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

By

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Abstract

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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; Turnner and Rabalais, 1991) nutrient dynamics in oligotrophic coastal waters are strongly dependent on internal recycling processes (Thingstad and Sakshaug., 1990; Ittekkot et al., 1991). These are linked to respiratory processes, much of which occurr 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, 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 (Meybeck, 1982; Cauwet and Martin, 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 (Fig. 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 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 to 250 ml, depending on phytoplankton biomass) was filtered through 0.45 µm Whatman GF/F filters for spectrofluorometric analysis of chlorophyll a concentration (Parsons et al., 1984). The filters were homogenised 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 6 cylindrical PVC tubes (cross-sectional exposed area = 31.81 cm^2) with an aspect ratio of 7.8 to prevent resuspension losses (Hargrave 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 seven 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 (∅ = 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 5 cores exposed to light (200 µmol 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 µmol L^{-1} for spectrophotometric determinations of PO_4^{3-} and $Si(OH)_4$, and 0.02 µmol L^{-1} for NO_3^- + NO_2^- analyses. Ammonium concentrations remained below detection limit (about 0.05 µmol 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 persulphate 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 δ^{13} C-POC analysis were filtered through pre-combusted (3 hours at 500 ºC) GF/F filters and frozen. Filters for δ^{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 900ºC for 3 hours, the resulting gases were distilled cryogenically in a vacuum line and the separated CO_2 was analysed on a VG SIRA II mass spectrometer. Precision δ^{13} C-POC of an internal laboratory standard was 1 SD = 0.06 ‰ O. The carbon isotope ratios are reported in per mil (‰) relative to PDB standard:

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

where $R = {}^{13}C:{}^{12}C$ 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 (0.6µm pore size) and dried for 12 hours 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 precombusted (400 °C for 2 h) GF/F filters, and kept frozen until analysis. DOC was determined on 2 ml samples, after acidification with 10 µl 85% H_3PO_4 and sparging with N_2 for 5 minutes, 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 conic 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 2 CO_3^- + HCO_3^- (V_2) titration points was recorded. Then DIC was calculated as :

$$\Sigma CO_2 = (V_2 - V_1) . [HCl] / (\text{ml of sample})$$

Planktonic community metabolism was estimated weekly along the two-year study. Water samples were carefully siphoned into fifteen 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 hr in the light (200 µmol photon m^{-2} s^{-1}) and the remaining five were incubated for 24 hr 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 µmol photons 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.

3.Results

Seawater temperature varied from a mean winter minimum of 11.1 °C to a mean summer maximum of 24.4 °C (Fig. 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 (Fig. 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 (Fig. 2b).

Dissolved inorganic nutrients varied greatly during the study, with high (up to 2 μM) nitrate concentrations during winter and low values (< 0.5 μM) during summer (Fig. 2c). Silicate concentrations remained low (< 1.0 μM) throughout 1997, but reached high concentrations (up to 2 μM) values during winter and summer 1996 (Fig. 2d). Phosphate concentrations remained low (< 1 μM) throughout the study (Fig. 2e). The average dissolved inorganic nitrogen concentration was similar to that of silicate at 0.6 μM, while phosphate concentration averaged 0.13 μM 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 (Fig. 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 (Fig. 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 1). DOC concentrations ranged from a minimum of 67 μM in winter to a maximum value of 160 μM 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 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} d^{-1}) in summer and low in winter, except for a highly productive event recorded in February 1997 (Fig. 5). Respiration rates were 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} y^{-1}, a respiration rate of 15.69 ± 3.71 mol C m^{-2} y^{-1} and a net benthic community production of 3.77 ± 0.33 mol C m^{-2} y^{-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 (Fig. 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} y^{-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} y^{-1} and the net planktonic community production was calculated at –8.67 ± 1.79 mol C m^{-2} y^{-1}, indicative of a heterotrophic planktonic compartment. Overall, integrated system gross primary production (pelagic + benthic) of 32.36 ± 4.83 mol C m^{-2} y^{-1} was in close balance with the integrated respiration rates of 37.26± 4.2 mol C m^{-2} y^{-1}, suggesting that the system is in metabolic balance, at least for the sampling station.

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 (Fig 6), averaging 14 g DW m^{-2} d^{-1}, but increased significantly in October, reaching a maximum in November of 96 g DW m^{-2} d^{-1} with a secondary local maximum of 33 g DW m^{-2} d^{-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 to 36.8 psu). The corresponding POC flux ranged over two orders of magnitude from 0.16 mmol C m^{-2} d^{-1} to a maximum of 60 mmol m^{-2} d^{-1}, and an average flux of 27.3 mmol C m^{-2} d^{-1} (Fig. 6). The depositional fluxes of PON, POP and bioSi were temporally variable (Fig. 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 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 (Fig. 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 (Figs. 2, 6 and 7). The ammonia efflux showed a contrasting pattern (Fig. 7).The annual release rate of N, P and Si was much lower (4 to 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.

4. 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 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 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 Fig. 2) when water mass circulation, influenced by the inflow of cold and low-salinity waters advected from continental slope waters off the Blanes canyon (Rojas et al., 1995; Masó and Tintoré, 1991; 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 heterotophic on an annual balance (Fig. 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 Fig. 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 (Fig. 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} yr^{-1}, Buscail et. al., 1990; 30.4 mol C m^{-2} yr^{-1}, Monaco 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 ± 0.92 ‰ $^{13}\delta$ C) than those found in sediment trap studies in the Western Mediterranean basin (Dauby et al., 1995) and than those characteristic of Mediterranean phytoplankton (Dauby 1989; Fontugne et al., 1981 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 Tables 2) using the equation:

$$\delta^{13}C_{\text{sediment trap}} = \delta^{13}C_{\text{terrestrial}} \cdot f + \delta^{13}C_{\text{plankton}} (1-f)$$

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} y^{-1} while respiratory losses in sediments removed 15.69 mol C m^{-2} y^{-1} resulting in a net accumulation (and export) of 13.7 mol C m^{-2} y^{-1} in the sediments at the Bay of Blanes (Fig. 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} yr^{-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, unpubl. 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 μmol S L^{-1}, Terrados et al. 1999), suggesting sulphate 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 (Rojas et al., 1995; Masó and Tintoré, 1991; 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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Table 1. Average (μmol 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				

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).

	Sedimenttrap fluxes Average ± SE	Sedimentary flux ratio	Sediment trap $\delta^{13}C$ Average ± SE
POC (mol m^{-2} y^{-1})	9.96 ± 2.4		-23.74 ± 0.92
PON (mol m^{-2} y^{-1})	0.81 ± 0.30		
POP (mol m^{-2} y^{-1})	0.06 ± 0.01		
bioS (mol m^{-2} y^{-1})	0.19 ± 0.07		
DW (gr m^{-2} y^{-1})	9349.22 ± 2823		
POC: bioS :PON:POP		159:50:12:1	
POC:PON		14	

Sediment –water fluxes (mol m^{-2} y^{-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} y^{-1})	15.7± 3.71

Figure headings

Fig.1. Location of the study area.

Fig.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.

Fig.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.

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

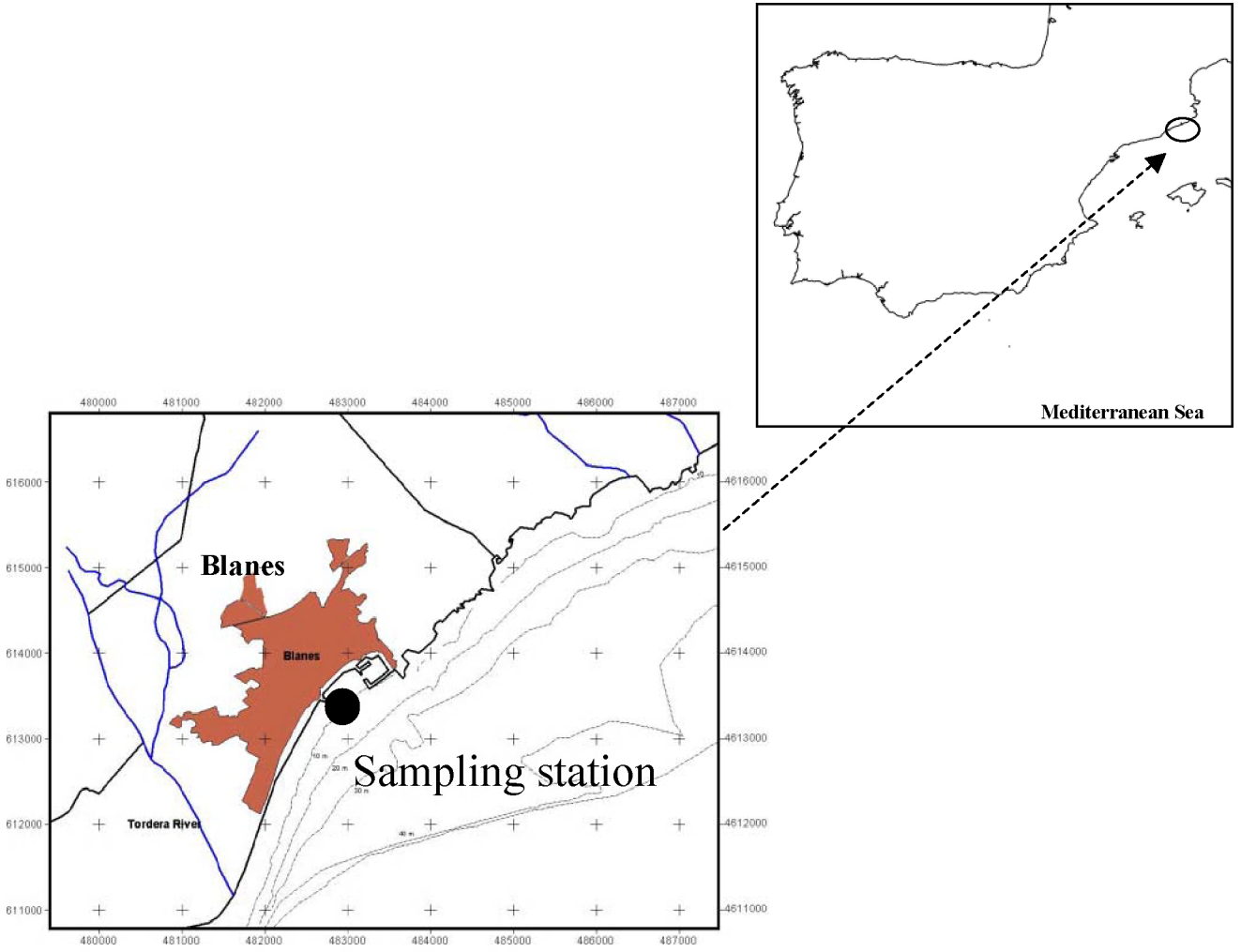
Fig.5. Mean monthly respiration (R), gross primary production (GPP) and net community production (NCP) for the pelagic and benthic compartments at the Bay of Blanes.

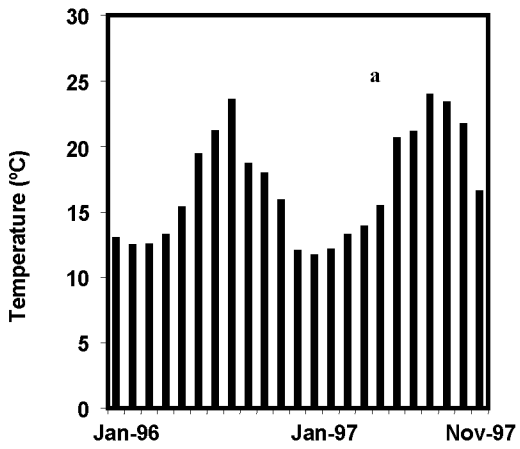
Fig.6. Total depositional fluxes of material (as dry weight DW), POC, PON, POP and BiO_2 at the Bay of Blanes.

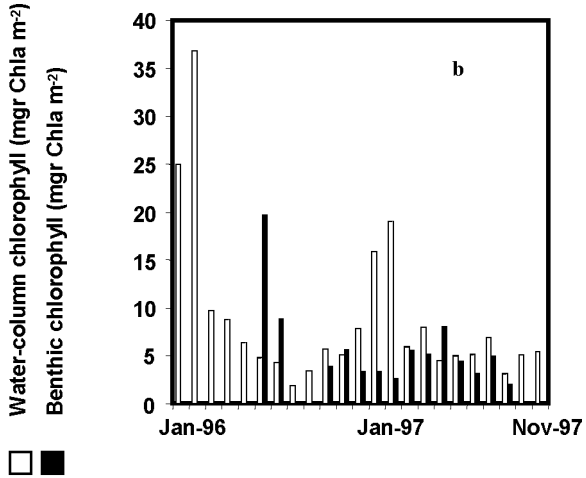
Fig. 7. Mean monthly sediment-water dissolved inorganic nutrient fluxes at the Bay of Blanes. Negative values denote uptake by the sediment compartment..

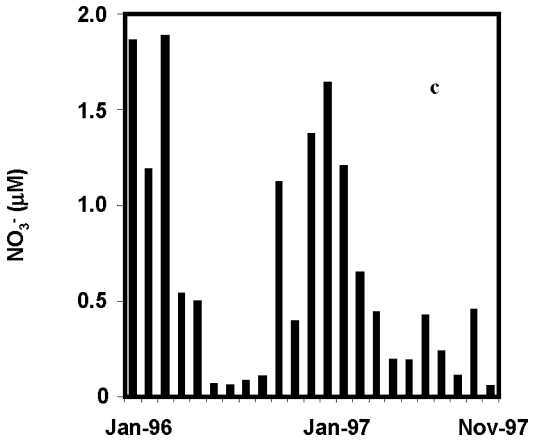
Fig. 8. A summary depiction of the carbon fluxes in the Blanes Bay (NW Mediterranean).

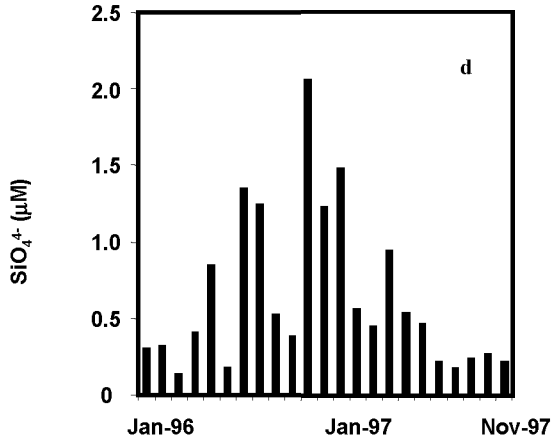
line figure

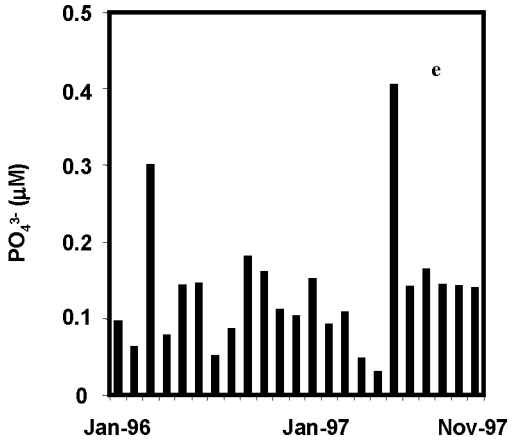

Mediterranean Sea
480000
481000
482000
483000
484000
485000
486000
487000
616000
615000
614000
613000
612000
611000
4616000
4615000
4614000
4613000
4612000
4611000
Blanes
Blanes
Tordera River
Sampling station

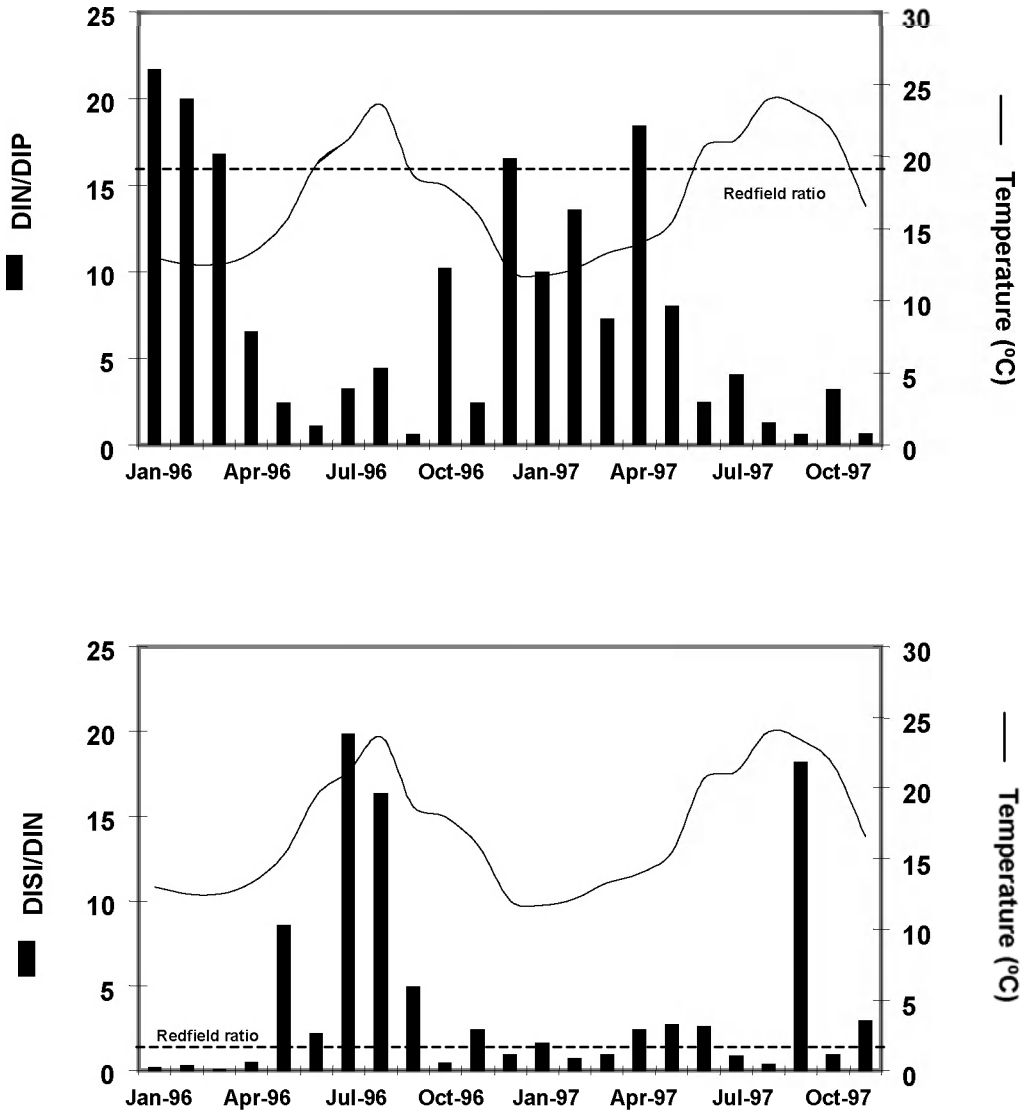

a
Temperature (°C)
30
25
20
15
10
5
0
Jan-96
Jan-97
Nov-97

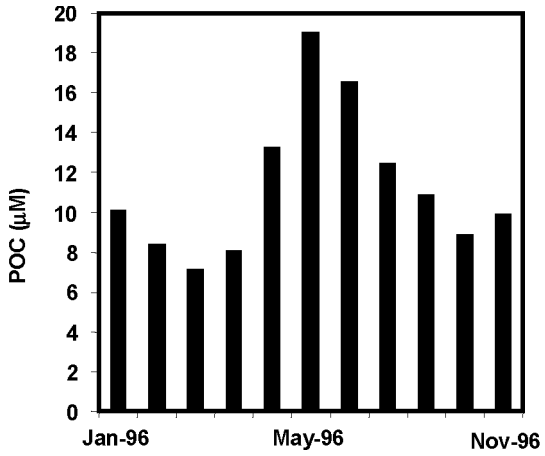

b
Water-column chlorophyll (mgr Chla m-2)
Benthic chlorophyll (mgr Chla m-2)
40
35
30
25
20
15
10
5
0
Jan-96
Jan-97
Nov-97

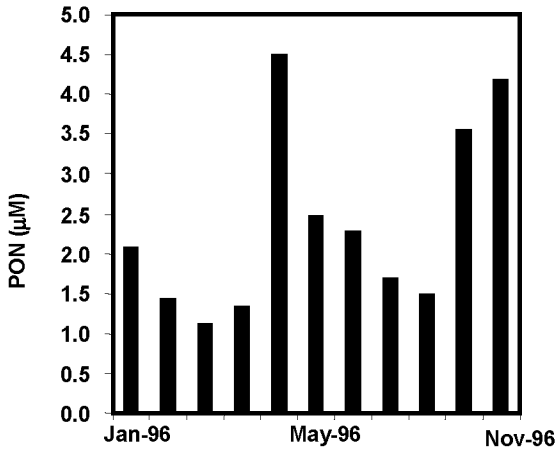

c
NO3- (µM)
2.0
1.5
1.0
0.5
0
Jan-96
Jan-97
Nov-97

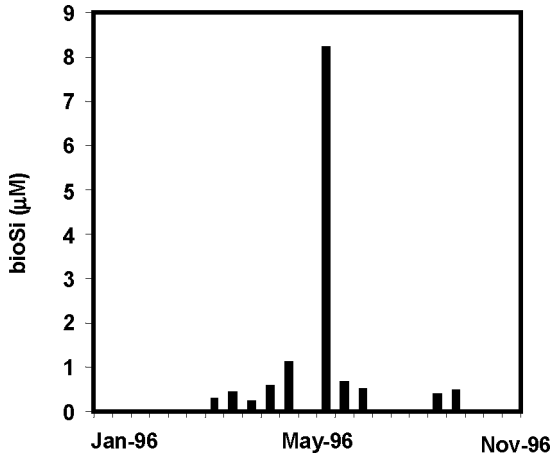

d
SiO4 4- (µM)
2.5
2.0
1.5
1.0
0.5
0
Jan-96
Jan-97
Nov-97

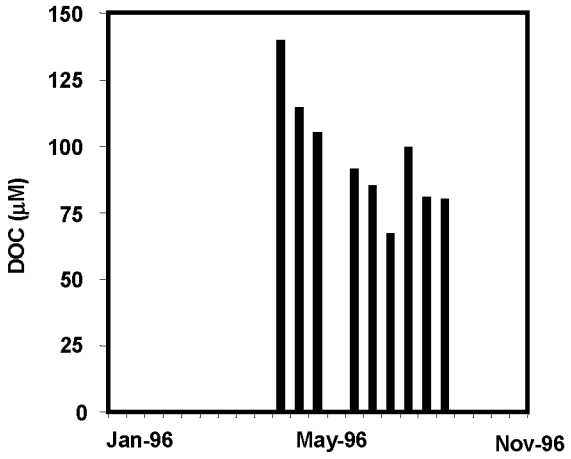

e
PO4 3- (µM)
0.5
0.4
0.3
0.2
0.1
0
Jan-96
Jan-97
Nov-97

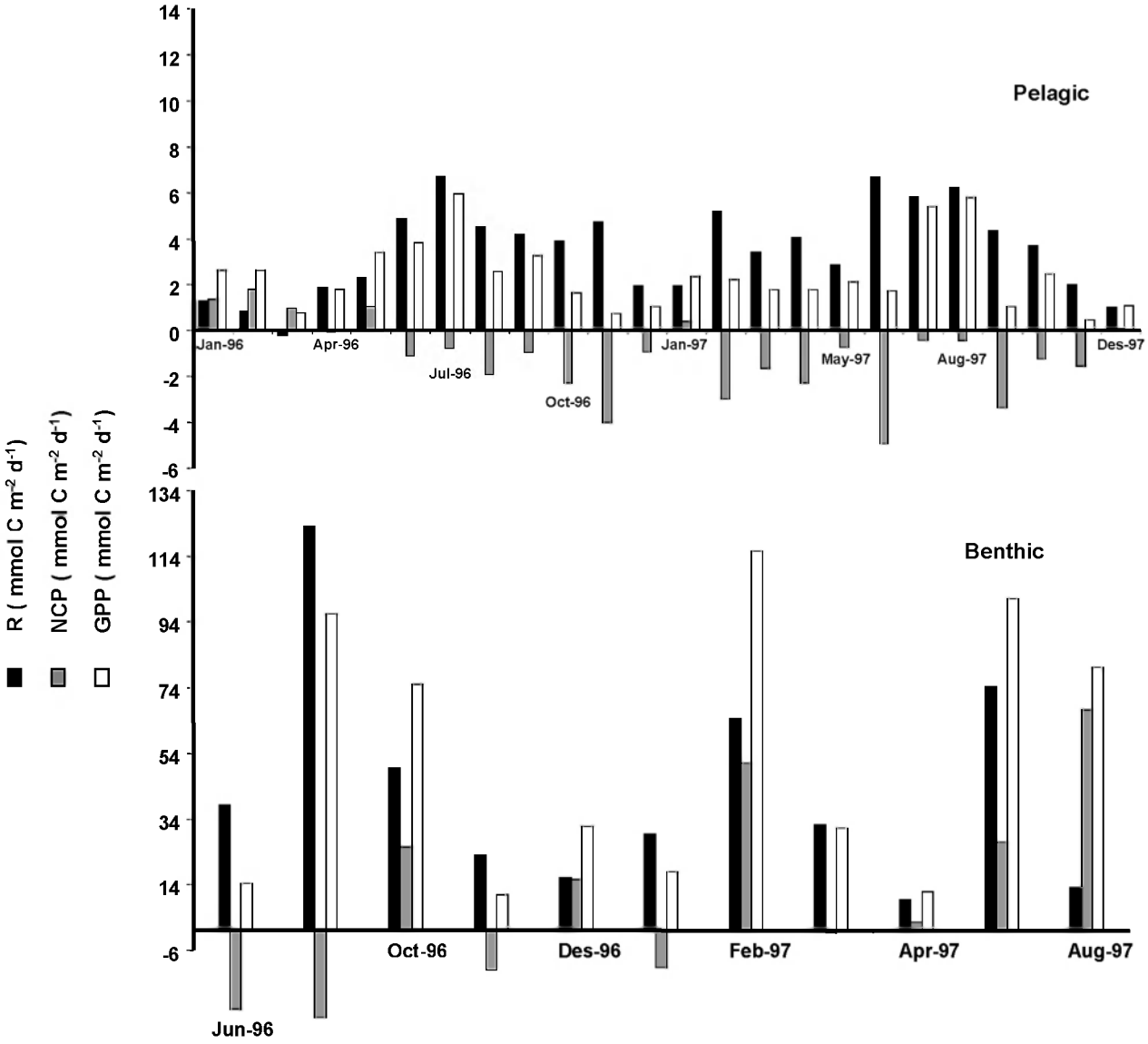

DIN/DIP
25
20
15
10
5
0
30
25
20
15
10
5
0
Redfield ratio
Temperature (°C)
Jan-96
Apr-96
Jul-96
Oct-96
Jan-97
Apr-97
Jul-97
Oct-97
DISI/DIN
25
20
15
10
5
0
30
25
20
15
10
5
0
Redfield ratio
Temperature (°C)
Jan-96
Apr-96
Jul-96
Oct-96
Jan-97
Apr-97
Jul-97
Oct-97

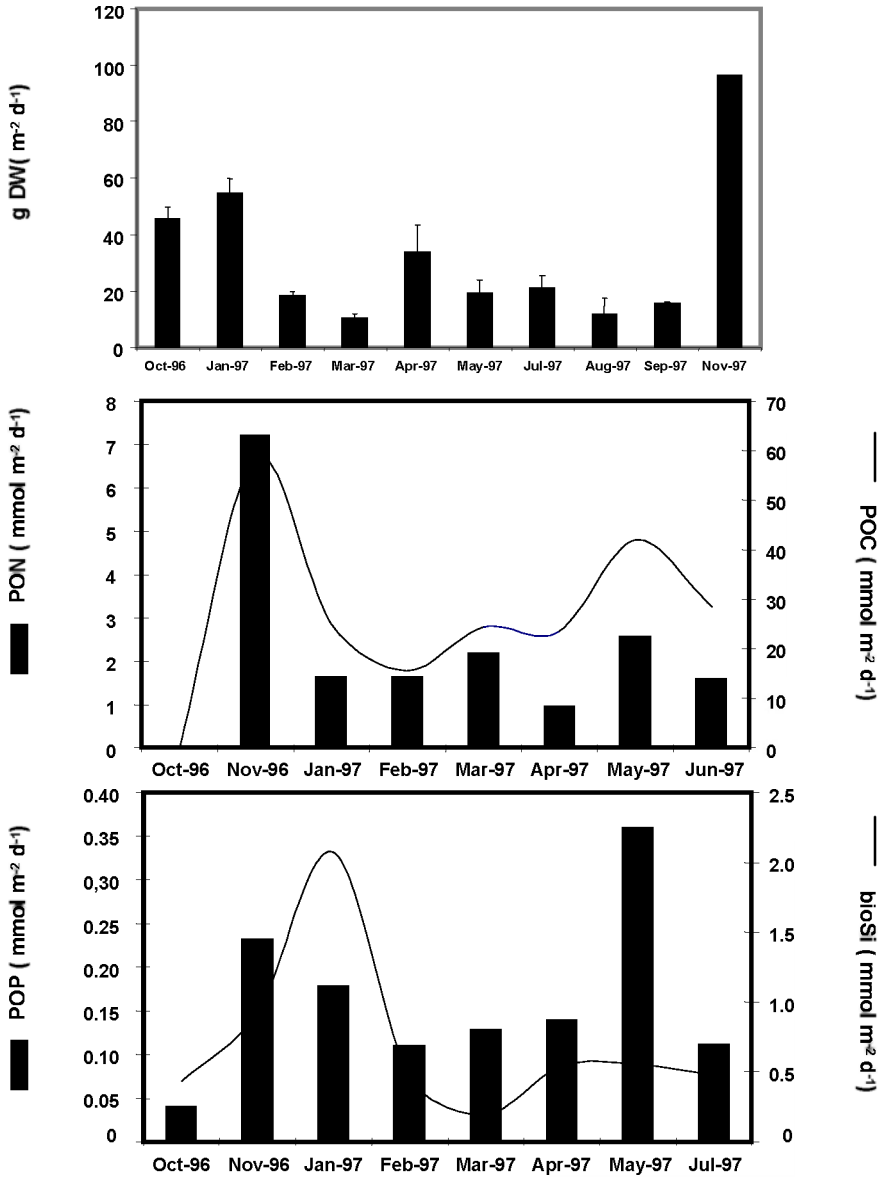

POC (µM)
20
18
16
14
12
10
8
6
4
2
0
Jan-96
May-96
Nov-96

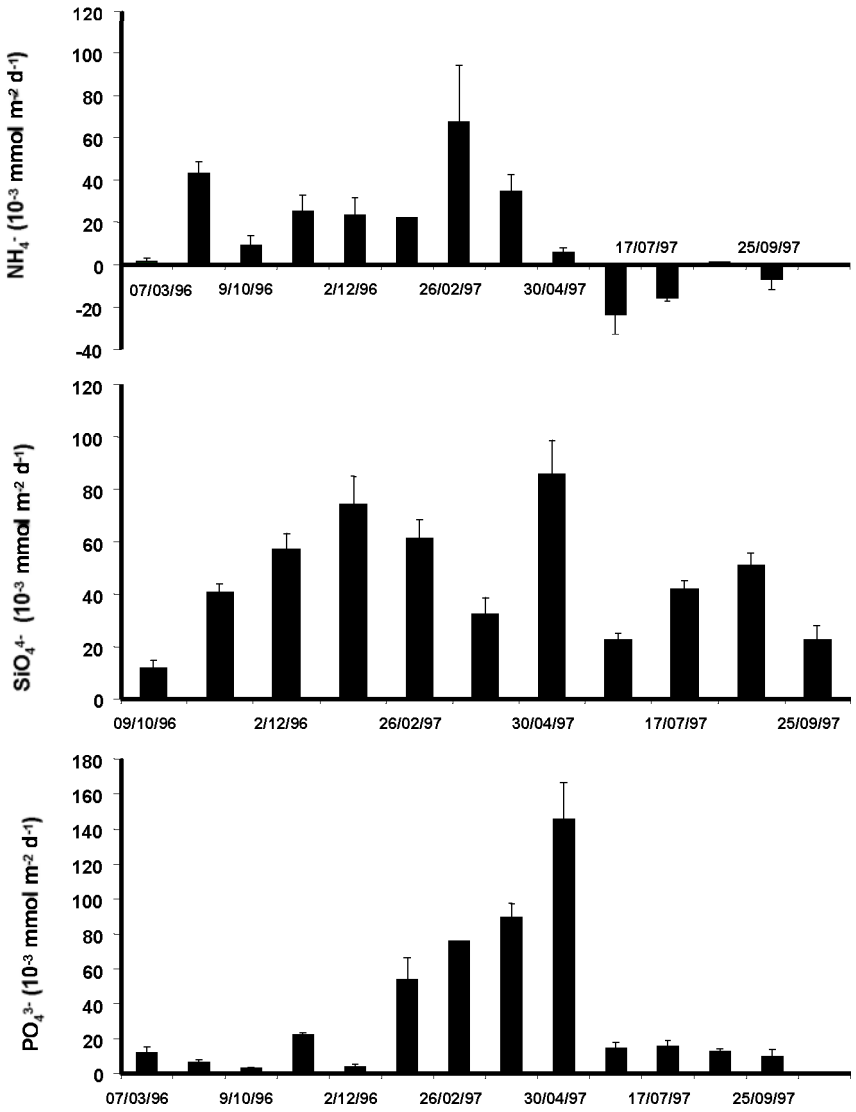

PON (µM)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Jan-96
May-96
Nov-96

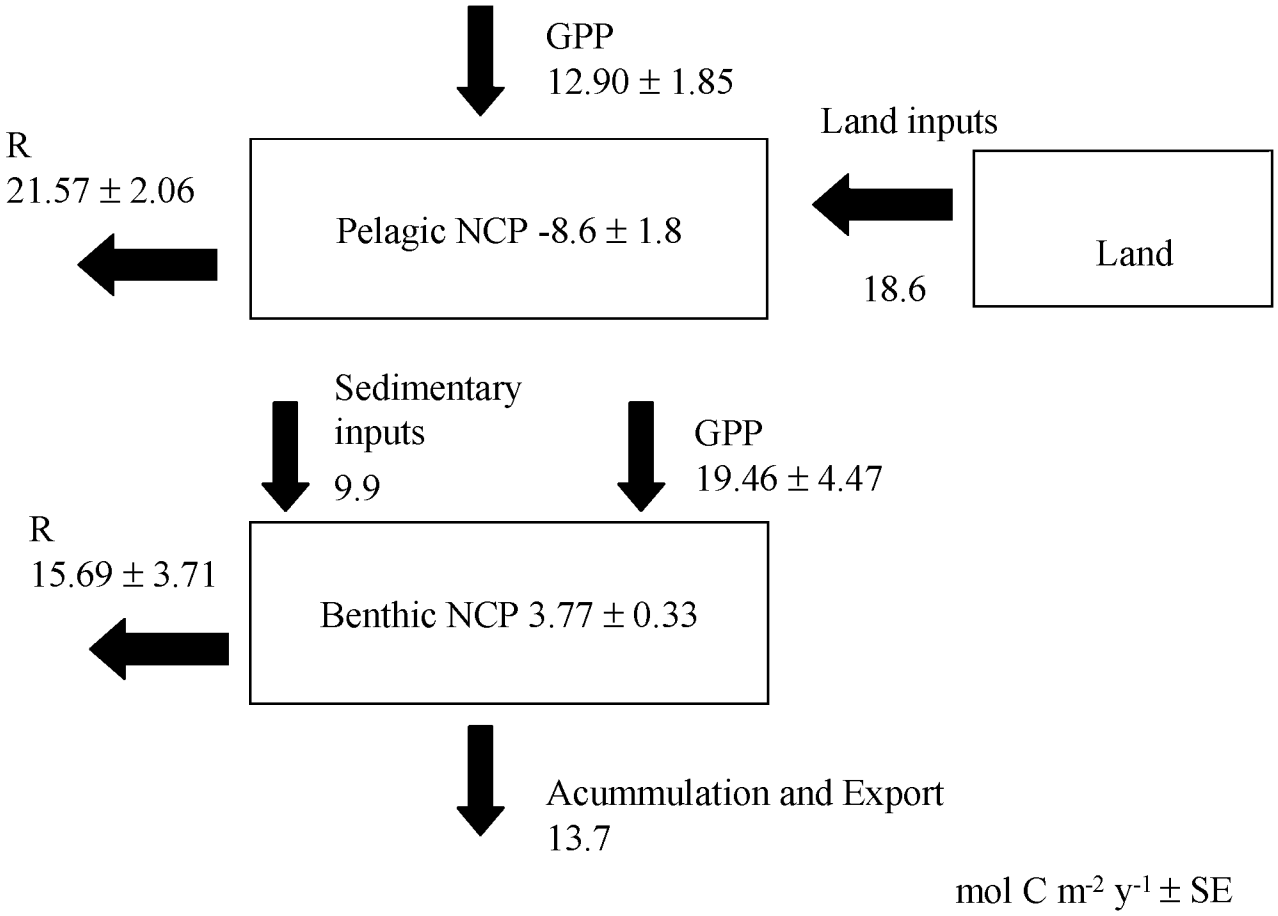

bioSi (µM)
9
8
7
6
5
4
3
2
1
0
Jan-96
May-96
Nov-96


DOC (µM)
150
125
100
75
50
25
0
Jan-96
May-96
Nov-96


R (mmol C m-2 d-1)
NCP (mmol C m-2 d-1)
GPP (mmol C m-2 d-1)
Pelagic
14
12
10
8
6
4
2
0
-2
-4
-6
Jan-96
Apr-96
Jul-96
Oct-96
Jan-97
May-97
Aug-97
Des-97
Benthic
134
114
94
74
54
34
14
-6
Jun-96
Oct-96
Des-96
Feb-97
Apr-97
Aug-97


g DW(m-2 d-1)
120
100
80
60
40
20
0
Oct-96
Jan-97
Feb-97
Mar-97
Apr-97
May-97
Jul-97
Aug-97
Sep-97
Nov-97
PON (mmol m-2 d-1)
POC (mmol m-2 d-1)
8
7
6
5
4
3
2
1
0
70
60
50
40
30
20
10
0
Oct-96
Nov-96
Jan-97
Feb-97
Mar-97
Apr-97
May-97
Jun-97
POP (mmol m-2 d-1)
bioSi (mmol m-2 d-1)
0.40
0.35
0,30
0.25
0.20
0.15
0.10
0.05
0
2.5
2.0
1.5
1.0
0.5
0
Oct-96
Nov-96
Jan-97
Feb-97
Mar-97
Apr-97
May-97
Jul-97


NH_4^- (10^{-3} mmol m^{-2} d^{-1})
120
100
80
60
40
20
0
-20
-40
07/03/96
9/10/96
2/12/96
26/02/97
30/04/97
17/07/97
25/09/97
SiO_4^{4-} (10^{-3} mmol m^{-2} d^{-1})
120
100
80
60
40
20
0
09/10/96
2/12/96
26/02/97
30/04/97
17/07/97
25/09/97
PO_4^{3-} (10^{-3} mmol m^{-2} d^{-1})
180
160
140
120
100
80
60
40
20
0
07/03/96
9/10/96
2/12/96
26/02/97
30/04/97
17/07/97
25/09/97


GPP
12.90 ± 1.85
Land inputs
R
21.57 ± 2.06
Pelagic NCP -8.6 ± 1.8
Land
18.6
Sedimentary
inputs
9.9
GPP
19.46 ± 4.47
R
15.69 ± 3.71
Benthic NCP 3.77 ± 0.33
Acummulation and Export
13.7
mol C m-2 y-1 ± SE

Actions taken to accommodate the comments from reviewer # 1

1. Reviewer: "*...there are a number of typos in the paper (for example, 'a know amount' instead of a known amount', punctuation problems, etc.) and these need to be fixed".*

Comment: We apologize for the fact that some, few, typos scaped our attention.

Action: The manuscript has been checked throgouhly once again to solve these problems.

2. Reviewer: *Importance of anaerobic metabolism in sediments:.... Iron reduction and coupled-denitrification could be very important in these sediments and both processes would challenge your conclusion that all benthic metabolism is aerobic. Do you have pore water iron (Fe2+) data or any estimates of coupled denitrification that could be used to evaluate this possibility? If not, you should discuss this possibility as best you can with the data you do have (O:N flux ratios - though I am very weary of this method - could be used if there is no other option).*

Comments: We agree that the evidence provided does not rule out anaerobic processes. We note, however, that we did not conclude that all metabolism is aerobic. Indeed, we explicitly identify denitrification as a potential factor accounting for the sedimentary N sink detected. Unfortunately, we lack Fe2+ data or estimates of coupled denitrification. The use of the O:N flux ratio would lead to confusion, for a meaningful ratio can be produced if considering dark processes alone *ratios (- 3140 O_2 :1 N, on average).* However, the benthic community is net autotrophic, so that the O:N flux ratio for the community is + *754 O_2 :1 N* which is opposite to that expected to derive from heterotrophic processes. Indeed, the apparent paradox of an autotrophic community that releases small amounts of inorganic nitrogen, ratner than being an N sink as expected, is derived from the need to consider benthic processes in concert with sedimentary inputs. Because of the possibility to add confusion, we have not added a discussion of O:N rations. Alternatively, we have produced a calculation of an upper limit to denitrification, based on the calculation of how much respiration would be associated to denitrification, shall all of the benthic N sink (i.e. difference between inputs and outputs derive from denitrification).

Action: We have altered the text to (1) indicate that sulphate reduction is likely to be unimportant in these sediments but that other anaerobic processes may be important, so

that the estimates of benthic respiration could be underestimated because of failure to account for anerobic processes, (the text now reads: "*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 µmol S L-1, Terrados et al. 1999), suggesting sulphate reduction to be unimportant, although other anaerobic pathways (e.g. denitrification) may still be important.")*; and (2) acknowledge that denitrification may be important, and provide a calculation of an upper limit to the respiration associated to this process, if denitrification was responsible for the all of the benthic N sink (the text now reads: "*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 , which should be added to the respiration estimated by oxygen consumption, which would still render the benthic community autotrophic").*

3. Reviewer: *Why were the benthic and pelagic samples incubated at the same irradiance (~200 µEinsteins)? If 200 µE is reaching the sediment surface, then I would think the "average" PAR in the water column is much higher than this. Did you run any water column incubations at higher PAR? If the pelagic compartment is autotrophic at higher PAR (which is what I would expect), your conclusions would change significantly. Please comment?.*

Coment: The reviewer is correct that the average PAR in the water column is much higher than 200 µE. However, the production by the pelagic community is saturated at irradiances ranging from 50 to 200 µmol photons m^{-2} s^{-1}, depending on the season (Satta et al. 1996), so that exposure to an increased irradiance would have no consequence for the estimated GPP nor the metabolic balance of the planktonic community.

Action: We now specify, in the methods section, the basis for choosing the fixed irradiance of *200 µEinsteins*

Reference:

Satta, M.P., S. Agustí, M.P. Mura, y C.M. **Duarte**. 1996. Gross planktonic primary production in the Bay of Blanes (1992-1994). In: **Duarte**, C.M. (ed.). Seasonality in the Blanes Bay: a paradigm of the northwest Mediterranean littoral. Publ. Espec. Inst. Esp. Oceanogr. 22: 31-38. Instituto Español de Occeanografía, Madrid.