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Carbonate chemistry in the coastal zone responds more strongly to eutrophication than to ocean acidification

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Abstract

The accumulation of anthropogenic CO_2 in the ocean has altered carbonate chemistry in surface waters since preindustrial times and is expected to continue to do so in the coming centuries. Changes in carbonate chemistry can modify the rates and fates of marine primary production and calcification. These modifications can in turn lead to feedback on increasing atmospheric CO_2. We show, using a numerical model, that in highly productive nearshore coastal marine environments, the effect of eutrophication on carbon cycling can counter the effect of ocean acidification on the carbonate chemistry of surface waters. Also, changes in river nutrient delivery due to management regulation policies can lead to stronger changes in carbonate chemistry than ocean acidification. Whether antagonistic or synergistic, the response of carbonate chemistry to changes of nutrient delivery to the coastal zone (increase or decrease, respectively) is stronger than ocean acidification.

The open ocean is a major sink of anthropogenic CO_2 (Sabine et al. 2004); however, the accumulation of anthropogenic CO_2 has altered carbonate chemistry in surface waters since preindustrial times, and is expected to continue to do so in the coming centuries (Orr et al. 2005). Ocean acidification of surface waters corresponds to the increase of $[CO_2]$ and of $[H^+]$, the decrease of pH and of $[CO_3^{2-}]$, and of the saturation state of calcite (Ω_{ca}) and aragonite (Ω_{ar}), all related to shifts in thermodynamic equilibria in response to the input of anthropogenic CO_2 from the atmosphere. Changes of the carbonate chemistry of surface waters related to ocean acidification can alter the rates and fates of primary production and calcification of numerous marine organisms and communities (Kleypas et al. 2006; Doney et al. 2009). Such changes can provide either positive or negative feedback on increasing atmospheric CO_2 by modifying the flux of CO_2 between the ocean and the atmosphere. The increase of $[CO_2]$ can favor the availability of inorganic carbon for primary producers, whereas the decrease of $[CO_3^{2-}]$, Ω_{ca}, and Ω_{ar} make the precipitation of $CaCO_3$ thermodynamically less favorable (or impossible spontaneously in $CaCO_3$-undersaturated conditions). An increase in primary production associated with efficient organic carbon export would induce a negative feedback on increasing atmospheric CO_2, according to:

$$CO_2 + H_2O \rightarrow CH_2O + O_2 \qquad (1)$$

A decrease in calcification would induce a negative feedback on increasing atmospheric CO_2, since $CaCO_3$ precipitation leads to the thermodynamic shift of HCO_3^- to CO_2, according to:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \qquad (2)$$

Besides changes in primary production and calcification, marine organisms and communities can also respond to ocean acidification through changes in N_2 fixation (Hutchins et al. 2007), shift in natural assemblages (Engel et al. 2008), an increase of export of organic matter to depth due to enhanced aggregation (Delille et al. 2005; Riebesell et al. 2007), or enhanced $CaCO_3$ dissolution in marine sediments (Andersson et al. 2003). All these processes could also provide a negative feedback on increasing atmospheric CO_2.

The coastal ocean hosts between ~ 15% and ~ 30% of oceanic primary production and ~ 80% of oceanic organic matter burial (Gattuso et al. 1998). It also hosts most of the benthic oceanic $CaCO_3$ production, ~ 20% of surface pelagic oceanic $CaCO_3$ stock (Balch et al. 2005), and ~ 50% of oceanic $CaCO_3$ deposition (Gattuso et al. 1998). Hence, the potential feedback on increasing atmospheric CO_2 related to the response of marine organisms and communities to the acidification of surface waters could be disproportionately much more important in the coastal ocean than in the open ocean. However, in the coastal ocean, the seawater carbonate chemistry is also expected to be strongly regulated by changes in biological activity related to the increase of anthropogenic nutrient delivery by rivers, groundwaters, and atmosphere (eutrophication), although to our best knowledge this has not been studied before. Here, we use the RIVERSTRAHLER-MIRO-CO_2 (R-MIRO-CO_2) coupled model (Gypens et al. 2009) to investigate the decadal changes of seawater carbonate chemistry variables related to the increase of atmospheric CO_2 and of nutrient delivery in the highly eutrophied Belgian coastal zone (BCZ) over the period 1951–1998.

Methods

The R-MIRO-CO_2 model results of the coupling between the RIVERSTRAHLER model (Billen et al. 2001), an idealized biogeochemical model of the river system, and MIRO-CO_2, a complex biogeochemical model

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Table 1. Description of the R-MIRO-CO_2 simulations.

Name and setup	Application
Reference simulation	
All forcings are unconstrained	Describes interannual variability and decadal changes of carbonate chemistry from 1951 to 1998 in the BCZ
Baseline simulation	
All forcings are maintained at the 1951 values	Allows analysis of spin-up and drift of the model
Wind simulation	
All forcings are maintained at the 1951 values except for wind speed	Allows analysis of the effect of changes in wind speed on the interannual variability and decadal changes of carbonate chemistry from 1951 to 1998 in the BCZ
SST simulation	
All forcings are maintained at the 1951 values except for SST	Allows analysis of the effect of changes in SST on the interannual variability and decadal changes of carbonate chemistry from 1951 to 1998 in the BCZ
River simulation	
All forcings are maintained at the 1951 values except for river loads of nutrients and carbon	Allows analysis of the effect of changes in river loads of nutrients and carbon on the interannual variability and decadal changes of carbonate chemistry from 1951 to 1998 in the BCZ
Atmospheric CO_2 simulation	
All forcings are maintained at the 1951 values except for atmospheric CO_2	Allows analysis of the effect of increasing atmospheric CO_2 on the interannual variability and decadal changes of carbonate chemistry from 1951 to 1998 in the BCZ

describing carbon and nutrient cycles in the marine domain (Gypens et al. 2004). The coupled model describes the biological transformation of C, N, P, and silicate along the river–coastal continuum as a function of meteorological conditions and changing human activity on the watershed. In the marine domain, MIRO-CO_2 describes the dynamics of phytoplankton (diatoms, nanoflagellates, and *Phaeocystis*); zooplankton (meso- and microzooplankton); degradation of dissolved and particulate organic matter (each with two classes of biodegradability); regeneration of inorganic nutrients (NO_3^-, NH_4^+, PO_4^{3-}, and $Si[OH]_4$) in the water column and the sediment; and dissolved inorganic carbon (DIC), total alkalinity (TA), partial pressure of CO_2 (pCO_2), pH, and air–sea CO_2 fluxes. The model is implemented in a multibox frame of the eastern English Channel and the BCZ, delineated on the basis of the hydrological regime and river inputs. The boundary conditions are provided by the simulations in the western English Channel. To take into account the cumulated nutrient enrichment of the Atlantic Ocean waters by the inputs from the Seine and Scheldt rivers, two successive boxes assumed homogeneous are considered: the Seine Bight and the BCZ. Each box is treated as an open system, receiving water and matter from the upward adjacent box and rivers (Seine or Scheldt) and exporting water and matter to the downward box.

Validation of the river loadings simulated by RIVERSTRAHLER from the Seine and Scheldt rivers during 1951–1998 is given by Billen et al. (2001, 2005). Validation of the key biogeochemical variables in the BCZ simulated by R-MIRO (forced by the Seine and Scheldt river loadings simulated by RIVERSTRAHLER) during 1951–1998 is given by Lancelot et al. (2007). Validation of the seasonality of the seawater carbonate chemistry simulated by MIRO-CO_2 for 1996–1999 is given by Gypens et al. (2004).

The reference simulation from 1951 to 1998 is obtained by constraining the model by daily wind speed, sea surface temperature (SST), monthly atmospheric pCO_2, daily global solar radiation (climatology for 1989–1999; Lancelot et al. 2005), 10-d RIVERSTRAHLER simulations for carbon and nutrient loads from the Seine and Scheldt (Billen et al. 2001, 2005), and river DIC and TA inputs from the Seine and Scheldt computed as a function of freshwater discharge (Gypens et al. 2009). Wind speed was obtained from the National Centers for Environmental Prediction reanalysis daily averages surface flux (http://www.cdc.noaa.gov/) at one station in the southern North Sea (3.75°E, 52.38°N). Atmospheric pCO_2 at Mace Head (53.55°N, 9.00°W, southern Ireland) was obtained from the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory air sampling network (http://www.cmdl.noaa.gov/) for the 1979–1998 period, and data for years before 1979 were reconstructed by assuming a similar annual growth rate as measured at Mauna Loa (http://www.esrl.noaa.gov/). Annual mean atmospheric pCO_2 increased from 30.6 Pa (302 parts per million [ppm]) to 36.2 Pa (357 ppm) between 1951 and 1998, at an average growth rate of 0.12 Pa yr^{-1} (1.2 ppm yr^{-1}). The long-term trend of annual SST was derived from ICES (2006), and the daily values were reconstructed on the basis of the mean seasonal cycle for the 1989–1999 period (Lancelot et al. 2005). Seawater carbonate chemistry computations on the basis of DIC and TA were performed on the total hydrogen ion pH scale using the carbonic acid dissociation constants of Mehrbach

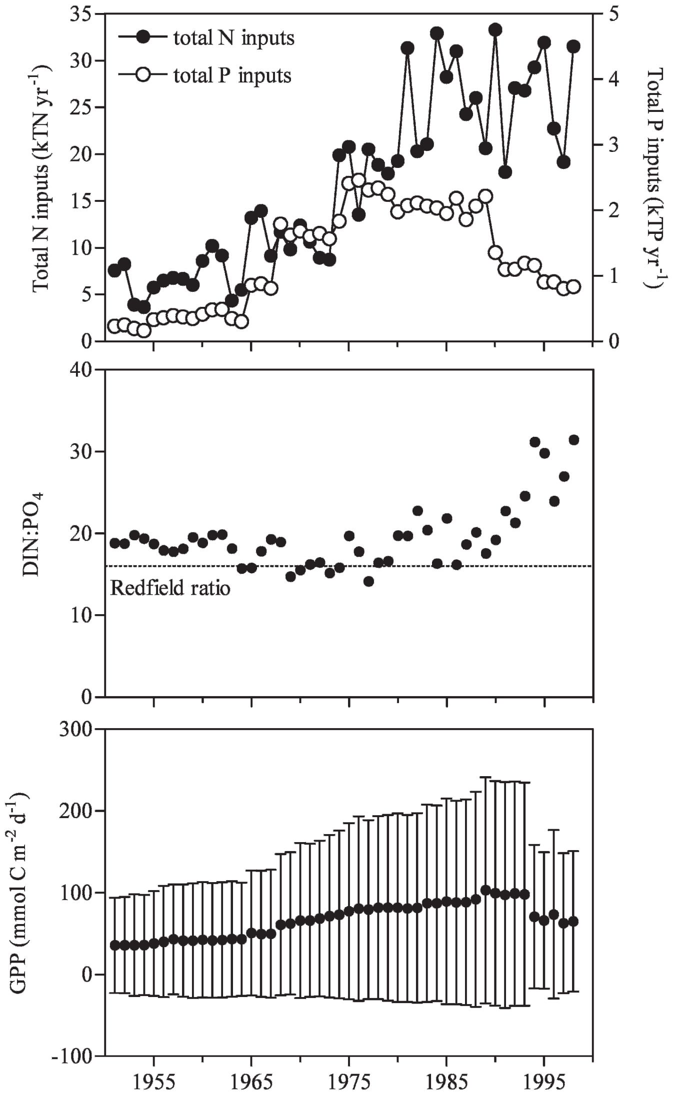

Fig. 1. Simulated evolution from 1951 to 1998 given by R-MIRO-CO$_2$ of annual nutrient river loads from the Scheldt, wintertime DIN : PO$_4$ ratio, and GPP in the BCZ. Error bars correspond to the standard deviation on the annual mean.

et al. (1973) refitted by Dickson and Millero (1987), and the calcite and aragonite solubility of Mucci (1983). Model simulations were performed over the 1951–1998 period after a 10-yr spin-up run. Five additional simulations described in Table 1 were carried out to analyze model stability and sensitivity to different forcings.

Results

From 1951 to 1998, three periods can be distinguished in terms of river inputs of N and P, quality of nutrient enrichment defined by wintertime ratio of dissolved inorganic nitrogen to phosphate (DIN : PO$_4$), and gross primary production (GPP) (Fig. 1). From 1951 to 1965, the annual increase of river nutrient loads and GPP was low. From 1965 to 1990, the river nutrient inputs increased and the wintertime DIN : PO$_4$ ratios remained close to phytoplankton requirements (Redfield ratio = 16 : 1), leading to an increase of GPP. From 1990 to 1998, the decrease of the total P river inputs (mainly due to removal of polyphosphates from washing powders) led to wintertime DIN : PO$_4$ ratios above the Redfield ratio, and to a P limitation and decline of primary production (Lancelot et al. 2007).

The reference simulation shows that from 1965 to 1990, when river nutrient loads increased with wintertime DIN : PO$_4$ ratio remaining close to the Redfield ratio, pH, Ω_{ca}, and Ω_{ar} increased while [CO$_2$] decreased (Fig. 2; Table 2), in response to increasing GPP (Fig. 1). After 1990, when GPP decreased (Fig. 1), pH, Ω_{ca}, and Ω_{ar} decreased and [CO$_2$] increased (Fig. 2; Table 2).

The baseline simulation shows that the model is stable, implying an adequate spin-up and no drift (Fig. 3). The wind simulation and the SST simulation show that changes in wind speed and SST induce low interannual variations of carbonate chemistry in surface waters of the BCZ from 1951 to 1998 (Fig. 3). The interannual variations (evaluated as the standard deviation of the mean of annual values for the 1951–1998 period) related to changes in SST are stronger than those due to changes in wind speed, respectively, ± 0.006 and ± 0.001 for pH, ± 0.04 and ± 0.01 for Ω_{ca}, ± 0.03 and ± 0.01 for Ω_{ar}, and equivalent for [CO$_2$], respectively, ± 0.07 μmol kg^{-1} and ± 0.06 μmol kg^{-1}.

The atmospheric CO$_2$ simulation shows that in absence of any other process than increasing atmospheric CO$_2$, a decrease of pH would have occurred at a rate of -0.00127 ± 0.00003 yr^{-1}, an increase of [CO$_2$] at a rate of 0.055 ± 0.001 μmol kg^{-1} yr^{-1}, and a decrease of Ω_{ca} and Ω_{ar} at a rate of -0.0103 ± 0.0002 yr^{-1} and -0.0066 ± 0.0001 yr^{-1}, respectively, in the BCZ from 1951 to 1998 (Fig. 2).

Between 1951 and 1990, the trends of seawater carbonate chemistry variables given by the reference simulation and the atmospheric CO$_2$ simulation are opposed (Figs. 2, 4; Table 2). Hence, eutrophication and related changes in carbon cycling (increase of GPP [Fig. 1], and a shift from net heterotrophy to net autotrophy [Gypens et al. 2009]) led to an effect on seawater carbonate chemistry that countered the effect of ocean acidification. This is confirmed by the parallelism between the reference simulation and the river simulation (Fig. 2). From 1951 to 1990, eutrophication alone (in absence of increasing atmospheric CO$_2$, river simulation) would have led to an increase of pH, Ω_{ca}, and Ω_{ar} of, respectively, 0.090, 0.92, and 0.59, and a decrease of [CO$_2$] of -2.7 μmol kg^{-1} (Fig. 4). From 1951 to 1990, the reference simulation shows a lower increase of pH, Ω_{ca}, and Ω_{ar} of, respectively, 0.041, 0.64, and 0.42, and a lower decrease of [CO$_2$] of -1.4 μmol kg^{-1} compared with the river simulation. The difference is mainly related to the invasion of atmospheric CO$_2$ given by the atmospheric CO$_2$ simulation that alone would have induced from 1951 to 1990 a decrease of pH, Ω_{ca}, and Ω_{ar} of, respectively, -0.044, -0.35, and -0.23 and an increase of [CO$_2$] of 1.9 μmol kg^{-1} (Fig. 4).

After 1990, when GPP decreased (Fig. 1), the decrease of pH, Ω_{ca}, and Ω_{ar}, and the increase of [CO$_2$] given by the reference simulation were highly significantly stronger than

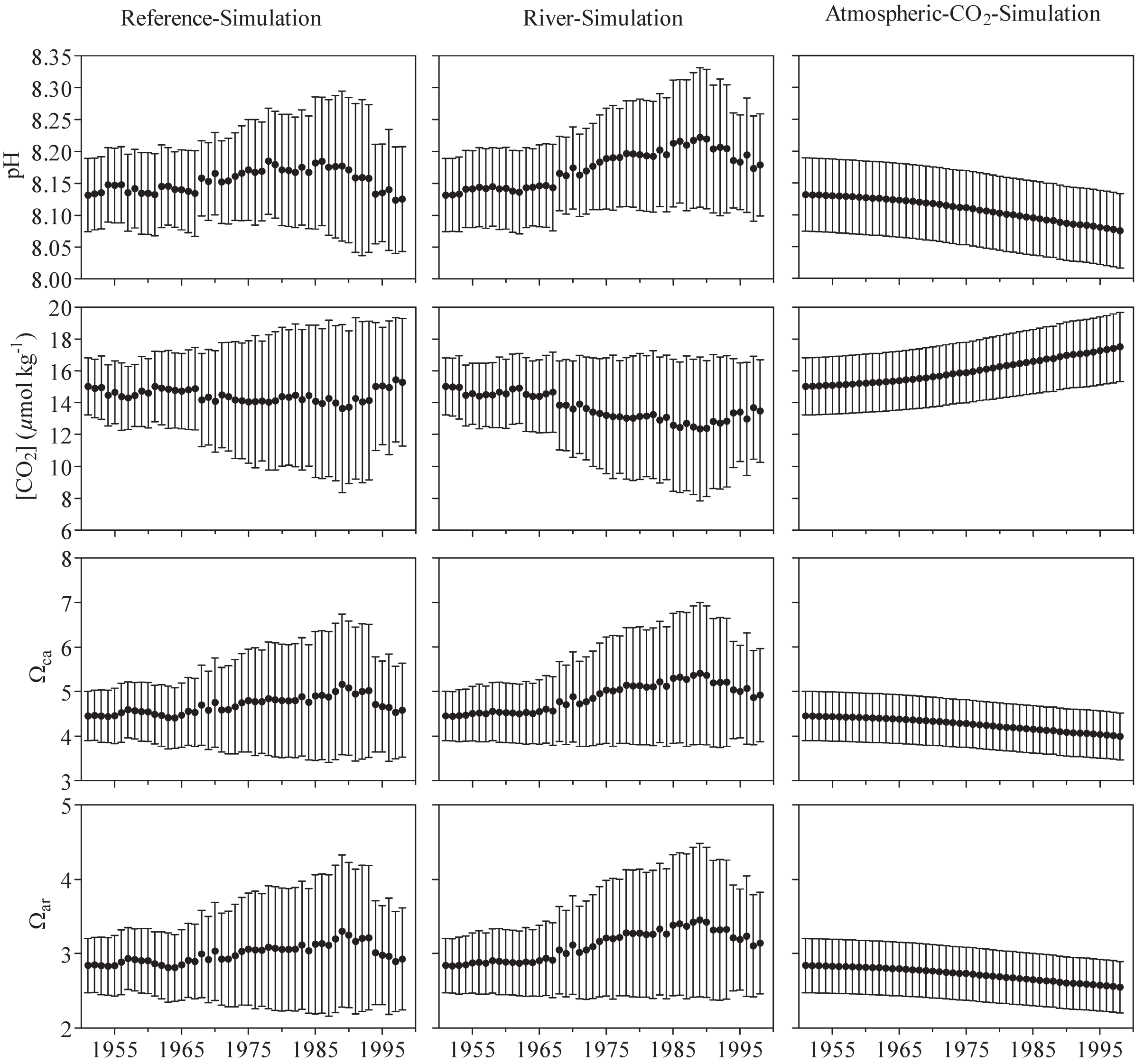

Fig. 2. Simulated evolution from 1951 to 1998 given by R-MIRO-CO$_2$ of annual pH, [CO$_2$], Ω_{ca}, and Ω_{ar} in the BCZ for the reference simulation, the river simulation, and the atmospheric CO$_2$ simulation (Table 1). Error bars correspond to the standard deviation on the annual mean.

the trends given by the atmospheric CO$_2$ simulation (Table 2). The values given by the reference simulation in 1998 compared with those in 1951 are slightly lower for pH (−0.005) and slightly higher for Ω_{ca}, Ω_{ar}, and [CO$_2$], respectively, 0.14, 0.10, and 0.2 μmol kg^{-1} (Fig. 4). In contrast, the values given by the atmospheric CO$_2$ simulation in 1998 compared with those in 1951 would have been distinctly lower for pH, Ω_{ca}, and Ω_{ar}, respec-

Table 2. Rate of change per year ± SE (r^2) of pH, [CO$_2$], Ω_{ca}, and Ω_{ar} simulated by R-MIRO-CO$_2$ in the BCZ for the reference simulation and the atmospheric CO$_2$ simulation (Table 1) for the 1951–1990 period when GPP increases, and for the 1990–1998 when GPP decreases (Fig. 1).

		Reference simulation	Atmospheric CO$_2$ simulation
pH	1951–1990	0.0013±0.0001(0.79)	−0.0012±0.0001(0.97)
	1990–1998	−0.0058±0.0008(0.87)	−0.0014±0.0001(0.98)
[CO$_2$]	1951–1990	−0.023±0.003(0.57)	0.051±0.001(0.97)
	1990–1998	0.208±0.033(0.85)	0.065±0.004(0.98)
Ω_{ca}	1951–1990	0.015±0.001(0.83)	−0.010±0.001(0.97)
	1990–1998	−0.072±0.011(0.86)	−0.011±0.001(0.98)
Ω_{ar}	1951–1990	0.010±0.001(0.82)	−0.006±0.001(0.97)
	1990–1998	−0.047±0.007(0.86)	−0.007±0.001(0.98)

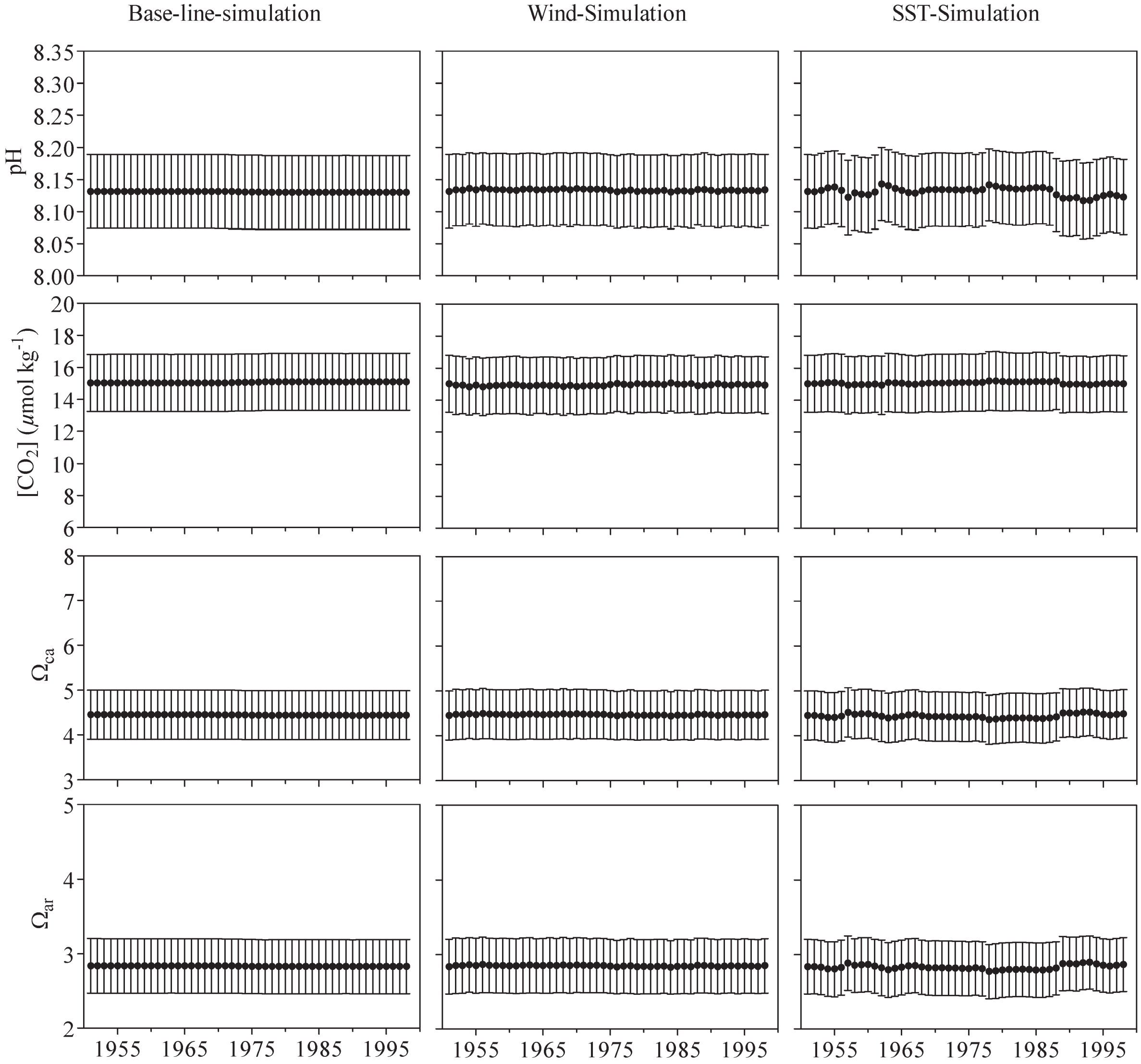

Fig. 3. Simulated evolution from 1951 to 1998 given by R-MIRO-CO_2 of annual pH, [CO_2], Ω_{ca}, and Ω_{ar} in the BCZ for the baseline simulation, the wind simulation, and the SST simulation (Table 1). Error bars correspond to the standard deviation on the annual mean.

tively, −0.055, −0.44, and −0.28, and distinctly higher for [CO_2], 2.4 μmol kg^{-1} (Fig. 4).

The trends in carbonate chemistry after 1990 are explained by the rapid shift of the BCZ ecosystem from net autotrophy to net heterotrophy (Gypens et al. 2009), related to the increase of the wintertime DIN : PO_4 ratio that limits primary production (Fig. 1). This shift from net autotrophy to net heterotrophy led to a net annual production of CO_2 at ecosystem level (Gypens et al. 2009), with a strong effect on seawater carbonate chemistry variables. This highlights that changes in river nutrient delivery loads due to management regulation policies can modify carbon cycling in the coastal zone, and lead to stronger changes in carbonate chemistry than ocean acidification.

Discussion

Temperate nearshore coastal areas that are usually strongly eutrophied, such as the Southern Bight of the North Sea and the adjacent English Channel, are characterized by important benthic calcification by organisms such as barnacles (480–1800 g $CaCO_3$ m^{-2} yr^{-1}, Gollety et al. 2008), brittle stars (680 g $CaCO_3$ m^{-2} yr^{-1}, Migné et al. 1998), mussels (11–43 g $CaCO_3$ m^{-2} yr^{-1}, F. Gazeau pers. comm. on the basis of the Netherlands National Institute for Coastal and Marine Management [RIKZ] database), oysters (330 g $CaCO_3$ m^{-2} yr^{-1}, F. Gazeau pers. comm. on the basis of the RIKZ database), cockles (8–24 g $CaCO_3$ m^{-2} yr^{-1}, F. Gazeau pers. comm. on the basis of the RIKZ database), and pelagic calcification by for instance coccolithophorids (100 g $CaCO_3$ m^{-2} yr^{-1} on the basis of Garcia-Soto et al. 1995). Some of these calcifying organisms such as bivalves play an important role in coastal biodiversity, and services and goods. Besides being important economic resources (fishery), they provide habitats for many benthic organisms, and constitute important resources for marine birds (Gutiérrez et al. 2003). From the results of controlled perturbation experiments, the calcification rates of most marine pelagic and benthic calcifiers are expected to decrease under ocean acidification (cocolithophorids [Delille et al. 2005]; mussels and oysters [Gazeau et al. 2007]). Hence, the effect of eutrophication on carbon cycling that counteracts the effect of ocean acidification, as simulated between 1951 and 1990 in the BCZ, could maintain favorable conditions of the carbonate chemistry for benthic and pelagic calcification in neashore coastal environments.

We used a relatively simplified physical description of the BCZ that could be improved by future work along several lines. Atmospheric deposition could be included in the simulations. The delivery of nutrients by atmospheric deposition has a small effect on primary production in the southern North Sea ($< 6\%$, de Leeuw et al. 2003). However, the deposition of anthropogenic nitrogen and sulfur could acidify coastal waters on the order of 10–50% of effect of ocean acidification on the basis of the simulations from an ocean global circulation model (OGCM) (Doney et al. 2007). Also, we assumed that surface waters of the North Atlantic Ocean (providing the oceanic boundary conditions of the simulations) followed the increase of atmospheric CO_2. However, pCO_2 and DIC in surface waters of North Atlantic Ocean could be increasing faster than atmospheric CO_2 because of reduction of the seawater buffering capacity (Thomas et al. 2007). The effect of the North Atlantic Oscillation (NAO) on seawater carbonate chemistry of the BCZ is to some extent accounted for in the simulations by the forcings (SST, wind speed, and freshwater discharge). However, NAO can also modulate on decadal timescales the secular trends of carbonate chemistry in the North Atlantic Ocean (Thomas et al. 2008), again affecting the boundary conditions of the model. These improvements would require the use of a three-dimensional (3-D) model of the southern North Sea, with a nesting in an OGCM to provide more detailed North Atlantic Ocean boundary conditions. The extension of 3-D modeling to the whole southern North Sea would require the historical reconstitution of river loads from other major rivers (Rhine and Thames) on the basis of monitoring data or catchment modeling with RIVERSTRAHLER or an equivalent model. Despite the simplified physical description of the BCZ we used in the present model, the simulations show marked and unexpected decadal and secular changes of the seawater carbonate chemistry in the southern North Sea. These findings need to be considered to evaluate the combined effect of future anthropogenic pressures (increasing atmospheric CO_2, eutrophication, …) on carbon cycling in coastal ecosystems.

Perturbation experiments on the effect of ocean acidification on primary production and calcification give results that are equivocal at organism and ecosystem levels (for coccolithophorids compare Delille et al. [2005], Riebesell et al. [2007], and Iglesias-Rodriguez et al. [2008]). Also, combined changes of seawater carbonate chemistry and other factors that are expected to vary with global change (micro- and macronutrients, light, and temperature) lead to nonlinear (synergistic or antagonistic) responses from marine organisms (Feng et al. 2008). This precludes us

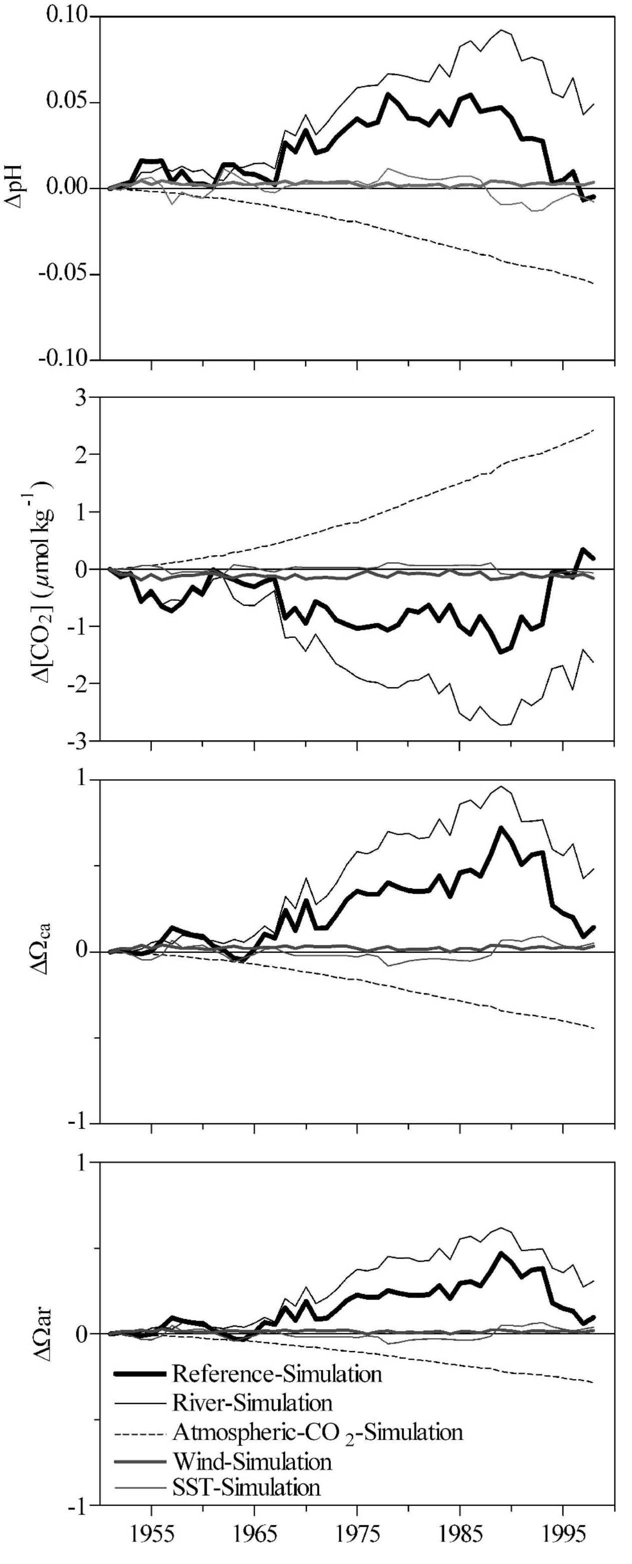

Fig. 4. Annual anomalies of pH, $[CO_2]$, Ω_{ca}, and Ω_{ar} given by the reference simulation, the river simulation, the atmospheric CO_2 simulation, the wind simulation, and the SST simulation with respect to the baseline simulation (Table 1) given by R-MIRO-CO_2 from 1951 to 1998 in the BCZ.

for the time being from robustly including potential biological feedback of ocean acidification in numerical models such as the one described here. Yet, we show that the increase of primary production due to eutrophication could counter the effects of ocean acidification on surface water carbonate chemistry in coastal environments. Also, the application of nutrient delivery regulation policies can lead to changes of carbonate chemistry that are faster than those related solely to ocean acidification. A shift toward P limitation of primary production due nutrient regulation policies, as described in the BCZ, have been also reported in several coastal environments such as the Gulf of Mexico and the Adriatic Sea (Justić et al. 1995), the Baltic Sea (Vichi et al. 2004), and the South China Sea (Ning et al. 2009), among others. Hence, the trends in carbonate chemistry described in the BCZ could be a general feature of numerous coastal environments. However, the response of carbonate chemistry in coastal environments will also to some extent be modulated by the seawater buffer capacity, in particular due to the bicarbonate content of freshwaters discharging into the coastal zone (Salisbury et al. 2008). Yet, such nutrient regulation policies have been mainly implemented in industrialized countries, while in emerging economy countries eutrophication can be supposed to continue to increase unregulated in coming decades. Other human activities such as the construction of dams can also change the delivery of nutrients to the coastal zone (Humborg et al. 1997), which can lead to rapid changes of primary production (Gong et al. 2006). The increase or decrease of nutrient delivery to the coastal zone will have, respectively, positive or adverse effects on carbonate chemistry countering or enhancing the effect of ocean acidification.

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