

## Metabolic CO<sub>2</sub> production in the Mediterranean Sea: A case study for estimating carbon budget in the sea\*

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**SUMMARY:** A synthesis of published metabolic CO<sub>2</sub> production rates determined in the water column of the Eastern Mediterranean Sea from 1993 to 1999 is reported with the aim of furnishing an overall picture of the remineralization processes occurring in the basin. The trends of the remineralization are also interpreted with respect to the so-called Eastern Mediterranean Transient (EMT) event. This study augments the sparse data set of respiration measurements, from oceanographic surveys, and highlights the tight coupling between biological processes and circulation patterns. In the photic zone, the rates decreased from West to East as well as from North to South. In the aphotic zone, the C remineralization trend followed the traditional routes of intermediate and deep waters in the Eastern Mediterranean Basin, and underwent the important modifications into the depths as a consequence of the EMT impact.

**Keywords:** ETS, metabolic production, remineralization, Mediterranean Sea, EMT

**RESUMEN:** PRODUCCIÓN DE CO<sub>2</sub> METABÓLICO EN EL MAR MEDITERRÁNEO: UN CASO DE ESTUDIO PARA ESTIMAR EL BALANCE DE CARBONO EN EL MAR. – Se realiza una síntesis de los datos publicados de tasas de producción metabólica en la columna de agua en el mar Mediterráneo Oriental desde 1993 a 1999, con el fin de proporcionar una imagen general de los procesos de remineralización que tienen lugar en la cuenca. Las tendencias de la remineralización se interpretan asimismo en relación con el llamado evento Transitorio del Mediterráneo Oriental (EMT). Este estudio aumenta los escasos conjuntos de datos de mediciones de respiración procedentes de campañas oceanográficas y destaca el estrecho acoplamiento entre procesos biológicos y pautas de circulación. En la zona fótica, las tasas decrecen de oeste a este así como de norte a sur. En la zona afótica, la tendencia de la remineralización de C siguió las rutas tradicionales de aguas intermedias y profundas en la cuenca oriental del Mediterráneo, y experimentó las importantes modificaciones en aguas profundas como consecuencia del impacto del EMT.

**Palabras clave:** ETS, producción metabólica de CO<sub>2</sub>, remineralización, mar Mediterráneo, EMT.

### INTRODUCTION

The biological pump controls the export of biogenic carbon from surface toward deeper layers in oceanic ecosystems. In simplified terms, the biological pump mechanism transforms the CO<sub>2</sub> into organic matter in the euphotic zone by means of

photosynthesis; the particulate fraction of this organic matter then sinks into the deeper waters where it can be remineralized to CO<sub>2</sub> or sequestered in the sediments (Longhurst and Harrison, 1989; Sundquist, 1985). The production, vertical flux and remineralization are theoretically balanced among themselves, so that the determination of any one of these rates facilitates the estimation of the others (Eppley and Peterson, 1979).

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Current knowledge of primary production is exhaustive when compared to that on the sinking and degradation of organic matter in the sea. In fact, only in the last twenty years have oceanographers turned towards the sinking and oxidation of organic matter. Moreover, information obtained from sediment-trap studies has not proved conclusive (Sundquist, 1985) because these studies take into account only particulate matter but neglect dissolved matter. Organic matter oxidation studies represent an additional neglected part of oceanographic knowledge. Since the oxygen consumption rates in the oligotrophic and deep waters are often below detection limits of the analytical methods traditionally used, assessment of these rates requires high resolution, in terms of analytical sensitivity. The assay of respiratory electron transfer activity provides this sensitivity. This activity is the biochemical basis of real respiration and can be determined at low biomass where direct measurements of respiration are currently impossible (Packard, 1971; Packard and Williams, 1981). Furthermore, it can be used to evaluate the oxidation of organic carbon in both dissolved and particulate phases and therefore provides an overall picture of the remineralization processes (Packard *et al.*, 1988; Christensen *et al.*, 1989).

Our research focused on determining metabolic CO<sub>2</sub> production in the Mediterranean Sea, a semi-enclosed basin where several ocean dynamic processes (i.e. intermediate and deep water formations, upwelling and so on) take place. Due to the small size of the Mediterranean, the relatively large role of lateral transport of organic matter from its shelf, and the brief residence time of its deep waters (Hopkins, 1978), this sea is an ideal basin for a mesoscale study of oceanic processes. During the study period, a transitory change in circulation occurred in the Eastern Mediterranean (Lascaratos *et al.*, 1999), the so-called Eastern Mediterranean Transient (EMT) event (Roether *et al.*, 1996; Klein *et al.*, 2000). The EMT event has replaced the East-

ern Mediterranean Deep Waters (EMDW) with younger waters of Aegean origin. This event produced a strong ecological impact on the deep biota of all the Eastern Mediterranean (Theocharis and Lascaratos, 2000), with an increasing level in productivity and nutrient concentration documented by Souvemeroglou *et al.* (1999), Psarra *et al.* (2000) and Tselepides *et al.* (2000).

In this paper, we report metabolic CO<sub>2</sub> production rates from different oceanographic surveys carried out in the Eastern Mediterranean Sea from 1993 to 1999. A general picture of the Mediterranean remineralization rates in the photic and aphotic zone is drawn from these data and related to the main Mediterranean water masses and CO<sub>2</sub> production rate estimates from the oceans.

## MATERIALS AND METHODS

References of the multidisciplinary cruises with details on the sampling protocols are shown in Table 1. For analysis of respiratory electron transfer system (ETS) activity, the water samples were pre-filtered through a 250 µm mesh net to remove large particles and were concentrated on GF/F Whatman glass fiber membrane filters at reduced pressure (<1/3 atm). The filters were immediately stored in liquid nitrogen until analysis (< 45 days) to prevent enzymatic decay (Ahmed *et al.*, 1976).

The ETS assay was performed according to the tetrazolium reduction technique extensively described elsewhere (Packard, 1971) as modified by Kenner and Ahmed (1975) for microplankton communities. The ETS measurements were corrected for *in situ* temperature using an Arrhenius activation energy of 15.8 Kcal mole<sup>-1</sup> (Packard *et al.*, 1975). To convert ETS values into oxygen utilisation rates (OUR), the currently used factor 0.15 was adopted in samples obtained from 5 to 200 m (Kenner and Ahmed, 1975). The water layers from 5 to 200 m are here referred to as euphotic zone, for better compar-

TABLE 1. – References of the sampling areas, cruises, periods sample sizes and water column sampling depths.

| Sampling area         | Cruise        | Period              | Sample size | Water column | References                  |
|-----------------------|---------------|---------------------|-------------|--------------|-----------------------------|
| Southern Adriatic Sea | AM3           | August 1993         | 32          | 0-1000       | Azzaro <i>et al.</i> , 1998 |
| Southern Adriatic Sea | MATER 6       | August 1998         | 27          | 0-1000       | Azzaro, 1998                |
| Southern Adriatic Sea | SINAPSI III   | Dec. 1998-Jan. 1999 | 10          | 0-1000       | Zaccone, 1999               |
| Ionian Sea            | POEM-LIWEX'95 | March-April 1995    | 14          | 0-3000       | La Ferla and Azzaro, 2001   |
| Ionian Sea            | MATER 6       | August 1998         | 21          | 0-3000       | Azzaro, 1998                |
| Ionian Sea            | SINAPSI III   | Dec. 1998-Jan. 1999 | 15          | 0-3000       | Zaccone, 1999               |
| Levantine Sea         | POEM-LIWEX'95 | March-April 1995    | 101         | 0-3000       | La Ferla and Azzaro, 2001   |

TABLE 2. – Summary of CDPR ranges determined in the studied surface areas (0-200m).

| Areas                 | Sample size (n) | CDPR min - max<br>mg C m <sup>-3</sup> h <sup>-1</sup> | CDPR<br>mean value | Reference                     |
|-----------------------|-----------------|--|--------------------|-------------------------------|
| Southern Adriatic Sea | 94              | 0.013 - 0.083  | 0.04               | La Ferla <i>et al.</i> , 1996 |
| Strait of Otranto     | 53              | 0.092 - 0.122  | 0.03               | La Ferla <i>et al.</i> , 1999 |
| Ionian Sea            | 24              | 0.019 - 0.163  | 0.05               | La Ferla <i>et al.</i> , 1996 |
| Levantine Sea         | 19              | 0.010 - 0.046  | 0.02               | Azzaro, 1997                  |

ison with other authors (Savenkoff *et al.*, 1993a; Lefèvre *et al.*, 1996; La Ferla *et al.*, 1996).

The ETS values from 200 m to the bottom were converted into OUR using the conversion factor of 0.43/5 (Packard *et al.*, 1988). The coefficient 0.43 derived from a study of five cultivable marine bacteria species by Christensen *et al.* (1980); the factor 1/5 is based on an ETS protocol (used in this study) five times more sensitive than the original version (Devol *et al.*, 1976).

Both the euphotic and aphotic OUR were converted to Carbon Dioxide Production Rate (CDPR) in carbon units by applying the following Equation:

$$\text{CDPR (mg C m}^{-3} \text{ h}^{-1}) = (\text{OUR ml O}_2 \text{ m}^{-3} \text{ h}^{-1} \times 12/22.4) \times (122/172)$$

where 12 is the C atomic weight, 22.4 the O<sub>2</sub> molar volume and 172/122 the Takahashi oxygen/carbon molar ratio (Takahashi *et al.*, 1985). We do not use the O/C molar ratio of 138/106 estimated by Redfield *et al.* (1963) for a better comparison with the references on respiratory rates in the Mediterranean Sea (Savenkoff *et al.*, 1993a; La Ferla *et al.*, 1996). Euphotic-integrated activity was calculated according to the trapezoidal method whereas aphotic carbon oxidation rate profile was outlined using the power functions of depth according to Packard *et al.* (1988):

$$R_i = A Z^B, \quad (1)$$

where A is the CDPR in mg C m<sup>-3</sup> d<sup>-1</sup>, Z is the depth below the surface in meters and B is the exponent of depth. The depth-integrated rate ( $\int R dz$  in mg C m<sup>-2</sup> d<sup>-1</sup>) in the water column was calculated within the depth interval between Z<sub>1</sub> and Z<sub>2</sub>, according to Christensen *et al.* (1989):

$$\int R dz = A (Z_2^{(B+1)} - Z_1^{(B+1)}) / (B+1). \quad (2)$$

The coefficients A and B are from Equation (1).

## RESULTS

### Photic zone

In Table 2 a summary of the CDPR ranges and mean values obtained in the upper 200 m of the Southern Adriatic Sea, Otranto Strait, Ionian Sea and Levantine Sea are reported. The mean values found in the Ionian Sea (CDPR: 0.05 C m<sup>-3</sup> h<sup>-1</sup>) were slightly higher, but comparable to the rates determined in the Southern Adriatic Sea (0.04 mg C m<sup>-3</sup> h<sup>-1</sup>) and in the Otranto Strait (0.03 mg C m<sup>-3</sup> h<sup>-1</sup>). Lower values occurred in the Levantine Sea (0.02 mg C m<sup>-3</sup> h<sup>-1</sup>).

### Aphotic zone

#### Southern Adriatic Sea

In Figure 1a, the CDPR values, integrated over the 400-1000 m layer from the Southern Adriatic Sea from 1993 to 1999 are reported. During August

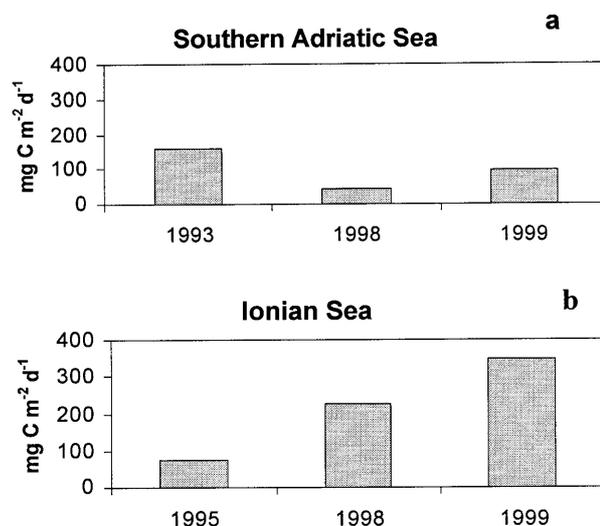


FIG. 1. – Carbon oxidation rates (mg C m<sup>-2</sup> d<sup>-1</sup>) determined by ETS activity in Southern Adriatic Sea, during 1993 (AM3 cruise), 1998 (MATER 6 cruise), and 1999 (SINAPSI III), and in Ionian Sea, during 1995 (POEM-LIWEX '95), 1998 (MATER 6) and 1999 (SINAPSI III).

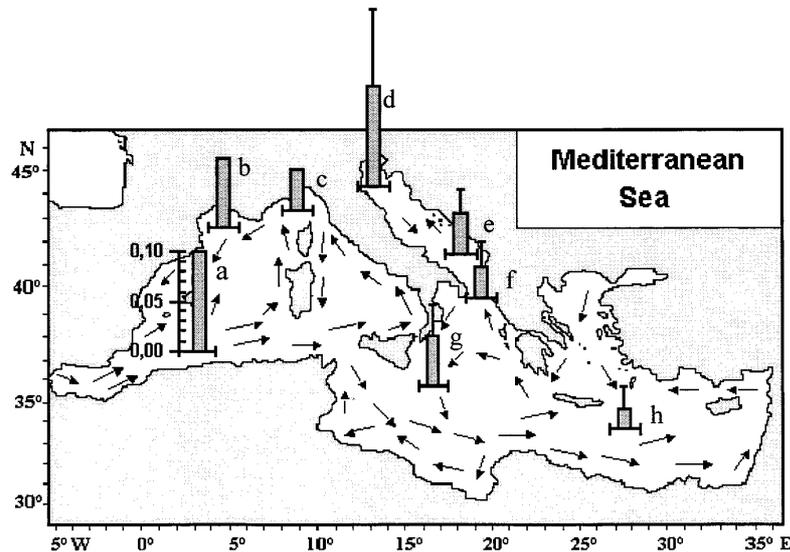


FIG. 2. – Surface circulation pattern and distribution of CDPR mean values ( $\text{mg C m}^{-3} \text{h}^{-1}$ ) in the Mediterranean Sea euphotic zones as estimated by various authors (a: Martínez *et al.*, 1990; b: Agustí and Cruzado, 1992; c: Slawyk *et al.*, 1976; d: La Ferla *et al.*, 2001; e and g: La Ferla *et al.*, 1996; f: La Ferla *et al.*, 1999; h: La Ferla and Azzaro, 2001).

1993, Azzaro *et al.* (1998) found a CDPR of  $158 \text{ mg C m}^{-2} \text{d}^{-1}$ , probably as a consequence of high mixing and homogeneity in the water column, which occurred in winter 1992 (Gacic *et al.*, 1998). In the 1993-1998 period, the convective renewal was generally scanty and as a consequence, the CDPR decreased by a factor three ( $50 \text{ mg C m}^{-2} \text{d}^{-1}$ ) in August 1998 in the same depth layer. On the contrary, in the following winter 1999, with an increase in the convective processes (Gacic *et al.*, 1998) the CDPR also increased ( $100 \text{ mg C m}^{-2} \text{d}^{-1}$ ).

#### Ionian Sea

Estimates of CDPR were made in February 1995 in St GEO 95 ( $35^{\circ}34.88\text{N}$ ,  $17^{\circ}14.99\text{E}$ ). The depth-integrated value in the depth layer between 200 and 2500 m was  $65 \text{ mg C m}^{-2} \text{d}^{-1}$  (Fig. 1b). The following data from the deep Ionian Sea –in August 1998 in St I 01 ( $38^{\circ}28.31\text{N}$ ,  $17^{\circ}58.35\text{E}$ )– produced rates three times higher ( $210 \text{ mg C m}^{-2} \text{d}^{-1}$ ). In 1999, the CDPR in the deep waters rose again to  $350 \text{ mg C m}^{-2} \text{d}^{-1}$  in St. GEO 99 ( $38^{\circ}28.31\text{N}$ ,  $17^{\circ}58.35\text{E}$ ).

#### Levantine Sea

Deep CDPR from 200 to 3000 m amounted to  $177.1 \text{ mg C m}^{-2} \text{d}^{-1}$  in the entire Levantine basin. At the depth interval 200-600 m, roughly corresponding to LIW, a CDPR of  $52.5 \text{ mg C m}^{-2} \text{d}^{-1}$  was found in the whole area. The mean CDPR values were  $67.4 \text{ mg C}$

$\text{m}^{-2} \text{d}^{-1}$  for the depth range between 600 and 1600 m and  $57.2 \text{ mg C m}^{-2} \text{d}^{-1}$  for the deeper layer (depth range 1600-3000 m) occupied by CDW (Fig. 3).

## DISCUSSION AND CONCLUSION

Figure 2 reports a summary of the CDPR mean values, extrapolated from data determined in different Mediterranean photic zones (0-200 m) by authors referenced in the legend. It also shows the surface water circulation pattern. Higher values were found in the Western Mediterranean (a: mean value,  $0.10 \text{ mg C m}^{-3} \text{h}^{-1}$ ), in the Gulf of Lyons (b:  $0.07 \text{ mg C m}^{-3} \text{h}^{-1}$ ) and in the Northern Adriatic Sea (d:  $0.09 \text{ mg C m}^{-3} \text{h}^{-1}$ ). Intermediate values were found in the Ionian Sea (g:  $0.05 \text{ mg C m}^{-3} \text{h}^{-1}$ ), in the Southern Adriatic and along the French Mediterranean Coast (e-c:  $0.04 \text{ mg C m}^{-3} \text{h}^{-1}$ ) as well as in the Otranto Strait (f:  $0.03 \text{ mg C m}^{-3} \text{h}^{-1}$ ). A lower CDPR was estimated for the Levantine Sea (h:  $0.02 \text{ mg C m}^{-3} \text{h}^{-1}$ ).

Due to the high net evaporation, the characteristics of the Atlantic surface waters (ASW) changed along their flow through the Gibraltar Strait to the east (Hopkins, 1978). Biomass, production, nutrients, and remote sensing activities detected by satellite sensors (Dowidar, 1984; Antoine *et al.*, 1995; Magazzù and Decembrini, 1995) gradually decrease from west to east, in the surface layers. Another source of high activity

originates in the riverine outflows in the Northern Adriatic and in the Gulf of Lyons. As a consequence, the oxidative processes in the surface Mediterranean waters decrease from West to East and from North to South associated with the Mediterranean circulation pattern (Martínez *et al.*, 1990; La Ferla *et al.*, 1996, 1999) and in agreement with the conceptual model proposed by Crise and Crispi (1998) on the coupling of physical forcing and biological processes.

The overall picture until 1995 derived from the volume specific CDPR for the entire Mediterranean Sea is schematically illustrated in Figure 3. In the euphotic zone between 0 and 200 m, later on called ASW (Atlantic Surface Water) from its site of origin, the water drifts from the Atlantic Ocean toward the Levantine basin. The oxidative rates decrease as discussed before. On the contrary, a gradual decrease in oxidative processes in the LIW layer, from the Levantine basin westward through the Ionian Sea and Western Basin was observed. Savenkoff *et al.* (1993a) stated that LIW waters of Mediterranean origin expanded out through the Straits of Gibraltar, in the north-east Atlantic. He depicts this layer as a salty tongue, plunging to depths where oxidative processes increased (33.7 mg C m<sup>-2</sup> d<sup>-1</sup> in the depth range between 600 and 1600 m). The authors explained this higher activity by the occurrence of the anticyclonic rotation of

Meddy Nicole, which would attract or entrap sedimenting particulate matter and thus significantly raise the oxidation rates.

Concerning the deep-waters (Fig. 3), these originated in the N-W Mediterranean Basin (Gulf of Lyons) and in the Southern Adriatic. In the N-W Mediterranean Sea, the deep-water oxidation rate (Lefèvre *et al.*, 1996) decreased with the spreading of the water mass from the origin site towards the entire Western basin (Christensen *et al.*, 1989). Within the Eastern Basin, the EMDW formation site is located in the Southern Adriatic Sea, from where the oxidation rate estimated by Azzaro *et al.* (1998) decreased while the waters spread towards the Ionian Basin (La Ferla and Azzaro, 2001). Continuing towards the Levantine sector of the Mediterranean basin, the EMDW, spreading in the upper 1600 m depth, showed lower oxidation rates. The input from the new CDW, that replaced the pre-existing deepest water mass below 1600 m depth, sustained an oxidation rate of 57.2 mg C m<sup>-2</sup> d<sup>-1</sup>.

With the aim of showing that the Mediterranean Sea could be considered suitable as a study basin for oceanic processes, Azzaro (1997) proposed the following power function (CDPR - mg C m<sup>-3</sup> d<sup>-1</sup> = 2.467 z<sup>-0.631</sup>) for extrapolating the vertical CDPR profile for the whole Mediterranean Sea from 100 m to the bottom. Christensen *et al.* (1989) already used this kind of representation for the CDPR in the

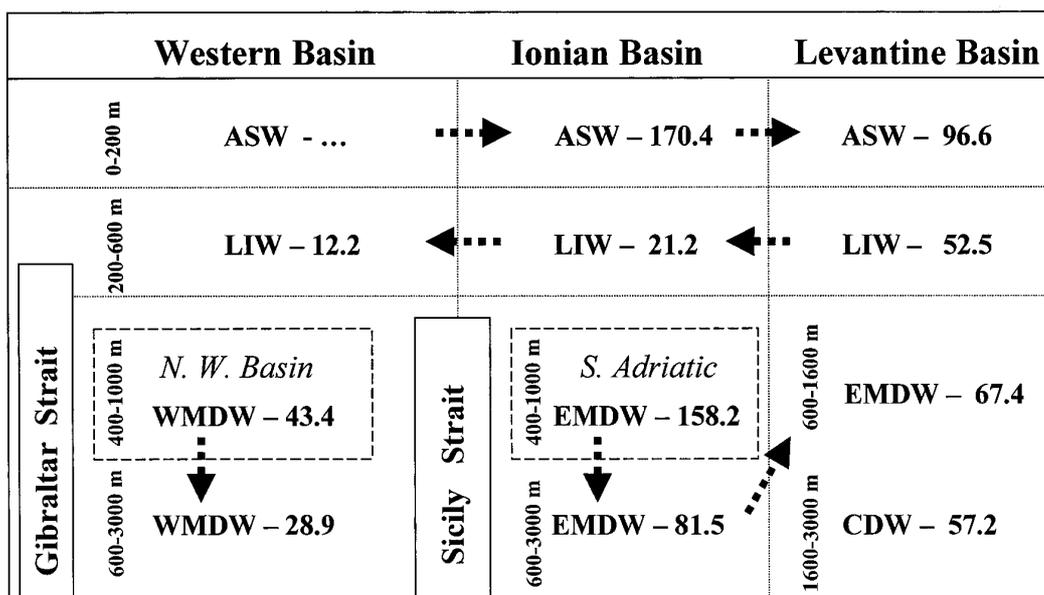
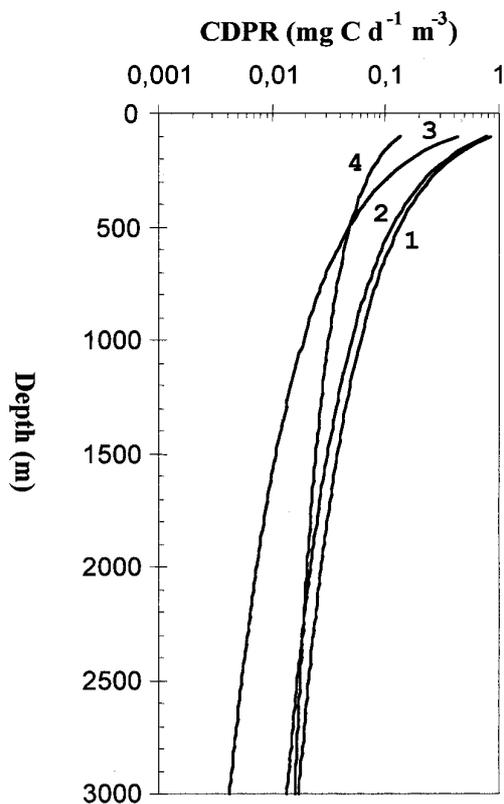


FIG. 3. – Schematic diagram summarising the coupling between CDPR (mg C m<sup>-2</sup> d<sup>-1</sup>) and the main Mediterranean water masses. Arrows indicate the direction of the water mass flux between boxes. The main body of the Mediterranean Sea is divided into the Western, Ionian and Levantine basins. Two additional sub-systems, in the dashed line boxes, represent the deep (NW Mediterranean Basin and Southern Adriatic) water formation areas. Data are calculated from: Lefèvre *et al.* (1996) and Christensen *et al.* (1989) for Western Basin water mass; Azzaro *et al.* (1998) for Southern Adriatic; La Ferla *et al.* (1996) and La Ferla and Azzaro (2001) for Ionian and Levantine water mass. Modified from La Ferla and Azzaro (2001).



1 Pacific Ocean      3 Atlantic Ocean  
2 Indian Ocean      4 Mediterranean Sea

FIG. 4. – Comparison of best-fit functions representing the depth dependence of CDPR in the Mediterranean Sea by Azzaro (1997), Atlantic and Pacific Oceans by Packard *et al.* (1988) and Indian Ocean by Naqvi *et al.* (1996).

Western Mediterranean Sea. Such integration of the data does not take into account the discontinuity of the respiratory rates along the water column due to the different microbial population structure with depth, such as those observed by Savenkoff *et al.* (1993b) for the Liguro-Provençal front (Western Mediterranean Sea). Furthermore, it does not account for the variability in the oxidative processes in the different sub-basins as previously described.

TABLE 3. – Ratios calculated between depth-integrated deep CDPR values (from 1500 to 2500 m) and depth-integrated shallow CDPR values (from 200 to 1200 m) in sites of the Mediterranean Sea, Atlantic, Pacific and Indian Oceans.

| Area              | Rdz ratio (%) | References                   |
|-------------------|---------------|------------------------------|
| Mediterranean Sea | 46.6          | Azzaro, 1997                 |
| Atlantic Ocean    | 14.9          | Packard <i>et al.</i> , 1988 |
| Pacific Ocean     | 21.1          | Packard <i>et al.</i> , 1988 |
| Indian Ocean      | 24.8          | Naqvi <i>et al.</i> , 1996   |

However, it well underlines the peculiarity of the deep Mediterranean waters with respect to other oceanic deep waters. In Figure 4, we compare the Mediterranean profile to those from Pacific, Atlantic and Indian oceans (Packard *et al.*, 1988; Naqvi *et al.*, 1996). The decrease with depth of the Mediterranean CDPR is exponential. However it is less pronounced than for Pacific and Indian waters since its exponent is less negative, as already computed by Christensen *et al.* (1989) for the Western Mediterranean Sea. Such evidence underlines the considerable importance of remineralization in the Mediterranean deep layers with respect to similar oceanic depths. Since the Mediterranean surface water is known for its oligotrophy, this pattern seems mainly caused by the important advective processes occurring in the Mediterranean rather than by export production from the upper layers. In Table 3, the ratios calculated between depth-integrated deep CDPR values (from 1500 to 2500 m) and shallow CDPR values (from 200 to 1200 m) in the Mediterranean Sea with respect to the oceans (before 1995) are reported. They clearly mark the peculiarity of this basin with regard to the deep remineralization processes as already referred by La Ferla *et al.* (in press). Such evidence is explained partially by the high temperatures of the Mediterranean deep water (~13°C), which accelerates microbial metabolism, and partially also by the availability of organic carbon suitable for remineralisation in the deep biota (Seritti *et al.*, in press).

Calculating the carbon budget in the Eastern Mediterranean Sea, we compare the remineralization patterns obtained by various authors (Fig. 5). Before 1987, Bethoux (1989) estimated a remineralization rate close to 32.9 mg C m<sup>-2</sup> d<sup>-1</sup> with a 3% increase per year. This trend was revised by Roether and Well (2001) who estimated higher rates in 1987. Our estimate in 1995 (74.5 mg C m<sup>-2</sup> d<sup>-1</sup>) was still higher than previous ones. Moreover, considerably higher remineralization occurred after EMT events: 226.7 and 349.9 mg C m<sup>-2</sup> d<sup>-1</sup> in 1998 and 1999, respectively. These findings highlight the accelerated remineralization rates in the Mediterranean depth. As a compensation, the intrusion of young waters with higher values of preformed oxygen negates the large spike in respiration (Klein *et al.*, 1999) so that the predicted anoxia is delayed.

In conclusion, assuming that the Mediterranean Sea has an area of 2.52 x 10<sup>12</sup> m<sup>2</sup> and assuming that the CDPR value (determined until 1995), extrapolated by integrating data from 200 to 1500 m (since the

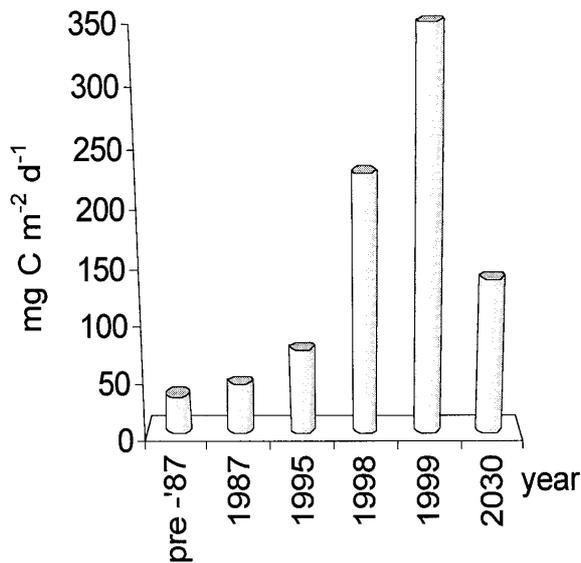


FIG. 5. – Remineralization rates determined in the Eastern Mediterranean Sea from prior to 1987, from 1987 to 1999 data and a projection to 2030. Pre-87 and 2030 data by Bethoux (1989); 1987 by Roether and Well (2001); 1995 by La Ferla and Azzaro (2001); 1998 by Azzaro (1998); 1999 by Zaccone (1998).

latter is the mean depth of the Mediterranean basin) is representative of the entire basin, a remineralization rate of  $47.9 \times 10^{12}$  g C yearly is estimated. This is higher than the previous calculation by Bethoux (1989), of  $29.8 \times 10^{12}$  g C  $y^{-1}$ , and represents the 0.2% of the global new production calculated from other ETS data (Packard *et al.*, 1988). However, the temporary EMT event and the yet-unknown evolution of the deep water renewal, just occurring in the Mediterranean Sea, do not permit closure of the carbon budget to date.

## ACKNOWLEDGEMENTS

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