is found in dissolved organic form.

Aminoacids are used as Nitrogen source by several marine phytoplankton (Fisher & Cowdell, 1982). However, the bulk of DON which exhibits the major fraction of TDN is not usable by phytoplankton assimilation. This fact is also shown in the western harbour from the weak correlation calculated between DON with chlorophyll-a content ($r= 0.1529$, $p< 0.001$).

The rate of decomposition of organic matter is increased as temperature rise, a good correlation was found between DON with water temperature ($r = 0.6190$, $p< 0.001$). High values of DON were consequently occurred in warm months due to the high phytoplankton crop as well as increased rate of decomposition of organic remains being 55.43 μM in May which is in agreement with the finding of Ruttner, 1968, Riley & Chester, 1971. Winter average, on the other hand, was relatively low ($< 10 \mu\text{M}$).

Regional averages showed a narrow range for most stations (20.62 - 25.14 μM), the inner harbour localities 1 & 8 gave higher averages ($> 30 \mu\text{M}$). With respect to annual average, a downwards decrease in DON content was recorded in the studied area (Table 1).

Comparing with the average of 11.87 μM in the eastern harbour (Aboul-Kassimj, 1987), the western harbour average of 24.72 μM is too high. The great amounts of DON detected at st. 8 during May up to 100 μM , were probably due to that most of DON represents the end product which is very resistant to further decomposition.

3) Total dissolved Nitrogen (TDN)

The TDN is the predominant fraction of TN. The annual average ratio of TDN/TN was nearly constant in the water column being around 68 %. A noticeable decrease in this ratio seawards was detected, starting from 76 % at st. 8 in the inner harbour, 70 % in the middle area to 66 % at El-Boughaz area. This explain the nature of the different effluent discharge into this basin. The amount of soluble Nitrogen compounds (organic + inorganic) brought by sewage in the inner part of the harbour is higher than that in drainage water received from outside of the harbour. The concentration of TDN in the harbour showed large scale variations (6.19 - 140-52 μM) with an annual average of 35.30 μM .

With respect to monthly variation, May average was the highest, being 61.97 μM , the rest of monthly data gave relative narrow range, 24.03 - 37.81 μM . The average as well as the values of TDN showed, in general, a decrease downwards (Table 1). TDN reflected also regional variations particularly in the surface water layer, stations 1,7 & 8 gave high averages, (40 - 80 μM), while the rest of localities averages were found below 40 μM .

Table (1) : Averages of K & P forms (u M) in Alexandria Western Harbour during the year 1989.

St. No.	Depth (m)	K							P				
		MO2	MO3	MO3	DOM	TD	PH	TM	DIP	DOP	TDP	PP	TP
St. No. 1	0	0.66	2.90	4.20	35.32	43.08	21.09	64.17	0.56	1.67	2.23	1.79	4.02
	5	0.73	3.23	5.57	30.81	40.34	11.78	52.12	0.42	1.07	1.49	0.92	2.41
0	b	0.52	4.43	4.80	25.34	35.09	12.21	47.27	0.43	0.99	1.42	0.66	2.08
	0	0.59	3.25	2.50	24.21	30.55	18.65	49.20	0.55	0.98	1.53	1.13	2.66
2	5	0.63	3.56	4.48	18.94	27.61	13.32	40.93	0.45	0.88	1.33	0.76	2.09
	b	0.54	4.36	5.01	16.33	26.24	13.81	40.05	0.48	1.00	1.48	0.60	2.08
3	0	0.65	3.04	4.10	28.49	36.28	13.76	50.04	0.74	0.96	1.70	1.21	2.91
	5	0.70	2.48	5.13	19.99	28.30	11.15	39.45	0.78	0.96	1.44	0.62	2.06
4	b	0.49	3.16	2.90	17.90	24.45	12.84	37.29	0.20	0.80	1.00	0.62	1.62
	0	0.96	4.16	3.90	23.52	32.54	20.60	53.14	0.83	1.12	1.95	1.59	3.54
5	5	1.10	3.23	5.08	18.88	28.29	14.65	42.94	0.46	0.96	1.42	0.67	2.09
	b	0.55	2.12	2.70	15.33	20.70	7.18	27.88	0.39	0.93	1.32	0.51	1.83
6	0	0.66	2.72	3.70	25.84	32.92	18.15	51.07	0.52	1.20	1.72	1.03	2.75
	5	1.17	3.32	3.03	17.51	25.03	18.97	44.00	0.23	0.92	1.15	0.64	1.79
7	b	0.68	3.59	2.40	13.33	20.00	18.44	38.44	0.22	0.76	0.98	0.53	1.51
	0	0.75	2.90	4.50	29.60	37.75	24.73	62.48	0.43	1.40	1.83	1.61	3.46
8	5	0.67	3.21	4.62	23.24	31.74	16.84	48.58	0.46	0.99	1.45	0.92	2.37
	b	0.63	4.11	5.30	16.70	26.74	17.76	44.50	0.30	1.14	1.44	0.46	1.90
9	0	1.07	9.27	8.90	31.53	50.77	23.28	74.05	0.62	0.93	1.55	0.86	2.41
	5	1.06	8.67	7.04	32.77	49.54	22.07	71.61	0.53	1.07	1.60	0.71	2.31
10	b	0.82	9.15	5.03	21.41	36.41	17.96	54.37	0.48	0.95	1.44	0.55	1.99
	0	1.21	24.84	6.60	43.85	76.50	21.03	97.53	2.37	3.80	6.17	1.56	7.73
11	5	0.77	9.10	7.94	25.02	42.73	17.99	60.72	0.83	1.66	2.49	1.69	4.18
	b	0.75	8.32	3.70	30.60	43.37	13.36	56.73	0.67	1.45	2.12	0.94	3.06
Total	Average	0.73	5.38	4.50	24.67	35.30	16.79	52.08	0.57	1.19	1.76	0.95	2.71

4) Particulate Nitrogen (PN)

Particulate Nitrogen in the sea may be organic as bacteria, plant and animal Nitrogen or inorganic, i.e., clays or others mineral and synthetic particles. This form of Nitrogen was widely fluctuated between 0.18 and 85.77 μM with an annual mean of 16.84 μM . As expected most of surface water sustained much particulate Nitrogen than bottom one, 1.42 folds in average. In the vicinity of sewers, as at st. 8, the surface values were 14 times greater than that of bottom during March & June. Among the stagnation period, a considerable amount of particulate matter sinks downwards, increase the amount of PN in the bottom water e.g. at stations 3 & 5 during August ($> 80 \mu\text{M}$).

PN showed significant variations in the harbour water, the middle part of the harbour showed the lowest PN, being 12.58 μM in average. At El-Noubaria area, (st. 6), the discharge of agricultural, industrial and domestic water brought considerable amounts of particulate substances raised the average of PN to about 20 μM .

5) Total Nitrogen (TN)

The amount of TN in the studied area ranged between 11.42 μM and 153.61 μM and averaged about 52 μM . Similar to TDN, DON and PN there was a significant trend in TN with time, where the values tend to follow more or less the water temperature. DIN, on the other, hand, showed no distinct pattern. TN in the harbour was characterized by relatively high averages ($> 50 - < 80 \mu\text{M}$) during the growing period of phytoplankton (May - October), the average for the rest of months were relatively low, being below 50 μM .

Horizontal as well as vertical variations in TN content were also observed. The values tend to decrease away from the sewers starting from 97.53 μM at st. 8 (surface) to 53.13 μM at st. 4. The amount of TN in the surface water, in general was mostly higher than that in the bottom one, reaching sometimes two or three folds.

Comparing with Aboul-Kassim (1987) average, the western harbour is much enriched with TN than the eastern harbour (4/3 fold). Two-third of TN is in dissolved forms while only one-third of it as particulate substances. The predominant dissolved Nitrogen in the western harbour is in organic form (70% of TDN) or nearly one-half of TN indicating the high proportion of humic substances. The use of fertilizers has increased considerably during the last decades and agriculture now contributes to high percentage of the TN-inputs comes from El-Noubaria canal as well as from El-Max pumping stations outside the harbour. The relation between TN and runoff is confirmed from the inversely correlation between TN with salinity ($r = -0.4749$, $p < 0.001$).

PHOSPHORUS FORMS:

1) Dissolved inorganic Phosphorus (DIP)

Similar to DIN, DIP is very important element limiting the growth and reproduction of phytoplankton (Riley & Chester, 1971). DIP when present in large content it cause eutrophication and may be considered as a potential pollutant.

A considerable amount of DIP was measured in the harbour water ranging from zero to 5.70 μM with an average values of 0.57 μM which is 32% of TDP or nearly 1/5 TP. The western harbour water is enriched with DIP much than the eastern harbour (Aboul-Kassim, 1987) or the open water infront of the studied area (Asaad, 1981).

The drainage water influx into the harbour during winter enriched with DIP resulting from the washing of Phosphorus fertilizers used for winter crops (Shaheen & Yosef, 1978) is a contributor to the February Peak (Nessim & Tadros, 1986). DIP tends to decrease downwards, the surface content is 35 times greater that of bottom one at the polluted area, st. 8, during May.

The supply of organic matter and detergents present in sewage is probably an important source of DIP. In El-Mahmoudia area the annual average of DIP in the surface water (2.12 μM) is 2 -4 times greater than that of any other localities. The significant inverse correlation between DIP and Salinity ($r = -0.2631$, $p < 0.001$) confirms this relation.

2) Dissolved organic Phosphorus (DOP)

Similar to DON, DOP is the major form of TDP, 68%, comprises 44% of TP. High values of DOP (up to 6.68 μM) were detected in the surface water during August, November and December. The lowest average was recorded in October, being 0.48 μM .

The annual averages, calculated for most localities, showed a narrow range (0.91 - 1.23 μM). The average value at the highly polluted area, st.8, is nearly doubled (Table 1). The surface value at this area reached sometimes five folds the bottom one.

A statistically significant correlation was found between DOP with chlorophyll-a biomass ($r = 0.2427$, $p < 0.001$). This explains the living organisms as a source of DOP in the sea.

The overall average of DOP content in the surface and bottom waters of 1.51 & 1.00 μM , respectively, are relatively high when compared with the finding of Aboul-Kassim (1987) in the eastern harbour or in many others marine environments.

3) Total dissolved Phosphorus, TDP

Most of the TP in the harbour water is found in dissolved forms (65 %). TDP varied between 0.12 and 11.02 μM with a mean of 1.76 μM which is twice as much as that in the eastern harbour (Aboul-Kassim, 1987) or higher than those in several marine waters (Armstrong & Tibbitts, 1968).

Similar to TDN condition, TDP/TP ratio averages showed a horizontal decrease seawards with insignificant vertical variations.

With regards to monthly variation, the February average was the highest while June and October gave the lowest averages (nearly 1/6). The annual average in the vicinity of sewers, st. 8, was nearly doubled that at any other studied localities.

4) Particulate Phosphorus (PP)

The insoluble and adsorbed phosphate in suspension (PP) was not widely varied. It ranges between 0.03 and 4.22 μM having an annual average of 0.94 μM . PP content is minor when compared with TDP, nearly one-half which is relatively too high to oceanic ratio.

With respect to monthly variation, June showed the lowest average, 0.49 μM while August gave the highest (1.51 μM).

The significant correlation calculated between PP content and each of oxidizable organic matter ($r = 0.2878$) and salinity ($r = -0.3202$, $p < 0.001$) indicate its origin. Statistically significant correlation computed between PP and chlorophyll-a content ($r = 0.3513$, $p < 0.001$) may explain the role of living organisms in relation to the insoluble P-fraction.

The continuous discharge of domestic water into the inner harbour, the drainage water influx at El-Boughaz area and effluent of El-Noubaria canal may be responsible for the high averages of PP at these localities (1.5 μM), the rest areas gave relatively low averages (0.86 - 1.21 μM).

5) Total Phosphorus, TP

The amount of TP in the harbour water varied from 0.18 to 12.49 uM with a mean value of 2.71 uM which is little exceeds than that in the eastern harbour (Aboul-Kassim, 1987). The monthly average showed two peaks; winter peak (February) just prior the phytoplankton bloom and the second in summer (August), being 5.11 & 4.16 uM respectively. The high P-uptake during blooming period resulted in low average in June (1.13 uM). The rest of months gave moderate values close to the general average of 2.4 uM.

The annual averages in most localities gave a narrow range (2.00 - 2.50 uM). Station 1 in the inner harbour as well as st. 6 in front of El-Noubaria canal had their waters little higher averages, while the mean of TP at st. 8 was nearly doubled (Table1).

The surface water, in general, was enriched with TP among the year, particularly near the sewers, st. 8, where the surface TP content was nearly ten folds that of the bottom during May. As in TN, TP show significant inverse correlation with salinity ($r = -0.5100, p < 0.001$) indicates its origin.

Generally, the concentration of TP is five times greater than DIP. It may suggest that organic P is ecologically important in the studied area. There is no bottom accumulation of phosphate at these localities under study. The harbour is relatively shallow and the euphotic zone extends down till bottom and continuous utilization of Phosphorus by phytoplankton is evident.

Statistical analysis:

The relation between total element and other forms content is shown in Figs. (2 & 3) and the regression equations are given as follows :

For Nitrogen :

- TN = 44.8932 + 0.5674 DIN.....(A)
- = 31.5092 + 0.9597 DON.....(B)
- = 16.5276 + 1.0584 TDN.....(C)
- = 32.1289 + 1.0643 PN.....(D)

For Phosphorus :

- TP = 1.9133 + 1.2172 DIP.....(A)
- = 1.2170 + 1.4516 DOP.....(B)
- = 0.7139 + 1.1399 TDP.....(C)
- = 1.4010 + 1.5582 PP.....(D)

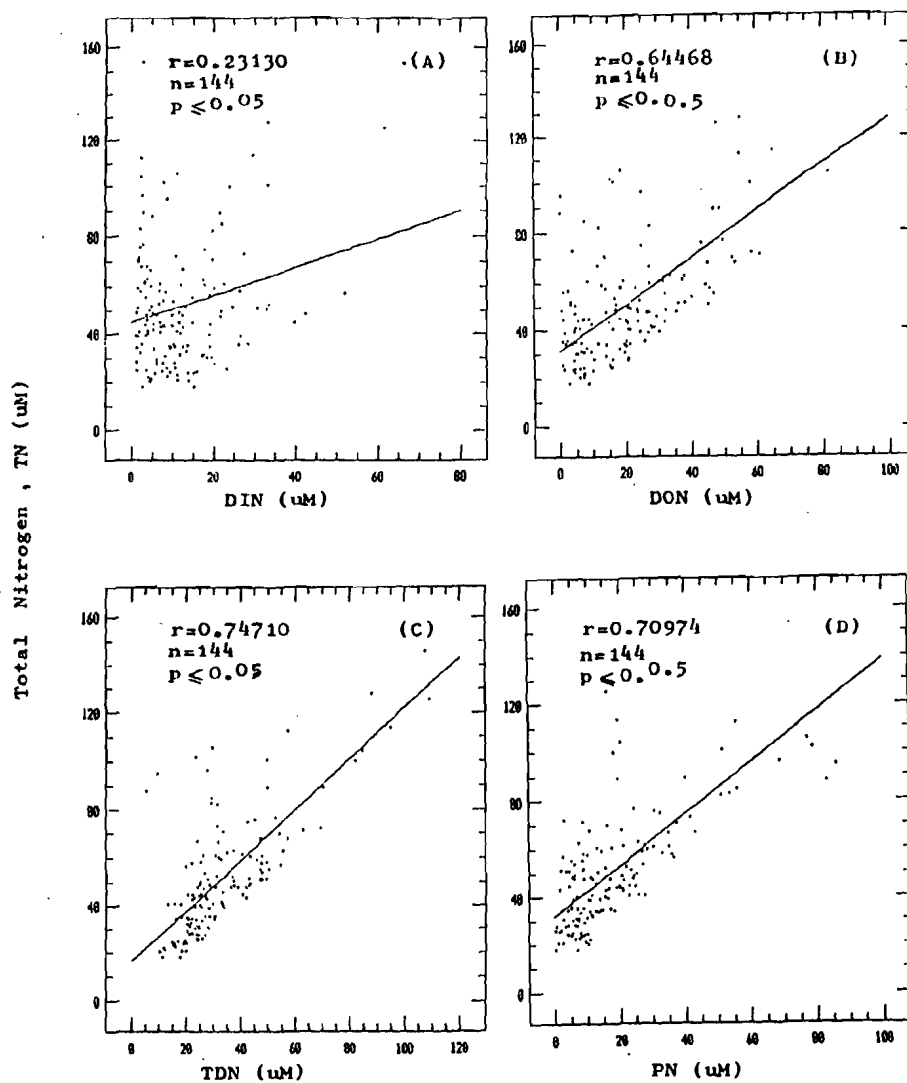


Fig. 2. Scatterplots relating Total Nitrogen , TN, with (A) DIN , (B) DON , (C) TDN and (D) PN in Alexandria western harbour waters during 1989 . .

Total Phosphorus , TP (μM)

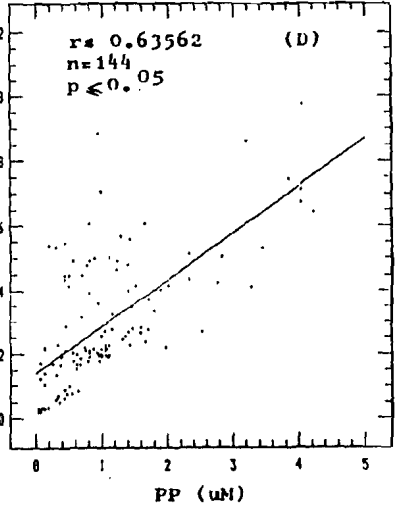
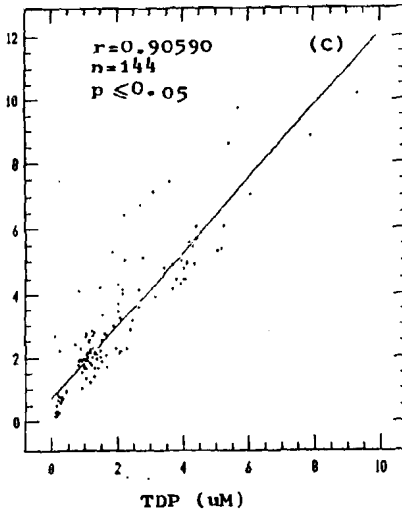
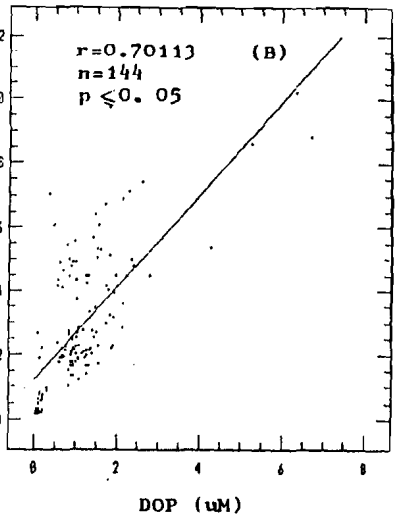
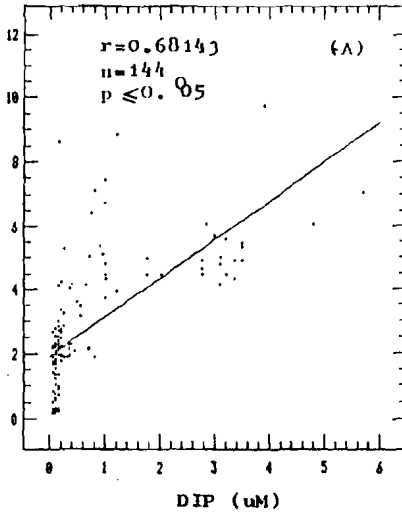


Fig. 3. Scatterplots relating Total Phosphorus , TP, with (A) DIP , (B) DOP , (C) TDP and (D) PP in Alexandria western harbour waters during 1989 .

It is evident from the linear model that the total forms of the two elements are strongly correlated with their dissolved forms comprising the major part of the elements. The dissolved organic Nitrogen is much significantly correlated with total Nitrogen when compared with DIN. In the case of Phosphorus, each of dissolved organic or inorganic forms are strong correlated with TP content.

Nitrogen : Phosphorus ratio

Many authors including Richards, 1958 and Redfield, 1958 are of the opinion that the normal oceanic N/P ratio is 16:1. However, the influx of the sewage, rivers, industrial and drainage effluents into the marine ecosystem is likely to influence organic and inorganic nutrient concentrations as well as their ratios and consequently affecting the primary production level and causing eutrophication. This phenomenon is very evident in the harbour, bays and semi-closed coastal areas. Whether N or P is the nutrient more likely to limit primary production is determined by the external supply ratio of both (Rhee, 1978, Tilman *et al.*, 1982 and Howarth, 1988).

The marine algae are considered to be Phosphorus-limited when the N/P ratio is > 6 and N-limited when the ratio is < 4.5 . In the range 4.5 - 6, the two nutrients are near the optimal assimilative proportion Chiaudani *et al.*, 1978. Accordingly, the results of TN/TP ratio evaluation on the western harbour showed about 96% are P-limited, about 1% is N-limited and about 3% of samples have an optimal assimilative proportion of nutrients. The ratios however between the dissolved inorganic forms, DIN/DIP gave more or less similar pattern where 90% are P-limited, 5% are N-limited and 5% with an optimal assimilative proportion.

For interpretative purposes, Grimm & Fisher (1986), and Galat (1990) assumed that potential Nitrogen limitation was at $TN/TP < 10$, potential Phosphorus limitation was at $TN/TP > 20$ and co-limitation was at $10 < TN : TP < 20$. According to this suggestion about the half of samples are P-limited while 15% are N-limited and 35% are P & N co-limitation. When the comparison include either TDN/TDP or DIN/DIP ratios instead of TN/TP, a pronounced deviation in the frequency was obtainable; 20% of samples were either N-limitation or N & P co-limitation and 60% are P-limitation. Actual nutrient limitation depends not only of N/P ratio but also on water soluble P or N is depleted (Grimm & Fisher, 1986).

N/P ratio showed, in general, noticeable seasonal as well as horizontal but not vertical variations. An abrupt increase in TN/TP ratio was detected in June (181 : 1). The ratio averages in both April & August are identical (21 : 1) while the October

average is nearly doubled. All these averages indicate P as a limiting factor (Galat, 1990). The ratio average of February, on the other hand, deviate markedly below the normal Richard ratio, being 8.5 : 1, the December value is closely nearer to the oceanic ratio.

Nitrogen was found in excess than Phosphorus during most months. Regionally, most of studied localities showed high TN/TP ratio average (40-85 : 1), the highly polluted area, st. 8, gave unexpected normal oceanic ratio while El-Boughaz area reflect a ratio average little higher than normal.

The total average ratio for the different forms during the year of study are not greatly differ, being; 48.6, 51.3 & 52.3 : 1 for TN/TP, TDN/TDP & DIN/DIP, respectively. These ratios averages were in a good agreement with the finding of Nessim (1990) in coastal Egyptian waters. Judging from these high N/P ratio in the western harbour as compared to Redfield value, one would expect potential Phosphorus limitation.

With respect to the value of N:P ratio obtained by Nessim & Tadros, 1986, the ratio increased in the last five years much than doubled.

REFERENCES

- Aboul-Kassim, T.A.T., 1987. Cycles of carbon, Nitrogen and Phosphorus in the marine environment in Alexandria region, M.Sc. Thesis, Alex. Univ., 233 pp.
- Armstrong, F.A.J. & S. Tibbits, 1968. Photochemical combustion of organic matter in sea water, for Nitrogen, Phosphorus and carbon determinations. *Mar. Biol. Ass. U.K.*, 48: 143-152.
- Asaad, F.N., 1981. Chemistry of the sea water, west of Alexandria. M. Sc. Thesis, Alex. Univ., 91 pp.
- Calvert, S.E. & E.B. Price, 1971. Upwelling and nutrient regeneration in the Benguella current. *Deep sea Res.*, 18: 505-523.
- Carpentar, E.J., C.C. Remesen & B.W. Schroeded, 1972,a. Comparison of laboratory and in situ measurments of urea decomposition by marine diatom. *J. Expl. Mar. Biol. Ecol.*, 8: 259-264.
- Carpentar, E.J. & S.W. Watson, 1972,b. Utilization of urea by some marine phytoplankters. *Limnol. Oceanogr.* 17: 265-269.

- Chiaudani, G. & M. Vighi, 1978. Metodologia standard di Saggio algare per 10 studio della acque marine. Quaderni dell'Instituto di Ricerca sulle acque n. 39:120.
- Dugdale, R.C., J.J. Georing, R.T. Barber, R.L. Smith and T.T. Packard, 1977. Denitrification and hydrogen sulphides in the Peru-upwelling region during 1976. *Deep sea Res.*, 24: 601-608.
- Eppley, R.W., E.H. Renger, E.L. Venrick & M.M. Mullin, 1973. A study of plankton dynamics and nutrient cycling in the central Gyre of the north Pacific Ocean. *Limnol. & Oceanogr.* 18 (4): 535-551.
- Fisher, N.S. & R.A. Cowdell, 1982. Growth of marine planktonic diatoms on inorganic and organic Nitrogen. *Mar. Biol.*, 72: 147-155.
- Galat, D.L., 1990. Seasonal and long - Term trends in Truckee River nutrient concentrations and loading to Pyramid Lake, Nevada: A terminal saline lake. *Wat. Res.* vol. 24 (8): 1031-1040.
- Grasshoff, K., 1976. *Methods of sea water analysis.* 317 pp.
- Grimm, N.B. & S.G. Fisher, 1986. Nitrogen limitation in a Sonoran desert stream. *J.N. Am. Benthol Soc.*, 5: 2-15.
- Howarth, R.W., 1988. Nutrient limitation of net primary production in marine ecosystems. *A Rev. Ecol.*, 19: 89-110.
- International Council for Exploration of the sea "ICES", 1972. *Cooperative Research Report. Series A, No. 29.*
- Kittredge, J.S., M. Horiguchi and P.M. Williams, 1969. In: *introduction to marine chemistry* by J.P. Riley and R. Chester (1971). Academic Press, London and New York.
- Koroleff, F., 1977. Simultaneous persulphate oxidation of Phosphorus and Nitrogen compounds in water: In Grasshoff, K. (Ed) *Report of the Baltic Intercalibration Workshop, Annex, Interim commission for the protection of the environment of the Baltic sea.*
- Martin, D.F., 1970. *Marine Chemistry. Theory and application.* Marcel Dekker, Inc., New York, vol. 2.

- McCarthy, J.J., 1971. The role of urea in marine phytoplankton ecology. ph. D. Thesis, Univ. Calif., San Diego.
- McCarthy, J.J., 1972. The uptake of urea by natural populations of marine phytoplankton. *Limnol & Oceanogr.* 17: 738-748.
- Nessim, R.B., 1990. Nutrient levels and chlorophyll-a content in Alexandria coastal waters. *Bull. Inst. of Oceanogr. & Fish., Egypt.* Vol. 17 (In press).
- Nessim, R.B. & A.B. Tadros, 1986. Distribution of nutrient salts in the water and porewater of the western harbour of Alexandria, Egypt. *Bull. Inst. Oceanogr. & Fish., Egypt*, 12: 165-174.
- Redfield, A.C., 1958. The biological control of chemical factors in the environment. *Amer. Sci.*, 46: 205-222.
- Rhee, G.Y., 1978. Effect of N:P atomic ratios and nitrate limitation on algal growth, cell composition and nitrate uptake. *Limnol. & Oceanogr.*, 23: 10-25.
- Richards, F.A., 1958. Dissolved silicate and related properties of some western north Atlantic and caribbean waters. *J. Mar. Res.*, 17: 449-457.
- Riley, J.P. & C. Chester, 1971. *Introduction Chemistry.* Academic Press., London and New York, 465 pp.
- Ruttner, F., 1968. *Fundamentals of Limnology.* Univ. of Toronto Press, 4th Ed., 295 pp.
- Shaheen, A.H. & S.F. Yosef, 1978. The effect of the Cessation of Nile flood on the hydrographic features of Lake Manzalah, Egypt. *Arch. Hydrobiol.*, 84 (3): 339-367.
- Smith, V.H., 1979. Nutrient dependence of primary productivity in Lakes. *Limnol. & Oceanogr.*, 24 (6): 1051-1064.
- Strickland, J.D.H. & T.R. Parsons, 1972. *A Practical handbook of sea water analysis.* Fish. Bd. Canada, Bull. 167, 2nd., Ed., 310 pp.
- Tilman, D. & Kilham, S.S. & P. Kilham, 1982. Phytoplankton community ecology: The role of limiting nutrients. *Ann. Rev. Ecol. Syst.*, 13: 249-372.

- Valderrama, J.C., 1981., The simultaneous analysis of total Nitrogen and total Phosphorus in natural waters. *Marine Chemistry*, 10: 109-122.
- Wafar, M.V.M., S. Wafar & V.P. Devassy, 1986. Nitrogenous nutrients and primary production in a tropical oceanic environment. *Bull. Mar. Sci.*, 38 (2): 273-284.
- Zaghloul, F. & R.B. Nessim, 1991. Eutrophication syndrome in the western harbour of Alexandria, Egypt. *The Bull. of the high Inst. of Public Health*. vol. XXI. No. 2: 257-271.
- Zentara, S.J. and D. Vamykowski, 1977. Latitudinal relationships among temperature and selected plant nutrients along the west coast of North and South America. *J. Mar. Res.*, 35 (2): 321-37.