

## Nutrient cycling in the south east Levantine basin of the eastern Mediterranean: Results from a phosphorus starved system

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### Abstract

The south east Levantine basin of the eastern Mediterranean is a uniquely P starved system with a nitrate:phosphate ratio in the deep water of 25–28:1, a PON:POP ratio of 27–32:1 and a DON:DOP<sub>UV</sub> ratio of ~100:1 (which probably represents a DON:DOP<sub>TOTAL</sub> of ~50:1). The C:N:P ratio of nutrients accumulated in the deep water from decomposed organic matter was 106:8.5–10.8:0.34–0.43 similar to the measured ratios for dissolved and particulate organic matter and much higher than the Redfield ratio. It is concluded that the P limitation of the eastern Mediterranean is due to the lack of P within the system and not in the preferential removal of P relative to N.

Results from the first extensive deployment of on-board nanomolar nutrient measurements in this low nutrient low chlorophyll system showed that free ammonia (50–80 nM) was present in the surface waters while nitrate was less than 10 nM, confirming the results obtained elsewhere in the CYCLOPS addition experiment results that grazing/nutrient recycling is a dominant process in this system. The total DIN:DIP ratio in the nutrient depleted waters above the chlorophyll maximum was predominantly greater than 16:1, suggesting that the system has not switched to N limitation. A primary nitrite maximum was observed immediately below the chlorophyll maximum at the top of the nutricline, which was similar to those found previously in oligotrophic ocean locations. Where nanomolar technology was deployed through the nutricline, it was found that the phosphocline started at the same depth as the nutricline for nitrate and silicate, a conclusion that would not have been made if only conventional micromolar technology had been available. An intercomparison of nutrient procedures suggested that freezing samples is acceptable for samples with a concentration above 20 nM (DIP) and 400 nM (nitrate and nitrite), which represent most of the previously published data from intermediate and deep waters from the Levantine basin. However for concentrations lower than this, which in practice

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means within the photic zone in the eastern Mediterranean, it is highly desirable to use on-board measurements and ideally the new nanomolar techniques.

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## 1. Introduction

Primary productivity in the eastern Mediterranean has been shown to be phosphorus limited (Krom et al., 1991). An important part of the evidence for this P limitation is that the nitrate:phosphate ratio in the deep water is 28:1 far in excess of the normal Redfield ratio found in deep water of the oceans (Redfield et al., 1963). Since the initial papers that noted this unusual N:P ratio, several authors have analysed inorganic nutrients in the deep water confirming this high N:P ratio (Kress and Herut, 2001; Kress et al., 2003). However, no previous study had been carried out in the eastern Mediterranean in which all the possible nutrient phases, including dissolved inorganic nutrients, dissolved organic nutrients and particulate organic nutrients had been measured simultaneously. It was thus possible, in this study, to determine whether the eastern Mediterranean is simply P starved or whether its unusual P limitation is due to cycling of nutrients between more labile and less labile reservoirs in some unusual combination.

Preformed nutrients have been used widely as a conservative, albeit calculated tracer to identify and follow water masses in the major oceans (Redfield et al., 1963; Broecker et al., 1985). The normal assumption used in the calculation is that nutrients are mixed into the surface waters in winter and because of the limited light available in the regions of oceanic deep water formation, they are then preserved in the descending water mass. It is also normally assumed in such calculations that the elemental ratio (O:C:N:P) of the decomposing organic matter is 138:106:16:1 (Redfield et al., 1963) or 175:106:16:1 (Takahashi et al., 1985). In the eastern Mediterranean, neither of these suppositions are correct. The eastern Mediterranean is the only region of subtropical water where deep water is being formed. As is characteristic of such regions, the phytoplankton bloom occurs in winter (November–March) during the many relatively warm sunny days (Krom et al., 2003). As a result the descending water has the characteristic of the nutrient depleted water which occurs during the phytoplankton bloom. We have used data available from the literature on the preformed nutrient concentration

of the descending water (Zavatarelli et al., 1998; Krasakopoulou et al., 1999) to calculate the elemental ratio of the decomposed organic matter found at this location.

Previous studies of the eastern Mediterranean in summer have shown that the surface waters above the chlorophyll maximum are low nutrient low chlorophyll (LNLC) with both nitrate and phosphate below detection limits of conventional automated technology. Recently, a new on-board nanomolar autoanalyser technology has been developed in which phosphate, nitrate and nitrite are determined at nanomolar levels (Woodward, 2002). The eastern Mediterranean was the ideal location for an extensive trial use of this technology because of the extremely low nutrient content particularly in the surface waters. We have used this technology here to provide new insights into the biogeochemical processes that exist within the upper layers of the water column.

This study was carried out as part of the CYCLOPS project in which phosphate was added to a patch of East Mediterranean surface water to investigate the nature of P limitation in the region. This Lagrangian experiment was carried out in a similar manner to the IRONEX and SOIREE experiments (Behrenfeld et al., 1996; Boyd et al., 2000) with the limiting nutrient, in this case phosphate, being added with SF<sub>6</sub> as an inert tracer to a 2 × 2 km<sup>2</sup> patch of seawater. The chemical and biological changes in the system were then tracked for 8 days until the patch had relaxed to a dilution in excess of 95%. The detailed results of the CYCLOPS P addition experiment are presented elsewhere in this volume (Krom et al., 2005). The data presented in this study describe the chemical conditions in the SE Levantine basin in general and the core of the Cyprus warm-core eddy at the time of the CYCLOPS experiment in early summer.

Most of the previous studies of the eastern Mediterranean involved the use of samples frozen soon after sampling, and then analysed subsequently in shore-based laboratories using conventional micromolar autoanalyser technology (Krom et al., 1991, 1992; Kress and Herut, 2001; Kress et al., 2003). This procedure was used in part because determination in a shore-based laboratory

enabled the best possible precision to be obtained which was necessary because of the very low levels of nutrients in both surface and deep waters. In this study, we have carried out a preliminary intercomparison study of on-board analysis vs. freezing samples followed by analysis in shore-based laboratories to enable reasonable estimates to be made of the value and limitation of previous results.

## 2. Sampling and methods

For reasons described in Krom et al. (2005), the centre of the Cyprus quasi-stationary warm-core eddy was chosen as the location for the CYCLOPS addition experiment. In this study, we are reporting the data from stations close to the centre of the eddy sampled before the phosphate was added and from “OUT” stations away from the fertilised patch but still in the eddy core. Although the effects of the patch were only seen in the surface layers, for the sake of simplicity, no data from “IN” patch stations are reported here. Together these data are described as eddy core stations. In addition, samples were taken from stations outside the eddy feature (Table 1).

Water samples were taken using a multi-sampler/carousel CTD system (Sea Bird Electronics) with 24 bottles, 10 l each. Physical data were gathered using the Sea Bird Electronics (SBE911plus) CTD profiler, equipped with oxygen and fluorometer sensors.

Water samples for dissolved oxygen were sampled and fixed using standard procedures (Kress and Herut, 2001). Dissolved oxygen was measured at sea using Carpenter–Winkler titration procedure

(Carpenter, 1965) and a radiometer automatic titrator (TTT80), equipped with a dual platinum electrode, in the dead-stop end point mode. The precision was 0.3% as determined by analysing replicate samples from the same Niskin bottle.

### 2.1. Dissolved nutrients

A suite of dissolved nutrients was determined on unmodified samples on-board ship within hours. Nitrate, nitrite, phosphate, ammonium and silicate were measured colorimetrically at micromolar concentrations using a conventional 5-channel Technicon AAII, segmented flow autoanalyser, with techniques developed for optimum sensitivity (Woodward, 1994; Woodward and Rees, 2001).

A colorimetric segmented flow analytical system, using a long path-length (2 m) liquid waveguide capillary cell (LWCC) as the detection flow-cell was used to measure for nanomolar phosphate, nitrite and nitrate (Woodward, 2002). The detection limit, defined as twice the standard deviation of the blank, for phosphate is 2 nM, nitrate + nitrite, 1 nM, and nitrite, 0.5 nM, and the precision was 0.2, 0.06 and 0.03 nM, respectively. For ammonium measurements the water samples analysed by the conventional Technicon autoanalyser were always below the detection limit, so we used a fluorimetric detection technique, following ammonia gas diffusion across a Teflon membrane (Jones, 1991; Woodward and Rees, 2001).

Duplicate samples for nutrient analysis were collected in 15 ml acid washed plastic scintillation

Table 1

Stations sampled for chemical parameters presented in this study showing those within the core of the eddy and those outside the eddy

Station no.	Type of station	Depth (m)	Additional parameters measured	Location
50	Outside eddy	0–1620	Dissolved organic matter, particulate organic matter	LAT = N33 04.79, LON = E31 50.33
68	Outside eddy	0–2600	Nanonutrients, dissolved organic matter, particulate organic matter	LAT = N33 43.44, LON = E32 12.61
26	Core of eddy	0–1600	Ammonium, dissolved organic matter, particulate organic matter	LAT = N33 20.10, LON = E32 17.46
58	Core of eddy	0–350	Nanonutrients, ammonium, dissolved organic matter, particulate organic matter	LAT = N33 17.37, LON = E32 15.30
67	Core of eddy	0–750	Nanonutrients, ammonium	LAT = N33 16.52, LON = E32 26.67

None of these stations were sampled from within the patch of the CYCLOPS addition experiment. Temperature, salinity, dissolved oxygen, chlorophyll and micromolar nutrients were measured at all stations.

vials and immediately frozen. In the laboratory (IOLR), nutrients were determined using a segmented flow Skalar, T SAN<sup>plus</sup> SYSTEM by the methods described by Krom et al. (1991) and Kress and Herut (2001). The instrument precision for nitrate + nitrite, phosphate and silicic acid was 20, 3 and 60 nM, respectively. The corresponding analytical limit of detection (two times the standard deviation of the blank) for the procedures is 7.5 nM for nitrate + nitrite, 8 nM for phosphate and 30 nM for silicic acid.

### 2.2. Dissolved organic matter (DOC and DON)

Polythene (powder-free) gloves were worn throughout handling procedures. Pre-cleaned all-glass syringe systems with Teflon tubing and an on-line stainless-steel unit containing 0.7 µm glass fibre filter (GFF) were used to collect the water samples directly from the CTD bottle. GF/F filters were combusted in an oven at 450 °C for at least 4 h. The samples were transferred to pre-combusted 10 ml glass ampoules, acidified with high-grade phosphoric acid and flame sealed. The glass ampoules containing the sample were stored cold (~4 °C) in the dark and transferred for analysis on-shore.

Samples were analysed by high temperature combustion (Alvarez-Saldago and Miller, 1998; Spyres et al., 2000). The acidified samples were purged with pure gas immediately prior to analysis for approximately 10 min to remove the inorganic carbon. A high temperature combustion system that has a Shimadzu TOC-5000A infrared gas analyser coupled to an Antek 7000 nitrogen-specific chemiluminescence detector was used for the simultaneous measurement of DOC and TDN. Deep Sargasso seawater (DW) samples were used daily as a check on instrument performance and accuracy. The estimated DOC concentration of the certified DW samples is  $44.0 \pm 1.5 \mu\text{M C}$ . The mean concentration and standard error for the DW samples analysed for each analytical run in this study was  $51 \pm 8 \mu\text{M C}$  ( $n = 7$ ). A daily blank correction was applied to the DOC measurements.

### 2.3. Dissolved organic phosphorus (DOP<sub>UV</sub>)

DOP<sub>UV</sub> was determined using a UV irradiation method adapted for use on-board ship. The unit consists of two 125 W Hg vapour lamp, two carousels of six quartz test tubes and a cooling fan. All equipments used to contain the samples

were cleaned with 10% hydrochloric acid for at least 24 h, and rinsed thoroughly with deionised water before use. Samples were taken from the CTD carousel in 125 ml high-density polyethylene (HDPE) bottles, which were rinsed with the sample before filling. Samples were filtered through 2 µm polycarbonate filters into the quartz tubes to the 10 ml mark, and the tubes were capped with custom-made Teflon screw tops. The samples irradiated for 40 min, cooled and transferred to 20 ml HDPE bottles, in which they were frozen immediately. The samples were irradiated and frozen within 1 h of the initial sampling time.

Frozen samples were defrosted at room temperature and shaken to avoid stratification, before analysis. A Bran and Luebbe autoanalyser (AAII) was used for the determination of phosphorus (P). The detection limit was 6 nM P ( $3 \times$  standard deviation of the blank). Precision (as relative standard deviation of replicates) was 2.8% (50 nM P), 4.3% (100 nM P) and 1.6% (200 nM P). DOP<sub>UV</sub> was determined by subtracting the concentration of dissolved inorganic-P (DIP) from that of total dissolved P after UV oxidation.

Recovery of model compounds was tested in the laboratory before use with a range of compounds, including easily oxidised phosphate esters and the refractive phosphonate, 2-aminoethylphosphonic acid (Table 2). Low nutrient seawater was used for the tests. Percentage recovery was comparable with two similar studies by Ormaza-Gonzalez and Statham (1996) and Thomson-Bulldis and Karl (1998). It can be seen from the results (Table 2) that the P–O–P bonds in both inorganic and organic polyphosphates are the most refractive, while P–O–C bonds, such as those in P esters, are the easiest to break. Recoveries were 99% and 100% recovery for the esters (P–O–C bonds), 85% for a phosphonate (P–C bond) and 54% for another P–C bonded molecule. The exact composition of organic P in seawater is unknown, but Kolowitz et al. (2001) detected a ratio of 25% phosphonates and 75% monoesters and diesters in ultra-filtered Pacific, Atlantic and North Sea samples. The process of ultra-filtration results in only a fraction of the total DOP pool being analysed. Diesters include the nucleic acids, DNA and RNA, but these are thought to make up a relatively small fraction of the DOP pool (Paul et al., 1987; Karl and Bailiff, 1989). Although total DOP (by persulphate oxidation—PO) was measured in our study, there were problems with noise in the data related to the

Table 2  
Percentage recovery of model DOP compounds for the UV procedure used in this study

	Percentage recovery of model compounds			
	Bond	This study	Ormaza-Gonzalez and Statham (1996)	Thomson-Bulldis and Karl (1998)
Trimetaphosphate	P–O–P	10	3	nd
Tripolyphosphate	P–O–P	15	20 (DIW)	18
Sodium pyrophosphate	P–O–P	10	nd	3
Adenosine-5'-triphosphate	P–O–P, P–O–C	28	3	35
Phosphonoacetic acid	P–C	54	nd	nd
2-Aminoethylphosphonic acid	P–C	85	82	81
O-phospho-DL-serine		88	nd	99
4-Nitrophenyl phosphate	P–O–C	99	90 (DIW)	nd
Lecithin	P–O–C	100	nd	89

All compounds were tested in seawater except those followed by deionised water (DIW). nd, no data.

combination of seawater and repeated use of plastic bottles (polypropylene). We have therefore chosen to disregard these data.

#### 2.4. Particulate organic matter (POC, PON and POP)

For particulate organic carbon (POC) and nitrogen (PON), 1–21 of samples were filtered through pre-combusted 25 mm Whatman GF/F GFFs and stored frozen. Before analysing the samples, filters were dried and treated with HCl fumes to remove carbonate. The samples were analysed on a Leeman Lab 440 CHN elemental analyser. Measurement of particulate P was modified after Koroleff (1976). Briefly, a suitable volume (usually 250 ml) was filtered onto a 47 mm, 0.2 µm pore-sized polycarbonate filters at low vacuum (<0.2 bar). Filters were suspended in 5 ml Milli-Q water in 10 ml polypropylene tubes and wet oxidised in acid persulphate. The low concentration of P in the filter blanks was subtracted from all samples. Released P was measured as SRP using the standard molybdenum blue technique and a 5 cm cuvette.

### 3. Analytical quality control discussion of frozen vs. unfrozen nutrients

It is axiomatic amongst marine chemists that analyse dissolved nutrients (nitrate, nitrite, phosphate, ammonium, silicic acid, etc.) that it is desirable to analyse seawater nutrients on-board ship as soon as possible after sampling. In this way, problems related to sample storage are negated or, at worst, minimised. Prior to this study most of the

nutrient data available from the Levantine basin was acquired from samples frozen prior to analysis in land-based laboratories (Krom et al., 1991, 1992; Kress and Herut, 2001; Kress et al., 2003). In this study, we sampled and measured DIP and total dissolved phosphate ( $TDP_{UV}$ ), nitrate + nitrite and silicic acid in various ways which allow intercomparisons to be made. A full and complete series of tests was not possible for practical reasons, but sufficient tests were made to allow preliminary conclusions to be drawn concerning the quality of the data produced and the procedures used.

Nanomolar and micromolar analyses for nitrate, nitrite and phosphate were carried out on-board ship within 2 h of sample collection with no storage procedure required (Woodward, 1994). The micromolar procedures used by Woodward and co-workers are quality controlled and monitored by participation in the QUASIMEME intercalibration programme. The nanomolar LWCC technique (Woodward, 2002) is too new to be part of a specific intercalibration exercise. However, in-house tests have been carried out to show that there is a good comparison between nanomolar and micromolar DIP for the range (20–100 nM) where both procedures are appropriate (Woodward, unpubl. data). We have used these phosphate data as the reference data for our other DIP results. For comparison, micromolar DIP analysis was carried out in which the samples were frozen on-board ship immediately after sampling and analysed on-shore some time later. This is the same procedure used originally by Krom et al. (1991, 1992, 1993) and used subsequently in a series of studies of nutrients in the eastern Mediterranean by Kress and Herut

(2001) and Kress et al. (2003). This procedure has been verified as part of the NOAA/NRC Inter-comparison for nutrients in seawater with good results (Willie and Clancy, 2000). In addition, interlaboratory comparisons also took place within the POEM-BC programme (Kress et al., 1991).

Micromolar nutrient data were compared between on-board measurements and frozen samples (Fig. 1). The results for nitrate + nitrite in the deep water are similar and consistent, with a slope close to 1 and with a correlation coefficient of 0.962. However, the results for the upper water mass (above 250 m) did not compare well. For samples with a concentration of less than 400 nM, the on-board samples were consistently lower. The difference became proportionately worse when the

concentration was lower. It was concluded that at concentrations less than 400 nM the frozen samples were not reliable. In addition to the nitrate and nitrite intercomparison, we performed the same intercomparison of the results for phosphate and silicic acid (Fig. 1). The slope of the phosphate line was close to the 1:1 line ( $r^2 = 0.846$ ) though there was considerable scatter below 20 nM. The silicic acid results of the frozen samples were slightly higher than those of on-board measurements, in particular at high concentrations, though overall the regression coefficient was 0.941. It was thus concluded that freezing samples are acceptable for samples with a concentration above 20 nM (DIP) and 400 nM (nitrate and nitrite) which represents most of the published data from intermediate and deep waters from the Levantine basin. However for concentrations lower than this, which in practice means within the photic zone in the eastern Mediterranean, it is highly desirable to use on-board measurements and ideally the nanomolar techniques (Woodward, 2002).

#### 4. Physical oceanography of the region

The physical oceanography of the region is summarised in Krom et al. (2003). Briefly, the surface layers of the eastern Mediterranean are represented by modified Atlantic water which flows east from the straits of Gibraltar and Sicily. This water is characterised as having relatively low salinity (36.15) and low nutrient content. As it flows east the salinity gradually increases. Beneath this surface layer is the Levantine Intermediate Water (LIW) with a salinity of  $\sim 39.15$  which is formed in the NE Levantine basin in winter and then flows to the west. Until 1989 the deep water of the Levantine basin (LDW) was formed exclusively in the N Adriatic in winter. This  $LDW_{ADR}$  has a salinity of 38.65 and a temperature of 13 °C. Starting in 1989 a new source of LDW originating in the Aegean was observed. This  $LDW_{AEG}$  has a salinity of 39.0 and a temperature of 14 °C.

The physical circulation is highly dynamic with a series of mesoscale features. The Cyprus eddy is a semi-permanent warm-core feature approximately 100 km in diameter situated south of Cyprus. It is characterised by an isothermal layer of relatively warm water to a depth of 300–500 m. There is deep winter mixing to the base of this isothermal layer in most winters.

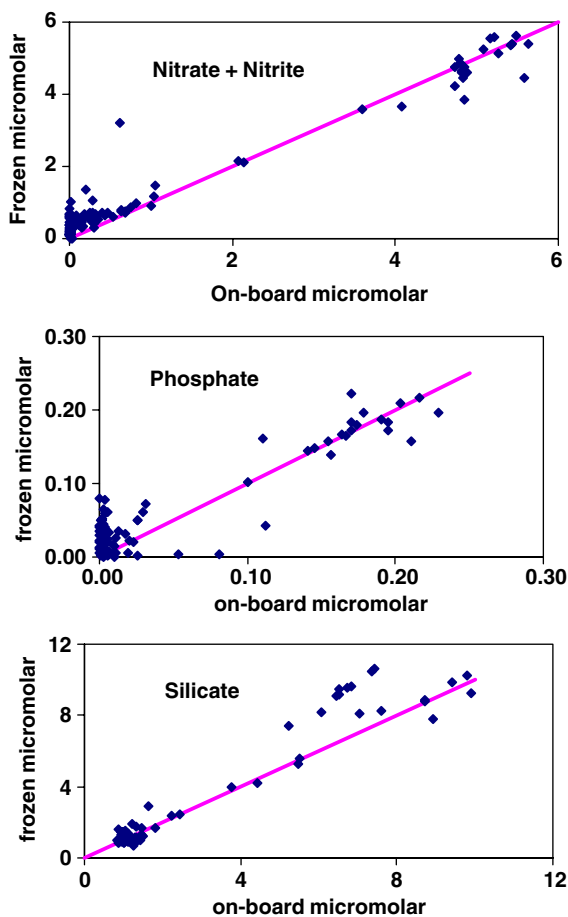


Fig. 1. Plot of nutrient samples (nitrate + nitrite, phosphate and silicate) analysed on-board ship within a few hours of sampling against samples frozen immediately and analysed subsequently in a shore-based laboratory. The line plotted is the 1:1 plot. The linear regression coefficient ( $r^2$ ) for nitrate + nitrite is 0.962, for phosphate is 0.846 and for silicate is 0.941.

## 5. Results

### 5.1. Stations outside the eddy

The vertical structure of stations 50 and 68 (outside the eddy) was typical of stations in the south eastern Levantine basin sampled in early summer (Krom et al., 1993; Kress and Herut, 2001). There was a seasonal thermocline beneath a shallow mixed layer (Fig. 2). The salinity minimum observed beneath the immediate surface layer was attributed to modified Atlantic water. From ~50 to 200 m there was an increase in salinity to a maximum representing LIW. The salinity and temperature then decreased to the Eastern Mediterranean Deep Water of Adriatic origin (EMDW<sub>ADR</sub>). At these stations there was then a relatively thin layer (~100 m) of EMDW formed in the Aegean Sea (EMDW<sub>AEG</sub>; Klein et al., 2003) at the bottom of the water column.

The surface layers of stations 50 and 68 to 70 m had a low but measurable amount of chlorophyll (20–50 ng/l) which increased to a maximum of 200 ng/l at 110 m depth (Table 4) and then decreased to background levels below 200 m. In the photic zone above the chlorophyll maximum in station 68, nitrate and phosphate as determined by conventional micromolar technology were below detection limits (Fig. 3). However, when phosphate was measured using nanomolar technology, there was a small (3–6 nM) but detectable concentration of phosphate present. Nitrate was not determined by nanomolar technology for these stations. In the same layers, ammonium was 65–70 nM which was higher than the concentrations present deeper within the water column. Silicate was present throughout the photic zone at a concentration of ~1.2  $\mu\text{M}$ .

At the base of the chlorophyll maximum (130–160 m), there was a sharp nitrite maximum of ~70 nM (Fig. 3). There was no associated change in ammonia-N concentration at this depth. The main nutricline starts at 130–160 m depth for nitrate, silicate and phosphate. Using conventional micromolar phosphate it appeared that the phosphocline was deeper than the nutricline and silicacline but when nanonutrient measurements were used, all nutrients increased simultaneously. There was a nutrient (nitrate and phosphate) maximum (Fig. 3) and dissolved oxygen minimum (Fig. 2) at approximately 500 m. The nutrients then decreased and the dissolved oxygen increased slightly throughout the EMDW<sub>ADR</sub>. Silicate increased throughout the depth profile to 1200 m. The silicate, phosphate and

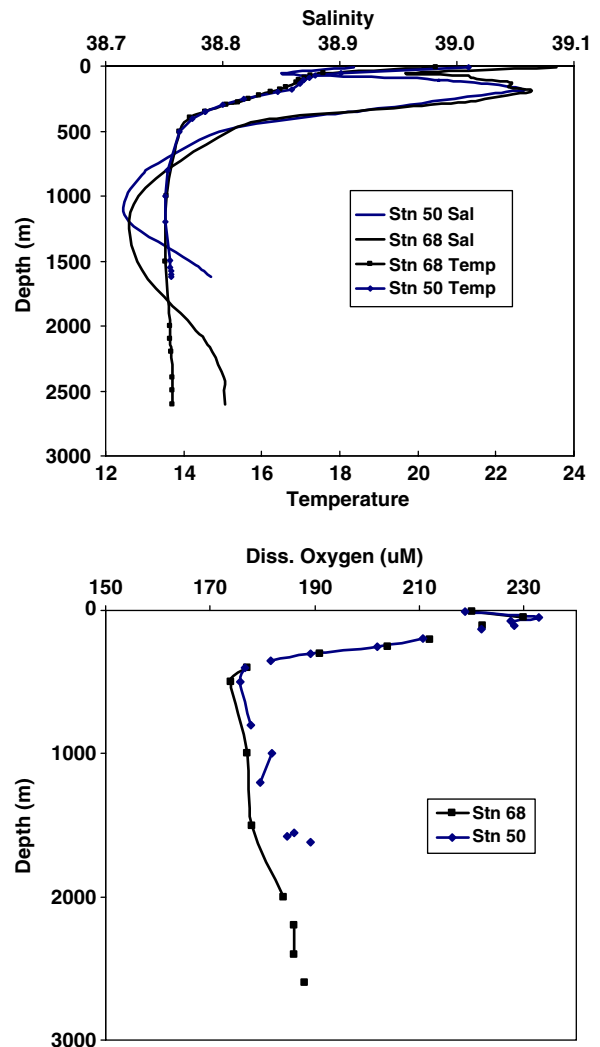


Fig. 2. Depth profiles of salinity and temperature, and dissolved oxygen from stations 68 and 50 situated outside the eddy.

nitrate content of the EMDW<sub>AEG</sub> was slightly lower than that for EMDW<sub>ADR</sub> while the dissolved oxygen content was slightly higher. Ammonium decreased to 59 nM at the base of the nutricline (400 m) and remained essentially constant at that concentration to the bottom of the profile.

### 5.2. Stations at the core of the eddy

The vertical structure of the stations at or close to the core of the warm-core eddy were typical of those found previously for the Cyprus eddy in early summer (Krom et al., 1993). There was a shallow sharp seasonal thermocline to a depth of ~30 m beneath a shallow mixed layer (Fig. 4). The salinity

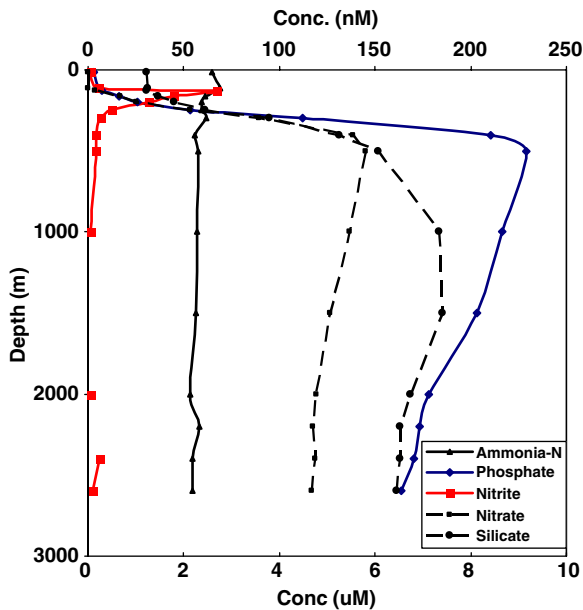


Fig. 3. Depth profile of ammonia-N, phosphate and nitrite measured by nanomolar technology (0–250 nM), and nitrate and silicate measured by micromolar technology (0–10  $\mu\text{M}$ ) from station 68 outside the eddy.

minimum observed beneath that layer is attributed to modified Atlantic water. From 25 to 150 m there was an increase in salinity. The isothermal layer characteristic of a warm-core eddy is found from 150 to 200–250 m. The precise depth of this isothermal layer depends on the particular station being sampled and how far it is from the geometric centre of the eddy as well as on the strength of the feature (Krom et al., 1993). Beneath the isothermal layer the salinity and temperature decrease to the  $\text{EMDW}_{\text{ADR}}$ . Beneath the  $\text{EMDW}_{\text{ADR}}$ , there was a thin layer ( $\sim 100$  m) of warmer and more saline water which is identified as  $\text{EMDW}_{\text{AEG}}$ .

The depth of the chlorophyll maximum was 120–140 m (Table 4). In the photic zone above the chlorophyll maximum, there was low but detectable levels of both nitrate (1–10 nM) and phosphate ( $< 2$ –5 nM) as determined by nanomolar technology (Fig. 5). At the same depths silicate was constant ( $\sim 1 \mu\text{M}$ ). Ammonia was present in the surface layers ( $\sim 80$  nM). At the base of the chlorophyll maximum there was a nitrite maximum (60–120 nM; Figs. 6 and 7). There was also a small but detectable increase in both nitrate (30–60 nM) and phosphate (3–5 nM; Figs. 5–7) associated with the seasonal nutricline (Krom et al., 1992, 1993). This is the layer of isothermal water which is formed during deep winter mixing and becomes isolated from the surface after the seasonal

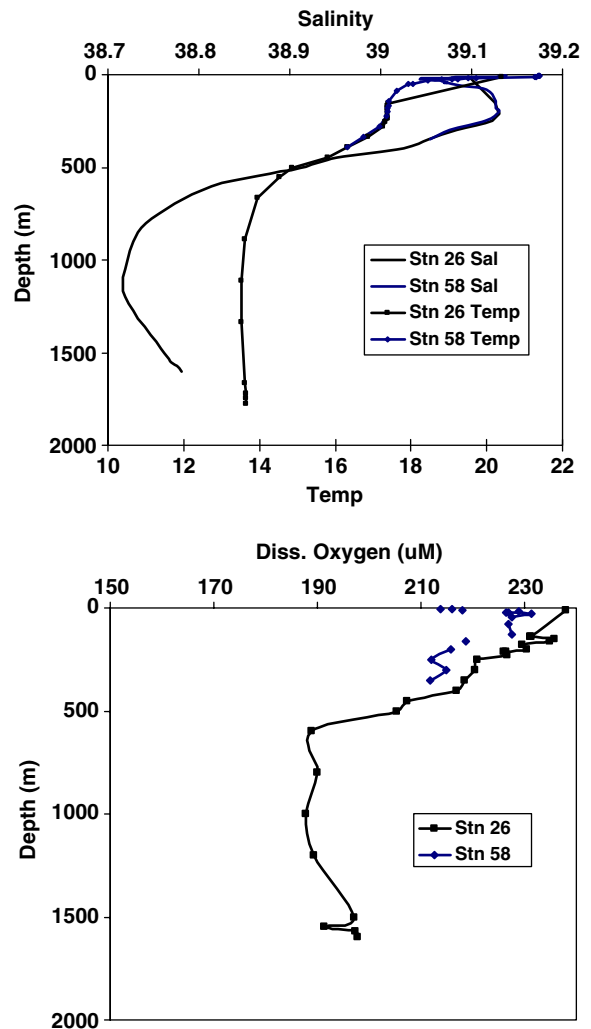


Fig. 4. Depth profiles of salinity and temperature, and dissolved oxygen from stations 58 and 26 situated in the core of the Cyprus warm-core eddy.

thermocline forms and deep winter mixing ceases. At station 58 (Fig. 5), there was a slight decrease in phosphate in this layer while in station 67 phosphate increased (Fig. 7). Beneath this layer, the permanent nutricline was found and the nutrient content increased to a maximum at 700 m (nitrate and phosphate). The dissolved oxygen minimum was found at 600 m.  $\text{EMDW}_{\text{AEG}}$  had lower phosphate, silicate and nitrate and higher dissolved oxygen than  $\text{EMDW}_{\text{ADR}}$  (Fig. 4).

### 5.3. Dissolved and particulate organic matter (DOM and POM)

A complete depth profile for DOM was obtained for four stations (44, 50, 64 and 68) outside the eddy

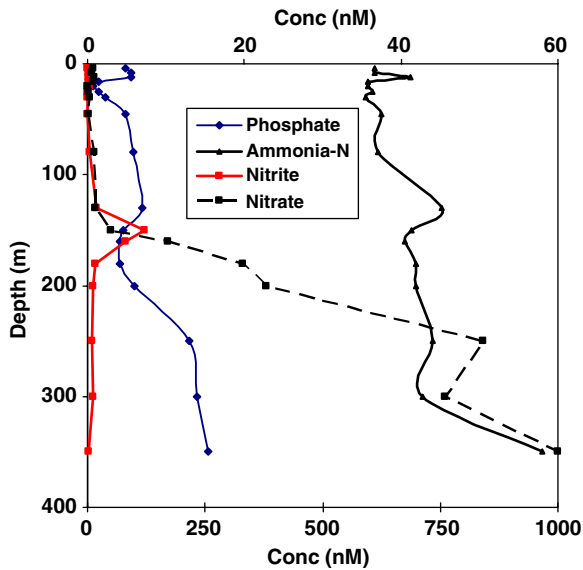


Fig. 5. Depth profile of ammonia-N and phosphate (0–60 nM) and nitrite and nitrate (0–1000 nM) measured by nanomolar technology from station 58 in the core of the Cyprus warm-core eddy.

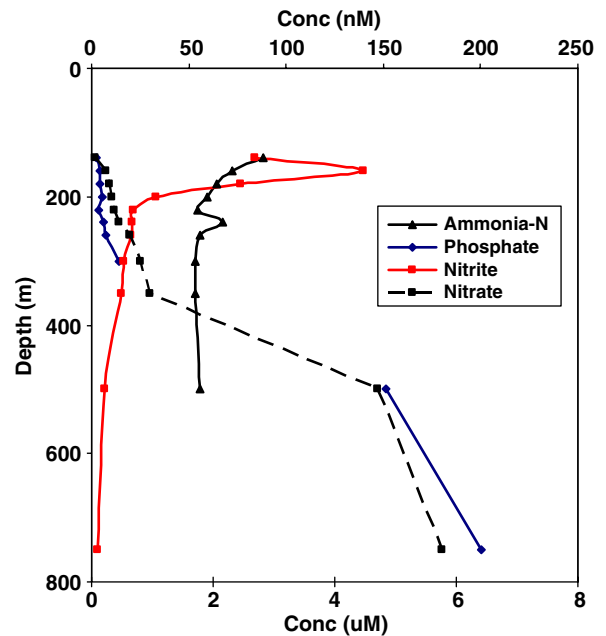


Fig. 7. Depth profile of ammonia-N, phosphate and nitrite measured by nanomolar technology (0–250 nM) and nitrate (0–8  $\mu$ M) measured by micromolar technology from station 67 in the core of the Cyprus warm-core eddy.

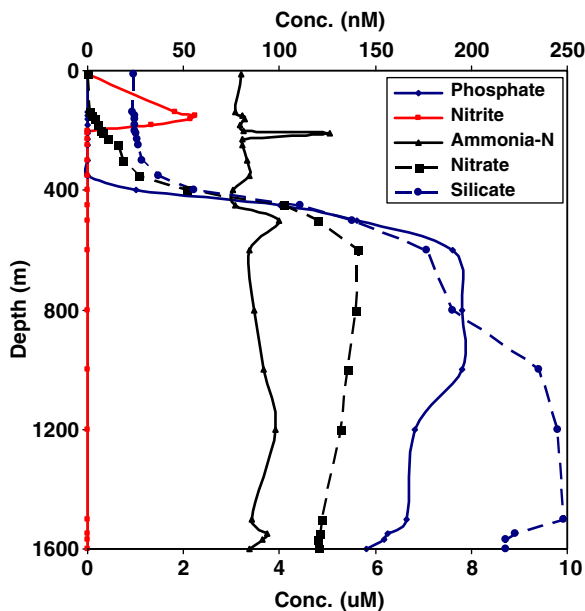


Fig. 6. Depth profile of ammonia-N and nitrite measured by nanomolar technology and phosphate measured by micromolar technology (0–250 nM) and nitrate and silicate (0–10  $\mu$ M) measured by micromolar technology from station 26 in the core of the Cyprus warm-core eddy.

(Fig. 8). DOC decreased rapidly from 60–110  $\mu$ M in the upper layers of the photic zone to a constant value of  $45 \pm 5$   $\mu$ M from 350 m to the bottom of the profile.

DON decreased from 4.5–11.5  $\mu$ M in the upper 50 m to a constant value of  $\sim 2$   $\mu$ M below 350 m depth. In contrast there was only a small decrease in DOP in the upper water column (<350 m) and then a relatively constant of  $\sim 50$  nM below that depth except for several anomalously high values at station 50 near the bottom of the profile. The resultant DOC:DON:DOP ratio in the photic zone was 106:8–13:0.05–0.06 changing to 106:6–8:0.2–0.3 at depth.

In the eddy core stations, except for a few apparently anomalously high values, DOC remained relatively constant at 60–100  $\mu$ M from the upper photic zone to the bottom of the isothermal layer and only began to decrease to a constant level of 45  $\mu$ M below 450 m (Fig. 9). DON values decreased rapidly from 5–10  $\mu$ M in the uppermost layers to  $\sim 2$   $\mu$ M below 300 m. As with the outside the eddy stations, DOP only decreased a relatively small amount from the uppermost photic zone (50–60 nM) to  $\sim 40$  nM at depth. There were also a number of anomalously scattered data close to the bottom of the water column (1500 m) in station 26. The resultant DOC:DON:DOP ratio in the photic zone was 106:4.3:0.11 changing to 106:9.1:0.10 at depth.

Carbon, nitrogen and phosphorus were determined in particulate matter collected from stations

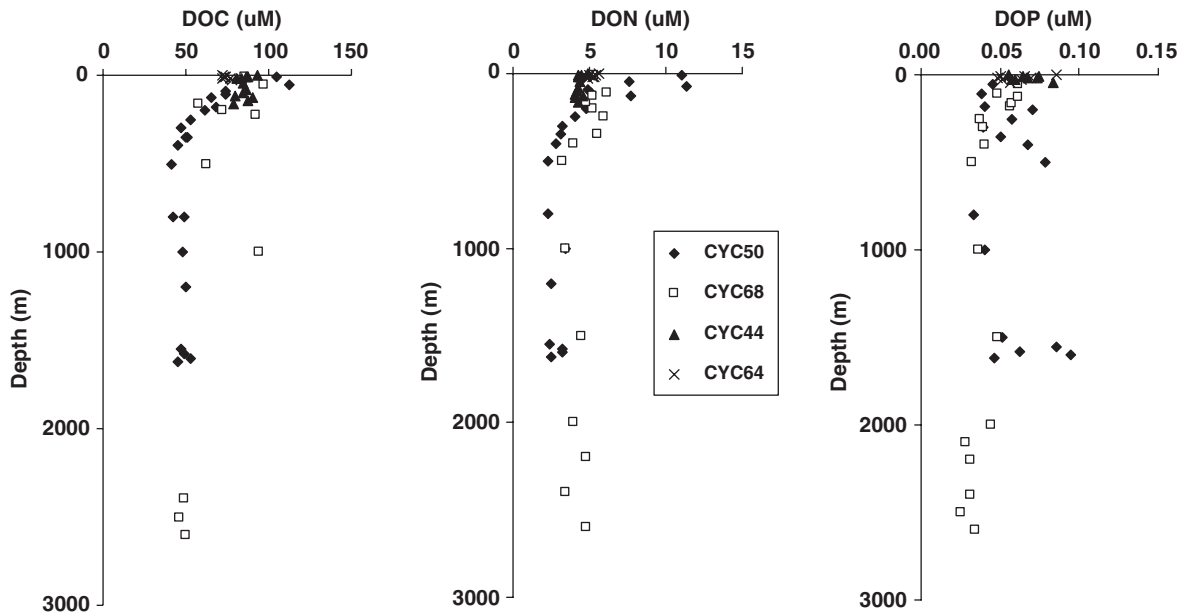


Fig. 8. Depth profile of DOC, DON and  $DOP_{UV}$  from stations 44, 50, 64 and 68 outside the Cyprus warm-core eddy.

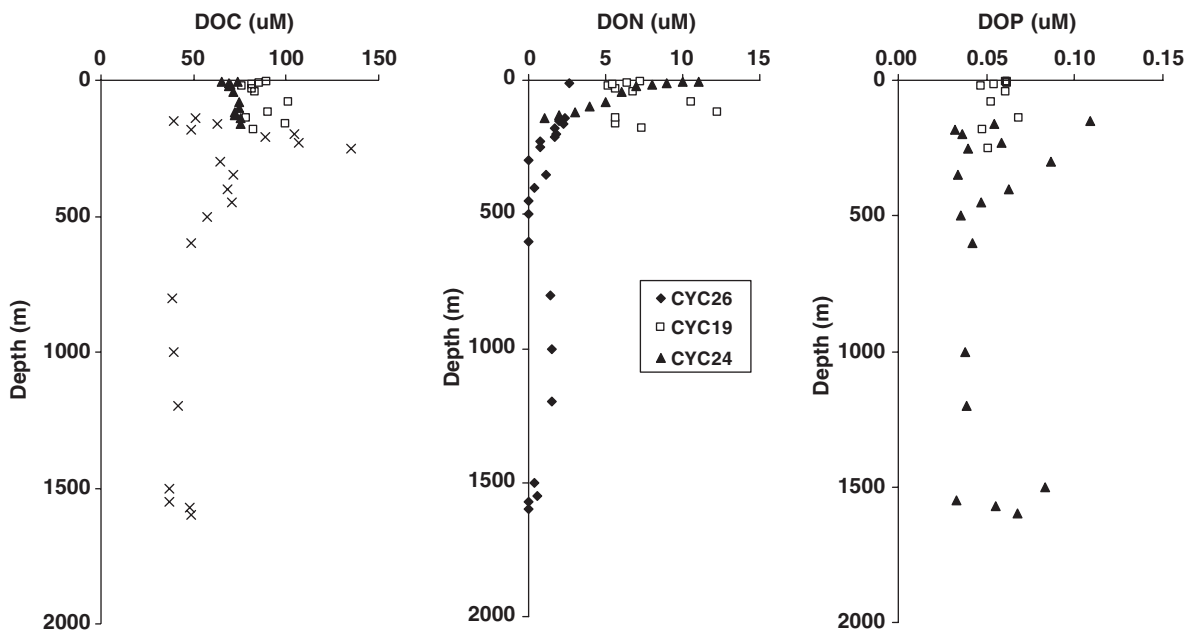


Fig. 9. Depth profile of DOC, DON and  $DOP_{UV}$  from stations 19, 24 and 26 in the core of the Cyprus warm-core eddy. NB: In station 26 below the nutricline, the total dissolved nitrogen was somewhat lower than the sum of nitrate + nitrite + ammonium. If the lowest value at 600 m was assumed to be zero, and the remaining data corrected correspondingly (i.e. add  $\sim 2 \mu\text{M}$ ), the values in the deep water became similar to those measured at stations outside the eddy.

both within the eddy core and outside the eddy. The results, summarised in Table 3, show that the POC in surface waters above the chlorophyll maximum

was  $3\text{--}3.7 \mu\text{M}$  decreasing to  $2.3\text{--}2.6 \mu\text{M}$  within the chlorophyll maximum to  $1.2\text{--}1.5 \mu\text{M}$  in the deep waters. PON values were  $0.39\text{--}0.32 \mu\text{M}$  above 70 m,

Table 3  
POC, PON and POP concentrations for particulate matter in the water column

Station and depth		POC ( $\mu\text{M}$ )	PON ( $\mu\text{M}$ )	POP (nM)	No. of samples
<i>Eddy core stations</i>					
Surface layer (0–50 m)	Aver.	3.7	0.39	9.1	28
	s.d.	1.2	0.12	2.5	
Chlorophyll maximum and just below (140–250 m)	Aver.	2.3	0.29	7.6	5
	s.d.	0.9	0.11	2.6	
Deep waters (350–1600 m)	Aver.	1.2	0.11	3.8	6
	s.d.	0.4	0.05	1.1	
<i>Outside eddy stations</i>					
Surface layer (70 m)	Aver.	3.0	0.32	n.m.	2
	s.d.	0.5	0.20		
Chlorophyll maximum and just below (130–250 m)	Aver.	2.6	0.30	n.m.	7
	s.d.	0.6	0.11		
Deep waters (350–2500 m)	Aver.	1.5	0.12	n.m.	13
	s.d.	0.34	0.05		

Average values  $\pm 1 \times$  s.d. given. All values in  $\mu\text{M}$ .

0.29–0.30  $\mu\text{M}$  within the chlorophyll maximum and 0.11–0.12  $\mu\text{M}$  in the deep waters. The POP values were only measured in the eddy core stations and were 9.1 nM decreasing to 7.6 nM at the chlorophyll maximum to 3.8 nM in the deep waters. Given the limited number of samples analysed there was no noticeable difference in the POM values between the eddy stations and outside the eddy.

## 6. Discussion

### 6.1. Dissolved inorganic nutrient profiles in the water column

In this study, for the first time in the eastern Mediterranean, a complete set of dissolved and particulate nutrient elements (C, N and P) were measured. In the eastern Mediterranean, the annual phytoplankton bloom takes place between November and March as soon as the dissolved nutrients are mixed into the photic zone (Krom et al., 2003). At the time of the winter bloom, when chlorophyll is distributed evenly throughout the mixed layer decreasing towards the base of the photic zone, phosphate is entirely depleted and significant concentrations of nitrate (300–1000 nM) remain. By May when this study was performed, summer conditions are firmly established with a strong seasonal thermocline and a well-developed deep

chlorophyll maximum. In the photic zone above the chlorophyll maximum, LNLC conditions have developed with both phosphate and nitrate below detection limits of conventional automated technology. Using nanomolar methods, there were low but detectable concentrations of ammonia (30–80 nM), while nitrate and nitrite was <1–10 nM and phosphate <2–4 nM. The presence of measurable ammonia in the photic zone while nitrate was close to or below detection limits suggests that grazing is an important process in this system since ammonia (and DON) are the first products of microbial grazing. A principal conclusion of the CYCLOPS addition experiment is that a very efficient grazing community is present that recycles bacterial and phytoplankton production rapidly (Thingstad et al., 2005). It has been estimated that export production is ~5% of gross primary production which is low for a basin with such a large dust flux (Carbo et al., 2005) and again emphasises the crucial importance of microbial grazing and recycling in this system.

The determination of total inorganic nutrients (DIN and DIP) by nanomolar technology enables N:P ratio to be calculated for surface waters. The ratio varied from 8.4 to 59, with five values below the Redfield ratio of 16:1 and four values above this ratio. The calculated N:P ratio at 80–120 m for IN patch stations sampled during the CYCLOPS experiment was greater than 16:1 for 21 out of 23

samples (Krom et al., 2005a). Since the P addition was confined to the Surface Mixed Layer (<20m), these data represent depths unaffected by P addition. Cavender-Bares et al. (2001) note that at the BATS station in the Sargasso Sea (N Atlantic), the system switches from P limitation in winter when the nitrate + nitrite:DIP > 16:1 to N limitation in summer when nitrate and nitrite:SRP < 16:1. This switch to N limitation caused the N<sub>2</sub> fixation observed at BATS in summer. In the eastern Mediterranean, it is known that there is excess N in winter. The results of this study in which the DIN:DIP ratio in the photic zone are predominantly greater than 16:1 suggest that under summer conditions also the water column remains short of DIP.

Silicate is present throughout the water column including in the photic zone. It has not been entirely depleted because the diatoms are only a very minor component of the phytoplankton biomass (Pitta et al., 2005). The total concentration of nutrients is so low that it favours the growth of nano- and picoplankton and mitigates against the growth of larger eukaryotic phytoplankton such as diatoms. The only significant blooms of diatoms in the eastern Mediterranean occur in coastal waters in winter and in the cores of cold core eddies such as the Rhodes gyre (Krom et al., 2003). Thus, it is unlikely that there are large enough populations of diatoms with symbiotic N fixers in the offshore waters of the eastern Mediterranean to allow significant N fixation as suggested by d'Alcala et al. (2003) to occur.

There was a prominent nitrite peak at the base of the chlorophyll maximum and at top of the permanent nutricline in the out of eddy stations and at the top of the seasonal nutricline in the eddy stations (Figs. 3, 6 and 7, Table 4). The location and magnitude of this peak were very similar to the

primary nitrite maximum (PNM) found at station ALOHA (Dore and Karl, 1996) and at BATS (Lipschultz et al., 1996). This PNM has been ascribed to a combination of incomplete assimilatory reduction of nitrate by phytoplankton and chemoautotrophic oxidation of ammonium by nitrifying bacteria. Without further detailed measurements it is not possible to determine the relative importance of these two processes in the development of the PNM here.

In stations outside the warm-core eddy, the permanent pycnocline and nutricline starts immediately below the chlorophyll maximum. However, in the warm-core eddy, the chlorophyll maximum is within the isothermal water layer and a seasonal nutricline which develops (Krom et al., 1993). The presence of a nitrite maximum at the top of this seasonal nutricline shows that the process that results in the production of nitrite occurred rapidly, within the past 6–8 weeks since the seasonal thermocline developed. The magnitudes of the nitrite peak at the eddy core stations are somewhat higher than that observed at stations 50 and 68 which have a permanent nitrite maximum. Similar short-term changes in the magnitude of the PNM are commonly found in such highly oligotrophic systems (Dore and Karl, 1996; Lipschultz et al., 1996).

Beneath this isothermal layer, there was a permanent nutricline. This is at 350–400 m in the eddy core compared with 150 m depth at stations outside the eddy. Using conventional micromolar technology, it appeared that the phosphocline was deeper in the water column than the nutricline or silicicline. However, when nanomolar technology was used (Figs. 5–7), it was evident that the phosphocline occurred at the same depth as the increase in the other nutrients. There is thus no evidence from the nutrient profiles of more rapid recycling of P relative to nitrate and silicate in these waters. The nutrient profile beneath the nutricline was similar to that observed previously in the region (Kress and Herut, 2001) with a nutrient (nitrate and phosphate) maximum at ~600 m.

## 6.2. Dissolved organic matter profiles in the water column

The concentration of DOC in the eastern Mediterranean is similar to that determined at station ALOHA in the N Pacific subtropical Gyre (data as presented in Hansell, 2002) with both

Table 4

Depth relationship between the chlorophyll maximum and the adjacent nitrite maximum

Station no.	Depth of chlorophyll maximum	Depth of nitrite maximum	Magnitude of the nitrite maximum (nM)
50 (outside eddy)	110	130	70 <sup>a</sup>
68 (outside eddy)	110	130	67 <sup>a</sup>
26 (core of eddy)	140	150	60 <sup>b</sup>
58 (core of eddy)	130	150	84 <sup>a</sup>
67 (core of eddy)	120	160	120 <sup>b</sup>

<sup>a</sup>Determined using nanomolar technology.

<sup>b</sup>Determined using micromolar technology.

Table 5

Concentration of DOC measured by High Temperature Oxidation in the eastern Mediterranean compared to values determined in other subtropical oligotrophic regions of the world's oceans

Location	Depth	DOC ( $\mu\text{M}$ )	Depth (m)	DOC ( $\mu\text{M}$ )	Reference
Eastern Mediterranean	Photic zone	65–100	500–1200	40–60	This study
N Pacific Central Gyre (ALOHA)	0–50 m	100–120	400	40	Hansell (2002)
Sargasso Sea (BATS)	0–50 m	60–70	400	40–50	Hansell (2002)
North-West Mediterranean	Surface	100	400	60	Raimbault et al. (1999a)
Ionian Sea	Surface	50–73	400	31–62	Seritti et al. (2003)

Table 6

Concentration of DON measured by High Temperature Oxidation in the eastern Mediterranean compared to values determined in other subtropical oligotrophic regions of the world's oceans

Location	Depth	DON ( $\mu\text{M}$ )	Depth (m)	DON ( $\mu\text{M}$ )	Reference
Eastern Mediterranean	Photic zone	3–11	500–1200	1–2	This study—HTC
Northern N Pacific	Surface	8–10	200–4000	6–8	Koike and Tupas (1993)—HTC
Equatorial Pacific	Upper 200 m	3–7			Raimbault et al. (1999b)—PO
Sargasso Sea	Surface	4–5.5	250–1000	2.1–5	Hansell and Carlson (2001)—UV
North-West Mediterranean	Surface	5	400	3	Raimbault et al. (1999a)—PO

systems having approximately 100  $\mu\text{M}$  in the surface waters and 40  $\mu\text{M}$  at depth (Table 5). The values of both are somewhat greater than those found in the Sargasso Sea where surface values are 60–70  $\mu\text{M}$  while values at 400 m are 40–50  $\mu\text{M}$  and in the Ionian Sea in winter with values of 50–73 and 31–62  $\mu\text{M}$  at depth (Table 5). Likewise the DON contents (Table 6) are similar to those measured elsewhere in the surface layers of open ocean waters such as the Northern N Pacific (Koike and Tupas, 1993). DON is determined by a variety of chemical procedures which result in determination of somewhat different chemical phases. The determinations of DON in the Equatorial Pacific and the Sargasso Sea have been carried out using PO and UV methods which are thus not strictly comparable with the high temperature oxidation (HTO) method used here. Nevertheless, the values seem to be of a similar order of magnitude in contrast to the data for DOP discussed below.

The amount of DOC (and DON) and their trends imply at least as a first hypothesis that the processes controlling their concentrations in the eastern Mediterranean might be similar to those observed in other subtropical ultra-oligotrophic systems. Vertical trends in DOC and DON have been interpreted elsewhere as being due to nutrient limited production of phytoplankton continuing to

fix carbon after running out of N and/or P. As some of this carbon leaks into the water column as a result of grazing or other processes, DOM with a high DOC/DON ratio accumulates. It is, however, somewhat surprising that the DOC and DON contents are as high as those determined in other tropical oceanic areas despite the fact that primary productivity levels are much lower (Krom et al., 2003) and light levels are high. Indeed, it has been found that a fraction of the DOC and DON is photolabile and its photochemical breakdown was shown to release inorganic N ( $\text{NH}_4^+$  and  $\text{NO}_2^-$ ) while there is also evidence of DOC photodegradation (Kitidis et al., pers. comm.). While DOC and DON are consumed by heterotrophic bacteria, this only occurs when phosphate is supplied. The result of the CYCLOPS addition experiment shows that in this system DOM consumption by heterotrophic bacteria is strongly P limited (Krom et al., 2005).

$\text{DOP}_{\text{UV}}$  is the largest reservoir of phosphorus within the surface water column, in general, and the photic zone in particular. Typically  $\text{DOP}_{\text{UV}}$  values are  $\sim 50$  nM in surface waters (Table 7) compared to a few nanomoles of DIP and 5–25 nM of particulate P. However, the concentration of  $\text{DOP}_{\text{UV}}$  is much lower than the amount found in other surface waters even within subtropical ocean gyres such as North Pacific subtropical gyre (Williams et al.,

Table 7

Concentration of  $\text{DOP}_{\text{UV}}$  measured by UV photooxidation in the eastern Mediterranean compared to values determined in other subtropical oligotrophic regions of the world's oceans

Location	Depth	DOP (nM)	Depth (m)	DOP (nM)	Reference
Eastern Mediterranean	Photic zone	50	500–1200	40	This study
N Pacific Subtropical Gyre	Surface	270	900	120	Williams et al. (1980)
N Pacific Subtropical Gyre	0–100 m	150–200	900	30	Smith et al. (1986)
Sargasso Sea	Surface	100–500			Cavender-Bares et al. (2001)
Sargasso Sea	Surface	74 ± 42			Wu et al. (2000)
North-West Mediterranean	Surface	130	400	bdl	Raimbault et al. (1999a)—PO

1980; Smith et al., 1986) or the Sargasso Sea (Wu et al., 2000; Cavender-Bares et al., 2001; Table 7). It is also somewhat lower than values measured in the NW Mediterranean (Raimbault et al., 1999a). This  $\text{DOP}_{\text{UV}}$  is biologically unreactive. Although N is present in the surface waters as free ammonia, there is only limited primary productivity. When ammonia was provided to “out of patch” water in a microcosm, no significant growth occurred (Zohary et al., 2005). Loh and Bauer (2000) used data from the eastern North Pacific Ocean to test the relative mineralisation rates of N relative to P and of N and P relative to C. They concluded that DOP is preferentially mineralised compared with DOC and DON resulting in increasing C:P and N:P ratios with depth. In contrast in the eastern Mediterranean there is a smaller decrease in  $\text{DOP}_{\text{UV}}$  with depth than that for either DON or DOC which decreases rapidly with depth implying that the labile DOP has already been recycled.

$\text{DOP}_{\text{UV}}$  measures only a proportion of the total DOP present in the water column. In the North Pacific, ~2/3 of the total DOP is present in a UV labile form (Thomas-Bulldis and Karl, 1998). Thus it is considered reasonable to assume that the  $\text{DOP}_{\text{UV}}$  measured in this study represents a minimum of 50% of the total DOP and probably contains most of the biologically available DOP. Thus, even if the total DOP is twice the measured  $\text{DOP}_{\text{UV}}$ , there was a drastic shortage of P relative to both C and N.

### 6.3. Elemental ratios of different organic matter phases in the water column

The DOC:DON:DOP ratio in the photic zone was 106:8–13:0.05–0.06 which is thus depleted in N and very depleted in P relative to the Redfield ratio. The C:N:P ratio of particulate matter was also very

much greater than the Redfield ratio (Table 8). High carbon:nutrient ratios are not uncommon in ultra-oligotrophic systems where carbon fixation continues after N and P become totally depleted. However, in this system, the samples are also severely depleted in P relative to N (N:P = 32–40). There is a systematic decrease in POM concentration with depth which reflects the progressive decomposition of labile organic matter mainly by bacterial consumption and respiration. As is noted above there is a parallel build up of dissolved nutrients and decrease in dissolved oxygen. The systematic increase in C:N ratio with depth suggests that N is being remineralised preferentially below the photic zone. Rather surprisingly the C:P values do not increase as fast as the C:N ratios suggesting that N is recycled more rapidly than P in the deeper zones of the water column. A similar pattern is found for DON and DOP. A possible explanation is that the rapid recycling of P occurs within the photic zone while N is recycled less rapidly on the time scale represented by the intermediate and deep waters.

Until recently (ca. 1990) all EMDW was formed in the Northern–Middle Adriatic in winter and then flowed out to fill the remainder of the deep waters of the eastern Mediterranean basin. Zavatarelli et al. (1998) have reviewed the seasonal nutrient data for the Adriatic Sea. In winter, they showed that the nitrate content in the deep Northern and Middle Adriatic contain 0.8–1  $\mu\text{M}$  nitrate. The same waters contain 50–75 nM of phosphate, very close to or at the limit of detection of the analytical method used. The water mass characteristics and nutrient content of this deep water is similar to the values determined by Kress and Herut (2001) and Kress et al. (2003) for the more extensive data sets collected across the Levantine basin. Assuming the original phosphate in the descending water was zero, then the

Table 8

C:N:P ratios of particulate organic matter sampled from the water column in the core of the eddy and outside the eddy: average values and  $1 \times$  s.d. are given

	C	N	P	No. of samples
<i>Eddy core stations</i>				
Surface layers (0–50 m)	106	11.31 0.908	0.284 0.095	28
Chlorophyll maximum (140–250 m)	106	12.92 1.746	0.401 0.212	5
Deep waters (350–1600 m)	106	9.612 1.126	0.36 0.127	6
<i>Out of eddy stations</i>				
Surface layers (70 m)	106	11.34	n.m.	2
Chlorophyll maximum (140–250 m)	106	12.29 4.19	n.m.	7
Deep waters (350–1600 m)	106	9.77 2.41	0.36	13

calculated C:N:P ratio of the organic matter which decomposed in the transit from the Adriatic to the SE Levantine basin is 106:8.8:0.34 assuming an O:org C ratio of 138:106 (Redfield et al., 1963) and 106:11.1:0.43 assuming an O:org C ratio of 175:106 (Takahashi et al., 1985). A similar calculation can be carried out for the EMDW that has recently formed in the Aegean Sea. In the Aegean Sea, the annual range of phosphate and nitrate concentration in the surface waters is bdl–0.05 and bdl–1  $\mu$ M, respectively (Krasakopoulou et al., 1999). Assuming the sinking waters have 1  $\mu$ M of nitrate and zero phosphate, this results in a similar C:N:P ratio for the decomposed organic matter of 106:8.5:0.34 or 106:10.8:0.43, respectively. If the preformed phosphate was 0.05  $\mu$ M then the content of the P in the decomposing organic matter would have been even lower.

Thus, the C:N:P ratio of the organic matter that has decomposed to provide the nutrients observed in the deep water (Table 9) is rather similar to the measured residual C:N:P ratio of the particulate matter in the deep water (106:9.6:0.36) and somewhat higher than the measured residual C:N:P ratio of dissolved organic matter (106:5.3:0.13). On the basis of these data either or both could be considered the source of the unusual ratio for the decomposed organic matter. It is, however, understood that the calculated C:N:P ratio of the decomposed organic matter is the sum of all of

the organic matter which has decomposed within that water mass during its passage from when it first descended from the surface to its present position in the eastern Mediterranean. Without specific data on the nutrient content of the POM and DOM along the entire transect particularly at the site where the water descended it is not possible to determine which of these sources of decomposing organic matter is more important.

#### 6.4. Eastern Mediterranean as a P starved system

The south eastern Levantine basin of the eastern Mediterranean is a uniquely P starved system. Prior to this study it was known that the nitrate:phosphate ratio in the deep water was 25–28:1 (Krom et al., 1991; Kress and Herut, 2001). In this study, similar nitrate:phosphate ratios were determined. The overall DIN:DIP ratio in the deep water is actually somewhat higher since a small but measurable concentration of ammonium (40–80 nM) was determined throughout the water column. In the nutrient depleted surface waters, the total DIN:DIP ratio, as determined by nanomolar technology was predominantly > 16:1. It has been shown here that the particulate matter throughout the water column has an N:P ratio of 27–32:1. The DON:DOP ratio was greater than 100:1. This is likely to be a maximum estimate since  $DOP_{UV}$  was determined rather than total DOP. In comparison to studies in

Table 9

Calculated elemental ratio of decomposed organic matter in Eastern Mediterranean Deep Water (EMDW)

Water mass	Carbon	Nitrogen	Phosphorus	No. of samples
EMDW <sub>ADR</sub> average <sup>a</sup>	106	8.8	0.34	6
EMDW <sub>ADR</sub> range <sup>a</sup>	106	8.2–9.4	0.27–0.40	6
EMDW <sub>ADR</sub> average <sup>b</sup>	106	11.1	0.43	6
EMDW <sub>ADR</sub> range <sup>b</sup>	106	10.4–12.0	0.34–0.51	6
EMDW <sub>AEg</sub> average <sup>a</sup>	106	8.5	0.34	6
EMDW <sub>AEg</sub> range <sup>a</sup>	106	7.9–9.1	0.29–0.39	6
EMDW <sub>AEg</sub> average <sup>b</sup>	106	10.8	0.43	6
EMDW <sub>AEg</sub> range <sup>b</sup>	106	10.3–11.5	0.39–0.49	6
Measured POM in the deep water	106	9.6	0.36	
Measured DOM in the deep water	106	8–13	0.05–0.06 0.1–0.12 <sup>c</sup>	

The calculation assumes that the descending water had an initial nitrate content of 1 μM and was entirely depleted in phosphate (Zavatarelli et al., 1998; Krasakopoulou et al., 1999).

<sup>a</sup>Calculated assuming an O:organic ratio of 138:106 (Redfield et al., 1963).

<sup>b</sup>Calculated assuming an O:organic ratio of 175:106 (Takahashi et al., 1975).

<sup>c</sup>Assuming that UV labile DOP is 50% of total DOP.

other oligotrophic waters (Thomson-Buldis and Karl, 1998), the total DOP might reasonably be assumed to be twice the DOP measured here and thus the DON:DOP ratio might be 50:1. Thus, all of the N:P ratios within the water column in this region are far in excess of the Redfield ratio of 16:1. Taking into account the limitations of a study carried out in one location and at one time it is concluded that there is no previously unidentified reservoir of biologically available P in the system. Furthermore, the N:P ratio of the decomposed organic matter, which represents a basin-wide integrated nutrient ratio is 23–30:1. The only large reservoir of P within the system of non-biologically labile P is the one which is supplied with Saharan dust (Herut et al., 1999). Carbo et al. (2005) have shown that there is evidence in this P starved system of significant remobilisation of inorganic ‘refractory’ P supplied in the Saharan dust probably in the photic zone. The P limitation of the eastern Mediterranean is thus due to the lack of P within the system and is not due to some unusual recycling processes within the system which is removing P relative to N. If N fixation is occurring as has been suggested by Bethoux et al. (1992) and Pantoja et al. (2002), then it is against a background of severe overall P starvation.

As a result of work carried out during the CYCLOPS programme, a new hypothesis has been presented to explain the P starved status of the eastern Mediterranean (Krom et al., 2004, 2005).

Krom et al. (2004) have carried out a total nutrient budget for the eastern Mediterranean and have shown that the N:P ratio of the nutrients supplied to the system is ~50:1, far in excess of the Redfield ratio. While globally microbial denitrification is known as an important process which causes the system to relax to the Redfield ratio of 16:1 (Tyrell, 1999), it has been suggested that this does not occur in the eastern Mediterranean. Denitrification requires sub-oxic to anoxic conditions. The eastern Mediterranean is ultra-oligotrophic, with very low levels of primary productivity. This is principally as a result of its unusual anti-estuarine circulation in which nutrients are net exported from the basin at the straits of Sicily within the LIW. This means that very little organic matter is produced and accumulated. Organic matter is required by denitrifying bacteria both to drive the system to the sub-oxic to anoxic conditions required for nitrate reduction and to provide the fuel for this microbial process. Since only very limited denitrification occurs, the N:P ratio does not relax back to the Redfield ratio and the system remains P starved. The data presented in this study are entirely consistent with this interpretation for the overall nutrient control of the system.

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