



## Whole-system metabolism and CO<sub>2</sub> fluxes in a Mediterranean Bay dominated by seagrass beds (Palma Bay, NW Mediterranean)

Frédéric Gazeau, C. M. Duarte, Jean-Pierre Gattuso, C. Barrón, N. Navarro, S. Ruiz, Y. T. Prairie, M. Calleja, B. Delille, M. Frankignoulle, et al.

### ► To cite this version:

Frédéric Gazeau, C. M. Duarte, Jean-Pierre Gattuso, C. Barrón, N. Navarro, et al.. Whole-system metabolism and CO<sub>2</sub> fluxes in a Mediterranean Bay dominated by seagrass beds (Palma Bay, NW Mediterranean). *Biogeosciences*, 2005, 2 (1), pp.43-60. 10.5194/bg-2-43-2005 . hal-00330308

**HAL Id: hal-00330308**

**<https://hal.science/hal-00330308>**

Submitted on 18 Jun 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Whole-system metabolism and CO<sub>2</sub> fluxes in a Mediterranean Bay dominated by seagrass beds (Palma Bay, NW Mediterranean)

F. Gazeau<sup>1,2,\*</sup>, C. M. Duarte<sup>3</sup>, J.-P. Gattuso<sup>2</sup>, C. Barrón<sup>3</sup>, N. Navarro<sup>3,\*\*</sup>, S. Ruiz<sup>3,\*\*\*</sup>, Y. T. Prairie<sup>4</sup>, M. Calleja<sup>3</sup>, B. Delille<sup>1</sup>, M. Frankignoulle<sup>1</sup>, and A. V. Borges<sup>1</sup>

<sup>1</sup>Unité d'Océanographie Chimique (B5), MARE, Université de Liège, B-4000 Sart Tilman, Belgium

<sup>2</sup>Laboratoire d'Océanographie de Villefranche, CNRS-Université de Paris 6, B. P. 28, F-06234 Villefranche-sur-mer Cedex, France

<sup>3</sup>IMEDEA (CSIC-UIB), Grupo de Oceanografía Interdisciplinar, Instituto Mediterráneo de Estudios Avanzados, C/Miquel Marqués 21, 07190 Esporles (Islas Baleares), Spain

<sup>4</sup>Département des sciences biologiques, Université du Québec à Montréal, Case postale 8888, succ. Centre-Ville, Montréal, H3C 3P8, Canada

\*present address: Netherlands Institute of Ecology (NIOO-KNAW), Postbus 140, 4400 AC Yerseke, The Netherlands

\*\*present address: Área de Biodiversidad y Conservación, ESCET, Universidad Rey Juan Carlos, C/ Tulipán s/n, Móstoles 28933, Madrid, Spain

\*\*\*present address: CLS Space Oceanography Division, Parc technologique du Canal, 8-10 Rue Hermès, 31526 Ramonville Cedex, France

Received: 1 September 2004 – Published in Biogeosciences Discussions: 26 October 2004

Revised: 31 January 2005 – Accepted: 17 February 2005 – Published: 23 February 2005

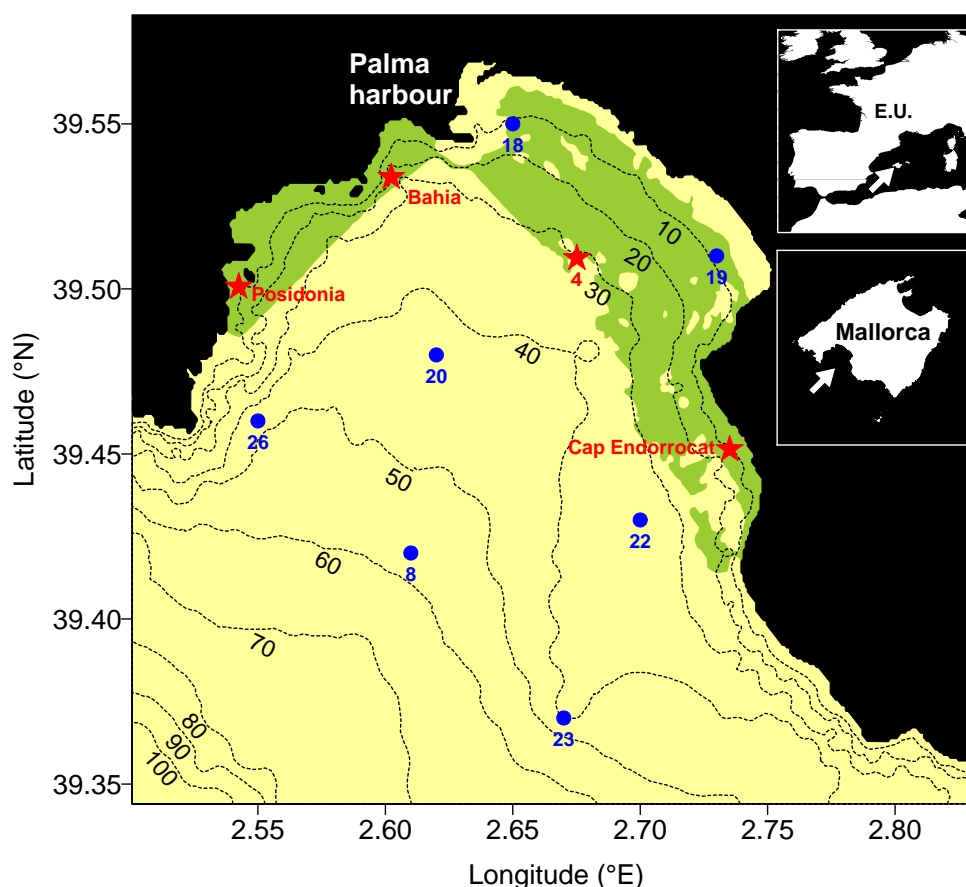
**Abstract.** Planktonic and benthic incubations (bare and *Posidonia oceanica* vegetated sediments) were performed at monthly intervals from March 2001 to October 2002 in a seagrass vegetated area of the Bay of Palma (Mallorca, Spain). Results showed a contrast between the planktonic compartment, which was on average near metabolic balance ( $-4.6 \pm 5.9 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ) and the benthic compartment, which was autotrophic ( $17.6 \pm 8.5 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ). During two cruises in March and June 2002, planktonic and benthic incubations were performed at several stations in the bay to estimate the whole-system metabolism and to examine its relationship with partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) and apparent oxygen utilisation (AOU) spatial patterns. Moreover, during the second cruise, when the residence time of water was long enough, net ecosystem production (NEP) estimates based on incubations were compared, over the *Posidonia oceanica* meadow, to rates derived from dissolved inorganic carbon (DIC) and oxygen (O<sub>2</sub>) mass balance budgets. These budgets provided NEP estimates in fair agreement with those derived from direct metabolic estimates based on incubated samples over the *Posidonia oceanica* meadow. Whereas the seagrass community was autotrophic, the excess organic carbon production therein could only balance the planktonic heterotrophy in shallow waters relative to the

maximum depth of the bay (55 m). This generated a horizontal gradient from autotrophic or balanced communities in the shallow seagrass-covered areas, to strongly heterotrophic communities in deeper areas of the bay. It seems therefore that, on an annual scale in the whole bay, the organic matter production by the *Posidonia oceanica* may not be sufficient to fully compensate the heterotrophy of the planktonic compartment, which may require external organic carbon inputs, most likely from land.

## 1 Introduction

The role of coastal ecosystems in carbon and nutrient fluxes can be conveniently summarised by their trophic balance, referring to the difference between the production of organic matter, as represented by the gross primary production (GPP) of the ecosystem and its degradation through community respiration (CR; Odum, 1956). Autotrophic systems, where  $\text{GPP} > |\text{CR}|$  (if CR is expressed in negative units), produce organic matter in excess and thereby act as sinks of inorganic nutrients and CO<sub>2</sub> from surrounding water. In contrast, heterotrophic ecosystems, where  $\text{GPP} < |\text{CR}|$ , rely on allochthonous inputs of organic matter and act as sources of inorganic nutrients and CO<sub>2</sub> to the surrounding water (Duarte and Prairie, 2005).

Correspondence to: F. Gazeau  
(f.gazeau@nioo.knaw.nl)



**Fig. 1.** Map of the Bay of Palma showing the bathymetry (dotted lines), the distribution of the *Posidonia oceanica* meadow (green area, adapted from Rey and Diaz del Rio, 1984), the four reference stations where incubations for metabolic processes and vertical profiles were carried out (red stars) and stations where only vertical profiles were carried out (blue circles).

The net flux of CO<sub>2</sub> across the air-water interface is modulated by this metabolic balance but also by external inputs of dissolved inorganic carbon (DIC; upwelling, river inputs...), calcium carbonate (CaCO<sub>3</sub>) precipitation/dissolution, and purely thermodynamic effects related to temperature changes or mixing of water masses with different chemical characteristics.

Coastal ecosystems contain highly productive communities, such as macrophyte beds which tend to be net autotrophic (Duarte and Cebrián, 1996; Gattuso et al., 1998; Hemminga and Duarte, 2000). As they also receive important inputs of organic matter from land, both GPP and |CR| tend to be elevated relative to open ocean waters (Duarte and Agustí, 1998; Gattuso et al., 1998; Hopkinson and Smith, 2005).

Smith and Hollibaugh (1993) argued that coastal ecosystems are a heterotrophic compartment of the biosphere. In contrast, other authors suggested that they produce organic matter in excess relative to local demands (Duarte and Cebrián, 1996; Gattuso et al., 1998; Wollast, 1998) and then act as sources of organic matter for the open ocean (Wollast, 1998; Liu et al., 2000; Chen et al., 2003). Duarte and

Agustí (1998) and Hopkinson and Smith (2005) concluded, on the basis of comparative analyses of several coastal communities, that the metabolic balance of coastal ecosystems would be dependent on their trophic status, with productive areas being more autotrophic.

However, oligotrophic coastal systems, with unproductive planktonic communities, often support highly productive benthic components. This implies that an assessment of their metabolism requires the integration of both benthic and planktonic compartments over relevant temporal and spatial scales. Nevertheless, an examination of coastal metabolism datasets (Duarte and Agustí, 1998; Gattuso et al., 1998; Hopkinson and Smith, 2005) reveals that most coastal communities were examined at small spatial scales (bottle incubations or benthic chambers) rather than based on research conducted at the ecosystem scale. This is largely attributable to the difficulties in encompassing the variability within ecosystems using discrete measurements and to extrapolate these estimates to large areas.

To overcome this problem, more integrative approaches, based on material mass balances at the ecosystem scale have been proposed (e.g. Land-Ocean Interaction in the Coastal

Zone, LOICZ approach, Gordon et al., 1996). However, these methods require salinity gradients to compute water exchanges and are, therefore, best used in estuarine systems and cannot be readily used in other coastal areas.

Assessments of the spatial and/or temporal variability of dissolved oxygen (O<sub>2</sub>) concentration and the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) may be also used to derive integrative estimates of net ecosystem production (NEP=GPP+CR). However, these estimates are not straightforward, as temperature changes, the history and residence time of water masses and other physical (e.g. Borges and Frankignoulle, 2001) and/or biogeochemical (e.g. Frankignoulle et al., 1996, 2001) factors may also affect O<sub>2</sub> concentration and pCO<sub>2</sub>. For instance, the computation of the CO<sub>2</sub> air-water flux can be critical in the estimation of NEP based on DIC budgets (Gazeau et al., 2005<sup>1</sup>), especially in coastal environments such as estuaries where simple parameterisations of the gas transfer velocity as a function of wind speed have been shown to be site specific (Borges et al., 2004). Thus, both approaches have their own limitations and, to our knowledge, no comparison of NEP estimates derived from GPP and CR incubation measurements and inferred from CO<sub>2</sub>/O<sub>2</sub> fluxes at the ecosystem scale have ever been made in the past.

In this paper, we present (1) results of benthic and planktonic metabolism at a fixed station over a seagrass meadow in the Bay of Palma (Mallorca, NW Mediterranean) from March 2001 to October 2002 and (2) estimates of whole system metabolism based on extensive surveys in the bay at two contrasting periods of the annual cycle in order to test the coherence between two approaches to quantify NEP (incubations and DIC/O<sub>2</sub> budgets).

## 2 Methods

### 2.1 Study site

The Bay of Palma (Mallorca, NW Mediterranean) is an oligotrophic system with a surface area of 217 km<sup>2</sup>, a width of 30 km and a mean depth of 28.5 m (Fig. 1). It receives negligible freshwater inputs and, in the absence of appreciable astronomical tides, exchanges with the offshore waters are dominated by wind stress (Ramis et al., 1990). The Bay of Palma contains extensive seagrass (*Posidonia oceanica*) meadows that extend down to 34 m depth and cover more than 30% of the bay (Fig. 1). As the water is rather clear (average±SE extinction coefficient=0.06±0.02 m<sup>-1</sup>; Navarro et al., 2004), the sediment remains within the euphotic layer throughout the bay. The city of Palma de Mallorca (385 000 permanent inhabitants) supports intense tourism activities and a large harbour.

<sup>1</sup>Gazeau, F., Gattuso, J.-P., Middelburg, J. J., Schiettecatte, L.-S., Brion, N., Frankignoulle, M., and Borges, A. V.: Planktonic and whole-system metabolism in a nutrient-rich estuary (The Scheldt Estuary), Estuaries, submitted, 2005.

Benthic and planktonic metabolisms were estimated, using in situ incubations, at a fixed station from March 2001 to November 2002 and at a grid of stations during two cruises in March (EUBAL-I) and June 2002 (EUBAL-II). During these two cruises, air-sea CO<sub>2</sub> and O<sub>2</sub> fluxes, and patterns of residual water currents were also examined.

### 2.2 Metabolism at a fixed station from March 2001 to October 2002

The community metabolism in a *Posidonia oceanica* meadow and unvegetated sediments were studied monthly from March 2001 to October 2002 using in situ benthic incubation chambers at the shallow (7 m depth) Posidonia station in the Western side of the bay (Fig. 1). Benthic incubations were set up in the vegetated (4 chambers) and unvegetated (3 chambers) sediment to estimate the net community production (NCP). The benthic chambers consisted of a PVC cylinder inserted in the sediment and a gas-tight polyethylene plastic bag fitted to the cylinder with a sampling port (Hansen et al., 2000). Water samples were withdrawn with syringes at the start of the incubation, just before sunset and right after sunrise. Samples for O<sub>2</sub> were transferred into Winkler bottles, fixed and measured by the Winkler technique following Carrit and Carpenter (1966), using an automated titration system (Mettler DL21 Auto-titrator) with potentiometric end-point detection (Oudot et al., 1988). The average precision achieved in replicates was %CV=0.29. In order to express dissolved O<sub>2</sub> changes per unit area, the volume of water enclosed in the benthic chambers was estimated from the dilution of a phosphate solution (0.25 mol l<sup>-1</sup>) in the benthic chambers and measurements of phosphate concentrations by spectrophotometry (Hansen and Koroleff, 1999) from samples collected after an equilibration period of 5 min. Dissolved O<sub>2</sub> changes, adjusted to 24 h, within the benthic chambers were used to calculate NCP. Further details and procedures are provided in Barrón et al. (2005)<sup>2</sup>.

Details on the procedure used to estimate the planktonic NCP at the same station from June 2001 to October 2002 are provided by Navarro et al. (2004).

### 2.3 Whole-system metabolism using different approaches during EUBAL-1 and -2

#### 2.3.1 Hydrography, current velocity and residence time

Five CTD (Conductivity Temperature Depth) surveys were conducted in the Bay of Palma during each of the EUBAL-I (1, 3, 7, 11 and 12 March 2002) and EUBAL-II (19, 21, 25, 26 and 27 June 2002) cruises. During the first survey of EUBAL-I, a total of 32 CTD casts were performed with an

<sup>2</sup>Barrón, C., Duarte, C. M., Frankignoulle, M., and Borges, A. V.: Organic carbon metabolism and carbonate dynamics in a Mediterranean seagrass (*Posidonia oceanica*) meadow, Biogeochem., submitted, 2005.

**Table 1.** Characteristics of the incubation stations during the EUBAL cruises in 2002. Salinity and temperature values were averaged and chlorophyll *a* concentrations were integrated throughout the water column. *K* is the light attenuation coefficient.

Station	Date	Bottom depth m	Salinity	Temperature °C	Integrated chlorophyll <i>a</i> mg m <sup>-2</sup>	Daily averaged surface irradiance μmol m <sup>-2</sup> s <sup>-1</sup>	<i>K</i> m <sup>-1</sup>
EUBAL-I							
Posidonia	04/03/2002	18	37.61	14.4	4.2	331	0.15
Bahia	06/03/2002	35	37.65	14.3	17.3	269	0.14
Station 4	08/03/2002	37	37.53	14.3	16.7	242	0.11
Cap Enderrocat	10/03/2002	20	37.62	14	11.4	761	0.14
EUBAL-II							
Posidonia	20/06/2002	13	37.80	22.6	3.3	1079	0.16
Bahia	22/06/2002	33	37.78	22.4	4.9	1017	0.09
Station 4	18/06/2002	33	37.76	20.8	2.6	960	0.08
Cap Enderrocat	24/06/2002	16	37.76	23	1.5	1110	0.09

average horizontal sampling resolution of 2.8×2.8 km. The other surveys consisted of 11 CTD casts each, reducing the sampling resolution to 5.2×5.2 km. Profiles were vertically averaged every 0.5 m. Direct current measurements were obtained on three surveys during EUBAL-I (1, 9 and 12 March 2002) and one survey during EUBAL-II (25 June 2002) with a ship-hull mounted 150 kHz RD instrument ADCP (Acoustic Doppler Current Profiler). This latter was set up to record currents from surface (10 m) to the bottom with a vertical resolution of 4 m and a 2 min ensemble period using the Transect Acquisition Software. In order to reduce the instrumental errors, raw ADCP data were averaged to 10 min ensembles. Absolute ADCP velocities were computed using bottom-tracking mode, which delivers accurate estimation of the ship velocity. Post-processing of ADCP data was carried out following the methodology described by Allen et al. (1997). Unfortunately, the ship was not equipped with a 3-D GPS (Global Positioning System) that provides accurate heading to account for the gyrocompass error. Hence, a typical error for a conventional gyrocompass of 2° (Griffiths, 1994) is assumed in the post-processing of ADCP data. The maximum error velocity has been estimated at about 4 cm s<sup>-1</sup>. The CTD observations were interpolated over a regular 0.5×0.5 km grid, using an objective analysis based on Optimal Statistical Interpolation. The two main parameters of this scheme are the characteristic scale and the cut-off length scale. The first determines the influence between observations and the second gives the filtering of scales which were not resolved by the sampling strategy. For the first CTD survey of EUBAL-I (dense sampling), the characteristic scale was set-up to 5 km and the cut-off scale to 10 km. For the other CTD surveys (coarse sampling), the scale derived from statistics was 7.5 km and the cut-off length scale was set to 15 km. For further details about this technique refer to Pedder (1993).

In order to have a qualitative view of the general circulation in the Mallorca channel, a database of daily sea surface temperature (SST) was compiled, for the EUBAL-I period, from Advanced Very High Resolution Radiometer (AVHRR) obtained from Instituto Espanyol de Oceanografia (<http://www.teledeteccion-oceanografica.net/>).

### 2.3.2 Whole-system metabolism based on incubations

Planktonic GPP and CR were measured at 4 stations in the bay during each of the EUBAL cruises (Fig. 1). Samples (5 replicates) were incubated in situ at 4 depths for 24 h in both transparent and dark 60 ml BOD bottles. O<sub>2</sub> concentrations were measured before and after incubation using an automated Winkler titration technique with potentiometric end-point detection. Analyses were performed with an Orion redox electrode (9778-SC) and a custom built titrator. Reagents and standardizations were similar to those described by Knap et al. (1996). Daily planktonic CR and NCP were estimated by regressing O<sub>2</sub> in the dark and transparent bottles against time, respectively. Daily GPP was estimated as the difference between NCP and CR.

At each station and incubation depth, samples were taken for chlorophyll *a*. Water was filtered through GF/F filters that were stored frozen until extraction and analysis by high-performance liquid chromatography (Barranguet et al., 1997). Light penetration in the water column was measured using a LI-COR spherical sensor (LI-193SA) and a LI-1400 data-logger twice during each incubation period. During two surveys on each cruise, vertical CTD (SeaBird SBE19) profiles of fluorescence (Chelsea and Sea tech sensors during EUBAL-I and -II, respectively) were performed at 11 stations in the bay (Fig. 1), and were calibrated using concomitant measurements of surface chlorophyll *a* concentration (same method as above). Surface irradiance was

measured every 15 min during each cruise using a LI-COR cosine corrected quantum sensor (LI-192SA) and a LI-1400 data-logger. Strong variations were observed during the first cruise, while during the second cruise light conditions were relatively constant (Table 1). As phytoplanktonic GPP is strongly dependent on the available light intensity, a correction was applied to compare results obtained under different light conditions during EUBAL-I. Relationships between daily GPP rates normalized per unit of chlorophyll *a* and the averaged daily irradiance were established for each station using the model of Platt et al. (1980). The resulting PI (production vs. irradiance) curves were then used to recalculate GPP for the mean daily surface irradiance over the whole campaign ( $421.5 \mu\text{mol m}^{-2} \text{s}^{-1}$ ).

During both EUBAL cruises, the community metabolism of *Posidonia oceanica* meadow and unvegetated sediment communities were studied at Posidonia (7 m) and Cap Endrocat stations (15 m) using in situ benthic incubations as described above (Sect. 2.2). Moreover, during EUBAL-II, incubations of both communities were performed along a depth gradient at Posidonia station (4, 7, 15 and 22 m). The variation of benthic NCP with depth at this station was upscaled to the entire bay using estimates of the surface area of vegetated and unvegetated sediments based on the detailed study of Rey and Diaz del Rio (1984), using a Geographic Information System (ArcView 3.2 software package).

### 2.3.3 CO<sub>2</sub>/O<sub>2</sub> fluxes and *Posidonia oceanica* meadow metabolism based on DIC and O<sub>2</sub> budgets

Underway parameters (seawater pCO<sub>2</sub>, O<sub>2</sub>, salinity and in situ temperature) were sampled with a frequency of 1 min from the seawater supply of the ship (pump inlet at a depth of about 2 m) during six surveys of the EUBAL-I cruise (1, 3, 7, 9, 11 and 12 March 2002) and during five surveys of the EUBAL-II cruise (19, 21, 25, 26 and 27 June 2002). Total alkalinity (TA) and O<sub>2</sub> were sampled from the seawater supply to cover the spatial variability during the surveys (on average 10 samples per survey). A non-dispersive infrared gas analyser (IRGA, LI-COR, LI-6262) was used to measure pCO<sub>2</sub> in wet air equilibrated with seawater. The IRGA was calibrated daily using three dry gas standards: pure nitrogen (0.0 ppm; Air Liquide Belgium) and two gas mixtures with a CO<sub>2</sub> molar fraction of 360.5 and 773.8 ppm (National Oceanic and Atmospheric Administration). The temperature at the outlet of the equilibrator was monitored with a platinum resistance thermometer (PT100, Metrohm) with an estimated accuracy of  $\pm 0.05^\circ\text{C}$  and pCO<sub>2</sub> values were corrected for the temperature difference between in situ seawater and water in the equilibrator using the algorithm proposed by Copin-Montégut (1988, 1989). The offset in temperature was typically  $0.5^\circ\text{C}$ . The accuracy of the pCO<sub>2</sub> measurement by equilibration is estimated to  $\pm 2$  ppm (cumulated errors on temperature correction and instrument calibration). For further details on the equilibrator design and performance tests

refer to Frankignoulle et al. (2001). A second IRGA was used to measure atmospheric pCO<sub>2</sub> sampled at the bow of the ship. TA was determined using the classical Gran electro-titration method, on 100 ml GF/F filtered samples with a reproducibility of  $\pm 2 \mu\text{mol kg}^{-1}$  and an estimated accuracy of  $\pm 3 \mu\text{mol kg}^{-1}$ . The measurement of pH was obtained using a combined electrode (Metrohm), calibrated on the Total Hydrogen Ion Concentration Scale ( $\text{mol kg SW}^{-1}$ ), using the buffers proposed by Dickson (1993). The reproducibility of pH measurement is estimated to  $\pm 0.004$  pH units. DIC was calculated from pCO<sub>2</sub> and TA with the dissociation constants of carbonic acid and borate from Roy et al. (1993), the dissociation constant of boric acid from Dickson (1990) and the CO<sub>2</sub> solubility coefficient of Weiss (1974). The accuracy of DIC computed from the pCO<sub>2</sub> and TA is estimated to  $\pm 5 \mu\text{mol kg}^{-1}$ . DIC was normalized to a constant salinity according to:

$$\text{DIC}_{37=37} = \frac{\text{DIC}_{\text{observed}}}{\text{Salinity}_{\text{observed}}} \quad (1)$$

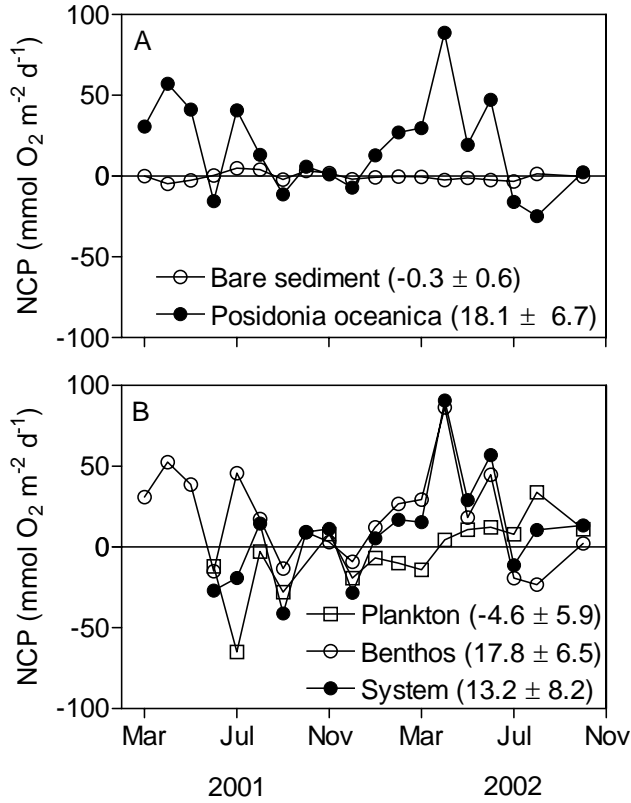
to remove the variations due to changes in salinity owing to mixing, evaporation or dilution. pCO<sub>2</sub> was normalized to a constant temperature using the algorithm proposed by Copin-Montégut (1988, 1989).

Discrete dissolved O<sub>2</sub> concentration was measured according to the Winkler method using a potentiometric end-point determination with an estimated accuracy of  $\pm 2 \mu\text{mol kg}^{-1}$ . Underway O<sub>2</sub> concentration was measured with a polarographic electrode (Oxyguard) calibrated against the discrete O<sub>2</sub> samples with an estimated accuracy of  $\pm 3 \mu\text{mol kg}^{-1}$ . Apparent oxygen utilisation (AOU) was computed using the concentration of O<sub>2</sub> at saturation calculated with the algorithm proposed by Benson and Krause (1984). Salinity and in situ temperature were measured using a SeaBird SBE21 thermosalinograph. The estimated errors on salinity and in situ temperature measurements are  $\pm 0.05$  and  $\pm 0.01^\circ\text{C}$ , respectively. Wind speed was measured at approximately 10 m height with a Batos (5 s sampling interval during EUBAL-I) and Aanderaa (1 min sampling interval during EUBAL-II) cup anemometer.

The air-sea CO<sub>2</sub> flux ( $F$ ;  $\text{mmol C m}^{-2} \text{d}^{-1}$ ) was computed from the air-sea gradient of pCO<sub>2</sub> ( $\Delta\text{pCO}_2 = \text{pCO}_2^{\text{water}} - \text{pCO}_2^{\text{atmosphere}}$ ; ppm), the gas transfer velocity ( $k$ ;  $\text{m d}^{-1}$ ) and the solubility coefficient of CO<sub>2</sub> ( $\alpha$ ;  $\text{mmol m}^{-3} \text{ppm}^{-1}$ ), using equation:

$$F = \alpha k \Delta\text{pCO}_2 \quad (2)$$

As a convention, a positive flux corresponds to a source for the atmosphere. Computations were made using various algorithms of  $k$  as a function of wind speed (Liss and Merlivat, 1986; Wanninkhof, 1992; Wanninkhof and McGillis, 1999; Nightingale et al., 2000; McGillis et al., 2001), although, we mainly discuss the values computed with the parametrization by Wanninkhof and McGillis (1999) for a consistent comparison with values from the Dyfamed station (Bégovic and



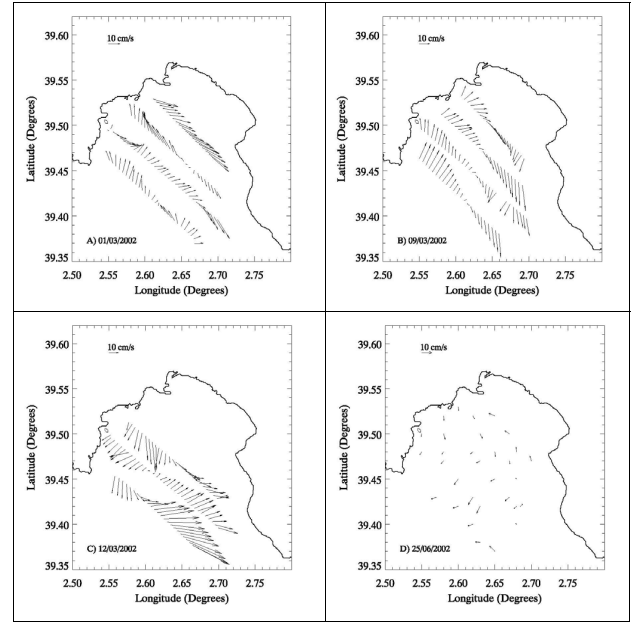
**Fig. 2.** (A) Monthly net community production (NCP) in the bare sediment and *Posidonia oceanica* communities. (B) Monthly NCP in the planktonic and benthic compartment as well as the combined net ecosystem production (system) at the Posidonia station (cf. Fig. 1). Whole period averages and associated standard errors are presented in the legends.

Copin-Montégut, 2002). For each survey, the  $\alpha \Delta p\text{CO}_2$  data were interpolated on a grid of  $0.0034^\circ \text{E} \times 0.0025^\circ \text{N}$ . To account for the strong non-linearity of the  $k$  parametrizations, the flux computations were carried out using hourly bins of wind speed (assuming that the whole area is uniformly submitted to wind speed measured anywhere during the survey) and then averaged for a given survey.

NEP over the *Posidonia oceanica* meadow was computed based on a DIC budget, according to the equation:

$$\text{NEP}_{\text{DIC}} = \frac{\left( \text{DIC}_{\text{bay}'} + t_{\text{bay}'} \frac{F_{\text{bay}'}}{\rho h_{\text{bay}'}} \right) - \left( \text{DIC}_{\text{pos}} + t_{\text{pos}} \frac{F_{\text{pos}}}{\rho h_{\text{pos}}} \right)}{t_{\text{pos}}} \quad (3)$$

where  $\text{NEP}_{\text{DIC}}$  is expressed in  $\text{mmol C m}^{-2} \text{d}^{-1}$ ,  $\rho$  is the water density ( $\text{kg m}^{-3}$ ),  $\text{DIC}_*$  is  $\text{DIC}_{37}$  ( $\text{mmol kg}^{-1}$ ),  $t_*$  is the water residence time (d),  $h_{\text{pos}}$  is the average water column height over the *Posidonia oceanica* meadow (m),  $h_{\text{bay}'}$  is the average mixed layer depth in the Bay of Palma (excluding the *Posidonia oceanica* meadow, m),  $F_*$  is the air-sea CO<sub>2</sub> exchange computed using the Wanninkhof and



**Fig. 3.** Current velocity distribution during EUBAL-I at 14 m for (A) 1 March 2002, (B) 9 March 2002 and (C) 12 March 2002; and EUBAL-II at 10 m (D) for 25 June 2002.

McGillis (1999)  $k$  parametrization, subscript *pos* denotes data over the *Posidonia oceanica* meadow and subscript *bay'* denotes data over the rest of the Bay of Palma (excluding the *Posidonia oceanica* meadow).

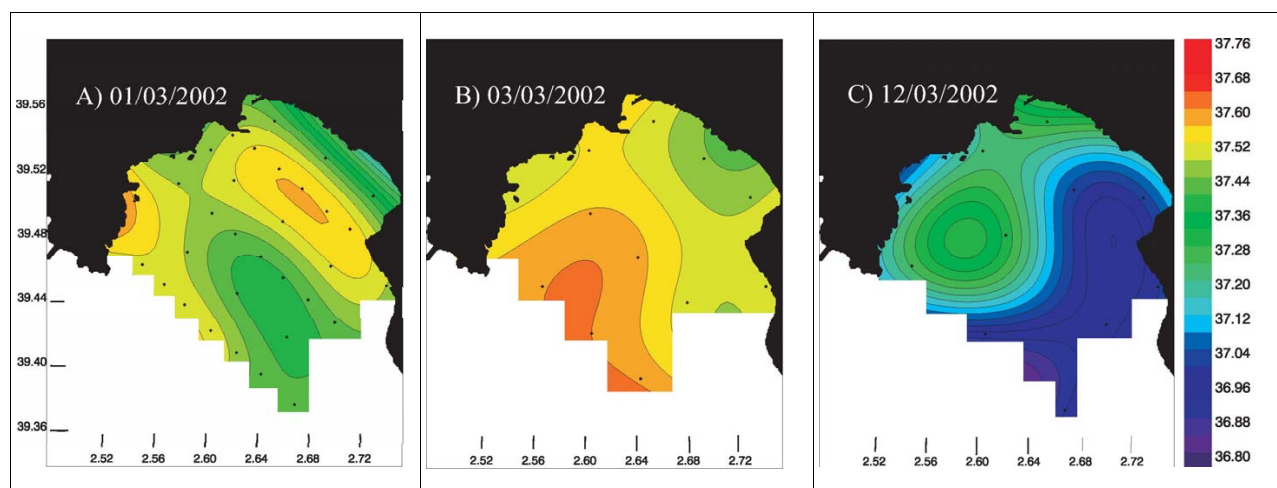
An identical equation was used to compute NEP from O<sub>2</sub> concentrations ( $\text{NEP}_{\text{O}_2}$  in  $\text{mmol O}_2 \text{ m}^{-2} \text{d}^{-1}$ ); the flux air-sea of O<sub>2</sub> was computed using the five  $k$  parametrizations mentioned above and the Schmidt number ( $Sc$ ) formulation for seawater given by Wanninkhof (1992), assuming a  $k$  dependency proportional to  $Sc^{-0.5}$ .

The relative water residence time over the *Posidonia oceanica* meadow and in the Bay of Palma (excluding the *Posidonia* meadow) were computed according to:

$$t_{\text{pos}} = t_{\text{total}} \frac{V_{\text{pos}}}{V_{\text{total}}} \quad (4)$$

$$t_{\text{bay}'} = t_{\text{total}} \frac{V_{\text{bay}'}}{V_{\text{total}}} \quad (5)$$

where  $V_*$  is the volume ( $\text{km}^3$ ),  $t_*$  is the water residence time (d), subscript *total* denotes data in the whole Bay of Palma, subscript *pos* denotes data over the *Posidonia oceanica* meadow and subscript *bay'* denotes data over the rest of the Bay of Palma (excluding the *Posidonia oceanica* meadow).



**Fig. 4.** Surface water salinity distributions during EUBAL-I for (A) 1 March 2002, (B) 3 March 2002; (C) 12 March 2002.

### 3 Results and discussion

#### 3.1 Metabolism at a fixed station from March 2001 to October 2002

Benthic and planktonic metabolism were studied at monthly intervals from March 2001 to October 2002 at *Posidonia* station (Fig. 1). The *Posidonia oceanica* community tended to be autotrophic and the bare sediment community tended to be heterotrophic during the study (Fig. 2a). The seagrass community ranged from heterotrophy with a lowest NCP in August 2002 ( $-24.7 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ) to autotrophy with a highest NCP in April 2002 ( $88.8 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ). Over the study duration, a NCP of  $18.1 \pm 5.2 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  was estimated. The unvegetated sediment community ranged from heterotrophy ( $-4.8 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  in April 2001) to autotrophy ( $5.0 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  in July 2001) with a mean NCP of  $-0.3 \pm 0.6 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ , therefore not significantly different from 0 ( $p > 0.05$ ).

The benthic community metabolism showed considerable variability along the study period, with the highest NCP found in spring and early summer (Fig. 2b). In contrast, the planktonic NCP showed no clear seasonality (Navarro et al., 2004). Indeed, most monthly NCP estimates in 2001 indicated a heterotrophy while those in 2002 suggested an autotrophy, related to high nutrient inputs in the bay due to frequent and severe storms according to Navarro et al. (2004). Overall, the NCP of the planktonic compartment averaged  $-4.6 \pm 5.9 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ , indicating metabolic balance (i.e.  $H_o$ : mean NCP=0,  $P > 0.05$ ), with a tendency towards heterotrophy (Navarro et al., 2004) whereas the benthic compartment was overall net autotrophic ( $17.8 \pm 6.5 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ). NEP (sum of benthic and planktonic NCP) was dominated by the benthic compartment in spring and summer, and by the planktonic community in fall and winter. At

an annual scale, NEP was nearly balanced, with a tendency towards autotrophy ( $13.2 \pm 8.2 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ).

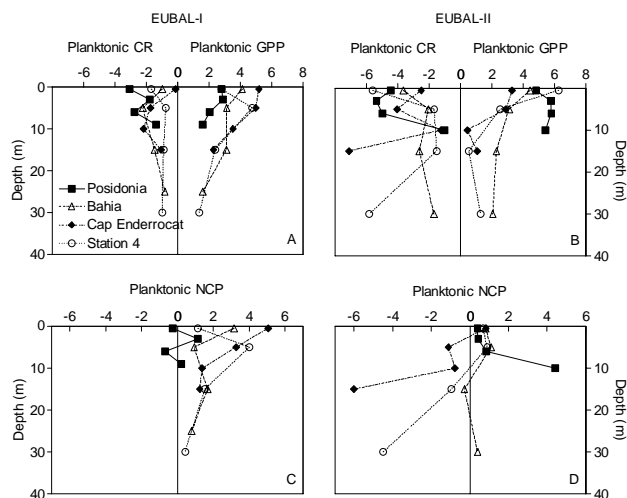
Navarro et al. (2004) suggested that the heterotrophy of the planktonic compartment at this station is fuelled by inputs of organic matter either derived from land or released by benthic communities. In this study, we estimated an overall positive NEP at this shallow station located over a *Posidonia oceanica* meadow indicating an organic matter production in excess and a possible sequestration in sediments or export to the deepest part of the bay.

#### 3.2 Whole-system metabolism during EUBAL-I and -2

##### 3.2.1 Hydrography, water currents and residence time

The horizontal velocity fields based on the ADCP surveys during the EUBAL-I and -II cruises differed considerably. In March, the flow pattern was initially characterised by a clear clockwise circulation with maximum velocities of 19 and  $22 \text{ cm s}^{-1}$ , on 1 March and 9 March 2002, respectively (Fig. 3a and b). The water entered the bay on its Western side, while the water outflow is dominant on the Eastern side. The circulation changed to the opposite direction towards the end of the cruise (12 March 2002; Fig. 3c) when the flow pattern became anticlockwise and the flow intensified to reach a value of  $40 \text{ cm s}^{-1}$ . This flow reversion was consistent with a shift between the start and the end of the cruise, from a relatively cool, high-salinity ( $37.5$  to  $37.6$ ) to a warmer and less saline surface water mass ( $+0.5^\circ\text{C}$ ;  $37.2$ ; Fig. 4). This pattern was evident both from CTD surveys and examination of AVHRR SST data (not shown). The flow pattern during EUBAL-II was similar to the one observed at the end of EUBAL-I, with a general anticlockwise circulation (Fig. 3d). Current velocities were, on average, lower than those during EUBAL-I ( $6\text{--}7 \text{ cm s}^{-1}$  vs.  $20\text{--}24 \text{ cm s}^{-1}$ ).



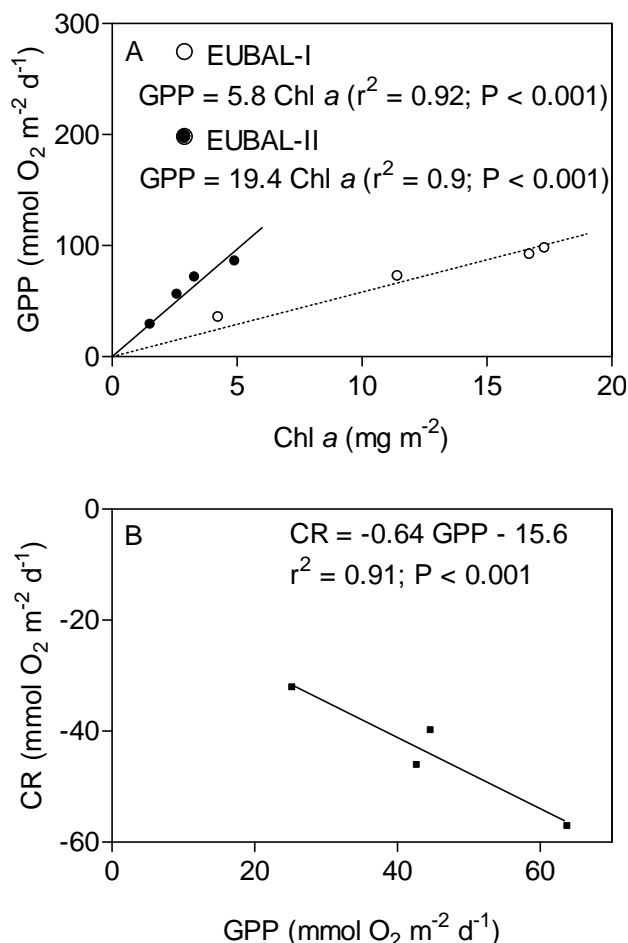


**Fig. 5.** Depth profiles of planktonic daily gross primary production (GPP), community respiration (CR) and net community production (NCP; all in  $\text{mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ ) measured at four stations (cf. Fig. 1) in the Bay of Palma during (A) and (C) EUBAL-I and (B) and (D) EUBAL-II cruises.

The water residence time in the Bay of Palma was estimated from the current velocities recorded during each survey. The average water residence time was much shorter during EUBAL-I ( $2.5 \pm 0.2 \text{ d}$ ) than during EUBAL-II (10 d). Due to the low velocities and the consequent noise during EUBAL-II, the computed residence time is subject to a strong uncertainty.

### 3.2.2 Whole-system metabolism based on incubations

Integrated chlorophyll *a* concentrations at the incubated stations were on average significantly higher in March than in June, except at Posidonia station which presented similar values during both cruises (Table 1). Minimal and maximal concentrations were found, respectively, at Cap Enderrocat station in June ( $1.5 \text{ mg m}^{-2}$ ) and at Bahia station in March ( $17.3 \text{ mg m}^{-2}$ ). Light attenuation coefficients (*K*) were rather low ( $< 0.16 \text{ m}^{-1}$  during both cruises) with slightly higher values in March, except for Posidonia station. During EUBAL-I, surface planktonic GPP rates ranged from  $2.8 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$  (Posidonia) to  $5.2 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$  (Cap Enderrocat) with an average value of  $3.7 \pm 1.2 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$  (Fig. 5a). During EUBAL-II, surface planktonic GPP rates were slightly higher (Fig. 5b; mean:  $4.7 \pm 1.2 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ ) with a minimal value at Cap Enderrocat ( $3.3 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ ) and a maximal one at station 4 ( $6.3 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ ). Average water-column planktonic CR strongly increased between March (Fig. 5a) and June (Fig. 5b), from  $-1.4 \pm 0.2 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$  to  $-3.2 \pm 0.3 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ , respectively. Higher vertical and horizontal gradients were found during the EUBAL-II cruise. Positive planktonic NCP rates were generally ob-



**Fig. 6.** (A) Linear relationships between integrated gross primary production (GPP) and integrated chlorophyll *a* concentrations (Chl *a*) at four stations (cf. Fig. 1) during EUBAL-I and -II cruises. (B) Linear relationship between GPP and community respiration (CR) integrated in the water column above the *Posidonia oceanica* meadow at four stations during the EUBAL-II cruise.

served in March with a maximal value in surface waters at Cap Enderrocat ( $5.1 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ ) while much more variable rates were measured in June with strongly heterotrophic conditions at depth in stations Cap Enderrocat and 4.

During EUBAL-I, maximal integrated planktonic GPP values were observed at stations Bahia and 4 ( $98$  and  $92 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ) and the minimal one at Posidonia station ( $36 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ , Table 2). During EUBAL-II, integrated planktonic GPP ranged from  $29 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  at Cap Enderrocat to  $86 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  at Bahia. Integrated planktonic CR showed a low spatial variability during the first cruise with a mean value of  $-35 \pm 4 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ . In contrast, during the second cruise, strong geographical variations were highlighted with a minimal value measured at Posidonia ( $-45 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ) and a maximal

**Table 2.** Water column averages and integrated planktonic gross primary production (GPP), community respiration (CR) and net community production (NCP) at four stations during the EUBAL-I and -II cruises. Averaged values ( $\pm$ SE) are also presented.

Station	Bottom depth m	GPP	CR	NCP	GPP	CR	NCP
		mmol O <sub>2</sub> m <sup>−3</sup> d <sup>−1</sup>			mmol O <sub>2</sub> m <sup>−2</sup> d <sup>−1</sup>		
EUBAL-I							
Posidonia	18	2.0	−1.8	0.2	36	−33	3
Bahia	35	2.8	−1.3	1.5	98	−45	53
Station 4	37	2.5	−0.9	1.5	92	−35	57
Cap Enderrocat	20	3.7	−1.4	2.3	73	−27	46
Mean (±SE)		2.8 (±0.4)	−1.4 (±0.2)	1.4 (±0.4)	75 (±14)	−35 (±4)	40 (±13)
EUBAL-II							
Posidonia	13	5.5	−3.5	2.1	72	−45	27
Bahia	33	2.6	−2.3	0.3	86	−75	11
Station 4	33	1.7	−3.2	−1.5	56	−107	−51
Cap Enderrocat	16	1.8	−3.7	−1.9	29	−59	−30
Mean (±SE)		2.9 (±0.9)	−3.2 (±0.3)	−0.3 (±0.9)	61 (±12)	−72 (±13)	−11 (±18)

one at station 4 ( $-107 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ). The planktonic compartment was autotrophic at all incubated stations during EUBAL-I while during EUBAL-II, two stations (Station 4 and Cap Enderrocat) presented a heterotrophic status.

Significant relationships were found between integrated planktonic GPP and integrated chlorophyll *a* concentration during both cruises (Fig. 6a). As chlorophyll *a* concentrations based on calibrated fluorescence profiles were estimated at 11 stations on two surveys during each cruise, these relationships were used to extrapolate GPP, integrated across the euphotic layer (34 m during EUBAL-I and 46 m during EUBAL-II) to the whole bay (Table 3). During both surveys in March, the lowest chlorophyll *a* values and consequently the lowest planktonic GPP were found at Posidonia and Cap Enderrocat stations while maximal rates were found in deep waters in the middle of the bay. During the second cruise, due to lower chlorophyll *a* concentrations, planktonic GPP were much lower and higher spatial variations were observed in comparison to March, reaching a mean value of  $33 \pm 9 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  (vs.  $93 \pm 9 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  during EUBAL-I) with highest values generally estimated over the *Posidonia oceanica* meadow.

During the first cruise, for all stations investigated during the surveys (except incubation stations), planktonic integrated CR rates were calculated by multiplying the mean volumetric rate observed during the incubations (at the 4 reference stations;  $-1.4 \pm 0.2 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ ) by the depth of each station. Planktonic integrated CR was, therefore, highest at deep stations reaching a maximal value at station 8 (60 m depth;  $-84 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ), but was always lower than planktonic GPP. Consequently, the planktonic compartment was autotrophic during EUBAL-I with an average value of  $48 \pm 9 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ .

Due to the strong heterogeneity in CR observed during EUBAL-II at the four incubated stations, the same procedure

was not applied. During this cruise, a significant relationship was observed between GPP and CR integrated across the water column, excluding the last incubated depth (Fig. 6b). CR rates measured near the bottom and therefore near the *Posidonia oceanica* meadow do not fit with this relationship. This suggests that near the bottom, planktonic CR may be fuelled by organic matter from the *Posidonia oceanica* meadow rather than by the planktonic production. Therefore, CR rates collected at the four incubated stations were upscaled only to the area covered by the *Posidonia oceanica* meadow, while integrated CR was calculated based on the estimated GPP in the rest of the bay where chlorophyll *a* and consequent GPP rates are much lower.

On average, integrated and extrapolated planktonic CR was similar in March and June ( $-43 \pm 5$  and  $-47 \pm 7 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ , respectively) but due to much lower GPP rates during EUBAL-II, the planktonic compartment was heterotrophic ( $-15 \pm 7 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ).

Seagrass communities were autotrophic at all depths during both cruises, with the highest NCP found at the shallowest station (Table 4). In contrast, bare sediment communities remained net heterotrophic during both cruises, except for the shallowest community investigated during EUBAL-II (4 m). The upscaled results suggest that the NCP of the *Posidonia oceanica* meadow was marginally autotrophic during EUBAL-I ( $6.5 \pm 9.9 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ) and significantly autotrophic, with an average NCP of  $26.3 \pm 8.0 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ , during EUBAL-II.

Combining these estimates with concurrent estimates of planktonic NCP over the *Posidonia oceanica* meadow (Stations Posidonia, Bahia, Cap Enderrocat, 4, 18 and 19), a NEP of  $63 \pm 24$  and  $10 \pm 22 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  was estimated in this area for EUBAL-I and -II, respectively.

Considering the entire bay, where the bare sediments and the seagrass meadow cover respectively 70 and 30% of the

**Table 3.** Integrated chlorophyll *a* (Chl *a*) concentrations, planktonic gross primary production (GPP), community respiration (CR) and net community production (NCP) estimated on two surveys during each of the EUBAL cruises in 2002.

Station	Date	Depth m	Chl <i>a</i> mg m <sup>-2</sup>	GPP	CR	NCP	GPP	CR	NCP
				mmol O <sub>2</sub> m <sup>-3</sup> d <sup>-1</sup>			mmol O <sub>2</sub> m <sup>-2</sup> d <sup>-1</sup>		
Posidonia	07/03	13	8	3.6	-1.8	1.8	47	-23	23
Bahia	"	34	16	2.7	-1.3	1.4	92	-44	48
Cap Enderrocat	"	12.5	3	1.4	-1.4	0.0	18	-18	0
4	"	33	15	2.6	-0.9	1.7	86	-30	56
8	"	60	15	1.5	-1.4	0.5	90	-84	6
18	"	12	14	6.8	-1.4	5.4	82	-17	65
19	"	11	8	4.2	-1.4	2.8	46	-15	31
20	"	45	15	1.9	-1.4	0.5	86	-63	23
22	"	33	15	2.6	-1.4	1.2	86	-46	40
23	"	41	15	2.1	-1.4	0.7	86	-57	29
26	"	50	16	1.9	-1.4	0.5	95	-70	25
Mean±SE	07/03		13±1	2.8±0.5	-1.4±0.1	1.5±0.5	74±8	-42±7	31±6
Posidonia	11/03	13	7	3.1	-1.8	1.3	40	-23	8
Bahia	"	34	30	5.1	-1.3	3.8	173	-44	129
Cap Enderrocat	"	12.5	9	4.2	-1.4	2.8	53	-18	25
4	"	33	35	6.2	-0.9	5.3	205	-30	168
8	"	60	19	1.8	-1.4	0.4	108	-84	21
18	"	12	12	5.8	-1.4	4.4	70	-17	52
19	"	11	15	7.9	-1.4	6.5	87	-15	71
20	"	45	24	3.1	-1.4	1.7	140	-63	72
22	"	33	22	3.9	-1.4	2.5	129	-46	79
23	"	41	16	2.3	-1.4	0.9	94	-57	32
26	"	50	23	2.7	-1.4	1.3	135	-70	59
Mean±SE	11/03		19±3	4.2±0.6	-1.4±0.1	2.8±0.6	112±15	-42±7	65±14
Posidonia	21/06	13	2.1	3.1	-3.5	-0.3	41	-45	-4
Bahia	"	34	4.2	2.4	-2.2	0.2	81	-75	6
Cap Enderrocat	"	12.5	0.5	0.8	-4.7	-3.9	10	-59	-49
4	"	33	0.8	0.5	-3.2	-2.8	16	-107	-91
8	"	60	0.5	0.2	-0.4	-0.2	10	-23	-13
18	"	12	4.1	6.6	-5.6	1.1	80	-67	13
19	"	11	0.9	1.6	-2.5	-0.9	17	-27	-19
20	"	45	1	0.4	-0.6	-0.2	19	-28	-9
22	"	33	0.1	0.1	-0.5	-0.4	2	-16	-14
23	"	41	0.1	0.0	-0.4	-0.4	2	-18	-16
26	"	50	0.4	0.2	-0.4	-0.3	8	-21	-13
Mean±SE	21/06		1±0	1.4±0.6	-2.2±0.6	-0.7±0.4	26±9	-44±9	-19±9
Posidonia	26/06	13	2.1	3.1	-3.5	-0.3	41	-45	-4
Bahia	"	34	7.1	4.1	-2.2	1.8	138	-75	63
Cap Enderrocat	"	12.5	0.5	0.8	-4.7	-3.9	10	-59	-49
4	"	33	0.8	0.5	-3.2	-2.8	16	-107	-91
8	"	60	0.3	0.1	-0.3	-0.2	6	-19	-14
18	"	12	8.5	13.7	-10.1	3.6	165	-121	44
19	"	11	1.2	2.1	-2.8	-0.7	23	-31	-8
20	"	45	0.6	0.3	-0.6	-0.3	12	-25	-14
22	"	33	0.7	0.4	-0.7	-0.3	14	-24	-10
23	"	41	0.4	0.2	-0.5	-0.3	8	-21	-13
26	"	50	0.2	0.1	-0.4	-0.3	4	-19	-16
Mean±SE	26/06		2±1	2.3±1.2	-2.6±0.9	-0.3±0.6	40±17	-50±11	-10±12
EUBAL-I Mean±SE	March		16±2	3.5±0.7	-1.4±0.1	2.2±0.4	93±9	-43±5	48±9
EUBAL-II Mean±SE	June		1.7±0	1.9±0.4	-2.4±0.1	-0.5±0.4	33±9	-47±7	-15±7

surface area, benthic NCP was estimated at  $1.6\pm3.0$  and  $8.6\pm3.2$  mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> for EUBAL-I and -II, respectively (Table 4). Therefore, a whole-system NEP of  $50\pm12$  and  $-6\pm10$  mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> was estimated in March and June, respectively, indicating that the Bay of Palma acted as a significant autotrophic ecosystem due to a high planktonic production in March and did not depart from metabolic balance in June despite a significantly autotrophic benthic compartment.

Interpolated maps of NEP in the bay of Palma during the 4 surveys conducted in March (Fig. 7) and June (Fig. 8) show

that maxima of net production were located in the northern and in the western areas in March and June, respectively.

### 3.2.3 Spatial and temporal variations of pCO<sub>2</sub>, TA, AOU and air-sea CO<sub>2</sub> fluxes

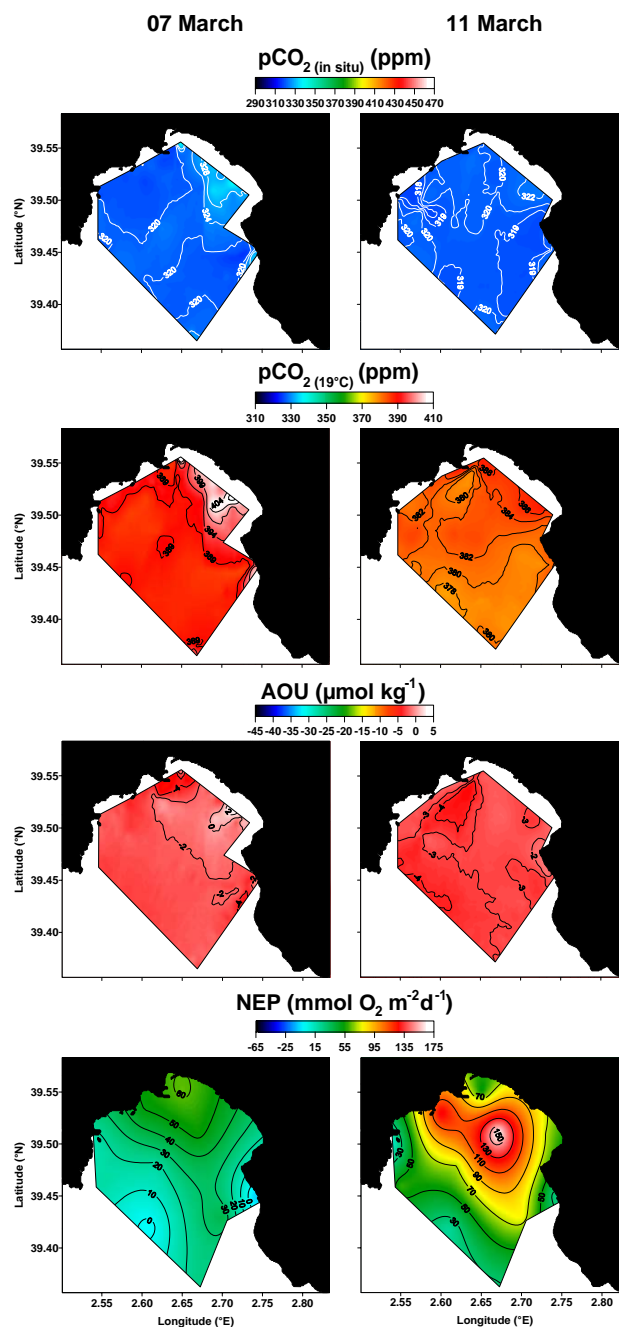
The comparison of pCO<sub>2</sub> among cruises required the normalization to a constant temperature, which in the present case should be 19°C (pCO<sub>2(19°C)</sub>). This is because temperature strongly affects the equilibrium constants of the carbonate system and, in particular, the solubility coefficient of CO<sub>2</sub>.

**Table 4.** Mean ( $\pm$ SE) benthic net community production (NCP) in March (EUBAL-I) and June 2002 (EUBAL-II).

Cruise	Community	Depth (m)	NCP±SE (mmol O <sub>2</sub> m <sup>-2</sup> d <sup>-1</sup> )
EUBAL-I	<i>P. oceanica</i>	7	29.7±10.8
		15	17.1±3.3
	Bare sediment	7	-0.3±0.2
		15	-0.4±0.1
<i>P. oceanica</i> meadow extrapolated			<b>6.5±9.9</b>
Bare sediment extrapolated			<b>-0.4±0.2</b>
Whole bay extrapolated			<b>1.6±3.0</b>
EUBAL-II	<i>P. oceanica</i>	4	44.2±13.6
		7	12.0±11.0
		15	24.6±3.9
		22	19.1±11.1
	Bare sediment	4	5.7±0.5
		7	-4.0±0.4
		15	-3.7±0.3
		22	-6.4±0.4
<i>P. oceanica</i> meadow extrapolated			<b>26.3±8.0</b>
Bare sediment extrapolated			<b>1.0±3.1</b>
Whole bay extrapolated			<b>8.6±3.2</b>

Indeed, a temperature increase of 1°C causes a pCO<sub>2</sub> rise of about 4%. Normalization of in situ pCO<sub>2</sub> (pCO<sub>2(in situ)</sub>) values to a constant temperature allows then to focus on potential biological controls of pCO<sub>2</sub>. No correlation was found between AOU and pCO<sub>2(in situ)</sub> (Fig. 9a) during the two EUBAL cruises taken together, while AOU and pCO<sub>2(19°C)</sub> (Fig. 9b) were strongly correlated which suggests that both variables were controlled by biological effects during these two cruises. The pCO<sub>2(19°C)</sub> and AOU values were on average lower during EUBAL-II than during EUBAL-I that could suggest a stronger NEP during the second cruise, which is clearly inconsistent with values derived from incubations (Sect. 3.2.2). This discrepancy can be explained by the input of water masses with different signatures during the two cruises and a much shorter water residence time in March (Sect. 3.2.1) which precludes a significant impact of the metabolism of the bay on pCO<sub>2(19°C)</sub> and AOU during this cruise. This highlights that, to infer on the metabolic status of a system, normalized pCO<sub>2</sub> (or DIC) and AOU signals must be interpreted with ancillary information on the chemical characteristics of the water mass entering the system and the water residence time and volume of the system. Only with such ancillary information, NEP can be computed from pCO<sub>2</sub> (or DIC) and AOU signals, as developed in Sect. 3.2.4 for the *Posidonia oceanica* meadow during EUBAL-II.

The observed pCO<sub>2(19°C)</sub> and AOU values were much lower than those at the Dyfamed station (located in the open

**Fig. 7.** Interpolated maps of pCO<sub>2(in situ)</sub>, pCO<sub>2</sub> normalized to a constant temperature (pCO<sub>2(19°C)</sub>) and Apparent Oxygen Utilisation (AOU) as well as net ecosystem production (NEP) in the Bay of Palma during two surveys of EUBAL-II.

waters of the Ligurian Sea, about 620 km North from the Bay of Palma) for the corresponding periods. This suggests that in the Western Mediterranean Sea, the continental shelf is more productive than the open oceanic waters.

During both EUBAL cruises, TA was well correlated to salinity (Fig. 9c) suggesting that CaCO<sub>3</sub>

**Table 5.** Mean±SD of AOU, pCO<sub>2</sub>, pCO<sub>2</sub> normalized to a constant temperature (pCO<sub>2(19°C)</sub>), DIC<sub>37</sub> (computed from continuous measurements of pCO<sub>2</sub> and salinity, and TA-salinity linear regression function in legend of Fig. 9), wind speed (*u*), the air-sea gradient of pCO<sub>2</sub> (ΔpCO<sub>2</sub>), in the surface waters, and atmospheric CO<sub>2</sub> flux computed using the gas transfer velocity given by Wanninkhof and McGillis (1999) (*F*), over the *Posidonia* meadow and in the rest of the bay, on the surveys carried out during the EUBAL-I and -II cruises. Data were interpolated using the Kriging procedure on a grid of 0.0034° E×0.0025° N and averaged.

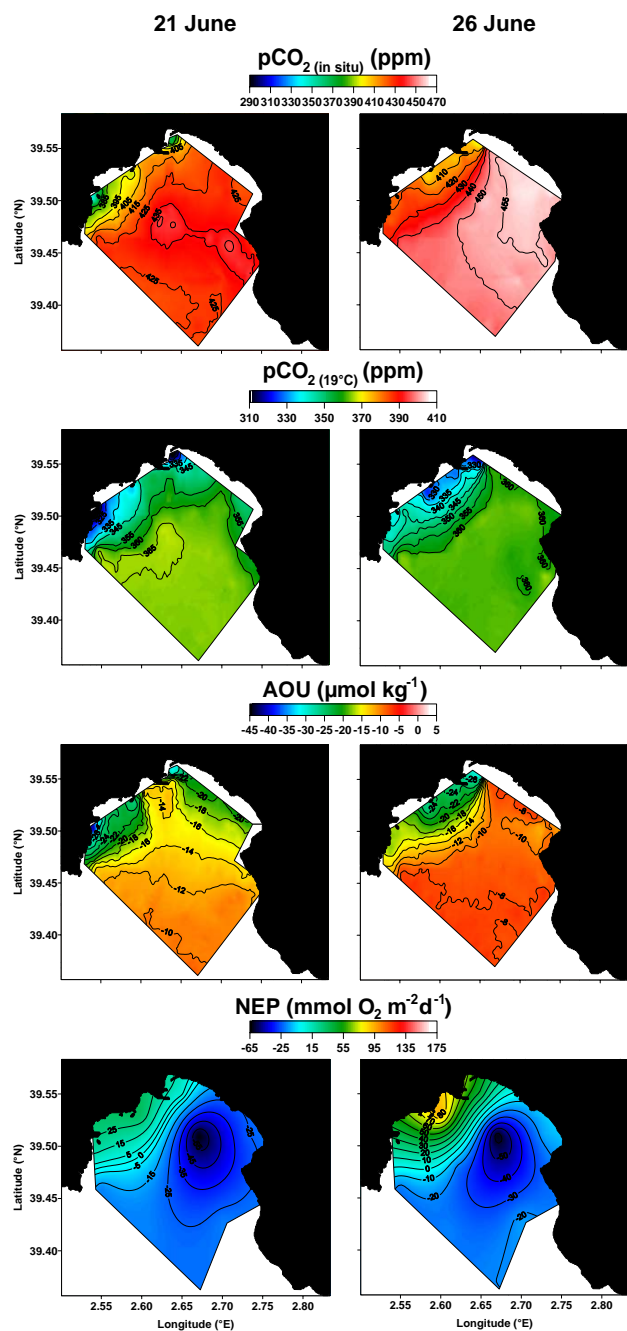
	AOU μmol kg <sup>-1</sup>	pCO <sub>2</sub> ppm	pCO <sub>2(19°C)</sub> ppm	DIC <sub>37</sub> μmol kg <sup>-1</sup>	ΔpCO <sub>2</sub> ppm	<i>u</i> m s <sup>-1</sup>	<i>F</i> mmol C m <sup>-2</sup> d <sup>-1</sup>
Bay (excluding <i>Posidonia</i> meadow)							
01/03/2002	-4.6±2.3	324±3	386±4	2142±2	-46±16	3.9±1.6	-1.0±0.9
04/03/2002	-10.5±1.8	320±2	384±3	2140±2	-64±1	6.9±1.8	-5.8±4.5
07/03/2002	-2.4±0.6	320±1	388±2	2144±1	-54±2	4.5±2.2	-1.9±2.3
09/03/2002	-0.8±0.9	320±1	386±3	2143±1	-57±3	2.9±0.9	-0.4±0.3
11/03/2002	-3.2±0.5	320±1	381±2	2140±1	-55±4	3.3±0.9	-0.5±0.4
12/03/2002	-4.2±0.9	321±2	380±2	2140±1	-53±7	3.3±1.0	-0.5±0.5
19/06/2002	-15.8±3.5	420±7	363±7	2121±4	50±12	4.7±2.1	1.7±1.4
21/06/2002	-13.3±3.3	426±10	361±7	2120±4	52±18	4.1±2.2	1.6±2.0
25/06/2002	-10.0±2.4	442±10	361±5	2118±3	82±10	6.3±1.4	5.9±3.4
26/06/2002	-10.5±4.0	444±11	358±8	2116±5	77±20	3.6±1.2	1.1±1.1
27/06/2002	-10.8±1.1	443±3	360±1	2119±1	83±3	5.4±1.4	3.6±2.5
<i>Posidonia</i> meadow							
01/03/2002	-6.1±2.4	323±2	384±3	2141±2	-56±17	3.9±1.6	-1.0±0.9
04/03/2002	-14.8±2.7	316±3	379±4	2138±2	-63±1	6.9±1.8	-5.7±4.5
07/03/2002	-2.0±1.6	323±5	395±6	2147±3	-54±4	4.5±2.2	-1.9±2.4
09/03/2002	0.0±0.6	323±8	394±10	2147±5	-58±9	2.9±0.9	-0.4±0.4
11/03/2002	-2.6±0.6	320±1	383±2	2141±1	-64±8	3.3±0.9	-0.6±0.5
12/03/2002	-4.2±1.1	321±3	379±2	2140±1	-59±12	3.3±1.0	-0.6±0.5
19/06/2002	-24.0±5.8	405±17	346±15	2110±10	40±21	4.7±2.1	1.4±1.1
21/06/2002	-18.0±4.7	420±18	351±13	2114±9	45±31	4.1±2.2	1.3±1.7
25/06/2002	-14.1±3.9	433±14	351±10	2111±7	74±15	6.3±1.4	5.3±3.1
26/06/2002	-12.6±5.8	445±18	354±12	2114±8	79±31	3.6±1.2	1.1±1.1
27/06/2002	-12.7±2.2	449±7	358±5	2117±3	87±11	5.4±1.4	3.7±2.6

precipitation/dissolution rates were too low and/or water residence time too short and/or the water volume too large to significantly affect surface water TA values. The linear regression function based on data from both EUBAL cruises was very similar to that reported by Copin-Montégut (1993) for the Alboran Sea.

Strong spatial gradients of pCO<sub>2(in situ)</sub>, pCO<sub>2(19°C)</sub> and AOU were observed during both EUBAL cruises (Figs. 7 and 8). During the six EUBAL-I surveys, pCO<sub>2(in situ)</sub>, pCO<sub>2(19°C)</sub> and AOU surface distributions exhibited variable patterns with no recurrent spatial features. Moreover, no clear relation was found between the spatial patterns of these variables and those of NEP derived from incubations (Fig. 7). This suggests either highly variable NEP in space and time and/or the advection of water masses with different pCO<sub>2(in situ)</sub>, pCO<sub>2(19°C)</sub> and AOU signatures. The latter explanation is consistent with changes in the water mass inferred from salinity and temperature and shifts of the residual current patterns observed between the start and the end of the

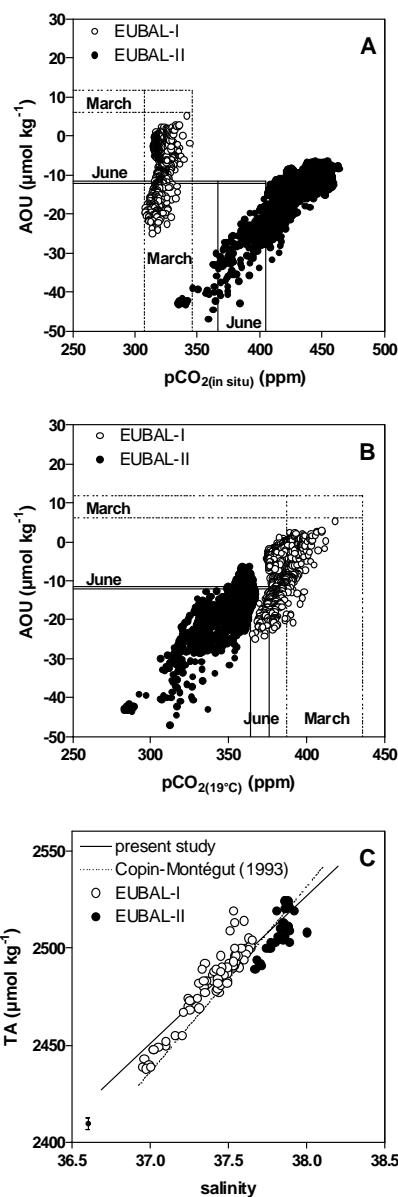
cruise (Sect. 3.2.1). In contrast, during the EUBAL-II surveys, pCO<sub>2(in situ)</sub>, pCO<sub>2(19°C)</sub> and AOU minima were systematically observed near-shore, above the *Posidonia oceanica* meadow (Fig. 8 and Table 5). Also, during the EUBAL-II surveys, lower near-shore values of pCO<sub>2(in situ)</sub>, pCO<sub>2(19°C)</sub> and AOU were systematically observed on the Western side of the bay in comparison to the Eastern side (Fig. 8). This is consistent with the anti-clockwise pattern of residual currents (Fig. 3), leading to an impoverishment in CO<sub>2</sub> and an enrichment in O<sub>2</sub> as the water mass is advected above the *Posidonia oceanica* meadow. Also, a higher NEP was observed on the Western side of the bay during two EUBAL-II surveys (Table 3 and Fig. 8).

The variability of the flux computations related to the choice of the *k* parametrization is huge as shown in other studies (e.g. Borges and Frankignoulle, 2002). The fluxes computed using the Wanninkhof and McGillis (1999) *k* parametrization were on average identical to those using the Liss and Merlivat (1986) *k* parametrization, and,

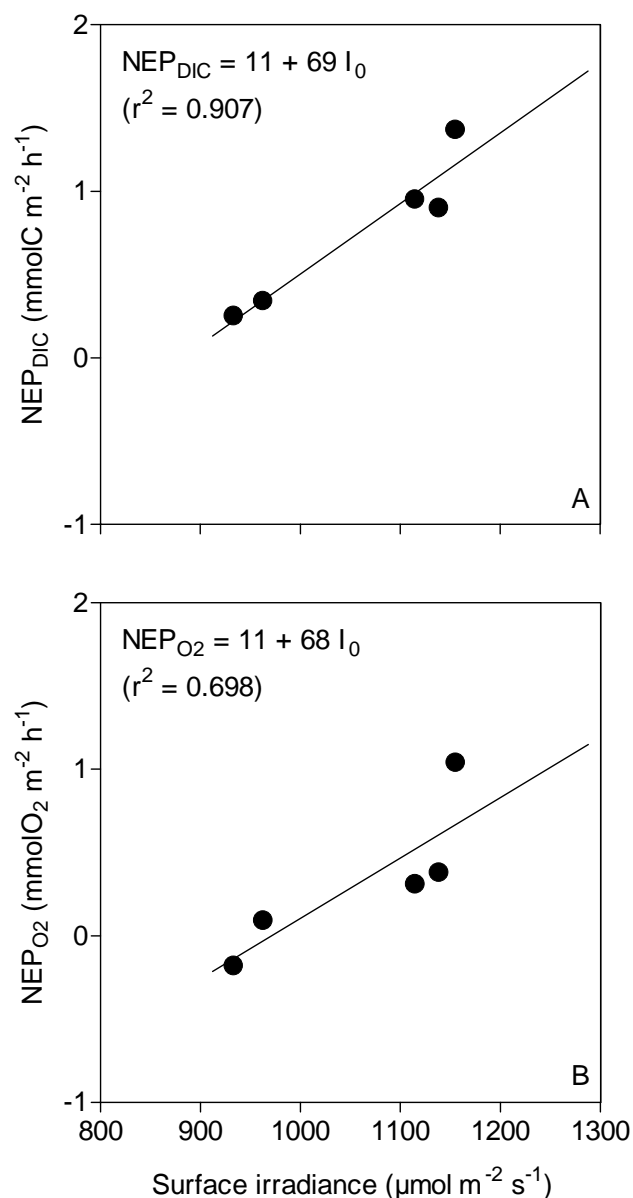


**Fig. 8.** Interpolated maps of  $p\text{CO}_2(\text{in situ})$ ,  $p\text{CO}_2$  normalized to a constant temperature ( $p\text{CO}_2(19^\circ\text{C})$ ) and Apparent Oxygen Utilisation (AOU) as well as net ecosystem production (NEP) in the Bay of Palma during two surveys of EUBAL-I.

corresponded to 57, 66 and 63% of those computed using, respectively, the  $k$  parametrization given by Wanninkhof (1992), Nightingale et al. (2000) and McGillis et al. (2001). The Bay of Palma was a sink for atmospheric CO<sub>2</sub> during EUBAL-I (on average  $-1.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) and a source during EUBAL-II (on average  $2.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ),



**Fig. 9.** (A) Apparent oxygen utilisation (AOU) versus  $p\text{CO}_2(\text{in situ})$  and (B) AOU versus  $p\text{CO}_2$  normalized to a constant temperature ( $p\text{CO}_2(19^\circ\text{C})$ ) in surface waters from all the surveys during EUBAL-I and II cruises. The range of variation of AOU and  $p\text{CO}_2(19^\circ\text{C})$  at the Dyfamed station for the March 1998–1999 and June 1998–1999 periods (Copin-Montégut and Bégovic, 2002; Bégovic and Copin-Montégut, 2002) are indicated by the horizontal and vertical lines. (C) Total alkalinity (TA) versus salinity in surface waters during the EUBAL-I and II cruises. Dotted line corresponds to the regression function reported by Copin-Montégut (1993) for the Alboran Sea ( $\text{TA} = -1072 (\pm 16) + 94.85 (\pm 0.4) \times \text{salinity}$ ) and the solid line corresponds to the regression function based on the EUBAL-I and II cruises ( $\text{TA} = -346 (\pm 7) + 75.6 (\pm 3) \times \text{salinity}$ ;  $r^2 = 0.869$ ;  $n = 119$ ;  $p < 0.0001$ ). The error bar on the lower left corner of the plot corresponds to the estimated accuracy on TA measurements.



**Fig. 10.**  $NEP_{DIC}$  (A) and  $NEP_{O_2}$  (B) over the *Posidonia oceanica* meadow versus surface irradiance ( $I_0$ ) during the EUBAL-II cruise.  $NEP_{DIC}$  and  $NEP_{O_2}$  data were adjusted linearly to 12:00 Universal Time (UT; all surveys ended in mid-afternoon, ranging from 14:30 to 16:45 UT). Surface irradiance was averaged from dawn to 12:00 UT.

Table 5). At the Dyfamed station, the CO<sub>2</sub> fluxes ranged between  $-2.9$  and  $-8.7$  mmol C m<sup>-2</sup> d<sup>-1</sup> in March 1998–1999 and between  $2.8$  and  $3.3$  mmol C m<sup>-2</sup> d<sup>-1</sup> in June 1998–1999 (Bégovic and Copin-Montégut, 2002). The stronger fluxes at Dyfamed are related to higher wind speeds since  $\Delta pCO_2$  values are more marked in the Bay of Palma:  $-56$  ppm during EUBAL-I ( $-39$  ppm at Dyfamed in March 1998–1999) and  $68$  ppm during EUBAL-II ( $20$  ppm at Dyfamed in June 1998–1999).

**Table 6.** Net ecosystem production (NEP), over the *Posidonia oceanica* meadow during the EUBAL-II cruise. DIC<sub>37</sub> and O<sub>2</sub> data were interpolated as explained in legend of Table 5. The uncertainty on NEP was computed assuming an error on  $t_{total}$  of  $\pm 1$  d.

	$NEP_{DIC}$ mmol C m <sup>-2</sup> d <sup>-1</sup>	$NEP_{O_2}$ mmol O <sub>2</sub> m <sup>-2</sup> d <sup>-1</sup>
19/06/2002	41±3	31±3
21/06/2002	25±2	10±1
25/06/2002	27±2	9±1
26/06/2002	9±1	2±1
27/06/2002	7±1	-5±1
Mean EUBAL-II	22±12	10±7

The temperature effect on the solubility coefficient of CO<sub>2</sub> strongly contributes to the seasonal variability of air-sea CO<sub>2</sub> flux in the Bay of Palma, as also shown in open oceanic waters (Dyfamed; Bégovic and Copin-Montégut, 2002) and other coastal waters (Bay of Calvi – Corsica; Frankignoulle, 1988) of the Western Mediterranean Sea. Indeed,  $pCO_2$  and  $\Delta pCO_2$  values were higher during EUBAL-II than EUBAL-I, although,  $pCO_{2(19^\circ C)}$  and DIC<sub>37</sub> were lower during EUBAL-II (Table 5). Thus, the fact that the Bay of Palma is a source of CO<sub>2</sub> in June seems to be largely related to a temperature effect, since  $pCO_{2(19^\circ C)}$  and AOU data were lower than in March (Figs. 7, 8, 9a and Table 5).

Our results also suggest that the potential impact of *Posidonia oceanica* meadows on the CO<sub>2</sub> air-sea flux budget in the Western Mediterranean continental shelf during summer could be small. The average CO<sub>2</sub> flux observed over the *Posidonia* meadow during EUBAL-II ( $2.54$  mmol C m<sup>-2</sup> d<sup>-1</sup>; Table 5) was only 10% lower than that for unvegetated areas during the same cruise ( $2.76$  mmol C m<sup>-2</sup> d<sup>-1</sup>). As *Posidonia oceanica* meadows are believed to cover about 25% of the shelf area (Bethoux and Copin-Montégut, 1986), they can only decrease the summertime CO<sub>2</sub> emission from the Mediterranean continental shelf by a modest 2.5%.

### 3.2.4 DIC- and O<sub>2</sub>-derived NEP estimates over the *Posidonia oceanica* meadow during EUBAL-II

As mentioned above,  $pCO_{2(in situ)}$ ,  $pCO_{2(19^\circ C)}$  and AOU surface distributions exhibited variable patterns with no recurrent spatial features during EUBAL-I. Moreover, the residence time of water was too low during this cruise to clearly identify an impact of the *Posidonia oceanica* meadow on these variables. Therefore, the DIC and O<sub>2</sub> mass balance budgets were not applied during this cruise.

NEP estimates over the *Posidonia oceanica* meadow during EUBAL-II based on surface water DIC<sub>37</sub> and O<sub>2</sub> were highly variable and the ecosystem metabolism ranges from a distinctly autotrophic to a nearly balanced status (Table 6).

The day-to-day variability of NEP seems to be mainly related to light availability, as there was a strong relationship between the NEP and surface irradiance (Fig. 10), which explained about 91 and 70% of the variance of, respectively, NEP<sub>DIC</sub> and NEP<sub>O<sub>2</sub></sub>. Based on these linear regressions and continuous surface irradiance measurements, NEP over the *Posidonia oceanica* meadow was integrated for the full duration of the EUBAL-II cruise (19–27 June): at  $22 \pm 12$  mmol C m<sup>-2</sup> d<sup>-1</sup> and  $10 \pm 7$  mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> for, respectively, NEP<sub>DIC</sub> and NEP<sub>O<sub>2</sub></sub>.

The difference between NEP<sub>DIC</sub> and NEP<sub>O<sub>2</sub></sub> could be related to net CaCO<sub>3</sub> production (net DIC consumption) that was not included in the DIC budget, since TA was assumed conservative for the purpose of the computations (Fig. 9c). Net CaCO<sub>3</sub> production was measured using in situ benthic chambers on 20 June 2002 at station Posidonia, yielding a value of 15 mmol C m<sup>-2</sup> d<sup>-1</sup> for the *Posidonia oceanica* vegetated community and 1 mmol C m<sup>-2</sup> d<sup>-1</sup> for bare sediments of the Bay of Palma (Barrón et al., 2005<sup>2</sup>). Based on the relative sea-floor coverage by these benthic communities, the integrated net CaCO<sub>3</sub> production between the shore and 30 m depth is 10 mmol C m<sup>-2</sup> d<sup>-1</sup> and corresponds to the difference between NEP<sub>DIC</sub> and NEP<sub>O<sub>2</sub></sub>.

The photosynthetic quotient (PQ) corresponds to the molar ratio of the release of O<sub>2</sub> to the consumption of DIC during photosynthesis while the respiratory quotient (RQ) corresponds to the molar ratio of the release of DIC to the consumption of O<sub>2</sub> during organic matter mineralization. As mentioned by Thamdrup and Canfield (2000), an important uncertainty in using O<sub>2</sub> uptake as a measure of mineralization in sediments lies in the assumption that anaerobic respiration and reoxidation of reduced inorganic species are at steady state. Holmer et al. (2003) reported that reduced sulfides are low both in the pore waters and in the particulate pools of seagrass sediments around Mallorca Island, suggesting that the previous assumption is realistic in these iron-poor and carbonate rich sediments. Therefore, in the present study, a RQ of 1 was assumed and the NEP<sub>O<sub>2</sub></sub> vs. NEP<sub>DIC</sub> ratio was used to compute a PQ value. As the difference between NEP<sub>DIC</sub> and NEP<sub>O<sub>2</sub></sub> is likely due to net CaCO<sub>3</sub> production, a PQ of ~1 is estimated. This would suggest that NEP over the *Posidonia oceanica* meadow is mainly related to the photosynthetic activity of the seagrass community. Indeed, one can compute a PQ of 1.08, based on the C:N:P elemental molar ratio of 956:39:1 reported by Atkinson and Smith (1983) for *Posidonia oceanica* leaves. The C:N:P elemental molar ratio of roots is 3550:61:1 (Atkinson and Smith, 1983) but the below-ground production of *Posidonia oceanica* is much lower than the above-ground production (about 10%; Duarte and Chiscano, 1999) and does not significantly affect the PQ estimate (PQ=1.03 for below-ground production, overall PQ≈1.08). Based on the C:N:P molar elemental composition of phytoplankton reported by Redfield (1963) and Hedges et al. (2002), the predicted PQ values are higher than 1, respectively, 1.30 and 1.45.

Error estimates on these NEP values (Table 6) are largely derived from the uncertainty on the water residence time. The analytical error on DIC<sub>37</sub> and O<sub>2</sub> should not significantly affect the NEP estimates, since the variables used in the computations are averages of a large number of observations (assuming that analytical errors are random and not systematic). The air-sea flux correction introduces a relatively small uncertainty in the computations. NEP<sub>DIC</sub> computed using the air-sea CO<sub>2</sub> fluxes calculated with Wanninkhof and McGillis (1999) *k* parametrization corresponds on average to 99.4, 102.7, 94.7 and 95.0% of NEP<sub>DIC</sub> computed using the *k* parametrizations given by, respectively, Liss and Merlivat (1986), Wanninkhof (1992), Nightingale et al. (2000) and McGillis et al. (2001). NEP<sub>O<sub>2</sub></sub> computed using the air-sea O<sub>2</sub> fluxes calculated with Wanninkhof and McGillis (1999) *k* parametrization corresponds on average to 98.5, 96.7, 96.5 and 97.2% of NEP<sub>O<sub>2</sub></sub> computed using the *k* parametrization given by, respectively, Liss and Merlivat (1986), Wanninkhof (1992), Nightingale et al. (2000) and McGillis et al. (2001).

This approach is attractive because it is based on large data sets that adequately resolve the spatial variability and considering potential sources of error associated to each method, these estimates (NEP<sub>DIC</sub>= $22 \pm 12$  mmol C m<sup>-2</sup> d<sup>-1</sup> and NEP<sub>O<sub>2</sub></sub>= $10 \pm 7$  mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>) are in fair agreement with the NEP estimate based on the upscaled incubation measurements of  $10 \pm 22$  mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> over the *Posidonia oceanica* meadow during this cruise (Sect. 3.2.2).

## 4 Conclusions

Results obtained, in the Bay of Palma, at one station located above a seagrass meadow over an annual cycle and at several stations during 2 cruises in March and June 2002 showed that benthic communities dominated by the seagrass *Posidonia oceanica* are autotrophic, whereas unvegetated sediment is near metabolic balance. The autotrophic nature of seagrass meadows is consistent with previous reports for these ecosystems (Duarte and Cebrián, 1996; Gattuso et al., 1998; Hemminga and Duarte, 2000; Barrón et al., 2005<sup>2</sup>). In contrast, the planktonic community seemed to be heterotrophic, except during phytoplankton blooms, as in March 2002 (EUBAL-I), the time of the spring bloom in the NW Mediterranean (Duarte et al., 1999). This is consistent with the fact that oligotrophic planktonic systems such as in the Western Mediterranean tend to be net heterotrophic (Duarte and Agustí, 1998). Consequently, even the shallow Posidonia station (7 m) was only slightly autotrophic at the annual time scale despite the contribution of the seagrass community. Moreover, the short water residence time in the bay suggests that the extended planktonic heterotrophic periods, that dominate most of the year, cannot be supported by carbon in excess accumulated during autotrophic periods. As such, the whole ecosystem might be, in general, near the



metabolic balance or slightly heterotrophic, especially during summer, when the strong increase in ecosystem community respiration, driven by the rise of temperature, greatly exceeds ecosystem gross primary production. This possible heterotrophic nature of the planktonic community and of the whole ecosystem must be supported by allochthonous organic carbon inputs, probably derived from the human population surrounding the Bay of Palma. Unfortunately, information on the amount of organic matter loading to this bay is lacking to test this hypothesis. However, inputs from land are expected to be low due to (1) low annual precipitation in the region (about 400 mm yr<sup>-1</sup>); (2) the lack of rivers and streams to deliver the run-off to the water, as the island is in a karstic area, where surface water percolates to ground waters; and (3) the zero-loss policy of urban waters, which are treated and then pumped back inland, although there are sporadic inputs during storm surges (Jansá et al., 1994).

Partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) normalized to a constant temperature and apparent oxygen utilisation (AOU) values decreased between the two cruises and suggested that the ecosystem is more productive in June than in March. This was clearly inconsistent with net ecosystem production (NEP) rates during these two periods based on incubations. This inconsistency is attributed to the inflow of water masses with different chemical signatures and to the relatively short residence time of the water mass in the bay that was different during the two cruises. The spatial patterns of pCO<sub>2</sub> and AOU were unrelated to those of NEP rates upscaled from O<sub>2</sub> incubations, during the March cruise when residence time of the water mass in the bay was less than 3 d. In contrast, during the summer cruise, the spatial patterns of pCO<sub>2</sub> and AOU were consistent with those of NEP upscaled from O<sub>2</sub> incubations.

When the water residence time in the bay was long enough (10 d in June), a mass balance approach allowed the derivation of NEP estimates that are in fair agreement with those derived from direct metabolic estimates from incubated samples over the *Posidonia oceanica* meadow. However, such a mass balance approach requires a detailed physical study to determine the water residence time that is the largest source of uncertainty in the computations. Air-water flux of CO<sub>2</sub> (or O<sub>2</sub>) introduced a relatively small error on the NEP estimates based on this method, in contrast with other ecosystems characterized by much larger air-water fluxes such as estuaries (e.g. Gazeau et al., 2005<sup>1</sup>).

**Acknowledgements.** We would like to thank U. Riebesell as well as R. Bellerby and two anonymous reviewers for their useful comments and suggestions on our manuscript.

This research was supported by the European Union in the framework of the EUROTROPH project (contract # EVK3-CT-2000-00040), and by a CNRS/CGRI/FNRS/CSIC cooperation. We thank the officers, crew and technical staff of the Tethys II and Mytilus for full collaboration during the EUBAL cruises, D. Tailliez for operating the rosette and CTD and processing the

data during EUBAL-I, C. Copin-Montégut for providing the DYFAMED dataset, R. Biondo, E. Libert, R. Martínez, M.-D. Pizay, R. Santiago and J.-M. Théate for technical support. A. V. Borges and M. Frankignoulle are, respectively, a post-doctoral researcher and a senior research associate at the FNRS. C. Barrón benefited from a grant from the Balearic government, and N. Navarro benefited from a fellowship from the Spanish Ministry of Education, Culture and Sports.

Edited by: U. Riebesell

## References

- Allen, J. T., Alderson, S. G., Ruiz, S., Nurser, A. G., and Griffiths, G.: Shipboard VM-ADCP observations during RRS Discovery cruise 224, Internal Document n°21, Southampton Oceanography Centre, 1997.
- Atkinson, M. J. and Smith, S. V.: C:N:P ratios of benthic marine plants, *Limn. Ocean.*, 28 (2), 568–574, 1983.
- Barranguet, C., Herman, P. M. J., and Sinke, J. J.: Microphytobenthos biomass and community composition studied by pigment biomarkers: importance and fate in the carbon cycle of a tidal flat, *J. Sea Res.*, 38, 59–70, 1997.
- Bégovic, M. and Copin-Montégut, C.: Processes controlling annual variations in the partial pressure of CO<sub>2</sub> in surface waters of the central northwestern Mediterranean Sea (Dyfamed site), *Deep-Sea II*, 49 (11), 2031–2047, 2002.
- Benson, B. B. and Krause, D. J.: The concentration and isotopic fractionation of oxygen dissolved in fresh water and seawater in equilibrium with the atmosphere, *Limn. Ocean.*, 29 (2), 620–632, 1984.
- Bethoux, J. P. and Copin-Montégut, G.: Biological fixation of atmospheric nitrogen in the Mediterranean Sea, *Limn. Ocean.*, 31 (6), 1353–1358, 1986.
- Borges, A. V. and Frankignoulle, M.: Short-term variations of the partial pressure of CO<sub>2</sub> in surface waters of the Galician upwelling system, *Prog. Ocean.*, 51 (2–4), 283–302, 2001.
- Borges, A. V. and Frankignoulle, M.: Distribution of surface carbon dioxide and air-sea exchange in the upwelling system off the Galician coast, *Global Biogeochem.*, 16 (2), art. no. 1020, doi:10.1029/2000GB001385, 2002.
- Borges, A. V., Delille, B., Schiettecatte, L.-S., Gazeau, F., Abril, G., and Frankignoulle, M.: Gas transfer velocities of CO<sub>2</sub> in three European estuaries (Randers Fjord, Scheldt and Thames), *Limn. Ocean.*, 49(5), 1630–1641, 2004.
- Carrit, D. E. and Carpenter, J. H.: Comparison and evaluation of currently employed modifications of the Winkler method for determining dissolved oxygen in seawater: a NASCO Report, *J. Marine Res.*, 24, 286–319, 1966.
- Chen, C. T. A., Liu, K. K., and Macdonald, R.: Continental margin exchanges, in: *Ocean biogeochemistry*, edited by: Fasham, M. J. R., Springer, 53–97, 2003.
- Copin-Montégut, C.: A new formula for the effect of temperature on the partial pressure of CO<sub>2</sub> in seawater, *Mar. Chem.*, 25, 29–37, 1988.
- Copin-Montégut, C.: A new formula for the effect of temperature on the partial pressure of carbon dioxide in seawater, *Corrigendum*, *Mar. Chem.*, 27, 143–144, 1989.

- Copin-Montégut, C.: Alkalinity and carbon budgets in the Mediterranean sea, *Global Biogeochem.*, 7 (3), 915–925, 1993.
- Dickson, A. G.: Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K, *Deep-Sea A*, 375 (4), 755–766, 1990.
- Dickson, A. G.: pH buffers for sea water media based on the total hydrogen ion concentration scale, *Deep-Sea I*, 40 (1), 107–118, 1993.
- Duarte, C. M. and Cebrián, J.: The fate of marine autotrophic production, *Limn. Ocean.*, 41 (8), 1758–1766, 1996.
- Duarte, C. M. and Agustí, S.: The CO<sub>2</sub> balance of unproductive aquatic ecosystems, *Science*, 281 (5374), 234–236, 1998.
- Duarte, C. M. and Chiscano, C. L.: Seagrass biomass and production: a reassessment, *Aqua Bot.*, 65, 159–174, 1999.
- Duarte, C. M. and Prairie, Y. T.: Prevalence of heterotrophy in aquatic systems, *Ecosystems*, in press, 2005.
- Duarte, C. M., Agustí, S., Kennedy, H., and Vaqué, D.: The Mediterranean climate as a template for Mediterranean marine ecosystems: the example of the northeast Spanish littoral, *Prog. Ocean.*, 44 (1–3), 245–270, 1999.
- Frankignoulle, M.: Field measurements of air-sea CO<sub>2</sub> exchange, *Limn. Ocean.*, 33 (2), 313–322, 1988.
- Frankignoulle, M., Borges, A., and Biondo, R.: A new design of equilibrator to monitor carbon dioxide in highly dynamic and turbid environments, *Water Res.*, 35 (4), 1344–1347, 2001.
- Frankignoulle, M., Gattuso, J.-P., Biondo, R., Bourge, I., Copin-Montégut, G., and Pichon, M.: Carbon fluxes in coral reefs. 2. Eulerian study of inorganic carbon dynamics and measurement of air-sea CO<sub>2</sub> exchanges, *Mar. Ecol.-Pr.*, 145 (1–3), 123–132, 1996.
- Gattuso, J.-P., Frankignoulle, M., and Wollast, R.: Carbon and carbonate metabolism in coastal aquatic ecosystems, *Ann. R. Ecol.*, 29, 405–434, 1998.
- Gordon, D. C. J., Boudreau, P. R., Mann, K. H., Ong, J.-E., Silvert, W. L., Smith, S. V., Wattayakorn, G., Wulff, F., and Yanagi, T.: LOICZ biogeochemical modelling guidelines, *LOICZ Reports & Studies*, 5, 1–96, 1996.
- Griffiths, G.: Using 3DF Ashtech GPS heading for improving underway ADCP data, *J. Atmos. Oc.*, 11, 1135–1143, 1994.
- Hansen, H. P. and Koroleff, F.: Determination of nutrients, in: *Methods of seawater analysis*, edited by: Grasshoff, K., Kremling, K., and Ehrhardt, M., Weinheim, Wiley-VCH Verlag, 159–226, 1999.
- Hansen, J. W., Thamdrup, B., and Jørgensen, B. B.: Anoxic incubation of sediment in gas-tight plastic bags: a method for biogeochemical process studies, *Mar. Ecol.-Pr.*, 208, 273–282, 2000.
- Hedges, J. I., Baldock, J. A., Gelinas, Y., Lee, C., Peterson, M. L., and Wakeham, S. G.: The biochemical and elemental compositions of marine plankton: a NMR perspective, *Mar. Chem.*, 78 (1), 47–63, 2002.
- Hemminga, M. A. and Duarte, C. M.: *Seagrass Ecology*, Cambridge University Press, Cambridge, 2000.
- Holmer, M., Duarte, C. M., and Marbá, N.: Sulfur cycling and seagrass (*Posidonia oceanica*) status in carbonate sediments, *Biogeochem.*, 66, 223–239, 2003.
- Hopkinson, C. S. J. and Smith, E. M.: Estuarine respiration: an overview of benthic, pelagic and whole system respiration, in: *Respiration in aquatic ecosystems*, edited by: del Giorgio, P. A. and Williams, L. P. J., Oxford, Oxford University Press, 123–147, 2005.
- Jansà, J., Lopez-Jurado, J. L., Amengual, R., Reñones, O., and Morillas, I.: Variación anual e interanual de los factores fisicoquímico-biológicos generales del medio pelágico de la Bahía de Palma (Islas Baleares, España) desde Mayo de 1988 hasta Mayo de 1992, *Informes técnicos*, Instituto Español de Oceanografía, 152, 1994.
- Knap, A. H., Michaels, A. E., Close, A., Ducklow, H. W., and Dickson, A. G. (Eds.): *Protocols for the Joint Global Ocean Flux Study (JGOFS) core measurements*, JGOFS Report No. 19, Bergen, Norway, Unesco, 1996.
- Liss, P. S. and Merlivat, L.: Air-sea gas exchange rates: introduction and synthesis, in: *The role of air-sea exchange in geochemical cycling*, edited by: Buat-Menard, P., Dordrecht, D. Reidel Publishing Company, 113–127, 1986.
- Liu, K. K., Iseki, K., and Chao, S. Y.: Continental margin carbon fluxes, in: *The changing ocean carbon cycle: a midterm synthesis of the Joint Global Ocean Flux Study*, edited by: Hanson, R. B., Ducklow, H. W., and Field, J. G., Cambridge University Press, 187–239, 2000.
- McGillis, W. R., Edson, J. B., Ware, J. D., Dacey, J. W. H., Hare, J. E., Fairall, C. W., and Wanninkhof, R.: Carbon dioxide flux techniques performed during GasEx-98, *Mar. Chem.*, 75, 267–280, 2001.
- Navarro, N., Agustí, S., and Duarte, C. M.: Plankton metabolism and DOC use in the Bay of Palma, NW Mediterranean Sea, *Aquat. Mic. E.*, 37, 47–54, 2004.
- Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S., Liddicoat, M. I., Boutin, J., and Upstill-Goddard, R. C.: In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem.*, 14 (1), 373–387, 2000.
- Odum, H. T.: Primary production in flowing waters, *Limn. Ocean.*, 1 (2), 102–117, 1956.
- Oudot, C., Gerard, R., Morin, P., and Gningue, I.: Precise shipboard determination of dissolved oxygen (Winkler procedure) for productivity studies with a commercial system, *Limn. Ocean.*, 33 (1), 146–150, 1988.
- Pedder, M. A.: Interpolation and filtering of spatial observations using successive corrections and Gaussian filters, *Monthly Weather Review*, 121, 2889–2902, 1993.
- Platt, T., Gallegos, C. L., and Harrison, W. G.: Photoinhibition of photosynthesis in natural assemblages of marine phytoplankton, *J. Marine Res.*, 38, 687–701, 1980.
- Ramis, C., Jansà, A., and Alonso, S.: Sea breeze in Mallorca, A numerical study, *Meteor. Atm.*, 42, 249–258, 1990.
- Redfield, A. C., Ketchum, B. H., and Richards, F. A.: The influence of organisms on the composition of sea-water, in: *The sea*, edited by: Hill, M. N., New York, Wiley, 2, 26–77, 1963.
- Rey, J. and Diaz del Rio, V.: Cartografía de los fondos marinos de la bahía de Palma (Baleares, España): distribución de las praderas vegetales y sedimentos superficiales, *International Workshop on Posidonia Oceanica Beds*, Porquerolles, 1984.
- Roy, R. N., Roy, L. N., Vogel, K. M., Porter-Moore, C., Pearson, T., Good, C. E., Millero, F. J., and Campbell, D. M.: The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C, *Mar. Chem.*, 44 (2–4), 249–267, 1993.
- Smith, S. V. and Hollibaugh, J. T.: Coastal metabolism and the

- oceanic organic carbon balance, *Rev. Geophys.*, 31 (1), 75–89, 1993.
- Thamdrup, B. and Canfield, D. E.: Benthic respiration in aquatic sediments, in: *Methods in ecosystem science*, edited by: Sala, O. E., Jackson, R. B., Mooney, H. A., and Howarth, R. W., New York, Springer, 86–103, 2000.
- Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, 97 (C5), 7373–7382, 1992.
- Wanninkhof, R. and McGillis, W. R.: A cubic relationship between air-sea CO<sub>2</sub> exchange and wind speed, *Geophys. Res. Lett.*, 26 (13), 1889–1892, 1999.
- Weiss, R. F.: Carbon dioxide in water and seawater: the solubility of a non-ideal gas, *Mar. Chem.*, 2, 203–215, 1974.
- Wollast, R.: Evaluation and comparison of the global carbon cycle in the coastal zone and in the open ocean, in: *The Sea*, edited by: Brink, K. H. and Robinson, A. R., New York, John Wiley & Sons, 10, 213–252, 1998.