OCEANOLOGICA ACTA 1990 - VOL. 13 - N° 3

Oxygen and nutrient observations in the Southern Tyrrhenian Sea

Mediterranean Sea
Tyrrhenian Sea
Oxygen
Nutrients

Mer Méditerranée
Mer Tyrrhénienne
Oxygène
Sels nutritifs

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Received 31/5/89, in revised form 26/12/89, accepted 16/1/90.

ABSTRACT

Water samples were collected for the analysis of oxygen, inorganic phosphorus and silicate, as an adjunct component of a circulation study of the Southern Tyrrhenian Sea. The vertical distribution of dissolved oxygen typically exhibited a sub-surface maxima around 50 m, and minima around 500 m. The apparent oxygen utilization increased from negative values in the euphotic zone to positive values of $\sim$ 1.4 ml/l in the underlying aphotic zone. Both the phosphates and silicates increased with depth to respective maxima of 0.2 and 8.4 µg-at/l. The oxygen maximum values were associated with the Tyrrhenian Atlantic Water (TAW), which was shown on the basis of its excess oxygen to have been supporting phytoplanktonic production at a rate of $\sim$ 1.5 mg C/m^3/day. The minimum oxygen values were found in the Levantine Intermediate Water (LIW). It was suggested that this was a result of oxygen consumption within the Strait of Sicily prior to entry into the Tyrrhenian Sea.

Oceanologica Acta, 1990. **13**, 3, 299-305.

RÉSUMÉ

Oxygène et sels nutritifs dans le sud de la Mer Tyrrhénienne

L'oxygène dissous, les phosphates et silicates inorganiques ont été dosés dans des échantillons d'eau pour compléter une étude de la circulation dans le sud de la Mer Tyrrhénienne. La répartition verticale de l'oxygène présente un maximum subsuperficiel caractéristique vers 50 m, et un minimum vers 500 m. L'utilisation apparente de l'oxygène, négative dans la couche euphotique, augmente avec la profondeur jusqu'à des valeurs positives de l'ordre de 1,4 ml/l dans la couche aphotique. Les concentrations en phosphates et en nitrates augmentent avec la profondeur jusqu'à des valeurs maximales de 0,2 et 8,4 µg-at/l respectivement. Le maximum d'oxygène est associé à l'Eau Atlantique Tyrrhénienne (TAW), où il correspond à une production phytoplanctonique d'environ 1,5 mg C/m^3/jour. Le minimum d'oxygène, observé dans l'Eau Intermédiaire Levantine (LIW), résulterait de la consommation d'oxygène dans le détroit de Sicile, avant l'entrée en Mer Tyrrhénienne.

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INTRODUCTION

In October 1983, the SACLANT Undersea Research Centre offered the Institute of Marine Environmental Science, Genoa, the opportunity to collect and analyse water samples as a complement to an experiment the Centre was conducting on the circulation of the Southern Tyrrhenian Sea. These waters have been much more studied with regard to their circulation and physical properties (Ovchinnikov, 1966; Tait, 1984; Hopkins, 1988) than to their chemical or biological properties. Several works (Jacobsen, 1912; McGill, 1965; Coste, 1971; and Bethoux, 1981) cite values of these properties but the coverage relative to the Southern Tyrrhenian and the distributions in the vertical are generally lacking. Although we were unable to complete the entire programmed sampling, due to logistical difficulties, the data presented here provide at least a preliminary description of the chemical properties of dissolved oxygen, silicate, and phosphate. The distribution of these properties are discussed relative to the resident water masses and the known circulations during autumn in the Southern Tyrrhenian Sea.

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EQUIPMENT AND METHODS

Hydrographic and chemical data were collected from two cruises: the R/V *Maria Paolina* (22 October-20 November 1984) and the R/V Magnaghi (2-25 October 1984). The station locations for these cruises from which water samples for chemical analysis were taken is shown in Figure 1. The area of coverage was not uniform, with stations being grouped in the Sardinian Channel, along the northwestern coast of Sicily, and with a scattering of stations in the eastern and central portions of the Southern Tyrrhenian. The CTD casts were made with a Neil Brown Instrument System Mk III instrument. The water samples were taken from a General Oceanics Rosette sampler with 5-l Niskin bottles. At each station, the samples for oxygen analysis were taken at six of the following standard depths: 5, 25, 50, 75, 100, 200, 250, 400, 500, 600, 700, 800, 1 000, 1 500, 2 000, and 2 500 m, and those for phosphate and silicate were taken at six or less of these depths. The oxygen concentrations were determined on board using the Winkler method, which has an estimated error of ~0.07 ml/l. The nutrients were frozen at −20°C and analysed in the laboratory using the Heteropoly blue method (with a Hach DR-2 spectrophotometer at low range, 0 to 2 µg-at/l) for the silicates and with a Varian 635 spectrophotometer for the phosphate analysis according to the methods of Strickland and Parsons (1972). Unfortunately the value of the nutrient data set was diminished by the freezing of the samples, which introduced some noise in the values, by the sparse sampling, and by the omission of the nitrogen nutrients. The physical data and methods are described in Hopkins and Zanasca (1988).

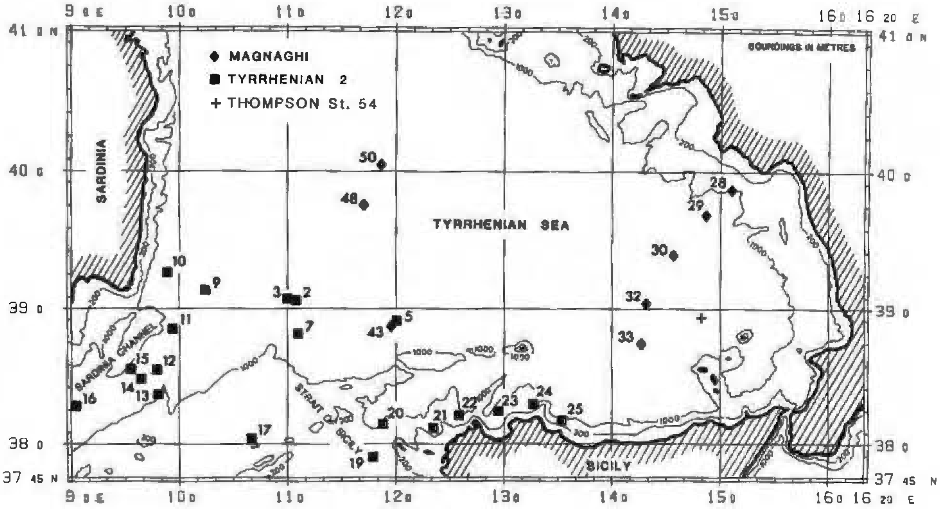

Figure 1

The location of the stations providing the data for the analyses reported on in the text.

VERTICAL WATER-MASS STRUCTURE

The vertical structure and water mass definition given by Hopkins (1988) will provide the basis for our discussion of the distribution of the observed chemical properties. The autumnal vertical structure is characterized by the superposition of five water masses each of different origin. An example of the vertical $T-S-O_2$ dependence together with the associated water mass is given in Figure 2. The vertical sequence of water masses is briefly described in the following paragraphs.

In the Tyrrhenian Sea, winter convective mixing produces a vertically homogeneous upper layer to depths of nearly 200 m or less, depending on the severity of the winter and the local vertical circulation. The water mass produced is the Tyrrhenian Intermediate Water (TIW). With the cessation of this deep mixing, two effects tend to modify the water type of the upper portion of the TIW and the lower portion remains as a remnant of the original TIW layer throughout the stratified season. From the CTD data of Hopkins and

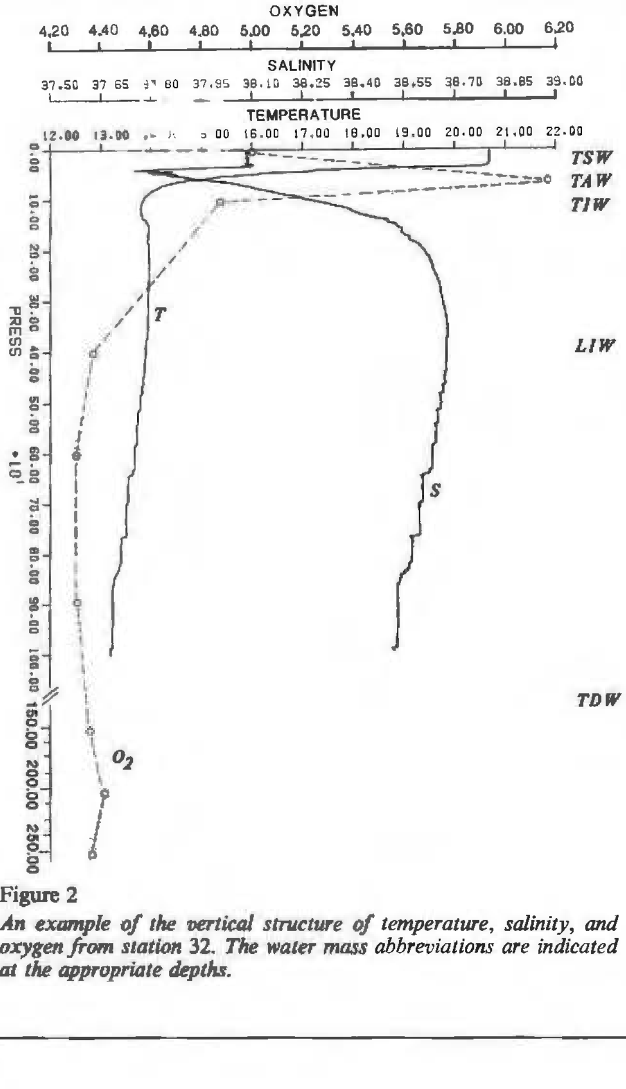

Figure 2

An example of the vertical structure of temperature, salinity, and oxygen from station 32. The water mass abbreviations are indicated at the appropriate depths.

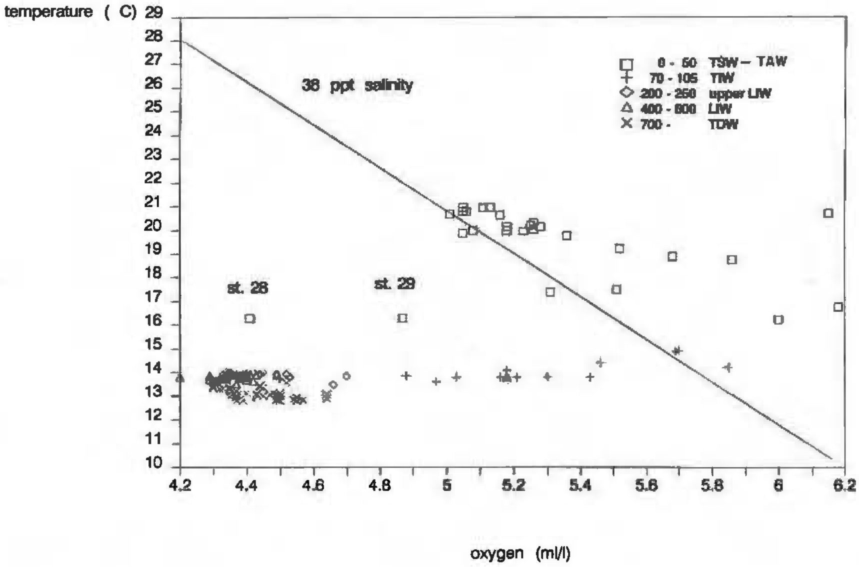

Figure 3
Temperature versus *dissolved oxygen diagram.*

Zanasca (1988), it occupied the depth range ~140 ± 40 m and had a water type of ~13.5°C and salinity ~38.4 ppt.

One of these modifying effects is that the entering lower-salinity surface waters of Atlantic origin are no longer convectively mixed into the resident TIW but begin to overlay it and form a less-dense surface layer. The thickness of this layer depends considerably on the local circulation. This water mass we identify as the Tyrrhenian Atlantic Water (TAW). It occupied the depth range of ~45±15 m and had a water type of ~17°C and salinity ~37.8 ppt.

The other effect, which occurs contemporaneously, gives rise to the Tyrrhenian Surface Water (TSW). The upper wind-mixed portion of the entering TAW diverges in water type from that below it and becomes warmer and saltier due to the combined influence of insolation and evaporation, respectively. By fall the surface (0-30 m) exhibited a water type of ~20°C and salinity ~38.0 ppt.

Below the TIW is found the thermohaline product of the Eastern Mediterranean, the Levantine Intermediate Water (LIW), that issues from the Strait of Sicily and occupies the depth range of ~200-700 m after entering the Tyrrhenian (Manzella *et al.*, 1988). The observed T – S mean values from the CTD data at the depth of the salinity maximum (~400) were ~13.9°C and salinity ~38.7 ppt.

Below the LIW the Tyrrhenian Deep Water (TDW) is found. It has its origin in the deep water of the Western Mediterranean that enters the Tyrrhenian through the Sardinian Channel and undergoes a slight water-type modification due to downwelled admixtures of LIW. The mean water type from the CTD data was ~12.8°C and salinity ~38.44 ppt.

OXYGEN AND NUTRIENT DISTRIBUTIONS

Dissolved oxygen

The vertical distribution of oxygen was characterised by a sub-surface maximum at ~50 m, a minimum at about 500 m, and thence slightly increasing to the bottom, as in Figure 2. The surface values taken from the 5 and 25-m bottle depths were saturated, but because of the warmer temperatures, appeared as relative minima in the vertical profile. The values from the 50-m depth were taken from below the thermocline and appeared as absolute maxima in the vertical, which appeared to be associated with the local salinity minimum of the TAW. Likewise, the minima observed at the ~500 m depths appeared to be associated with the salinity maximum of the LIW. Samples taken from the TDW at depths below 700 m had slightly higher values, from 4.2 to 4.7 ml/l. As a consequence of these associations with the Tyrrhenian water masses, a certain distinct grouping is evident in the oxygen-temperature scatter diagram (Fig. 3 and Tab. 1). The centroid of the TDW points (> 700 m) was cooler and slightly more oxygenated than that of the LIW (400-600 m). A clear distinction can be seen between the LIW and the TIW (70-105 m) and also between the TIW and the euphotic layer above it, the TSW and TAW (0-

Table 1
Water mass properties of sampled (bottle) depth ranges. Standard deviations are given for the nutrient values.

Depth (m)	T (°C)	S (ppt)	O_2 (ml/l)	SiO_2 (μg-at/l)	PO_4 (μg-at/l)	Si : P
0-25, TSW	20.32	38.03	5.23	1.64 ± .53	0.09 ± .02	19.70 ± 5.6
50, TAW	17.32	37.89	5.48	1.70 ± .57	0.08 ± .00	25.98 ± 3.0
70-105, TIW	14.03	38.16	5.19	1.54 ± .34	0.09 ± .01	20.98 ± 4.9
200-250, LIW	13.89	38.55	4.46	4.72 ± .69	0.20 ± .05	24.94 ± 5.2
400-600, LIW	13.80	38.66	4.39	6.08 ± .95	0.19 ± .03	33.62 ± 4.8
700, TDW	13.12	38.50	4.43	8.44 ± .74	0.22 ± .06	40.61 ± 10.8

50 m). Among the water masses, the oxygen variability in the TSW is the greatest. This is due to the greater variability in the factors controlling the oxygen concentration, *i.e.:* the variation in the water type of the wind-mixed surface layer and in the amount of *in situ* production.

In the transect formed by stations 33-28, there was a tendency for the sub-surface oxygen maximum to vanish to the northeast towards the coast. Thus, the values observed at stations 28 and 29 appear to be part of a trend rather than strictly an anomaly. In addition, the deeper absolute oxygen minimum of these two stations was observed higher in the water column, between the depths of 100 and 200 m, but it still coincided with the depth of the LIW salinity maximum. Similarly, for certain stations in the southwestern region, *e.g.* station 9, the sub-surface maximum appeared higher in the water column at 25 m. At stations 7, 10 and 11 the maximum oxygen values at 75 m were undersaturated, implying that, for these stations, a sub-surface maximum must have existed between the bottle depths of 10 and 75 m.

The oxygen-minimum values of ~4.4 ml/l were found in the lower portions of the LIW (between 400 and 600 m in Tab. 1). Throughout most of the northwest-southeast transect of the Tyrrhenian taken during the March *Atlantis* 265 cruise (Miller *et al.*, 1970), the LIW oxygen minimum was a prominent feature in all but a few of the stations. It was not observed in the single southeastern station of the March *Thompson* cruise (Pastouzo, 1971), *see* Figure 1. Our dissolved oxygen values at or below 2 000 m averaged to 4.43 ml/l, a value which compares well with both the 4.45 ml/l value for TDW taken from an average of the 2 000-3 000 m values of the *Atlantis* 265 cruise and the 4.44 ml/l at 2 000-2 500 m from the *Thompson* station 54. Within the accuracy of the observational method, no west-to-east oxygen gradient in the TDW was perceptible.

Nutrients

The concentrations of inorganic phosphorus were very low in the surface layer, confirming previous observations (Coste, 1971; Bethoux, 1981; Pastouzo, 1971). Below the surface, the concentrations increased slightly to the depth of the LIW where the 400-600 m values averaged to 0.19 μg-at P/l. Below the LIW the values increased to a TDW average (2 000 m) of 0.22 μg-at P/l (Tab. 1). We note that the our deep phosphate values were low compared to those of the *Thompson* data, which are also indicated in Figure 4. Since the agreement through most of the water column was close, we are not certain as to the source of this difference.

The silicates showed a sharp increase with depth: from values of 1-2 μg at/l at the surface, to values of 8-9 μg at/l in the deep water. The average Si : P ratio for all the sampled values was 31.4. The scatter diagram is shown in Figure 4, which has an *r*-squared value of 0.6 for the 70 observations. Similar values for the Si : P ratio have been reported: *e.g.*, ratios of 32.4 and 29.9 for the Ionian Sea (McGill, 1965); 26.8 for the Tyrrhenian Sea (station 54, Pastouzo, 1971). We note that if we omit the deep values for which the PO4 values are suspect, the average ratio would be 27.7 with an *r*-squared value of 0.7 for 52 the observations. Although the Si values tend to monotonically increase with depth, those of salinity do not, consequently the Si − S scatter diagram is nonlinear (Fig. 5). The *Thompson* data are added in Figure 5 for comparison.

AOU

At all stations the AOU (Redfield *et al.*, 1963) increased with depth. It was negative in the upper 75 m, except at stations 28 and 29 where at 50 m the values were positive at 1.1 and 0.6 ml/l, respectively. Below 200 m the AOU is almost constant, with values around 1.40 ml/l, suggesting little active oxidation of organic substances sinking from the upper layers.

DISCUSSION

TAW production

Because of the oligotrophic nature of the Tyrrhenian surface waters the sub-surface concentrations of nutrients and oxygen are more noticeably dominated by

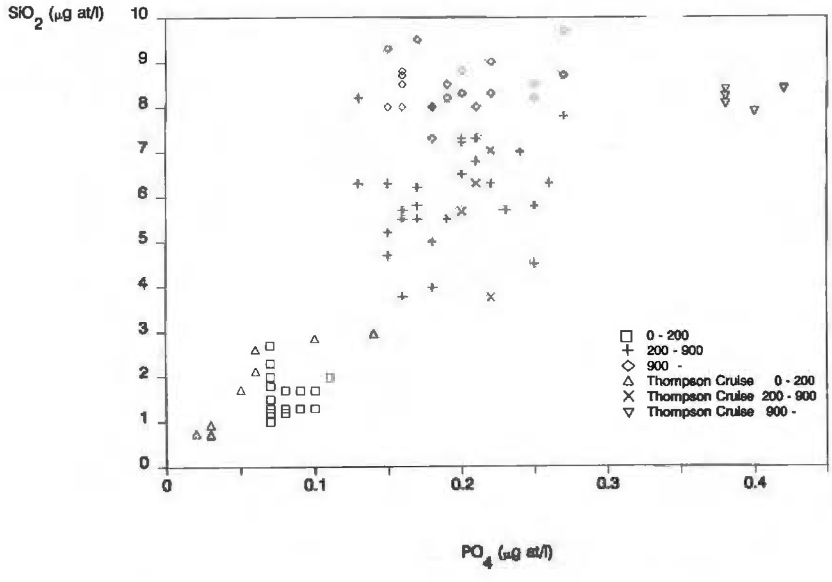

Figure 4

Silicate versus phosphate diagram. The values from station 54 of the Thompson are also included for comparison.

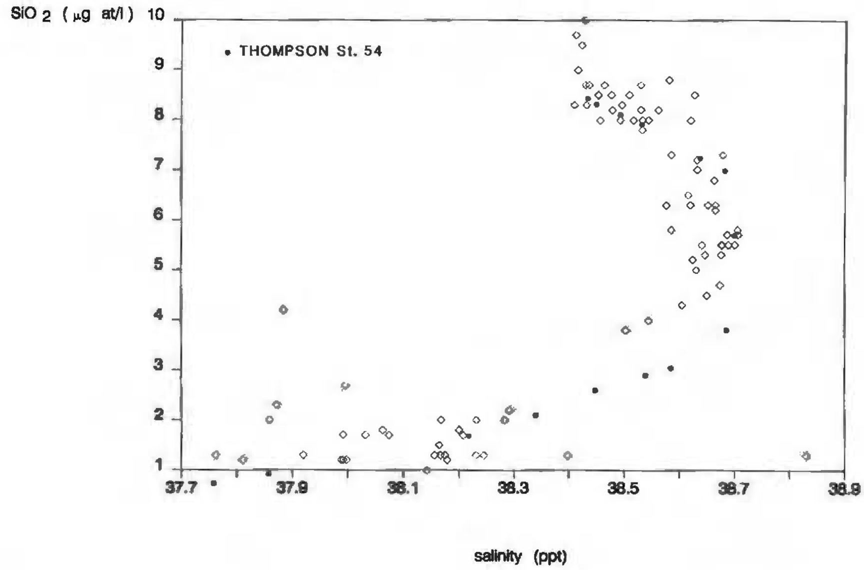

Figure 5
Silicate versus *salinity diagram.*

horizontal or advective processes and consequently depend the specific history of their associated water mass. In fact, an estimate of the photosynthetic production in the TAW is possible with certain assumptions concerning the history of the upper-layer water masses. As we have noted, the samples from the TAW have lesser values of AOU than those from the TIW. We suggest that this was because the TAW was found overlaying the TIW at depths where photosynthetic production was possible, and because any equilibration between the TAW and the atmosphere at least had postdated that of the TIW. We can estimate the amount of oxygen produced in the TAW as a result of in-situ photosynthesis using the conservation of mass equation for oxygen,

$$\frac{\Delta O_2}{\Delta t} = \text{production} - \text{respiration} + \text{mixing},$$

where O_2 is given by the difference between the observed and the initial oxygen values.

We have estimated the end-winter T − S values as follows: for the TIW, core values were taken from the CTD casts (Hopkins and Zanasca, 1988); and for the NAW, winter values were taken from outside the Sardinian channel (Miller *et al.*, 1970); (Tab. 3). From the oxygen data, we chose the 10 samples that were clearly from the TIW (*i. e.* having a temperature minimum) and the 7 samples that were from the NAW (*i. e.* having a salinity minimum). As can be seen in Table 2, the TIW saturation values remained virtually unchanged due to the compensating effects of a loss in salinity and a gain in temperature (mixture with TAW) and therefore any effects of mixing have been minimized. The TIW samples were mostly from the 100 m bottle depth and therefore from below the euphotic zone. Consequently, we assume that the difference between the core TIW oxygen value and the observed TIW mean value reflects the *in situ* respiration, which in this case is the same as AOU value of the TIW or 0.75 ml/l.

Table 2
Temperature, salinity and oxygen values used to estimate the productivity in the TAW mass. The T and S values were taken from the CTD casts rather than from the discrete bottle depths as in Table 1.

Water Mass	T (°C)	S (ppt)	O_2 sat. (ml/l)	O_2 obs. (ml/l)	AOU (ml/l)
Core TIW	13.45	38.4	5.76	–	–
Observed TIW	13.79	38.22	5.76	5.01	0.75
Outside TAW	14.00	36.80	5.82	–	–
Observed TAW	16.60	37.50	5.38	5.48	−0.10

Table 3
Regional differences in chemical properties of LIW, WMDW and TDW all data from T.G. Thompson (*Pastouzo*, 1971).

Region	Property	LIW	WMDW	TDW
Ionian Station 53	Depth	125-400	–	–
	AOU	0.90	–	–
	O_2	4.73	–	–
	PO_4	0.07	–	–
	SiO_4	3.00	–	–
Southern Tyrrhenian Station 54	Depth	300-700	–	1 500-2 500
	AOU	1.20	–	1.39
	O_2	4.47	–	4.41
	PO_4	0.22	–	0.40
	SiO_2	6.01	–	8.34
Western Mediterranean Station 55	Depth	–	1 500-2 500	–
	AOU	–	1.30	–
	O_2	–	4.50	–
	PO_4	–	0.31	–
	SiO_2	–	7.52	–

The T−S values of the TAW observed in the fall were significantly different from their presumed springtime vaules outside the Tyrrhenian (Tab. 2) suggesting that some mixing had occurred. The amount of oxygen loss by mixing was simply estimated as proportional to the salinity gained by mixing, as follows:

$$\text{TAW } O_2 \text{ mixing loss} = 5.82\ \text{ml/l} \times \frac{36.8-37.5}{36.8} = -0.11\ \text{ml/l}.$$

Using a value of 0.75 ml/l and −0.11 ml/l for the respiration and mixing terms, respectively, gives a production of 0.51 ml/l/Δt. We consider this production as having occurred over the six-month period extending from the beginning of the stratified season in April. Thus, we compute an O_2 production rate of $\sim$2.8 ml/m^3/*d*.

Using a 1 mg C equivalent of 1.87 ml O_2, we estimate a production rate of $\sim$1.5 mg C/m^3/d for this subsurface TAW layer. Magazzu' *et al.* (1975) reported an annual averages of ^{14}C measurements from 7 stations taken along the northern coast of Sicily. As these were given as hourly rates, we have used a factor of four (*cf.* Shulenberger and Reid, 1981) to convert them to daily values thereby obtaining a value of $\sim$1.2 mg C/m^3/d for the $\sim$50 m depth. Magazzu' *et al.* also gave monthly values of the vertically integrated production, which showed little variation between the stratified and unstratified seasons. However, at 50 m we expect that the annual average would be less than the mean for the stratified season, *i.e.* we expect that our value should exceed their annual averaged value. Despite the reasonably close agreement, the two results can not be strictly compared due to the differences in method and the differences between an average from a fixed location and an average taken from a moving water mass.

Although the TAW was subjected to some mixing, probably more from the TSW above it, neither the TAW nor the TIW had at any time greater concentrations of nutrients. We note that the initial nutrient concentrations of the winter mixed layer were low, on the order of 0.03-04 μg-at/l $P-PO_4$ (Pastouzo, 1971). Therefore, we can not expect that the TAW production was supported through any upwelling or mixing process. On the other hand, the winter PO4 values observed outside the Tyrrhenian are on the order of 0.10-.15 μg-at/l P−PO4 (Coste, 1971). If we consider that 0.1 μgat/l $P-PO_4$ was consumed during the 6 month period, the carbon equivalent fixed would be 0.7 mg C/m^3/d. Further, if this rate is considered to represent the new production and the above value of 1.5 mg C/m$_3$/d is considered to represent the total production, then we obtain a value of 46% for Epply's factor (Eppley and Peterson, 1979). This compares with the Epply's factor of 36% cited for the Ligurian Sea by Minas and Bonin (1988). Production at the base of the euphotic zone during the stratified season has been cited from studies elsewhere in the Mediterranean by Minas (1970), Velasquez (1981), Unesco (1983).

AOU in the LIW and TDW

As noted in Figure 6, the AOU below the 200 m sampling depth remains nearly constant at around 1.4 ml/l. Actually, our AOU values from the LIW were slightly less at 1.32 ml/l than those of the 1.39 ml/l of the TDW; and the same tendency existed in the spring values of the *Thompson* of 1.20 and 1.39 ml/l, respectively (Tab. 3). Nevertheless, the closeness of the AOU values for these two water masses bears comment, as their pathways to the Tyrrhenian and thereby the histories of their oxygen balances are completely different.

The LIW originates in the Levantine Sea and takes a fairly shallow ($\sim$0-400 m) route westward through the Strait of Sicily to the Tyrrhenian; whereas the WMDW originates in the Ligurian-Provincial Basin where it sinks to deep levels (> 1 500 m) and spreads southward before entering the Tyrrhenian and becoming the TDW. In general, the approximately equal value of AOU for the two water masses could be interpreted as simply indicating the same relative age. However, the vertical O_2 minimum is associated with the LIW core tends to give an impression that the LIW is older or a more active layer of remineralization than the underlying TDW. In contrast, we suggest that the LIW is probably the younger water mass and that it is

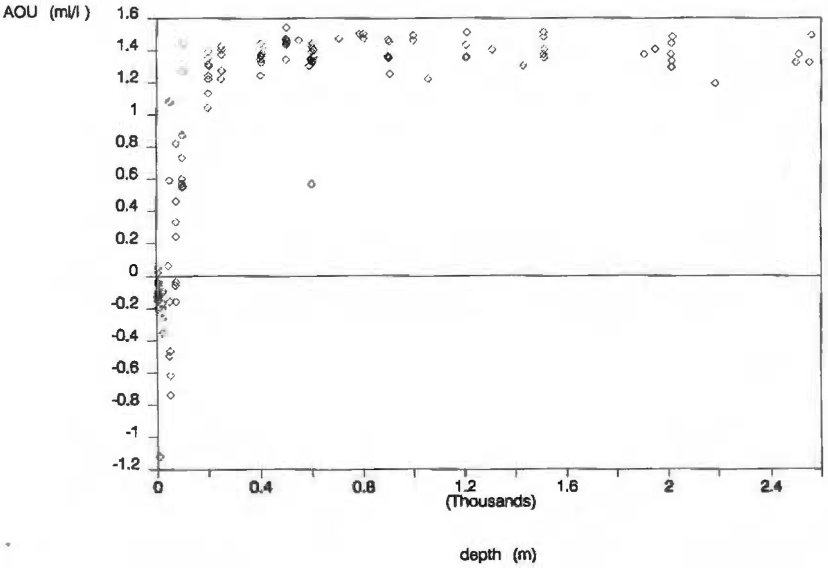

Figure 6
Apparent oxygen utilization versus *depth diagram.*

largely modified with respect to its oxygen content prior to its entry to the Tyrrhenian within the Strait of Sicily.

In Table 3 we have given parameter averages for the deep water masses of the western Ionian, southern Tyrrhenian and southern Ligurian-Provincial Seas as reported from the three respective *Thompson* stations. The AOU and nutrient values increased considerably from the Ionian to the Tyrrhenian. We suggest that most of this change occured as a result of remineralization during the transit of the LIW through the Strait of Sicily. The volume ratio of the euphotic to aphotic (LIW) layers is much larger in the strait than in the open sea and where the LIW residence time can be ~5 months (Manzella *et al.*, 1988).

A much smaller increase in AOU and nutrient values is found between the WMDW and the TDW. How much of this increase occurred as a result of remineralization external and internal to the Tyrrhenian Sea is not known. However, the absense of a detectable west-to-east gradient in our deep oxygen values suggests that little *in situ* oxygen consumption occurred during the spreading of the entering deep water from the Sardinian Channel into the Tyrrhenian basin. Hopkins (1988) suggests that the depression of oxygen in the TDW, relative to the WMDW is more due to admixture of downwelled LIW than by the *in situ* deep respiration.

CONCLUSIONS

The distributions of oxygen, phosphate, and silicate from the late stratified season in the Southern Tyrrhenian have been investigated and compared with other reported distributions. Although the data sampling was not very comprehensive, we have attempted to demonstrate the importance of the horizontal circulations in controlling the vertical distribution of these variables. This is assumed to be an indication that the surface biological processes and the resulting vertical fluxes of organic matter in the Tyrrhenian Sea do not obliterate the signals in the chemical parameters introduced as a result of horizontal advective fluxes from external sources.

An oxygen maximum was associated with the TAW that was located in the lower portion of the euphotic layer. Calculations of the oxygen utilization of the TAW gave an estimate of 0.5 ml/l oxygen excess over a six month period or approximately a 1.5 mg $C/m^3/d$ rate of photosynthetic production. The nutrient source is considered to have been that associated with the original (outside) nutrient content of the TAW rather than any local upwelling from the TIW below.

The oxygen minimum values were associated with the LIW. It was suggested that this minimum was largely an artifact of a proportionately large oxygen utilization occurring during the LIW's transit of the Strait of Sicily. The minimum is established also as a result of the relatively high values of the WMDW, which is the source water for the underlying TDW. Local production in the Tyrrhenian probably enhances this tendency for a vertical minimum with greater remineralization occurring in the LIW.

Acknowledgements

The authors would like to thank the Saclantcen technicians, particularly, Briano Tornarelli for the assistance in the data collection and analysis, to thank Maurizio Ribera for his help with the manuscript, and to express their appreciation to the officers and crew of both the R/V Marina Paolina and the R/V Magnaghi.

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