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The effect of cold- and warm-core eddies on the distribution and stoichiometry of dissolved nutrients in the northeastern Mediterranean

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Abstract

The nutrient distribution and phytoplankton production in the Levantine Sea of the eastern Mediterranean are principally determined by the duration and the intensity of deep winter mixing in the quasi-permanent anticyclonic and cyclonic eddies. In the seasons of stratification, a nutrient-poor aphotic layer is formed between the euphotic zone and the nutricline; interestingly, it consistently extends down to depths of about 29.0–29.05 isopycnal surfaces, but nearly vanishes in the core of the cyclonic Rhodes Gyre (RG) due to the upwelling of the Levantine deep water (LDW) up to the base of the euphotic zone. Accordingly, the nutricline is much sharper and shallower in the cyclonic RG; nevertheless, it is consistently established between the density surfaces of 29.00–29.05 and 29.15 throughout the basin. In the severe winters of 1992 and 1993, the upper 1000 m of the cyclonic Rhodes Gyre was occupied by the LDW with its associated chemical properties and abnormally high nutrient concentrations ($NO_3 = 3.8–4.7 \mu M$; $PO_4 = 0.14–0.16 \mu M$ and $Si = 7.3–7.8 \mu M$) were observed in the euphotic zone. However, the surface nutrient concentrations of the anticyclonic regions were raised merely from the summer–autumn values of < 0.02 and nearly $0.2 \mu M$ to about 0.03 and $0.8 \mu M$ for phosphate and nitrate, respectively. The molar ratios of nitrate to phosphate in the water column range between 5 and 20 in the euphotic zone but exhibit well-defined peak values (as large as 40–120) at the top of the nutricline (corresponding to nearly the depths of the 29.05 isopycnal surfaces) for most of the year. Such prominent maxima are the result of the apparent shift between the onsets of the nitracline and phosphacline due to as yet undefined factors. Below the nutricline the N/P ratios decrease regularly and reach an almost constant deep value ($= 28$) over the basin. The mean ratio, derived from linear regression of the pooled phosphate and nitrate data from March 1991 to March 1994 is about 23.6, substantially higher than deep ocean values.

Keywords: dissolved nutrients; N/P ratio; eddy fields; East Mediterranean

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1. Introduction

The Mediterranean Sea is well known to be one of the world's oligotrophic seas due to the limited nutrient supply to its surface waters both from its lower layers and from external sources (the Atlantic inflow, riverine discharges and atmospheric input) (Redfield et al., 1963; Mc Gill, 1965, 1969; Bethoux and Copin-Montegut, 1988; Coste et al., 1988; Loye-Pilot et al., 1990; Bethoux et al., 1992). Ac-

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cording to the estimates of Coste et al. (1988) and Bethoux and Copin-Montegut (1988), the Atlantic inflow through Gibraltar accounts for only 20% of the nutrients exported from the Mediterranean via the strait undercurrent; the rest is compensated by terrestrial and atmospheric inputs. The majority of rivers and the Atlantic inflow principally feed the western Mediterranean surface layer (UNEP, 1988; Bethoux and Copin-Montegut, 1988; Bethoux et al., 1992) and annual primary production in the western basin is of the order of 80 g C/m^2 (Minas et al., 1993), comparable to open ocean values, whereas the estimates for the south- and northeastern Mediterranean are as low as 18 g C/m^2 (Berman et al., 1984) and 16 g C/m^2 (Ediger, 1995) due to the very limited inputs from external sources.

The nutrient regime of the eastern Mediterranean has been studied extensively in recent years (Krom et al., 1991a,b, 1992, 1993; Salihoğlu et al., 1990; Yılmaz et al., 1994) though the biological data are too limited to reach reliable conclusions about the spatial and temporal variability of phytoplankton production (PP) and biomass. PP in the eastern basin is dominated by the input from the lower layers especially by wintertime vertical mixing (Krom et al., 1992). The phytoplankton biomass and PP are relatively higher in the cyclonic regions where the nutricline ascends to the base of the euphotic zone (Salihoğlu et al., 1990; Yılmaz et al., 1994; Ediger and Yılmaz, 1996). In the anticyclonic regions the nutricline is situated at greater depths (as deep as 400–500 m) (Salihoğlu et al., 1990; Yılmaz et al., 1994), limiting the nutrient input to the surface waters during winter mixing. Primary production obtained by direct measurements is < 20 g $C/m^2/yr$ for the eastern basin (Berman et al., 1984; Ediger, 1995) and interestingly, these values are less than the indirect estimates based on seasonal changes of nutrient concentrations in the upper layer waters of anticyclonic eddies (Ediger, 1995). Limited winter data have revealed that sub-basin scale deep convective mixing processes are observed in severe winters, significantly altering the hydrochemical properties of the upper water column from the surface down to at least 1000 m. Thus, the surface layer of the entire cyclonic Rhodes Gyre (RG) was occupied by the relatively nutrient-rich Levantine deep water (LDW) under the prolonged unfavorable winter conditions observed in 1987 (Gertman et al., 1990), 1992 (Sur et al., 1993) and 1993. However, in the anticyclonic

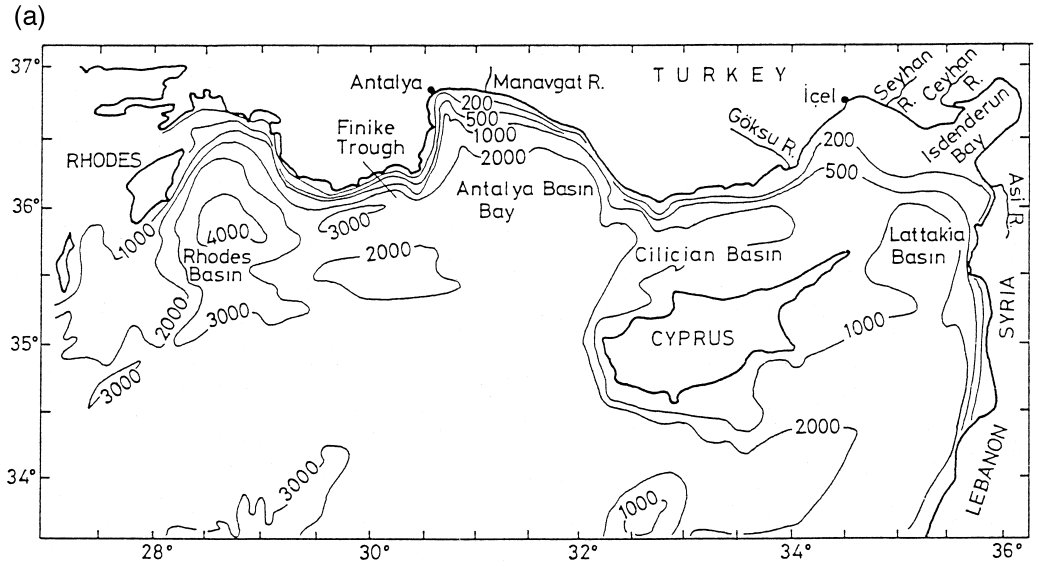

Fig. 1. (a) The bottom topography and geography of the Levantine Basin. (b) The station network in the northern Levantine Basin from March 1991 to March 1994. The stations are plotted with different symbols where ▲ and □ show hydrographic and nutrient stations respectively. The stations for which the profiles are given in Figs. 3 and 4 are depicted by the symbol ‘‘○’’. The stations visited during February 1993 are surrounded by a dashed line in the July 1993 map.

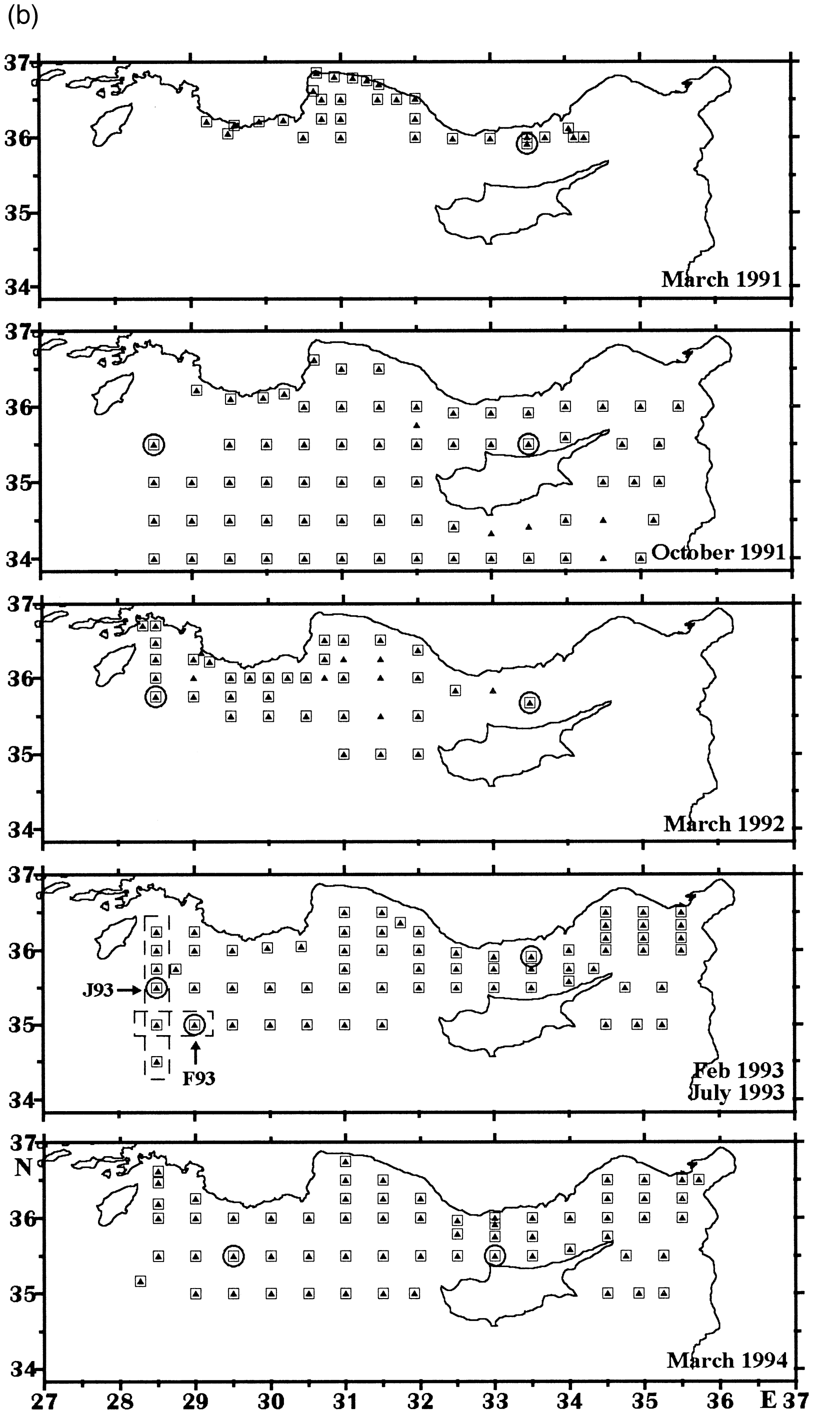

Fig. 1 (continued).

eddies, the nutrient supply from the lower layer to the upper productive waters (the euphotic zone) by convective vertical mixing is relatively limited due to the establishment of a permanent nutricline much below the euphotic zone, as deep as 400–500 m, though it shallows at peripheral regions (Salihoğlu et al., 1990; Krom et al., 1991a, 1992, 1993; Yılmaz et al., 1994; Ediger and Yılmaz, 1996). Accordingly, in the RG, the nutricline and LDW rise up into the euphotic zone throughout the whole year and the nutricline even decomposes when the LDW rises to the surface in severe winters. This is known to be the major internal nutrient source for the Levantine Basin. Or in other words, the deep waters in the Levantine basin, even though relatively poor in nutrients, are still richer in nutrient contents than the surface waters of the Levantine, and that is why deep mixing is so important in terms of transport of nutrients into the productive upper layer.

In the Mediterranean deep waters, molar ratios of nitrate to phosphate are anomalously high and range from 22.5 in the western basin (Coste et al., 1984) to 28 in the eastern Mediterranean deep waters (Krom et al., 1991a). These high ratios have been attributed to atmospheric nitrogen fixation by specific plankton, bacteria and *Posidonia oceanica* in the nutrient-poor surface waters of the Mediterranean (Bethoux and Copin-Montegut, 1986; Dugdale and Wilkerson, 1988). This process is suggested to lead to the export of biogenic particles with anomalously high N/P ratios from the surface waters in the western basin (Bethoux and Copin-Montegut, 1988; Bethoux, 1989). However, the low N/P ratios of sestons from the productive upper layer of the eastern Mediterranean (Abdel-Moati, 1990; Ediger, 1995) do not corroborate this suggestion. Only limited systematic and basin-wide studies of the hydrochemistry of the northern Levantine Sea are available to understand the inter-annual and sub-basin scale variabilities (Salihoğlu et al., 1990; Yılmaz et al., 1994). We discuss here some aspects of the primary nutrient elements (nitrate, phosphate and silicate) in the northern Levantine basin, based on the data obtained during 1991–1994; specifically, seasonal variations of hydrochemical features and molar ratios of nutrients in the water columns of cyclonic and anticyclonic eddies. Moreover, composite profiles obtained from the basin-wide chemical data plotted against temperature, salinity and water density permit us to define the boundaries of hydrochemically different water masses, irrespective of the regions.

2. Methodology

2.1. Area of study

Basin-wide surveys in the northern Levantine part of the eastern Mediterranean (Fig. 1a) were performed seasonally and the data of representative cruises (March 1991, October 1991, March 1992, February 1993, July 1993 and March 1994) were evaluated (Fig. 1b). The summer cruises covered nearly the entire basin, but in late winters only a limited area was visited due to unfavorable working conditions such as occurred in February 1993. A couple of stations could be visited along the 28°30′ north–south transect in the Rhodes region during this cruise.

2.2. Sampling and analysis

Sea water samples were collected in General Oceanic Niskin bottles mounted on a rosette attached to a SEA-BIRD Model 9 CTD probe measuring water pressure, temperature and conductivity in situ. Dissolved oxygen (DO) was determined by conventional Winkler titration. Nutrient subsamples from the bottle casts were put into 50–100 mL HDPE bottles (pre-cleaned by 10% HCl). The seawater samples for nitrate and phosphate determination were kept frozen (-20°C), whereas those for silicate were kept cool ($+4$°C) in the dark until the analysis. The nutrient measurements were carried out using a Technicon Model, two-channel autoanalyzer; the methods followed were very similar to those described in Strickland and Parsons (1972) and Grasshof et al. (1983). The detection limits achieved using low concentration samples were 0.02, 0.05 and 0.3μM for phosphate, nitrate and reactive silicate, respectively. Nitrite concentrations measured at selected locations were very close to the detection limits or below it. Thus the nitrate + nitrite data presented here are effectively all nitrate. The reliability of the nutrient measurements has been confirmed by the results obtained from an international intercomparison exercise (ICES, 1995).

3. Results and discussion

3.1. Hydrographic properties

The Levantine basin circulation, described by a new synthesis (Özsoy et al., 1989, 1991, 1993; Robinson et al., 1991, 1992; Sur et al., 1993) based on recently collected data, consists of a series of dynamically interacting sub-basin scale eddies (the Rhodes cyclonic, Mersa Matruh anticyclonic and Shikmona anticyclonic gyres) and embedded coherent structures (the Anaximander, Antalya, Cilician and southwest Cretan anticyclonic eddies) fed by bifurcating jet flows (the Central Levantine Basin Current and Asia Minor Current, AMC). The cyclonic Rhodes Gyre (RG) is a permanent member of the Levantine basin circulation, with a cold dome hydrographic structure (Özsoy et al., 1989, 1991, 1993; Tziperman and Malanotte-Rizzoli, 1991). The main water types (Hecht et al., 1988; Özsoy et al., 1989) seasonally maintained in the circulation system are the Levantine surface water (LSW), identified with the mixed layer during stratification seasons, the Atlantic water (AW) reaching the Levantine basin from its origin in the Atlantic Ocean, the Levantine intermediate water (LIW), which is locally produced in the northern Levantine basin and the Levantine deep water (LDW). Recently, wintertime deep water formation and convective overturning have been shown to occur in the RG (Gertman et al., 1990; Sur et al., 1993). General circulation patterns and eddies are shown for selected seasons for example for an autumn month (October 1991) when most of the general and permanent structures are clearly observed and for a mixing period when deep water formation and/or a kind of chimney formation was observed (March 1992) in the RG (Fig. 2).

Before dealing with the chemical data from the northern Levantine basin, we attempt to identify the hydrographic features in the upper water column (down to 1000 m) of both the Rhodes cyclonic and the Cilician anticyclonic eddies. It should be noted

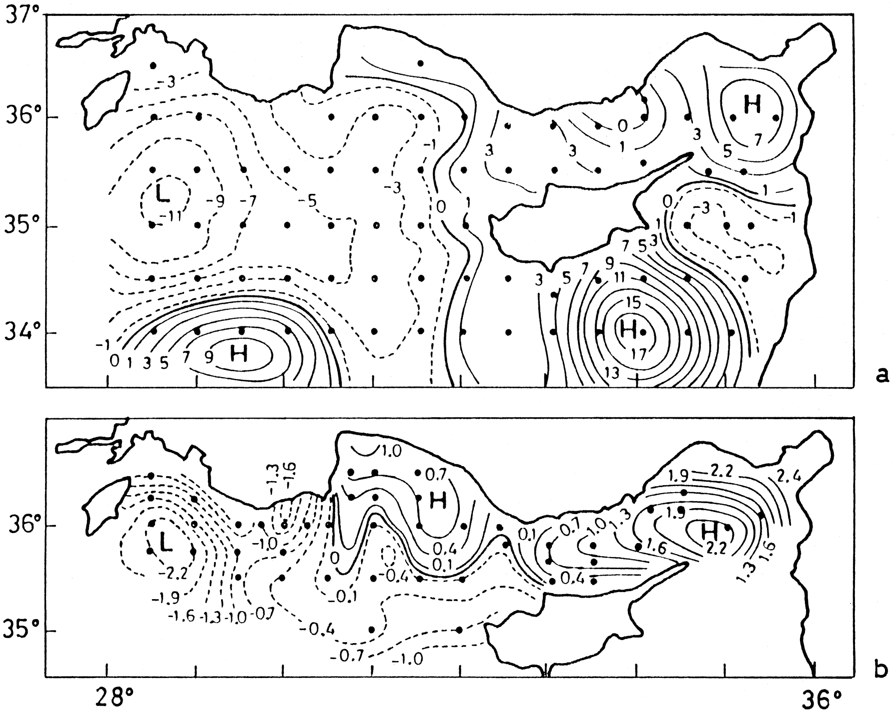

Fig. 2. The surface geopotential height referenced to a 1000 decibar level of no motion during (a) October 1991 and (b) March 1992. Dynamic topography contours are given in centimeters and have different spacings in the two surveys. "L" and "H" show low (cyclonic) and high (anticyclonic) pressure areas (modified from Sur et al., 1993).

here that the permanent core of an anticyclonic eddy (Mersa Matruh) was observed in the southern part of the Rhodes cyclone but this area could only be visited once. Therefore the Cilician basin was selected as representative of an anticyclonic region where in general small scale eddies are observed and the AMC is the most prominent dynamical feature. The emphasis on the effect of deep winter mixing in the water column was provided especially by the RG. With this goal, typical vertical profiles of temperature, salinity and water density (sigma-theta) obtained during summer–autumn and late winter periods are illustrated in Fig. 3.

In the RG, the salinity profiles displayed an apparent seasonality (Fig. 3a). During the stratification seasons, the salty surface layer was separated from the less saline LDW. The halocline was established at 25–50 m during the stratification seasons whereas it appeared at 50–100 m in anticyclonic eddies (Fig. 3b). In winter months, the halocline moved upward in parallel to the vertical movement of LDW; thus it was formed either at shallower depths (e.g. at 15–20 m) in mild winters (e.g. in March 1994) or disappeared completely as experienced during the severe winters of 1992 and 1993 (Fig. 3a). This was the result of the occupation of the surface layer by LDW, leading to the formation of a vertically uniform water column (down to at least 1000 m) in terms of hydrographic and chemical properties. The region of deep convection and homogenization coin-

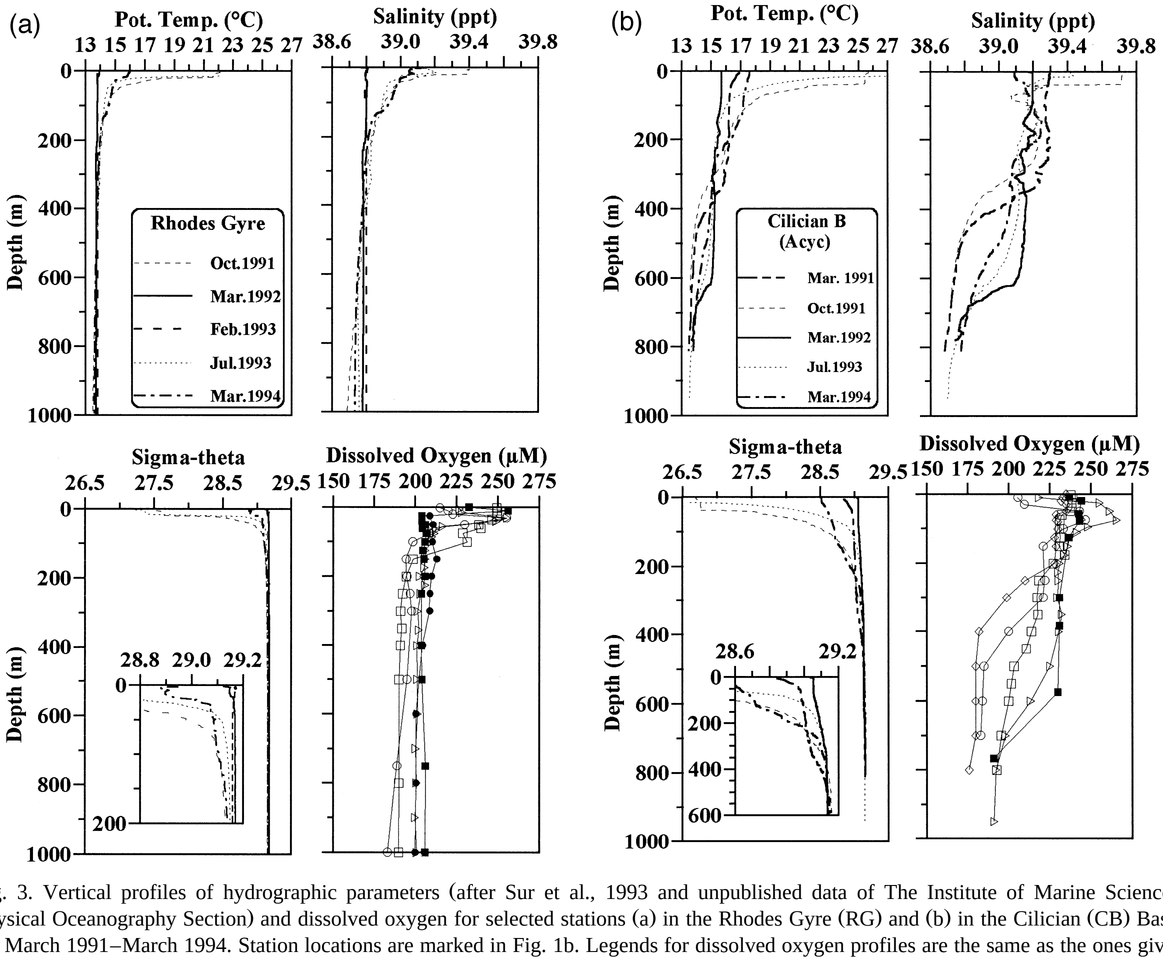

Fig. 3. Vertical profiles of hydrographic parameters (after Sur et al., 1993 and unpublished data of The Institute of Marine Sciences, Physical Oceanography Section) and dissolved oxygen for selected stations (a) in the Rhodes Gyre (RG) and (b) in the Cilician (CB) Basin for March 1991–March 1994. Station locations are marked in Fig. 1b. Legends for dissolved oxygen profiles are the same as the ones given in Fig. 4.

cided with the permanent dome structure of the RG as reported by Sur et al. (1993). In addition, deep convective mixing during the prolonged winter conditions of 1992–1993 modified the temperature and salinity of LDW, which increased slightly by ~ 0.1°C and ~ 0.1 ppt at depths > 500 m, relative to the values measured in other years or seasons (Fig. 3a). In early spring (after a mild winter), in the upper water column the LDW was topped by relatively warmer and more saline waters and the surface mixed layer was separated from the LDW by a strong halocline towards the summer months. As shown in Fig. 3a, temperature and salinity contents of LDW decreased very slowly with depth, from 14.5°C and 38.9 ppt at the base of the halocline to 13.7°C and 38.7 ppt at 1000 m, though the density remained almost constant at the levels of 29.10–29.17. The deep convective mixing in severe winters permitted the ventilation of the upper layer, extending down to 600–700 m in the anticyclonic eddies but to at least 1000 m in the RG (Fig. 3a,b). The oxygen content of LDW increased from its characteristic value of 175–180 to 210μM during this ventilation due to the strong convective mixing.

In the Cilician anticyclonic eddy, there appeared distinctly different water masses in the upper 1000 m throughout the year as definitely characterized by Hecht et al. (1988) and Özsoy et al. (1989). The surface layer was occupied by more saline ($S =$ 39.4–39.8 ppt) and warmer (Pot. $T =$ 26–28°C) waters than the RG ($S =$ 39.2–39.4 ppt, Pot. $T =$ 22–24°C) during summer and autumn. The surface layer was separated from the less saline Atlantic origin waters by a seasonal halocline (Fig. 3b). The occurrence of salty and warm surface waters in the Levantine basin is the result of the high rate of evaporation much exceeding fresh water input to the system (Özsoy et al., 1989). The relatively cool and less saline surface waters observed in the core of the Rhodes cyclonic eddy is the result of doming, mixing and even overturning of the LDW which may reach as far as the surface layer and this region therefore constitutes a unique system within the entire Levantine basin. The seasonal thermohaline feature formed below the mixed surface layer appeared at a depth of 25 m in March 1991 and at 50 m in March 1994; it was observed to be further down during the summer months and was situated at 100 m in October 1991 (Fig. 3b). Cooling of the surface layer allowed the disappearance of both the thermohaline feature and the signature of the Atlantic waters during late autumn (Fig. 3b). The less saline waters of Atlantic origin top a more saline and warmer (characterized by $S =$ 39.1 ppt and Pot. $T =$ 15.5°C) intermediate layer, the so-called the Levantine intermediate water (LIW). It has been suggested (Özsoy et al., 1989, 1991, 1992; Brenner et al., 1991) that LIW is formed locally in the RG in the northern Levantine basin during storm events in cold winter months and spreads along its peripheries and sinks down to 300–700 m in the anticyclonic areas; examples are presented in Fig. 3b. The less saline deep waters are separated from the LIW layer by a permanent halocline in the anticyclonic eddies. The thickness of the halocline changed from summer to winter, depending on the magnitude and duration of deep convective mixing in winter; for example the halocline became as thin as 50 m in the severe winter of 1992 (Fig. 3b). Deep winter mixing in 1992 also modified the hydrographic properties of the entire water column extending down to at least 700 m in the Cilician anticyclonic region. The surface layer became less saline when the LIW mixed with the surface layer and the temperature and salinity remained almost constant ($S =$ 39.1–39.2 ppt and Pot. $T =$ 15.7°C) down to 600–700 m. The lower parts of this mixed layer possessed more saline and warmer waters with respect to waters of almost the same depths during other winters and during summer–autumn periods. In other words, the convective winter mixing influenced the LDW through the permanent halocline in the Cilician anticyclonic eddy in the winter of 1992 (Fig. 3b). Below such depths (600–700 m) the LDW possessed its characteristic temperature, salinity and densities throughout the whole basin and for all other years excluding the Rhodes chimney for 1992 and 1993.

3.2. Dissolved nutrients

Nutrient concentrations measured in the upper 1000 m of the northern Levantine basin exhibited remarkable variations with depth, region and season (Fig. 4). The layer-averaged concentrations of dissolved nutrients and N/P ($NO_3 + NO_2/PO_4$) molar ratios estimated for the euphotic zone and LDW

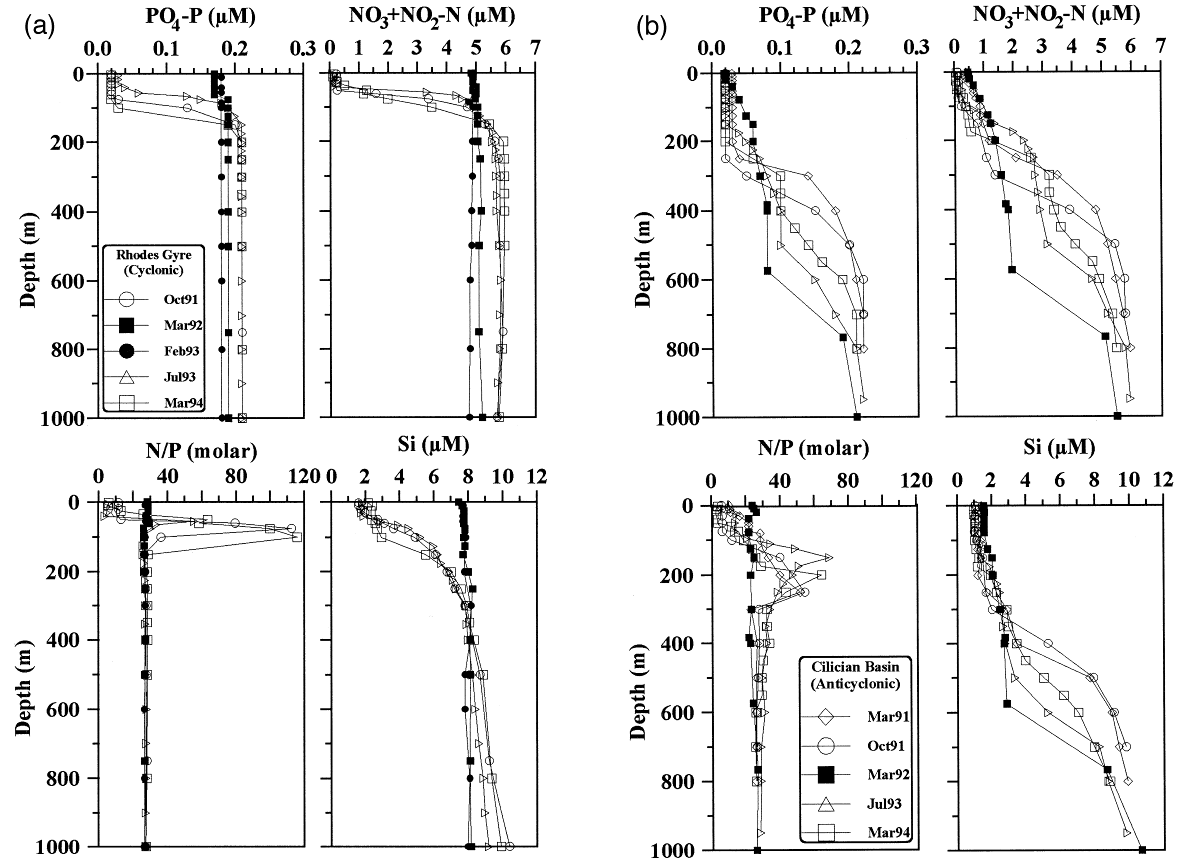

Fig. 4. Vertical profiles of dissolved nutrients and N/P (molar ratio of total oxidized nitrogen to orthophosphate) for selected stations in (a) the Rhodes Gyre (RG) and (b) the Cilician anticyclonic (CB) regions for March 1991–March 1994. Station locations are marked in Fig. 1b.

down to 1000 m are given in Table 1 for different seasons and years. The average values for March 1992 were determined on a regional basis due to the disappearance of the halocline in the Rhodes cyclonic gyre. Only data from the Rhodes region are presented for the February 1993 cruise.

3.2.1. The Rhodes cyclonic gyre

The surface waters of the Rhodes cyclonic region are poor in nutrients for most of the year as are the other areas of the Levantine basin (Fig. 4a, Table 1). The depth-averaged values for the euphotic zone were 0.2μM for nitrate and nearly 0.02μM or less for phosphate in stratification seasons (October 1991 and July 1993) (Table 1). The silicate values always exceeded 1μM (but <2μM) in the euphotic zone throughout the year (Fig. 4a, Table 1). In mild winters (1991, 1994), the upper layer, overlying the quasi-permanent nutricline, was also poor in nutrients ($NO_3 + NO_2 = 0.4$–0.6μM, $PO_4 = 0.02$–0.03μM) in early spring and this property was prominent for the whole basin (Fig. 4, Table 1). This was attributed to photosynthetic consumption and subsequent export of nutrient-associated biogenic particles into the lower layers.

Interestingly, in the cold winters of 1992 and 1993, the surface water cooling was sufficiently prolonged for the upwelling of relatively nutrient-rich LDW as far as the surface; therefore nutrient concentrations of the surface layer were similar to those measured in LDW. Concentrations in the euphotic zone were recorded as high as 0.16 for phosphate, 4.7 for nitrate and 7.8μM for reactive silicate (Fig. 4a and Table 1). These extreme values were 5–10

Table 1
The average concentrations of dissolved nutrient elements and N/P molar ratios ($NO_3 + NO_2/PO_4$) for the top 1000 m of the northern Levantine Basin; eddy fields were taken into account only for March 1992 when significant differences were observed

Date	Eddy field [a]	Water layer [b]	PO_4-P (μM)	$NO_3 + NO_2$-N (μM)	$Si(OH)_4$-Si (μM)	N/P (molar)
March 1991	Whole	EZ (75 m)	0.03 ± 0.01	0.58 ± 0.54	1.53 ± 0.57	19.3
	Basin	LDW	0.19 ± 0.04	5.38 ± 0.68	9.68 ± 2.36	28.3
October 1991	Whole	EZ (85 m)	0.02 ± 0.01	0.21 ± 0.23	1.33 ± 0.30	10.5
	Basin	LDW	0.20 ± 0.04	5.54 ± 0.91	9.74 ± 1.10	27.7
March 1992	RG	EZ (59 m)	0.16 ± 0.02	4.66 ± 0.41	7.81 ± 0.43	29.1
	(CYC)	LDW	0.17 ± 0.03	4.71 ± 0.56	8.17 ± 0.35	27.7
	Antalya	EZ (55 m)	0.06 ± 0.02	1.70 ± 0.88	2.87 ± 0.78	28.3
	Bay (P + F)	LDW	0.16 ± 0.05	4.60 ± 0.96	7.97 ± 2.10	28.7
	CB	EZ (66 m)	0.03 ± 0.01	0.76 ± 0.26	1.65 ± 0.23	25.3
	(ACYC)	LDW	0.17 ± 0.03	4.78 ± 0.70	8.42 ± 1.46	28.1
February 1993	RG	EZ (60 m)	0.14 ± 0.02	3.82 ± 0.65	7.25 ± 0.73	27.3
	(CYC)	LDW	0.17 ± 0.02	4.59 ± 0.39	8.68 ± 0.93	27.0
July 1993	Whole	EZ (85 m)	0.02 ± 0.01	0.16 ± 0.07	1.52 ± 0.96	8.0
	Basin	LDW	0.20 ± 0.03	5.53 ± 0.30	9.58 ± 1.09	27.7
March 1994	Whole	EZ (88 m)	0.02 ± 0.01	0.40 ± 0.39	1.61 ± 0.48	20.0
	Basin	LDW	0.20 ± 0.01	5.50 ± 0.35	9.69 ± 0.97	27.5

[a] RG (CYC): Rhodes Gyre, cyclonic eddy region.
Antalya Bay (P + F): the region between the Rhodes Gyre and the Cilician Basin (Fig. 1aFig. 2) where in general the extension of the Rhodes cyclonic eddy and its peripheral (P) zones, small-scale anticyclonic eddies, frontal (F) zones and Asia minor current (AMC) are observed.
CB (ACYC): Cilician Basin where in general AMC and small-scale anticyclonic eddies are observed.

[b] EZ: euphotic zone. The mean thickness of the euphotic zone is given in parentheses for the corresponding month (Ediger, 1995).
LDW: Levantine deep water. The water column below $\sigma_t = 29.15$. Or below ~ 100 m in the Rhodes cyclonic region and below 250–700 m in anticyclonic regions surrounding the Rhodes Gyre.

times greater than those recorded in March 1991 and 1994 throughout the whole basin when the LDW was topped by more saline and warmer waters (Fig. 3) under much less severe winter conditions. The deep convective mixing in the winters of 1992 and 1993, also modified the hydrochemical properties of LDW, relative to those determined in mild winters and stratification seasons. Under the prolonged deep winter mixing, the entire water column (down to at least 1000 m) was ventilated, as clearly shown by the DO profiles in Fig. 3a. On the contrary, the nutrient content of LDW decreased noticeably (Fig. 4a and Table 1) due to its dilution with nutrient-poor surface waters during the overturnings of LDW in the core of the Rhodes cyclone. Briefly, its phosphate concentration was reduced by 0.03μM, whereas the decreases in nitrate and silicate concentrations were nearly 0.8 and 1.5μM respectively with respect to the average values; for example, in October 1991 the concentrations were $PO_4 = 0.2\mu$M, $NO_3 + NO_2 = 5.5\mu$M and Si = 9.7μM.

A relatively steep nutrient gradient zone, the so-called nutricline, formed quasi-permanently at the base of the euphotic zone in the Rhodes cyclonic region. The nutricline formation is essentially the result of the mixing of nutrient-poor, saltier surface waters with the nutrient-enriched, less saline LDW (Figs. 3a and 4a). Accordingly, the base of the nutricline is determined by the upwelling of LDW in the northern Levantine basin. If LDW reaches as far as the surface, the quasi-permanent nutricline disappears, as occurred in the winters of 1992 and 1993. During these periods, the entire water column from surface down to at least 1000 m displayed vertically homogeneous hydrochemical features as a result of deep convective mixing (Fig. 3aFig. 4a).

3.2.2. The anticyclonic eddy

Nutrient concentrations of the surface waters were very low during summer and autumn in the Cilician basin where, in general, anticyclonic eddies and AMC are observed (Figs. 2 and 4b and Table 1). The surface values rose slightly due to input from the lower layers by deep convective mixing which actually affected the whole Levantine basin during the cold winter of 1992 (Sur et al., 1993). The nitrate concentration increased from ~0.2μM (summer–autumn surface concentration level) to 0.8μM during March 1992 while it increased only to 0.4–0.6μM during mild winters of March 1991 and March 1994. However, the seasonal changes in phosphate concentration were less pronounced than the changes in nitrate, due to the inefficiency of the analytical method at concentrations below 0.02μM. In other words, the winter phosphate content of the Levantine surface waters are very close to the detection limit of the method (0.02μM). Similarly, increases in the silicate content of the surface layer during mild winters were less pronounced than those which appeared in the nitrate data; the average concentrations varied insignificantly (from 1.3–1.5μM in July–October to levels of 1.5–1.6μM in mild winters of 1991 and 1994) (Table 1). The seasonal changes in the surface concentrations were more pronounced in and off Antalya bay where, in general, the extension of the Rhodes cyclone plus its peripheries and frontal zones are observed (Fig. 2). The surface nitrate values increased from 0.2μM (summer–autumn level) to ~2μM in March 1992, due to the lateral input from the Rhodes cyclone as well as vertical convective mixing. Similar increases were recorded in the phosphate and silicate concentrations from undetectable levels (< 0.02μM) to 0.06μM and from 1.3–1.5μM to 2.9μM, respectively (Table 1).

Throughout the year, the aphotic layer extending from the base of the euphotic zone down to the top of the main nutricline established within the LIW layer was also relatively poor in dissolved nutrients (Figs. 3b and 4b). This layer is termed the ‘‘nutrient deficient aphotic layer’’ (NDAL) and it coincides with the LIW layer. A seasonal nutricline separated the productive surface waters from the NDAL or nutrient-poor LIW layer which, vertically, is almost isohaline and isothermal during the stratification seasons (Figs. 3b and 4b). The nutrient concentrations in NDAL change little with depth but seasonal and interannual changes are quite significant depending upon the intensity of winter mixing determined by the climatology and the related hydrodynamical regime of the Levantine basin (Fig. 4b). For example, during the severe winter of 1992 and the summer of 1993 (following the 1993 severe winter), the NDAL was apparently enriched with inorganic nutrients, relative to its content for example in October 1991, due to input from the lower layers through the nutricline. During this period, the thickness of the LIW and NDAL also increased markedly and was observed to enlarge down to 600–700 m (Figs. 3b and 4b). When the saltier surface waters were mixed thoroughly with the LIW by winter convective mixing, a net export of nutrients occurred from the LIW to the productive surface layer. In other words, the euphotic zone and NDAL mixed with each other and a homogeneous water column formed down to the main nutricline. The winter mixing provided a small increase in the salinity but some decrease in the nutrient content of the LIW layer (Figs. 3b and 4b). The LIW layer is stagnant during the stratification seasons (starting from late spring to late autumn) and it receives a net input of labile particulate nutrient from the productive surface layer. During this period, the inorganic nutrient content of LIW is expected to increase slightly. For instance, the nitrate concentrations of the LIW or the NDAL were observed to vary seasonally from 0.5–1.0μM (in March 1991 and March 1994) to 1.0–1.5μM in October 1991 and up to 3μM in July 1993. The seasonal nutricline (especially the nitracline) was very pronounced in July 1993 due to marked increases in the nitrate content of the LIW by the input from the LDW via the main nutricline during the severe winter of 1993. Similarly, the phosphate concentration of this layer showed seasonal changes (e.g. from 0.02–0.03 up to 0.1μM). However, the seasonal change in the silicate content of the LIW was less pronounced (e.g. from 1.5 to 3.5μM). This may have resulted from the smaller decay of silicious biogenic materials than of nitrogenous biogenic compounds oxidized in the LIW layer during the late spring–late autumn period. Comparable seasonalities were also observed in LIW situated in the core of a permanent anticyclone in the southern Levantine Sea (Krom et al., 1992).

The main nutricline is established just below the LIW layer, coinciding with the permanent halocline formed within the LIW–LDW interface (Figs. 3b and 4b). The thickness and the depths of the nutricline boundaries vary with season, depending on the duration and intensity of winter mixing in the basin. The nutricline weakens and deepens under severe winter conditions due to greater chemical input from the LDW to the LIW as occurred in March 1992 (Fig. 4b). The main nutricline appeared at shallower depths (200–250 m) in the less severe winters of 1991 and 1994, deepened to 500–700 m in March 1992 and July 1993 (Fig. 4b), in parallel to the deepening of LIW layers during these periods (Fig. 3b).

In the LDW, below the quasi-permanent nutricline, nitrate and phosphate concentrations remained almost constant with depth (down to at least 1000 m), whereas silicate profiles still displayed a gradual increase with depth (Fig. 4b). The basin-wide average concentrations of dissolved nutrients for the LDW layer are given in Table 1. The average LDW concentrations were determined as 0.2μM for phosphate, 5.5μM for nitrate and 9.7μM for silicate, which are very consistent with those reported for the southeastern Mediterranean deep waters (Dowidar, 1984; Krom et al., 1991a,b, 1992, 1993). The phosphate and nitrate concentrations appeared to be markedly less than the concentrations ($PO_4 = 0.38\mu M$; $NO_3 + NO_2 = 7.6\mu M$) reported for the western Mediterranean deep waters but silicate concentrations are at comparable levels (Mc Gill, 1965; Delmas and Treguer, 1984; Bethoux et al., 1992). And they are all much lower than those found typically at similar depths in other oceans (Weiss et al., 1983).

3.2.3. Basin-wide vertical distributions

The chemical properties of the upper water column (the top 1000 m) in the Levantine Sea appeared to exhibit distinctly different vertical features in the cyclonic and anticyclonic eddies. As is clearly seen from the selected hydrographical and hydrochemical profiles in Figs. 3 and 4, the scale of spatial and temporal changes in the thickness of both LIW (NDAL) and the main nutricline as well as the LDW–LIW interface are principally determined by changes in the hydrophysical forces and hydrological features of the Levantine basin. Based on the close correlations observed between the chemical and hydrographic features, all the basin-wide nutrient data (obtained in the upper 1000 m) have been examined with respect to temperature, salinity and water density (sigma-theta) irrespective of sampling locations. The composite profiles produced from the combined data sets are depicted in Fig. 5. These vertical features would lead us to define not only the boundaries of the hydrochemically different water masses but also the ranges of the nutrient concentrations in the physically similar or different water masses over the Levantine basin. For instance, the very low nutrient concentrations appearing in the upper nutricline represent data from the less saline Atlantic waters (AW) topping the more saline LIW during the stratification seasons (Fig. 5a).

The density-dependent nutrient profiles clearly show that the nutrient-poor upper layer (euphotic zone plus NDAL) extends consistently down to the depths of the 29.00–29.05 density surfaces, independent of region and the time of year (Fig. 5b). Salinities and temperatures at the base of this layer were in the range of 15.5–16.0°C and 39.1–39.2 ppt over the entire Levantine basin (Fig. 5a). Comparison of the nutrient profiles in Fig. 5b (with the enlarged sigma-theta scales) reveals that the phosphate gradient zone appears at isopycnal surfaces nearly 0.05 density units greater than the nitracline (and silicacline). This apparent shift between the nitracline and phosphacline onsets may have resulted either from selective accumulation of labile nitrogen or from selective removal of reactive phosphate at the base of the quasi-permanent pycnocline. Heterotrophic and chemosynthetic activities in the lower pycnocline may contribute to the selective accumulation of labile dissolved organic nitrogen which eventually oxidized to nitrate and may have caused high nitrate concentrations relative to phosphate.

The nutrient gradient zone (the nutricline) extends down to the first appearance of the 29.15 density surface which defines the upper boundary of LDW throughout the entire Levantine basin (Özsoy et al., 1989, 1991). At the base of the main nutricline, LDW has a salinity of 38.7 ppt and a temperature of 13.8°C (Figs. 3–5). The main nutricline is a permanent feature of the anticyclonic eddy and is always much below the euphotic zone; though it appears quasi-permanently at the lower boundary of the euphotic zone in the cyclonic Rhodes Gyre. When LDW reaches as far as the surface in severe winters (such as occurred in 1992 and 1993), the nutricline

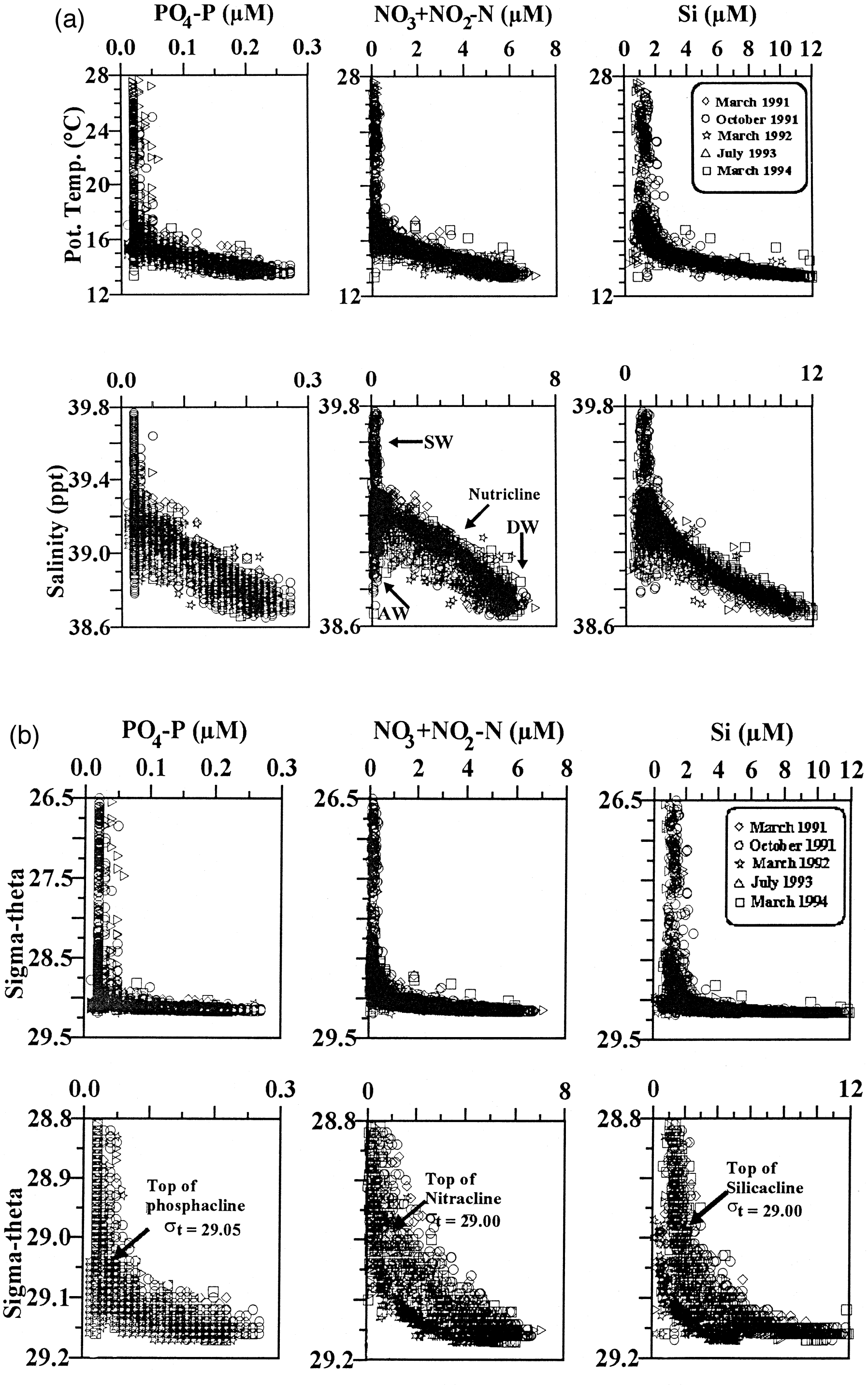

Fig. 5. The plots of dissolved nutrients versus temperature and salinity (a) and versus sigma-theta (b) for the whole northern Levantine basin for March 1991–March 1994. In section (b), the same plots are presented using different (enlarged) scales.

decomposes and a homogenous water column forms (Figs. 3 and 4).

The composite profiles displayed in Fig. 5 also indicate that the nutrient concentrations are markedly scattered in the nutrient gradient zone; e.g., different concentrations were recorded for different location at similar water density or salinity surfaces. The scatter, however, was more pronounced in the salinity-dependent nutrient profiles because water masses with similar densities had regionally and seasonally varying salinities and temperatures (Fig. 5). The general lateral circulation of the Levantine basin does not permit the LIW masses of different ages and slightly different chemical concentrations to mix thoroughly along the similar isopycnal surfaces. Thus, the nutricline formed with spatially and temporally variable thickness has different chemical concentrations at a given density and/or salinity surface from one location to another and from one year to another depending on the climatological conditions.

3.3. *N/P ratios*

The molar ratios of nitrate to phosphate (N/P) in the water column of the Levantine basin vary substantially with depth (Fig. 4 and Table 1). In the euphotic zone, the ratio generally ranged between 5 and 20. It should be noted here that the lower ratios for the euphotic zone were mostly obtained by assuming phosphate concentrations of about 0.02μM, whenever the samples contained nearly undetectable phosphate values with the present analytical method ($< 0.02 \mu$M). Therefore, the low ratios derived from such low phosphate data were probably underestimates for the stratification seasons. When the surface waters were enriched with nutrients by input from the lower layer during severe winters of 1992 and 1993; the phosphate concentrations exceeded the detection limit ($> 0.02 \mu$M), leading to reliable and relatively high N/P ratios of 25–29 (Fig. 4 and Table 1).

Below the euphotic zone, the ratios exhibited anomalously high values (N/P = 40–120) at the top of the nutricline during mild winters and stratification seasons (Fig. 4 and Table 1). The peak ratios originated from the apparent shift between the onsets of the nitracline and phosphacline depths. In addition, they were situated at much shallower depths (50–100 m) in the Rhodes cyclonic region than in the core of the anticyclonic eddies (150–300 m) (Fig. 4). In the cores of the Mersa Matruh and Shikmona anticyclonic eddies, the N/P peak was observed to remain at 500–600 m during October 1991. Interestingly, the N/P maxima consistently appeared at specific salinity and density surfaces of nearly 39.1 ppt and 29.05, respectively (Fig. 6). The ratios then decreased steadily at the LIW–LDW interface down to the specific density surface ($\sigma_t =$ 29.15). Below this surface or in the LDW, the basin-wide average of the N/P ratios remained almost constant and ranged merely between 27.0 and 28.5 (= 28 on average) (Table 1).

Similar anomalous peak ratios were reported by Krom et al. (1992) for the southern Levantine basin; they attributed these maxima to the preferential uptake of reactive phosphate by planktonic species. As was emphasized above, though the maximum ratios

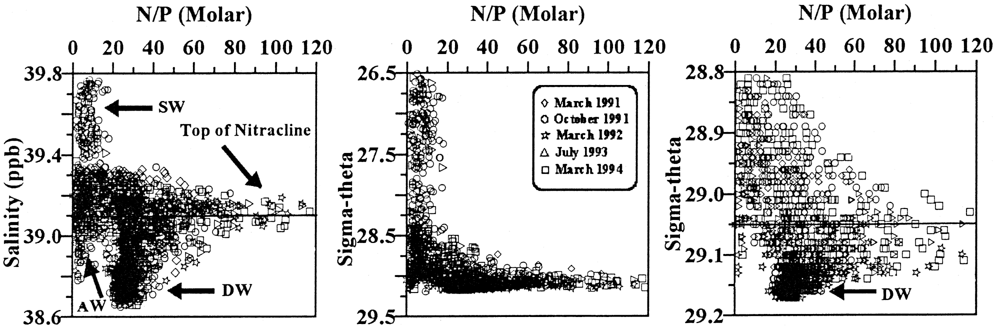

Fig. 6. Salinity and sigma-theta (with enlarged scale at the third panel) versus N/P ratio for the whole northern Levantine Basin for March 1991–March 1994.

appear at markedly different depths (from 50 m to 600 m) regionally, they were always situated at the 29.05 isopycnal surface. This finding weakens the suggestion of preferential uptake of phosphate by photosynthesis because there is no light at such depths for photosynthetic production in anticyclonic regions. Instead, it suggests a selective nitrogen accumulation by heterotrophic or chemosynthetic activities which might be intensified within the indicated density range. This phenomenon needs further investigation.

In the LDW, the ratios were in the range of 27.0–28.5, higher than the N/P ratios (between 10–18) determined in the particulate matter (PM) from the surface waters of the northern Levantine basin for the same period (Ediger, 1995). They were much higher than the ratios in the deep oceans, e.g. N/P = 15.2 for N. Atlantic deep waters (Bainbridge, 1981) but similar to ratios (N/P = 28.1) which were reported for the southern Levantine basin (Krom et al., 1991a). This finding strongly suggests that the higher N/P ratios obtained in the deep waters of the Levantine basin have originated from as yet undefined factors but not from the decay of biogenic PM exported from the surface. Negative preformed values of phosphate derived from the dissolved oxygen–phosphate regressions (Krom et al., 1991b) indicate the oxidation of nitrogen-rich organic matter (both in particulate and dissolved forms) in the entire water column of the LDW. These findings suggest that the principal factor determining the high N/P ratios measured in LDW may originate from the anomalously high N/P ratios of labile nutrients in the upper layer which sink to deeper layers. Confirmation of this requires examination of the principal chemical properties of LDW at the source point.

Mean molar N/P ratios, estimated from the slope of the linear regression analysis of nutrient data from LIW depths to the upper LDW depths, were about 23.6 for the period of 1991–1994 (Fig. 7). This value was found to be very similar to the value given for the southern Levantine basin (= 22.9) (Krom et al., 1991a) and higher than the N/P ratio (= 19.1) for the western Mediterranean (Coste et al., 1984) and the one (= 14.5) for the north Atlantic deep waters (Bainbridge, 1981). The anomalously high N/P ratio observed in the LDW suggest that the input from the deep layer may result in a phosphorus-limited primary production in the Levantine basin.

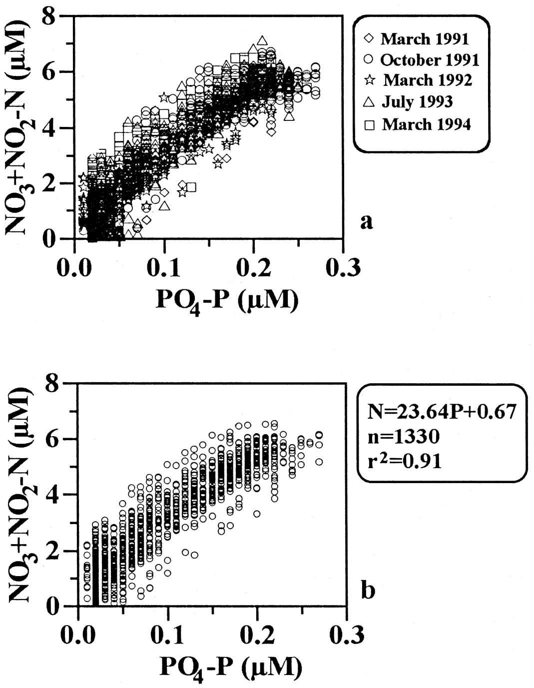

Fig. 7. Correlation between nitrate + nitrite and orthophosphate for the whole data (a) and for the linear portion of the data (excluding the data of the nutrient deficient euphotic zone and of the deep water corresponding to a sigma-theta of >29.15) (b) for March 1991–March 1994.

4. Conclusions

Under severe (prolonged cold) winter conditions, the Levantine deep waters rise up to the surface in the Rhodes cyclonic gyre, resulting in vertically homogeneous hydrochemical features down to at least 1000 m (a chimney formation). This phenomenon enriches the surface layer in nutrients. However, the percentage of transported nutrient remaining in the productive zone and utilized in photosynthetic production until it is topped by the lateral flows from the adjacent regions in early spring is poorly understood. The phytoplankton biomass (in terms of chlorophyll-a and particulate organic carbon) and the primary production rate measurements during the same period showed high values (comparable to western concentrations) not in the core of Rhodes Gyre but at its peripheries and frontal zones (Ediger, 1995; Ediger and Yılmaz, 1996).

Quasi-permanent nutriclines appear at specific density surfaces throughout the Levantine basin even though their depths are well known to vary markedly in space and time. Interestingly, the upper boundary of the phosphate gradient zone is situated at greater density surfaces —by nearly 0.05 units— than the nitracline. This shift, due to as yet undefined factors, also resulted in the appearance of anomalously high N/P ratios in the upper nitracline depths.

The Levantine deep waters have relatively high N/P ratios (~ 28), greatly exceeding the oxidative ratios of nitrate to phosphate in the deep oceans (Takahashi et al., 1985). Relatively low N/P ratios —with respect to Redfield ratios— determined in biogenic particles from the Levantine surface layer suggest that there should be another source for the observed high N/P ratios in the LDW. The most probable source is the sinking water, selectively enriched with labile, dissolved organic and inorganic nitrogen constituents.

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