# AN ESTIMATE OF THE ENVIRONMENTAL STATUS OF LEBANESE LITTORAL WATERS USING NUTRIENTS AND CHLOROPHYLL-A AS INDICATORS

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(Received 26 June 2007 - Accepted 7 November 2007)

### ABSTRACT

In the aim to estimate the environmental status and to detect the signs of eutrophication in the Lebanese coastal waters using nutrients and chlorophyll-a as indicators, surface water analysis was run monthly for a period of 12 months, from March 2005 till February 2006, along 18 stations that extend from Tripoli in the north, to Naqoura in the south. Physico-chemical and biological parameters of the water samples were also studied.

During this period, the temperature followed its normal cycle usually noted in the Lebanese waters; whereas salinity varied spatially and temporally presenting sometimes low values due to the rivers inputs. Significant fluctuations of nutrients and chl-a concentrations were observed in most of the stations and during year cycle. High levels of nitrate (30.68  $\mu$ *M/L*) were observed at stations located near river and sewers, whereas high levels of orthophosphates (5.17  $\mu$ M/L) were detected in zones around the Selaata factory. However the high values of phosphate and nitrate at some sites have caused an important increase in the primary production as shown by high chlorophyll-a concentrations (15.02 mg/m<sup>3</sup>). According to the results and in relation with continental input and the first trophic level which react to this man-made disturbance, stations can be divided into 5 categories: reference (mean values of P-PO4 <0.15  $\mu$ M/L, N-NO2 < 0.05  $\mu$ M/L, N-NO3 < 0.34  $\mu$ M/L and chl-a < 0.12 mg/m<sup>3</sup>), slightly enriched, enriched indirectly by river input or phosphorus input, directly by river input and directly by sewage input stations. Three stations are classified as moderately eutrophied whereas the other stations present a weak eutrophication. The principal component analysis confirms this result by showing the factors influencing on the various parameters and determining the existing correlation among them. Consequently, the concentrations of nutrients and chlorophyll-a biomass can be considered good indicators to assess the environmental status of the sites.

Keywords: Lebanese coastal waters, chlorophyll-*a*, nutrients, eutrophication, biological indicators, environmental status assessment

# **INTRODUCTION**

Like many coastal areas in the Mediterranean, the status of the Lebanese coast is in some way declining through over-exploitation for various uses and different kinds of pollution; the current uses of marine coastal areas are unsustainable. In fact, the high demographic increase in the coastal area led to a rapid expansion of the urban areas. Beach resorts, large commercial and industrial units and ports cover almost 56 km of the coastline (MoE/LEDO/ECODIT, 2001). In the absence of operational wastewater treatment plants, effluents from coastal agglomerations are directly discharged into the sea while effluents from inland communities are disposed in rivers, streams, on open land or underground. Currently, there are 53 identified wastewater outfalls along the coast (CDR/LACECO, 2000). Most outfalls extend only a couple of meters or terminate at the surface of the water (MoE/LEDO/ECODIT, 2001). Moreover, waters drained by rivers carry pollutants such as organics, nutrients, fertilizers, etc... its ultimate destination being coastal waters. It has been recognized that coastal eutrophication from rivers is nowadays one of the most crucial environmental problems (Ganoulis et al., 1996). Agricultural activities may overload soils with fertilizers and pesticides. Washing off the soil by rainfall produces large concentrations of nitrate, phosphate and toxic chemicals in rivers and coastal waters. Waste disposal in marine water affects and alters the chemical and physical characteristics of the water in question. By-products of urban, agricultural and industrial development and untreated effluents from these sources released into the coastal waters initiate the process of eutrophication. The underlying processes of eutrophication are basically natural, yet when its causes are anthropogenic the result may lead to considerable ecosystem disturbance (Cruzado, 1992).

Despite the common understanding of its causes and effects, there is no consensus definition of coastal eutrophication (Andersen *et al.*, 2006). The European Commission (EC) directive defines eutrophication as "the enrichment of water by nutrients, especially nitrogen and/or phosphorus, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of water concerned (EC, 1991). Jorgensen and Richardson (1996) pointed out that when eutrophication is spoken of, it is anthropopogenic eutrophication that is of interest. Stressing the importance of coastal water quality protection, Andersen *et al.* (2006) have recently suggested that eutrophication be defined as 'the enrichment of water by nutrients, especially nitrogen and/or phosphorus and organic matter, causing an increased growth of algae and higher forms of plant life to produce an unacceptable deviation in structure, function and stability of organisms present in the water and to the quality of water concerned, compared to reference conditions. In their opinion, this re-definition will lead to revisions of existing coastal zone monitoring studies (Smith, 2007).

Nutrient enrichment, mainly phosphate and nitrate, causes the development of algal blooms which are in many respects similar to the red tides that arise as a result of natural causes. In this way phytoplankton which are minute plants, are the first trophic level in the marine ecosystem to react to man-made disturbance of the natural equilibrium. The result of eutrophication may be either beneficial or detrimental to marine life depending on the species composition, time of the year and environmental conditions (Cruzado, 1992). Eutrophication is beneficial if the increase in primary productivity results in a balanced and gradual development of multi species algal populations that are capable of sustaining higher trophic levels in the marine food chain. Some species can be toxic to fish, invertebrates and even humans (Hallegraff, 2003).

The symptoms of eutrophication may not be the same all around the world but the cause is always the same: excessive nutrient inputs. However not every nutrient input leads to eutrophication. The question now is: do the conditions prevailing in Lebanese coastal waters determine or help the development of coastal eutrophication?

Collection and analysis of water data are the basis for an assessment of ecological status of a given water body and the risk of pollution and presence of eutrophication. The obtained information can be used for environmental status assessment of ecosystem and for comparisons on regional or global scales. Ecological indicators are important tools in the early detection of changes in the steady state of marine ecosystems. Which ecological and biological indices should be adopted for environmental evaluation system of marine coastal areas? Measurements of nutrient concentrations (especially nitrogen and phosphorus) and algal biomass (using concentrations of chl-*a* and/or algal biovolume) are essential parameters in any effort to manage and monitor coastal zone eutrophication. Nutrients and chl-*a* as relevant quality elements are mandatory in some European directives and recommended in others. Andersen *et al.* (2006) have proposed that measurements of primary productivity should also be added as a mandatory component of these efforts. Smith (2007) suggests that volumetric productivity may provide a more sensitive and a more valuable tool to monitor both the current and future trophic states of estuarine, coastal and offshore marine ecosystems.

A study carried out in South Lebanon using phytoplankton population as an ecological indicator for the assessment of coastal water quality shows that qualitative and quantitative studies of phytoplankton are still important elements (tools) in estimating the level of eutrophication in the littoral environment (Abboud-Abi Saab et al., 2005); but on the other hand, cell count is time consuming thus limiting the number of samples analyzed. The phytoplankton biomass expressed as chl-a levels is also considered to be another way of monitoring eutrophication due to the pigment composition being the active element of autotrophic cells. In addition, phytoplankton investigations conducted earlier in the Lebanese coastal waters mainly focused on the qualitative and quantitative aspects of diatoms and dinoflagellates and their relationships to environmental factors (Abboud-Abi Saab, 1985; 1986; Abboud-Abi Saab et al., 2005). To date, there are few local quantitative data sets on chla distribution in the waters of the Lebanese coast (Abboud-Abi Saab, 1986; 1992; Fakhri et al., 2005). Small cell phytoplankton ( $<2\mu$ m) were found to contribute significantly to the total biomass, photosynthesis and food web in the oligothrophic waters (Abboud-Abi Saab, 1988; Berman et al., 1984 ; Li et al., 1993; Bell & Kaleff , 2001); this way most of picoplanktonic populations will be retained in the filters.

The aim of the present study is: 1) to study the spatial and seasonal variations of nutrients and chlorophyll-*a* along the Lebanese coast; 2) to attempt to set reference condition standards with the objective of enabling the assessment of ecological quality according to these standards. Reference condition is in this context defined as a description of biological quality elements that exist, or would exist, at high status, with or without minor disturbances caused by human activities (EC, 2003).

#### MATERIALS AND METHODES

Eighteen stations were chosen as part of the National Monitoring Program of the National Center for Marine Sciences, covering a large part of the Lebanese coast extending from Tripoli in the north to Naqoura in the south (Fig.1). The characteristics and the coordina-



Figure 1. Sampling sites of chlorophyll-a and nutrients in the Lebanese coastal waters.

tes of the stations are presented in Table 1. Surface samples near sea shore were collected monthly in the morning for a period of one year from March 2005 to February 2006 using 10L sampler at surface level. The temperature was immediately recorded. Salinity was measured using an induction salinometer and presented on a practical salinity scale. Fresh samples of nutrients were brought to the laboratory in ice boxes in darkness where the samples were stored at  $-20^{\circ}$ C. Orthophosphates (P-PO4) were analyzed according to Murphy and Riley (1962), nitrite (N-NO2) to Bendschneider and Robinson (1952) and nitrate (N-NO3) to Strikland and Parsons (1968) with a small modification consisting of utilizing ammonium chloride as activator (Grasshoff, 1961). Samples for measuring of total chlorophyll-a (chl-*a*) were filtered through a Whatmann GF/C filter at low pressure. Pigments were then extracted in 90% acetone for 24h in the cold and the dark. The concentration was determined by a spectrophotometer according to the monochromatic method of Lorenzen (1967). The volume of sea water filtered varied between 1 and 4 liters according to stations. The biomass is expressed in quantity of chl-*a* over volume of sea water (mg/m<sup>3</sup>).

#### Statistical analysis of data

Data of one biological and 5 environmental parameters measured in 215 samples from 18 stations were organized in a matrix of correlation using SPSS. The averages were subjected to principal component analysis (PCA).

# TABLE 1

Town	Code	Longitude	Latitude	Location	Bottom Type
Tripoli	TRI-20	35° 44.160	34° 22.054	Deir Natour-Las-salinas	Rocky
	TRI-21	35° 42.851	34° 18.592	Hiri	Sandy
Batroun	BAT-9	35° 39.189	34° 16.570	Effluent Selaata	Rocky
	BAT-14	35° 39.413 <sup>°</sup>	34° 15.090	Mid-bay	Rocky
Byblos	BYB-10	35° 38.578	34° 07.406	Near Oursin	pebbles
	BYB-14	35° 38.896	34° 06.864	Tam-Tam	Sandy
	BYB-20	35° 39.035	34° 06.142	Fidar Bridge	Sandy
	BYB-22	35° 38.539	34° 03.625	Nahr-Ibrahim	River mouth
Jounieh	JUN-13	35° 37.424	34° 01.777	Tabarja	Rocky
	JUN-20	35° 38.630 <sup>°</sup>	34° 00.635	Roman Bridge	Sandy/pebbles
Antelias	JUN-40	35° 34.970 <sup>°</sup>	33° 55.020	Antelias River	Sandy
Beirut	BEY-11	35° 28.518	33° 54.120	AUB	Rocky
	BEY-20	35° 28.760 <sup>°</sup>	33° 52.767	Ramlet Baida	Sandy
Damour	DAM-10	35° 26.617	33° 42.818	North Damour river	define
Saida	SDA-12	35° 22.931	33° 34.708	Baladiye Beach Sandy	
Sour	SUR-8	35° 18.171	33° 28.032	Facing Electricity	Rocky
	SUR-12	35° 12.536	33° 15.610	Istiraha House public beach	Sandy
Naqoura	NAQ-10	35° 07.254	33° 06.977	Istiraha Private	Rocky

# Description Coordinates and Characteristics of the 18 Stations Monitored on the Lebanese Littoral Waters between March 2005 and February 2006

#### RESULTS

Descriptive statistics (mean, standard deviation, minimum and maximum values) of the parameters measured at the 18 stations studied between March 2005 and February 2006 in the Lebanese coastal area are given in Table 2 while standard errors are given in the Figures.

## **Spatial variations**

The average values ( $\pm$  SD) of temperature varied from 21.88 °C ( $\pm$ 5.70) at Byb-22 to 23.59°C ( $\pm$ 4.26) at Byb-14 and the annual range from a minimum of 15°C (Byb-22) to a maximum 30.8°C (Bey-20). The average values ( $\pm$  SD) of salinity varied between 30.31 $\pm$ 10.99 at Byb-22 and 39.31 $\pm$ 0.27 at Naq-10. A maximum of 39.68 was noted in September at Nak-10 and a minimum of 38.86 in May at Byb-22. The average values ( $\pm$  SD) of the pH varied between 8.09 ( $\pm$  0.06) at station Jun-40 and 8.25 ( $\pm$  0.05) at Bey-11. A minimum of 8.03 is reached in August at Jun-40 whereas a maximum of 8.36 is noted in May at Byb-22 (Table 2).

The mean values (± SE) of nitrite varied from 0.03 (± 0.01)  $\mu$ M/L at Tri-20 to 0.68 (± 0.15)  $\mu$ M/L at Jun-40 (Fig.2a). The values ranged between undetectable concentrations (Tri-20, Naq-10) and 1.71  $\mu$ M/L (Jun-40). For nitrate, the mean values (± SE) vary from 0.31 (± 0.07)  $\mu$ M/L at Tri-20 to 10.69 (± 2.14) at Dam-10 and 10.49 ((± 2.97)  $\mu$ M/L at Byb-22 (Fig. 2b).

# TABLE 2

# Descriptive Statistics (Mean, Standard Deviation, Minimum and Maximum Values) of the Parameters Measured at the 18 Stations Studied between March 2005 and February 2006 in the Lebanese Littoral Area

	T°C	Salinity	pH	N-NO2	N-NO3	P-PO4	Chl a
Stations		· ·	-	(µM/L)	(µM/L)	(µM/L)	$(mg/m^3)$
TRI-20	$22.52 \pm 4.6$	39.13±0.27	$8.23\pm0.03$	0.03 ±0.03	0.31 ±0.24	0.46±0.28	0.22 ± 0.23
	17-29.2	38.66-39.51	8.2 - 8.28	0.00-0.08	0.14-0.97	0.13-0.89	0.01 - 0.72
TRI-21	22.80±4.98	38.26±1.64	$8.18 \pm 0.03$	$0.07 \pm 0.03$	$238 \pm 404$	0.82±0.39	0.46 +0.33
	17-29.5	34.25-39.42	8.11 - 8.21	$0.07 \pm 0.03$ 0.02 - 0.13	0.11-12.27	0.26-1.52	0.1 - 1.03
BAT-9	22.21+4.75	38.28+1.96	8.21 + 0.04	$0.09 \pm 0.06$	3.21 + 3.42	1.12+1.15	$0.22 \pm 0.12$
	17-29.3	32.35-39.52	8.14 - 8.26	0.01 - 0.18	0.21 - 9.56	0.20-3.72	0.06 - 0.39
D	22.88±4.88	38.91±0.43	$8.23 \pm 0.04$	$0.08 \pm 0.05$	$0.91 \pm 1.02$	0.31±0.19	$0.09 \pm 0.08$
BAT-14	17.5-30	37.97-39.36	8.17 - 8.28	0.02 - 0.18	0.20 - 3.70	0.13-0.78	0.01-0.23
DVD 10	22.98±4.5	38.68±0.76	$8.21 \pm 0.04$	$0.12\pm0.07$	$1.32 \pm 1.16$	0.19±0.06	$0.20 \pm 0.21$
BYB-10	17.5-30.2	37.39-39.54	8.15 - 8.27	0.02 - 0.25	0.24 - 3.72	0.10-0.30	0.05 - 0.73
BYB-14	23.59±4.26	38.41±0.92	$8.19\pm0.02$	$0.12\pm0.06$	$6.32\pm6.36$	0.21±0.06	$0.76\pm0.92$
	18.5-30	36.57-39.23	8.15 - 8.22	0.06-0.22	1.29-17.88	0.29-0.12	3.36 - 0.06
BYB-20	$23.43 \pm 4.27$	37.78±1.57	$8.21\pm0.03$	$0.12\pm0.05$	$5.11 \pm 5.38$	$0.22 \pm 0.08$	$0.45\pm0.39$
	18-30	34.94-39.13	8.17 - 8.25	0.04-0.19	1.06 -19.73	0.11-0.38	0.03 - 1.34
	21 88+5 70	30 31+10 99	$8.21 \pm 0.08$	$0.12 \pm 0.09$	$10.49 \pm$	0 27+0 08	$0.28 \pm 0.22$
BYB-22	15-30	8 86-38 92	8 13 - 8 36	0.01-0.34	10.29	0.15-0.40	$0.20 \pm 0.22$ 0.05 - 0.87
	10 00	0.000 20072	0.12 0.20	0.01 0.01	0.97 - 30.68	0110 0110	0.02 0.07
Jun-13	22.85±4.74	39.05±0.38	$8.18 \pm 0.03$	$0.12 \pm 0.06$	$0.81 \pm 0.34$	0.43±0.64	$0.36 \pm 0.46$
oun no	17.4-30	38.40-39.46	8.14 - 8.21	0.03- 0.23	0.39 – 1.71	0.13-2.45	0.06 – 1.71
Jun-20	23.02±4.67	38.52±0.52	$8.18\pm0.03$	$0.10\pm0.07$	$4.19\pm3.69$	$0.22\pm0.05$	$0.50\pm0.27$
	17.5-30	37.68-39.14	8.14 - 8.23	0.02- 0.20	0.48- 13.05	0.10-0.28	0.06- 0.99
Jun-40	23.53±4.69	36.11±3.24	$8.09\pm0.06$	$0.68 \pm 0.53$	$8.49 \pm 7.93$	$2.88 \pm 2.11$	$1.83 \pm 2.12$
J UII-40	18-30.3	28.19-39.16	8.03 - 8.17	0.13-1.71	0.83-26.72	0.43-5.17	0.02 - 6.33
BEY-11	$23.27 \pm 4.84$	39.18±0.22	$8.25\pm0.05$	$0.12 \pm 0.07$	$0.74 \pm 0.78$	$0.22 \pm 0.08$	$0.12 \pm 0.10$
	17.5-30.5	38.83-39.48	8.19 - 8.33	0.03-0.25	0.20-3.03	0.09-0.36	0.02 - 0.33
BEY-20	23.5±4.95	38.77±0.48	$8.14 \pm 0.04$	$0.53 \pm 0.34$	$3.58 \pm 3.64$	$1.52 \pm 1.32$	$0.96 \pm 1.51$
	17-30.8	37.86-39.4	8.08 - 8.21	0.07-1.14	0.73-14.15	0.39-3.93	0.03 - 5.36
DAM-	22.41±4.32	38.45±0.52	$8.20\pm0.01$	$0.14 \pm 0.08$	$10.69 \pm 7.4$	0.23±0.08	$0.47 \pm 0.28$
10	17.2-29.3	37.20-39.12	8.17 - 8.21	0.05-0.29	3.38-24.33	0.11-0.42	0.09 - 1.01
SDA-12	$22.79 \pm 4.66$	38.87±0.27	$8.18 \pm 0.04$	$0.22 \pm 0.11$	$2.66 \pm 1.48$	$0.52 \pm 0.37$	$2.73 \pm 4.17$
	17.4 -30	38.16-39.24	8.13 - 8.23	0.09- 0.38	0.96 - 6.05	0.17-1.27	0.13 - 15.02
SUR-8	$22.75 \pm 4.89$	38.76±0.55	$8.18 \pm 0.06$	$0.22 \pm 0.13$	$3.90 \pm 3.07$	$0.21\pm0.11$	$0.56 \pm 0.49$
	17-30	37.13-39.36	8.1 - 8.27	0.03 - 0.40	0.29-10.24	0.08-0.44	0.09 - 1.41
SUR-12	22.80±4.81	38.95±0.28	$8.20 \pm 0.02$	$0.23 \pm 0.13$	4.72 ±5.69	0.20±0.05	$0.42 \pm 0.30$
	17.2-30.1	38.53-39.46	8.17 - 8.23	0.5-0.52	0.52-21.21	0.12-0.28	0.1 - 0.95
NAQ-	23.14±4.68	39.31±0.27	$8.24\pm0.03$	$0.05\pm0.05$	$0.34 \pm 0.45$	0.14±0.05	$0.11 \pm 0.08$
10	17.5-30.1	58.91-39.68	8.19 - 8.28	0.0-0.16	0.13-1.76	0.04-0.20	0 01- 0.3

A maximum of 30.68  $\mu$ M/L is noted at Byb-22 and a minimum of 0.11  $\mu$ M/L is noted at Tri-21. The average values (± SE) of orthophosphates varied between 0.14 (± 0.01)  $\mu$ M/L at Naq-10 and 2.88  $\mu$ M/L (± 0.61) at Jun-40. The values ranged between 0.038 and 5.17  $\mu$ M/L respectively at Naq-10 and Jun-40 (Fig. 3a).





Figure 2. Spatial distribution of nitrite (a) and nitrate (b) (± SE) at the different sampling sites in the Lebanese littoral waters (March 2005 - February 2006).

#### Seasonal variations

The annual average of N-NO2 concentration in all stations ranged between 0.09 (±0.01)  $\mu$ M/L in April and 0.23 (±0.05)  $\mu$ M/L in September; the highest values are noted in September, October and November (Fig. 4a). For nitrate, the values varied between 1.5 (±0.45) in June and 8.46 (±2.21)  $\mu$ M/L in February. All average values are lowest than 5



 $\mu$ M/L except in May, November and February (Fig. 4b). The annual average of orthophosphates concentrations ranged between 0.27 (±0.04)  $\mu$ M/L in December and 0.94 (±0.33)  $\mu$ M/L in May. The highest average values are noted between May and November and the lowest are noted in March, April and January (Fig. 5a).

Figure 3. Spatial distribution of orthophosphate (a) and chl-*a* (b) ( $\pm$  SE) at the different sampling sites in the Lebanese littoral waters (March 2005 - February 2006).

The annual average of chl-*a* concentration ranged between 0.12 ( $\pm 0.02$ ) mg/m<sup>3</sup> in November and 1.31 ( $\pm 0.82$ ) mg/m<sup>3</sup> in June (Fig. 5b). The average values were highest during spring and early summer (June–August) with gradual increasing from March and gradual decreasing from September to reach the annual minimum in November. Low mean values are also noted in December-January followed by a pre-spring bloom in February.

The Pearson correlation analysis (n = 215) showed that chl-*a* was positively and strongly correlated at P< 0.001 with orthophosphates (r = 0.29), nitrite (r = 0.296) and at P< 0.05 with nitrate (r = 0.150) and with temperature (r = 0.163).

# DISCUSSION

The mean value of temperature in most of stations is not always comparable to the annual mean value ( $\pm$ SD) noted in the Lebanese water which is of 23.5°C ( $\pm$  4.3) (Abboud-Abi Saab *et al.*, 2004). The low temperatures noted at Byb-22 and Dam-10 are due to the influence of fresh waters of the Damour and Nahr Ibrahim rivers which are colder at the mixing site with marine water.





According to previous results, the values of salinities match with the majority of these results found in Lebanese coastal waters (Abboud-Abi Saab, 1985; Abboud-Abi Saab *et al.*, 2005). The minimum observed at Byb-22 in spring is due to the input of Nahr Ibrahim River (this minimum corresponds with the minimum of temperature at this station). The contribution of fresh water in winter causes a strong reduction in the salinity noted by high

values of the standard deviation. The fresh water discharged sometimes by the factory of Selaata, causes a drop in salinity to a minimum of 32 at station BAT-9 located near the factory (Table 2). Station Jun-40 also presents a low average of 36.5 due to the contributions of the sewers and Antelias River. The other stations have almost comparable values.



Figure 5. All-site monthly mean values of orthophosphates (a) and chl - a (b) (± SE) in the Lebanese littoral waters (March 2005 - February 2006).

Significant fluctuations in nutrient concentrations were observed in most of the stations. The two peaks of orthophosphates observed at Jun-40 and Bey-20 (1.52  $\mu$ M/L) are due to the presence of sewage in these stations. The impact of the phosphate discharges of the Selaata factory on the quality of water is also marked at station Bat-9 located near the factory and those in its proximity (Tri-21 and Tri-20) in the direction of the current. It seems more logical that under such conditions nitrogen is the prevailing limiting factor and not phosphate as proposed by Berland *et al.* (1980); however more research is required in order to understand and apply the limiting concept adequately.

The peaks of nitrite in Jun-40 and Bey-20 are due to domestic sewage and the peaks of nitrate observed in Byb-22, Jun-40 and Dam-10 are due to the discharges of the rivers of Nahr Ibrahim, Antelias and Damour respectively and which are usually rich in nitrate. Station Byb-14 has also a high nitrate average due to the influence of Nahr Ibrahim River and the effect of the wind which drives the water current towards north of station Byb-22. All these stations presented also a wide range of standard deviations due to high monthly variations. The stations situated relatively out of the direct continental input like Tri-20, Bat-14, Bey-11 and Naq-10, present very weak nitrite and nitrate values lower than  $1\mu$ M/L. In none of the stations, the value of nitrate exceeded  $35\mu$ M/L; according to Buson (1999), a mechanism of transfer towards the atmosphere exists in the cycle of nitrate thus prohibiting their accumulation in marine water.

In his recapitulation paper about eutrophication in the Mediterranean Sea, Stirn (1988), in listing the factors enhancing algal growth and production, noted that a typical value for Open Ocean for orthophosphates in surface layers is 0.1  $\mu$ M/L (much less in tropical area and much more in upwelling area). Values for the Mediterranean Sea are extremely low, typically below 0.05  $\mu$ M/L in the euphotic zones and at highest 0.3  $\mu$ M/l in the deepest waters (*ibid.*). Average normal concentrations in euphotic layers of productive temperate coastal waters are around 0.3 $\mu$ M/L. In coastal waters which are directly polluted by sewage or similar effluents, the concentrations of phosphorus are as a rule dramatically increased (*ibid.*). In very coastal urbanized area, marine algae are normally exposed to a continual supply and the concentration is higher than open sea. According to UNEP (1988), the concentrations of phosphorus in surface waters of the Mediterranean Sea are extremely low: showing values of 0.03  $\mu$ M/L or less for P-PO4; typical concentrations for eutrophic coastal waters are above 0.15  $\mu$ M/L and for highly eutrophied systems well beyond 0.3  $\mu$ M/L. Seven stations have averages higher than 0.3  $\mu$ M/L (Table 2), therefore these stations will be considered strongly eutrophized in case of orthophosphates.

In surface waters of the Mediterranean Sea, the concentrations are about 0.1  $\mu$ M/L of N-NO3 and 0.1  $\mu$ M/L of N-NO2; concerning nitrogen in the form of inorganic compounds, it is quite depleted; generally, the concentrations are about 0.1  $\mu$ M/L of N-NO3; in eutrophic waters, concentrations are usually increased at least by a factor of 2 and in heavily eutrophied coastal waters by a factor of more than 5; in waters which are directly polluted by sewage or substantially mixed with river discharges, the concentrations are as a rule, much higher, *i.e.*, above 35  $\mu$ M/L (UNEP, 1988).

In marine and coastal waters, increased nutrient loads result in increase of phytoplankton biomass and changes in phytoplankton species (EEA, 2003). The concentrations are generally highest in estuaries and close to river mouths or big cities, and lowest in open marine waters mirroring the pattern of nutrient concentrations (*ibid.*).

It is important to mention the conditions prevailing and the factors in favor of the delay of eutrophication despite the presence of high level of nutrients: there are no large rivers in Lebanon and so the discharges of sewage from the rivers are not significant. The continental shelf is very narrow, edging deep waters, and hence the dispersion of nutrient is relatively easy. Therefore, widespread offshore eutrophication cannot be expected. In addition, when the water temperature is high and favorable for development of toxic algae, rivers are almost dry in the summer and their inputs are generally very modest. It is mostly in the spring season that the temperature rises causing the snow to melt thus adding fresh water to the sea. The

discharges from the rivers and snowmelt from the mountains are beneficial to the primary production. The reason for this is that the addition of fresh water with the nutrient is limited to the spring period and to the coastal area. Whereas when nutrients are needed in the summer, they are not available (Abboud-Abi Saab, 1996). A study has revealed that the very littoral Lebanese water is affected by sewage discharged and urbanization; thus the phytoplankton populations are more affected by human activities rather than the thermal cycle (Abboud-Abi Saab *et al.*, 2005). The geomorphology of coastal environment is an important factor in the intensity of the eutrophication impact. Harbors and closed shallow bays, rivers and estuaries and lagoons are suitable for the negative effect of eutrophication and the development of toxic algae such as in the Eastern harbor of Alexandria noted by Halim *et al.* (1980) since decades. In Lebanon, there are no closed bays and water is being continuously mixed thus preventing conditions of eutrophication; water mixing helps the dispersion of nutrients and pollutants. In addition, oligotrophic conditions in most open areas in the Mediterranean accommodate relatively high loads of domestic inputs.

In attempting to establish national standard values for nutrients in the Lebanese coastal waters, only station Naq-10 which is maybe not affected directly by continental input, presented a level of orthophosphates <0.15  $\mu$ M/l; about 10 stations are slightly affected and have around 0.2-0.7  $\mu$ M/L; the remaining stations which presented an annual mean > 0. 43 $\mu$ M/L are directly affected by sewage input such as Sda-12, Bey-20, Jun-40 and sporadically Jun-13; also all stations from Bat-14 towards North are directly or during the presence of North wind affected by Selaata plant. The above values compared with normal conditions in the Mediterranean are actually high and sometimes very high. Orthophosphate in these littoral waters cannot be a limiting factor.

For nitrite, most values are less than 0.1  $\mu$ M/L. For nitrate, lower annual means are 0.34 and 0.39  $\mu$ M/L respectively in Tri -20 and Naq -10 and can be considered as standard values. Few stations such as Bat-14, Jun13, Bey-11 have mean values <1  $\mu$ M/L. Due to numerous rivers and coastal springs (CNRS/CNRSL, 1999), most of the coastal area is affected at different levels and during a period of the year by fresh waters; for this reason in most stations, nitrate levels are > than 2.5  $\mu$ M/L and can reach about 10.6  $\mu$ M/L as annual mean near river mouths (Table 2).

Comparing these results of nitrate, the principal inorganic forms of nitrogen, to those found in euphotic layers of coastal waters, is between 2-5  $\mu$ M/L and in tropical surface layers the concentrations are much lower, except in upwelling areas. Some of these values, except for stations affected directly by river, are comparable to those found in oligothrophic southern basin of Adriatic sea with 1  $\mu$ M/L, in eutrophic North Adriatic with 1.5  $\mu$ M/L (Vucak-Skrivanic-Stirn,1982) and in highly eutrophic NW Adriatic with 4  $\mu$ M/L (Franco, 1983). Generally, in coastal waters which are directly polluted by sewage or significantly mixed with rivers discharges, the concentrations are generally much higher as in the case of Jun-40 and Sda-12.

For chl-*a*, all mean values obtained did not exceed 1 mg/m<sup>3</sup> except for the three noted peaks at Sda-12, Jun-40 and Bey-20 respectively in the areas of Saïda, Antelias and Ramlet El Bayda and are due to the strong urbanization and the harmful effect of the untreated used waters. Moreover, these stations have maximum chlorophyll-a values between 5 and 20 mg/m<sup>3</sup> (Table 2); according to Bricker *et al.* (1999), waters of these three stations are

classified as moderately eutrophied whereas the other stations present a weak eutrophication because their maximum values are lower than  $5 \text{ mg/m}^3$ .

It should be mentionned that nutrients are also used by macroalgae especially in spring when there is a high development of green algae such as *Enteromorpha* or *Ulva*. This phenomenon is becoming more frequent in the rocky area of the Lebanese coast and a high competition between microalgae and macroalgae is noted in this situation.

Comparing to the recent results carried in stations situated near the factory of Selataa (Fakhri *et al.*, 2005), the results in some littoral stations are lower than in some offshore stations presented in their work. In spring, values of 2.5mg/m3 are noted in coastal area in surface water and  $3.5 \text{ mg/m}^3$  at 30m in May in Jounieh Bay (Abboud-Abi Saab, 1986) while in spring and in another littoral and open to the sea station, chl-*a* varied between 0.1 and 1 mg/m<sup>3</sup> (Abboud-Abi Saab, 1992).

Comparing to some results in Mediterranean Sea, high concentrations are found in polluted area either in occidental or oriental basins; a maximum of 6.5 mg/m<sup>3</sup> is noted in Iskandaroun Bay in Turkey (Yilmaz *et al.*, 1992), 9.6 mg/m<sup>3</sup> in Abu –Qir Bay in Egypt (Nessim & El-Deek, 1993), 5.14 mg/m<sup>3</sup> in coastal basin of Alexandria Egypt (Aboul-Kassim *et al.* (1992), 9.5 mg/m<sup>3</sup> in North Adriatic (Franco & Michelato, 1992) and 15.5 mg/m<sup>3</sup> in Golf of la Spezia in Italy.

The stations Naq-10 and Bat-14 presented an annual average between 0.09 and 0.12 mg/m<sup>3</sup>; these values are comparable to those of offshore stations (paper in preparation) and can be considered as standard stations or standard references. In spite of the significant correlation found between nutrients and chl-a, which show the lower average rates of chl-a. The stations which show the lower averages of chl-a did not always present the lower means of orthophosphates and nitrate such as in Bat-14; five other stations (Tri-20; Bat-9; Byb-10; Byb-22 and Jun-13) having mean values between 0.2 and 0.36 mg/m<sup>3</sup> are considered as slightly enriched either by orthophosphates or nitrogen. The highest annual mean > 1 mg/m<sup>3</sup> and values reaching 15 mg/m<sup>3</sup> are noted in the stations affected by sewage; these sources bring nitrogen and orthophosphates, both essential elements for phytoplankton development followed by stations affected indirectly by rivers or fresh water input such as Tri-21, Byb-14, Byb-20, Jun-20, Sur -8 and Sur-12 which presented mean values between 0.42 and 0.56  $mg/m^3$  of chl-a; except for the station Byb -14 which presented an average of 0.76  $mg/m^3$ ; previous research in this station showed a high density and high diversity in phytoplankton populations. It should also be noted that among these categories of similar environmental conditions, it seems that, the mean values in sandy stations are higher than in rocky stations because nutrients according to sea state can easily be resuspended in water column during mixing waters and thus contribute to the primary production in pelagic waters.

The stations affected directly by rivers and which presented a high value of nitrate did not show a high concentration of chl-*a*; this is due to the high turbulence prevailing in the proximity of the estuaries; when nutrients are available primary producers need a minimum of water clarity and stability to develop; this situation was noted by Coste (1975) and Abboud–Abi Saab et *al.* (1999-2002). On the other hand, the water of the river presents a low value in orthophosphates, a necessary element for the primary production (Khalaf, 1986; Abboud–Abi Saab et *al.*, 1999-2002; Khalaf & Slim, 2005). In this study, stations enriched only by orthophosphates did not also show remarkable values of chl-*a*.

The principal component analysis (PCA) applied to the average of all parameters in each station confirmed most of these findings and give us a comprehensive scheme of the factors affecting this coastal environment. The first two factors have explained a wide fraction of the total variability (75%). In the variable projection plot of F1/F2 (Fig. 6) the first factor (44% of variability) may be considered as representative of the sewage's influence and stations Sda-12, Bey-20 and Jun-40 are present. The second factor F2 (31%) is more representative of the river's influence and Byb-22 and Dam-10 are present; all other stations are brought together (Fig. 7). In discarding these five stations, more details can be obtained concerning the other stations. Other distribution is shown; 3 other groups can be distinguished: Tri-21 and Bat-9 are together and are the stations which present a high average of orthophosphates due to the plant of Selaata; the second is formed by Byb-14, Byb-20, Jun-20, Sur-8 and Sur-12 slightly enriched by fresh water or nitrate ; the last one formed by Tri-20, Bat-14, Byb-10, Jun-13, Bey-11 and Naq-10 are considered as relatively reference stations.



Figure 6. Plane-space of factors F1 and F2 of principal component analysis (structure of stations).



Figure 7. Plane-space of factors F1 and F2 of principal component analysis (structure of stations, 5 stations discarded).

# CONCLUSION

According to these results and in relation to continental inputs, sites can be divided into 5 categories: (i) sites influenced directly by urban sewage inputs, (ii) directly by river input, (iii) enriched indirectly by river inputs or phosphorus input, (iv) slightly enriched by continental input and (v) sites – references. In a general view there are some moderate inshore eutrophication and heavily eutrophied local systems. In the south and north of the Lebanese coast where the human settlements are scattered and modestly inhabited, there is in principle no risk of substantial eutrophication.

Results of the present work will be considered as a baseline for further studies. The coming years will therefore be a learning process about interannual variations. Further work is needed to consolidate these standard national values. Also, further study should be focused on another important step that is to define what constitutes an acceptable deviation.

Finally, signs of eutrophication should be monitored not only in pelagic environment but also in the benthic communities since an increase in the development of monospecific green algae has been noted in many Lebanese rocky zones especially in terraces during spring period; that is why it is considered vital that science and management are integrated to ensure that the directive becomes a strong legal instrument for the protection and whenever necessary for the restoration of the ecological status of Lebanese coastal waters.

#### ACKNOWLEDGEMENTS

We gratefully acknowledge all our colleagues from the National Center for Marine Sciences working in the Monitoring Program.

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