

# Effect of Domestic Pollution on the Distribution of Nitrogenous and Phosphorus Species in the Coastal Mediterranean Region in front of the Eastern Harbor of Alexandria, Egypt

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## ABSTRACT

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The coastal Mediterranean region in front of Alexandria is subjected to water exchanges with Eastern Harbor throughout El-Boughaz and El-Silselah openings. Surface and bottom water samples were collected seasonally from this area to investigate the influence of discharged domestic wastes on the levels of nitrogenous and phosphorus species. The extensive waste discharges, mainly from Kayet Bay outfall, increased dissolved inorganic phosphorus (DIP), dissolved organic phosphorus (DOP) and particulate phosphorus (PP), especially at the near shore locations. However, the regression equations of DOP with salinity and of PP with suspended particles indicate that DOP and PP might also be associated with biological activities. The ratio of DIP/DOP indicates predominance of DOP. The maximum nitrate and nitrite averages near El-Silselah outfall reflect their high contents in its discharges. The regression equations versus salinity indicate that nitrate was mainly derived from this outfall, which was not the only contributor of nitrite. Abundance of ammonium was similar to that of nitrate. The annual mean surface nitrite, nitrate and ammonium concentrations were higher than the bottom means, reflecting the direct influence of discharged wastes. The maximum surface and bottom dissolved organic nitrogen (DON) averages in front of El-Silselah outfall indicate its main external anthropogenic origin. However, the positive correlations of DON with salinity, pH and ammonium in the bottom water possibly reflect the DON source from living organisms. The highest particulate nitrogen (PN) averages were in the vicinity of Kayet Bay discharges. The regression equation between PN and suspended particles confirms external input of PN.

**ADDITIONAL INDEX WORDS:** *Man's impact, eutrophication, marine basin.*

## INTRODUCTION

During the last four decades, the coastal waters of Alexandria have been subjected to extensive discharges of untreated industrial, agricultural and sewage wastewaters. About 183x106m<sup>3</sup> of untreated domestic sewage and wastewaters are discharged annually from land-based sources into the coastal waters of Alexandria (SAID and MAIYZA, 1987). Anthropogenic nutrient inputs play an important role in the high productivity and biomass of the coastal zone of Alexandria relative to its continental shelf (ABOUL-KASSIM, 1987). DOWIDAR *et al.*, (1990) reported the importance of land-based sources on the phosphorus species and budget in a heavily polluted Eastern Harbor of Alexandria. The data obtained from previous studies showed that these waters were suffering from risks of deterioration, as a result of increase in degradation of the coastal water quality (YOUNES, 1997; YOUNES *et al.*, 1997, YOUNES and ROMANO, 1999; ROMANO *et al.*, 1999). This work, a part of the MED-POL Program (Phase II), was designed to investigate the distribution of dissolved and particulate fractions of phosphorus and nitrogen in the study area. The estimation of the present levels of nutrients delivered to the study area via domestic inputs is a tool to evaluate the role of land-based sources as major contributors of pollutants to this area.

## STUDY AREA

The coastal Mediterranean region in front of Alexandria has no distinct boundaries. It lies between 29° 52' 29° 55' E and 31° 13' 31° 16' N. This study area with a maximum depth of 22 m is subjected to exchanges of waters with the open coastal seawater of Alexandria and with the Eastern Harbor throughout the two harbor's outlets (El-Boughaz and El-Silselah). It receives from 0.15 0.20 X 106 m<sup>3</sup> /day of untreated domestic wastes throughout the main sewage tube at Kayet Bay Fort. This pumping station is the metropolitan sewage pumping station of

the central part of Alexandria. There are some subsidiary branches of the sewage pumping station, which open directly at the shore and lie about 100 m east of the main sewage tube. These branches are used only during rainy days in winter (SHRIADACH, 1982).

## METHODS

Surface and bottom water samples were collected seasonally during April 1991 to January 1992 from the study area along three transects perpendicular to the coast line. According to the maximum depth, from 2 to 3 stations were sampled along each transect. The surface samples were collected using a silicon / teflon manual water pump at 30 cm below the water surface to avoid floating matter. The bottom samples were collected by a 5 liters PVC Niskin water sampler at 30 cm above the sea bottom to avoid disturbance of sediments. The water samples were kept in 2 liters acid-cleaned PET bottles, as described by PAI *et al.* (1990). Immediately before sampling, the bottles were rinsed with a portion of the seawater samples. The bottles were then tightly closed and the samples were frozen at -20°C until analyses could be performed. Millipore membrane filter papers (0.45 µm porosity, 47 mm diameter) were used to separate the dissolved from particulate nutrient fractions. Nutrient salts were determined colorimetrically using Bauch & Lomb Spectronic 2000 double beam spectrophotometer. Dissolved inorganic phosphorus (DIP), nitrate, nitrite and ammonium were determined according to SRICKLAND and PARSONS (1972). Total dissolved nitrogen (TDN), total nitrogen (TN), total dissolved phosphorus (TDP) and total phosphorus (TP) were determined according to the method described by VALDERAMA (1981). Dissolved organic nitrogen (DON), dissolved inorganic nitrogen (DIN), particulate nitrogen (PN), dissolved organic phosphorus (DOP) and particulate phosphorus (PP) were determined by calculations. The concentrations of nutrients were expressed in µM.

Table 1. Regional average concentrations and annual means of DIP, DOP and PP in surface (S) and bottom (B) waters of the study area.

Stations	Depths	DIP ( $\mu\text{M}$ )	DOP ( $\mu\text{M}$ )	PP ( $\mu\text{M}$ )
I	S	0.99	1.16	4.15
	B	0.20	1.25	0.38
II	S	0.39	0.78	1.31
	B	0.18	0.25	0.54
III	S	0.20	0.37	2.34
	B	0.20	0.78	0.50
IV	S	2.00	2.69	2.05
	B	0.28	0.30	1.74
V	S	0.28	0.62	1.58
	B	0.11	0.61	0.38
VI	S	0.75	0.48	1.15
	B	0.16	1.02	0.60
VII	S	0.25	0.79	1.52
	B	0.21	0.67	0.23
Annual means	S	$0.69 \pm 0.60$	$0.98 \pm 0.62$	$2.01 \pm 1.36$
	B	$0.19 \pm 0.05$	$0.70 \pm 0.64$	$0.62 \pm 0.39$

## RESULTS

### Phosphorus Species

Station IV showed the highest regional average DIP value of 2.00 and 0.28  $\mu\text{M}$  in the surface and bottom water, respectively (Table 1). The maximum seasonal average DIP value for the bottom water appeared in July was one fourth that for the surface water in October. DIP showed comparatively low annual surface and bottom means of  $0.69 \pm 0.60$  and  $0.19 \pm 0.05$   $\mu\text{M}$ , respectively (Table 1). The contribution of DIP to TDP was 53% for the surface water and 45% for the bottom water.

The maximum surface regional average DOP value was 2.69  $\mu\text{M}$  at station IV. However, the regional averages for the bottom water ranged from 0.25 to 1.25  $\mu\text{M}$  at stations II and I, respectively (Table 1). For the bottom water, the peak of seasonal DOP average value in April was followed by three minima of nearly similar magnitude around 0.3  $\mu\text{M}$  in July, October and January. The annual DOP means for the bottom and surface samples ( $0.70 \pm 0.64$  and  $0.98 \pm 0.62$   $\mu\text{M}$ ) were considerably higher than those of DIP (Table 1). Contrary to DIP, DOP contributed 46 and 55% of TDP for the surface and bottom waters; the contribution of DOP was more in the bottom than in the surface water layer and vice versa.

The high PP value in July at station IV was reflected on the highest bottom regional average value of 1.74  $\mu\text{M}$  (Table 1). In the surface water, the seasonal regional averages value of PP ranged widely from 1.06  $\mu\text{M}$  in April to 4.37  $\mu\text{M}$  in October. For the bottom water, the peak was also shown in October (1.14  $\mu\text{M}$ ), while the minimum seasonal average appeared in January (0.16  $\mu\text{M}$ ). The annual mean surface value of PP ( $2.01 \pm 1.36$   $\mu\text{M}$ ) was more than three times higher than that of  $0.62 \pm 0.39$   $\mu\text{M}$  for the bottom water (Table 1).

### Nitrogenous Species

The surface water showed a wide difference in the regional nitrate averages, fluctuating between 0.65  $\mu\text{M}$  at station VI and 4.32  $\mu\text{M}$  at station IV. The alteration in the regional bottom nitrate averages was minor compared with that in the surface water. They ranged from 0.78  $\mu\text{M}$  at station III to 2.65  $\mu\text{M}$  at station V (Table 2). The seasonal average nitrate values ranged from 1.30  $\mu\text{M}$  in April to 3.53  $\mu\text{M}$  in July for the surface water and from 1.01  $\mu\text{M}$  in January to 3.18  $\mu\text{M}$  in October. The annual surface mean nitrate concentration was  $2.40 \pm 0.85$   $\mu\text{M}$ , while that for the bottom water was  $1.80 \pm 0.85$   $\mu\text{M}$  (Table 2). On the average, about half of DIN in both surface and bottom waters was nitrate and DON was mostly the predominant fraction of TDN in both water layers rather than DIN.

The regional bottom nitrite average varied from 0.12  $\mu\text{M}$  at station III to 0.33  $\mu\text{M}$  at stations IV and VI. For the surface water, they ranged from 0.17  $\mu\text{M}$  at station VII to 0.90  $\mu\text{M}$  at station IV (Table 2). The peak of seasonal surface nitrite average was obtained in July (0.60  $\mu\text{M}$ ), while the minimum average of 0.13  $\mu\text{M}$  appeared in April. The bottom water gave also a peak in July (0.46  $\mu\text{M}$ ), while the minimum of 0.06 appeared in January. The annual surface and bottom nitrite means of  $0.35 \pm 0.18$  and  $0.22 \pm 0.16$   $\mu\text{M}$ , respectively were calculated (Table 2). In the surface water, the contribution of nitrite / DIN was 6%, while nitrite / TDN was very low (0.2%). In the bottom water, nitrite / DIN constituted 5% and nitrite / TDN was only 0.1%.

The maximum surface and bottom regional average ammonium values were found at station I; 16.01 and 5.21  $\mu\text{M}$ , respectively (Table 2). However, the minimum surface regional average (2.39  $\mu\text{M}$ ) appeared at station III and that for the bottom water of 1.29  $\mu\text{M}$  at station VII. The seasonal average ammonium concentrations in the surface water ranged from

Table 2. Regional average concentrations and annual means of  $\text{NO}_3$ ,  $\text{NO}_2$ ,  $\text{NH}_4$ , DON and PN in surface (S) and bottom (B) waters of the study area.

Stations	Depths	$\text{NO}_3$ ( $\mu\text{M}$ )	$\text{NO}_2$ ( $\mu\text{M}$ )	$\text{NH}_4$ ( $\mu\text{M}$ )	DON ( $\mu\text{M}$ )	PN ( $\mu\text{M}$ )
I	S	2.35	0.24	16.01	225.41	27.65
	B	1.85	0.15	5.21	226.13	81.38
II	S	2.22	0.21	6.21	182.78	75.55
	B	2.23	0.17	4.14	213.21	37.85
III	S	4.06	0.22	2.39	217.79	59.33
	B	0.78	0.12	2.62	234.51	45.28
IV	S	4.32	0.90	7.32	205.51	58.18
	B	1.86	0.33	3.53	247.10	59.35
V	S	2.25	0.27	2.93	239.43	72.28
	B	2.65	0.21	2.88	198.11	15.99
VI	S	0.65	0.34	3.15	218.29	59.10
	B	1.75	0.33	1.99	222.24	61.05
VII	S	1.00	0.17	2.41	233.44	60.55
	B	1.59	0.18	1.29	239.49	78.03
Annual means	S	$2.40 \pm 0.85$	$0.35 \pm 0.18$	$5.77 \pm 4.52$	$217.52 \pm 55.25$	$58.95 \pm 20.18$
	B	$1.80 \pm 0.85$	$0.22 \pm 0.16$	$3.09 \pm 3.03$	$225.83 \pm 33.64$	$54.13 \pm 12.95$

0.02  $\mu\text{M}$  in January to 12.34  $\mu\text{M}$  in July. These averages varied in the bottom water from 0.02  $\mu\text{M}$  in January to 7.16  $\mu\text{M}$  in April. The surface water showed an annual nitrite mean of  $5.77 \pm 4.52 \mu\text{M}$ , which was nearly double that of  $3.09 \pm 3.03 \mu\text{M}$  for the bottom water (Table 2). The surface ammonium constituted 49% of DIN and 3% of TDN. However, these contributions in the bottom water were 40 and 1%, respectively.

The regional surface average DON values ranged from 182.78  $\mu\text{M}$  at station II to 239.40  $\mu\text{M}$  at station V. However, the regional bottom averages varied from 198.11  $\mu\text{M}$  at station V to 247.10  $\mu\text{M}$  at station IV (Table 2). In April, the peaks of seasonal DON averages for the surface and bottom waters reached 279.96 and 264.20  $\mu\text{M}$ , respectively. However, the minimum seasonal averages for both water layers appeared in January (129.24 and 171.72  $\mu\text{M}$ , respectively). The annual surface DON mean value ( $217.52 \pm 55.25 \mu\text{M}$ ) was slightly lower than that of  $225.83 \pm 33.64 \mu\text{M}$  for the bottom water (Table 2). DON/TDN and DON/TN for the surface water were 96 and 76%, respectively. In the bottom water, DON constituted 98 and 79% of TDN and TN, respectively.

The surface water at stations I and II exhibited the minimum (27.65  $\mu\text{M}$ ) and maximum (75.55  $\mu\text{M}$ ) regional average PN values. A fluctuation in the bottom regional average PN values appeared at stations V and I, ranging from 15.99 to 81.38  $\mu\text{M}$ , respectively (Table 2). In the surface water, the seasonal average PN values varied from 25.24  $\mu\text{M}$  in October to 78.87  $\mu\text{M}$  in July. These averages in the bottom water varied from 33.63  $\mu\text{M}$  in October to 67.40  $\mu\text{M}$  in January. Nearly similar annual mean PN values were calculated for the surface and bottom waters ( $58.95 \pm 20.18$  and  $54.13 \pm 12.95 \mu\text{M}$ , respectively), as shown in Table 2. PN/TN constituted 22% in the surface water and 20% in the bottom water.

## DISCUSSIONS

### Phosphorus Species

Silselah outfall was responsible for the maximum surface and bottom regional DIP averages of 2.00 and 0.28  $\mu\text{M}$  at station IV (Table 1). The study area is subjected to extensive inputs of untreated domestic sewage discharges which affected the DIP levels, especially at the near shore stations. Such effect decreased seaward in both water layers. This fact is confirmed using the regression equation with salinity;  $\text{DIP} (\mu\text{M}) = 1.43 \cdot 0.022 \text{ S } \%$  for the surface water and  $\text{DIP} (\mu\text{M}) = 0.038 + 0.006 \text{ S } \%$  for the bottom water (YOUNES, 1997). These equations confirm that these outfalls were almost responsible for the DIP level in the study area, despite the effects of biological activities and/or remobilization from the bottom sediments and detritus fractions which might have contributed to DIP to a less extent. The increase in the surface annual mean DIP concentration ( $0.69 \pm 0.60 \mu\text{M}$ ) compared to that of  $0.19 \pm 0.05 \mu\text{M}$  for the bottom water (Table 1) might be due to adsorption of the bottom DIP onto suspended particles and sediments and/or the high phosphate enriched freshwater invasion to the surface water layer.

The ratios of DIP/DOP in the surface and bottom waters were 0.8:1 and 0.3:1, respectively, indicating the predominance of DOP. The maximum surface regional DOP value (2.69  $\mu\text{M}$ ) at station IV, located opposite to Silselah outfall and that of 1.25  $\mu\text{M}$  for the bottom water at station I, located opposite to Kayet Bay outfall (Table 1) show that DOP was associated with the untreated domestic discharges via both outfalls. Similar to DIP, the DOP values for both water layers showed a marked decrease seaward. The regression equations relating DOP to S‰;  $\text{DOP} (\mu\text{M}) = 4.239 \cdot 0.098 \text{ S } \%$  and  $\text{DOP} (\mu\text{M}) = 0.147 + 0.015 \text{ S } \%$  for the surface and bottom waters, respectively, indicate that DOP levels in the study area might be also associated with biological activities. The maximum seasonal average DOP in April confirms that DOP might be associated with high biological activities in spring. The slight increase in the annual surface mean DOP value ( $0.98 \pm 0.62 \mu\text{M}$ ) compared to that for the bottom water ( $0.70 \pm 0.64 \mu\text{M}$ ), as shown in Table 1 resulted most probably from biological activities taking place in the

surface water.

The highest surface and bottom seasonal PP averages appeared in October possibly coincided with the intensive biological activities and/or external freshwater inputs associated with organic and suspended matter. The maximum surface regional average PP value (4.15  $\mu\text{M}$ ) appeared at station I, located opposite to Kayet Bay outfall, and that of 1.74  $\mu\text{M}$  for the bottom water appeared at station IV, located opposite to Silselah outfall (Table 1). According to YOUNES, (1997), the regression equation between total suspended matter (TSM) and PP for the water column is:  $\text{TSM} (\text{mg/l}) = 20.609 \cdot 0.774 \text{ PP} (\mu\text{M})$ . This confirms that untreated domestic wastes discharging from these outfalls might not be the main sources of PP in the study area. The annual mean surface PP value ( $2.01 \pm 1.36 \mu\text{M}$ ) was more than three times higher than that of  $0.62 \pm 0.39 \mu\text{M}$  for the bottom water (Table 1). This might illustrate that biological activities played an important role in the vertical and/or horizontal distribution of PP.

### Nitrogenous Species

The surface nitrate constituted 45% of DIN and 55% in the bottom water. Station IV, located opposite to Silselah outfall, exhibited the maximum surface regional average nitrate value (4.32  $\mu\text{M}$ ), indicating the high nitrate content in the untreated domestic sewage derived from this outfall. The regression equation versus S‰ ( $\text{NO}_3 (\mu\text{M}) = 2.395 + 0.25 \cdot 10^{-3} \text{ S } \%$ ) shows that nitrate was mainly derived from Silselah outfall associated with anthropogenic inputs. Station V showed the highest regional average bottom nitrate value (2.65  $\mu\text{M}$ ). The regression equation versus salinity ( $\text{NO}_3 (\mu\text{M}) = 1.086 + 0.020 \text{ S } \%$ ), indicates that the bottom nitrate levels were also derived from external sources; Silselah and Kayet Bay outfalls and/or to a lesser extent from remobilization of the sediments and detritus fractions. However, the nitrification process in the well oxygenated water might probably take place in elevating the nitrate levels in the bottom water (YOUNES, 1997). The maximum seasonal surface average nitrate value (3.53  $\mu\text{M}$ ) in July is considered to be lower than the expected value from domestic discharges. This might be ascribed by phytoplankton uptake. STRICKLAND *et al.* (1970) attributed the increase in plant nutrient utilization to heating of the water column. The increase in the surface mean nitrate ( $2.40 \pm 0.85 \mu\text{M}$ ) compared to that of  $1.80 \pm 0.85 \mu\text{M}$  for the bottom water coincided mostly with biological activities.

The maximum regional average nitrite values of 0.90 and 0.33  $\mu\text{M}$  in the surface and bottom waters at station IV, located opposite to Silselah outfall (Table 2) indicates that nitrite originated mainly from the discharges of this outfall. The regression equations versus salinity for the surface and bottom waters;  $\text{NO}_2 (\mu\text{M}) = 0.509 \cdot 0.005 \text{ S } \%$  and  $\text{NO}_2 (\mu\text{M}) = -0.221 + 0.012 \text{ S } \%$ , respectively (YOUNES, 1997), indicate that Silselah outfall was not the only contributor of nitrite to the study area. The trend of nitrite distribution showed a decline seaward. It was also concluded that the surface nitrite annual mean ( $0.35 \pm 0.18 \mu\text{M}$ ) was relatively higher compared with that for the bottom water ( $0.22 \pm 0.16 \mu\text{M}$ ), as shown in Table 2. Nitrite concentrations for the surface and bottom waters showed statistically significant positive correlation with DIP ( $r = 0.699$  and  $0.737$ ,  $P < 0.001$ ), indicating that nitrite might be derived from the same origin.

Abundance of ammonium was similar to that of nitrate. Ammonium constituted 49 and 40% of DIN in the surface and bottom waters, respectively. The maximum regional surface ammonium average of 16.01  $\mu\text{M}$  and that for the bottom water of 5.21  $\mu\text{M}$  was observed at station I, located opposite to Kayet Bay outfall. High averages were also found in the surface and bottom waters at station IV, located opposite to Silselah outfalls (Table 2). This confirms that ammonium might be significantly associated with the inputs from these outfalls. Ammonium exhibited a positive correlation with TSM in the surface water. For the bottom water, however, it showed a positive correlation with pH and DIP (YOUNES, 1997). These in addition to the decreasing trend of ammonium seaward suggest that

ammonium might be also derived from other external sources; via water derived from the western polluted Mex Bay by the long shore current. Accordingly, the surface annual ammonium mean value ( $5.77 \pm 4.52 \mu\text{M}$ ) was higher than bottom mean of  $3.09 \pm 3.03 \mu\text{M}$  (Table 2).

The maximum surface and bottom regional DON averages of 239.40 and 247.10  $\mu\text{M}$  at stations V and IV along the transect of Silsilah outfall indicate that domestic wastewaters might be the main source of DON in the study area. RILEY and CHESTER (1971) showed that most of organic nitrogen compounds probably enter into the water as a result of protein decomposition during decay of organic tissues. However, the bottom DON showed several positive correlations with:  $\text{S}\%$  ( $P < 0.01$ ), pH ( $P < 0.01$ ), as pointed out by YOUNES (1997) and  $\text{NH}_4$  ( $P < 0.01$ ). This might indicate that living organisms were considered as important sources of DON in which high DON compounds may also enter into the water as extra cellular metabolites of phytoplankton (RILEY and CHESTER, 1971). Accordingly, it is difficult to trace the dispersion behavior and distribution of DON in such water. The decrease in the annual surface DON mean ( $217.52 \pm 55.25 \mu\text{M}$ ) compared to that of  $225.83 \pm 33.64 \mu\text{M}$  for the bottom water might be resulted from sinking of organic nitrogen compounds to the bottom, where they were incorporated in the sediments as bottom humus (RILEY and CHESTER, 1971).

Table 2 shows that the maximum regional PN averages were found in the surface water at station II ( $75.55 \mu\text{M}$ ) and in the bottom water at station I ( $81.83 \mu\text{M}$ ). These two locations were subjected directly to untreated domestic discharges derived from Kayet Bay outfall. A significant negative correlation existed between PN and PP in the surface water ( $r = -0.599$ ,  $P < 0.001$ ). The regression equation between PN and TSM;  $\text{TSM} (\text{mg/l}) = 17.372 + 0.039 \text{PN} (\mu\text{M})$  confirms the external input of PN through domestic outfalls.

## CONCLUSIONS

Estimation of the present levels of nutrient species delivered in large amounts to the study area via domestic wastewater discharges represents a tool for evaluating the role of land-based sources as major contributors of domestic pollution to this area. The budget of nutrients in this area is controlled by; 1) inputs from domestic discharges; 2) release from bottom sediments and detritus of living organisms; 3) precipitation; 4) exchange with open seawater and Eastern Harbor; 5) uptake by organisms. Kayet Bay and Silsilah outfalls are mainly responsible for the highest levels of nutrient species, as confirmed from the marked decline in their concentrations

seaward. Besides, biological activities might play a role in the distribution of nutrients in the study area.

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