

# Dissolved nutrients, preformed nutrients and calculated elemental ratios in the South-East Mediterranean Sea

Dissolved nutrients  
Preformed nutrients  
Elemental ratios  
Eddy  
SE Mediterranean  
Sels dissous  
Sels préformés  
Rapports élémentaires  
Tourbillon  
SE Méditerranée

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## ABSTRACT

The Mediterranean Sea has been described as the most impoverished large body of water in the world. Number of studies have determined nutrient concentration in the western and central Mediterranean; in this preliminary study, we present data from 25 stations in the Levantine basin of the eastern Mediterranean. The surface layer, to a depth of 150 m, had a silicic acid content of 1-2  $\mu\text{M}$  and a nitrate concentration of less than 1  $\mu\text{M}$ , while the maximum reached at depth was 5.4-6.5  $\mu\text{M}$  nitrate and 9.9-14.6  $\mu\text{M}$  nitrate and 9.9-14.6  $\mu\text{M}$  silicic acid except for three stations close to the Egyptian coast where a value of 17  $\mu\text{M}$  was reached. There was sometimes a small nitrate maximum (0.1-0.5  $\mu\text{M}$ ) at 600 m (400-800 m). Based on temperature, salinity and dissolved nutrient data, a warm-core eddy was found south of Cyprus in a position similar to that observed previously. Preformed nutrients calculated in the usual manner gave negative values and could not be used as a tracer for water mass type. The elemental ratio (O:N) for decomposing organic matter was calculated to be 138:11.0-13.0 which is considerably different from the usual Redfield ratio.

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## RÉSUMÉ

Sels nutritifs dissous et préformés, rapports élémentaires calculés dans le sud-est de la Méditerranée

Les eaux de la mer Méditerranée sont parmi les plus pauvres de l'océan mondial. La concentration en sels nutritifs dans les bassins occidental et central a fait l'objet de nombreux travaux. Pour la Méditerranée orientale, cet article présente les données obtenues en 25 stations du bassin Levantin. Dans la couche superficielle jusqu'à 150 m, la teneur en acide silicique est de 1 à 2  $\mu\text{M}$  et la teneur en nitrate est inférieure à 1  $\mu\text{M}$ ; en profondeur, la concentration en nitrate atteint un maximum de 5,4 à 6,5  $\mu\text{M}$  et la concentration en acide silicique s'élève jusqu'à 9,9 à 14,6  $\mu\text{M}$ , sauf en trois stations proches de la côte égyptienne où elle atteint 17  $\mu\text{M}$ . Un petit maximum de nitrate (0,1 à 0,5  $\mu\text{M}$ ) a été observé quelquefois à 600 m (de 400 à 800 m). La température, la salinité et les sels nutritifs dissous révèlent la présence d'un tourbillon chaud dont la position au sud de Chypre a été observée précédemment. La teneur en sels nutritifs préformés dont le calcul donne des valeurs négatives ne peut être utilisée comme traceur des masses d'eau. Le rapport élémentaire (O:N) pour la matière organique en décomposition 138:11,0-13,0 est très différente de la valeur habituelle du rapport de Redfield.

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## INTRODUCTION

The Mediterranean Sea has been described as the most impoverished large body of water in terms of dissolved nutrients (Redfield *et al.* 1963). A number of studies

which have determined the nutrient concentrations in the western Mediterranean Sea (including Schink, 1967; Miller *et al.* 1970; Coste *et al.* 1984) and in the central Mediterranean (Miller *et al.* 1970; Cescon and Macchi, 1973; Weiss *et al.* 1983, Hydes *et al.* 1988). However

there are very few published data available on nutrient concentrations in the eastern (Levantine) basin of the Mediterranean (Morcos and El-Rayis, 1973). In this preliminary study, dissolved nutrient data are presented from a cruise of the R/V *Shikmona* in the Levantine basin south of Cyprus in August-September 1987.

Mesoscale eddies have been recognized and studied as potentially important oceanographic features (Robinson, 1983). Recently, eddy features have been discovered in the Levantine basin of the eastern Mediterranean Sea (Robinson *et al.* 1987; Brenner *et al.* 1986). Fox and Kester (1986) noted that dissolved nutrients can be used to identify and delineate such mesoscale eddy features. In this study, we have used dissolved nutrient as well as temperature profiles to demonstrate the presence of such mesoscale features in the Mediterranean and to provide a first description of their basic chemical features.

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; Minster and Boulahdid, 1988). The normal assumption used in the calculation is that the O:C:N elemental ratio of the decomposing matter is 138:106:16 (Redfield *et al.* 1963) or 175:106:16 (Takahashi *et al.* 1975). Recent studies have suggested that the N:P ratio of the waters of the S.E. Levantine basin are unusually high (Krom *et al.* in prep a). An aim of this study was to determine whether preformed nutrients could be used as a tracer for the major water masses in the area. If, as preliminary calculations showed, preformed nutrients gave unusual negative

values, a second aim was to suggest the reason for this, and the implications concerning the elemental ratio of decomposing organic matter in the area.

## METHODS

### Area of study

Field observations were taken at a number of stations as part of a cruise of the R/V *Shikmona* to this area in August-September 1987. Of these stations, 25 were sampled for dissolved nutrients. Figure 1 shows the locations of the stations under study.

Water samples were collected with a General Oceanics rosette, equipped with ten 1.5 l Niskin bottles. Pressure, temperature and conductivity of the samples were measured *in situ* by a Neil Brow CTD coupled to the rosette. The data acquired by the CTD were depicted in real time on a plotter and stored on magnetic tape for later detailed analysis. Salinity was also determined ashore using a Guildline salinometer with an accuracy of  $\pm 0.003$  ppt. These salinities, together with the temperatures and the depths measured by the reversing thermometers, were used to calibrate the CTD data. The CTD salinities were calculated using the definition and algorithm of practical salinity (Unesco, 1981).

### Sampling and analysis

The water was sampled for nutrients as soon as the rosette was taken on board. Samples were collected in

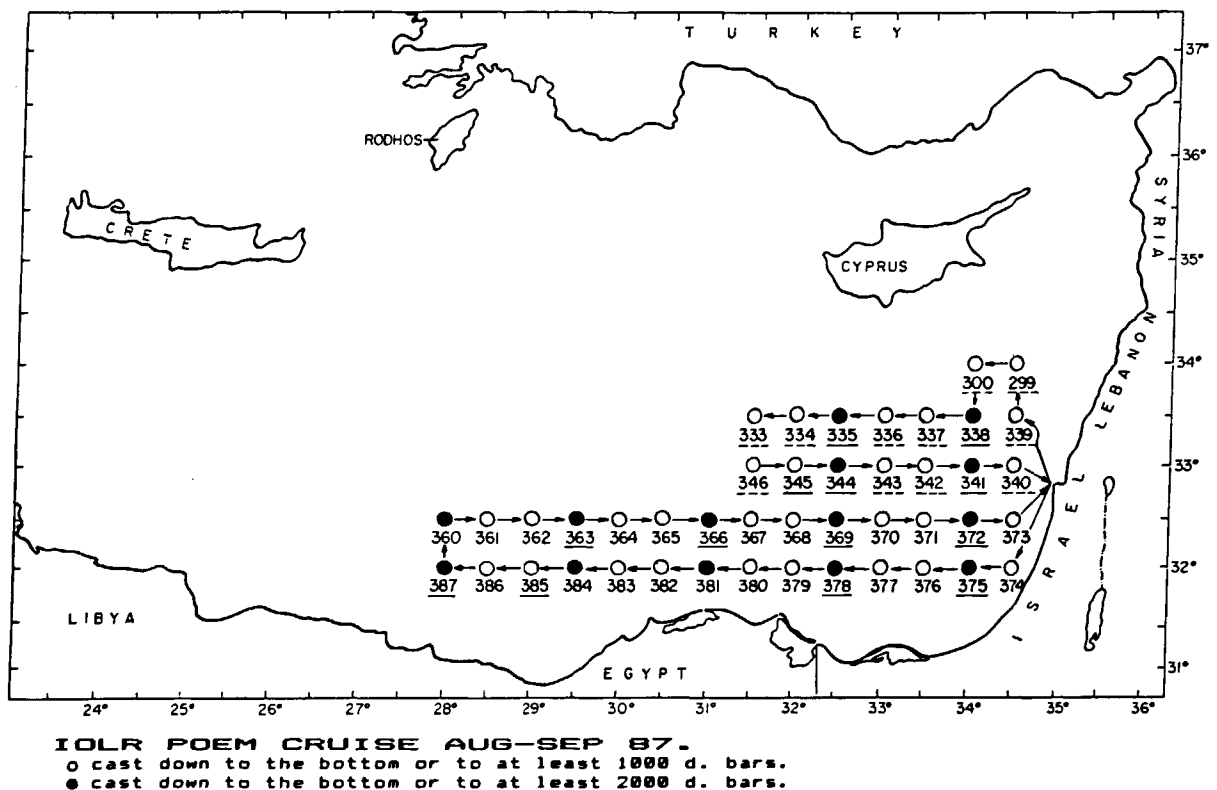


Figure 1  
 Map of sampling locations for cruise POEM-05 (August-September 1987).

15-ml plastic scintillation vials which were new and had been prewashed with 10% hydrochloric acid. The samples bottles were rinsed twice with the sample, filled with sample, and then immediately frozen. In the laboratory, the samples were thawed for 24 hours prior to determination of dissolved nutrients (Macdonald and McLaughlin, 1982). Subsequent tests showed no measurable difference between samples thawed for 24 hours and those thawed and measured immediately. Nutrient determinations were carried out on a rapid flow analysis Alpkem system by the methods described in the Alpkem manual with slight modifications. The precisions achieved using replicate samples collected in the field were  $0.12 \mu\text{M}$  (1 s) for Silicic acid and replicate sea water standards and  $0.07 \mu\text{M}$  (1 s) for nitrate+nitrite. Nitrite was measured on several profiles. The results were all below  $0.07 \mu\text{M}$ , which was close to the detection limits for the procedure used. Thus all data measured as nitrate+nitrite are effectively all nitrate.

In a sample preservation experiment, frozen samples were compared with samples measured within 1-3 hours of collection. The average difference found was  $0.1\text{-}0.2 \mu\text{M}$  for silicic acid and nitrate in surface samples, and  $0.5\text{-}0.7 \mu\text{M}$  for nitrate and  $0.2\text{-}0.4 \mu\text{M}$  for

silicic acid on the deep samples (500 m). On the basis of this experiment it was decided not to attempt to correct the measured data for this small and somewhat variable effect. Dissolved oxygen was measured on board ship by a Winkler titration carried out in the 30 ml sampling bottle without transfer (Carritt and Carpenter, 1966).

## RESULTS

Figures 2 and 3 show the vertical profiles of dissolved nutrients, temperature and salinity from station 333, chosen as typical of most of the stations. The isothermal and isohaline ( $T=26\text{-}28 \text{ C}$ ,  $S=39.1\text{-}39.4$ ) mixed layer extended from the surface to a depth of 30 m. The seasonal thermocline extended from the base of this mixed layer to approximately 150 m. A pronounced salinity minimum associated with the Atlantic water ( $S=38.7\text{-}38.8$ ) appeared near the base of the

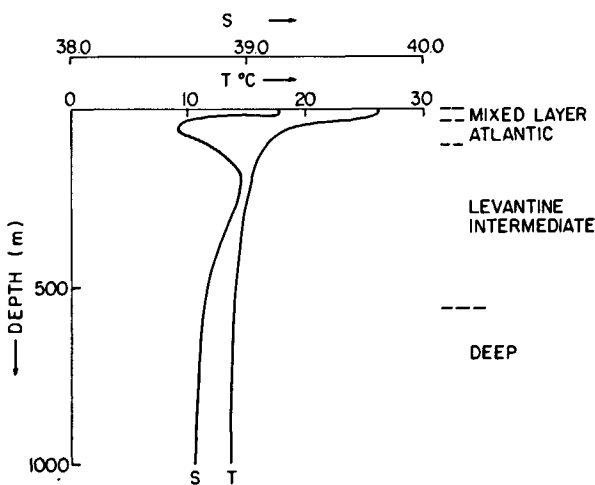
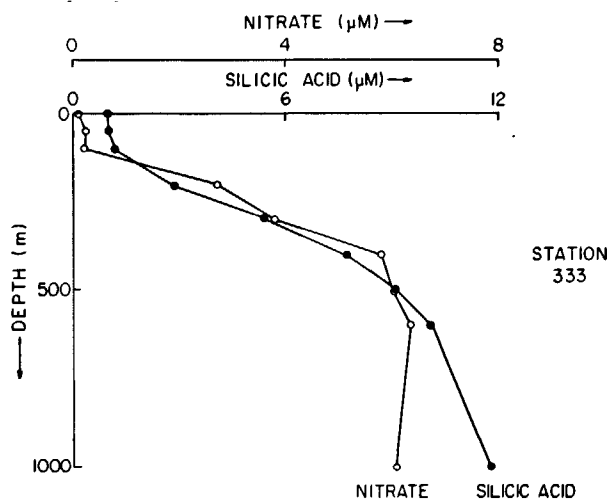


Figure 2  
Vertical chemical and physical profiles at station 333 considered typical of the Levantine Basin of the Eastern Mediterranean sea.

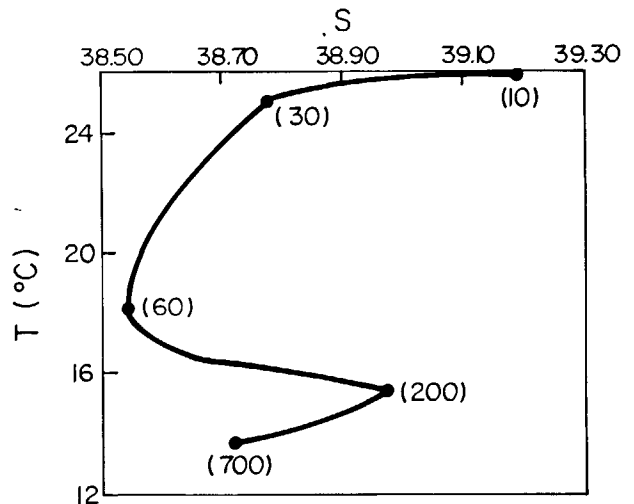


Figure 3  
 $T\text{-}S$  plot for Station 333 considered typical of the Levantine basin.

thermocline (Fig. 4). These temperature and salinity profiles are characteristic of summertime in the Levantine basin (Hecht *et al.* 1988). From the surface to 100 m, the euphotic zone, the distribution of nitrate was homogeneous with a value of  $<1 \mu\text{M}$  and silicate  $1 \mu\text{M}$ . The layer of high salinity Levantine Intermediate Water (LIW) from 150 to 500 m contained the nutricline with nitrate increasing to  $5\text{-}7 \mu\text{M}$  and silicic acid increasing to  $6\text{-}11.6 \mu\text{M}$ . The depth of the nutricline and the gradient varied somewhat between stations. There was a small nitrate maximum at most of the stations where suitable depths were sampled (11 out of 15). The maximum was most frequently at 600 m but ranged between 400 and 800 m. It was  $0.1\text{-}0.5 \mu\text{M}$  higher than the value at 1000 m. The silicic acid continued to increase below 500 m but at a somewhat slower rate. At 1000 m, the silicic acid content had reached a value of  $9.9\text{-}14.6 \mu\text{M}$ . At three stations closest to the Egyptian coast, 378, 385, and 387, silicic acid increased to  $12\text{-}17 \mu\text{M}$  by 500 m.

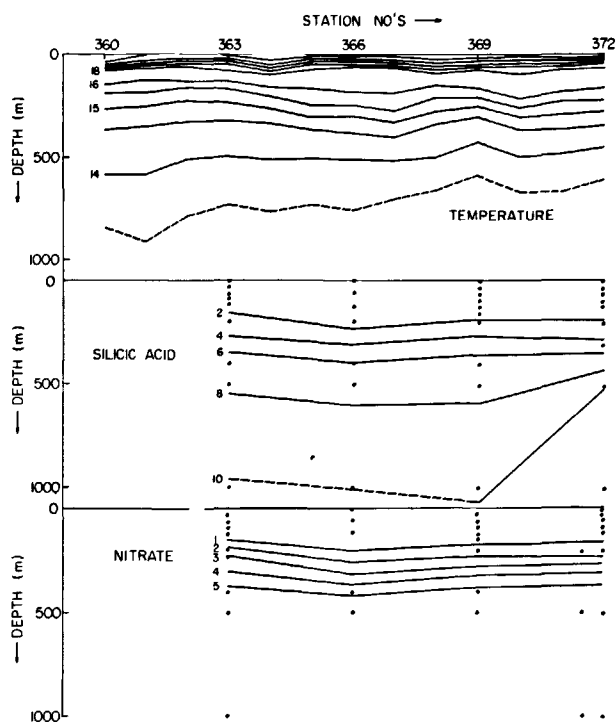


Figure 4  
Vertical cross sections of temperature, silicic acid and nitrate along the eastern Mediterranean Sea, 32.5 N.

DISCUSSION

The values of dissolved nutrients at depth (1000 m) were much lower than those found typically at similar depths in other oceans: 40  $\mu\text{M}$  nitrate in the Pacific and Indian Oceans and 20  $\mu\text{M}$  nitrate in the Atlantic Ocean; 130  $\mu\text{M}$  silicic acid in the Pacific and Indian Oceans and 40-100  $\mu\text{M}$  silicic acid in the Atlantic Ocean (Spencer, 1975, Weiss *et al.* 1983). The values found in this study are comparable to and possibly somewhat higher than those measured previously in the central Mediterranean. Miller *et al.* (1970) found levels of silicic acid of 8-10 and 4-5  $\mu\text{M}$  for nitrate in a transect from Crete, south to the Libyan coast, while Weiss *et al.* (1983) measured levels of 8.5  $\mu\text{M}$  for silicic acid and 4.7  $\mu\text{M}$  for nitrate at 1000 m at GEOSECS

station 404 south of Italy at 35 35'N; 17 15'E. Hydes *et al.* (1988) found concentrations for silicic acid of 10.6  $\mu\text{M}$  and for nitrate 5.3  $\mu\text{M}$  at 1000 m at 33 54'N; 26 02'E south of Crete. These data were sampled and measured by automated methods on board ship. The data from this study are thus comparable with previous studies which enabled Redfield *et al.* (1963) to describe the Mediterranean Sea as the most impoverished large body of water in the world in terms of dissolved nutrients.

On the track (32 30'N), which was similar in form to that of the southernmost track (32 N; not shown here), there was no evidence of any mesoscale features in this region (Fig. 4). On the track at 33 N (not shown here) and even more so on the track at 33 30' N, clearly defined mesoscale features were recognized (Fig. 5). Centred on station 338, there was a depression of the temperature, and salinity contours associated with a warm core eddy (Brenner, 1989). The nutrient contours, nitrate and silicic acid, were similarly depressed in the centre of the eddy. The position of this eddy was similar to that found on previous cruises to the area (Robinson *et al.* 1987; Hecht *et al.* 1988; Brenner, 1989). The presence of this quasi-permanent feature has been confirmed by a series of subsequent cruises to the area, designed to obtain detailed information on the structure and dynamics of this eddy (Brenner *et al.* 1990; Krom *et al.* in prep. b).

Preformed nutrients are defined as the nutrients present in the water when they sank beneath the euphotic zone and are generally determined by the following relation:

$$N(\text{preformed}) = N(\text{measured}) - N(\text{respired})$$

where N (respired) is calculated from  $\text{AOU}/R_n$ .  $R_n$  is the ratio of oxygen consumed to nutrient produced during decomposition of organic matter (Redfield *et al.* 1963).

If this calculation is carried out for waters from the southeast Levantine basin, a negative value for preformed nutrients is obtained. This occurs whether Redfield ratio of 138:16 is used (Fig. 6a) and also occurs, though to a lesser extent if the higher ratio of 175:16 suggested by Takahashi *et al.* (1985) is used (Fig. 6b).

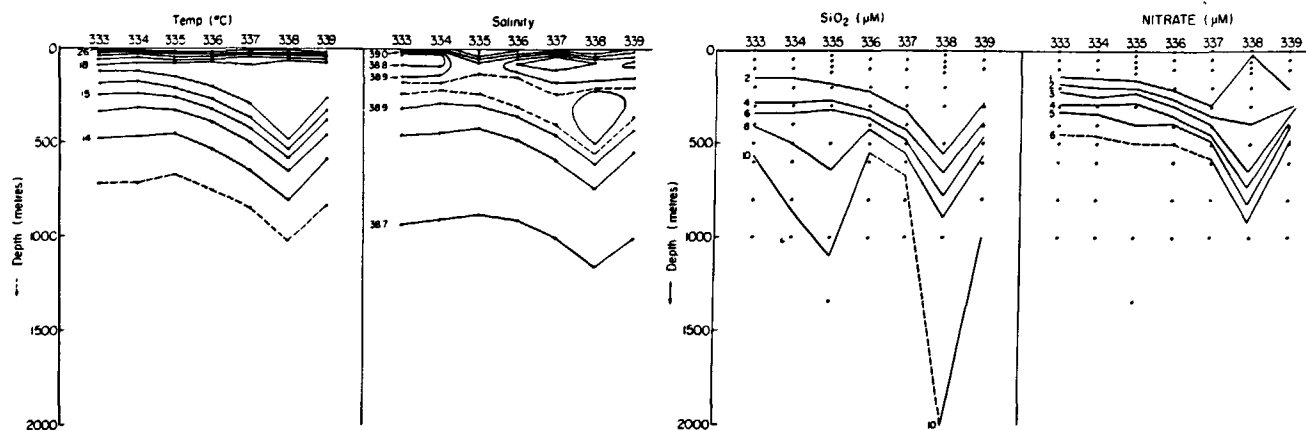


Figure 5  
Vertical cross sections of temperature, salinity, silicic acid and nitrate along the eastern Mediterranean Sea, 33.5 N. A warm core eddy can be seen centred at station 338.

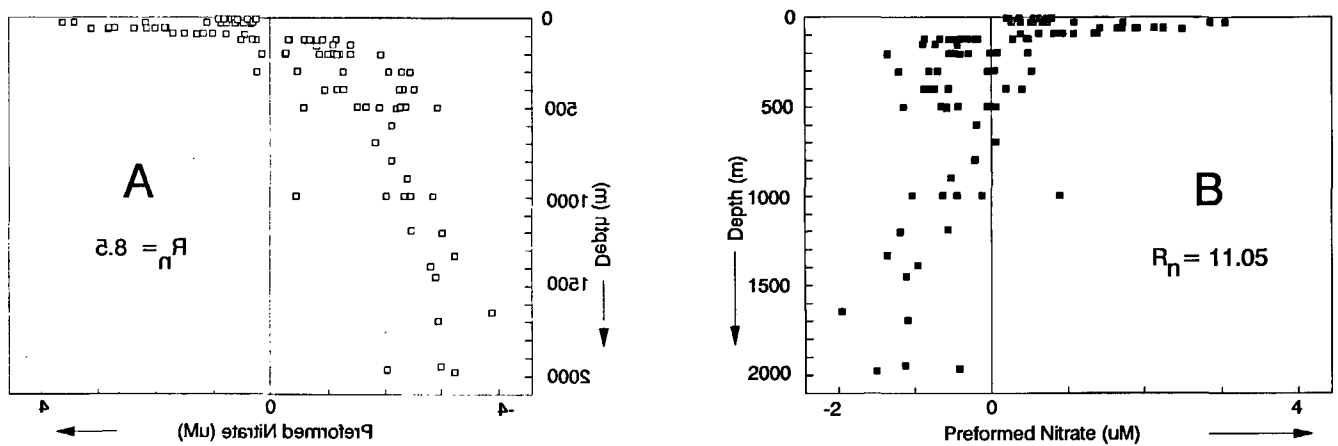


Figure 6

Plot of Preformed Nitrate vs. Depth. Preformed Nitrate was calculated in Figure 6a assuming an O:N of 8.6 (Redfield et al. 1963) and in Figure 6b assuming a ratio of 11.0 (Takahashi et al. 1985).

Similar profiles have been found when this calculation is carried out on data from the Cyprus eddy (Krom *et al.* in prep.) or on the data from GEOSECS 404 (Weiss *et al.* 1983). Negative preformed nutrients cannot exist and thus one or more of the assumptions made in the calculations cannot be valid for the eastern Mediterranean.

One possible explanation is that the value used for AOU is too high, *i.e.* that a process occurs which produces oxygen without consuming nutrients. Warming of water by solar radiation below a depth in the water column at which it can equilibrate with the atmosphere is a process which might occur in the very clear waters of the eastern Mediterranean. However such warming would result in too low, not too high, AOU.

A second possibility is that nutrients are being removed from the water column without production of oxygen. Nutrient uptake has been shown to occur in the depth range 120-200 m in the Levantine basin is the reason for the extreme values for the N:P ratio (up to 120) found in that depth range (Krom *et al.* in prep. a). That depth range is below the 0.05% light level and net active photosynthesis no longer occurs. This process can explain the particularly negative values for preformed nutrients found in this depth zone but not below this depth. The third and most plausible explanation of the negative preformed nutrients is that the elemental ratio used to calculate them was too low. In order to estimate this ratio, it was assumed that the value for the preformed nutrients throughout the eastern Mediterranean was zero and hence the elemental ratio was the slope of AOU:N below 200 m. This assumption is the same as that used by Redfield *et al.* (1963). The slope of the scattergram resulted in a calculated ratio of O:N=138:11.0 (Fig. 7), while the ratio required to bring all the preformed nitrate, except those in the depth range 120-200 m, to zero was 138:13.0. This ratio is similar to that suggested by Takahashi *et al.* (1985).

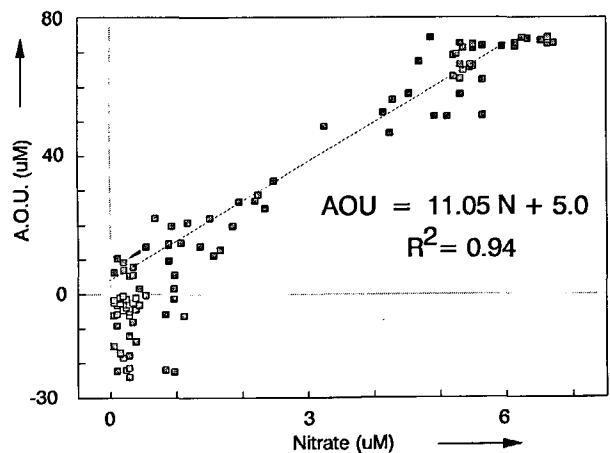


Figure 7

Scattergram of Apparent Oxygen Utilization vs Nitrate for the S.E. Levantine basin.

No determinations exist for the elemental composition of particulate matter in the Levantine basin. Copin-Montegut and Copin-Montegut (1983) observed that the C:N ratio for particulate matter in the N.W. basin of the Mediterranean were significantly higher than were found in the major oceans of the world and that the elemental ratio (N:P) in the water column was similar to that of the particulate matter in the area. The calculation carried out in this study suggests that O:C:N ratio in the eastern Mediterranean is unusually high and that the usual Redfield ratio may not be valid for the elemental composition of organic matter in this area.

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