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# Nutrient dynamics and ecosystem metabolism in the Bay of Blanes (NW Mediterranean)

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**Abstract.** The dynamics of the nutrient pools and their stoichiometry as well as their control by ecosystem metabolism (benthic and planktonic) and benthic–pelagic exchanges (sedimentation rates and sediment waterfluxes) were examined in the Mediterranean littoral (Blanes Bay, NE Spain). Dissolved organic nitrogen comprised about half of the nitrogen present in the water column and the carbon pool was dominated by the inorganic pool (95% of the carbon present in the water column). The dissolved and particulate organic pools were deficient in P relative to C and N, indicating a rapid recycling of P from organic matter. The pelagic compartment was heterotrophic, supported by significant allochthonous inputs of land material, which also contributed greatly to the sedimentary inputs (37% of total sedimenting carbon). In contrast, the benthic compartment was autotrophic, with the excess net benthic community production balancing the deficit in pelagic community production, leading to metabolic equilibrium at the station studied. Sedimentary inputs of nitrogen, phosphorus and silicon exceeded the benthic release, indicating that the benthic compartment acted as a sink for nutrients, consistent with its autotrophic nature. Carbon inputs to the benthic compartment also exceeded requirements, due to the allochthonous subsidies to the system, so that the benthic compartment stored or exported organic carbon.

## Introduction

Widespread eutrophication has stimulated research on nutrient dynamics in coastal ecosystems (e.g. Smith and Hollibaugh 1989; Justic et al. 1995; Nixon et al. 1995; Vidal et al. 1999a). However, the resulting knowledge is biased towards nutrient-rich or eutrophied systems (Rosenberg 1985; Westernhagen et al. 1986; Andersson and Rydberg 1988; Vidal et al. 1999a), and accounts of nutrient dynamics in oligotrophic coastal waters are still few. Whereas nutrient dynamics in eutrophied coastal systems are dominated by allochthonous inputs (Marchetti et al. 1989; Turner and Rabalais 1991) nutrient dynamics in oligotrophic coastal waters are strongly dependent on internal recycling processes (Thingstad and Sakshaug 1990; Ittekkot and Laane 1991). These are linked to respiratory processes, much of which occur in the sediments (Smith

and Hollibaugh 1993; Heip et al. 1995), thereby requiring a close coupling between benthic and pelagic nutrient cycling and metabolism. The extent of the coupling between benthic and pelagic nutrient cycling and metabolism may change seasonally because of the possible stimulation of respiration rates with increasing temperature, which may lead to faster nutrient recycling. However, winter mixing may also supply nutrients entrained from deeper offshore waters to the coastal zone of temperate regions, relaxing the dependence on remineralization as a source of nutrients in winter.

The Mediterranean littoral zone is still largely oligotrophic, although eutrophication problems are also increasing in the Mediterranean (Vidal et al. 1999a; UNEP 2000). Moreover, because of the characteristic episodic nature of rainfall in the Mediterranean region (e.g. Duarte et al. 1999), nutrient inputs from land occur in pulses (Bavestrello et al. 1995; Buscail et al. 1995), rather than as a continuous supply. As a consequence, the nutrient dynamics of the Mediterranean coastal waters are dependent, as those of coastal waters elsewhere, on the complex interplay between land inputs, marine supply in winter and recycling processes from the sediments. Each of these sources involve a differential partitioning between the various nutrient pools involved, with land-derived inputs delivering both organic and inorganic nutrients (Cauwet and Martin 1982; Meybeck 1982; Cauwet et al. 1990), and marine supply and sediment release delivering inorganic nutrients. As a consequence, the concentrations of nutrients, their stoichiometric balance and the partitioning between inorganic and organic (dissolved and particulate) nutrient pools all may vary significantly over time, likely leading to complex biogeochemical dynamics in Mediterranean littoral waters.

Here we contribute to our knowledge on nutrient dynamics in temperate oligotrophic coastal waters by assessing the nutrient partitioning in the Bay of Blanes (NW Mediterranean). To this end we describe the dynamics of the nutrient pools and their stoichiometry as well as their control by ecosystem metabolism (benthic and planktonic) and benthic–pelagic exchanges (sedimentation rates and sediment water fluxes).

## Methods

The study was conducted in the Bay of Blanes located in the North Western Mediterranean Spanish coast (Figure 1; 41°40.19′ N 2°47.11′E), an open, oligotrophic coastal area (cf. Duarte et al. 1999; Lucea et al. 2003). The Bay of Blanes receives terrestrial inputs from the Tordera River as well as urban runoff from the town of Blanes, which receives a high number of tourists during summer. The sediments in the Bay are sandy, with an average organic content of 0.4% of the dry weight and remain oxic to a depth of about 10 cm (Marbá and Duarte 2001).

Subsurface water samples were collected weekly between 1996 and 1997 from a permanent station 1 km offshore, at a depth of 15 m, where the water column

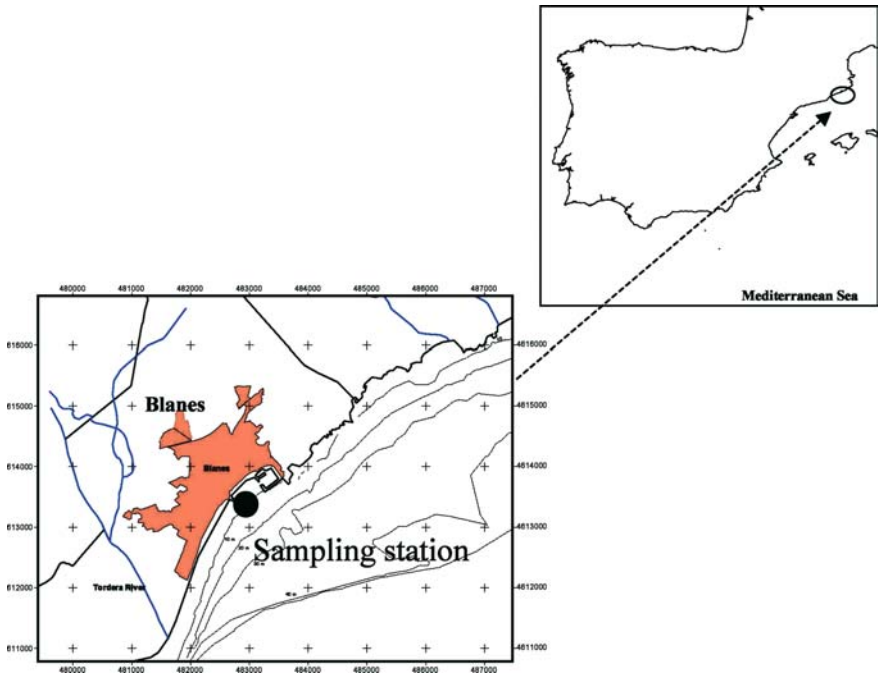


*Figure 1.* Location of the study area.

remains well mixed throughout the year (Lucea et al. 2003). Samples, collected on acid-washed polyethylene bottles were taken to the laboratory and processed within 30 min from collection. Samples for dissolved nutrient analyses were immediately frozen. Samples for particulate organic carbon (POC), nitrogen (PON) and phosphorus (POP) analyses were filtered (about 2 L) through pre-combusted Whatman GF/C glass fiber filters and stored frozen for subsequent analyses. A variable water volume (50–250 mL, depending on phytoplankton biomass) was filtered through 0.45 $\mu$m Whatman GF/F filters for spectrofluorometric analysis of chlorophyll *a* concentration (Parsons et al. 1984). The filters were homogenized and kept refrigerated for ca. 6 h in the dark while pigments were extracted in 90% acetone. Fluorescence was measured, following extraction, in a Turner Designs fluorometer calibrated with pure chlorophyll *a* (Sigma Co.)

The downward particle flux was measured at monthly intervals between October 1996 and November 1997 using sediment traps. The sediment traps consisted of six cylindrical PVC tubes (cross-sectional exposed area = 31.81 $cm^2$) with an aspect ratio of 7.8 to prevent resuspension losses (Hardgrave and Burns 1979; Blomquist and Hakanson 1981). The array of traps were mounted on a 1 m diameter stainless steel circular frame inserted into the sediments so as to raise the mouth of the traps 1.5 above

the sediment surface. This placed the traps, above the depth where sediment is resuspended during storms (Gacia et al. 1999, 2002). The traps were deployed by SCUBA divers for a total period of 7 days, and capped before returning them to the surface. At the laboratory the content of the tubes was filtered through 25 mm pre-combusted GF/F filters, which were subsequently dried for 24 h at 60 °C and used for POC, PON, POP and biogenic silica (bioSi) determinations.

Each month SCUBA divers collected 10 plexiglass corers (Ø = 4.3 cm; $H$ = 33 cm) containing 8 cm of sediments, which were brought to the laboratory to estimate sediment water fluxes, and the water overlying the sediments replaced by water collected from the sampling station before the flux measurements were initiated. Flux measurements were conducted by incubating the cores at *in situ* temperature for 24 h, with five cores exposed to light (200 $\mu$mol photon $m^{-2}$ $s^{-1}$, the average incident irradiance on the sediments at the sampling station), while the rest were kept in the dark. Dissolved inorganic $PO_4^{3-}$, $NH_4^+$, $NO_3^-$ $Si(OH)_4$ and $O_2$ fluxes were determined from the changes in concentrations from the beginning to the end of the incubation period. Nitrate fluxes were consistently within the error of the replicates so that nitrogen fluxes are represented by the ammonium fluxes alone. Oxygen concentrations remained above 4 mg $L^{-1}$ throughout the experiments, precluding the development of anoxic conditions.

Samples for nutrient analysis were thawed and $PO_4^{3-}$ and $Si(OH)_4$ concentrations were measured spectrophotometrically using a 10-cm cuvette cell (Koroleff 1976; Grasshoff 1983). $NO_3^-$ + $NO_2^-$ concentrations were determined by the colorimetric methods of Grasshoff (1983). The detection limit of dissolved nutrient concentrations were 0.01 mol $L^{-1}$ for spectrophotometric determinations of $PO_4^{3-}$ and $Si(OH)_4$, and 0.02 mol $L^{-1}$ for $NO_3^-$ + $NO_2^-$ analyses. Ammonium concentrations remained below detection limit (about 0.05 mol $L^{-1}$) throughout most of the study. Filters for POC and PON analyses were exposed to concentrated hydrochloric acid fumes for 30 min to remove any inorganic carbon, which may interfere with the analysis. Measurements were carried out using a Perkin-Elmer 240 CHN analyzer. Samples for POP determination were oxidized in acidic persulfate solution and then analyzed as soluble reactive phosphorus following the methods outlined in Murphy and Riley (1962) and Solórzano and Sharp (1980).

The samples for $\delta^{13}$C-POC analysis were filtered through pre-combusted (3 h at 500 °C) GF/F filters and frozen. Filters for $\delta^{13}$C-POC analyses were fumed with concentrated hydrochloric acid overnight to remove calcium carbonate, dried and loaded into small pre-combusted quartz tube with Cu, CuO and Ag foil and subsequently placed inside a larger quartz tube, which was evacuated and sealed. The samples were combusted at 900 °C for 3 hours, the resulting gases were distilled cryogenically in a vacuum line and the separated $CO_2$ was analyzed on a VG SIRA II mass spectrometer. Precision $\delta^{13}$C-POC of an internal laboratory standard was 1SD = 0.06‰ O. The carbon isotope

ratios are reported in per mil (‰) relative to PDB standard:

$$\delta^{13}\mathrm{C} = [(R_{\mathrm{sample}}/R_{\mathrm{standard}}) - 1] \times 1000$$

where $R = {}^{13}\mathrm{C}{:}{}^{12}\mathrm{C}$ ratio.

Dissolved organic nitrogen (DON) and phosphorus (DOP) concentrations were estimated as the difference between the total dissolved nutrient pools and the dissolved inorganic nutrient concentrations. Biogenic silica samples were filtered through a 47 mm polycarbonate Nuclepore filter (0.6 $\mu$m pore size) and dried for 12 h at 60 °C. The determination of biogenic silica followed the NaOH/HF digestion method (Ragueneau and Tréguer 1994).

Samples for DOC analyses were filtered through pre-combusted (400 °C for 2 h) GF/F filters, and kept frozen until analysis. DOC was determined on 2 mL samples, after acidification with 10 $\mu$L 85% $H_3PO_4$ and sparging with $N_2$ for 5 min, by high temperature oxidation using an MQ1001 TOC analyzer (Qian and Mopper 1996). Dissolved inorganic carbon (DIC) was determined by a potentiometric method using a Mettler DL21 automatic titration device. A known amount of seawater was placed into a conical flask where it was titrated with a solution of 0.1 N HCl at *in situ* temperature. The acid was prepared with an accuracy of 0.0002 mol $L^{-1}$ to which sodium dichloride and sodium sulfate were added to approximate the solution to the ionic strength of sea water, so as to maintain the activity coefficients constant during the titration (Grasshof 1983). The volume dispensed by the burette (mL) and the signal (mv) were recorded automatically to calculate the first derivative (mv/mL) which represents the smallest gradient in the flat part of the titration curve. The reagent consumption for the $CO_3^-(V_1)$ and $2CO_3^- + HCO_3^-(V_2)$ titration points was recorded. Then DIC was calculated as

$$\sum \mathrm{CO}_2 = (V_2 - V_1) \cdot [\mathrm{HCl}]/(\mathrm{ml\ of\ sample})$$

Planktonic community metabolism was estimated weekly along the 2-year study. Water samples were carefully siphoned into 15 125-mL narrow-mouthed Winkler bottles. Five of the bottles were immediately processed to measure the initial oxygen content present in the samples, five transparent ones were incubated for 24 h in the light (200 $\mu$mol photon $m^{-2}$ $s^{-1}$) and the remaining five were incubated for 24 h in the dark at *in situ* temperature. The production by the pelagic community at Blanes Bay is saturated at irradiances ranging from 50 to 200 $\mu$mol photon $m^{-2}$ $s^{-1}$, depending on the season (Satta et al. 1996a), so that exposure to an increased irradiance would have no consequence for the estimated GPP nor the metabolic balance of the planktonic community. Dissolved oxygen concentration was measured using high-precision Winkler titration after Carrit and Carpenter (1966), using a Mettler DL21 automatic titration device for the potentiometric (redox electrode) end-point detection (Oudot et al. 1988). The average coefficient of variation of the dissolved oxygen concentration was about 0.35% and the resulting detection limit for net production and respiration was about 0.0009 mg $O_2$ $L^{-1}$ $h^{-1}$. Oxygen evolution

rates were converted into carbon incorporation assuming a photosynthetic and respiratory quotient of 1, and were converted to daily values using the observed corresponding photoperiod. Respiration rates ($R$) were determined from the oxygen change in the dark bottles, net community production (NCP) was determined from the oxygen change in the clear bottles, corrected for photoperiod, and gross primary production (GPP) was calculated as the sum of $R$ and $P$. The same procedure was followed for determining benthic community metabolism from core incubations. The estimates of benthic respiration rates may underestimate the total rates, as anaerobic processes were unaccounted for.

## Results

Seawater temperature varied from a mean winter minimum of 11.1 °C to a mean summer maximum of 24.4 °C (Figure 2a). CTD profiles showed that the water column at the sampling station remained well mixed in this exposed location throughout the study, as the summer thermocline was established offshore at about 40 m depth. The chlorophyll $a$ concentration showed late winter maxima in the water column (Figure 2b), corresponding to the main algal bloom in these waters (Duarte et al. 1999). The sediments, which remained well-illuminated due to the high transparency of these waters (Duarte et al. 1999), throughout the study, also supported an important microphytobenthic community, with a chlorophyll density half, on average, those of the water column, but that were comparable or even exceeded those in the water column during spring and summer (Figure 2b).

Dissolved inorganic nutrients varied greatly during the study, with high (up to 2 $\mu$M) nitrate concentrations during winter and low values (<0.5 $\mu$M) during summer (Figure 2c). Silicate concentrations remained low (<1.0 $\mu$M) throughout 1997, but reached high concentrations (up to 2 $\mu$M) values during winter and summer 1996 (Figure 2d). Phosphate concentrations remained low (<1 $\mu$M) throughout the study (Figure 2e). The average dissolved inorganic nitrogen concentration was similar to that of silicate at 0.6 $\mu$M, while phosphate concentration averaged 0.13 $\mu$M along the study period (Table 1). The ratio between silicate and dissolved inorganic nitrogen also showed a clear seasonality, with generally low values (<4), except for sporadic high values (up to 20) during summer, when the nitrate pool is depleted. These patterns resulted in consistent changes in the inorganic nutrient ratios, with the N:P ratio being close to the Redfield ratio of 16 during the winter period and much lower (<5) between May and August (Figure 3).

The elemental concentrations in the particulate pool were lower during winter, and reached the maximum values during spring and late summer, with biogenic silicon concentrations showing a clear peak in early winter (Figure 4). The average concentration of bioSi was similar to that of PON (Table 1), but the particulate material was relatively enriched in N relative to C and P, having a lower C/N and a higher N/P ratio than the dissolved inorganic pool (Table

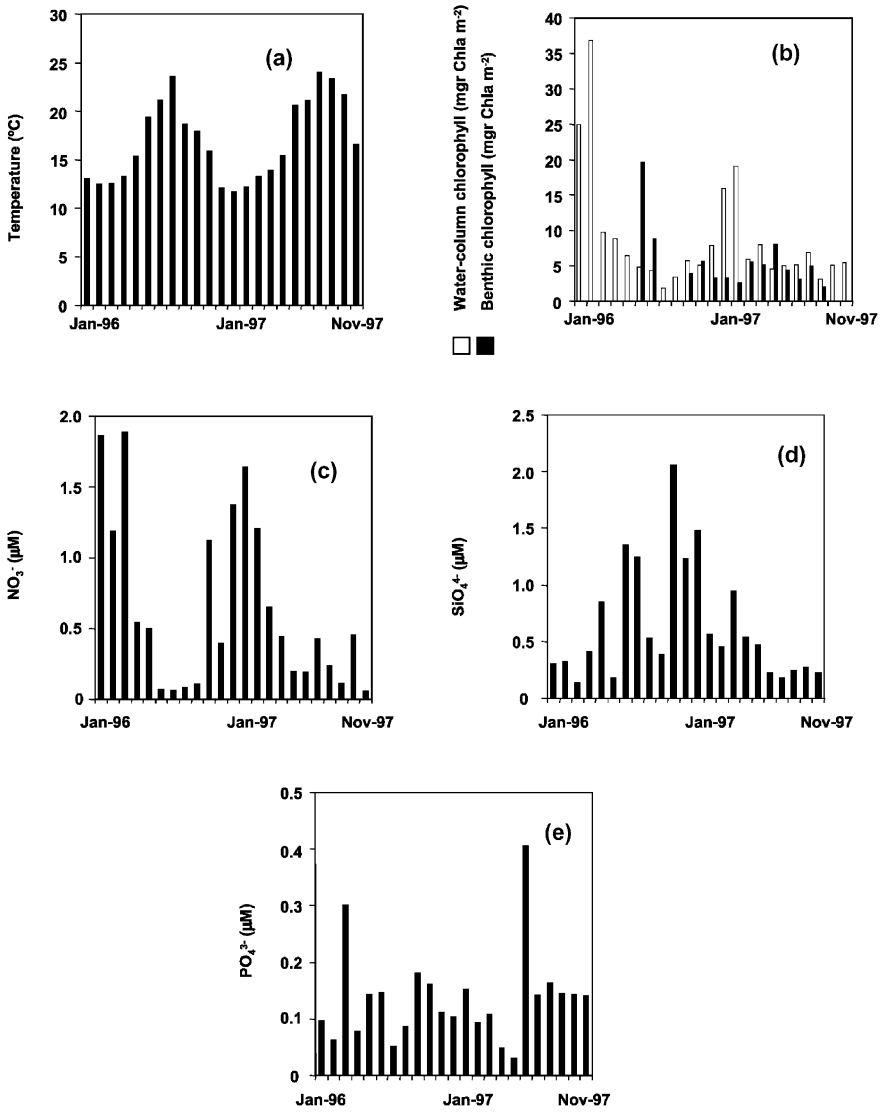


*Figure 2.* Temporal variation of mean monthly dissolved inorganic and particulate organic nutrient concentrations, surface seawater temperature and water-column and benthic chlorophyll *a* concentration in the Blanes Bay for 1996 to 1997.

1). DOC concentrations ranged from a minimum of 67 $\mu$M in winter to a maximum value of 160 $\mu$M observed in spring and late summer. DOC values were comparable to open ocean concentrations. DON and DOP concentrations showed a similar pattern, with the average DON and DOP concentrations being comparable to those of PON and POP (Table 1), and dissolved

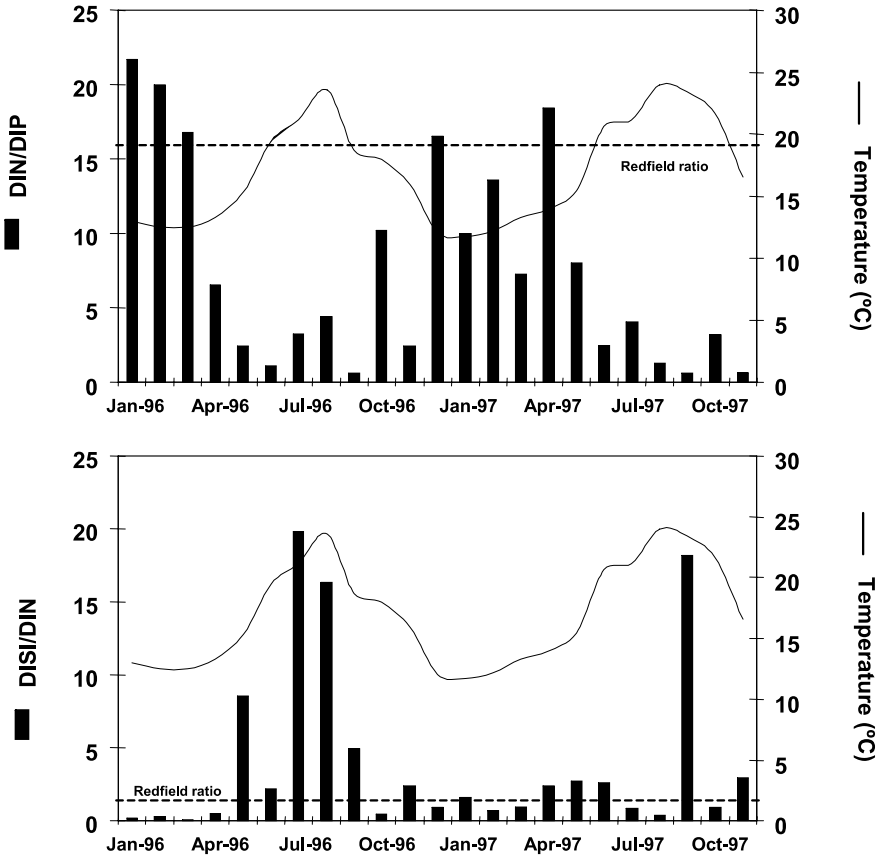


*Figure 3*. Temporal variation of of mean monthly of dissolved inorganic nutrient ratios in the Blanes Bay. The solid lines indicate the Redfield N/P and Si/N ratios.

organic nutrients reaching the highest concentrations in late summer. In contrast, carbon was dominated by the inorganic pool, which comprised, on average 95% of the carbon present in the water column (Table 1), phosphorus showed a balanced partitioning between the three different pools (Table 1), and nitrogen was dominated by the dissolved organic pool, which comprised about half of the total nitrogen present in the water column (Table 1). The stable carbon isotope value of the POC material was $-26.02‰$ (Table 1), similar to values of Mediterranean land vegetation (Dauby 1989), suggesting an important contribution of land-derived material.

The benthic community was autotrophic ($P > R$) in 6 of the 11 experiments conducted. Gross benthic primary production rates were highest (up to 98 mmol C $m^{-2}$ $day^{-1}$) in summer and low in winter, except for a highly productive event recorded in February 1997 (Figure 5). Respiration rates were

*Table 1.* Average ($\mu$mol $L^{-1}$ ± SE) nutrient concentrations and average ratios for particulate organic matter, dissolved inorganic and dissolved organic matter pools in the Bay of Blanes (1996–1997). Isotopic composition values are expressed in ‰.

| Element | DIM | DOM | POM | Elemental ratios | Average ratios | Pool ratios | Average ratios |
|---|---|---|---|---|---|---|---|
| C | 2409.8 ± 41.5 | 91.94 ± 5.7 | 11.17 ± 0.75 | DIN/DIP | 7 | DIC:DOC | 26 |
| N | 0.64 ± 0.09 | 2.59 ± 0.4 | 2.12 ± 0.18 | DISi/DIN | 4 | DIN:DON | 0.25 |
| P | 0.13 ± 0.02 | 0.1 ± 0.02 | 0.12 ± 0.01 | DOC/DON | 35 | DIP:DOP | 1.3 |
| | | | | DON/DOP | 24 | | |
| Si | 0.61 ± 0.08 | | | POC/PON | 6 | | |
| BioS | | | 1.89 ± 0.78 | PON/POP | 22 | | |
| | | | | DISi:DIN:DIP | 14:7:1 | DIC:DOC:POC | 219:8:1 |
| | | | | DOC:DON:DOP | 857:24:1 | DIN:DON:PON | 0.32:1.3:1 |
| | | | | POC:bioS:PON:POP | 124:31:22:1 | DIP:DOP:POP | 1:0.8:1 |
| $\delta^{13}$C (land derived material) | | | −26.02 ± 0.02 | | | | |

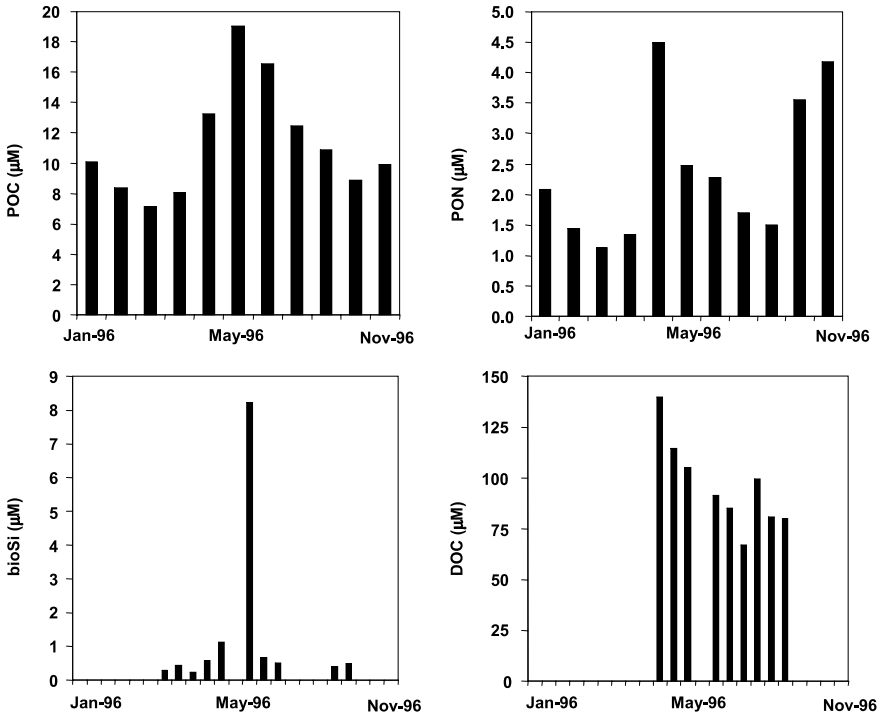


*Figure 4*. Temporal variation of mean monthly of POC, PON, POP and biogenic silica (bioSi) concentrations in the Blanes Bay for 1996 to 1997.

also highest in summer with the $P/R$ ratio averaging 1.5 ± 0.5, yielding an annual gross primary production of 19.46 ± 4.47 mol C $m^{-2}$ $year^{-1}$, a respiration rate of 15.69 ± 3.71 mol C $m^{-2}$ $year^{-1}$ and a net benthic community production of 3.77 ± 0.33 mol C $m^{-2}$ $year^{-1}$. In contrast, the pelagic compartment was heterotrophic, with a seasonal pattern characterized by high respiration and gross production rates in summer and lower values in winter (Figure 5). Planktonic respiration exceeded gross primary production in 40% of the 24 months of observation,with an average $P/R$ ratio of 0.64 ± 0.07. The annual pelagic gross primary production (12.90 ± 1.85 mol C $m^{-2}$ $year^{-1}$) was of the same order of magnitude than the benthic gross primary production, the annual pelagic respiration rate was 21.57 ± 2.06 mol C $m^{-2}$ $year^{-1}$ and the net planktonic community production was calculated at −8.67 ± 1.79 mol C $m^{-2}$ $year^{-1}$, indicative of a heterotrophic planktonic compartment. Overall, integrated system gross primary production (pelagic + benthic) of 32.36 ± 4.83 mol C $m^{-2}$ $year^{-1}$ was in close balance with the integrated respiration rates of 37.26 ± 4.2 mol C $m^{-2}$ $year^{-1}$, suggesting that the system is in metabolic balance, at least for the sampling station.

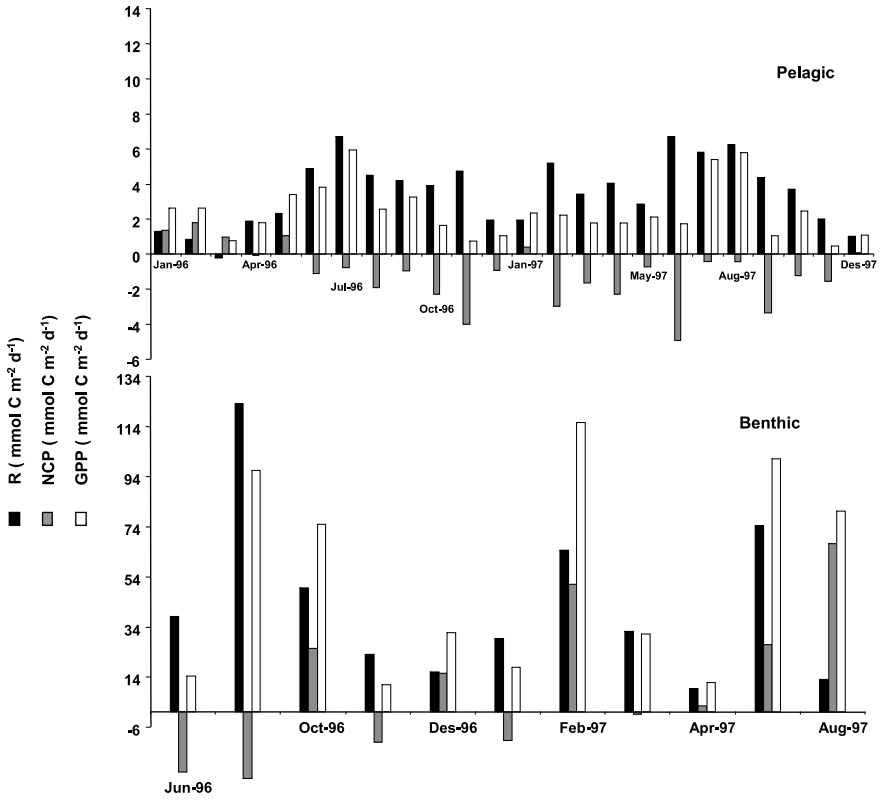


*Figure 5*. Mean monthly respiration (R), gross primary production (GPP) and net community production (NCP) for the pelagic and benthic compartments at the Bay of Blanes.

In addition to the organic inputs derived from its significant gross production, the benthic compartment received an important sedimentary input of organic matter. The bulk sedimentation was relatively low from the beginning of February to mid-September (Figure 6), averaging 14 g DW $m^{-2}$ $day^{-1}$, but increased significantly in October, reaching a maximum in November of 96 g DW $m^{-2}$ $day^{-1}$ with a secondary local maximum of 33 g DW $m^{-2}$ $day^{-1}$ in April. These peaks coincided with periods of intense rain and discharge from the Tordera River to the Bay of Blanes, clearly indicated by relatively low salinity values (34.5–36.8 psu). The corresponding POC flux ranged over two orders of magnitude from 0.16 mmol C $m^{-2}$ $day^{-1}$ to a maximum of 60 mmol $m^{-2}$ $day^{-1}$, and an average flux of 27.3 mmol C $m^{-2}$ $day^{-1}$ (Figure 6). The depositional fluxes of PON, POP and bioSi were temporally variable (Figure 6), and showed stoichiometric relationships indicative of a sedimentary flux relatively enriched in organic carbon and, particularly, bioSi, and depleted in nitrogen and phosphorus relative to the sestonic pool (Tables 1 and 2). The stable carbon isotope values in the material

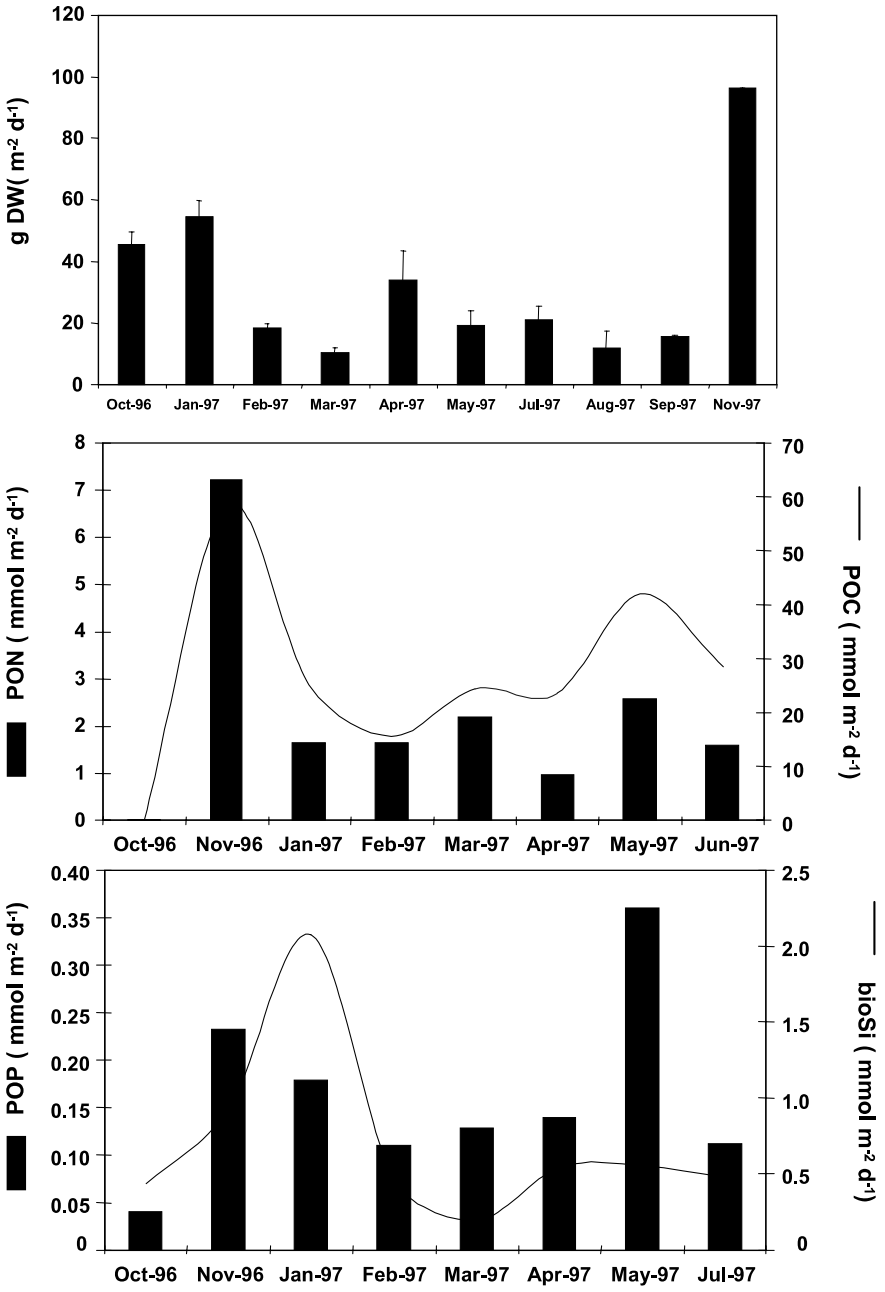


*Figure 6*. Total depositional fluxes of material (as dry weight DW), POC, PON, POP and $BiO_2$ at the Bay of Blanes.

*Table 2.* Mean ± SE sedimentary fluxes of material and sediment water fluxes in the Bay of Blanes (1996). Isotopic composition values are expressed in ‰. Average nutrient fluxes and respiration of sedimentary record in Blanes Bay (1996).

| | Sediment trap fluxes Average ± SE | Sedimentary flux ratio | Sediment trap $\delta^{13}C$ Average ± SE |
|---|---|---|---|
| POC (mol $m^{-2}$ $year^{-1}$) | 9.96 ± 2.4 | | −23.74 ± 0.92 |
| PON (mol $m^{-2}$ $year^{-1}$) | 0.81 ± 0.30 | | |
| POP (mol $m^{-2}$ $year^{-1}$) | 0.06 ± 0.01 | | |
| bioS (mol $m^{-2}$ $year^{-1}$) | 0.19 ± 0.07 | | |
| DW (g $m^{-2}$ $year^{-1}$) | 9349.22 ± 2823 | | |
| POC:bioS:PON:POP | | 159:50:12:1 | |
| POC:PON | | 14 | |
| Sediment water fluxes (mol $m^{-2}$ $year^{-1}$) | | | Average ± SE |
| $PO_4^{3-}$ | | | 0.013 ± 0.005 |
| $SiO_4^{4-}$ | | | 0.016 ± 0.002 |
| $NH_4^{+}$ | | | 0.005 ± 0.003 |
| Respiration (mol C $m^{-2}$ $year^{-1}$) | | | 15.7 ± 3.71 |

collected in the sediment trap (Table 2) were similar to that in the seston, and tended to be lighter, resembling that of land-derived carbon (−26.02 ± 0.02‰), during periods of high sedimentary flux, which corresponded with high river discharge.

Benthic remineralization processes released modest, but significant amounts of nutrients to the water column, despite the net autotrophic metabolism of the sediment community (Table 2). The sediment nutrient efflux varied by two-orders of magnitude along the study for silicate, phosphate and ammonium (Figure 7). The sediment efflux of silicate and phosphate followed similar patterns, with high release rates following the collapse of the winter phytoplankton bloom as well as after episodes of intense discharge from the Tordera River (Figures 2, 6 and 7). The ammonia efflux showed a contrasting pattern (Figure 7). The annual release rate of N, P and Si was much lower (4–100-fold) than the corresponding depositional supply ($p < 0.05$ for all elements, Table 2), particularly so for nitrogen, showing a high nutrient retention – or possibly loss through denitrification in the case of nitrogen – in the benthic compartment.

## Discussion

The Bay of Blanes showed elevated nutrient concentrations relative to the open ocean, where summer dissolved inorganic nutrient concentrations are typically below detection limit, except for silicate (Lucea et al. 2003). The elevated nutrient concentrations in the Bay of Blanes likely derive from inputs from

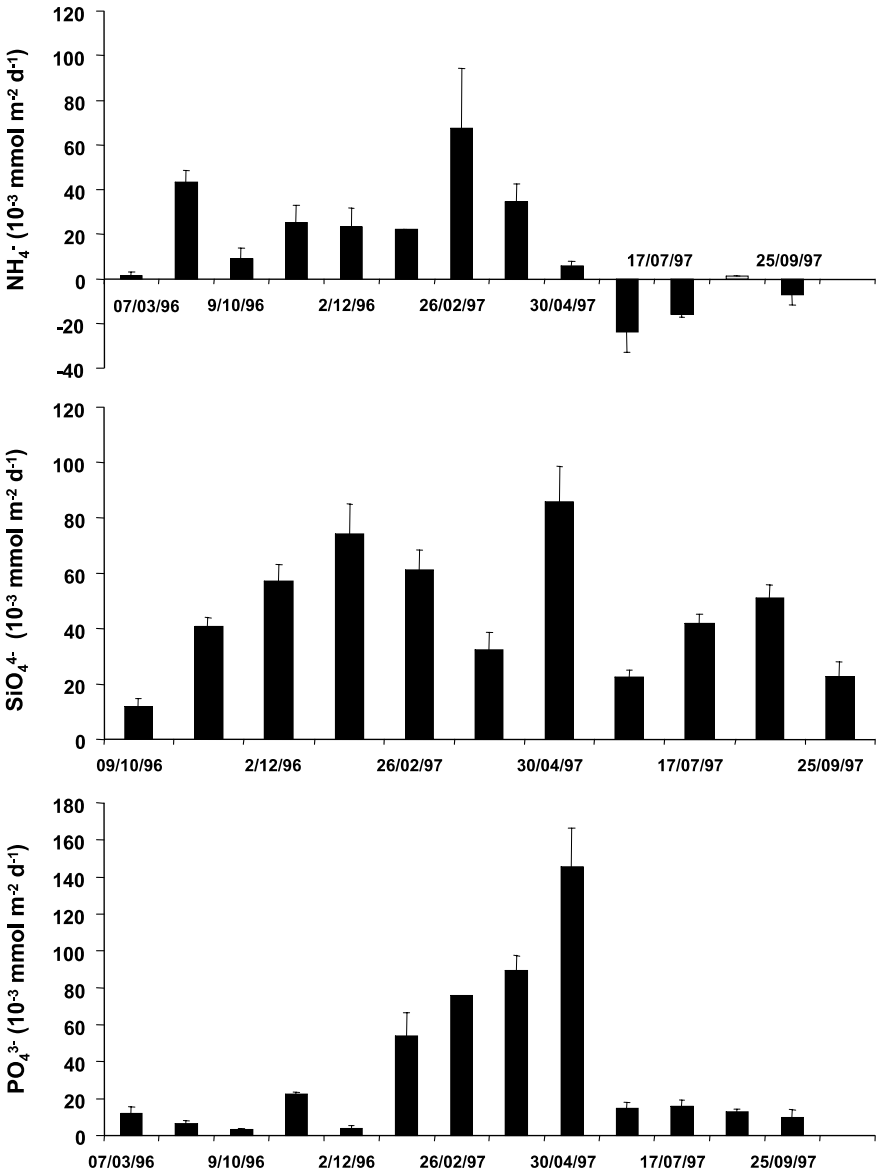


*Figure 7.* Mean monthly sediment–water dissolved inorganic nutrient fluxes at the Bay of Blanes. Negative values denote uptake by the sediment compartment.

land, through the combined discharges of the Tordera River and urban discharges from the town of Blanes.

The average elemental ratios in the total particulate and dissolved organic pools are indicative of acute phosphorus depletion in the Bay of Blanes (see

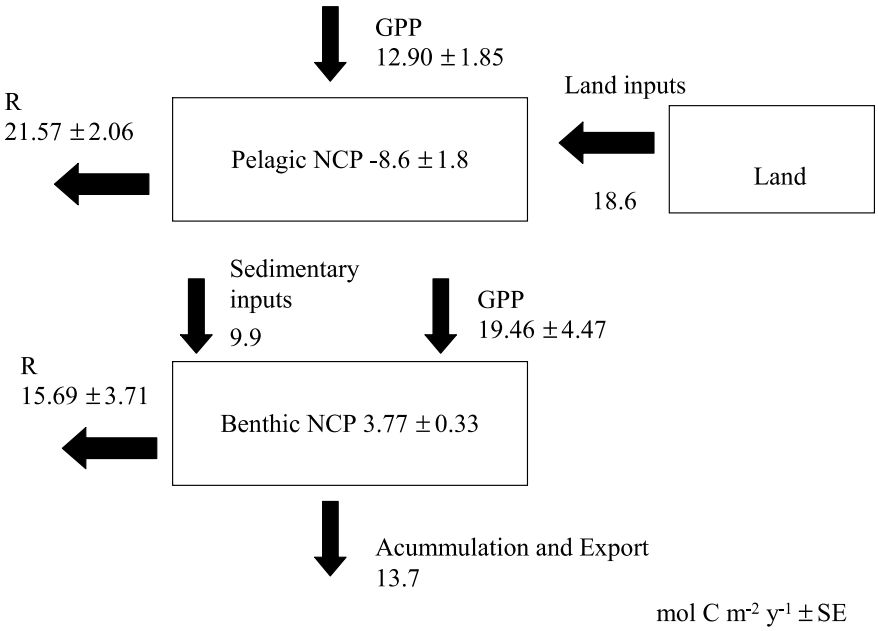


*Figure 8*. A summary depiction of the carbon fluxes in the Blanes Bay (NW Mediterranean).

Table 1), a general feature of the biogenic layer in the Mediterranean sea (Berland et al. 1980; Minas et al. 1988; Krom et al. 1999; Lucea et al. 2003), although this is not reflected in the DIN:DIP ratios, which are relatively low. This situation varied seasonally, with no evidence of such deficiency in winter (see Figure 2) when water mass circulation, influenced by the inflow of cold and low-salinity waters advected from continental slope waters off the Blanes canyon (Masó and Tintoré 1991; Rojas et al. 1995; Granata et al. 1999), entrains deeper waters into the littoral zone yielding DIN:DIP ratios higher than the average value of 7. Relatively high amounts of silica delivered from episodic land inputs enhance the relative phosphorus depletion, showing an important role of events of high rainfall and river discharge in determining the nutrient partitioning within the water column.

In addition to the important role of the exchanges and inputs with land and the ocean, the local stoichiometric C, N, P and Si ratios in the Blanes Bay are also dependent on local ecosystem processes. Nutrient assimilation by phytoplankton is responsible for the decline of nutrients from winter to summer. On the other hand, organic matter release by phytoplankton cell lysis (Agustí and Duarte 2000), would yield an increase in dissolved organic carbon from spring to summer and a greater importance of dissolved organic over inorganic nutrients in the water column during summer. The elemental ratios in the dissolved organic pool (DOC:DON = 35 and DOC:DOP = 875) are indicative of a faster recycling rates for nitrogen and, particularly phosphorus, than

for carbon. The DOC:DON:DOP ratio in the Bay of Blanes was somehow lower than the average ratio reported for the biogenic layers of the NW Mediterranean (DOC:DON:DOP = 1984:66:1; Lucea et al. 2003) which suggests a more labile pool of DOM and consequently more oxidative activity in the waters of the Bay of Blanes than in the open ocean.

Indeed, the pelagic component in the Bay of Blanes was found to be heterotrophic on an annual balance (Figure 8), as reported for this system in the past (Satta et al. 1996b). Planktonic and benthic respiration rates were within the mid range of rates reported for other coastal pelagic communities (Hopkinson and Smith 2004). Planktonic respiration rates were particularly high in the summer (see Figure 4), also consistent with previous results (Satta et al. 1996b), suggesting an important recycling of nutrients within the water column. The faster recycling of nutrients relative to carbon in the organic matter pool is also reflected in the differences in the average elemental ratios between the sestonic material, with POC:PON ratios similar or below the Redfield value of 6.6 (cf. Table 1) in summer, when nitrate is depleted, compared to the average POC:PON ratio of the sedimenting material of 12 (see Table 2). This situation coincides with the seasonal minimum in sedimentation values (Figure 6). Indeed, the finding of a significant sedimentary flux despite the observation of an heterotrophic planktonic component implies an important allochthonous input of materials to support this sedimentary flux. The estimated annual organic carbon deposition at Blanes Bay (Table 2) was lower than sedimentation rates previously reported for the continental shelf margin of the Northwestern Mediterranean (15.2 mol C $m^{-2}$ $year^{-1}$, Buscail et al. 1990; 30.4 mol C $m^{-2}$ $year^{-1}$, Mónaco et al. 1990). The likely source of organic matter is the adjacent terrestrial compartment through the inputs by the Tordera River. This suggestion was tested through the evaluation of the sources of organic carbon as derived from the stable isotope signatures. The average isotopic composition of organic carbon in the sedimentary flux deposition was more negative ($-23.74 \pm 0.92‰$ $\delta^{13}C$) than those found in sediment trap studies in the Western Mediterranean basin (Dauby et al. 1995) and than those characteristic of Mediterranean phytoplankton (Fontugne and Duplessy 1981; Dauby 1989 and Faganeli et al. 1994). These comparisons suggested an important terrestrial component in the sedimentary flux. We calculated the relative contribution of planktonic material and terrestrial-derived material (see Table 1) to the settling carbon flux (see Table 2) using the equation:

$$\delta^{13}C_{\text{sedimenttrap}} = \delta^{13}C_{\text{terrestrial·f}} + \delta^{13}C_{\text{plankton}}(1 - f)$$

where $f$ is the fraction derived from terrestrial land-derived material, and $\delta^{13}C_{\text{plankton}}$ is the stable carbon isotope signature of Mediterranean phytoplankton, taken to be $-22.4‰$ (Dauby 1989).These calculations indicated that terrestrial materials contributed 37% of the total sedimentary flux, also accounting for the highest carbon:nutrient ratios in the trapped material (Table 2) relative to those in the water column (Table1). These calculations support

our conclusion that the net heterotrophic nature of the pelagic compartment of the Bay of Blanes is, therefore, driven by land inputs.The total organic carbon inputs to the sediment (sedimentation rate + gross community production) was estimated at 29.36 mol C $m^{-2}$ $year^{-1}$ while respiratory losses in sediments removed 15.69 mol C $m^{-2}$ $year^{-1}$ resulting in a net accumulation (and export) of 13.7 mol C $m^{-2}$ $year^{-1}$ in the sediments at the Bay of Blanes (Figure 7). Whereas some of the organic carbon deficit of the pelagic compartment in the Bay of Blanes may be met by transference of the excess production of the benthic community, possibly as dissolved organic carbon, the net accumulation of organic carbon in the sediments requires inputs from land. Because some of the land inputs of organic carbon may be exported out of the Bay of Blanes, these are estimated at 18.6 mol C $m^{-2}$ $year^{-1}$. These results indicate that allochthonous inputs, equivalent to about 50% of the total system GPP in the Bay of Blanes, are comparable to average values for most river-affected coastal systems, whereby inputs from land tend to exceed 14% of GPP (Hopkinson and Smith 2004), often rendering coastal ecosystems heterotrophic (Hopkinson 1985; Smith and Holibaugh 1993; Hopkinson and Smith 2004).

The mass balance calculations derived here contain uncertainty derived from various sources of error; (1) spatial heterogeneity within the Bay of Blanes, (2) uncertainties about the quotients used to transform oxygen-based rates into carbon-based rates, and (3) absence of data on some potentially important fluxes, such as sediment release of dissolved organic constituents. Preliminary synoptic surveys at multiple stations within the Bay of Blanes showed pelagic (e.g. nutrient and chlorophyll *a* concentrations) and benthic (organic and chlorophyll *a* concentrations) properties to be relatively invariant within the Bay (Duarte, unpublished data), except for the presence of a relatively small area seasonally vegetated with sparse stands of the seagrass *Cymodocea nodosa* (Marbá and Duarte 2001). Hence, the results presented here, although representative, cannot be readily extrapolated to the entire Bay. Oxygen uptake may underestimate benthic respiration whenever anaerobic metabolism has a substantial contribution to total respiration (cf. Heip et al. 1995; Hopkinson and Smith 2004). The sediments at Blanes Bay present positive redox potentials down to 10 cm (Terrados et al. 1999; Marbá and Duarte 2001), and are characterized by low sulfide concentrations (2 $\mu$mol S $L^{-1}$, Terrados et al. 1999), suggesting sulfate reduction to be unimportant, although other anaerobic pathways (e.g. denitrification) may still be important.

In agreement with the finding of an important storage rate of organic carbon in the sediments at the Bay of Blanes, the benthic compartment acted as a sink for P, Si and, particularly N at the annual time scale, with the sediment efflux of these elements being much lower than the inputs to the sediments by sedimentation processes. An upper limit to denitrification can be calculated by assuming all of the benthic N sink (sedimentary inputs minus sediment water efflux) of 0.81 mol N $m^{-2}$ $year^{-1}$ to be derived from denitrification. This would involve an associated respiration of 1.01 mol N $m^{-2}$ $year^{-1}$ (cf. Schlesinger 1991), which should be added to the respiration estimated by oxygen

consumption. Consideration of this potential anaerobic respiratory C loss would still render the benthic community autotrophic. The potentially important denitrification losses would be expected to be conducive to N deficiency in the dissolved inorganic water pool, consistent with observations, and, therefore, a dependence on external inputs, through riverine inputs, to which N supplied by mixing and entrainment of deeper off-shore waters adds in winter. The dissolved and particulate organic pools were, in contrast, deficient in P, indicating a rapid recycling of P from organic matter, consistent with observations in other oligotrophic ecosystems (Vidal et al. 1999b; Cañellas et al. 2000).

In conclusion, our study reveals that the Bay of Blanes remains oligotrophic despite substantial inputs of organic carbon and, therefore, nutrients from land. The reasons for the lack of eutrophication symptoms are multiple, (1) the high dilution rate of Blanes Bay waters with off-shore waters resulting from the dynamics imposed by the adjacent submarine canyon (Masó and Tintoré 1991; Rojas et al. 1995; Granata et al. 1999), (2) the heterotrophic nature of the planktonic community which prevents the accumulation of organic matter in the system, and (3) the role of sediments as a sink for C, N, P and Si. In contrast, the benthic compartment is autotrophic and receives important sedimentary inputs of organic carbon, with an important contribution of land-derived carbon. These results highlight the important coupling between the benthic and water column compartments in determining the metabolism and biogeochemical behavior of oligotrophic littoral ecosystems.

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