Biogeochemical Budgets in the Eastern Boundary Current System of the North Atlantic: Evidences of Net Heterotrophy and Nitrogen Fixation

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Abstract

Thermohaline and chemical data from three WOCE cruises conducted in 1997/98 define the MedBox region, bounded by the Strait of Gibraltar, 24°N, 41°N and 22°W. The carbon budget indicates that the MedBox is a heterotrophic region, where carbon is mineralised at a net rate of 17±11 g C m⁻² yr⁻¹, supported by the input of allochthonous organic matter, mainly in the dissolved form, from the adjacent ocean. Dissolved organic carbon accounts for 90% of the organic carbon demand. In vitro measurements to estimate the net community production of the study area differ largely from our geochemical budget estimation, likely reflecting different spatial and temporal scales and/or terms or processes not taken into account by both methods. The nitrogen budget of the MedBox pointed to a significant atmospheric input via N₂ fixation (3.4±3.1 g N m⁻² yr⁻¹).
Introduction

The metabolic state of the ocean is defined as the balance between in situ gross primary production (GPP) and total respiration (R); a system is autotrophic if it produces more organic matter than it consumes, and heterotrophic if organic matter consumption exceeds in situ production. Assessing whether the ocean, from the local to the global scale, is heterotrophic or autotrophic still remains a burning issue. Contrasting conclusions are achieved depending on the approach used: 1) regional budgets of nutrient salts (e.g., Álvarez et al. 2002) or organic matter (e.g., Hansell et al. 2004a) versus 2) extrapolation of in vitro net community production (NCP) estimates relying on empirical relationships between GPP (Williams 1998) or net primary production (del Giorgio et al. 1997) and total (Duarte and Agustí 1998; Williams 1998) or bacterial (del Giorgio et al. 1997) R. Results from the empirical relationships between in vitro GPP and R in oligotrophic waters by the oxygen light/dark incubation method range from net heterotrophy (del Giorgio et al. 1997; Duarte and Agustí 1998) to metabolic balance (Williams 1998). In this sense, there is ongoing discussion about the suitability of the field data (Williams 1998), the data processing (Duarte et al. 1998), the decoupling between GPP and R, the plankton community structure (Serret et al. 2001) and the intermittent nature of GPP on the in vitro approaches. NCP estimates based on the seasonal changes of inorganic carbon, nutrient salts, and dissolved oxygen in the euphotic layer or integrating sediment trap data suggest that the upper ocean is autotrophic, producing organic matter that is exported downwards.

More research is needed to discern whether mass balance and in vitro NCP estimates are comparable; specifically whether 1) in vitro estimates are representative for the same temporal and spatial scales than mass balance estimates; and 2) allochthonous input of organic matter from the coastal margins and the atmosphere or the photochemical production of labile DOM from deep DOM transported into the upper ocean could account for the differences between the two approaches.
Along with light, nitrogen, N, is the main factor limiting the primary and export production in the oceans. The biological pump removes reduced N from the euphotic zone, which is oxidized to nitrate at deeper levels and transported back by upwelling and turbulent mixing. Other sources of N to the euphotic zone are wet and dry deposition of combined N from the atmosphere, riverine inputs, and atmospheric N₂ fixation by marine diazotrophs. The latter was previously considered a negligible process but it is now a subject of intense debate and it has been proposed to balance the N budget in the ocean (Gruber 2005 and references therein).

The organisms responsible for N₂ fixation are taxonomically, physiologically, and ecologically diverse, including, bacteria (phototrophs, heterotrophs, chemolithotroph); heterocystous and non-heterocystous cyanobacteria and Archeae (see the review by Karl et al. 2002). Much of the oceanic research about N₂ fixation has been focused on the relatively conspicuous, non-heterocystous, filamentous cyanobacterium *Trichodesmium* (Capone et al. 2005) but other N₂ fixing organisms could substantially contribute to the N budget (Zehr et al. 2000).

N₂ fixation depends on the expression of the enzyme system nitrogenase, which synthesis and expression are ultimately determined by a range of physiological and ecological variables such as oxygen concentration, availability of enzyme cofactors (Fe and Mo), sufficient supply of energy, etc. (Karl et al. 2002 and references therein). N₂ fixation is neither temporally nor spatially uniform. Therefore, as for many processes in oceanography, it suffers from undersampling because of its occurrence as stochastic and heterogeneous blooms that are difficult to detect or model. Additionally, all species with the genetic potential for N₂ fixation have not already been identified. The difficulty to obtain statistically scaled data bases has led to a clear underestimation of N₂ fixation in much of the recent research (Karl et al. 2002). In that review, the relevance of diazotrophic production as a source of new N in the subtropical gyres of the North Atlantic and North Pacific is highlighted, being much higher that previously estimated.
This source of new N will support net production and export of organic matter from the euphotic zone, with a direct effect on the carbon cycle. This fact leads to relevant consequences in relation to the N₂ fixation-climate feedback hypothesis proposed by Michaels et al. (2001): N₂ fixation affects the concentration of the green house gas CO₂ in the atmosphere on time scales of decades to millennia; CO₂ influences climate and, in turn, climate controls the supply of Fe in dust to the ocean and the stratification of the upper ocean.

The most recent and comprehensive compilation of direct and indirect estimates of N₂ fixation in the North Atlantic is given in Capone et al. (2005). They arrived at a N₂ fixation rate in the Atlantic between 2 and 9 \(10^{12}\) mol N yr⁻¹ reconciling isotopic budgets, direct N₂ fixation rates extrapolated and several indirect geochemical estimates except for that given by Hansell et al. (2004b).

Here we evaluate the mass balances of carbon and nitrogen in a box closing the boundary current system of the Eastern North Atlantic with the aim of evaluating the metabolic status of the region. The results presented here complement the work by Álvarez et al. (2005, hereinafter APSB) on the role the region as an anthropogenic carbon sink.

Material and methods

The data set and the methods used here are common to APSB. Therefore, only the most relevant and new aspects will be highlighted; we refer the reader to APSB for a thorough description of the data set and velocity field methodology.

A three sided box was created around the Strait of Gibraltar (Fig. 1). Hydrographic and chemical data from three WOCE cruises undertaken in 1997 and 1998 were used to create the named MedBox 98. Details about the analytical methods and quality control are given in the corresponding cruise report and related works (see Table 1 in APSB).
The estimation of the velocity field is a crucial step to obtain reliable mass and chemical transports. We refer again to APSB for a thorough explanation. Briefly, the velocity field is approximated geostrophically using a reference level at $\sigma_3 = 41.49$, nearly equivalent to 3,200 dbar. From this initial velocity field, an inverse model is run: an underdetermined system of linear equations is solved to satisfy some constraints and resolved by singular value decomposition. The model constraints are: i) mass conservation for the whole water column; ii) mass salt and heat conservation for six deep layers below 2,500 dbar; and iii) no deep water formation within the MedBox.

The nutrient transports are obtained integrating the velocity field times the nutrient distributions along the MedBox walls for the whole water column. Positive values indicate transports into the MedBox and negative values out of it.

Biogeochemical budgets

We will focus on the region between the Strait of Gibraltar and the MedBox walls, hereinafter, MedBox region. To discern whether it behaves as a nutrient source or trap, mass balances are set out taking into account the transports across all the open boundaries of the study box. In this section, we formulate regional-averaged balances assuming steady state conditions for all the chemical variables except inorganic carbon, which is affected by the transient entry of anthropogenic carbon ($C_{\text{ANT}}$) into the MedBox (e.g., APSB).

The balance of any species, $C$, can be formulated as follows:

$$\frac{dC}{dt} = I - O + \text{NCP}_C = 0.$$  \hspace{1cm} (1)

Under steady state conditions, the balance of inputs ($I$) minus outputs ($O$) of $C$ must be equal to the net community production of $C$ within the study box ($\text{NCP}_C$). $I$ and $O$ refer to the fluxes across the open boundaries of the region: the MedBox walls, the Strait of Gibraltar, the surrounding continents and the air-sea interface.
We obtained outward (into the North Atlantic) transports of nitrate (NO$_3$), phosphate (PO$_4$), alkalinity (TA), and total inorganic carbon (TIC) across the MedBox walls, of -30 ± 3, -1.0 ± 0.3, -31 ± 16, and -130 ± 13 kmol s$^{-1}$, respectively. The TA and TIC transports were calculated constraining the salt transport across the MedBox walls to zero, in order to minimize the effect of the salt imbalance on the estimate of the NCP of organic and inorganic carbon.

The NO$_3$ transport across the Strait of Gibraltar has been calculated by different authors providing a range of values. Ribera d’Alcalà et al. (2003) estimated that 8.5±4.1 kmol s$^{-1}$ of NO$_3$ flow across the Strait of Gibraltar, obtained from a wide range of nutrient and water transport determinations.

In the case of the air-sea interface, two possible N sources can be considered: N$_2$ fixation and air-sea NOX deposition. Regarding nitrogen fixation, a recent work by Mahaffey et al. (2003) justified the low abundance of $^{15}$N relative to $^{14}$N between 26ºW and 32ºN along 20ºW on basis of the existence of N$_2$ fixers, but did not quantify any rate. Lipschultz and Owens (1996) calculated a N$_2$ fixation rate of about 1.142 kmol s$^{-1}$ between 31ºN and 50ºN; proportionally, about 0.2 kmol s$^{-1}$ within the MedBox. Regarding the air-sea deposition of NO$_3$, Prospero et al. (1996) evaluated the air-sea deposition of nutrients to the North Atlantic using an atmospheric chemical model. From their Table 3, we proportionally calculated an air-sea input of 0.3 kmol s$^{-1}$ within the MedBox.

In order to get a better estimation of the N riverine input, we combined river discharges from Baumgartner and Reichel (1975) with the NO$_3$ concentrations of the Tajo, Guadiana and Guadalquivir river mouths from Kempe et al. (1991) and we estimated a NO$_3$ plus ammonium input of 0.3 kmol s$^{-1}$.

Combining the former estimations in Eq. 1, the NCP of NO$_3$ (NCP$_{NO_3}$) within the MedBox region results to be 21 ± 5 kmol s$^{-1}$ or 15 ± 4 mg N m$^{-2}$ d$^{-1}$ (Fig. 2a) which should be produced.
from the decomposition of organic matter imported from the surrounding Mediterranean Sea and Eastern North Atlantic interior.

Assuming that the distribution of organic N in the Eastern North Atlantic varies more with depth than with latitude, the total transport of organic N across the MedBox can be ascribed to the Ekman and overturning transports (APSB). Estimations of particulate (PON) and dissolved organic nitrogen (DON) fluxes across the MedBox walls can be calculated from field measurements in the Eastern North Atlantic-Azores Front region by Doval et al. (2001). The Ekman and overturning transports across the box are 0.25 Sv and 3 Sv, respectively (APSB) and surface PON and DON concentrations are taken from Table 1 in Doval et al. (2001): 0.4 and 5.3 μmol L⁻¹, respectively. The vertical gradient (estimated as the difference between the mean concentration below 500 m and that in the upper 200 m) of both variables (0.22 and 1.3 μmol L⁻¹) was also taken from Doval et al. (2001). The result is that about 6 ± 4 kmol s⁻¹ of organic N are transported into the MedBox.

The only estimate of organic N in the Strait of Gibraltar is from Coste et al. (1988), used by Ribera D’Alcalà et al. (2003): 1.5±3.5 kmol s⁻¹ into the MedBox. The river input of DON and PON is estimated using a mean C:N ratio in riverine organic matter of 20 and 8.5, respectively (Meybeck 1982) and the dissolved (DOC) and particulate organic carbon (POC) concentrations in the Sado and Douro (Abril et al. 2002) as representative for the rivers flowing into the MedBox. About 0.16 kmol s⁻¹ of PON and DON are introduced into the MedBox by these rivers. In addition, this small quantity is mostly refractory: about two thirds have lifetimes of several decades. So the river input of organic nitrogen can be neglected.

The burial of organic carbon for the Canary and Iberian basin areas, about 0.016 g C m⁻² yr⁻¹, was estimated by Seiter et al. (2005). Using the mean C:N ratio of 10 in surface sediments of the region given by Meggers et al. (2002), we estimate that 0.007 kmol s⁻¹ of organic N is buried in the MedBox. Atmospheric inputs of organic N, especially DON, have been suggested
to be an important term in the global N budget (Prospero et al. 1996). These authors estimated that 8 mmol N m$^{-2}$ yr$^{-1}$ deposit in the Northeast Atlantic Ocean, corresponding to about 0.7 kmol s$^{-1}$ in the MedBox area. Combining all the estimates for organic N in Eq. 1, we obtain a NCP of about -8 ± 4 kmol s$^{-1}$ (Fig. 2b).

Summing up, we have a net consumption of 8 ± 4 kmol s$^{-1}$ of organic N and a net production of 21 ± 5 kmol s$^{-1}$ of NO$_3$ within the MedBox (Fig. 2a, b). Consequently, an excess of 13 ± 7 kmol s$^{-1}$ or 9 ± 5 mg N m$^{-2}$ d$^{-1}$ of NO$_3$ are produced within the MedBox. Where do they come from? The most plausible hypothesis is that they come from an underestimated organic N source via N$_2$ fixation.

If this hypothesis is correct, the nitrogen imbalance should not be reflected in the phosphorus and carbon budgets. Unfortunately, we lack of organic phosphorus measurements in the MedBox. Therefore, we can only set up a PO$_4$ budget. The transport across the Strait of Gibraltar into the MedBox is 0.35±0.2 kmol s$^{-1}$ (Ribera d’Alcalà et al. 2003) and the transport across the MedBox is -1.0±0.3 kmol s$^{-1}$. The Saharan dust has a low percentage of phosphorus and there are no estimates of PO$_4$ deposition; the river input of phosphorous is quite small: 0.054±0.01 kmol s$^{-1}$, 75% as PO$_4$ (Meybeck 1982). Therefore, we estimate a NCP of PO$_4$ (NCP$_{PO4}$) of 0.6±0.4 kmol s$^{-1}$.

Since we are interested in the NCP of organic carbon (NCP$_{org}$), the TIC budget (NCP$_{TIC}$) has to be corrected for the dissolution/precipitation of calcium carbonate by means of the potential alkalinity (TA$_p$) budget (NCP$_{TAp}$) within the MedBox region. The definition of TA$_p$ by Fraga and Álvarez-Salgado (2005) takes into account the influence of N$_2$ fixation and the organic constituents of marine phytoplankton. Therefore, NCP$_{TAp}$ is:

$$\text{NCP}_{TAp} = \text{NCP}_{TA} + 0.92 \cdot \text{NCP}_{NH4} + 0.08 \cdot \text{NCP}_{N2} + 1.01 \cdot \text{NCP}_{NO2} + 1.08 \cdot \text{NCP}_{NO3} + 0.23 \cdot \text{NCP}_{PO4}$$

(2)
where NCP$_{NH4}$ is the NCP of ammonium, NCP$_{N2}$ the NCP of N$_2$, and NCP$_{NO2}$ the NCP of nitrite.

We assume that the nitrite and ammonium contribution to TAP$_P$ in this region is negligible. The only missing term in Eq. 2 is NCP$_{TA}$, which can be calculated with Eq. 1 for TA.

The atmospheric input of TA due to the air-sea exchange of CO$_2$ is zero; other TA exchanges across this interface are acid rain and calcite deposition by the Saharan dust. They decrease and increase, respectively the TA budget within the MedBox. However, no estimates are available and we assume they are negligible and/or compensated. The transport of TA across the Strait of Gibraltar is 122±10 kmol s$^{-1}$ into the MedBox, using the methodology and TA data in Dafner et al. (2001), with zero salt transport. The transport across the MedBox is -31±16 kmol s$^{-1}$ into the North Atlantic, and the river input of bicarbonate is estimated to be 25±10 kmol s$^{-1}$ using data from the GEM-CO$_2$ model by Amiotte-Suchet et al. (2003). Consequently, the resulting NCP$_{TA}$ within the MedBox is -116±21 kmol s$^{-1}$.

To solve Eq. 2 within the MedBox, we need to differentiate between the TAP$_P$ change due to NO$_3$ production from organic matter imported from the Eastern North Atlantic interior (8 ± 4 kmol s$^{-1}$) and organic matter originated from N$_2$ fixation (assumed to be 13 ± 7 kmol s$^{-1}$) and to consider also the NCP of PO$_4$ (0.6±0.4 kmol s$^{-1}$). Consequently:

$$\text{NPT} = (-116±21) - 0.08 \cdot (13±7) + 1.08 \cdot [(8±4) + (13±7)] + 0.23 \cdot (0.6±0.4) = -94±22 \text{ kmol s}^{-1}$$

Therefore, we infer a TAP$_P$ consumption equivalent to a NCP of CaCO$_3$ of 47±11 kmol s$^{-1}$ or 10±3 g C m$^{-2}$ yr$^{-1}$. Since the MedBox has high surface productivity and lies above the lysocline, accumulation rates of this order of magnitude are expected according to Milliman (1993). Meggers et al. (2002) found high percentages of carbonate in the sediments of the Canary Islands region mainly as calcite.

We then proceed with the TIC budget (Fig. 2c) using the approach in Álvarez et al. (2003), where the balance of O minus I of inorganic carbon across the boundaries (air-sea interface, Strait of Gibraltar, MedBox walls, sediments, ocean-land interface) should balance the NCP$_{TIC}$
minus the accumulation of $C_{\text{ANT}}$ within the region, which was estimated by APSB in $66 \pm 21$ kmol s$^{-1}$. Since the Azores region was a weak CO$_2$ sink of about $0.38$ mmol m$^{-2}$ d$^{-1}$ (Ríos et al. 2005), we use this estimate to infer an air to sea CO$_2$ flux within the MedBox of $7.5 \pm 4$ kmol s$^{-1}$. The TIC transport across the Strait of Gibraltar is $138 \pm 10$ kmol s$^{-1}$ into the MedBox according to Dafner et al. (2001), and $-130 \pm 13$ kmol s$^{-1}$ across the MedBox boundaries. The NCP and the river input of CaCO$_3$ were estimated previously as $-47 \pm 11$ and $25 \pm 10$ kmol s$^{-1}$, respectively. Consequently, $73 \pm 33$ kmol s$^{-1}$ of CO$_2$ (Fig. 2c) are produced within the MedBox. Does it come from the organic carbon mineralized within the region?

The transport of organic carbon across the Strait of Gibraltar into the Mediterranean Sea of $-9.5 \pm 8$ kmol s$^{-1}$ was taken from Dafner et al. (2001). The burial of organic carbon for the Canary and Iberian basins was estimated by Seiter et al. (2005) to be about $0.016$ g C yr$^{-1}$ m$^{-2}$, i.e., $0.07 \pm 0.01$ kmol C s$^{-1}$. The organic carbon transport across the MedBox was estimated, as for the case of organic nitrogen, using the particulate and dissolved organic carbon data from Doval et al. (2001) and the transports by APSB, resulting in an inflow of $76 \pm 20$ kmol s$^{-1}$ into the MedBox. The river input of organic carbon was extrapolated from organic carbon data given by Abril et al. (2002) in the Sado and Douro to the river input in the MedBox by Baumgartner and Reichel (1975), $2.5 \pm 2$ kmol s$^{-1}$. Given these data, the NCP of organic carbon within the MedBox is $-69 \pm 20$ kmol s$^{-1}$ (Fig. 2d).

The production of inorganic carbon ($73 \pm 33$ kmol s$^{-1}$) practically compensates the consumption of organic carbon imported from the Mediterranean Sea and the Atlantic Ocean ($69 \pm 20$ kmol s$^{-1}$), yielding an imbalance of $-4 \pm 39$ kmol s$^{-1}$, which is practically zero within reasonable error bars. Therefore, we conclude that the carbon budget within the MedBox is balanced (Fig. 2c,d).
Discussion

$N_2$ fixation. The NO$_3$ transport across the MedBox walls is under the large uncertainties expected for any mass balance across an oceanic section. In the particular case of the MedBox, the uncertainties are due to the mass transport across the walls (synoptic assumption, seasonality, error in the inverse model constraints, etc.) and the NO$_3$ concentrations (seasonality, steady state assumption in the budget, etc.) along the walls. The same uncertainties are applicable to the Strait of Gibraltar. The river input and air-sea NO$_3$ deposition are one order of magnitude lower than the transports, so they are less influential in calculating the NCP of NO$_3$. The estimated NCP of NO$_3$ coming from the regeneration of organic N produced by $N_2$ fixers mainly relies on the difference between the NO$_3$ and organic N transports across the MedBox walls and Strait of Gibraltar. Consequently, the $N_2$ fixation rate obtained in this work should be taken with caution.

The net rate of $N_2$ fixation for the MedBox area (13 ± 7 kmol s$^{-1}$, 0.24±0.13 mol N m$^{-2}$ yr$^{-1}$ or 658±354 $\mu$mol N m$^{-2}$ d$^{-1}$) is high compared to early estimates using the acetylene reduction technique in the subtropical North Atlantic, which range from 0.29 to 6.2 $\mu$mol m$^{-2}$ d$^{-1}$. However, more recent direct measurements and indirect estimates compiled by Capone et al. (2005) range between 111 and 3,110 $\mu$mol m$^{-2}$ d$^{-1}$. Although our estimated $N_2$ fixation rate is feasible, is the MedBox area favourable for the development of diazotrophs? and are there any direct or indirect evidences of $N_2$ fixation in the region?

Mixed layer depths in the MedBox region are around 30 m during spring and summer and 100 m during fall and winter (Monterey and Levitus 1997). The World Ocean Atlas 2001 gives temperatures from 15 to 20°C in spring, 19 to 23°C in summer, 17 to 24°C in fall and 14 to 21°C in winter at 30 meters, with NO$_3$ always below 1 $\mu$mol L$^{-1}$ in spring, summer and fall. Regarding dust inputs, the southern limit of the MedBox (28°-29°N) is located on the northern boundary of the main dust cloud from the Sahara desert and receives episodic pulses with peaks mainly in winter and summer/fall (Pérez-Marrero et al. 2002). The whole MedBox area is affected by...
Sahara dust deposition ranging from 1.5 to 6 g m\(^{-2}\) yr\(^{-1}\) (e.g., Mahowald et al. 2005) which provide trace elements and macronutrients to the surface North Atlantic ocean and specifically to the study area (e.g., Baker et al. 2003).

In general, there are few direct determinations of \(N_2\) fixing by diazotrophs; to our knowledge, only two recent works show direct evidences of \(N_2\) fixation in the eastern North Atlantic: i) Mahaffey et al. (2003) found particulate organic matter with a low abundance of \(^{15}\text{N}\) relative to \(^{14}\text{N}\) between 26\(^\circ\)N and 32\(^\circ\)N along 20\(^\circ\)W, which associates with a predominance of phytopigments from cyanobacteria and prochlorophytes and elevated \(\text{NO}_3\) to \(\text{PO}_4\) ratios in the upper thermocline; ii) Tyrrell et al. (2003) found high abundances of \textit{Trichodesmium} spp. in the eastern North Atlantic between 0 and 15\(^\circ\)N, but also significant concentrations up to 30\(^\circ\)N. Citing Mahaffey et al. (2003), this apparent inconsistency might be due to utilisation of inorganic nutrients by \textit{Trichodesmium} spp., the presence of other \(N_2\) fixing cyanobacteria and the temporal variability in \(N_2\) fixation. On the contrary, Neuer et al. (2002) did not detect a high N:P ratio in the seasonal evolution of nutrients of the upper 200 m at the ESTOC station (29\(^{\circ}\)10’N, 15\(^{\circ}\)30’W near the Canary Islands), this fact along with the high \(\delta^{15}\text{N}\) isotope values in suspended organic matter collected with sediment trap at ESTOC led them to conclude that \(N_2\) fixation cannot be the dominant source of nitrogen for primary production in the region.

Regarding indirect evidences, the distribution of the \(N^*\) parameter (\(= (\text{NO}_3 -16 \cdot \text{PO}_4 + 2.90) \cdot 0.87\)) in the North Atlantic (Gruber and Sarmiento 1997) at the isopycnals \(\sigma_0 = 26.5\) (Subtropical Mode Water) and \(\sigma_0 = 27.1\) (Subpolar Mode Water), show positive values in the MedBox region, pointing to \(N_2\) fixing as the cause for the \(\text{NO}_3\) excess. Although the work by Vidal et al. (1999) studies an area south of the MedBox, they calculated high downward fluxes of DON from the euphotic zone around 15\(^\circ\)N associated with abundant \textit{Trichodesmium} populations. Lee et al. (2002) quantified the net carbon production due to \(N_2\) fixing in \(\text{NO}_3\)-depleted tropical and subtropical waters with temperatures >20\(^\circ\)C from the decrease in normalized total inorganic
carbon in the mixed layer, estimating the highest rates in the western tropical North Atlantic with a negligible contribution in the MedBox. The study by Hansell et al. (2004\textit{b}) found negative values of DINxs (= NO$_3$ -16 · PO$_4$) along $\sigma_0 = 26.5$ and slightly positive values at $\sigma_0 = 27$, indicating a low input in the MedBox region by N$_2$ fixation. Model studies trying to reproduce the \textit{Trichodesmium} distribution, biomass and fixation rates do not predict any signal in the study area.

Environmental conditions for the development of N$_2$ fixing organisms seem to be positive within the MedBox. In addition, geochemical evidences (low $^{15}$N signal in particulate organic matter and high nitrate to phosphate ratios) also point to the occurrence of N$_2$ fixation, although the abundance of \textit{Trichodesmium} could be relatively low (Tyrrell et al. 2003) or very sporadic. Consequently, other N$_2$ fixing organisms may be mainly responsible for the inferred rate of N$_2$ fixation within the MedBox (Zehr et al. 2000). Clearly, more widespread and interdisciplinary research about marine N$_2$ fixation is needed.

\textit{Heterotrophy.} According to the carbon and nitrogen mass balances, the MedBox is a heterotrophic region, which exports nutrients and CO$_2$ to the adjacent open ocean. The net rate of carbon regeneration within the MedBox is $73 \pm 33$ kmol C s$^{-1}$, $17 \pm 8$ g C m$^{-2}$ yr$^{-1}$ or $47 \pm 21$ mg C m$^{-2}$ d$^{-1}$ which is supported mainly by the input of allochthonous organic matter from the adjacent ocean. This statement needs confirmation; all the terms in the organic carbon budget are rough estimations. Seasonal transports of organic carbon at the Strait of Gibraltar and water column measurements along the MedBox are needed to calculate a reliable transport across the boundaries and to evaluate the exchange between the MedBox and the Atlantic Ocean interior. Another source of uncertainty when setting an organic carbon budget is the atmospheric deposition.

The present day respiration of DOC within the MedBox, about 65 kmol C s$^{-1}$, could explain about 90% of the inorganic carbon produced within the MedBox ($73 \pm 33$ kmol C s$^{-1}$). It
should be considered that a kind of overturning circulation occurs in this region: the formation of Mediterranean Water, which drags to depth anthropogenic carbon (APSB). We hypothesize that it is also dragging DOC to intermediate depths, where it is mineralized. Such a high contribution of DOC to the respiration at intermediate levels greatly exceeds the global estimate of about 25% by Aristegui et al. (2002), based on a compilation of world ocean AOU and DOC data in the 100 to 1000 m depth range but it is consistent with the high DOC consumption rates obtained in areas of intermediate (Hansell et al. 2002) and deep water formation (Hansell and Carlson 1998).

Using an area-weighted mean primary production (PP) for the North East Atlantic (NASE) and Canary Island upwelling system (CNRY) regions (Longhurst et al. 1995), we obtain an average PP of 1000±200 kmol C s⁻¹ for the MedBox, or 610±122 mg C m⁻² d⁻¹. This value is in agreement with recent estimates in the Iberian and Canary upwelling regions and the oligotrophic Eastern North Atlantic.

In order to estimate the plankton community respiration (R), we applied the empirical equations relating PP and R by Williams (1998) and Duarte and Agustí (1998), representing the lower and the upper limits for R in the photic layer of the open ocean, respectively. The latter propose an equation for the open ocean and a general one for all aquatic systems. The equation given in Duarte et al. (2001), representative for the subtropical Northeast Atlantic, is also evaluated. Table 1 shows the estimated R and the resulting carbon deficit (R - PP) in the photic layer of the MedBox. Slight autotrophy is only obtained following Williams (1998); the other approximations yield heterotrophy, especially the general equation by Duarte and Agustí (1998). The estimations for open ocean waters by Duarte and Agustí (1998) and for the subtropical Eastern North Atlantic by Duarte et al. (2001) yielded similar numbers. These rates would be lower limits as they only estimate R in the photic layer. R in the mesopelagic and deep ocean is not included within these empirical relationships. Even so, if we assume that the heterotrophy within the MedBox, calculated for the entire water column, being 1.4±0.7 mol C m⁻² yr⁻¹ (17±8 g
C m\(^{-2}\) yr\(^{-1}\)) occurs in the photic layer, our estimated R is one order of magnitude lower than the calculated in Table 1. Direct estimates of the NCP of the photic layer from experimental in vitro experiments in the subtropical gyre of the Eastern North Atlantic provide a wide range of values from -96 to -456 g C m\(^{-2}\) yr\(^{-1}\) (Duarte et al. 2001).

We can perform a budget for the respiration minus organic matter production in the whole water column of our study region in the same way as del Giorgio and Duarte (2002) for the open ocean, but using measurements in the subtropical Eastern North Atlantic. The respiration in the photic zone is evaluated to be between 64-97 mmol C m\(^{-2}\) d\(^{-1}\) (Aristegui et al. 2005) and 89-136 mmol C m\(^{-2}\) d\(^{-1}\) (Duarte et al. 2001). R values in the mesopelagic and deep ocean are 68±8 mmol C m\(^{-2}\) d\(^{-1}\) and 55±5 mmol C m\(^{-2}\) d\(^{-1}\) (Aristegui et al. 2005), respectively. The respiration of mesozooplankton is evaluated as 5% of the sum of the former estimations (del Giorgio and Duarte 2002), i.e., 10 ± 4 mmol C m\(^{-2}\) d\(^{-1}\). Overall, from in vitro experiments performed in the subtropical Eastern North Atlantic, the water column respiration should be 213 ± 21 mmol C m\(^{-2}\) d\(^{-1}\). The production of organic carbon in the MedBox was 610 ± 122 mg C m\(^{-2}\) d\(^{-1}\) (51 ± 10 mmol C m\(^{-2}\) d\(^{-1}\)) mainly based on \(^{14}\)C measurements. According to del Giorgio and Duarte (2002) these estimations can be incremented by about 48% to account for the algal respiration and DOC production. Therefore, the total organic carbon production will be 76 ± 18 mmol C m\(^{-2}\) d\(^{-1}\) and the water column NCP 137 ± 28 mmol C m\(^{-2}\) d\(^{-1}\). Compared to our estimation (3.7 ± 1.7 mmol C m\(^{-2}\) d\(^{-1}\)) this number is two orders of magnitude higher.

Direct estimates and empirical predictions from in vitro measurements of the heterotrophy of the pelagic subtropical Eastern North Atlantic are at odds with our geochemical estimate. A similar result was obtained by Hansell et al. (2004b) north of 24.5°N in the North Atlantic. We emphasize that geochemical and in vitro studies relate to different spatial and temporal scales. An agreement between them is a current challenge for the oceanographic research community.
Mineralization processes overcome photosynthesis in the MedBox region and NO₃, PO₄ and CO₂ are produced at 21 ± 5, 0.6 ± 0.4 and 73 ± 33 kmol s⁻¹ (17 ± 8 g C m⁻² yr⁻¹), respectively. The potential alkalinity budget suggests a net production of 47 ± 11 kmol s⁻¹ of CaCO₃, which could be converted into a CaCO₃ net production rate of 11 ± 3 g C m⁻² yr⁻¹.

Organic nitrogen and carbon budgets are inferred from the literature; therefore, they will remain tentative until direct organic matter measurements are done along the MedBox boundaries. Seasonal transports of organic matter at the Strait of Gibraltar and organic matter profiles along a MedBox-like cruise should be the subject of future research programmes. Despite this, the mass balances of organic species provide consistent and interesting results. In the case of nitrogen, only 8 ± 4 kmol s⁻¹ of NO₃ come from the decomposition of organic nitrogen within the MedBox, consequently, an external source of nitrogen of 13 ± 7 kmol s⁻¹ is needed. The most likely source of allochthonous nitrogen towards the MedBox is N₂ fixation, introducing nitrogen within the region at a rate of 9 ± 5 mg N m⁻² d⁻¹. Environmental conditions, euphotic layer temperature and nitrate depletion, mixed layer depth and dust inputs from the Sahara are positive for the development of N₂ fixing organisms. However, both direct and indirect studies support and disregard the possibility of N₂ fixation in the subtropical Eastern North Atlantic. In the case of carbon, the inferred consumption of organic carbon compensates the CO₂ produced within the MedBox: the carbon budget is in balance.

Our water column estimate for the heterotrophy within the MedBox region, 17 ± 8 g C m⁻² yr⁻¹, is one order of magnitude lower than direct or empirical estimates from in vitro experiments in the euphotic layer of the region. Even more, considering the whole water column, in vitro-derived estimates are two orders of magnitude higher than our estimate. Three possibilities arise: a) the mass balance approach integrates wider temporal and spatial scales while in vitro experiments reflect daily instant and local conditions and the intermittent nature of the ocean, so both approaches cannot be compared; b) the mass balance approach is not taking into account a
source of allochthonous labile organic carbon from the atmosphere as suggested in a recent work by Dachs et al. (2005); c) the disagreement between mass balance and in vitro NCP estimates could be reduced if instantaneous measurements are scaled according to the community structure (Serret et al. 2001).
References


Table 1. Plankton community respiration in the photic layer of the open ocean according to different equations, relating primary production (PP) and respiration (R), applied to a mean PP in the MedBox of 610±122 mg C m$^{-2}$ d$^{-1}$ or 19±4 mol C m$^{-2}$ yr$^{-1}$. The carbon deficit (R-P) is also shown; positive (negative) values indicate heterotrophy (autotrophy). The photosynthesis quotient is assumed to be 1, and the depth of the photic layer, 150 meters. The carbon deficit obtained in this study was 1.4±0.7 mol C m$^{-2}$ yr$^{-1}$.

<table>
<thead>
<tr>
<th>Equation</th>
<th>R (mmol O$_2$ m$^{-2}$ d$^{-1}$)</th>
<th>R (mol C m$^{-2}$ yr$^{-1}$)</th>
<th>Carbon deficit (mol C m$^{-2}$ yr$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R = 0.73 \cdot P + 4.57$</td>
<td>42 ± 12</td>
<td>15 ± 4</td>
<td>-4 ± 6</td>
<td>Williams (1998)</td>
</tr>
<tr>
<td>$R = 0.2 \cdot P^{0.5}$</td>
<td>0.021 ± 0.009</td>
<td>36 ± 16</td>
<td>17 ± 17</td>
<td>Open ocean Duarte &amp; Agustí (1998)</td>
</tr>
<tr>
<td>$R = 1.0 \cdot P^{0.78}$</td>
<td>0.029 ± 0.008</td>
<td>50 ± 15</td>
<td>31 ± 16</td>
<td>Overall aquatic systems Duarte &amp; Agustí (1998)</td>
</tr>
<tr>
<td>$\log (P/R) = -3.9 + 1.12 \cdot \log(P)$</td>
<td>3226 ± 1638</td>
<td>37 ± 19</td>
<td>18 ± 19</td>
<td>Eastern North Atlantic Duarte et al. (2001)</td>
</tr>
</tbody>
</table>
FIGURE LEGENDS

Figure 1. Location of the station pairs comprising the MedBox walls (circles). The MedBox region is defined between the Strait of Gibraltar and the MedBox walls.

Figure 2. Schematic panels showing the (a) nitrate (NO$_3$), (b) organic nitrogen (N$_{org}$), (c) total inorganic carbon (TIC) and (d) organic carbon (C$_{org}$) budgets in the MedBox region.
FIGURE 1
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FIGURE 2.
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