

EFFECT OF RIVERINE NUTRIENTS ON COASTAL WATER ECOSYSTEMS: A CASE STUDY FROM THE NORTHEASTERN MEDITERRANEAN SHELF

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SUMMARY

Hydro-chemical data were obtained from a shallow and deep water station in the Turkish shelf zone of the NE Mediterranean with approximately monthly intervals from January to December 2002. The shallow station (0.5 miles off the coast) is influenced directly by the small Lamas River having high nitrate (63-121 μM) and silicate (52-118 μM) values, but very low phosphate concentrations (30-760 nM). Thus, nitrate and silicate concentrations of the shallow station are extremely variable and much higher than those in the upper layer (0-50 m) of the deep station. Similarly, the phosphate concentrations, measured using the high-sensitivity magnesium-induced coprecipitation (MAGIC) method, fluctuate markedly between 20 and 180 nM in the shallow water, but vary little (15-30 nM) in the deep water samples. Particulate organic matter (POM) abundance increases markedly from the shallow to the deep station. However, chemical composition (C/N ratio) of bulk POM in the shelf waters ranges between 7 and 13, displaying small temporal fluctuations at the nutrient-depleted deep station.

KEYWORDS: Nutrients, particulate organic matter, NE Mediterranean shelf, riverine input.

INTRODUCTION

The eastern Mediterranean is a typical example of oligotrophic seas as a result of the limited nutrient input to its surface waters from internal and external sources [1, 2]. It is characterized by unusually high nitrate/phosphate (N/P = 25-28) ratios in waters of the intermediate and deep layers [3-7]. This has been attributed to the high dissolved inorganic nitrogen to phosphate (N/P) ratios in the atmospheric sources (dry + wet depositions) and the Mediterranean rivers [8, 9]. However, there is indeed no selec-

tive enrichment of nitrogen in the POM pool of the eastern Mediterranean, even in the cyclonic Rhodes gyre during the spring bloom [10]. In other words, there should be other physical and biochemical processes for maintenance of the high N/P ratio in deep waters of the Mediterranean [9-11].

Various studies carried out elsewhere indicate wide fluctuations in nutrient and particulate organic contents, depending on the season, nutrient flux and geographical location [7, 11]. The increased discharges of phosphorus from land-based sources have apparently influenced the nutrient cycles in coastal regions during the last several decades [11-13]. For example, elevated nutrient loads from rivers and direct discharges of untreated domestic and industrial wastes gave rise to severe eutrophication in the Iskenderun and Mersin Bays of the NE Mediterranean [14, 15]. However, there have been limited systematic data from the Turkish coastal margin to assess temporal variations in the shelf ecosystem. This paper gives a brief evaluation of hydro-chemical data to elucidate the river effects on the NE Mediterranean shelf ecosystem.

MATERIALS AND METHODS

The study area and the locations of the two water stations on the Turkish continental shelf are shown in Fig. 1. The total depths of the shallow (34°16'E, 36°34'N) and the deep station (34°23'E, 36°30'N) were approximately 20 and 200 m. They were visited monthly during January to December 2002 (except March) to obtain time-series data. A Sea-Bird model CTD probe was used for *in situ* measurements of pressure, salinity and temperature. Water samples for chemical analyses were collected from standard or selected depths using 5 or 30 L Niskin bottles. Sub-samples for nutrients were transferred to acid-washed plastic (HDPE) bottles and kept frozen or cool in the dark until analysis.

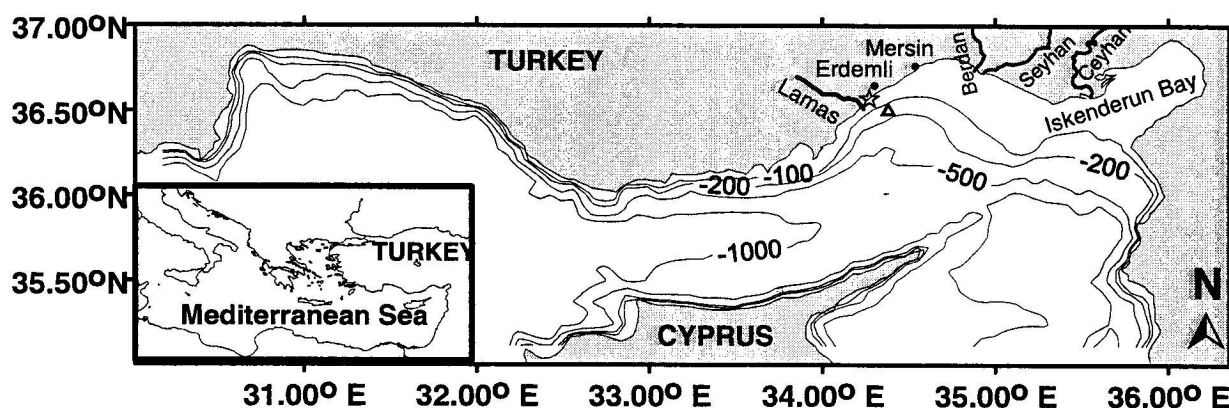


FIGURE 1 - The locations of the shallow (☆) and deep (Δ) water stations on the shelf in front of Erdemli.

The measurements of nitrate (nitrate+nitrite), phosphate and dissolved reactive silicate in seawater and river water samples were carried out using a Technicon model 3-channel auto-analyzer [16]. The detection limits of the automated technique are 20 nM, 0.05 μ M and 0.20 μ M for phosphate, nitrate and silicate, respectively. However, the direct automated analysis is not sensitive enough for precise determinations of the very low (<20-30 nM) phosphate concentration of the eastern Mediterranean upper layer waters. Therefore, the magnesium-induced coprecipitation (MAGIC) technique recently developed by Karl and Tien [17] for phosphate-depleted surface waters, which is much more sensitive (detection limit 1.0 nM) than the automated method, has also been applied for the first time to determine these low phosphate levels.

Water samples for particulate organic carbon (POC) and nitrogen (PON) analysis were filtered through pre-ignited Whatman GF/F-type filters. All the filters with particles were kept frozen (-20 °C), then dried overnight at about 50 °C and stored in a vacuum desiccator until analysis. POC and PON measurements were performed by the dry combustion technique [18], using a Carlo Erba Model 1108 CHN analyzer.

RESULTS AND DISCUSSION

Hydrographic Properties

The depth distributions of salinity and temperature measured monthly in front of Erdemli in the NE Mediterranean shelf water, at the shallow and deep station, are illustrated in Fig. 2. The salinity profiles in Fig. 2a reveal that the shallow station (0.5 miles off the coast) is apparently influenced by the Lamas River having a volume flux of about 2.2×10^8 m³ per year. The evidence for the riverine input is relatively low saline surface waters (34.46-38.74 psu) overlying deep water (36.92-39.40 psu). The two-layer hydrographic feature at the shallow station almost disappears in winter due to strong mixing events.

Surface water temperature displays a large seasonal variation, ranging from 16-19 °C in winter to 28-31 °C in the July-August period (Fig. 2b).

Salinity profiles from the deep station on the shelf-break zone, however, display a different vertical structure in summer-autumn period (Fig. 2c). The near-surface layer is occupied by more saline water (39.3-39.6 psu) between July and October, due to the excessive evaporation with respect to the water column below the seasonal thermocline characterized by salinity of 38.9-39.1 psu. In other words, the hydrographic properties of the outer shelf are principally dominated by the circulations in the surface mixed layer [19]. In April-May, however, the near-surface is occupied by less saline waters, indicating the river effects. The December profiles show that the cooler and less saline waters of Atlantic origin [4, 10] may occasionally occupy the intermediate depths of the NE Mediterranean shelf by the lateral intrusions (Fig. 2c-d). In winter, when the surface waters cool down sufficiently, the entire water column in the shelf-break zone is homogenized thoroughly. Thus, temperature and salinity possess vertically uniform structure in deep parts of the NE Mediterranean.

Biochemical Properties

The shallow station is directly influenced by the small Lamas River having high nitrate (63-121 μ M; mean of 2-year data 93 μ M) and reactive silicate (52-118 μ M; mean 91 μ M), but very low phosphate (30-760 nM; mean 190 nM) concentrations. The highest phosphate values were recorded in turbid river waters, implying partial dissolution of phosphates adsorbed on suspended particles during filtration. The nitrate to phosphate (N/P) molar ratio of the river water is abnormally high and variable, ranging from 71 in turbid samples to 3500 in P-depleted waters, whereas the silicate/nitrate ratio varies slightly between 0.67 and 1.22 (annual mean 1.01). Time series data from the shallow station are depicted in Fig. 3 at the surface and 10 m water depth, indicating prominent seasonal fluctuations in salinity, nutrients and particulate concentrations. The surface

nitrate reached maximum values of $5.30\text{--}8.87\ \mu\text{M}$ in the rainy January–April period, when the riverine input markedly exceeds the removal by biological activities in the sea (Fig. 3). Not unexpectedly, concurrent rises in phosphate and reactive silicate levels occurred in January. The phosphate reached the peak values of $183\ \text{nM}$ at surface water and $116\ \text{nM}$ at $10\ \text{m}$ depth. The secondary phosphate level rise in May coincides with the particulate maximum in the nitrate-depleted water column (Fig. 3). In May, the near-surface layer ($0\text{--}7\ \text{m}$) was occupied by less saline waters, because the river-fed shallow zone also received some rainfall before the field survey. The rain-water sampled on May 11, 2002 contained the expected values of nitrate ($66\ \mu\text{M}$) and ammonia ($40\ \mu\text{M}$), but very low silicate ($0.77\ \mu\text{M}$) and abnormally high phosphate

($3740\ \text{nM}$) concentrations. In addition to the direct input onto the sea surface, the rainfall with high phosphates of the Saharan origin [20, 21] was very likely to modify the nutrient content of the Lamas River. Thus, the phosphate-rich spring rains and also the river inflow could markedly increase the phosphate content of the near-surface water in May. The N/P molar ratio in the shallow water fluctuates drastically with both season and depth. The surface water ratios ranged from 3.1 to 96.7 in winter, declining to the lowest level (2.9) during the May bloom. Then it increased again to levels of 102.6 in August and remained almost constant between 33 and 37 by late November. The ratio dropped again to a minimum value of 3.1 in December, when nitrates were consumed by biological activities.

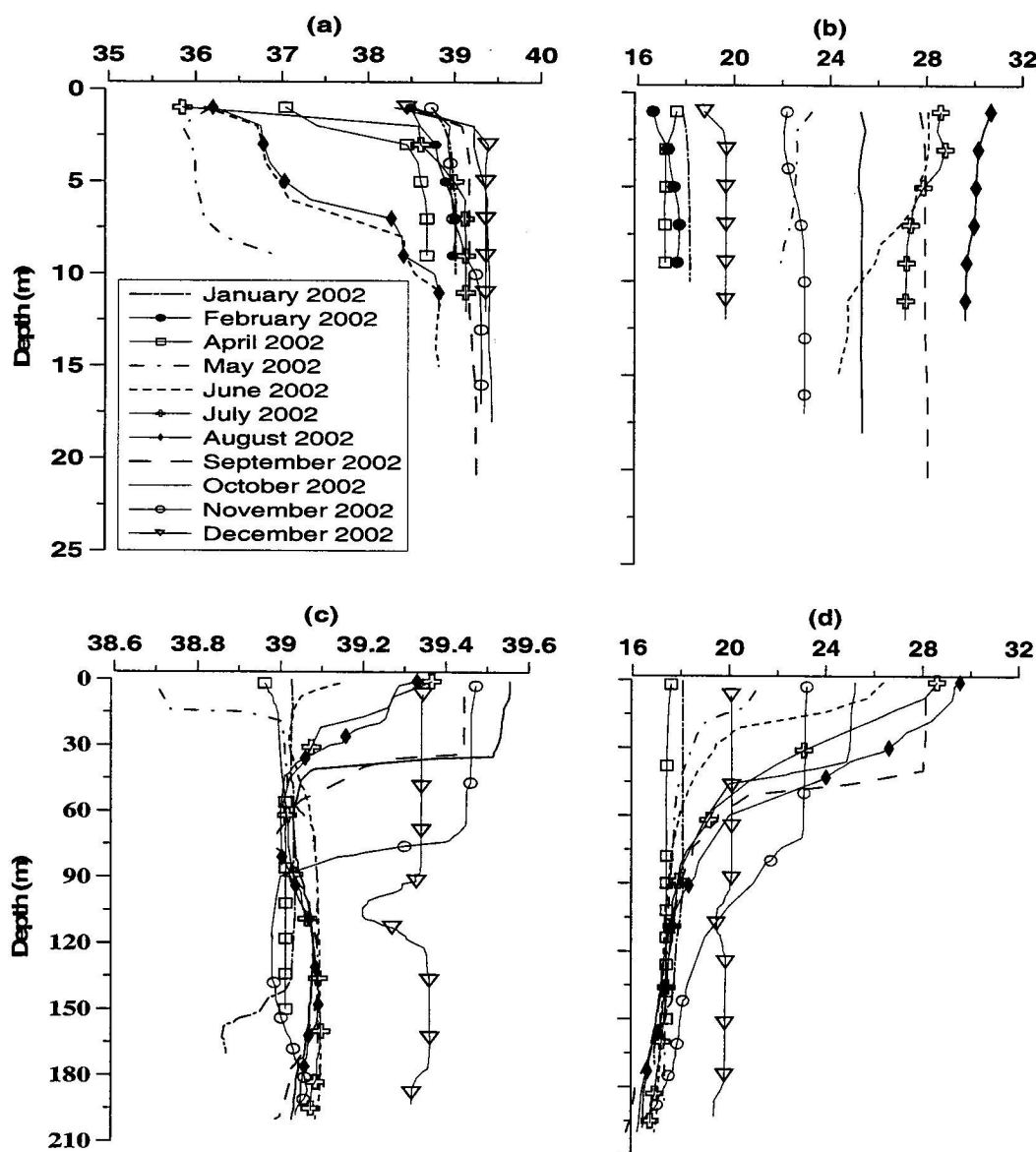


FIGURE 2 - Monthly variations of salinity and temperature with depth at the shallow (a, b) and the deep water stations (c, d) of the NE Mediterranean shelf in 2002.

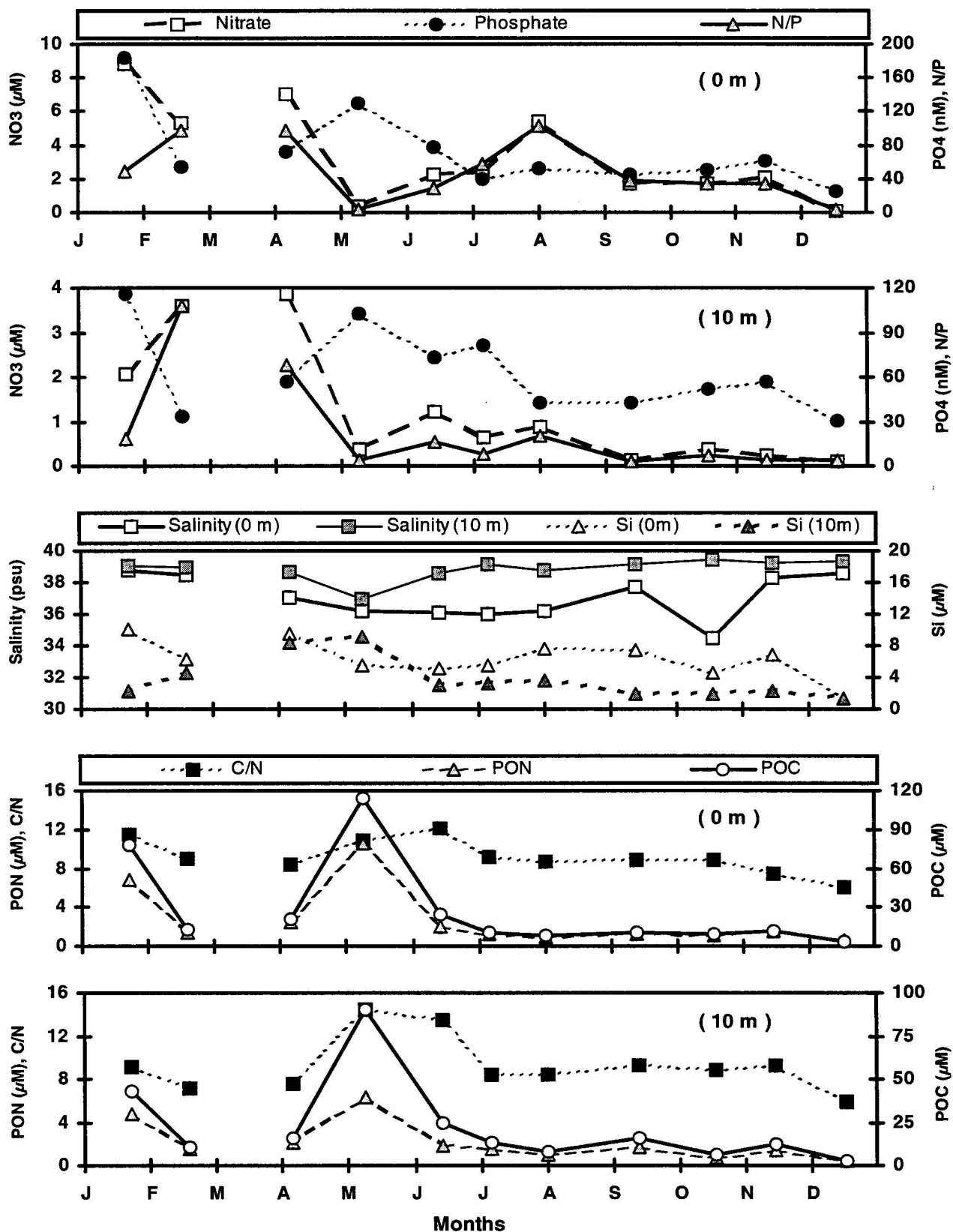


FIGURE 3 - Monthly variations of nutrients, salinity and POM concentrations at the surface and 10 m water depth at the shallow station.

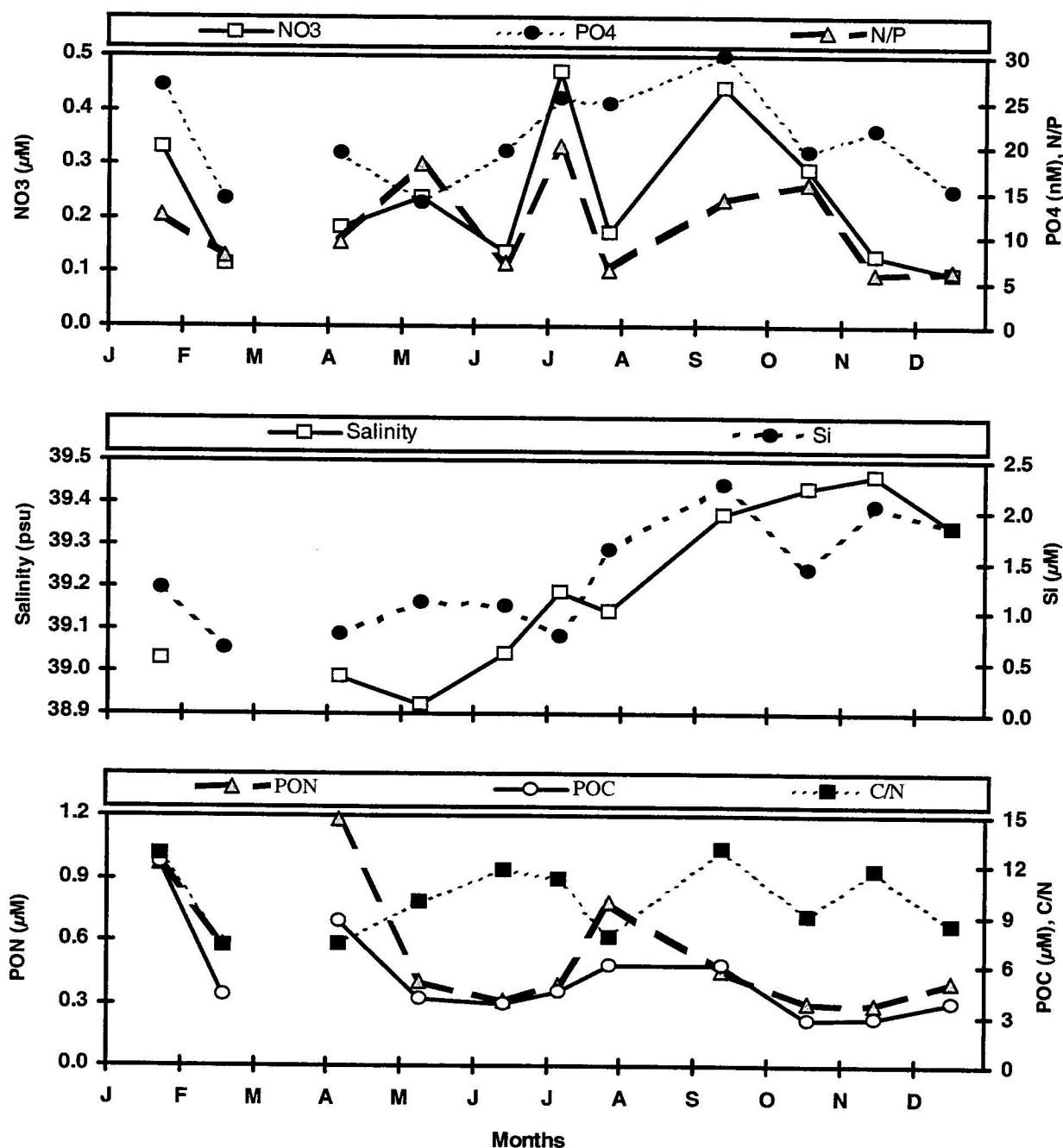


FIGURE 4 - Monthly variations of depth-averaged nutrients, salinity and POM concentrations in the upper layer (0-50 m) waters of the deep station.

In the dry summer-autumn period, the shallow waters are expected to become poor in dissolved inorganic nutrients due to insufficient supply from external sources. However, during June-November, when the near-surface waters were not mixed thoroughly, the nitrate (2.04-5.42 μM) and silicate (4.55-7.69 μM) contents of the less saline surface waters were apparently higher than the near-bottom values (Fig. 3). In this period, the surface phosphate (40-77 nM) concentrations of the shallow station were comparable to

the near-bottom values of 43-81 nM (Fig. 3). These nutrient values of the shallow zone are consistent with those reported from other coastal margins influenced by riverine inputs [12-15, 18].

Figure 3 also illustrates the time-series POM data (in terms of POC and PON) in the shallow zone. The annual POC values in the surface water varied markedly from 3.47 μM in December to 114.06 μM in May. PON values

displayed a similar temporal fluctuation, ranging from 0.57 μM to 10.49 μM , slightly exceeding the near-bottom (10 m depth) values. POM concentrations attained pronounced peaks in January, when the nutrient concentrations in the ambient water reached the highest levels due to increased riverine input. However, the major POC and PON maxima were observed in May, when the short-term spring rains supplied nutrients to the shallow waters (Fig. 3). Then POM concentrations apparently declined to levels of 10–15 μM for POC and 1–2 μM for PON in summer-autumn season. The lowest particulate matter values were recorded in December indicating low phytoplankton production in the nutrient-depleted shallow waters during summer-autumn months (Fig. 3), when the riverine input displayed a decreasing trend. Chemical composition (C/N ratio) of bulk POM was in the range of 6–13, increasing apparently in May, when the POM level attained a marked maximum during post-bloom period (chl-a: 1.15 $\mu\text{g/L}$).

Salinity and chemical data depicted in Fig. 4 are the depth-averaged values for the upper layer (0–50 m) of the shelf-break zone, exhibiting less temporal variations than the time-series data of the shallow station. The annual nutrient values were in the ranges of 0.09–0.47 μM , 0.64–2.26 μM , and 13.7–30 nM for nitrate, reactive silicate and phosphate, respectively. The fluctuating nitrate values increased slightly in July, September and October, then dropped to the lowest levels of about 0.09–0.13 μM in November–December. The phosphate was rather constant during the dry period from June to November and consistent with the shallow water values. Contrary to the shallow station, nutrient concentrations in the upper layer of the deep station do not show any significant increase from autumn to late winter. This possibly suggests limited input from different sources.

Upper layer-averaged concentrations of bulk POM varied between 2.7–12.1 μM for POC and 0.32–1.18 μM for PON, exhibiting remarkable increases in January, April and August 2002. The winter rise was in a good harmony with the nutrient peaks observed in the ambient waters, indicating the increased role of new production in the POM pool. The POM rise in April was also most probably fueled by the riverine input as supported by concurrent decreases in the upper layer salinity. The POM showed a short peak in August, when the salinity of the nutrient-depleted upper layer displayed a descending trend as compared to the salinity values in July and autumn (Fig. 4), suggesting limited input from the major Turkish rivers (Seyhan, Ceyhan). POM concentrations reduced to a minimum level in the late autumn, when the upper layer waters were depleted in nutrients. These findings indicate that the outer shelf zone received limited nutrient input from both rivers and deeper layers during the entire year. C/N molar ratio for the shelf-break POM varied between 7 and 13, comparable to the ratios of bulk POM in the shallow waters fed by Lamas River.

In conclusion, both the phosphate-depleted river inflow and spring rains with P-rich Saharan dust highly

influence the hydrological and biochemical properties of the shallow zone of the NE Mediterranean shelf. Therefore, the nutrient and particulate contents of the shallow zone drastically exceed the offshore values, especially during the rainy winter-spring period. Though the outer shelf water is always poor in nutrients and biogenic particles, the chemical composition (C/N ratio) of bulk POM displays small local differences on the shelf.

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