

# Carbon dynamics and CO<sub>2</sub> air-sea exchanges in the eutrophied coastal waters of the Southern Bight of the North Sea: a modelling study

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**Abstract.** A description of the carbonate system has been incorporated in the MIRO biogeochemical model to investigate the contribution of diatom and *Phaeocystis* blooms to the seasonal dynamics of air-sea CO<sub>2</sub> exchanges in the Eastern Channel and Southern Bight of the North Sea, with focus on the eutrophied Belgian coastal waters. For this application, the model was implemented in a simplified three-box representation of the hydrodynamics with the open ocean boundary box 'Western English Channel' (WCH) and the 'French Coastal Zone' (FCZ) and 'Belgian Coastal Zone' (BCZ) boxes receiving carbon and nutrients from the rivers Seine and Scheldt, respectively. Results were obtained by running the model for the 1996–1999 period. The simulated partial pressures of CO<sub>2</sub> (pCO<sub>2</sub>) were successfully compared with data recorded over the same period in the central BCZ at station 330 (51°26.05' N; 002°48.50' E). Budget calculations based on model simulations of carbon flow rates indicated for BCZ a low annual sink of atmospheric CO<sub>2</sub> (−0.17 mol C m<sup>−2</sup> y<sup>−1</sup>). On the opposite, surface water pCO<sub>2</sub> in WCH was estimated to be at annual equilibrium with respect to atmospheric CO<sub>2</sub>. The relative contribution of biological, chemical and physical processes to the modelled seasonal variability of pCO<sub>2</sub> in BCZ was further explored by running model scenarios with separate closures of biological activities and/or river inputs of carbon. The suppression of biological processes reversed direction of the CO<sub>2</sub> flux in BCZ that became, on an annual scale, a significant source for atmospheric CO<sub>2</sub> (+0.53 mol C m<sup>−2</sup> y<sup>−1</sup>). Overall biological activity had a stronger influence on the modelled seasonal cycle of pCO<sub>2</sub> than temperature. Especially *Phaeocystis* colonies which growth in spring were associated with an important sink of atmospheric CO<sub>2</sub> that counteracted the temperature-driven increase of pCO<sub>2</sub> at this period of the year. However, river inputs of organic and inorganic carbon

were shown to increase the surface water pCO<sub>2</sub> and hence the emission of CO<sub>2</sub> to the atmosphere. Same calculations conducted in WCH, showed that temperature was the main factor controlling the seasonal pCO<sub>2</sub> cycle in these open ocean waters. The effect of interannual variations of fresh water discharge (and related nutrient and carbon inputs), temperature and wind speed was further explored by running scenarios with forcing typical of two contrasted years (1996 and 1999). Based on these simulations, the model predicts significant variations in the intensity and direction of the annual air-sea CO<sub>2</sub> flux.

## 1 Introduction

Coastal waters are heavily impacted by nutrients and carbon inputs from rivers and estuaries that stimulate production and remineralization of organic matter. They also intensively exchange nutrients, and inorganic and organic carbon with the open ocean across marginal boundaries (e.g. Thomas et al., 2004a). Consequently, these areas play a key role in the global carbon cycle by linking the terrestrial, oceanic and atmospheric reservoirs (Gattuso et al., 1998; Mackenzie et al., 2004). There is nowadays a great uncertainty on the overall role of coastal ecosystems to act as a sink or a source for atmospheric CO<sub>2</sub> due to the large variability of recorded air-sea CO<sub>2</sub> exchanges across latitudinal and ecosystem gradients. Existing data of CO<sub>2</sub> air-sea fluxes suggest that temperate marginal seas act as sinks for atmospheric CO<sub>2</sub> (Tsunogai et al., 1999; Frankignoulle and Borges, 2001a; Borges and Frankignoulle, 2002a; DeGrandpre et al., 2002; Thomas et al., 2004a, b). On the contrary sub-tropical marginal seas (Cai et al., 2003) and near-shore aquatic ecosystems influenced by terrestrial inputs such as inner and outer estuaries (Frankignoulle et al., 1998; Cai et al., 2000; Raymond et al., 2000; Borges and Frankignoulle 2002b; Bouillon et al., 2003), mangroves (Borges et al., 2003) and non-estuarine

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salt marshes (Wang and Cai, 2004) act as sources of CO<sub>2</sub> to the atmosphere. However, the paucity of field data prevents the comprehensive biogeochemical description of the very diverse coastal ecosystems that is needed for the integration of CO<sub>2</sub> fluxes on a global scale. Furthermore, little is known on the seasonal and interannual variability of CO<sub>2</sub> dynamics and fluxes in coastal ecosystems, although it has been shown to be highly significant in open oceanic waters in relation to large scale climatic forcings acting at various time-scales (e.g. Takahashi et al., 2003). In the absence of long term time-series, these aspects of CO<sub>2</sub> cycling in coastal ecosystems can only be approached with modelling tools (e.g. Janson and Allen, 2002). Up to now, little mechanistic modelling effort has been devoted to the description of the dynamics of dissolved inorganic carbon (DIC) in coastal environments (Walsh et al., 1994, 1996; Mackenzie et al., 2004).

The North Sea is amongst the best-studied coastal areas in the World, with respect to its physical, chemical and biological characteristics. However, the spatio-temporal monitoring of DIC has been limited to near-shore waters such as the German Bight, the Wadden Sea or the Belgian coastal zone (Hoppema, 1991; Borges and Frankignoulle, 1999, 2002b; Brasse et al., 2002). Recently the seasonality of pCO<sub>2</sub> has been investigated in the whole North Sea (Thomas et al., 2004b). On this basis a detailed carbon budget that identifies the major players in the large scale air-sea CO<sub>2</sub> fluxes has been established (Thomas et al., 2004b). Results point the Southern Bight as distinct from the Northern North Sea in terms of organic and inorganic carbon cycling. This is related to both their different hydrographic features (permanently well-mixed shallow versus seasonally-stratified water column, in the South and North, respectively) and the influence of rivers inputs that are concentrated in the Southern Bight.

The Belgian coastal zone (BCZ) located in the Southern Bight of the North Sea is a highly dynamic system with water masses resulting from the variable mixing between the inflowing southwest Atlantic waters through the Strait of Dover and the Scheldt freshwater and nutrient inputs. The inflowing Atlantic waters are themselves enriched with nutrient inputs from the river Seine (Lancelot et al., 1987). The river inputs characterized by a large excess of nitrate over phosphate and silicate are shaping the structure and the functioning of the ecosystem characterized by the dominance of undesirable recurrent blooms of non-siliceous phytoplankton like *Phaeocystis* colonies (Lancelot, 1995).

In this paper, we test a complex biogeochemical model (MIRO-CO<sub>2</sub>) to investigate the present-day impact of land-based nutrients and carbon inputs from the Seine and Scheldt rivers on the functioning of the *Phaeocystis*-dominated ecosystem of the Southern Bight of the North Sea and the related air-sea CO<sub>2</sub> exchanges. The model is run over the 1996–1999 period when existing field data of CO<sub>2</sub> partial pressure (pCO<sub>2</sub>) allow model validation. We further conduct

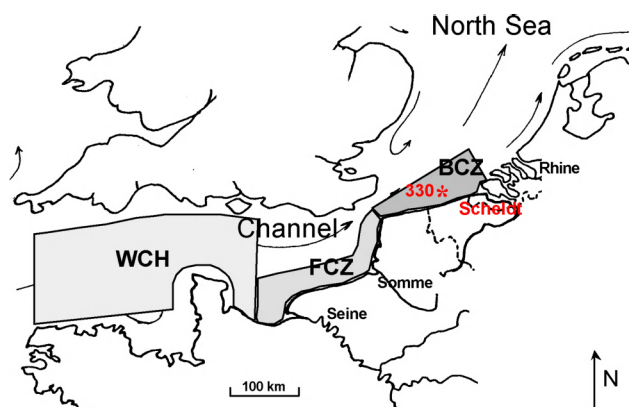
model scenarios to evaluate the respective contribution of biological, chemical and physical processes to the seasonal and annual variability of pCO<sub>2</sub>. Finally, we investigate the impact of the hydro-climatic constraints (river inputs, temperature, wind stress) on the pCO<sub>2</sub> seasonal dynamics by running scenarios with contrasting but realistic meteorological conditions.

## 2 Material and method

### 2.1 Model description

The MIRO-CO<sub>2</sub> biogeochemical model results of the coupling of the detailed biogeochemical MIRO model (Lancelot et al., 2004) with the physico-chemical module of Hannon et al. (2001) detailing the seawater carbonate system and air-sea CO<sub>2</sub> exchange. MIRO is a mechanistic model that describes C, N, P and Si cycling through aggregated components of the *Phaeocystis*-dominated ecosystem of the North Sea. It includes thirty-two state variables assembled in four modules expressing the dynamics of phytoplankton, zooplankton, organic matter degradation and nutrients (NO<sub>3</sub>, NH<sub>4</sub>, PO<sub>4</sub> and SiO), regeneration by bacteria in the water column and the sediment. The phytoplankton module considers three phytoplankton groups (diatoms, free-living autotrophic nanoflagellates and *Phaeocystis* colonies) the growth physiology of which is described according to the AQUAPHY model of Lancelot et al. (1991). The latter model considers 3 intracellular constituents (small metabolites, reserve material, functional and structural metabolites) and distinguishes different processes: photosynthesis, reserve synthesis and catabolism, growth and associated nutrient uptake, respiration and lysis. The zooplankton module details the dynamics of two groups: the microzooplankton feeding on free-living autotrophic nanoflagellates and bacteria and the mesozooplankton grazing on diatoms and microzooplankton. *Phaeocystis* colonies escape grazing, but are submitted to colony disruption which releases in the ambient nanoflagellated cells and organic matter. The degradation of organic matter by planktonic bacteria is described according to the HSB model (Billen and Servais, 1989), considering two classes of biodegradability for both dissolved and particulate organic matter. Benthic organic matter degradation and nutrient recycling are calculated using the algorithms developed by Lancelot and Billen (1985) and Billen et al. (1989).

The physico-chemical module of Hannon et al. (2001) details the carbonate system in seawater and calculates CO<sub>2</sub> exchange between the surface water and the atmosphere. The speciation of the carbonate system (in particular pCO<sub>2</sub>) is calculated based on the knowledge of DIC and total alkalinity (TA), using stoichiometric relationships and apparent equilibrium constants, which are function of temperature, pressure and salinity (Weiss, 1974; Millero et al., 1993). DIC and TA are computed taking into account, respectively, the

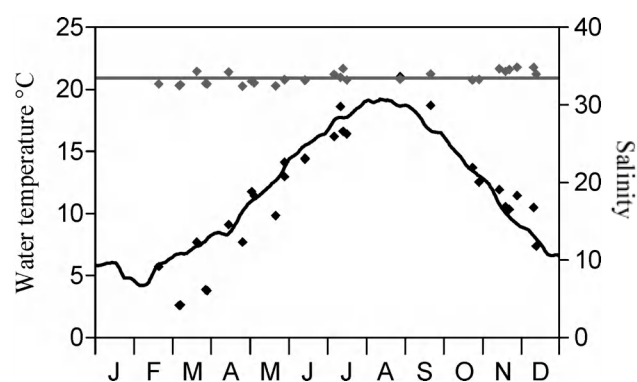


**Fig. 1.** Map of the studied area showing the MIRO multi-box frame (adapted from Lancelot et al., 2004) and the location of the station 330 (51°26.05' N; 002°48.50' E).

biological uptake or release of carbon and the phytoplankton assimilation of nitrate, all provided by the MIRO model. Air-sea CO<sub>2</sub> fluxes are calculated from the pCO<sub>2</sub> gradient across the air-sea interface and the gas transfer velocity estimated from wind speed and using the parameterisation of Nightingale et al. (2000). The latter was chosen among several existing empirical formulations since it was established from dual tracer experiments in the Southern Bight of the North Sea.

## 2.2 Model runs

The MIRO-CO<sub>2</sub> model was applied in the coastal domain of the eastern English Channel and Southern Bight of the North Sea, between the Baie de Seine and the northern limit of BCZ (Fig. 1). The model was implemented in a multi-box frame delineated on the basis of the hydrological regime and the river inputs. In order to take into account the cumulated nutrient enrichment of Atlantic waters by the Seine and Scheldt rivers, two successive boxes, assumed to be homogeneous, were chosen from the Baie de Seine to the BCZ (Fig. 1). Each successive box was characterized by its own area, depth, water temperature and average salinity, light conditions and water residence time and was treated as an open system, receiving water from the southern adjacent box and exporting water to the northern box (Lancelot et al., 2004). The boundary conditions were provided by the results of the calculations performed for the conditions existing in the Western Channel area, considered as a quasi-oceanic closed system. Initial conditions of nutrients were extracted from the database of Radach et al. (1995). Initial conditions of DIC (2070 mmol C m<sup>-3</sup>) and total alkalinity (2290 mmol m<sup>-3</sup>) were estimated from existing data in the area for the 1996–1999 period (Borges and Frankignoulle, 2003). The seasonal variation of the state variables was calculated by solving the equations expressing mass conservation, according to the Euler procedure, with a time step of



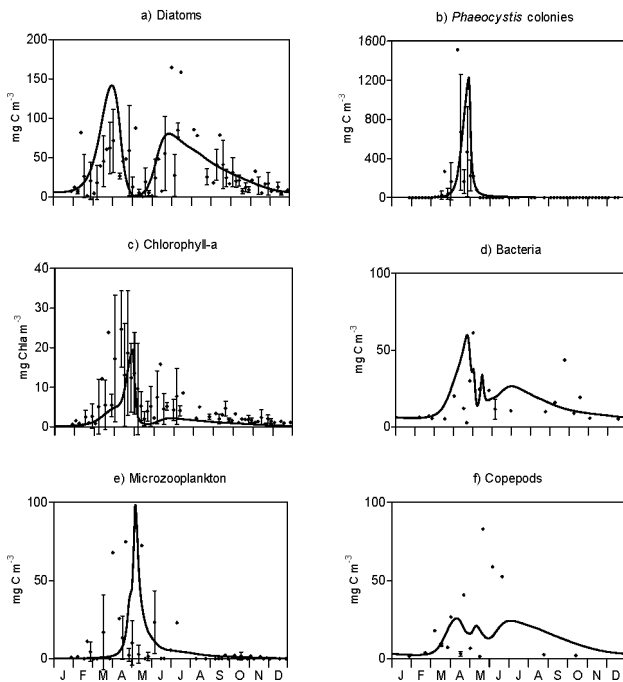
**Fig. 2.** Modelled (solid line for BCZ) and observed (♦ at station 330) temperature (black) and salinity (grey).

15 min. Conservation equations and parameters are detailed in Lancelot et al. (2004).

Model simulations were run with 1996–1999 climatological forcings for hydro-meteorological conditions and river inputs. These functions were computed from recorded daily global solar radiation (Oostende Station, Institut Royal de Météorologie, Belgium), seawater temperature and monthly nutrient loads for the rivers Seine (Cellule Antipollution de Rouen du Service de la Navigation de la Seine, France) and Scheldt [Institute for Inland Water Management and Waste Water Treatment, The Netherlands) and Department of Environment and Infrastructure (Ministry of Flemish Community, Belgium). Organic carbon loads by the Scheldt were retrieved from the Dutch water base (<http://www.waterbase.nl>). For the river Seine, we used data described in Servais et al. (2003). Land-based fluxes of DIC and TA were estimated based on a compilation of DIC and TA concentrations in the Seine and the Scheldt rivers (Frankignoulle et al., 1996, 1998; Frankignoulle and Borges, 2001b; Abril, personal communication) and river discharges, making use of the “apparent zero end-member” method (Kaul and Froelich, 1984). Atmospheric pCO<sub>2</sub> was extracted from the Mace Head (53°33' N 9°00' W, Southern Ireland) and the National Oceanic and Atmospheric Administration/climate Monitoring and Diagnostics Laboratory/Carbon Cycle Greenhouse Gases Group (NOAA/CMDL/CCGG) air sampling network (available at <http://www.cmdl.noaa.gov/>). Wind speed at 50.0° N 6.0° W was provided by the Pacific Fisheries Environmental Laboratory (PFEL) and is based on Fleet Numerical Meteorology and Oceanography Center (FNMOC) synoptic pressure fields.

## 2.3 Validation data

Model results were daily-averaged and compared with available data sets in the central BCZ at the station 330 (51°26.05 N; 02°48.50 E) for the 1996–1999 period. Over this period, nutrients, phytoplankton and chlorophyll data



**Fig. 3.** Model results in BCZ (solid line) and observations 5-day average and standard deviation over 1996–1999 (♦) of (a) diatoms, (b) *Phaeocystis* colonies, (c) Chlorophyll-*a*, (d) bacteria, (e) microzooplankton and (f) copepods at the station 330 for the 1996–1999 period.

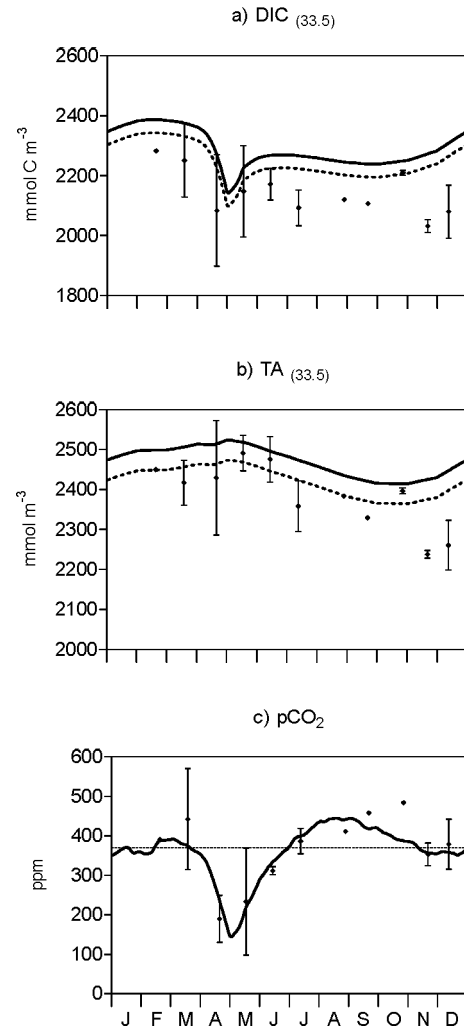
were collected at a weekly frequency except during winter when bimonthly (Rousseau, 2000). DIC was calculated from TA and pCO<sub>2</sub> measured between 1996 and 1999 in the BCZ and WCH (Borges and Frankignoulle, 1999, 2002b, 2003). Due to the inherent discrepancy between in situ temperature at the time of pCO<sub>2</sub> measurement and that imposed by the climatological forcing of the model (Fig. 2), field data of pCO<sub>2</sub> were corrected with respect to the modelled temperature. Similarly, DIC and TA data obtained at station 330 were normalized to the mean BCZ salinity of 33.5 imposed by the chosen box-model implementation in order to overcome the effect of salinity discrepancy (Fig. 2). The normalized DIC and TA are written DIC<sub>(33.5)</sub> and TA<sub>(33.5)</sub>.

### 3 Results and discussion

#### 3.1 Model validation

##### 3.1.1 Biological state variables

Figure 3 compares MIRO-CO<sub>2</sub> predictions of diatom (Fig. 3a) and *Phaeocystis* (Fig. 3b) biomass, total phytoplankton (mg Chl *a* m<sup>-3</sup>, Fig. 3c), bacteria (Fig. 3d), microzooplankton (Fig. 3e) and copepods (Fig. 3f) biomass with field data collected between 1996 and 1999. The model



**Fig. 4.** Model results (solid line) and observations (♦) of (a) dissolved inorganic carbon DIC<sub>(33.5)</sub>, (b) total alkalinity TA<sub>(33.5)</sub> and (c) surface water pCO<sub>2</sub>. The dotted line corresponds to the atmospheric equilibrium. Modelled results of sensitivity test were added (dotted line) on (a) DIC<sub>(33.5)</sub>, (b) TA<sub>(33.5)</sub> plots.

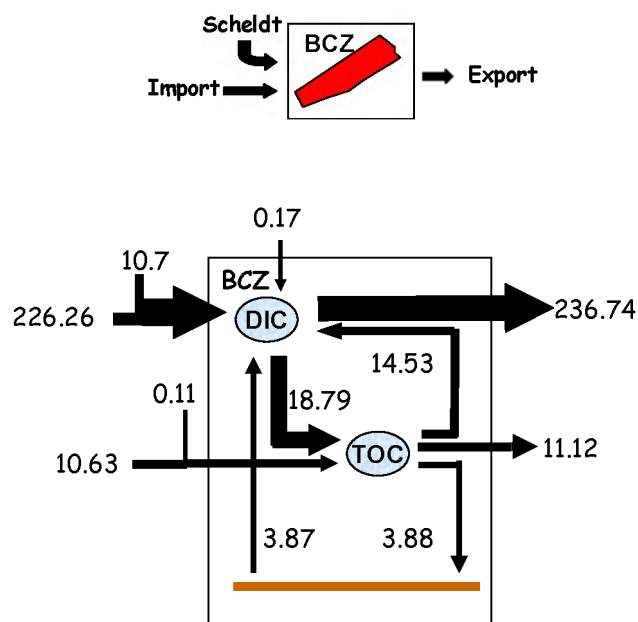
describes reasonably well the main trends (timing and magnitude) of the diatom-*Phaeocystis*-diatom succession: spring diatoms (Fig. 3a) initiate the phytoplankton bloom in early March and are followed by *Phaeocystis* colonies (Fig. 3b) which reach concentrations of 20 mg Chl *a* m<sup>-3</sup> in April (Fig. 3c). Summer diatoms bloom after *Phaeocystis* decline and maintain up to fall. In agreement with observations, MIRO-CO<sub>2</sub> results show non-negligible concentration of diatoms all over the year (Fig. 3a) contrasting with the unique bloom of *Phaeocystis* in spring (Fig. 3b). Phytoplankton decline in spring stimulates the development of diverse heterotrophs such as bacteria (Fig. 3d), microzooplankton (Fig. 3e) and copepods (Fig. 3f). The seasonal succession and magnitude of spring bacteria and microzooplankton biomass are well captured by the model. However, biomass

reached by copepods and bacteria in spring and fall, respectively, are not properly simulated. These weaknesses of the model are discussed in Lancelot et al. (2004) and is mainly attributed to some mismatch between the simulated seasonal succession of copepods and their prey which might be related to some unreliable description of either the mortality process and fate of *Phaeocystis* colonies and derived matter and/or the copepod feeding function. Experimental work in this matter is in progress.

### 3.1.2 Carbonate chemistry

Figure 4 compares MIRO-CO<sub>2</sub> simulations of DIC<sub>(33.5)</sub> (Fig. 4a), TA<sub>(33.5)</sub> (Fig. 4b) and surface water pCO<sub>2</sub> (Fig. 4c) with field observations. The seasonal evolution of DIC<sub>(33.5)</sub> and TA<sub>(33.5)</sub> is reasonably well captured by the model but concentrations obtained overestimate field data, especially in winter and late fall (Fig. 4a, b) when biological activity is low (Fig. 3). The simulated DIC<sub>(33.5)</sub> clearly reaches lowest values at the time of *Phaeocystis* bloom maximum (Fig. 3b; Fig. 4a) and increases in mid-May when heterotrophs prevail over autotrophs (Fig. 4a; Fig. 3d, e, f). In agreement the highest TA<sub>(33.5)</sub> values (Fig. 4a) are modelled in end April-early May when phytoplankton biomass is elevated (Fig. 3a, b, c) and consumes NO<sub>3</sub>. Lowest TA<sub>(33.5)</sub> are simulated in late fall (Fig. 4b) when phytoplankton growth has ceased but heterotrophic process and nitrification are still operating. The observed seasonal signal of TA<sub>(33.5)</sub> is well represented (Fig. 4b) but the modelled amplitude (110 mmol m<sup>-3</sup>) is weak compared to that suggested by field data (~200 mmol m<sup>-3</sup>, Fig. 4b), mainly because of the failure of the model to capture the observed late fall-winter minima (Fig. 4b). At the annual scale, Atlantic waters bring 96% of TA in BCZ and river loads and biological processes contribute 3.9% and 0.1%, respectively. Sensitivity tests with varying initial TA corresponding to the range of observed values in WCH (Borges and Frankignoulle, 2003) indicate that a reduction of WCH initial conditions of TA by less than 2% improves significantly model simulations of DIC (Fig. 4a) and TA (Fig. 4b) in winter while fall observations remain overestimated by the model (Fig. 4a, b). Elevated modelled TA in fall could result from an overestimation of river inputs during this period. At that time of the year (October to January), river discharge is high and inputs of TA account for 45% of annual river loads. Due to the importance of biological processes on magnitude and seasonal variability of DIC, modification of DIC initial value in the Western Channel has no impact on DIC magnitude in the Belgian coastal zone.

The discrepancies in the BCZ between observed and modelled DIC and TA are due to the structure of the model since initial conditions are not forced in the BCZ but result from the transformations of chemical water properties from the WCH (model initial conditions) due to river inputs and biological activity during transport through the FCZ and BCZ



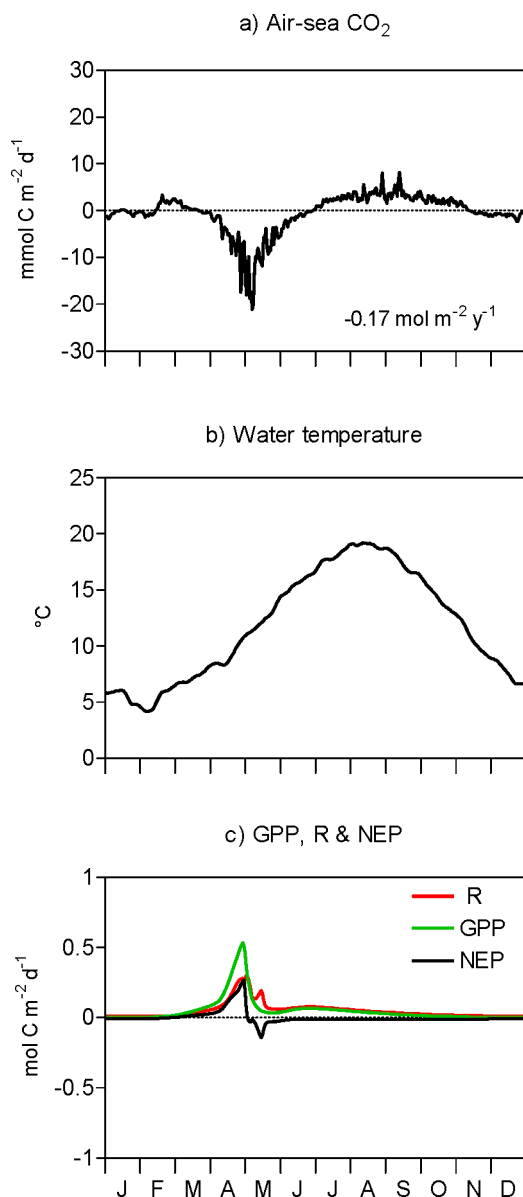
**Fig. 5.** Annual budget of C flows at the scale of the BCZ (mol C m<sup>-2</sup> y<sup>-1</sup>).

boxes. Altogether, these discrepancies between observed and modelled DIC and TA have no influence on the magnitude and seasonal evolution of the modelled pCO<sub>2</sub>.

The comparison between modelled and measured pCO<sub>2</sub> (Fig. 4c) shows that our model is able to describe the observed seasonal variability, both in time and amplitude. The latter (defined as the difference between the maximum and minimum values) is evaluated at 300 ppm with pCO<sub>2</sub> values ranging between 445 ppm in summer and 145 ppm in spring (Fig. 4c). Model pCO<sub>2</sub> values generally agree fairly well with observations except in fall when field data are significantly higher than modelled values. Over the winter season, modelled surface pCO<sub>2</sub> are close to saturation (Fig. 4c). A marked decrease of pCO<sub>2</sub> is simulated in early March and coincides with the onset of the diatom bloom (Fig. 4c; Fig. 3a) and pCO<sub>2</sub> reaches its minimum (145 ppm) during the *Phaeocystis* bloom (Fig. 4c; Fig. 3b). Modelled pCO<sub>2</sub> increases as *Phaeocystis* declines and values above saturation with respect to atmospheric CO<sub>2</sub> are reached in July up to the end of October (Fig. 4c). The model early decrease of surface water pCO<sub>2</sub> in September compared to observations might be due to some underestimation of modelled bacterial biomass (and related activity) during fall (Fig. 3d).

### 3.2 Carbon budget

An annual budget of C flows was constructed for BCZ based on time integration of MIRO daily simulations of biological activities (photosynthesis and planktonic and benthic respiration), Atlantic inputs, Scheldt loads and air-sea CO<sub>2</sub> fluxes. Results of these calculations (Fig. 5)



**Fig. 6.** Seasonal evolution of **(a)** modelled air-sea CO<sub>2</sub> flux, **(b)** mean water temperature for the 1996–1999 period and **(c)** gross primary production (GPP), total respiration (R) and net ecosystem production (NEP) computed for BCZ from MIRO-CO<sub>2</sub> daily simulations of biological activities.

highlight the importance of Atlantic inputs of inorganic ( $226.26 \text{ mol C m}^{-2} \text{ y}^{-1}$ ) and organic ( $10.63 \text{ mol C m}^{-2} \text{ y}^{-1}$ ) carbon representing, respectively, 95 and 99% of total inputs to BCZ. River Scheldt inputs contributes to 4.5 and 1% of total DIC and TOC inputs, respectively. The uptake of atmospheric CO<sub>2</sub> is low ( $-0.17 \text{ mol C m}^{-2} \text{ y}^{-1}$ ) i.e. less than 0.1% of the total input of DIC. Autotrophic processes fix some 8% of the annual input of DIC ( $18.79 \text{ mol C m}^{-2} \text{ y}^{-1}$ ) from which 77 and 20% is remineralized in the water column

and sediment, respectively (Fig. 5). At the annual scale BCZ exports to the North some  $0.38 \text{ mol C m}^{-2} \text{ y}^{-1}$  as TOC while little carbon is buried in the sediment ( $0.01 \text{ mol C m}^{-2} \text{ y}^{-1}$ ).

### 3.3 Physical and biological controls of surface water pCO<sub>2</sub> and air-sea CO<sub>2</sub> fluxes in central BCZ at the seasonal and annual scales

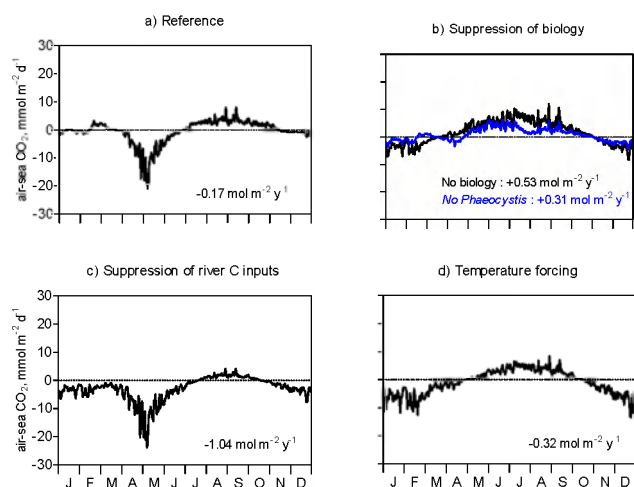
Physical and biological mechanisms regulating pCO<sub>2</sub> (Fig. 4c) and air-sea exchanges of CO<sub>2</sub> (Fig. 6a) in central BCZ were first investigated based on the comparative analysis of MIRO-CO<sub>2</sub> daily forcing of temperature (Fig. 6b) and predictions of biological features (gross primary production GPP, community respiration R (including autotrophic and heterotrophic planktonic and benthic respiration) and net ecosystem production NEP (the difference between GPP and R), Fig. 6c). In winter (November to late February), NEP and R are close to zero (Fig. 6c) and pCO<sub>2</sub> fluctuations (Fig. 4c) are modulated by river inputs of carbon and seawater temperature (Fig. 6b). The system is near equilibrium and air-sea CO<sub>2</sub> fluxes are close to zero (Fig. 6a). From mid-March to end April, NEP is high enough to reverse the positive effect of temperature increase on pCO<sub>2</sub> that reaches extremely low values with respect to saturation (Fig. 4c; Fig. 6b, c). In accordance, our model calculates for this period an important sink of atmospheric CO<sub>2</sub> in central BCZ (up to  $-20 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ; Fig. 6a). In May, NEP is strongly negative (i.e. the system is heterotrophic) and surface water pCO<sub>2</sub> increases due to both respiration and temperature increase (Fig. 4c; Fig. 6b, c). As a consequence the system evolves progressively from a sink of atmospheric CO<sub>2</sub> during spring to a source during the period end of June to November (Fig. 6a). After November, the system is again close equilibrium (Fig. 6a). Overall MIRO-CO<sub>2</sub> estimates a weak annual sink of atmospheric CO<sub>2</sub> of  $-0.17 \text{ mol C m}^{-2} \text{ y}^{-1}$ .

As a first attempt to appraise the relative importance of physical and biological controls of surface water pCO<sub>2</sub>, we used the approach of Takahashi et al. (2002) that separates the seasonal effect of ‘net biology’ from that of temperature. As defined by these authors the ‘net biology’ effect includes the effect of biological processes, TA variation due to nitrate utilization, air-sea exchange of CO<sub>2</sub> and an addition of DIC and TA by external forcing (river inputs in the present study). Removal of the temperature effect on pCO<sub>2</sub> simulations is obtained after normalization of modelled daily values of pCO<sub>2</sub> to the annual mean temperature ( $11.9^{\circ}\text{C}$ ) using the equation:

$$\text{pCO}_2 \text{ at } T_{\text{mean}} = \text{pCO}_2_{\text{mod}} \cdot \exp[0.0423 \cdot (T_{\text{mean}} - T_{\text{mod}})], \quad (1)$$

where  $T_{\text{mean}}$  and  $T_{\text{mod}}$  are, respectively, the climatological annual mean and daily temperature (in  $^{\circ}\text{C}$ ) used in model runs.



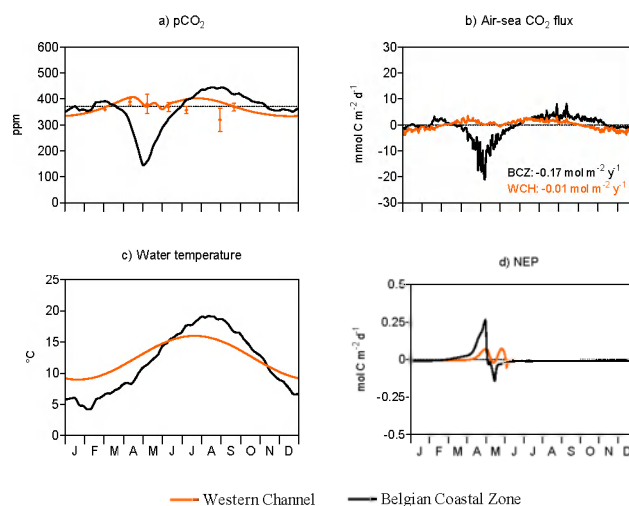


**Fig. 7.** Seasonal evolution of MIRO-CO<sub>2</sub> pCO<sub>2</sub> computed for (a) the reference run and by closing (b) biological processes or only *Phaeocystis* growth. (c) river inputs of inorganic and organic carbon or (d) both biological processes and carbon inputs. The annual integrated CO<sub>2</sub> air-sea flux calculated for each scenario is indicated on the corresponding plot.

The seasonal effect of temperature on pCO<sub>2</sub> is further estimated by attributing to the mean annual pCO<sub>2</sub> deduced from model runs (i.e. 360 ppm) a correction factor based on the difference between  $T_{mod}$  and  $T_{mean}$  as above. According to these calculations, the effect of biology on pCO<sub>2</sub>, represented by the seasonal amplitude of pCO<sub>2</sub> values corrected to the mean annual temperature, is estimated at 350 ppm (150 ppm in May to 500 ppm in February). The effect of temperature change is less, 230 ppm (260 ppm in January–February to 490 ppm in July–August). The relative importance of the temperature and ‘net biology’ effect (T/B) is given by the ratio between the above seasonal amplitudes and is evaluated at 0.66. Thus, based on MIRO-CO<sub>2</sub> results we conclude that temperature contributed less to the seasonal pCO<sub>2</sub> variability of central BCZ in 1996–1999 than biological processes. However in areas influenced by river inputs of carbon and nutrients such as BCZ, the approach of Takahashi et al. (2002) includes their impact in the so-called ‘net biology’ effect.

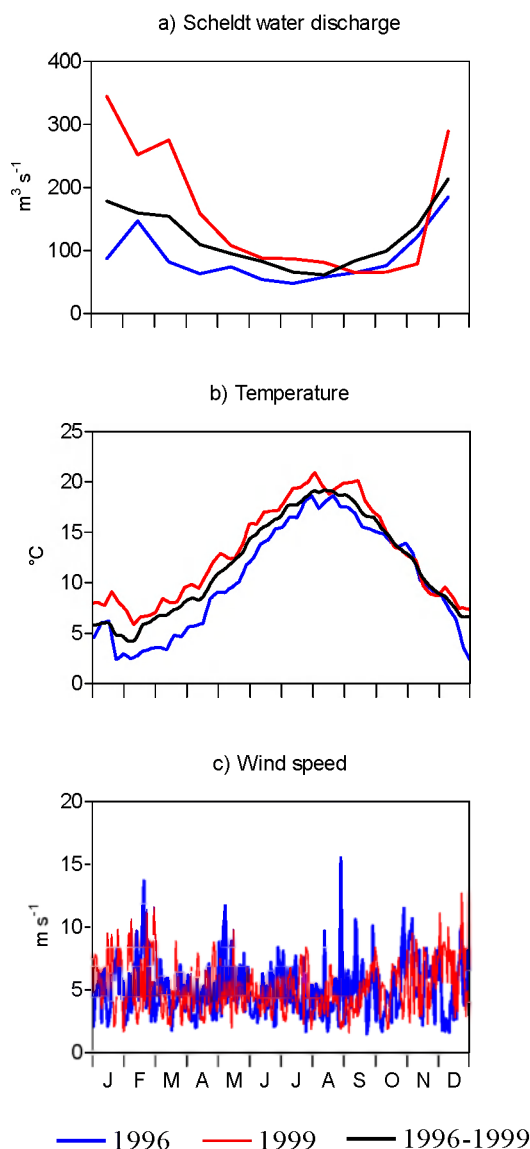
As an alternate approach to resolve these contributions, we compared MIRO-CO<sub>2</sub> reference 1996–1999 simulations of the seasonal evolution of surface water pCO<sub>2</sub> in BCZ and the related annual air-sea CO<sub>2</sub> fluxes (Fig. 7a) with those obtained by closing separately biological processes, *Phaeocystis* only (Fig. 7b) and the river inputs of organic and inorganic carbon (Fig. 7c). For the latter scenario the river nutrient inputs were maintained. A supplementary MIRO-CO<sub>2</sub> scenario with closing both biological processes and river inputs of carbon was conducted to extract the solely thermodynamic effect of temperature change on pCO<sub>2</sub> (Fig. 7d).

Suppressing biological processes predicts in BCZ a significant annual source of atmospheric CO<sub>2</sub> (+0.53 mol C m<sup>-2</sup>



**Fig. 8.** Seasonal evolution of MIRO-CO<sub>2</sub> simulations of daily (a) pCO<sub>2</sub>, (b) air-sea CO<sub>2</sub> flux, (c) water temperature and (d) net ecosystem production computed for WCH and BCZ boxes. Model results of pCO<sub>2</sub> in WCH (solid line) are compared with available observations in that area (♦). The dotted line, in the pCO<sub>2</sub> plots, corresponds to atmospheric pCO<sub>2</sub>. The calculated annual CO<sub>2</sub> air-sea flux is added to each plot of air-sea CO<sub>2</sub> flux.

y<sup>-1</sup>, Fig. 7b). This suggests that biology is responsible for the annual sink predicted in BCZ (Fig. 7a) by taking up to 0.7 mol C m<sup>-2</sup> y<sup>-1</sup> of atmospheric CO<sub>2</sub>. In the absence of biology, seasonal evolution of water pCO<sub>2</sub> is mainly determined by temperature and water CO<sub>2</sub> super-saturation with respect to the atmosphere is simulated in summer (Fig. 7b) when water temperature is elevated (Fig. 6b). Additional comparison with scenarios closing separately *Phaeocystis* colonies estimates at more than 50% the contribution of their bloom to this uptake (−0.47 mol C m<sup>-2</sup> y<sup>-1</sup>, Fig. 7b). Comparison with the reference run (Fig. 6a) indicates that the simulated water CO<sub>2</sub> under-saturation in spring is mainly associated with *Phaeocystis* colony growth. Spring diatoms also contribute to spring water CO<sub>2</sub> undersaturation (Fig. 7b) but to a lesser extent. Suppression of river inputs of organic and inorganic carbon has no detectable influence on the seasonal evolution of pCO<sub>2</sub> but increases significantly the annual CO<sub>2</sub> sink obtained with the reference run (Fig. 7a, c). River inputs of carbon thus represent a significant source of atmospheric CO<sub>2</sub> (+0.87 mol C m<sup>-2</sup> y<sup>-1</sup>) that is partly counteracted by biology on an annual scale (−0.7 mol C m<sup>-2</sup> y<sup>-1</sup>). Finally our scenarios predict an annual sink of atmospheric CO<sub>2</sub> of −0.32 mol C m<sup>-2</sup> y<sup>-1</sup> associated to the seasonal signal of temperature only (Fig. 7d). All together these scenarios show the predominance of different controls of pCO<sub>2</sub> and air-sea CO<sub>2</sub> exchanges in central BCZ along the season. Clearly river inputs of carbon are responsible for the simulated emission of CO<sub>2</sub> to the atmosphere in late winter, counteracting the effect of decreasing temperature (Fig. 7c,

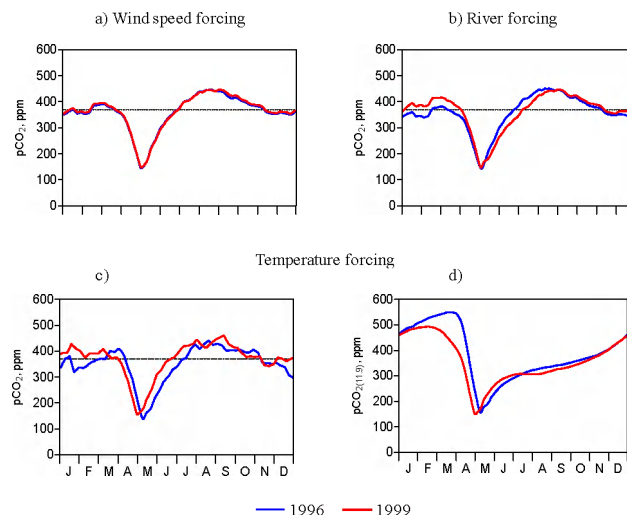


**Fig. 9.** Seasonal cycle of (a) Scheldt fresh water discharge, (b) water temperature and (c) wind speed for 1996 and 1999 compared to the climatological reference (for (a) Scheldt discharge and (b) water temperature).

d). NEP mostly that associated to *Phaeocystis* colonies explains the predicted CO<sub>2</sub> sink in spring which, under these conditions of temperature should have been a CO<sub>2</sub> source towards the atmosphere (Fig. 7a, b). During summer, temperature first and then C remineralization are the most important controls (Fig. 7b, d).

### 3.4 Role of land-based nutrients

In order to better appraise the role of land-based nutrients and carbon in modulating the seasonal cycle of surface water pCO<sub>2</sub> and air-sea CO<sub>2</sub> fluxes, we compared model



**Fig. 10.** Seasonal evolution of MIRO-CO<sub>2</sub> pCO<sub>2</sub> obtained with changing (a) wind speed, (b) river carbon and nutrient loads (c) water temperature of 1996 and 1999 and (d) same as (c) but normalized to BCZ average temperature of 11.9°C. The dotted line corresponds to atmospheric equilibrium.

results in central BCZ with those obtained for the WCH boundary conditions (Fig. 8). For this purpose simulations of pCO<sub>2</sub> (Fig. 8a) and air-sea CO<sub>2</sub> exchanges (Fig. 8b) in both areas were compared with the temperature forcing (Fig. 8c) and the simulated NEP (Fig. 8d). In the WCH, a fairly good agreement is observed between daily simulations of pCO<sub>2</sub> and available field data (Fig. 8a). As a general trend surface water pCO<sub>2</sub> in WCH is driven by temperature variation, being under-saturated with respect to the atmosphere between October and mid-March and over-saturated during spring-summer (Fig. 8a). Over the latter period, two small decreases in pCO<sub>2</sub> are simulated, coinciding with events of elevated NEP (Fig. 8d) that are counteracting the effect of temperature increase (Fig. 8a, c, d). However and contrary to BCZ, the simulated pCO<sub>2</sub> never reaches under-saturated values in spring due to the low productivity of WCH compared to BCZ (Fig. 8a). At the annual scale indeed BCZ is net autotrophic (integrated NEP=+0.38 mol C m<sup>-2</sup> y<sup>-1</sup>) while WCH is close to metabolic balance (integrated NEP ~0 mol C m<sup>-2</sup> y<sup>-1</sup>). Accordingly, WCH is almost in equilibrium with respect to atmospheric CO<sub>2</sub> (-0.01 mol C m<sup>-2</sup> y<sup>-1</sup>; Fig. 8b) when BCZ acts as a sink for atmospheric CO<sub>2</sub> (-0.17 mol C m<sup>-2</sup> y<sup>-1</sup>).

Applying the approach of Takahashi et al. (2002) to WCH simulations allows us to conclude that temperature variation over the year contributes more to pCO<sub>2</sub> seasonal variation than biology (T/B=1.21). Comparing this result with T/B obtained in BCZ (0.66) points to the major contribution of nutrient river inputs (i.e. coastal eutrophication) in counteracting the temperature control on surface water pCO<sub>2</sub>.



**Table 1.** Comparison between annual integrations of air-sea CO<sub>2</sub> fluxes, gross primary production (GPP), respiration (R) and net ecosystem production (NEP) computed for the reference run (1996–1999) and those obtained with separate modification to the reference of 1996 and 1999 river nutrient and carbon loads or temperature or wind speed forcing. The relative importance of temperature and biology effect on pCO<sub>2</sub> is expressed by the ratio T/B.

	Reference	Wind speed		River discharge		Temperature	
	1996–1999	1996	1999	1996	1999	1996	1999
Air-sea CO <sub>2</sub> flux, mol C m <sup>-2</sup> y <sup>-1</sup>	−0.17	−0.20	−0.14	−0.24	−0.05	−0.39	+0.04
GPP, mol C m <sup>-2</sup> y <sup>-1</sup>	18.8	18.8	18.8	17.2	21.9	17.1	19.7
R, mol C m <sup>-2</sup> y <sup>-1</sup>	18.4	18.4	18.4	16.9	21.4	16.7	19.3
NEP, mol C m <sup>-2</sup> y <sup>-1</sup>	+0.38	+0.38	+0.38	+0.32	+0.56	+0.44	+0.42
T/B	0.66	0.66	0.65	0.68	0.6	0.68	0.69

### 3.5 Sensitivity to external present-day forcings

In this section we explore to what extent changing meteorological conditions (rainfall (i.e. river discharge), temperature, wind stress) could alter the seasonal and annual dynamics of pCO<sub>2</sub> in coastal waters. For this application, we choose to compare MIRO-CO<sub>2</sub> reference simulations relative to the 1996–1999 climatological year with results obtained when running the model with changing one by one either the river inputs of carbon or the water temperature or the wind speed forcing corresponding to the most contrasted “meteorological” years for the period (the dry 1996 and wet 1999 year). For each simulation, the other forcing were maintained equal to the reference 1996–1999 mean value. Over 1996–1999, nutrient loads were very variable, modulated by freshwater discharge that was higher in 1999 compared to 1996 (Fig. 9a). Nutrient concentrations in the Seine and Scheldt rivers were indeed unchanged over this period. Similarly, concentrations of organic and inorganic carbon were assumed constant. Significantly higher temperatures were observed in 1999 compared to 1996, especially between January and August (Fig. 9b). Daily wind speeds were quite variable with however a similar annual average of 5.05 and 5.16 m s<sup>-1</sup> in 1996 and 1999, respectively (Fig. 9c).

The relative impact of each forcing was explored based on a comparison of modelled pCO<sub>2</sub> along the season (Fig. 10) and MIRO-CO<sub>2</sub> annual budget of biological activity (GPP, R and NEP) and air-sea CO<sub>2</sub> flux (Table 1). Generally, the seasonal trends and magnitude of pCO<sub>2</sub> variations were not significantly modified. However, significant changes in the intensity and direction of the annual air-sea CO<sub>2</sub> flux were simulated (Table 1).

#### 3.5.1 Wind speed forcing

We found a negligible effect of wind speed on the seasonal cycle of pCO<sub>2</sub> (Fig. 10a), since this forcing does not control NEP and temperature in our model (Table 1). Still, these model scenarios reveal that the daily variations of wind speed impacted significantly on the annual budget of air-sea

CO<sub>2</sub> (18%; Table 1). The largest sink is predicted in 1996 (−0.2 mol C m<sup>-2</sup> y<sup>-1</sup>, Table 1) and corresponds to lower gas transfer velocity, (8.38 and 8.58 cm h<sup>-1</sup> (normalized to a Schmidt number of 600) in 1996 than in 1999, respectively).

#### 3.5.2 River forcing

Comparison of seasonal simulations of water pCO<sub>2</sub> obtained with 1996 and 1999 river loads, shows for 1996 lower values between January and March, similar in May and higher from May to August (Fig. 10b). The lower late winter pCO<sub>2</sub> simulated in 1996 are mostly due to the lower DIC river inputs as biological activity in winter is low. The initial winter pCO<sub>2</sub> value in 1996 also probably explains why minimal pCO<sub>2</sub> values simulated in spring are very similar for both years (Fig. 10b), although the maximum NEP value obtained during the *Phaeocystis* bloom is higher in 1999 than 1996 (0.28 mol C m<sup>-2</sup> d<sup>-1</sup> in 1999 compared to 0.21 mol C m<sup>-2</sup> d<sup>-1</sup> in 1996, not shown).

On an annual base we calculated a lower sink for atmospheric CO<sub>2</sub> in 1999 compared to 1996 (Table 1) which contrasts with the elevated NEP simulated in 1999 (Table 1) in response to the higher riverine nutrient inputs. This has to be related to the higher DIC river inputs in 1999 that induce higher initial pCO<sub>2</sub> values in winter (Fig. 10b). Altogether this scenario points the dual role of river inputs on the seasonal dynamics of pCO<sub>2</sub> in eutrophied coastal waters by modulating their carbon and nutrient conditions.

#### 3.5.3 Temperature forcing

Clearly, the difference in time and magnitude of surface water pCO<sub>2</sub> simulated in 1996 and 1999 (Fig. 10c) corresponds with temperature records deviation over the period January-to-July (Fig. 9b). Over this period temperature is significantly higher in 1999 than in 1996 (~3°C, Fig. 9b). In order to eliminate the temperature effect, modelled pCO<sub>2</sub> were normalized to the mean BCZ temperature (11.9°C, Fig. 10d). From January to February, the lower pCO<sub>2</sub> simulated in 1996 are clearly due to lower temperature compared to 1999

(Fig. 10d). The 9 days delay obtained for the minimal simulated pCO<sub>2</sub> values in spring (Fig. 10d) is related to the late onset of *Phaeocystis* bloom in 1996 as a consequence of the temperature dependence of GPP. On an annual base, NEP is lower in 1999 than in 1996 (Table 1), in spite of a higher GPP in 1999 than in 1996 (Table 1), due to the stronger temperature dependence of heterotrophic processes.

The shift from an annual sink in 1996 to a source in 1999 of atmospheric CO<sub>2</sub> (Table 1) is related to a combination of temperature effect on the carbon chemistry and biology (increased respiration at higher temperature). Their relative importance can be assessed through the calculation of the T/B i.e. the ratio between  $\Delta p\text{CO}_{2(\text{temp})}$  and  $\Delta p\text{CO}_{2(\text{bio})}$  (Table 1). This suggests a higher temperature effect on biology than carbon chemistry. Indeed the T/B increase from 0.68 in 1996 to 0.69 in 1999 (Table 1) is due to a higher difference between  $\Delta p\text{CO}_{2(\text{bio})}$  (362 ppm in 1996 compared to 353 ppm in 1999) than  $\Delta p\text{CO}_{2(\text{temp})}$  (247 ppm in 1996 and 244 ppm in 1999).

#### 4 Conclusions

The MIRO-CO<sub>2</sub> simulations, by showing stronger seasonal signals of pCO<sub>2</sub> and related air-sea CO<sub>2</sub> fluxes in the carbon and nutrient-enriched BCZ compared to more oceanic waters (WCH), is giving additional support to observation-based conclusions on the key role of coastal areas in the global carbon cycle (e.g. Frankignoulle and Borges, 2001a). We also demonstrated the advantage of model simulations and sensitivity analysis for the identification of the major physical and biological mechanisms controlling the seasonal dynamics of surface water pCO<sub>2</sub> and their external forcing. In particular, we highlighted the significance of the *Phaeocystis* bloom in the spring-time drawn-down of atmospheric CO<sub>2</sub>. The model also allows us to explore how the intensity and direction of the annual air-sea CO<sub>2</sub> flux was changed in relation to realistic variations of environmental forcing such as water temperature, fresh water discharge or wind speed.

Model results revealed that the seasonal variation of pCO<sub>2</sub> in the BCZ is strongly driven by nutrient-enriched biological activity in spring that counteracts the effect of temperature increase. On an annual scale for the 1996–1999 period, the solely river inputs of organic and inorganic carbon are driving a source of CO<sub>2</sub> of +0.87 mol C m<sup>-2</sup> y<sup>-1</sup> that is balanced by an atmospheric CO<sub>2</sub> uptake of -0.7 and -0.32 mol C m<sup>-2</sup> y<sup>-1</sup> due to nutrient stimulated NEP and temperature change, respectively. Globally an annual weak sink is predicted for BCZ. However, based on a sensitivity analysis, we also showed that the present-day interannual variations of fresh water discharge (and related land-based nutrient and carbon inputs) and water temperature might have a significant impact on the air-sea CO<sub>2</sub> fluxes in the BCZ.

These simulations clearly illustrate the potentially significant but complex variations of CO<sub>2</sub> fluxes in near-shore coastal ecosystems in response to small environmental changes within the range of present-day variability. These variations in CO<sub>2</sub> fluxes are a small glimpse of those that can be expected from environmental changes predicted in the near future in context of global change and/or of management strategies.

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