The relevant time scales in estimating the air–sea CO2 exchange in a mid-latitude region

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Accepted 24 November 2001

Abstract

A 1D biogeochemical model simulating the nitrogen and carbon cycles is validated, using continuous observations obtained with the Carioca buoy (sea surface temperature (SST), pCO2, fluorescence) at the DYFAMED station (NW Mediterranean Sea) in 1995–1997, as well as other in situ data. Although the average surface pCO2 is generally slightly over-saturated (8 ± 8 μatm), the NW Mediterranean Sea is a weak sink for atmospheric CO2 (0.15 ± 0.07 mol C m–2 yr–1), because the highest fluxes occur in winter and spring during the period of under-saturation when the winds are strong. The seasonal cycle is modulated by synoptic events (Mistral bursts), which can have a strong impact on the behaviour of the system and on the fluxes in winter and spring. While the atmospheric forcing constrains the annual balances and fluxes of tracers and CO2, the winter pre-conditioning of the bloom plays a major role in driving the interannual variability. Sensitivity analyses indicate that atmospheric forcing in this highly variable region should be averaged over periods of no longer than one week to simulate the biological and air–sea CO2 fluxes correctly. Also, because the model used is rather simple, this time scale is an upper limit. The sampling period must be no greater than a few days in order to estimate the CO2 fluxes with an error smaller than 20%. In the NW Mediterranean Sea, it is difficult to use “satellite proxies” (SST, sea colour) to estimate annual air–sea CO2 fluxes because SST does not vary much in winter and during the beginning of the bloom, while chlorophyll can either remain low (winter) or change rapidly (beginning of the bloom). At least several direct observations of pCO2 are needed during winter to define “initial conditions”. © 2002 Published by Elsevier Science Ltd.

1. Introduction

Human activity is responsible for modifications of the atmospheric composition, and concentrations of several trace gases which play a significant role in the radiative balance of the lower atmo-

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Although supposedly more constrained than the flux with the terrestrial biosphere, the net CO₂ flux between the atmosphere and the ocean is nevertheless characterised by large uncertainties (1.9 ± 0.6 Gt C yr⁻¹ for the 1980s: IPCC). Such a result comes partly from the strong natural variability of the ocean surface pCO₂; the seasonal air–sea flux is almost two orders of magnitude larger than the flux due to anthropogenic perturbation (Sarmiento and Sundquist, 1992). Moreover, due to the strong coupling between ocean dynamics and biological activity, the mesoscale variability of surface pCO₂ can be as large as basin-scale variations (Watson et al., 1991; Lévy, 1996). Therefore, it is extremely difficult to estimate large-scale air–sea CO₂ fluxes by means of direct observations. If models can be used for such purposes (Sarmiento et al., 1992; Maier-Reimer and Hasselmann, 1987), the results are strongly dependent on the simplified hypotheses used, as well on the scales resolved, and they need data to be validated.

The use of automated devices able to make observations at high frequency can partly solve this issue. Such a device, the Carioca buoy, measures pCO₂, as well as other relevant parameters, such as sea surface temperature (SST) and fluorescence (Lefèvre et al., 1993). It was deployed in 1995, 1996 and 1997, at the DYFAMED station (Fig. 1), which is a long time-series station in the NW Mediterranean Sea (France—JGOFS), that has given rise to several studies (Copin-Montégut and Avril, 1993; Miquel et al., 1994; Lévy et al., 1998; Andersen and Prieur, 2000). The Carioca data are presented and discussed in Hood and Merlivat (2000), who have shown that this part of the Mediterranean Sea is a weak sink of atmospheric CO₂.

In this work, we validate a simple 1D nitrogen–carbon model using the Carioca data, and analyse the variability of the biological and air–sea CO₂ fluxes at different time scales (synoptic, seasonal and interannual). Afterwards, we quantify the impact of the frequency of the atmospheric forcing driving the dynamic model on the estimates of the major biogeochemical fluxes, using sensitivity runs. Finally, from the model results, we address different issues dealing with the estimate of air–sea CO₂ flux from data—the sampling frequency and the use of satellite “proxies” (i.e. SST and sea colour).

2. The setting of the simulation

The biogeochemical model used in this study is a NNPZD-DOM model (nitrate, ammonium, phytoplankton, zooplankton, detritus, dissolved organic matter). It contains the minimum number of generic compartments in order to represent at first order the basic biogeochemical fluxes. Nitrate and ammonium allow the estimation of new and regenerated production, zooplankton mortality and detrital sedimentation feed the particle export flux, and winter mixing of accumulated semi-refractory DOM is associated with the dissolved export flux, which can be the major export flux in the Mediterranean Sea (Copin-Montégut and Avril, 1993; Avril, 2002). Compared to other more complete models (Fasham et al., 1990; Lévy et al., 1998), bacterial production is not explicitly taken into account. This simplification can accelerate the nitrogen regeneration in the model, which means that the f-ratio tends to be under-estimated (Lévy, 1996). The basic equations are presented in Appendix A, as well as the associated equations.
for carbon. The coupling between the nitrogen and the carbon cycles uses mostly Redfield ratio considerations, whereas the C/Chl ratio is assumed to be constant.

The biogeochemical model is imbedded in a 1D physical model, which simulates the time evolution of temperature, salinity and turbulent kinetic energy (TKE); the only dynamic process taken into account is vertical diffusion. The mixing coefficient is obtained diagnostically from the TKE, with a 1.5 closure scheme in the Mellor Yamada nomenclature (Gaspar et al., 1990). It is the same parameterisation that is used in the Primitive Equation model developed at Laboratoire d'Océanographie Dynamique et de Climatologie (LODYC) (Blanke and Delecluse, 1993). The model simulates tracer evolution from the surface to 300 m, with a vertical resolution of 5 m, the bottom layer being closed.

The simulation is forced by the ECMWF atmospheric data (Fig. 2), which give the wind stress and heat fluxes every 6 h. The heat fluxes are split into a solar penetrative forcing (short-wave radiation) and a surface non-penetrative flux (long-wave radiation + latent and sensible heat fluxes). Because surface atmospheric fluxes are not exact, to avoid a strong drift of the model, a regular hybrid formulation is used. A corrective feedback term is added to the heat atmospheric forcing, which tends to make the SST close to data. The surface boundary conditions for salinity only take into account that corrective term, as no explicit E-P term is considered. Although the DYFAMED station can be considered as a first approximation to behave like a 1D vertical system (Lévy et al., 1998; Andersen and Prieur, 2000), deep convection in winter cannot be obtained easily by the negative atmospheric fluxes used in this study. Therefore, in February, the temperature and salinity profiles are forced to be close to the data by a restoring term. In fact, convection and restratification are associated with barotropic–baroclinic instabilities, which are 3D processes: the added term could be an implicit way to take into account these processes.

The biogeochemical tracers are vertically mixed by the same diffusion coefficient as temperature and salinity. Except for CO₂, there is no flux at the air–sea interface. As the zooplankton mortality is instantaneously exported out of the system (Eq. (A.4)), nitrogen is not conserved. Therefore, as for temperature and salinity, dissolved tracers, like nitrate, dissolved organic nitrogen (DON), dissolved inorganic carbon (DIC) and alkalinity, are restored in winter towards climatological homogeneous profiles. The values of these profiles correspond to the averaged value below 200 m, according to the DYFAMED data (6 mmol N m⁻³ for nitrate, 4 mmol N m⁻³ for DON—48 mmol C m⁻³ for DOC—2300 mmol C m⁻³ and 2584 mmol C m⁻³ for DIC and alkalinity). The carbonate equations, which give the partial pressure of CO₂ in terms of DIC and alkalinity, are obtained from Dickson and Millero (1987), with CO₂ solubility given by Weiss (1974). The air–sea CO₂ fluxes are computed from wind speeds using the Liss and Merlivat (1986) relationship. A sensitivity run also was performed with the Wanninkhof (1992) quadratic relationship. Computations show that after 2 yr, the system reaches an annual steady state. Therefore, the standard run (STD) is made of three repeated 1995 years, followed by the years 1996 and 1997: only the three last years of the run are analysed.

3. The simulation: validation

Validation against DYFAMED data can be only qualitative, as the temporal coverage of the nitrate and chlorophyll profiles is no better than monthly. Figs. 3 and 4 compare several temperature, nitrate and chlorophyll profiles in 1995, 1996 and 1997. Although the model results differ from the data in the details, the basic seasonal variability, as well as some significant basic features, are well reproduced. Temperature profiles seem to show that the thermocline in summer is not stratified enough (Fig. 3), which might result from the 1D TKE closure scheme used to parameterise the vertical diffusion coefficient, or from the vertical resolution. The nitracline is correctly simulated except in summer 1995, where it is a little too deep, and the time evolution of the nitrate profiles agrees with the data (Fig. 3). During winter, the restoring term towards an
uniform concentration in February along with vigorous mixing homogenise too strongly the nitrate profiles in the model. The chlorophyll variability in depth and time is also reasonable, with a deep chlorophyll maximum in summer and fall (Fig. 4). High-frequency atmospheric forcing is able to modify very quickly the stratification at the end of the winter, which has a strong impact on the onset of the bloom. On April 10, 1995, and March 2, 1997, high chlorophyll concentrations were simulated. These values come after the sharp shallowing of the mixed layer (ML), leading to the spring bloom (Fig. 7a: days 100 and 790, respectively). The data tend to show the onset of the bloom at the same period, but with smaller chlorophyll concentrations (Figs. 4a and c).

Although the exact timing of the bloom could be shifted in the model, a light-dependent C/Chl ratio (Lévy et al., 1998) might partly explain the high model chlorophyll concentrations. The C/Chl ratio is known to increase with light availability (Doney et al., 1996; Geider et al., 1996). With a ratio of 150 mg C (mg Chl)$^{-1}$ (compared to 55 mg C (mg Chl)$^{-1}$ used in the model, generally associated with the Deep Chlorophyll Maximum—Table 5), the surface Chl concentrations simulated could be divided by a factor 3. On April 5, 1996, the temperature profile is not very stratified, but nitrate and chlorophyll profiles show that the bloom has already started, both in the data and in the model.
Table 1 shows the annual average of some major biological fluxes. Over the three-year period, total production amounts to $138.7 \text{gCm}^{-2}\text{yr}^{-1}/\text{C}_0$, which is larger than the flux obtained for the year 1991 by Lévy et al. (1998) with a more complex model, but remains in the range of different estimates coming from either in situ measurements or satellite data—from $78 \text{gCm}^{-2}\text{yr}^{-1}$ (Minas, 1970) to $157.7 \text{gCm}^{-2}\text{yr}^{-1}$ (Antoine et al., 1995) for the whole western basin. At DYFAMED, the average annual primary production during the years 1993–1999 is equal to $156 \text{gCm}^{-2}\text{yr}^{-1}/\text{C}_0$ (Marty and Chiaverini, 2001). The organic matter is exported mostly as DOM, in agreement with previous estimates: although less pronounced, the role of DOM in export fluxes also has been emphasised in several other oligotrophic areas (Carlson et al., 1994; Emerson et al., 1997). The averaged particle export is equal to $3.9 \text{gCm}^{-2}\text{yr}^{-1}/\text{C}_0$, which can be compared to $4.0 \text{gCm}^{-2}\text{yr}^{-1}$ between 1987 and 1990, estimated from sediment traps (Miquel et al., 1994). In agreement with the data presented in Copin-Montégut and Avril (1993), the estimate of the DOC export flux has an average of $14.3 \text{gCm}^{-2}\text{yr}^{-1}$ (based on a DOM C/N ratio of 12). An updated estimate of the DOC export flux amounts to $12 \text{gCm}^{-2}\text{yr}^{-1}$ (Avril, 2002).

In 1997, the Carioca buoy measured fluorescence during the bloom and at the end of the year. These data are shown with the surface chlorophyll...
obtained in the simulation in Fig. 5. Compared either with Carioca or DYFAMED data, the bloom in the model does not last long enough. An analysis of the run shows that, in 1997, the intensity of the bloom is partly controlled by zooplankton grazing, before being strongly constrained by nutrient limitation. Therefore, during the bloom, the coupling between primary and secondary productions could be too strong in the model. Nevertheless, if the grazing pressure is decreased, chlorophyll concentrations during summer in the sub-surface maximum become too high. It appears that generic phytoplankton and zooplankton cannot simulate correctly the seasonal variability, closely linked to species succession. That shortcoming could be “corrected” by changing the grazing parameters with time, making the coupling between primary and secondary productions more efficient during summer compared to spring. That sensitivity study goes beyond the scope of this study and is not presented here. Assuming a linear relationship between fluorescence and chlorophyll concentrations, as it is implicitly done on Fig. 5, the winter fluorescence observations tend to indicate blooms that are either not present or less intense in the model. This comes certainly from the restoring term on the physical tracers, which are applied during that period: the ML dynamics is smoothed by this added term, the ML forced to remain deep, and transient blooms absent by lack of stratification.

The SST, surface $p$CO$_2$, and surface $p$CO$_2$ at 13°C during the three years considered are presented in Figs. 6a–c, along with the Carioca data. The low-frequency (seasonal) patterns of the SST are correctly reproduced. Nevertheless,
oscillations with periods of several days clearly seen in the data are much smoother in the model outputs. These oscillations are associated with a succession of atmospheric depressions (strong winds and heat loss—Fig. 2) and quiet periods. They are mostly observed after the shallowing of the ML, at the end of the spring and during summer, when the thermodynamical response of the upper ocean is fast. The lack of variability in the model tends to show that the ML dynamics are not perfectly simulated with the TKE closure scheme and the vertical resolution used. As already noted, the thermocline is too diffuse at the base of the ML, which could partly explain the SST low variability. Figs. 6a and b emphasise the major role played by the SST in driving surface $p$CO$_2$ mainly during summer. When $p$CO$_2$ is corrected from the temperature effect according to the relationship of Takahashi et al. (1993), there is a decrease of 80–100 $\mu$atm in $p$CO$_2$, between winter and summer (Fig. 6c). This variation is mostly due to variations in surface DIC, resulting mostly from biological uptake. That decrease can be compared to the total observed increase of 120 $\mu$atm in 1996 and 1997 and of about 200 $\mu$atm in 1995. Of opposite sign, the SST effect is about twice the biological effect.

When data are available in summer (1995 and 1997), they show a systematic decrease in $p$CO$_2$ at 13°C. Although a decrease can be seen in the model results as well, it is much less pronounced (Figs. 6b and c): between days 200 (07/19) and 238 (08/16) in 1995, this decrease amounts to 25.1 $\mu$atm (7.5 $\mu$atm) in the CARIOLCA data set (simulation), and between days 176 (06/16) and 300 (10/27) in 1997, it amounts to 49.6 $\mu$atm.
The impact of salinity and alkalinity variability is rather small on the time evolution of \( pCO_2 \) in the model. That means that most of the variability of \( pCO_2 \) at 13°C is driven by DIC changes. During summer, only gas exchange (over-saturation due to high SST) and biological uptake could explain a decrease in DIC. As the Liss and Merlivat (1986) gas transfer velocity is about half of the relationship of Wanninkhof, a sensitivity study (run WAN) has been done by using the Wanninkhof (1992) formulation. The decrease in \( pCO_2 \) at 13°C is enhanced (up to 18.8 and 35.4 μatm for the two periods considered in 1995 and 1997). It still does not reach the decrease observed in the data (Fig. 6c). In fact, this apparent contradiction (decrease in DIC with no nutrient in the euphotic layer) already has been observed and thoroughly discussed in another oligotrophic area, the BATS station (Gruber et al., 1998). Different hypotheses have been proposed, like the accumulation of carbon in the C-enriched DOM pool (Bégoovic and Copin-Montégut, 2002), the role of nitrogen fixers (cyanobacteria), or nitrogen atmospheric deposition. Although no data are available at the DYFAMED station, it is likely that the same processes are at play in the same type of ecosystem. As the model considers a C/N larger in the DOM pool than in the other pools (12.0 compared to 6.6), the first process is implicitly taken into account: the simulation seems to show that the C accumulation in the dissolved organic matter (DOM) cannot explain the observed decrease in DIC in summer.

Figs. 6b and c display also the \( pCO_2 \) evolution of a sensitivity study, which has taken into account an additional source of new production. Every year, during the oligotrophic period, between days 150 and 300, the phytoplankton growth rate is increased by 5% without considering the nutrient limitation term, as if nitrogen was added to the system and entirely

<table>
<thead>
<tr>
<th></th>
<th>Run 1995</th>
<th>1996</th>
<th>1997</th>
<th>Mean (deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP STD INIT</td>
<td>51.9</td>
<td>46.7</td>
<td>44.7</td>
<td>47.8 (3.7)</td>
</tr>
<tr>
<td>TP STD INIT</td>
<td>136.9</td>
<td>141.8</td>
<td>137.5</td>
<td>138.7 (2.7)</td>
</tr>
<tr>
<td>Exp. part. STD INIT</td>
<td>3.23</td>
<td>3.77</td>
<td>4.67</td>
<td>3.89 (0.73)</td>
</tr>
<tr>
<td>Exp. DOC STD INIT</td>
<td>10.2</td>
<td>19.7</td>
<td>13.1</td>
<td>14.3 (4.9)</td>
</tr>
<tr>
<td>ΔpCO₂ STD INIT</td>
<td>15.2</td>
<td>−0.2</td>
<td>8.4</td>
<td>7.8 (7.7)</td>
</tr>
<tr>
<td>Air–sea flux STD INIT</td>
<td>0.112</td>
<td>0.306</td>
<td>0.199</td>
<td>0.148 (0.072)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.202</td>
<td>0.175</td>
<td>0.0017</td>
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NP = NO₃ production in g C m⁻² yr⁻¹.
TP = total production in g C m⁻² yr⁻¹.
Exp. part. = export of large particles (zooplankton mortality) in g C m⁻² yr⁻¹ at 200 m.
Exp. DOC = export of DOM in g C m⁻² yr⁻¹ at 200 m.
ΔpCO₂ = air–sea \( pCO_2 \) difference in μatm (\( pCO_2 \) atm = 350 μatm).
Air–sea flux = \( CO_2 \) air–sea exchange in mol C m⁻² yr⁻¹.
STD: Standard run with winter-restoring of dissolved tracer profiles towards the average of the data below 200 m.
INIT: Run with winter-restoring of dissolved tracer profiles towards in situ observations.
Mean (deviation): average (standard deviation) of the three years.

(20.0 μatm). The impact of salinity and alkalinity variability is rather small on the time evolution of \( pCO_2 \) in the model. That means that most of the variability of \( pCO_2 \) at 13°C is driven by DIC changes. During summer, only gas exchange (over-saturation due to high SST) and biological uptake could explain a decrease in DIC. As the Liss and Merlivat (1986) gas transfer velocity is about half of the relationship of Wanninkhof, a sensitivity study (run WAN) has been done by using the Wanninkhof (1992) formulation. The decrease in \( pCO_2 \) at 13°C is enhanced (up to 18.8 and 35.4 μatm for the two periods considered in 1995 and 1997). It still does not reach the decrease observed in the data (Fig. 6c). In fact, this apparent contradiction (decrease in DIC with no nutrient in the euphotic layer) already has been observed and thoroughly discussed in another oligotrophic area, the BATS station (Gruber et al., 1998). Different hypotheses have been proposed, like the accumulation of carbon in the C-enriched DOM pool (Bégoovic and Copin-Montégut, 2002), the role of nitrogen fixers (cyanobacteria), or nitrogen atmospheric deposition. Although no data are available at the DYFAMED station, it is likely that the same processes are at play in the same type of ecosystem. As the model considers a C/N larger in the DOM pool than in the other pools (12.0 compared to 6.6), the first process is implicitly taken into account: the simulation seems to show that the C accumulation in the dissolved organic matter (DOM) cannot explain the observed decrease in DIC in summer. Figs. 6b and c display also the \( pCO_2 \) evolution of a sensitivity study, which has taken into account an additional source of new production. Every year, during the oligotrophic period, between days 150 and 300, the phytoplankton growth rate is increased by 5% without considering the nutrient limitation term, as if nitrogen was added to the system and entirely
Fig. 4. Chlorophyll profiles. Model results vs. data. Same as Fig. 3 (mg Chl m$^{-3}$).
assimilated (run N2FIX). DIC decrease in summer is then enhanced. The results show that the time variations of $pCO_2$ are in better agreement with the data (decrease of 20.0 and 42.3 μatm during the two periods considered in 1995 and 1997). The total new production due to new nitrogen uptake amounts to about 10 g C m$^{-2}$ yr$^{-1}$, which can be compared to the annual nitrate uptake of 45–50 g C m$^{-2}$ yr$^{-1}$ or to the total production of 140 g C m$^{-2}$ yr$^{-1}$. This new added production is entirely exported, mostly through DOM diffusion in winter, the increase in large particle sedimentation being small.

Alkalinity is a fundamental parameter in estimating $pCO_2$. An increase in alkalinity could a priori decrease $pCO_2$ during summer. Correlation between alkalinity and salinity is generally strong at the regional scale (Copin-Montégut and Begovic, 2002). Moreover, growth of coccolithophorids is associated with a strong decrease (increase) in alkalinity ($pCO_2$). Therefore, changes in alkalinity cannot be ruled out in explaining the decrease in $pCO_2$ during summer. In the present run, salinity is poorly simulated, as the E-P atmospheric forcing is not considered. Being driven by the atmospheric water cycle, the errors associated with this forcing are very high, which is a major issue for $CO_2$ simulations: it is the main reason for using restoring towards observations for sea surface salinity (SSS), a classical procedure in ocean modelling. Local precipitation can decrease (increase) the salinity and the alkalinity ($pCO_2$) substantially: these transient events could partly explain the high $pCO_2$ values observed in January 1996 and not simulated in the model (Fig. 6c). Salinity is always high in the Mediterranean Sea, and its low-frequency seasonal variability is taken into account by the restoring terms in the simulation. For instance, in 1997, between days 176 and 300, SSS increases by 0.15 PSU, implying an increase of alkalinity of 15 mmol kg$^{-1}$ using the linear relationship of Copin-Montégut and Begovic (2002). The associated decrease in surface $pCO_2$ amounts to ~12 μatm, which is
non-negligible compared to the observed decrease of 50 μatm. Although precise data do not exist, it is not likely that growth of calcareous plankton could greatly influence the time evolution of surface $pCO_2$ at DYFAMED. To match a decrease of surface $pCO_2$, the end of the bloom must be characterised by a coccolithophorid-dominant ecosystem, and summer by a non-calcareous ecosystem. Copin-Montégut and Bégovic (2002) noted that the absence of seasonal variation in the salinity–alkalinity relationship can be explained by a weak impact of biological activity on alkalinity. In the simulation, a classical rain ratio of 0.1 has been used, which implies an increase in alkalinity due to the decrease in primary production from spring to summer. The alkalinity distribution is therefore driven by dynamics (vertical diffusion) and biological activity (primary production and respiration): its variability is too low (by μmol kg$^{-1}$) to strongly constrain the surface $pCO_2$.

4. Seasonal and interannual variability

Figs. 7a shows the annual variations of several basic biogeochemical parameters during the years of the simulation. The annual cycle can be decomposed into three main periods. From December to February, the pre-bloom conditions prevail: SST is low, the ML deepens, nutrients are high, and biological stocks and fluxes reach their lowest levels, which results from deep ML and light limitation. During favourable situations, some localised blooms can occur (when the ML is still shallow and is deepening in November–December, for instance). Generally, because of low SST, $pCO_2$ is below atmospheric levels, and the ocean takes up atmospheric CO$_2$. During the following months, as heat fluxes become positive, the upper ocean becomes stratified, and a classical spring bloom occurs, with high $f$-ratios (up to 90% averaged over the 100 m). After several weeks, primary production decreases by lack of
nutrients, and phytoplankton is mostly grazed by zooplankton. During that period, there is a drawdown of surface $pCO_2$ of 40–80 μatm, and CO$_2$ invasion into the ocean. In summer and fall, the stratification is strong, nutrients are limiting, there is some loss through sedimentation, and the system is based on regenerated production. $pCO_2$ follows the SST evolution, and CO$_2$ is mostly degassing to the atmosphere. Globally, although the average surface $pCO_2$ is larger than the atmospheric CO$_2$, the ocean takes up carbon dioxide on an annual basis. The winds are much higher during winter and spring (Fig. 2) periods during which the ocean is under-saturated. CO$_2$ over-saturation during summer is not strong enough to compensate for the weak transfer velocities.

This general annual pattern undergoes interannual variations, mostly during the spring bloom. Year 1996 is characterised by a shallower ML during the convection phase (Fig. 7a), as well as a bloom which starts later (mid-March day 450—compared to the beginning of February in 1995 and 1997—days 40 and 790). Stratification of the seasonal thermocline is temporarily stopped by
atmospheric events, mostly in 1995, but also in 1997. At this period of the year, the upper ocean is not yet very well stratified, and deep mixing can occur even if the atmospheric forcing is only weakly negative (small heat loss for the ocean). On 10 February 1997 (day 771), a strong depression stops the development of the bloom for several days, whereas, in 1995, several events in February–March end in disrupting the bloom for almost two weeks. In fact, the bloom due to the definitive shallowing of the ML is delayed to mid-March (like in 1996).

Annual values of several biogeochemical parameters (Table 1) indicate strong interannual variability in the seasonal cycle, but the integrated annual biological productions are more steady. The relative variability, estimated over only three years, reaches 2% and 8% for the total and new production, but is larger for the export fluxes (19% and 34%, respectively, for the particle and dissolved fluxes—not shown). At first order, one might explain the lack of variability by the fact that the “initial load” of nitrate in winter is almost the same every year, as the profiles are imposed to get close to a constant value of $6 \text{ mmol m}^{-3}$ during deep convection. Variability in physical forcing, i.e., in the ML dynamics, can modify nitrate upward fluxes and primary production during the spring and autumn blooms, but the main constraint is still the initial amount of nutrient at the beginning of the year. In order to test this hypothesis, and to better describe interannual variability, a sensitivity run was done by imposing nitrate winter profiles coming from real data (run INIT). During this run, the pre-bloom amount of nitrate is increased by 15% in 1995, and decreased by 23% in 1996 and 1997. Validation of this run is shown in the figures already discussed (Figs. 3 and 4). The differences in nitrate and chlorophyll profiles against data are not significant, which means that validation of such models need a better time resolution of the data coverage, or different types of data, more sensitive than nitrogen stocks. Nevertheless, modifications of biogeochemical fluxes are not negligible: the interannual variability is increased by a factor 2–6, depending upon the parameter studied. The major biological fluxes (new and total production, Table 1) have been modified according to the changes in the initial pre-bloom concentrations of nitrate. With regard to the $p\text{CO}_2$ and air–sea $\text{CO}_2$ fluxes, results in Fig. 6b indicate that the drawdown of $p\text{CO}_2$ during the bloom is increased or decreased following the modifications of production during that period. The post-bloom shift in $p\text{CO}_2$ is kept more or less constant during summer, as the upper ocean system is almost closed, except for loss by gas transfer. Therefore, the air–sea fluxes are modified accordingly, which means that they are increased in 1995 and decreased in 1996 and 1997, becoming almost negligible during 1997 (Table 1).
5. Role of the atmospheric forcing

High-frequency events of several days, like Mistral bursts, can potentially modify the time evolution of the ML dynamics and the biological fluxes. The basic simulations have shown that such events exist in the atmospheric forcing at least in 1995 and 1997 in winter and spring (Fig. 7a). Previous discussions have shown that, with SST, the spring bloom intensity and timing is a major factor which constrains the evolution of surface $p$CO$_2$. Moreover, data obtained during JGOFS process studies have emphasised the role of quiet periods in the onset of the bloom during winter (Garside and Garside, 1993; Townsend et al., 1992). Finally, CO$_2$ fluxes result from the product of the transfer velocity and of the air–sea $p$CO$_2$ gradient. This non-linear relationship certainly controls the forcing frequency necessary to obtain unbiased fluxes. The question addressed here deals with this threshold frequency below which the surface fluxes are correctly estimated, and the
processes at play in the variations of the CO₂ fluxes in terms of the atmospheric forcing frequency.

In order to quantify the influence of the frequency of the atmospheric forcing, several sensitivity studies were performed by smoothing the wind stress and the heat fluxes. The ECMWF atmospheric forcing have a time resolution of 6 h. Different simulations were done by averaging these fluxes for periods between 1 and 30 days (hereafter referred to as d). Fig. 7 displays the time evolution of several relevant parameters for 3- and 30-d averaged forcing (simulations F03 and F30, respectively). Changes in the ML depth during winter and spring modify the biological fluxes. In 1997, in the F03 run, the bloom intensity is greatly (Fig. 7a) decreased, whereas the complex winter–spring bloom in 1995 has entirely disappeared in the F30 run (Fig. 7b), to give rise to a more standard bloom (in the run with a 15-d forcing, that behaviour is already present, and with a 7-d forcing, there is only a weak signature of a first bloom at the end of February). Even if the SST surface restoring is not modified, SST is changed up to +1.5°C during spring in the F03 run. A longer forcing period seems to imply a cooler SST during summer, which is much more significant in the F30 run than in the F03 one (mostly in 1997). These changes in ML dynamics, SST and primary production have impact on the surface pCO₂, which is different by 20 µatm (70 µatm) in the F03 (F30) simulation. The pCO₂ changes at 13°C show that, in summer, a large part of the increase in pCO₂ with increasing forcing period is controlled by SST, whereas the decrease during spring comes from the vertical dynamical fluxes and primary production.

The relative variations of the annual averages of some main biological fluxes due to the changes in the forcing period are presented in Fig. 8 and Table 2. As already pointed out, the three years studied behave differently. Years 1995 and 1997 undergo the largest decrease in annual production, which can partly be associated with the initial higher variability of the ML dynamics during winter and spring. On the contrary, year 1996 does not display much sensitivity to the forcing period, as the ML dynamics does not change very much with the forcing period (Fig. 7b). The mean pCO₂ tends to increase in 1995, as well as in 1996, whereas it decreases slightly in 1997. As the gas transfer velocity depends upon the mean wind in the model, it tends to decrease dramatically with increased forcing period. As a result, the air–sea CO₂ flux follows the same trend, with nevertheless a strong modulation coming from the pCO₂ gradient. For instance, in 1996, the flux decrease is weak and begins only for a forcing period of
about 15d: there is a compensation between the changes in surface $pCO_2$ (increased air–sea gradient) and in the gas transfer velocity. Although less pronounced, that mechanism takes place in 1995 as well: the air–sea flux is larger for forcing period ranging from 1 to 10d. At DYFAMED, in 1995–1997, in order to estimate the annual $CO_2$ air–sea flux with an error smaller than 20%, the atmospheric forcing period should be of the order of a week (from several days in 1997 and 1995 to almost a month in 1996).

6. Estimation of $CO_2$ fluxes

6.1. Sampling period

During the JGOFS years, several long time-series stations have been deployed in different oceanic regions, like BATS in the sub-tropical North Atlantic Ocean (Michaels et al., 1994; Michaels and Knap, 1996), HOT in the sub-tropical North Pacific Ocean (Karl and Lukas, 1996), DYFAMED in the Mediterranean Sea (Miquel et al., 1993; Copin-Montégut and Avril, 1993; Hood and Merlivat, 2000; Marty et al., 2002) or KERFIX in the Indian sector of the Southern Ocean (Fiala et al., 1998). These stations are visited on a regular basis, when core and more specific parameters are measured. Moreover, satellite data allow a global and synoptic coverage of parameters, like wind, SST or chlorophyll. Mapping these parameters can be used to estimate biogeochemical fluxes, like air–sea $CO_2$ transfer (Boutin et al., 1999; Stephens et al., 1995; Antoine and Morel, 1995). Following Antoine and Morel (1995), the issue, which can be addressed by modelling, deals with the frequency of measurements or mapping needed to get a robust estimate of fluxes. In order to answer this question, annual $CO_2$ air–sea exchange was computed by under-sampling the data set given by the daily results of the model. For each sampling period ($x\, d$, with $x$ ranging from 1 to 60), the $CO_2$ flux was determined by averaging the set of all the possible subsets, the date of the first sample varying from day 1 to day $x$:

$$F_{x_i} = \frac{1}{N_x} \sum_{k} f_{i+k-x},$$

where $k$ varies from 0 to $k_f$, with $k_f x \leq 365$ and $(k_f + 1)x > 365$, and $N_x$ is the number of samples.

<table>
<thead>
<tr>
<th>Sensitivity simulations with varying atmospheric forcing frequency</th>
<th>Run</th>
<th>1995</th>
<th>1996</th>
<th>1997</th>
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<tbody>
<tr>
<td>NP</td>
<td>STD</td>
<td>51.9</td>
<td>46.7</td>
<td>44.7</td>
</tr>
<tr>
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<td>49.7</td>
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</tr>
<tr>
<td>F03</td>
<td>48.8</td>
<td>46.0</td>
<td>42.8</td>
<td></td>
</tr>
<tr>
<td>F07</td>
<td>44.9</td>
<td>46.2</td>
<td>43.4</td>
<td></td>
</tr>
<tr>
<td>F15</td>
<td>43.6</td>
<td>45.7</td>
<td>43.5</td>
<td></td>
</tr>
<tr>
<td>F30</td>
<td>41.3</td>
<td>45.2</td>
<td>43.4</td>
<td></td>
</tr>
<tr>
<td>TP</td>
<td>STD</td>
<td>136.9</td>
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</tr>
<tr>
<td>F01</td>
<td>132.9</td>
<td>141.6</td>
<td>129.9</td>
<td></td>
</tr>
<tr>
<td>F03</td>
<td>132.2</td>
<td>140.7</td>
<td>128.0</td>
<td></td>
</tr>
<tr>
<td>F07</td>
<td>124.8</td>
<td>140.8</td>
<td>127.2</td>
<td></td>
</tr>
<tr>
<td>F15</td>
<td>124.4</td>
<td>140.3</td>
<td>127.3</td>
<td></td>
</tr>
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<td>F30</td>
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<td>128.4</td>
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<tr>
<td>Transfer velocity</td>
<td>STD</td>
<td>6.01</td>
<td>8.08</td>
<td>10.16</td>
</tr>
<tr>
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<td>5.20</td>
<td>7.19</td>
<td>9.52</td>
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<td>4.31</td>
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<td>8.51</td>
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<td>3.65</td>
<td>5.31</td>
<td></td>
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<tr>
<td>$\Delta pCO_2$</td>
<td>STD</td>
<td>15.2</td>
<td>−0.2</td>
<td>8.4</td>
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<tr>
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<td>2.2</td>
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<td>7.1</td>
<td></td>
</tr>
<tr>
<td>F30</td>
<td>24.2</td>
<td>0.9</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>Air–sea flux</td>
<td>STD</td>
<td>0.112</td>
<td>0.306</td>
<td>0.199</td>
</tr>
<tr>
<td>F01</td>
<td>0.120</td>
<td>0.309</td>
<td>0.163</td>
<td></td>
</tr>
<tr>
<td>F03</td>
<td>0.120</td>
<td>0.312</td>
<td>0.153</td>
<td></td>
</tr>
<tr>
<td>F07</td>
<td>0.130</td>
<td>0.308</td>
<td>0.134</td>
<td></td>
</tr>
<tr>
<td>F15</td>
<td>0.095</td>
<td>0.284</td>
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</tr>
<tr>
<td>F30</td>
<td>0.064</td>
<td>0.196</td>
<td>0.102</td>
<td></td>
</tr>
</tbody>
</table>

NP = NO3 production in g C m$^{-2}$ yr$^{-1}$.
TP = total production in g C m$^{-2}$ yr$^{-1}$.
Transfer velocity in cm h$^{-1}$.
$\Delta pCO_2 =$ air–sea $pCO_2$ difference in μatm ($pCO_2$ atm = 350-μatm).
Air–sea flux = $CO_2$ air–sea exchange in mol C m$^{-2}$ yr$^{-1}$.
STD: standard run with 6h atmospheric forcing.
$F_{xx}$: run with atmospheric forcing averaged over $xx$ days.
For the sampling period \( x \), the sub-set of the estimates is obtained by varying \( i_0 \) from 1 to \( x \). The standard deviation of the \( x \) mean fluxes determined for each different sampling period is plotted in Fig. 9. The variance increases regularly with \( x \): it reaches 100% of the flux for a sub-sampling period of about 18, 45 and 15 d for, respectively, 1995, 1996 and 1997. If an accuracy better than 20% is required, the sub-sampling period must be at most a few days. These results can be compared to those obtained by Garçon et al. (1992), who performed a similar exercise for a model at Ocean Station P (NE Pacific Ocean). From their Fig. 10, one sees that the minimum sampling period is longer (around two weeks). The regional hydrodynamical conditions are quite different between the North Pacific Ocean and the Mediterranean Sea, where the seasonal signal and the intensity of the bloom are much larger, with strong variability due to wind bursts. Sub-sampling a highly varying system can strongly alias averages (Wunsch, 1996).

In these calculations, it has been assumed that the daily observations of wind and \( pCO_2 \) are synoptic. In fact, satellite data or atmospheric models produce wind fields at different time-scales (generally at higher frequency) than \( pCO_2 \) observations. New estimates of \( CO_2 \) air–sea exchange have been performed assuming wind distributions averaged over one week, like those that can be obtained with global satellite data. The results (not shown) indicate that the fluxes are not strongly aliased in 1996 (an under-estimation of <10% when the sampling period of \( pCO_2 \), \( \Delta T \), is smaller than 40 d), but the years 1995 and 1997 behave quite differently. The misfit with the “true” flux (computed with a daily sampling of both wind and \( pCO_2 \)) is always larger than 10%. As already noted (Fig. 9), the error associated with the air–sea estimations increases with \( \Delta T \): in 1995 and 1997, it reaches 20% with \( \Delta T \) of 3 and 4 d, respectively, and >100% for \( \Delta T \) of 16 and 13 d, respectively. The year 1996 is characterised by a much smaller error (<20% when \( \Delta T \) is below 12 d, and >50% when \( \Delta T \) is above 33 d). As already noted, the difference between the years are related to the variability of the atmospheric forcing.

### 6.2. Satellite proxies

Recently, different authors used correlation between parameters observed from satellites to estimate air–sea \( CO_2 \) fluxes (Stephens et al., 1995; Boutin et al., 1999). As surface \( pCO_2 \) is driven by dynamic, thermodynamic and biological processes, it is hoped that these parameters can be obtained in terms of other parameters, which are visible from space and which are controlled by the same processes. In the following, the feasibility of this statistical approach is tested at DYFAMED using the model results. Fig. 10a displays the
surface \( p\text{CO}_2 \) distribution in terms of SST. As already noted by Hood and Merlivat (2000), the different regimes or seasons are characterised by specific relationships between \( p\text{CO}_2 \) and SST. During the warming season (red), the increase in SST is associated with an increase in \( p\text{CO}_2 \); vertical transfer of carbon across the base of the shallow ML is small, and only the SST effect on solubility has a significant impact. The same process applies for the decrease in SST and \( p\text{CO}_2 \) at the end of the summer and during fall (black). Nevertheless, the \( p\text{CO}_2 \) level is lower, as some carbon has been lost by air–sea exchanges during summer, even if its intensity is small. At the end of the fall, SST is low, and deep mixing brings up carbon. There is an increase in \( p\text{CO}_2 \) without large variations of SST (blue). Finally, the development of the spring bloom is emphasised by a decrease in \( p\text{CO}_2 \) without significant increase in SST (green).

When the thermodynamic effect is strong, during summer and fall, correlation between SST and \( p\text{CO}_2 \) are high. During winter and spring, this correlation is less obvious and tends to show a large interannual variability. In order to go a step further, the SST signal is removed by computing \( p\text{CO}_2 \) at 13°C, and Fig. 10b shows the evolution of this corrected \( p\text{CO}_2 \) against surface chlorophyll, another parameter that can be estimated from space. During most of the year, the chlorophyll concentrations are low and constant, whereas \( p\text{CO}_2 \) at 13°C can change by 100 μatm. This is obvious in winter, when DIC and nitrate are brought to the surface without any biological activity. It also can be seen in summer, although on a smaller scale. The fact that \( p\text{CO}_2 \) at 13°C is variable during that period shows that the SST control on \( p\text{CO}_2 \) is not complete, and that vertical exchange, alkalinity variations and air–sea fluxes cannot be entirely negligible. Large variations of \( p\text{CO}_2 \) at 13°C with low, almost constant, surface chlorophyll during most of the year make the usefulness of sea-surface colour data questionable in estimating air–sea CO2 exchange, at least in the Mediterranean Sea. During the bloom, changes in surface chlorophyll are significant, but the interannual variability is also important. A unique and simple relationship between \( p\text{CO}_2 \) at 13°C is difficult to obtain. Moreover, the fall bloom shows a different relationship, with \( p\text{CO}_2 \) values lower than those obtained during the spring bloom.

To test this approach further, a study was made, following Hood and Merlivat (2000) who have used seasonal \( p\text{CO}_2 \)–SST correlation in order to estimate air–sea \( p\text{CO}_2 \) fluxes. In the present work, each year was divided into four periods. The
Table 3
Date of the beginning of the different periods using SST and surface Chla

<table>
<thead>
<tr>
<th>Period</th>
<th>01/01/95</th>
<th>12/24/95</th>
<th>12/15/96</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bloom</td>
<td>03/30/95</td>
<td>03/28/96</td>
<td>02/19/97</td>
</tr>
<tr>
<td>Warming</td>
<td>05/27/95</td>
<td>05/25/96</td>
<td>04/01/97</td>
</tr>
<tr>
<td>Cooling</td>
<td>08/05/95</td>
<td>09/01/96</td>
<td>09/10/97</td>
</tr>
</tbody>
</table>

criteria chosen to define these periods take into account only SST and surface chlorophyll concentrations in order to be consistent with the use of satellite data. The beginning of the bloom is defined by a chlorophyll threshold value (> 0.10 mg Chl m⁻³). The post-bloom period starts when the surface chlorophyll becomes smaller than 1/10 of the maximum chlorophyll concentration. The warming period ends when SST begins to decrease. Finally, the winter period starts when SST is smaller than a threshold value (in this case, 14°C). Table 3 gives the limits of the different periods for each year. A first basic experiment used all the data, by fitting the surface $p$CO₂ with a second-degree polynomial function against SST for each period (Hood and Merlivat, 2000). If comparisons between $p$CO₂ estimated from correlation between SST and $p$CO₂ obtained from the model are qualitatively good (not shown), the major problems come from the winter and the bloom periods, as SST does not vary much during this time of the year. Table 4 indicates that the air–sea CO₂ fluxes obtained are close to the exact fluxes, coming from the model results, mostly for 1995 and 1996 with a bias <5%. In 1997, the results are not as good, the bias decreasing down to -25%.

In fact, to test the method properly, it is necessary to apply the relationship to data sets that have not been used to estimate the parameters of the correlation. Therefore, the same computations were made, but only one or two years are used to fit $p$CO₂ against SST, and the surface $p$CO₂, as well as the air–sea fluxes, were estimated for the other years. Table 4 shows the results for different combinations of years. When year 1997 is used, the results are dramatically poorer. Even if the results using this year are not taken into account, the annual air–sea CO₂ fluxes can only be estimated to a factor 2 when the data are not used in the fitting, the error decreasing to <10% if the data are used in the fitting. Therefore, the good results obtained with the global fitting must be tempered by the sensitivity tests undertaken by sub-sampling the data set.

7. Conclusion

This work has allowed validation of simple biogeochemical model of the carbon cycle in a highly variable region (NW Mediterranean Sea), using data obtained with the Carioca buoy in 1995–1997. Although some shortcomings have
been emphasised, the agreement between the model results and the data is good. Although the annual surface \( pCO_2 \) is slightly over-saturated, the DYFAMED region is a weak atmospheric CO\(_2\) sink, due to strong winds during winter and spring. As in other regions, a non-Redfieldian process seems to be responsible for a DIC and \( pCO_2 \) decrease in summer, occurring with almost no surface nitrate. Nevertheless, mostly through its correlation with salinity, alkalinity could partly explain that decrease: that emphasises the need to have more reliable fresh water fluxes, as SSS must be accurately simulated. During spring, the bloom decreases surface \( pCO_2 \) half as much as the increase due to SST variation in summer.

Interannual variability of the biological fluxes is driven by the pre-bloom conditions, i.e. the winter nitrate concentrations, the timing of the bloom, and high-frequency events of several days occurring during that period. The simple model used has only a generic phytoplankton and it is not possible to simulate different species, like diatoms. Therefore, due to the fast export kinetics of this plankton (Kiorboe et al., 1996), the impact of the high-frequency events on biological fluxes may have been under-estimated in this study (Townsend et al., 1994).

The sampling period of data must be adapted in order to obtain unbiased estimates of air–sea CO\(_2\) fluxes. In a highly variable region with a strong seasonal cycle, this time scale should be no larger than a few days, or a week, if the sampling is representative of the daily average. Only automated in situ devices like Carioca buoys can achieve this sampling frequency. Wind variability is the crucial parameter because of the non-linearity between gas transfer and wind velocity, but surface \( pCO_2 \) strongly modulates the CO\(_2\) flux. Although the model shows some diurnal variability, the 6-h atmospheric forcing and the “diffusive” behaviour of the model prevented the analysis of the role of diurnal variations on the sampling strategy. Diurnal variations could have an impact on the onset of the bloom and export fluxes as well (Taylor and Stephens, 1993; Andersen and Prieur, 2000).

At least in the NW Mediterranean Sea, it is difficult to use satellite data such as SST and sea colour in order to estimate surface \( pCO_2 \). In fact, during the oligotrophic period, the correlation between \( pCO_2 \) and SST is unsurprisingly good, but during the ‘cold’ period, SST is almost constant, surface chlorophyll is low or not very well correlated to \( pCO_2 \). By increasing the DIC concentration in the ML, the vertical dynamics drive surface \( pCO_2 \), without any strong signature on SST (in an area of deep convection) and chlorophyll. Moreover, the interannual variability, partly associated with winter tracer concentrations, makes the problem more intricate. No satellite “proxy” of winter conditions and \( pCO_2 \) values are available. In mid-latitude regions, it might be necessary to get systematic in situ measurements during winter in order to reset the correlation with satellite data during the other seasons. As already pointed out by Antoine and Morel (1995) the previous history of the water column is crucial in the determination of the evolution of surface \( pCO_2 \).

Acknowledgements

The authors are grateful to Jean Claude Marty and Claire Copin-Montégut for providing the DYFAMED data. Discussions with Steve Emerson, as well as comments on the first version of the paper, were appreciated and very helpful in improving the manuscript. Numerous relevant comments by Nicolas Metzl and Jacqueline Boutin were also greatly appreciated by the authors. Funding for this study was provided by French-JGOFS (now PROOF) program, and the European Community, in the framework of the MAST program, MATER.

Appendix A. Biogeochemical model

The prognostic equation for each tracer can be split into a dynamical part and a biological part. The dynamics take into account vertical mixing, and restoring term during winter. The biogeochemical model is based on six components: nitrate (N), ammonium (A), phytoplankton (P), zooplankton (Z), detritus (D), dissolved organic
matter (DOM). The non-conservative biological terms distribute nitrogen and carbon between the components. All the components have the same constant C/N ratio ($R_{dphy}$), except DOM which has a large C/N ratio ($R_{dDOM}$). Eqs. (A.1)–(A.6) show the biogeochemical fluxes taken into account in the conservation equations for nitrogen, and (A.7) and (A.8) for carbon. (Parameter values are shown in Table 5.)

### A.1. Nitrate

\[ \frac{dN}{dt} = -JL_{NO_3}L_M P + R_{NH_4} A. \]  
(A.1)

The first term represents the nitrate sink due to primary production, which is limited by nitrate ($L_{NO_3}$) and deep mixing ($L_M$), and the second term nitrification, due to bacterial activity.

### A.2. Ammonium

\[ \frac{dA}{dt} = -JL_{NH_4}L_M P - R_{NH_4} A + \left(1 - \frac{R_{dphy}}{R_{dDOM}}\right)PP \]
\[ + \left(z_d \mu_d + (1 - z_d)\left(1 - \frac{R_{dphy}}{R_{dDOM}}\right)\mu_d\right)LT D \]
\[ + R_{DOM}(DON - DON_0). \]  
(A.2)

The first two terms are ammonium sink (regenerated production and nitrification), whereas the source terms represent zooplankton excretion (Eq. (A.4)), detritus bacterial mineralisation limited by temperature (Eq. (A.5)), and DOM oxidation (A.6). The other source term (A.3) comes from nitrogen phytoplankton exudation which is not transferred to the DOM pool, due to the different C/N ratios of the two compartments. If the two ratios are equal, there is no phytoplankton contribution to ammonium source, and all the phytoplankton exudation feeds the DOM.

### A.3. Phytoplankton

\[ \frac{dP}{dt} = J(L_{NO_3} + L_{NH_4})L_M P - \gamma \left(1 - \frac{R_{dphy}}{R_{dDOM}}\right)PP \]
\[ - \gamma \frac{R_{dphy}}{R_{dDOM}} PP - G_{phy} Z - \mu_p P. \]  
(A.3)

The only source term for phytoplankton is total primary production. The first two sink terms represent exudation towards ammonium and DON: the sum of both terms is equal to $\gamma PP$, where PP is the total primary production. The third term represents grazing by zooplankton, and the last one mortality.

### A.4. Zooplankton

\[ \frac{dZ}{dt} = (G_{phy} + G_{det})Z - \delta_{phy} G_{phy} Z - \delta_{det} G_{det} Z \]
\[ - m_z (1 - \exp(-AZ))Z^2 \]
\[ - \tau_z (1 - \gamma) \left(1 - \frac{R_{dphy}}{R_{dDOM}}\right) \mu_z Z \]
\[ - \tau_z \left(1 - \gamma\left(1 - \frac{R_{dphy}}{R_{dDOM}}\right)\mu_d\right)LT D \]
\[ - (1 - \tau_z) \frac{R_{dphy}}{R_{dDOM}} Z. \]  
(A.4)

Zooplankton grows by grazing phytoplankton and detritus. Part of this grazing is lost to the detritus compartment, as faecal pellets: that sink is represented by the first two negative terms. The following one simulates the zooplankton mortality, which takes into account mostly transfer towards higher trophic levels (closing term). This flux is supposed to be exported towards the deep ocean instantaneously, by means of very large particles: it is a net loss for the system. The last terms represent zooplankton excretion and exudation. In fact, the sum of the three terms is equal to $\mu_z Z$: $z_d$ is the proportion excreted as ammonium in carbon units, whereas $(1 - z_d)$ is exuded towards DOM. Considerations on C/N ratios demand to split that last term into two parts for nitrogen (same procedure than for phytoplankton). Finally, during winter, as there is no more phytoplankton, neither detritus, zooplankton might decrease to extremely low values, which can prevent its development next year. Therefore, a threshold value ($E_{z0}$) is imposed: when this value is reached, the sink terms are not considered. In fact, in the runs undertaken in this study, that condition has never been used.
A.5. Detritus

\[
\frac{dD}{dt} = \mu_P P + \delta_{\text{phy}} G_{\text{phy}} Z + \delta_{\text{det}} G_{\text{det}} Z - G_{\text{det}} Z - \left( z_d \mu_d + (1 - z_d) \left( 1 - \frac{R_{\text{phy}}}{R_{\text{DOM}}} \right) \mu_d \right) L_T D \\
- (1 - z_d) L_T \mu_d \frac{R_{\text{phy}}}{R_{\text{DOM}}} D. \tag{A.5}
\]

Detritus are fed by phytoplankton mortality and faecal pellets. They are grazed by zooplankton and are either mineralised towards ammonium or “broken” into DOM. The same considerations for C/N ratios of zooplankton hold for detritus. Another physical sink term must be added: under gravity, particles sink out of the euphotic layer with a sedimentation velocity \( V_d \).

A.6. Dissolved organic nitrogen

\[
\frac{d\text{DON}}{dt} = - R_{\text{DOM}} (\text{DON} - \text{DON}_0) + \gamma \frac{R_{\text{phy}}}{R_{\text{DOM}}} PP +os \left( 1 - z_d \right) \frac{R_{\text{phy}}}{R_{\text{DOM}}} \mu_z Z \\\n+ (1 - z_d) \frac{R_{\text{phy}}}{R_{\text{DOM}}} \mu_d D. \tag{A.6}
\]

The sources of DON come from phytoplankton, zooplankton and detritus, and DON is mineralised.
in ammonium. Only the semi-labile part is considered: DON\textsubscript{0} is the background concentration of refractory DON.

### A.7. Dissolved inorganic carbon

\[
\frac{d\text{DIC}}{dt} = (-J(L_{\text{NO}_3} + L_{\text{NH}_4})L_M P(1 + \rho_{\text{CaCO}_3}) \\
+ \gamma(1 - \frac{\text{Rd}_\text{phy}}{\text{Rd}_\text{DOM}}) \text{PP} \\
+ (\gamma z_\text{phy} + (1 - \gamma) \mu_z Z + \gamma z_\text{d} L_T D) \text{Rd}_\text{phy} \\
+ R_{\text{DOM}}(\text{DON} - \text{DON}_0) \text{Rd}_\text{DOM} \\
+ \text{air}_\text{flux}). \tag{A.7}
\]

DIC is produced by respiration and excretion products of zooplankton and detritus, and by DOM mineralisation. The loss of DIC is due to primary production, which is increased by a factor \((1 + \rho_{\text{CaCO}_3})\), which takes into account calcium carbonate formation (coccolithophorids). Part of DIC can be exchanged with the atmosphere by CO\textsubscript{2} gas transfer (Eq. (A.19)).

### A.8. Alkalinity

\[
\frac{d\text{Alk}}{dt} = J(L_{\text{NO}_3} - L_{\text{NH}_4})L_M P - 2\rho_{\text{CaCO}_3} \text{PP} \text{Rd}_\text{phy} \\
+ \gamma(1 - \frac{\text{Rd}_\text{phy}}{\text{Rd}_\text{DOM}}) \text{PP} \\
+ (\gamma z_\text{phy} + (1 - \gamma) (1 - \frac{\text{Rd}_\text{phy}}{\text{Rd}_\text{DOM}}) \mu_z) Z \\
+ (\gamma z_\text{d} + (1 - \gamma) (1 - \frac{\text{Rd}_\text{phy}}{\text{Rd}_\text{DOM}}) \mu_d) L_T D \\
+ R_{\text{DOM}}(\text{DON} - \text{DON}_0). \tag{A.8}
\]

The alkalinity terms take into account the fact that when a mole of nitrate (ammonium) is assimilated, there is an increase (decrease) of an equivalent mole of alkalinity (Morel and Hering, 1993), due to production of a mole of OH\textsuperscript{-} (H\textsubscript{3}O\textsuperscript{+}). Moreover, formation of a mole of calcite implies a doubled decrease of alkalinity (Morel and Hering, 1993).

### A.9. Limitation terms

\[
L_{\text{NH}_4} = \frac{A}{A + K_A}, \tag{A.9}
\]

\[
L_{\text{NH}_4} + L_{\text{NO}_3} = \frac{A + N}{A + N + K_A} \tag{A.10}
\]

\[
=> L_{\text{NO}_3} = \frac{K_A N}{(A + K_A)(A + N + K_A)}, \tag{A.11}
\]

\[
L_T = \frac{a_T(T - T_{\text{opt}})}{A} \tag{A.12}
\]

The nitrate and ammonium limitation terms are parameterised according to Hurtt and Armstrong (1996).

When the ML is significantly greater than the euphotic layer, photosynthesis is strongly inhibited by light availability during the phytoplankton cell trajectories. That effect is taken into account explicitly by the limitation term \(L_M\). This parameter is equal to 1 when the ML depth, \(Z_M\) is shallower than the euphotic layer depth \(Z_E\), and to 0.1 when \(Z_M > 2Z_E\). In between, \(L_M\) varies linearly with \(Z_M / Z_E\). This choice is based on a study using an ensemble Lagrangian approach (André, 1990), and has been validated at the DYFAMED station with a more complex model (Lévy et al., 1998): it has been shown that, without that limitation term, in the NW Mediterranean Sea, the chlorophyll concentration during winter cannot be decreased to realistic values, even by modifying “free” parameters of the model.

### A.10. Photosynthesis

The phytoplankton maximum growth rate is modelled in terms of light according to Morel (1991) as a function of photosynthetic usable radiation (PUR), computed from the photosynthetic available radiation (PAR). The PAR is predicted from the phytoplankton pigment content according to the algorithm of Morel (1988) (same as Eqs. (A.9)–(A.12)):

\[
L_{\text{NH}_4} = \frac{A}{A + K_A}, \tag{A.9}
\]

\[
L_{\text{NH}_4} + L_{\text{NO}_3} = \frac{A + N}{A + N + K_A} \tag{A.10}
\]

\[
=> L_{\text{NO}_3} = \frac{K_A N}{(A + K_A)(A + N + K_A)}, \tag{A.11}
\]

\[
L_T = \frac{a_T(T - T_{\text{opt}})}{A} \tag{A.12}
\]
A.11. Zooplankton grazing

The grazing terms are similar to the formulation presented by Fasham et al. (1990), and used in Lévy et al. (1998): zooplankton feeds preferentially on the most abundant food organisms.

\[ G_{\text{phy}} = g_f T \frac{p_{\text{phy}}}{K_z + F} P, \]
\[ G_{\text{det}} = g_f T \frac{p_{\text{det}}}{K_z + F} D, \]

with
\[ p_{\text{phy}} = \frac{\pi_{\text{phy}} P}{\pi_{\text{phy}} P + \pi_{\text{det}} D}, \]
\[ p_{\text{det}} = \frac{\pi_{\text{det}} D}{\pi_{\text{phy}} P + \pi_{\text{det}} D}, \]
\[ F = \frac{\pi_{\text{phy}} P^2 + \pi_{\text{det}} D^2}{\pi_{\text{phy}} P + \pi_{\text{det}} D}, \]
\[ f_T = \left( \frac{T_{\text{max}} - T}{T_{\text{max}} - T_{\text{opt}}} \right) \frac{(T_{\text{max}} - T_{\text{opt}}) R_g}{R_g} \]
\[ \times \exp \left( \frac{T - T_{\text{opt}}}{R_g} \right). \]

The parameters \( p_{\text{phy}} \) and \( p_{\text{det}} \) are the preferences and \( f_T \) is the temperature limitation of zooplankton growth rate.

A.12. CO₂ air–sea flux

According to the classical formulation, the gas transfer between the atmosphere and the ocean is given by
\[ K(D_g, u) \text{sol}(\text{SST}, \text{SSS})(p_{\text{CO}}^{\text{atm}} - p_{\text{CO}}^{\text{oc}}). \]

\( K \) is the gas transfer velocity, which depends on the molecular diffusion of the gas considered \( D_g \), and on the wind velocity, \( u \). This parameter is still not very well known, and different formulations are presently used. In most of the simulations presented in this paper, the parameterisation comes from Liss and Merlivat (1986), with the exception of the WAN run, which has used Wanninkhof (1992). sol is the gas solubility, which depends on temperature and salinity (Weiss, 1974). \( p_{\text{CO}}^{\text{atm}} \) and \( p_{\text{CO}}^{\text{oc}} \) represent the CO₂ partial pressure, respectively, in the atmosphere and in the ocean. \( p_{\text{CO}}^{\text{oc}} \) is computed from the surface concentrations of DIC and alkalinity according to the dissociation constants given by Dickson and Millero (1987).

References


