

IMPACT OF NATURAL AND ARTIFICIAL CHEMICAL INPUTS ON THE MARINE ECOSYSTEM OF BATROUN REGION (NORTH LEBANON)

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ABSTRACT

This paper is an attempt at studying the interaction of a seasonal river and the discharges of a major chemical plant in the Batroun region in North Lebanon.

Surface water analysis was done monthly for a period of 14 months from May 2001 till June 2002, along 13 stations (10 along the shore and 3 on a horizontal transect from the factory). The ranges of the hydrological and hydro-biological parameters were as follow: 16.3 to 32°C for temperature, 26.34 to 39.53‰ for salinity, 6.33 to 8.30 for pH, 81.85 to 110.7% for dissolved oxygen saturation, 0.02 to 25.36 µg/L for nitrate, 0.01 to 54.65 µg/L for phosphate and 0.01 to 2.52 mg.m⁻³ for chlorophyll-a respectively. Results show that nitrate values follow a decreasing gradient from the mouth of the river in winter and spring. Phosphate values decrease as one moves away from the discharge points of the plant. The buffering capacity of seawater did not prevent the increase in seawater acidity to abnormally high levels and the acid discharge from the factory to its immediate proximity has created a local ecologically deliterious factor that was marked out at primary production level represented by chlorophyll-a concentrations. The high levels of nutrients essential for phytoplankton development did not result in high chlorophyll-a concentrations. The reduction in chlorophyll-a concentrations was the consequence of the dystrophic condition caused by the unbalance in nutrients distribution and the destructive effect of acid discharges at primary production level.

The hydrodynamic and geomorphologic position of any marine zone, the flow rate and concentrations of the different continental discharges will interfere in the level of its contamination.

Keywords: Levantine basin, North Lebanon, chemical contamination, river, chlorophyll-a, dystrophy

INTRODUCTION

The Eastern Mediterranean basin, in particular the Levantine basin, is one of the most oligotrophic regions in the world (Berman *et al.*, 1984; Krom *et al.*, 1991) with nutrient deficits especially in nitrate and phosphate which are essential for primary production (Berland *et al.*, 1978; Bethoux *et al.*, 1992; Yilmaz *et al.*, 1992; Tselepides *et al.*, 2000). This situation also characterizes the Lebanese coast where hydrology is strongly conditioned by summer wind pattern that often prohibits the upwelling of the nutrient-enriched deeper waters.

The major sources of these chemicals are the agrochemicals reaching the sea through rivers, run-off waters or rainfall, or as the by-products wastes from factories and domestic sewers, which currently flow along the coast without any treatment.

There are two major sources of contamination in the Batroun region. The first is the chemical plant established in 1957 in Selaata to the North of Batroun, and characterized by its heavy production of phosphoric acid, triple superphosphate, simple superphosphate, aluminum sulfate and sulfuric acid. The by-products like phosphor-gypsum and sulphuric acid are directly discharged in coastal waters near the plant (Al-Hajj and Muscat, 2000). This plant uses 840 Tons of phosphate rocks per day (Abboud-Abi Saab and Dargham, 1998). Huge amounts of phosphate are rejected into the seawater (Abboud-Abi Saab and Attallah, 1996). The second source is the Al-Jaouz seasonal River, located to the north of Batroun (about 400m to the south of Selaata chemical plant) with a mean annual flow of $2.84\text{m}^3\text{s}^{-1}$ (UNDP, 1970). Its watershed is less urbanized and not industrialized, and the nutrient load it carries originates essentially from agrochemicals.

The wastewater produced at this plant interacts with Al-Jaouz river waters loaded with fertilizers, at the study zone, thus making it possible to study its impact and influence on the chemical composition of marine waters and on primary productivity. Previous studies conducted in the region (Abboud-Abi Saab, 1985; 1986) have not detected any eutrophication despite the fact that this region is also considered "a hot spot" (H.H Kouyoumjian; personal communication).

The purpose of this paper is to study the impact of these sources on the physico-chemical and biological characteristics of the zone under different hydrological conditions, and by using chlorophyll-a as an indicator.

MATERIALS AND METHODS

The studied area is located in the northern part of the Lebanese coast opposite Al-Jaouz River and the chemical plant of Selaata (Figure 1). Thirteen stations were chosen for sampling. Stations M01 to M10 were roughly distributed along the coastline, from Batroun harbor exit till the jetty, 300m to the north of the plant. The distance between successive stations is being 200m. Stations M11, M12 and M13 were positioned along a transect to the west from station M09 extending 1Km offshore. Their location and characteristics are given in Table 1. Samples were collected monthly from May 2001 till June 2002, using a small fishing boat. Geographical coordinates were determined with a portable G.P.S type Garmin 45.

Hydrological and hydro-biological parameters were measured directly in the field by three probes fitted with a multi-parameter type "WTW Multiline P4". The first probe was for

water temperature ($^{\circ}\text{C}$) and salinity (‰) measurements. It was calibrated using a salinometer, type Beckman R S7-C model. The second probe was for pH measurement, calibrated with two WTW buffer solutions 4.0 and 7.0 directly before sampling. The third one was for dissolved oxygen determination. The *in situ* values were compared with parallel laboratory analysis on water sub-samples using Winkler's method as modified by Carpenter (1965).

For nitrate, phosphate and salinity analyses, water samples were directly collected at -30cm. Sub-samples for nutrient determination were frozen at -20°C until manual analysis where orthophosphate was analyzed by the colorimetric method of Murphy and Riley (1962), and nitrate by the method of Bendschneider and Robinson (1952). Chlorophyll-a concentrations were determined on Whatman GF/F filters by spectrophotometry after extraction in 90%-acetone/water (V/V) (Lorenzen, 1967).

The meteorological data (air temperature, wind speed and wind direction) were received monthly from the National Meteorological Station at Tripoli (25 Km to the North of Batroun).

Descriptive statistics, t-tests, correlation and model adjustments were conducted using Excel® Analysis Tools Pack. To determine the dominance of each parameter, Principal Components Analysis (PCA) was conducted by using the SPSS® statistics program for Windows®.

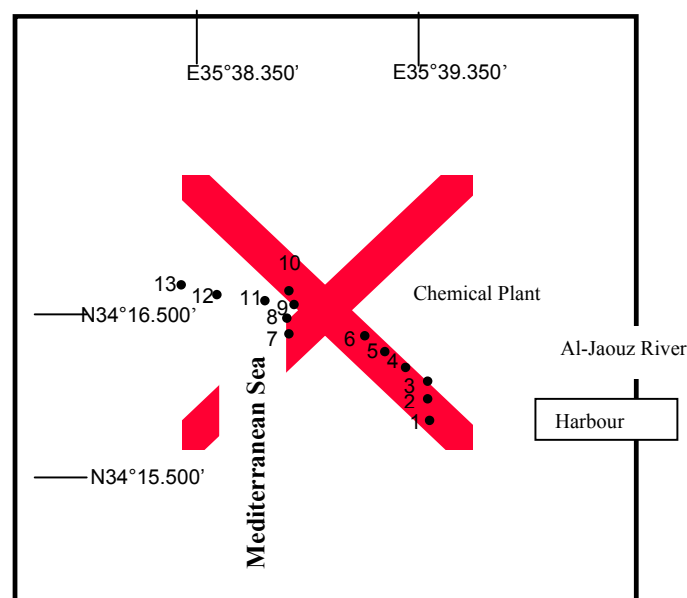


TABLE 1
Description and Coordinates of the 13 Stations

Stations	Coordinates	Bottom type and Depth (m)	Location
M01	N 34° 15,533' E 35° 39,361'	Rocky with big areas of sand, 10m	50m from the exit of the harbor of Batroun
M02	N 34° 15,684' E 35° 39,357'	Rocky with big areas of Sand, 10.5m	125m far from the coast
M03	N 34° 15,824' E 35° 39,359'	Dunes of sand, 7.5m	150m far from the coast and 200m from the tongue of El-Jaouz river
M04	N 34° 16,003' E 35° 39,339'	Sandy, 6m	140m in front of the tongue of the river and 400m from the south wall of the plant
M05	N 34° 16,160' E 35° 39,304'	Sandy, 6m	100m far from the coast and 200m from the discharge at the south wall of the plant
M06	N 34° 16,317' E 35° 39,280'	Sandy, 5m	50m far from the coast and 50m in front of a small discharge at plant south wall
M07	N 34° 16,377' E 35° 39,119'	Sand and gravel, 11m	60m in front of the west wall of the plant and to the south of cooling discharge
M08	N 34° 16,440' E 35° 39,102'	White layer of gypsum and gravel, 6m	50m in front of the west wall of the plant and to the north of cooling discharge
M09	N 34° 16,579' E 35° 39,132'	Rocky with small areas of sand, 5m	100m in front the principal discharge, north side of the plant
M10	N 34° 16,748' E 35° 39,214'	Rocky with big areas of sand, 4m	50m south of the jetty and 100m from the coast
M11	N 34° 16,583' E 35° 39,004'	Rocky, 7.5m	200m offshore from station M9
M12	N 34° 16,672' E 35° 38,734'	Rocky with small area of sand, 16m	600m offshore from station M9
M13	N 34° 16,834' E 35° 38,370'	Rocky with large areas of fine gravel, 24m	1200m offshore from station M9

RESULTS

Mean annual values (including annual evolution) and other statistical data of each station are presented in Table 3 and in figures 2 to 6.

Meteorological data

The weather data showed that throughout the sampling period the predominant winds were westerly, southwesterly and northerly. Wind speeds range between 0.2 and 4m.s⁻¹ (Table 2)

Temperature

Except for station M09 where seawater temperature reached 32°C, all the other stations showed normal annual variation ranging between 16.2°C in winter and 30°C in summer (Figure 2). The mean annual temperature was higher in station M09 than in the other stations ($0.5 \leq \Delta T \leq 1.08$; Table 3). Distance from the plant or the river discharge point had no bearing on temperature ($P < 0.05$).

TABLE 2
Dominant Wind Speed and Wind Direction on Each of the 14 Sampling Date During the
Period of Experiment (May 2001- June 2002)

Date	Wind Speed m.s ⁻¹	Wind Direction
17-May-2001	3	N
12-Jun-2001	2	W-NW
24-Jul-2001	3.4	W-NW
14-Aug-2001	3.5	W
11-Sep-2001	2.4	N
19-Oct-2001	1	NW
16-Nov-2001	3	SW
22-Dec-2001	1.5	NE
18-Jan-2002	1.6	NE
15-Feb-2002	2.25	SW
19-Mar-2002	0.2	-
15-Apr-2002	2.8	SW
20-May-2002	2.6	NW
24-Jun-2002	2.6	W

Salinity

Salinity at the river mouth was shown to fluctuate seasonally depending on rainfall. Station M04 showed the extreme annual variation with the lowest recorded value in April 2002 (26.34 ‰). The impact of freshwater dilution decreased to the west and to south while proceeding far from the river mouth. A small decrease in salinity was registered in front of the discharge points of the chemical plant, however, with no measurable seasonal trend (Figure 2). Stations M01, M02, M12 and M13 (significantly different from station M04 at $p < 0.05$), showed similar mean values throughout the year (38.92‰, 38.97‰, 38.99‰, 39.00‰) respectively (Table 3).

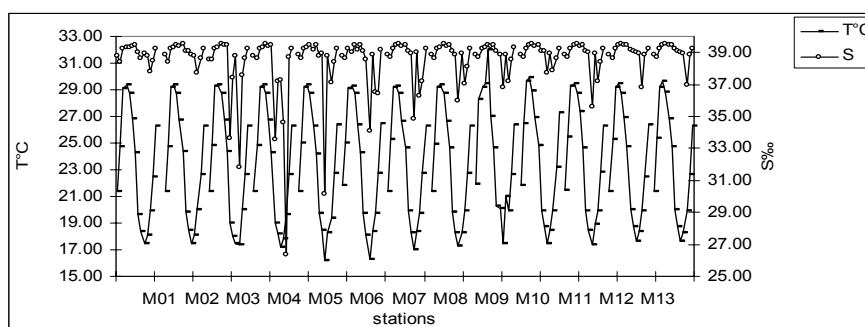


Figure 2. Variation of water temperature and salinity in all stations (May2001-June 2002).

pH

Out of plant influence, pH values ranged between 8.0 and 8.3 throughout the year. The relation between temperature and pH was only significant at station M04 where pH decreased with increasing temperatures ($R^2=0.825$; $p<0.001$). Very low pH values (6.33, 7.49 and 7.36 respectively) were sometimes measured in stations M06, M09 and M10 close to the chemical plant (Figure 3). The mean annual pH values $\pm$ standard deviation at these 3 stations (7.78 ± 0.71 , 7.83 ± 0.19 and 7.93 ± 0.27 respectively) showed high variability throughout the sampling sorties (Table 3).

Dissolved oxygen

A maximum of 110.7% was measured in December 2001 and a minimum of 81.9% in August 2001 at station M01 (Figure 3). The lowest annual mean percentage of saturation was recorded at station M01, in front of Batroun harbor exit (92.9%) and the highest at the further station M13 (110.68%) (Table 3). The annual mean trend appeared to be homogenous, without any clear seasonal influence on primary production enhancement. There appear to be only significant differences between stations M01 and M13 at $p<0.05$.

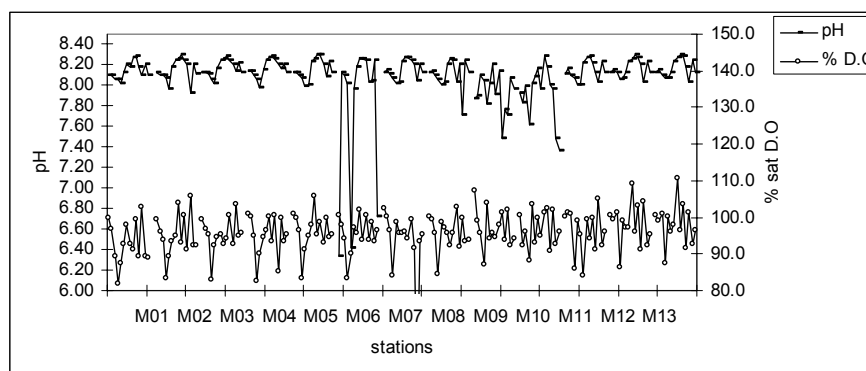


Figure 3. Variation of pH and % of saturation of dissolved oxygen in all stations (May 2001-June 2002).

Orthophosphate

Orthophosphate concentrations are plotted in Figure 4. Maximum mean values $\pm$ sd of 3.83 ± 4.87 , 4.73 ± 7.73 , 15.24 ± 11.40 , and $18.67 \pm 18.34 \mu\text{g}\cdot\text{L}^{-1}$ were respectively measured in M06, M08, M09 and M10 stations, near the plant (Table 3). At the south side of the chemical plant, a north to south dilution gradient of orthophosphate was detected. Seawater orthophosphate levels were inversely proportional to the distance from the factory as one moves from M06 ($3.13 \mu\text{g}\cdot\text{L}^{-1}$) to station M03 ($1.3 \mu\text{g}\cdot\text{L}^{-1}$) ($R^2=0.887$, $p<0.05$). In front of the river, poor orthophosphate enrichment was noted (Figure 5).

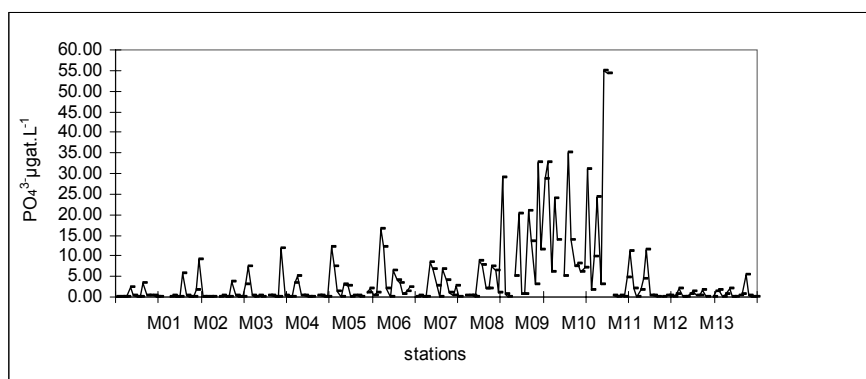


Figure 4. Variation of phosphate concentrations in all stations (May 2001-June 2002).

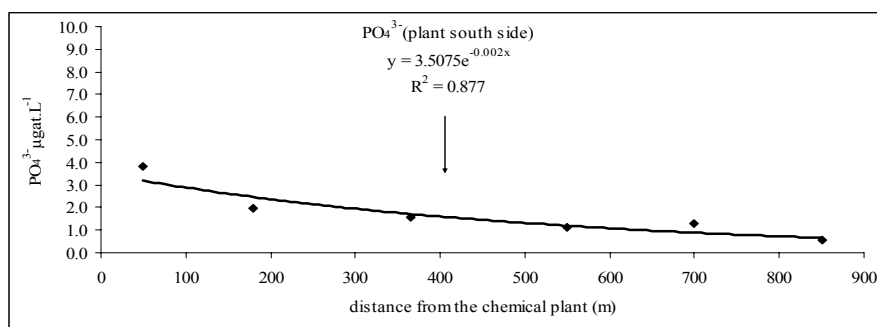


Figure 5. Correlation between phosphate concentrations and distance of stations from the south side of the chemical plant at Batroun region, showing the north-to-south dilution of phosphate (May 2001-June 2002).

Nitrate

Figure 6 shows the seasonal effect of Al-Jaouz River on nitrate levels. A maximum value of $25.36 \mu\text{g}\cdot\text{L}^{-1}$ was measured at station M04 in April 2002, while a minimum level of 0.02 was observed at the furthest station M13 - the least influenced by river flow. Strong variability was detected at stations M04 ($4.40 \pm 7.40 \mu\text{g}\cdot\text{L}^{-1}$) followed by M03, M05 and M06, while weak variability was found at M02 ($0.42 \pm 0.27 \mu\text{g}\cdot\text{L}^{-1}$) (Table 3). The relation between nitrate concentrations and the northward distance from the river was significant ($R^2=0.703$; $p<0.05$) (Figure 7). A light enhancement of nitrate levels was observed at Batroun harbor exit (M01) as compared to M02 and M10 to M13 stations, which exhibited oligotrophic nitrate levels throughout this study.

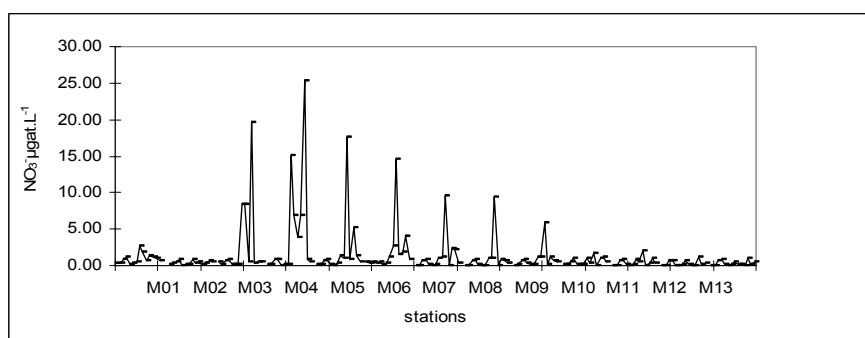


Figure 6. Variation of nitrate concentrations in all stations (May 2001-June 2002).

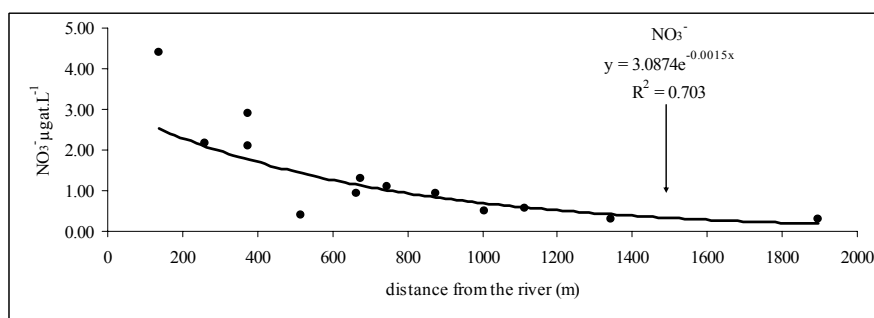


Figure 7. Correlation between nitrate concentrations in coastal waters at Batroun and distance of stations from the river Al-Jaouz showing the trend of nitrate dilution (May 2001-June 2002).

Chlorophyll-a Measurements

Figure 8 shows monthly chlorophyll-a concentrations. A clear spring peak (April 2002) was observed in almost all the stations, however, with low levels at stations M06, M07, M08 and M13. Stations located out of the continental influences (M01, M02 and M11), in front of the river mouth (M03, M04 and M05) and near the northwest wall of the chemical plant (M09 and M10) exhibited the highest chlorophyll-a mean concentrations varying between 0.27 and 0.38 $\text{mg}\cdot\text{m}^{-3}$. Lowest values, ranging between 0.17 and 0.23 $\text{mg}\cdot\text{m}^{-3}$, were measured at stations M06, M07, M08, M12 and M13 (Table 3). The stations closest to the harbor exit, M01 and M02, showed an increase in chlorophyll-a concentrations due to the possibility that the water inside the harbor may contain wastewater from different human activities.

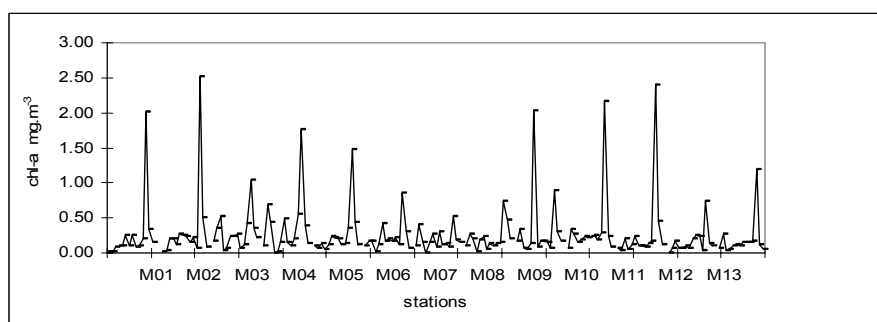


Figure 8. Variation of chlorophyll-a concentrations in all stations (May2001-June 2002).

TABLE 3
Summary of Average Data ($\pm$ SD) from Monthly Samples for Hydrological Parameters and Chl-a at the Different Stations (May2001- June 2002)

	T°C	S ‰	pH	% D.O	PO ₄ ³⁻ (μ -gat.L ⁻¹)	NO ₃ ⁻ (μ gat.L ⁻¹)	Chl-a (mg.m ⁻³)
M01	23.34 $\pm$ 4.28	38.92 $\pm$ 0.47	8.14 $\pm$ 0.08	92.94 $\pm$ 5.83	0.55 $\pm$ 1.02	0.92 $\pm$ 0.68	0.27 $\pm$ 0.51
M02	23.38 $\pm$ 4.26	38.97 $\pm$ 0.48	8.15 $\pm$ 0.11	94.98 $\pm$ 5.86	1.27 $\pm$ 2.71	0.42 $\pm$ 0.27	0.35 $\pm$ 0.64
M03	23.25 $\pm$ 4.44	37.94 $\pm$ 2.35	8.17 $\pm$ 0.08	95.14 $\pm$ 4.78	1.13 $\pm$ 2.16	2.92 $\pm$ 5.59	0.29 $\pm$ 0.26
M04	23.23 $\pm$ 4.43	37.24 $\pm$ 3.65	8.17 $\pm$ 0.09	94.87 $\pm$ 5.66	1.60 $\pm$ 3.34	4.40 $\pm$ 7.40	0.38 $\pm$ 0.45
M05	23.24 $\pm$ 4.42	38.26 $\pm$ 2.41	8.15 $\pm$ 0.10	96.27 $\pm$ 5.24	1.97 $\pm$ 3.53	2.16 $\pm$ 4.65	0.27 $\pm$ 0.36
M06	23.29 $\pm$ 4.39	38.32 $\pm$ 1.55	7.78 $\pm$ 0.71	95.57 $\pm$ 4.77	3.83 $\pm$ 4.87	2.10 $\pm$ 3.78	0.23 $\pm$ 0.21
M07	23.39 $\pm$ 4.32	38.52 $\pm$ 1.40	8.15 $\pm$ 0.09	95.96 $\pm$ 4.53	2.37 $\pm$ 2.98	1.31 $\pm$ 2.48	0.19 $\pm$ 0.14
M08	23.39 $\pm$ 4.29	38.70 $\pm$ 1.02	8.11 $\pm$ 0.14	95.81 $\pm$ 4.54	4.73 $\pm$ 7.73	1.09 $\pm$ 2.43	0.19 $\pm$ 0.19
M09	24.31 $\pm$ 4.45	38.80 $\pm$ 0.81	7.93 $\pm$ 0.19	97.08 $\pm$ 5.24	15.24 $\pm$ 11.40	0.94 $\pm$ 1.50	0.36 $\pm$ 0.53
M10	23.81 $\pm$ 4.43	38.95 $\pm$ 0.57	7.92 $\pm$ 0.27	96.66 $\pm$ 4.95	18.67 $\pm$ 18.34	0.57 $\pm$ 0.52	0.38 $\pm$ 0.53
M11	23.59 $\pm$ 4.28	8.73 $\pm$ 1.08	8.14 $\pm$ 0.09	96.08 $\pm$ 6.07	2.65 $\pm$ 4.01	0.51 $\pm$ 0.53	0.31 $\pm$ 0.61
M12	23.51 $\pm$ 4.25	38.99 $\pm$ 0.68	8.16 $\pm$ 0.08	98.07 $\pm$ 5.82	0.55 $\pm$ 0.65	0.30 $\pm$ 0.34	0.17 $\pm$ 0.18
M13	23.52 $\pm$ 4.27	39.00 $\pm$ 0.64	8.16 $\pm$ 0.09	98.22 $\pm$ 5.63	0.92 $\pm$ 1.43	0.30 $\pm$ 0.33	0.21 $\pm$ 0.29

Statistical Treatment

Data from the 13 stations were subjected to principal component analysis (PCA). The first three factors have explained a wide fraction of the total variability (77.5%). In the variable projection plot of F1/F2 (Figure 9) the first factor (42% of variability) was positively determined by nitrate concentrations and dissolved oxygen values, and negatively marked by temperature and salinity. Their projection in this F1/F2 space was closely located near F1 (X-axis) and never to F2 (Y-axis). The major F1 axis may be considered as representing the river's influence because these parameters were usually associated with the river flow characteristics (decrease in salinity and increase in nitrate and dissolved oxygen values). The second factor F2 (20.3% of the total variability) appeared to be strongly and positively determined by phosphate concentrations and inversely by the pH point that could be identified as representative of the chemical plant influence. In the F2/F3 plot (Figure 10), F3 (15.17% of the total variability) exhibited a strong opposition between dissolved oxygen and salinity on

one side, temperature and nitrate on the other and might be interpreted as the seasonal cycle and its consequences on the time evolution of coastal marine water.

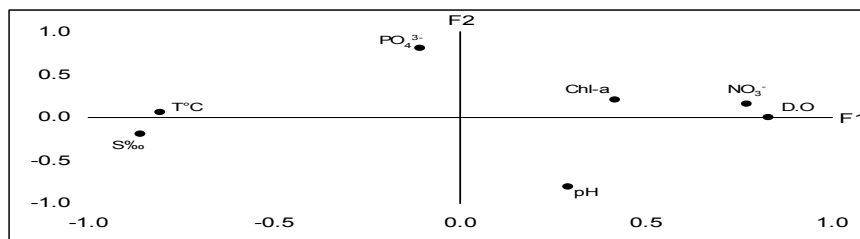


Figure 9. Plane – space of factors F1 and F2 of Principal Component Analysis (structure of variables).

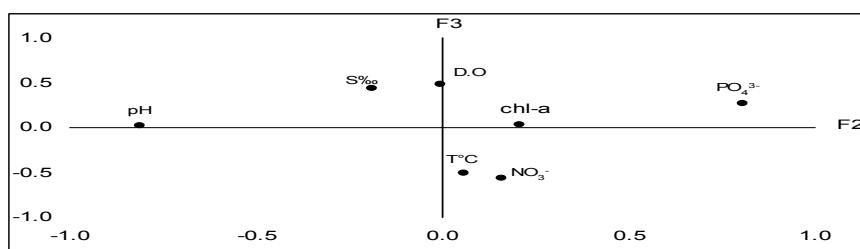


Figure 10 Plane – space of factors F2 and F3 of Principal Component Analysis (structure of variables).

DISCUSSION

Temperature showed an expected marked seasonal cycle with a minimum in winter and maximum in summer. The annual range of variation is in accordance with the previously reported data (Abboud-Abi Saab, 2002). The two sources of continental inputs have differently signed their respective influence. Lowest temperatures were recorded in winter in the vicinity of Al-Jaouz River as it was reported in outflows of Mediterranean rivers (Abboud-Abi Saab *et al.*, 1999-2002; Younes *et al.*, 2003). On the other hand, a significant increase in seawater mean temperature ($\Delta T=1^{\circ}C$) was noted at station M09, as a result of the higher temperatures of the industrial wastewater discharged at the northwest side of the chemical plant. It is a small but significant change of one of the hydrological parameters induced by the plant's activity.

The influence of the river on salinity annual cycle was mainly noted in winter and spring. Lowest salinity values accompanied with strong variability were measured at station M04 in front of the river tongue. The dilution effect was regularly reaching M03 and M05 located at the same distance from both sides of the discharge point of the river. The dilution plume was mainly conditioned by wind and river flow. In February 2002, due to both high river flow rate and strong southerly winds, the fresh water plume reached station M11 (35.59‰; Table 2), a distance considered important for a small river. In contrast, the effect of

plant discharges on salinity was not evident.

In the studied area, the river dilution plume could be considered as a structural element of prime importance for seasonal evolution of surface seawater and for the associated biological consequences. This is confirmed by PCA analysis results where F1 factor was widely determined by low temperature and salinity levels on one side, and on the other, by high dissolved oxygen saturation percentages and nitrate levels. In the current study the dissolved oxygen annual distribution, classically linked to salinity and temperature distributions (Skelvan *et al.*, 2001), was physically conditioned (higher percentage in winter and lower in summer) and linked with temperature at a significant level ($R^2=0.827$; $p<0.001$) and did not appear to be seasonally determined by the biological activity (Lalli and Parsons, 1993).

As it was reported from recent long-time series measurements in coastal shallow waters (Bensoussan *et al.*, 2004, in press), the dissolved oxygen and pH (an indirect estimator of CO_2 concentrations; pH increases when CO_2 concentrations decreases) natural variations are linked in seawater at different time scales (from day to seasons), due to the opposite dynamics of dissolved gas utilization by autotrophic and heterotrophic biomass (O_2 production and CO_2 consumption by photosynthetic processes in light and conversely in dark). So, natural variability of pH is limited by the biological activity level as well as by the buffer effect of all the present salts in seawater. But, in this study, if most of the pH values were included inside the range of variations, commonly reported in literature (8.1 to 8.3), these distributions were deeply lowered at the nearest plant stations (M06, M09 and M10). For example, some values as low as 6.2 were measured at station M06. Taking into account the strong buffering effect of seawater, such low pH values constitute certainly a clear and intense signature of the chemical plant activity. Two sources of acid were flowing out of the plant. The first one originated from plant's south wall (in front of station M06). This small-sized emissary seemed to be of local importance because of its weak observed flow rate and did not influence the pH level and its variability at the other stations (its effect was delimited to M06 station). The second source of acid was coming out of the northwest wall of the factory, in front of station M09. In most of the cases, the measured pH at M09 was higher than that found at M06, but the flow strength of this emissary contributed to extend its impact to other surrounding stations such as M10. Undoubtedly, the pH modification of seawater in this studied area is one of the main influences of Selaata chemical plant. These pH changes might have probable consequences upon biological activities of living organisms represented by chlorophyll alteration.

The Lebanese Levantine basin is a part of the eastern Mediterranean basin, considered to be one of the most oligotrophic water bodies in the world (Berland *et al.*, 1988). The $\text{PO}_4^{3-}\text{-P}$ concentrations are in the range of $0.01\text{-}0.24\mu\text{g}\cdot\text{L}^{-1}$, depending on the depth and location, and the level of $\text{NO}_3^- + \text{NO}_2^- \text{-N}$ ranges from 0.05 to $6\mu\text{g}\cdot\text{L}^{-1}$. The eastern-basin coastal zones are locally enriched with nutrients through different sources like rivers (Yilmaz *et al.*, 1992) and like industrial effluents such as fertilizer plants. The major part of anthropogenic nutrients reaching seawater, and particularly the phosphate forms, is discharged from acidic industrial effluents (Bethoux *et al.*, 1992; Herut *et al.*, 2000).

The PCA had clearly differentiated two main continental sources that structured the Batroun marine environment, both with their specific associated loads: Al-Jaouz River and the chemical plant at Selaata. This study provides evidence that the factory represents the main source of orthophosphate in Batroun coastal seawater, and the river does not contribute to this

supply. In fact, orthophosphate concentrations in surface waters were inversely correlated to the distance from the emissaries of the plant ($R^2=0.8415$; $p<0.05$) and the best fit for the relationship is the exponential form, a model that describes well a dynamic dilution from a continental water flow (Figure 7). Moreover, when all the monthly data of the M10 sampling station are considered, orthophosphate concentrations are inversely but significantly linked to pH values ($R^2=0.767$; $p<0.01$). Due to stronger variability in pH or orthophosphate values, such a relationship was not found near the two main sources of phosphate compounds; they were located respectively in front of station M06 and station M09 and their input level appeared to be different, as the probable consequence of their own concentrations and strength of discharge. The M06 location was 2.5 times closer to the source of phosphate than M09, but the concentrations of phosphate at M09 were 4 times greater than those found at station M06. The south-wall emissary of the plant was exhibiting weaker flow and orthophosphate concentrations than the one at the northwest side. The orthophosphate level often recorded in front of the Batroun harbor exit (higher than that of nitrate), and in relation with a slight decrease in salinity, provides evidence for the contamination by phosphate compounds present in domestic detergents.

The Al-Jaouz River adds no significant amounts of phosphates into the seawater, but huge amounts of nitrate, a phenomenon reported by many workers in the field e.g. Chen *et al.* (2001). The Al-Jaouz River drains numerous agricultural lands where nitrates are used as major fertilizers. The nitrate mass brought yearly to Batroun seawater are estimated at $270 \times 10^7 \mu\text{g}$ (Abboud-Abi Saab *et al.*, 1999-2002). The origin of this nitrate enrichment is first evidenced by the nitrate-salinity inverse correlation either when the whole set of data was considered or when only seawater samples with nitrate concentrations higher than $1 \mu\text{g} \cdot \text{L}^{-1}$ ($p<0.05$) were selected. This is assessed by the study of the spatial distribution of the nitrate mean values in relation to their distance from station M04. The relation, of exponential form, is highly significant ($r^2=0.7311$; $p<0.05$). The dilution of river nitrate inputs is more progressive when going northward than southward as the possible consequence of southwest wind dominance and by the general current direction south- north along the Lebanese coastal waters.

The oligotrophy of the eastern Mediterranean is due to the lack in nutrients, particularly in nitrates (Denis-Karafistan *et al.*, 1998), which are essential for marine primary production. This relative poverty induces consecutive low levels of chlorophyll. Coastal zones are generally richer as attested by chlorophyll concentrations viewed by satellite sensors, and particularly in front of the river mouths (Younes *et al.*, 2003); but the coastal waters, north of Batroun, seemed to constitute a particular case in this general scheme. Despite the fact that its waters were enriched, permanently, by huge amount of phosphate from the chemical plant and, seasonally, by the river nitrate inputs, the chlorophyll-a mean concentrations remain modest and comparable to other reported values for the Levantine surface waters (Yacobi *et al.*, 1995). Spring-limited phytoplankton blooms can be detected, with different amplitudes, in almost all the stations by their highest mean chlorophyll-a concentrations (note that a part of the chlorophyll-a concentrations measured in front of the river should not be associated to marine phytoplankton cells but also to a contribution of freshwater phytoplankton populations drained by the river flows). The chlorophyll-a levels were weaker and erratic near the plant (M06 to M08), despite light nitrate enrichment from the river and strong phosphate input from the plant. On the other hand, stations (M12 and M13) that exhibited low nitrate and phosphate levels, have exhibited throughout the year a significant signal for chlorophyll-a concentrations. In the studied area the situation appeared to be controversial. As it is well known that the

increase in accumulating input of nutrients like nitrogen and phosphorous in seawater *via* land run off rivers and man-made sources should result in a ‘fertilization’ of the seawater in coastal regions and subsequently enhances primary production. But this might lead to severe trophic problems when one nutrient form becomes predominant (Yilmaz *et al.*, 1992; Justić *et al.*, 1995). A dystrophy phenomenon might be suspected due to unbalanced distribution of nutrients when the N/P ratio, selective criteria for phytoplankton growth (Berland *et al.*, 1978; 1980), is considered. This ratio was higher around the river and extremely lower nearby the plant than the normal ratio (15:1) (Redfield *et al.*, 1963) and may have a limited effect on phytoplankton development. The pH factor was at the origin of environmental problems because of the permanent stress to which the cells were subjected due to high acidity near the chemical plant. This low pH could limit the local photosynthetic process of chlorophyll assimilation.

CONCLUSION

This study is an attempt to define the main sources of contamination to which coastal waters around Batroun are subjected and their environmental impact. Each specific influence may be considered as well as their common interferences. Two main and strong influences were structuring Batroun coastal area: the fresh water of Al-Jaouz River and the wastewaters of Selaata chemical plant. The industry was exerting a local impact on the biochemical processes by different ways and, for example by increasing artificially the temperature of the surrounding water, while the river was interfering naturally by its own thermal annual cycle. At a local space scale, the buffer capacity of seawater did not prevent the increase in seawater acidity to high levels, and the acid discharge from the factory to its immediate proximity has created a local and destructive factor for ecology that was marked out at primary production level represented by chlorophyll-a concentrations. The large amount of nitrate reaching the seawater in some stations near the river and the great inflow of phosphate from the plant into others did not provide the expected favorable conditions for phytoplankton development than other oligotrophic places without such nutrient supplies. In fact, they often conduct to a dystrophic situation where N/P ratio is frequently unbalanced. Many factors such as the hydrodynamic and geomorphologic position of every station, the flow rate and concentrations of the different continental discharges, interfere in the levels contamination.

If the level of industrial activity at Selaata, and the seasonal activity of Al-Jaouz River are taken into consideration, their contamination impact remains at a critical level, but on the other hand it may be considered as more space limited than expected in pelagic ecosystem. This may induce the use of other sampling strategies with immediate effects such as on-line measurements and drague drifting operations. Sediment analysis is necessary to reveal the permanent impact of the industrial input deposition and the seasonal effect of the river on the benthic ecosystem.

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