Chapter 3
Present Day Carbon Dioxide Fluxes in the Coastal Ocean and Possible Feedbacks Under Global Change

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Abstract The present day contemporary CO_2 fluxes in shelf seas could be significant for the global carbon cycle, since available estimates converge to a sink of ~0.3 PgC yr^{-1} corresponding to 21% of most recent estimate of contemporary sink of atmospheric CO_2 in open oceans of 1.4 PgC yr^{-1}. These estimates are prone to large uncertainty mainly due to inadequate representation of the spatial variability and need to be improved based on more data, requiring a concerted global observational effort. The potential feedbacks on increasing atmospheric CO_2 from changes in carbon flows in the coastal ocean could be disproportionately higher than in the open ocean. The changes in carbon flows and related potential feedbacks in the coastal ocean could be driven by 3 main processes: i) changes in coastal physics; ii) changes in land-used, waste water inputs, agricultural fertilizers and changes in hydrological cycle; iii) changes in seawater carbonate chemistry (ocean acidification). These potential feedbacks remain largely unquantified due to a poor understanding of the underlying mechanisms, or lack of modelling to quantify them. Based on reported evaluations and back of the envelop calculations, it is suggested that changes of biological activity due the increased nutrient delivery by rivers would provide by 2100 a negative feedback on increasing atmospheric CO_2 of the order of magnitude of the present day sink for atmospheric CO_2. This negative feedback on increasing atmospheric CO_2 would be one order of magnitude higher than negative feedback due to the decrease of either pelagic or benthic calcification related to ocean acidification, and than the negative feedback related to dissolution of $CaCO_3$ in sediments. The increase of export production could also provide a significant feedback to increasing atmospheric CO_2, although based on the conclusions from a single perturbation experiment. Feedbacks on increasing atmospheric CO_2 due to effects of C cycling in continental shelf seas related to changes in circulation or stratification could be important but remain to be quantified.

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P. Duarte and J.M. Santana-Casiano (eds.), *Oceans and the Atmospheric Carbon Content*,
DOI 10.1007/978-90-481-9821-4_3,

Keywords Carbon dioxide fluxes • Green house gases • Global change • Coastal ocean • Coastal environments • Feedbacks • Land use • Waste water inputs • Agricultural fertilizers • Hydrological cycle • Atmospheric deposition • Ocean acidification

Warming of the climate system is unequivocal based on observational evidence from all continents and most oceans (increases in global average air and ocean temperatures, melting of snow and ice, and increasing global average sea level) (IPCC 2007a). The observed increase in global average temperatures since the industrial revolution is very likely due to increasing concentrations in the atmosphere of anthropogenic green house gases (GHG). Global GHG emissions are expected to continue to grow over the next few decades, and warming and climate change in the near and long term will have a variety of negative impacts such as: changes in terrestrial and marine ecosystems (increased risk of species extinction, changes in ecosystem structure and function, loss of biodiversity, loss of ecosystem goods and services,…), changes in crop productivity, increasing risks on coasts (coastal erosion, floods,…), increasing exposure to extreme weather events (heat waves, heavy precipitation events, incidence of extreme high sea level,…), effects on health status of millions of people (increases in malnutrition, diseases, injury due to extreme weather events,…), exacerbate current stresses on water resources,… (IPCC 2007b).

Carbon dioxide (CO_2) is the most important anthropogenic GHG accounting for 77% of total anthropogenic GHG emissions in 2004 (IPCC 2007a). For the 2000–2006 period, 9.1 PgC $year^{-1}$ (PgC = 10^{15} gC) of CO_2 were emitted to the atmosphere mainly from fossil fuel combustion and cement production (7.6 PgC $year^{-1}$) and land use change (1.5 PgC $year^{-1}$). About 4.1 PgC $year^{-1}$ accumulated in the atmosphere, the land biosphere is supposed to have absorbed 2.8 PgC $year^{-1}$, and the oceans have absorbed the remaining 2.2 PgC $year^{-1}$ (Canadell et al. 2007). Hence, oceans are a major component of the global CO_2 cycle. However, the oceans are also vulnerable to climate change with potential changes in their capacity to absorb anthropogenic CO_2. These vulnerabilities include surface warming and related changes in circulation that will impact directly the chemical and physical oceanic CO_2 pumps. Changes in ocean physics are also expected to modify the vertical inputs of inorganic nutrients and light availability (increasing stratification), hence, affecting primary production and ecosystem structure, and modifying the biological CO_2 pump. The latter is also expected to respond to changes of seawater carbonate chemistry (ocean acidification) that could modify the rates and fates of primary production and calcification of numerous organisms.

Coastal environments only represent 7% of the total oceanic surface area, however, they are biogeochemically more dynamic, and probably more vulnerable to climate changes than the open ocean. Whatever the responses of the open ocean to climate changes, they will propagate on the coastal ocean. Superimposed on this "background open oceanic forcing", the coastal ocean will also respond to changes of fluxes from the land biosphere through rivers, ground waters and atmospheric deposition of major biogeochemical elements (carbon, nitrogen, phosphorous, silica) in organic and inorganic forms. Physical settings specific to the coastal ocean (coastal

upwelling, sea-ice,…) are also expected to respond to climate change probably leading to unique and local changes in carbon cycling. Finally, due to the shallowness of the coastal ocean, the benthic compartment will respond to changes of carbon cycling in surface waters on much shorter time scales than in the open ocean.

This chapter focuses on CO_2 cycling in the coastal ocean, briefly summarizing the current knowledge on the present day fluxes, and focussing more in depth on the possible evolution and feedbacks under global change.

3.1 Present Day Carbon Dioxide Fluxes in the Coastal Ocean

Continental shelf seas receive massive inputs of organic matter and nutrients from land, exchange large amounts of matter and energy with the open ocean across continental slopes and constitute one of the most biogeochemically active areas of the biosphere. The coastal ocean hosts between ~15% and ~30% of oceanic primary production and ~80% of oceanic organic matter burial (e.g. Gattuso et al. 1998a). It also hosts most of the benthic oceanic calcium carbonate ($CaCO_3$) production, ~20% of surface pelagic oceanic $CaCO_3$ stock (Balch et al. 2005), and ~50% of oceanic $CaCO_3$ deposition (Gattuso et al. 1998a). Hence, carbon (C) flows in the coastal ocean are disproportionately high in comparison with its surface area (~7% of total oceanic surface area). Intense air–water carbon dioxide (CO_2) exchanges can then be expected in the coastal ocean and could be significant for CO_2 flux budgets at regional (Frankignoulle and Borges 2001; Borges et al. 2006) and global scales (Table 3.1).

The contemporary flux of CO_2 between the coastal ocean and the atmosphere has been evaluated by several authors based on the global extrapolation of a flux value from a single shelf sea or from the compilation of literature data in several shelf seas (Table 3.1). The most recent evaluations converge towards a sink of atmospheric CO_2 of about 0.3 PgC year^{-1}. This CO_2 sink would be highly significant, corresponding to 21% of the most recent estimate of contemporary sink of atmospheric CO_2 in open oceans of 1.4 PgC year^{-1} (Takahashi et al. 2009).

Yet, these estimates based on literature compilations suffer from several caveats, one of the most important being the lack of data to adequately cover the full spatial extent of the coastal ocean and the diversity of biogeochemical C cycling related to extremely contrasted physical and biogeochemical settings. Indeed, the distribution of CO_2 flux data in shelf seas reported in literature is biased towards the mid-latitudes of the Northern Hemisphere. Data are lacking in large portions of the coastal ocean such as the Russian Arctic coast, the Eastern South America coast, the Eastern Africa coast, large sections of the Western Africa coast and large sections of the Antarctic coast.

Further, due to the high dynamic range of seasonal and spatial variations of the partial pressure of CO_2 (pCO_2) in coastal environments (Fig. 3.1), reported air–sea CO_2 fluxes can be biased by inadequate spatial or temporal coverage. For instance, in the Southern Bight of the North Sea where Thomas et al. (2004) reported a

Table 3.1 Reported estimates of the sink for atmospheric CO_2 in the coastal ocean (excluding near-shore environments)

CO_2 sink ($PgC\ year^{-1}$)	Reference	Comment
–1.0	Tsunogai et al. (1999)	Based on the global extrapolation of the average air–sea CO_2 flux in the East China Sea computed from five cruises (February 1993, October 1993, August 1993, November 1995 and September 1996). The annual air–sea CO_2 flux of Tsunogai et al. (1999) (2.9 $molC\ m^{-2}\ year^{-1}$) has been revised to a lower value (1.2 $molC\ m^{-2}\ year^{-1}$, Wang et al. 2000) based on a better coverage of the seasonal cycle and use of gas transfer velocities computed from wind speed rather than a constant value.
–0.40	Thomas et al. (2004)	Based on the global extrapolation of the average air–sea CO_2 flux in the North Sea (1.4 $molC\ m^{-2}\ year^{-1}$) computed from four cruises (September 2001, November 2001, February 2002, May 2002).
–0.37	Borges (2005)	Based on the compilation of annually integrated air–sea CO_2 fluxes in 15 shelf seas as reported in literature using partial pressure of CO_2 (pCO_2) measurements, scaled by latitudinal bands of 30° based on surface areas reported by Walsh (1988). Surface areas between 30°S and 30°N are under-estimated.
–0.45	Borges et al. (2005)	Based on the compilation of annually integrated air–sea CO_2 fluxes in 17 shelf seas as reported in literature using pCO_2 measurements, scaled by latitudinal bands of 30° based on surface areas reported by Walsh (1988). Air–sea CO_2 fluxes were recomputed to an uniform gas transfer velocity parameterization. Surface areas between 30°S and 30°N are under-estimated.
–0.22	Cai et al. (2006)	Based on the compilation of air–sea CO_2 fluxes in 29 shelf seas, scaled by 7 shelf provinces using classification and surface areas reported by Walsh (1988). Not all the air–sea CO_2 fluxes have a full annual coverage, and some of the fluxes are derived from C mass balance and not pCO_2 measurements.
–0.33 to –0.35	Chen and Borges (2009)	Based on the compilation of air–sea CO_2 fluxes in 58 shelf seas, scaled using a global average or by shelf provinces using classification and surface areas reported by Jahnke (2009). Not all the air–sea CO_2 fluxes have a full annual coverage and some of the fluxes are derived from C mass balance and not pCO_2 measurements.

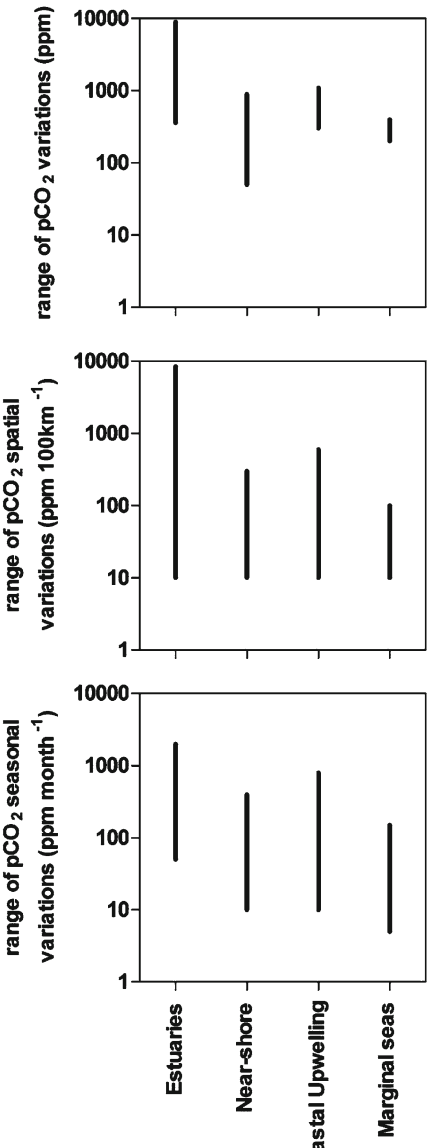

Fig. 3.1 Dynamic range of the partial pressure of CO_2 (pCO_2) variations across coastal ecosystems, of pCO_2 spatial gradients and of pCO_2 seasonal changes in estuaries (based on Frankignoulle et al. 1998; Bouillon et al. 2003), in near-shore ecosystems (based on Borges and Frankignoulle 2002a; Cai et al. 2003), and coastal upwelling systems (based on Friedrich et al. 2002, 2008; Goyet et al. 1998; Borges and Frankignoulle 2002b)

source of CO_2 based on a data-set with a lower temporal coverage than the one of Schiettecatte et al. (2007) who reported a sink of atmospheric CO_2. Another example is in the US South Atlantic Bight, where Cai et al. (2003) reported a source of CO_2 based on a data-set with a lower spatial resolution than the one of Jiang et al. (2008a) who reported a sink of atmospheric CO_2.

Inter-annual variations of air–sea CO_2 fluxes in the coastal ocean can be significant although they have been seldom investigated due to the lack of adequate data-sets. In continental shelf seas, these inter-annual variations can be due to large scale climate oscillations such as the El Niño Southern Oscillation (ENSO) (Ianson and Allen 2002; Friederich et al. 2002) or such as the Southern Annular Mode (SAM) (Borges et al. 2008a). In the case of the California current, the change of ENSO phases can lead to a reversal of the direction of annual air–sea CO_2 fluxes (Friederich et al. 2002). In near-shore ecosystems, inter-annual variations of air–sea CO_2 fluxes can be due to variable river influence (Borges and Frankignoulle 1999; Gypens et al. 2004; Borges et al. 2008b; Salisbury et al. 2009).

Contemporary air–sea CO_2 fluxes deduced from field measurements of pCO_2 are the combination of natural (pre-industrial) air–sea CO_2 flux signal and a perturbation air–sea CO_2 flux signal related to the anthropogenic increase of atmospheric CO_2. The pre-industrial air–sea CO_2 fluxes can be roughly evaluated by the mass balance of carbon inputs and outputs for the whole ocean (open and coastal) at global scale (e.g. Sarmiento and Sundquist 1992). In the open ocean, the inventory of anthropogenic dissolved inorganic carbon (DIC) can be evaluated by several back-calculation techniques (e.g. Vázquez-Rodríguez et al. 2009) that allow deriving a pre-formed DIC value that is removed from the observed DIC value, the difference corresponding to the anthropogenic DIC signal. The evaluation of a pre-formed DIC value relies on the analysis of chemical variables in water masses that are assumed to be devoid of anthropogenic DIC (deep waters). Due to the shallowness of the coastal ocean, it is impossible to evaluate pre-formed DIC values. Further, in the coastal ocean the anthropogenic air–sea CO_2 flux signal is expected to be influenced by other perturbations besides the increase of atmospheric CO_2, such as changes in nutrient inputs by atmospheric deposition or by rivers. The only attempts to evaluate the anthropogenic CO_2 sink in the coastal ocean have been made with two modelling studies. Mackenzie et al. (2004) used a single box model of the coastal ocean and evaluated the sink of anthropogenic CO_2 to 0.17 PgC $year^{-1}$. Bopp et al. (2008) used a high resolution ocean model (0.5° × 0.5°) and evaluated the sink of anthropogenic CO_2 in the coastal ocean to 0.13 PgC $year^{-1}$. Hence, the coastal ocean presently contributes between 6% and 11% of the sink of anthropogenic CO_2 in the open ocean, ranging between 1.5 and 2.2 PgC $year^{-1}$ (Sarmiento et al. 2000; Gloor et al. 2003; Quay et al. 2003; Gurney et al. 2004; Sabine et al. 2004; Patra et al. 2005; Gruber et al. 2009).

The proximal coastal ocean (estuaries, bays, salt-marshes, mangroves, and other near-shore ecosystems) is directly influenced by terrestrial inputs of DIC, nutrients and organic carbon. At ecosystem level, the aquatic compartment of these environments is net heterotrophic, consuming more organic carbon than the autochtonous gross primary production (GPP) (Odum and Hoskin 1958; Odum and Wilson 1962;

Heip et al. 1995; Kemp et al. 1997; Gattuso et al. 1998a; Gazeau et al. 2004; Hopkinson and Smith 2005). Accordingly, the aquatic compartment of these ecosystems is a source of CO_2 to the atmosphere (Frankignoulle et al. 1998, Borges et al. 2003; Abril and Borges 2004; Wang and Cai 2004). The contribution of CO_2 inputs by rivers to the overall estuarine emission is generally low (Borges et al. 2006; Jiang et al. 2008b). The overall source of CO_2 from near-shore ecosystems has been evaluated to ~0.50 PgC year^{-1}, mainly related to the emission of CO_2 to the atmosphere from estuaries (~0.36 PgC year^{-1}) (e.g. Chen and Borges 2009). These estimations also suffer from the same caveats as those for continental shelf seas. Data distribution is biased towards the temperate regions of the Northern Hemisphere, and most estuaries where CO_2 fluxes have been evaluated are macrotidal estuaries, while data in other types of estuarine environments (fjords, fjards, lagoons, micro-tidal estuaries,…) are scarce. Further, the dynamic range of pCO_2 variations in estuaries is very marked (Fig. 3.1) and issues of adequate spatial and temporal coverage are even more critical. Also, there is a large uncertainty related to value of estuarine surface area used to scale the CO_2 flux data as discussed by Abril and Borges (2004) and Borges (2005). Yet, the estimate of the emission of CO_2 from estuaries based on the scaled CO_2 flux data is in reasonable agreement with the estimate based on the input of river CO_2 and the degradation during estuarine transit of particulate (POC) and dissolved organic carbon (DOC) as discussed by Abril and Borges (2004), Borges (2005) and Chen and Borges (2009).

3.2 Possible Evolution and Feedbacks Under Global Change

Figure 3.2 depicts a conceptual diagram of the different anthropogenic forcings on the coastal ocean that can modify the sources and sinks of carbon and ultimately provide a feedback on increasing atmospheric CO_2. Hereafter, the impact of these forcings and potential associated feedbacks will be discussed in relation to air–sea CO_2 fluxes in the coastal ocean, when documented, and roughly quantified, when possible (Table 3.2).

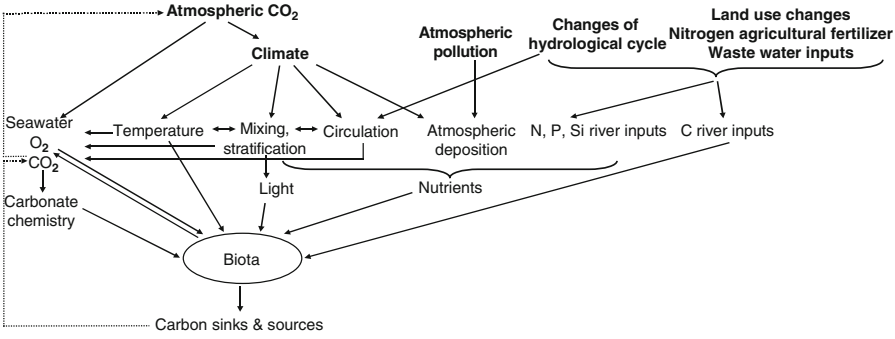

Fig. 3.2 Conceptual diagram of global change forcings on C cycling of the coastal ocean (*bold*), and feedbacks on increasing atmospheric CO_2 (Adapated from Riebesell 2007)

Table 3.2 Global change forcings on carbon cycling of the coastal ocean and associated feedback on increasing atmospheric CO_2 by year 2100. Refer to text for details on evaluation of sign and quantification of feedbacks

Global change forcings	Feedback	PgC year^{-1}	Comment
Changes in coastal physics			
Enhanced stratification	– ?	?	1
Enhanced (?) coastal upwelling	+ ?	?	2
Impact of expanding OMZ in coastal upwelling regions	+	?	3
Enhancement of air–sea CO_2 fluxes related to Arctic sea-ice retreat	–	0.002	4
Changes in land-used, waste water inputs, agricultural fertilizers and changes in hydrological cycle			
Increase of river organic carbon delivery to the Arctic Ocean	+	?	
Increase of river nutrients delivery to the Arctic Ocean	–	?	
Global increase in river nutrient and organic matter delivery	–	0.200	5
Global increase in nutrient atmospheric deposition	–	?	6
Expanding hypoxic and anoxic zones	+	?	3
Changes in seawater carbonate chemistry (ocean acidification)			
Decrease of benthic calcification			
Coral reefs	–	0.015–0.026	
Other benthic environments	–	0.025–0.046	
Decrease of pelagic calcification			
Coccolithophorids	–	0.013–0.019	
Other pelagic calcifiers	–	?	
Dissolution of metastable $CaCO_3$ in sediment porewaters	–	0.022	7
Enhancement of primary production and export production due increasing $[CO_2]$	–	0.108–0.216	8

1. Negative feedback only reported in Tasman shelf assuming pCO_2 behaviour during warm years is representative of response to global warming, if extrapolated globally would produce a negative feed-back of the order of ~0.1 PgC year^{-1}.
2. Assuming exact opposite response of model output with decreasing upwelling favourable winds.
3. Assuming enhanced denitrification leading to decreased primary production.
4. Feedback computed for the next decade and not until 2100.
5. The enhancement of primary production by nutrient inputs balances the additional CO_2 production by organic matter inputs.
6. Not taking into account enhancement of acidification of surface waters by sulphur atmospheric deposition.
7. Based on Andersson et al. (2003).
8. Based on a single mesocosm experiment with mixed diatom and coccolithophorid assemblage.

Several changes in coastal ocean physics are expected with global warming that can change C cycling and air–sea CO_2 fluxes, such as increasing stratification, enhanced coastal upwelling, expanding oxygen minimum zones, retreat of sea-ice and changes in freshwater delivery (Section 3.2.1).

Changes in land use, waste water inputs, agricultural fertilizers, hydrological cycle and atmospheric deposition increase the delivery of inorganic and organic carbon, and nutrients to the coastal ocean, and modify C flows (enhanced primary production and hypoxia/anoxia) and air–sea CO_2 fluxes in the coastal ocean with potential feedbacks on increasing atmospheric CO_2 (Section 3.2.2).

Changes in seawater carbonate chemistry in response to increasing atmospheric CO_2 content can change the rates and fates of primary production and calcification at organism and ecosystem community levels, modifying C flows and air–sea CO_2 fluxes in the coastal ocean with potential feedbacks on increasing atmospheric CO_2 (Section 3.2.3).

Finally, anthropogenic impacts on specific near-shore coastal ecosystems (coral reefs, seagrass meadows and mangroves) can alter C flows in these ecosystems (Section 3.2.4).

3.2.1 Changes in Coastal Ocean Physics

It has been hypothesized (Bakun 1990) and modelled (Snyder et al. 2003; Diffenbaugh et al. 2004) that the intensity and duration of coastal upwelling will increase in future due to climate change. Increasing land–sea thermal contrasts will increase alongshore winds driving Ekman upwelling. Locally, other factors such as decadal fluctuations in surface heat fluxes can modulate the response to increasing upwelling favorable winds and lead to increased stratification and surface ocean warming, as evidenced in the California Current in relation to the Pacific Decadal Oscillation (Di Lorenzo et al. 2005; Field et al. 2006). Yet, there is observational evidence in several coastal upwelling systems that suggest a general increasing trend in upwelling with global warming (Anderson et al. 2002; Mendelssohn and Schwing 2002; Goes et al. 2005; Santos et al. 2005; McGregor et al. 2007).

The response of air–sea CO_2 fluxes to increased upwelling is difficult to predict and can go both ways. Stronger vertical inputs of DIC would drive the system to emit more CO_2 to the atmosphere, while enhanced nutrient inputs would drive higher primary production, export production and a sink for atmospheric CO_2. Plattner et al. (2004) modelled the impact of decreasing upwelling favorable winds on C flows in the California Current system. Model results show that a 50% reduction of wind stress induces a ~50% decrease in net primary production and in export production; yet, the source of CO_2 to the atmosphere also decreases by about ~50% due to the decrease of vertical inputs of DIC and the decrease of the gas transfer velocity, providing a negative feedback on increasing atmospheric CO_2. However, the increase of upwelling favorable winds does not necessarily imply that the

ecosystem will respond by an increase of primary production. Increased upwelling winds can also lead to a reduction of light exposure due to deeper mixed layers and to an increase offshore advection of phytoplankton (Largier et al. 2006). Nevertheless, a time series in Monterey Bay (California) shows since 1993 an increasing trend in pCO_2 that is faster than the one expected from the equilibration with increasing atmospheric CO_2, in parallel with a decreasing trend in sea surface temperature (SST) and an increasing trend in chlorophyll-a (Francisco Chavez and Gernot Friederich, 2009, personal communication). This would suggest an increasing trend in upwelling and primary production with an increase in pCO_2 values, leading to an overall positive feedback on increasing atmospheric CO_2.

Climate change is expected to lead to a decrease of oxygen (O_2) content in the oceans due to the slowing down of the thermohaline circulation and decreasing solubility of O_2 (due to surface warming) of the source waters of intermediate and deep layers (Bopp et al. 2002; Matear and Hirst 2003). This will lead to the expansion of oxygen minimum zones (OMZ) as confirmed by historical observations (Bograd et al. 2008; Stramma et al. 2008). OMZ are associated to major coastal upwelling regions such as the Humbolt current, the Benguela current, the Canary current and the Arabian Sea. The upwelling source waters in coastal upwelling areas associated to OMZ are sources of CO_2 to the atmosphere because denitrification leads to lower concentrations of nitrate and excess of DIC relative to nitrogen (Fig. 3.3). Hence, coastal upwelling areas associated to OMZ are sources of atmospheric CO_2 such as the Arabian Sea (Goyet et al. 1998) and the Peruvian and Chilean coasts (Friederich et al. 2008; Paulmier et al. 2008). Coastal upwelling areas devoid of OMZ such as the Iberian coastal upwelling system (Borges and Frankignoulle 2002a) or with deep OMZ such as the Oregon coast (Hales et al. 2005) are sinks for atmospheric CO_2. The future horizontal and vertical expansion of OMZ is then expected to provide a positive feedback on increasing atmospheric CO_2 due to enhanced CO_2 emissions from coastal upwelling systems.

Sarmiento et al. (1998) showed that future increase in stratification reduces the thermohaline circulation and open oceanic uptake of anthropogenic CO_2. Yet, the ocean will also respond to increased stratification by changes in export production (Sarmiento et al. 1998; Bopp et al. 2001; Le Quéré et al. 2002, 2003) and in the vertical input of DIC, which potentially can provide feedbacks on increasing atmospheric CO_2. The comparison of negative and positive SST anomaly phases of the large scale climatic oscillations (ENSO, SAM,…) can be used as a natural laboratory to determine how marine biogeochemistry could respond to future increase in SST and stratification in the oceans (Le Quéré et al. 2002, 2003). However, time-series of pCO_2 with the adequate temporal resolution and duration to work out seasonal and inter-annual variations are extremely scarce in continental shelf seas. Borges et al. (2008a) constructed a time-series of pCO_2 and air–sea CO_2 fluxes in the Tasman continental shelf based on the analysis of anomalies of pCO_2 and SST from a data-set of 22 cruises spanning from 1991 to 2003. Over the Tasman continental shelf, during positive phases of SAM, there is a decrease of wind speed that leads to increasing SST and stratification (Fig. 3.4). The increase of stratification leads to a decrease of vertical inputs of DIC and overall decrease in pCO_2 and

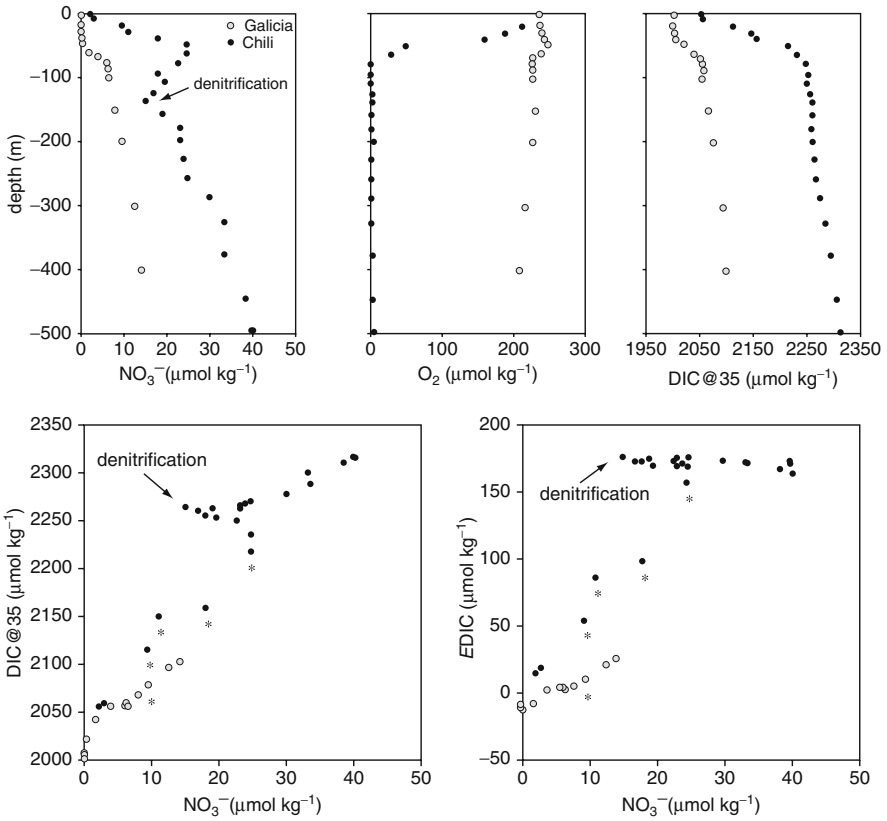

Fig. 3.3 Vertical profiles in the top 500 m of nitrate (NO_3^-), dissolved oxygen (O_2), dissolved inorganic carbon normalized to a salinity of 35 (DIC@35), DIC@35 vs NO_3^-, excess DIC (*E*DIC) vs NO_3^- at the continental shelf break of the Galician (–9.54°E 42.15°N) and Chilean (–77.59°E –12.45°N) upwelling systems. Chilean data were extracted from the Global Ocean Data Analysis Project (Key et al. 2004), Galician data are from the OMEX-II project (Borges and Frankignoulle 2002a). EDIC was computed as the difference between observed DIC and DIC computed from total alkalinity and atmospheric CO_2, and provides an estimate of CO_2 outgassing if the water mass is upwelled. Asterisks indicate the depths from which water can be upwelled (10–50 m in the Chilean upwelling system based on Paulmier et al. (2008) and 200 m in the Galician upwelling system based on Borges and Frankignoulle (2002a)). For a given NO_3^- value (indicative of potential primary production), DIC@35 and *E*DIC (indicative of potential CO_2 outgassing) are higher in the Chilean upwelling system than in the Galician upwelling, probably in relation to denitrification associated to the marked oxygen minimum zone in the Chilean upwelling system. This could explain that the Chilean upwelling system behaves as a source of CO_2 (Friederich et al. 2008) and the Galician upwelling system as a sink of CO_2 (Borges and Frankignoulle 2002a)

increase in the sink for atmospheric CO_2 (Fig. 3.4). Hirst (1999) modelled an increase of SST at the latitude of the Tasman continental shelf of about 2°C by 2100. If we assume that the response of air–sea CO_2 fluxes to inter-annual positive anomalies of SST are representative of the response of air–sea CO_2 fluxes under global warming, this would lead to an enhancement of the sink of atmospheric CO_2

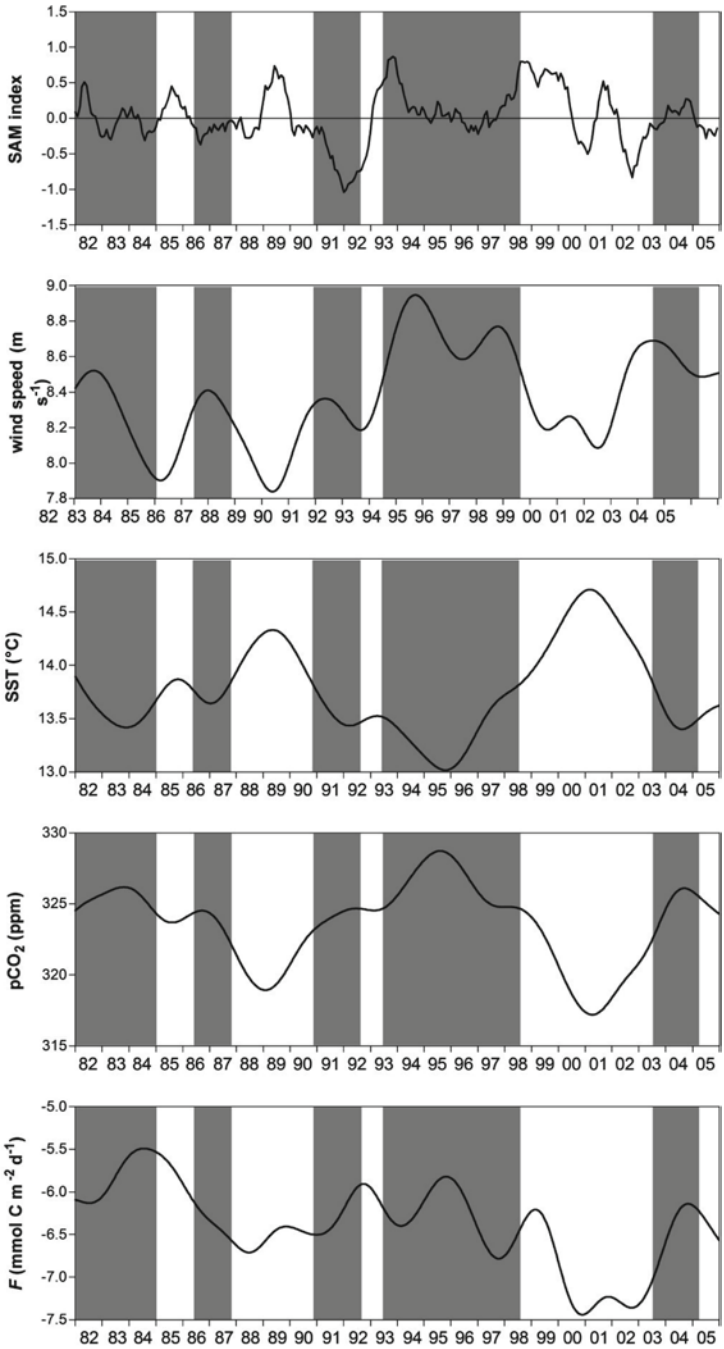

Fig. 3.4 Time-series from 1982 to 2005 of Southern Annular Mode (SAM) index and of deseasonalized sea surface temperature (SST), partial pressure of CO_2 (pCO_2) and air–sea CO_2 fluxes (F) in the Tasman continental shelf (adapted from Borges et al. 2008a). Grey areas correspond to periods of sustained negative SST anomalies

in the Tasman continental shelf of about 36%. Assuming all continental shelves respond similarly this would lead to a major feedback on increasing atmospheric CO_2 from a present day sink of 0.3–0.4 PgC year^{-1} by 2100. However, it is extremely unlikely that all continental shelves will respond by an increase in the sink of atmospheric CO_2 with increasing stratification. More data acquisition and analysis are required to characterize the possible responses of air–sea CO_2 fluxes to changes in stratification in continental shelf seas.

Climate changes will probably strongly affect C cycling and air–sea CO_2 fluxes in the Arctic Ocean that at present time has been evaluated as a sink for atmospheric CO_2 (Pipko et al. 2002; Murata and Takizawa 2003; Bates 2006; Bates et al. 2005; 2006; Else et al. 2008; Murata et al. 2008). Bates et al. (2006) found a positive relationship between air–sea CO_2 fluxes and the ice–sea cover in the Chukchi Sea. Assuming that this relationship could be used to predict the evolution of air–sea CO_2 fluxes with the future predicted sea-ice retreat, these authors estimated that the sink of atmospheric CO_2 in the Arctic Ocean would increase in the coming decade by 0.002 PgC year^{-1} compounded each year. However, it is also expected that future changes in temperature will modulate air–sea CO_2 fluxes directly through the thermodynamic change of pCO_2. Future changes in temperature will indirectly modulate air–sea CO_2 fluxes through changes in circulation (combined with salinity changes due to sea-ice retreat and changes in fresh-water delivery) that will affect DIC transport (horizontally and vertically) and will also affect biological activity and C flows.

3.2.2 Changes in Land Use, Waste Water Inputs, Agricultural Fertilizers, Hydrological Cycle and Atmospheric Deposition

A major change in C flows and air–sea CO_2 fluxes can be expected from the mobilization of terrestrial matter and transport by rivers to the Arctic Ocean. The Arctic Ocean receives almost 10% of global river discharge and about 0.025 PgC year^{-1} of terrestrial DOC (Opshal et al. 1999). Arctic river basins may store up to ~50% of the global soil organic carbon (Macdonald et al. 2006), with permafrost soils storing about 400 PgC (Davidson and Janssens 2006). An increase of fresh water discharge to the Arctic during the last 60 years has been reported (Peterson et al. 2002) and could continue to increase in future (McClelland et al. 2004). This could enhance organic carbon delivery by rivers to the Arctic Ocean that could be further increased by mobilization of soil organic carbon with permafrost thawing (Frey and Smith 2005). The DOC delivered during ice-out is mostly young (Benner et al. 2004; Raymond et al. 2007) and labile (Holmes et al. 2008). Hence, the degradation of the additional organic carbon delivered by rivers to the Arctic Ocean with climate changes would provide a positive feedback on increasing atmospheric CO_2 that could be significant but yet unquantified (Frey and McClelland 2009). On the other hand, the river delivery of dissolved inorganic nutrients (McClelland et al. 2007) and possibly dissolved organic nutrients (Frey and McClelland 2009) to the Arctic

Ocean could also increase with climate change. This could stimulate primary production and provide a negative feedback on increasing atmospheric CO_2 that could also be significant and is yet unquantified.

Changes in land use and waste water inputs have increased river nutrient contents (Green et al. 2004; Seitzinger et al. 2005) and are expected to continue to increase in future (Seitzinger et al. 2002; Galloway et al. 2004). The delivery of nutrients to the coastal ocean will also be modified by predicted future increasing global freshwater flow due to changes in the hydrological cycle (Douville et al. 2002; Labat et al. 2004; Milly et al. 2005; Aerts et al. 2006; Huntington 2006). However, future changes in freshwater flow will show regional differences, in general with an increase at high-latitudes and tropical latitudes and a decrease at mid-latitudes (Milly et al. 2005). The freshwater delivery to the coastal ocean will be further modulated by damming and other water diversion activities (Vörösmarty and Sahagian 2000; Vörösmarty et al. 2003).

It is established that nutrient delivery by rivers to the coastal ocean has increased during the past century and is expected to continue to increase in the future. This could lead to an enhancement of primary production and a negative feedback on increasing atmospheric CO_2. On the other hand, increased organic matter river loadings are expected to fuel heterotrophic activity in the coastal ocean and provide a positive feedback on increasing atmospheric CO_2. Yet, the balance between these two processes seems to be a negative feedback on increasing atmospheric CO_2 due to the enhancement of net ecosystem production (NEP). Based on a simple one-box model of the coastal ocean, Mackenzie et al. (2004) have evaluated the negative feedback on increasing atmospheric CO_2 by 2100 at ~0.20 PgC $year^{-1}$. Moreover, it has been recently reported that the impact of anthropogenic nitrogen atmospheric deposition on primary production has been under-estimated (Duce et al. 2008), hence the future increase in NEP and related negative feedback on increasing atmospheric CO_2 could be stronger. Based on a coupled general circulation model, da Cunha et al. (2007) have shown that variable river inputs of nutrients have little impact on C cycling in the open ocean, hence, this impact seems to be confined to the coastal ocean. Gypens et al. (2009) have shown, based on a regional model, that nutrient reduction policies can lead to a strong decrease of primary production and NEP and a positive feedback increasing atmospheric CO_2. However, at a global scale, the anthropogenic delivery of nutrients to the coastal zone and concomitant enhancement of NEP and sink of atmospheric CO_2 is expected to continue to increase. The environmental policies actually implemented in watersheds of developed countries are not expected to be implemented for decades in emergent countries.

Changes in land use on watersheds and in freshwater flow can also alter the delivery of bicarbonate (and total alkalinity (TA)) from rivers to the coastal ocean (Cai 2003; Raymond and Cole 2003; Raymond et al. 2008; Cai et al. 2008; Gislason et al. 2009). This in itself constitutes a sink for atmospheric CO_2 on the watershed if related to enhanced $CaCO_3$ weathering. However, it is unclear how this could affect the coastal ocean CO_2 sink, although an increase of the seawater buffering capacity can be expected. This will also be probably modulated by the changes in

DIC:TA ratio in river water (Cai et al. 2008). Also, it has been suggested that TA generation in near-shore environments (Cai and Wang 1998) could contribute to enhance the seawater buffering capacity and enhance the sink for atmospheric CO_2 in the coastal ocean (Fennel et al. 2008; Thomas et al. 2009).

An important consequence of eutrophication is the development of hypoxic or anoxic regions in coastal ecosystems (Diaz and Rosenberg 2008). In semi-enclosed seas permanently stratified, hypoxia is a perennial feature (Baltic Sea and Black Sea), while in seasonally stratified systems hypoxia is a seasonal feature, occurring usually in summer when temperature (and stratification) and organic matter availability are highest (Gulf of Mexico and East China Sea). In permanently well-mixed continental shelf seas, even highly eutrophicated such as the Southern Bight of the North Sea, hypoxia does not occur. However, in well-mixed (macro-tidal) estuaries, low oxygen levels and even hypoxia can occur mainly in maximum turbidity zones (e.g. Herman and Heip 1999), such as in the Scheldt estuary in the 1970s when eutrophication was highest (e.g. Soetaert et al. 2006). In estuaries, hypoxia can occur seasonally but also at daily time-scales (during the night) (Tyler et al. 2009). Hypoxia and anoxia have important consequences on benthic biomass and biodiversity with potential impacts on fisheries (Diaz and Rosenberg 2008). The impact on air–sea CO_2 fluxes is difficult to evaluate, yet, by analogy with OMZ (Section 3.2.2) it is expected that the enhancement of denitrification at low oxygen levels will lead to a net CO_2 production due to removal of nitrate and production of CO_2. Denitrification will also increase TA and increase the buffering capacity of seawater and decrease the seawater pCO_2 (Fennel et al. 2008; Thomas et al. 2009). This can lead to a negative feedback on increasing atmospheric CO_2. Yet, the model of Fennel et al. (2008) in the northwest North Atlantic continental shelf shows that the contribution of TA generation by benthic denitrification to the enhancement of the CO_2 sink (0.07 mmolC m^{-2} $year^{-1}$) is one order of magnitude lower than the decrease of the CO_2 sink due to lower primary production related to the removal of nitrate (0.17 mmolC m^{-2} $year^{-1}$). Hence, the expansion of hypoxic or anoxic zones in coastal environments that has been observed since the 1960s (Diaz and Rosenberg 2008) and could increase in future with sustained eutrophication, can be expected to lead to a positive feedback on increasing atmospheric CO_2 due to denitrification.

3.2.3 Changes in Seawater Carbonate Chemistry

Ocean acidification of surface waters corresponds to the increase of $[CO_2]$ and of $[H^+]$, the decrease of pH, of $[CO_3^{2-}]$, and of the saturation state (Ω) 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. The $CaCO_3$ production of benthic and planktonic calcifiers is expected to decrease with decreasing Ω due to ocean acidification (refer to reviews by Raven et al. (2005), Kleypas et al. (2006),

Fabry et al. (2008), Doney et al. (2009)). This is expected to provide a negative feedback on increasing atmospheric CO_2 since calcification leads to a shift from the bicarbonate to the CO_2 pool according to

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

Furthermore, ocean acidification is expected to lead to an enhancement of shallow-water $CaCO_3$ dissolution in the porewaters within sediments (Andersson et al. 2003), also providing a negative feedback on increasing atmospheric CO_2.

On the other hand, primary production of some pelagic (e.g. Riebesell et al. 1993; Qiu and Gao 2002) and benthic (e.g. Gao et al. 1993; Zimmerman et al. 1997) non-calcifying autotrophs could increase with $[CO_2]$. An increase in primary production associated to efficient organic carbon export would induce a negative feedback on increasing atmospheric CO_2, according to

$$CO_2+H_2O \rightarrow CH_2O+O_2$$

Besides changes in primary production and calcification, marine organisms and communities can also respond to ocean acidification through changes in N_2 fixation (e.g. Hutchins et al. 2007), shift in natural assemblages (e.g. Boyd and Doney 2002; Tortell et al. 2002; Engel et al. 2008) and an increase of export of organic matter to depth due to enhanced aggregation (e.g. Engel et al. 2004; Delille et al. 2005; Riebesell et al. 2007). All these processes could also provide a negative feedback on increasing atmospheric CO_2.

Since the coastal ocean hosts a disproportionately more important biological activity than the open ocean, the potential feedbacks on increasing atmospheric CO_2 related to the response of marine organisms and communities to the acidification of surface waters are expected to be disproportionately much more important in the coastal ocean than in the open ocean. Further, in coastal environments the acidification of surface waters could be enhanced compared to the open ocean due to anthropogenic atmospheric nitrogen and sulfur deposition (Doney et al. 2007), influence of river discharge (Gledhill et al. 2008; Salisbury et al. 2008) or related to upwelling of DIC rich waters (Feely et al. 2008).

During high-runoff, near-shore coastal environments influenced by estuaries can be exposed seasonally to low Ω values. Salisbury et al. (2008) showed that during high-runoff the plume of Kennebec river (Gulf of Maine) shows very low Ω values down to 0.4 associated to salinities down to 8. However, most rivers show Ω values above 1 for salinities above 10 (Salisbury et al. 2008), hence, river plumes under-saturated in $CaCO_3$ are not the common feature. Yet, in Arctic rivers Ω values are lower ($\Omega > 1$ for salinities > 25). Hence, the increase of Arctic river runoff under global warming (Section 3.2.2) could lead to an extension of river plumes with low Ω values in the Arctic Ocean. However, river plumes are also typically eutrophicated, leading to an increase in primary production with an effect on carbonate chemistry (Gypens et al. 2009; Borges and Gypens 2010). Figure 3.5 shows the decadal changes of carbonate chemistry in the Southern North Sea. From the 1950s to the mid 1980s when GPP

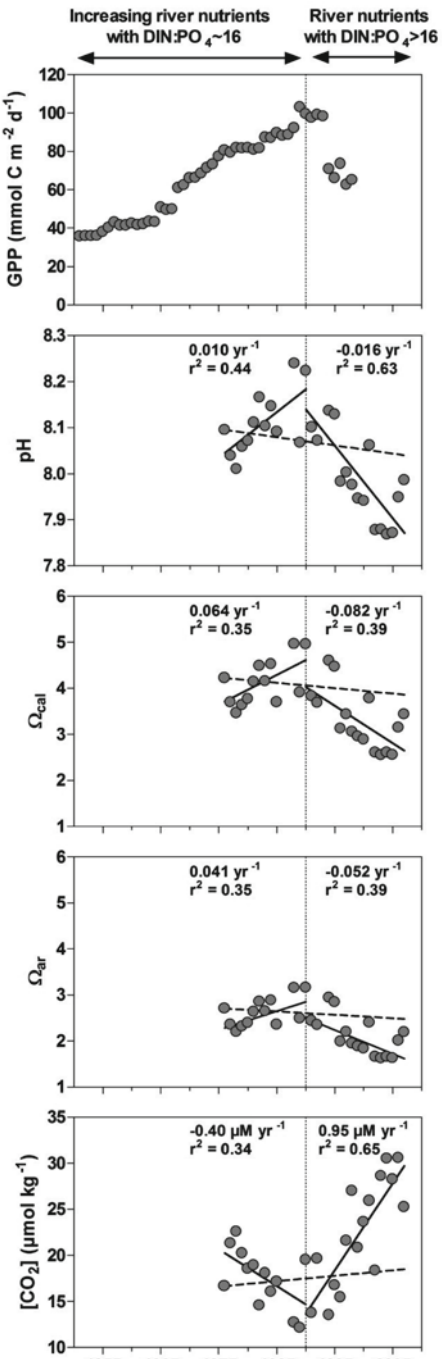

Fig. 3.5 Time series in the Southern North Sea of annual means of modelled gross primary production (GPP) by Gypens et al. (2009) and measured pH at a fixed station (3.2206°E 51.6586°N) from the Rijkswaterstaat database (measurements every 15 days from 1976 to 1987, and every month from 1988 to 2007; due to low seasonal coverage, years 1986, 1987 and 1993 were excluded from analysis). pH was converted from the National Bureau of Standards Scale to the Total Hydrogen Ion Scale. [CO_2], saturation state of calcite (Ω_{cal}) and of aragonite (Ω_{ar}) were computed from measured pH, salinity and temperature, calculated total alkalinity (from salinity based on the climatological relationship given by Borges et al. (2008b)), the carbonic acid dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987), the calcite and aragonite solubility of Mucci (1983). Solid lines correspond to linear regressions prior and after 1990, dotted line corresponds to the theoretical evolution of variables in surface waters had followed the increase of atmospheric CO_2 from the conditions of 1976. Periods prior and after 1990 can be distinguished based on the ratio of dissolved inorganic nitrogen (DIN) to phosphate (PO_4) of nutrient river delivery

increased due to eutrophication, there is an increasing trend in pH, in Ω_{ca} and in Ω_{ar} and a decreasing trend in [CO_2], while the equilibration of surface waters with increasing atmospheric CO_2 would have lead to the opposite trends. After the mid 1980s when phosphorus removal policies were implemented, primary production in the Southern Bight of the North Sea became increasingly limited by phosphorus availability, GPP decreased and the ecosystem shifted from net autotrophy to net heterotrophy (Gypens et al. 2009). The decrease of pH, Ω_{ca} and Ω_{ar} and the increase of [CO_2] were actually faster then those expected from the equilibration of surface waters with increasing atmospheric CO_2 (Fig. 3.5). Hence, the effect of eutrophication on carbon cycling that counter-acts the effect of ocean acidification could maintain carbonate chemistry conditions that remain favorable for benthic and pelagic calcification in near-shore coastal environments. Also, the application of nutrient delivery regulation policies can lead to transient changes of carbonate chemistry that are faster than those related solely to ocean acidification. Such 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.

The response of calcifiers to ocean acidification has been to some extent relatively well documented. Based on the upper bound value global calcification rate from coral reefs of 0.11 PgC $year^{-1}$ (Milliman and Droxler 1996) and assuming a decrease by 2100 of calcification ranging from 22% (Gattuso et al. 1998b) to 40% (Andersson et al. 2005), and using a molar ratio of CO_2 production to calcification (Ψ) of 0.6 (Frankigoulle et al. 1994), the negative feedback on increasing atmospheric can be roughly evaluated to range between 0.015 and 0.026 PgC $year^{-1}$. Benthic calcification in other coastal environments than coral reefs has been evaluated to 0.19 PgC $year^{-1}$ (Milliman and Droxler 1996), and assuming a similar range of decrease of calcification (22–40%) by 2100, the negative feedback on increasing atmospheric can be roughly evaluated to range between 0.025 and 0.046 PgC $year^{-1}$ (using a Ψ of 0.6).

Balch et al. (2007) recently estimated global pelagic calcification to 1.6 ± 0.3 Pg C $year^{-1}$, based on remote sensing data. This implies that coccolithophorids would be the single most important pelagic calcifier in the oceans, as other estimates of global pelagic calcification range between 0.7 PgC $year^{-1}$ based on historical accumulation rates and sediment trap data (Milliman et al. 1999) and 1.4 PgC $year^{-1}$, based on seasonal cycle of TA in the euphotic zone (Lee 2001). A global estimate of pelagic calcification is unavailable for the coastal ocean, but on first approximation, it can be evaluated to 0.38 ± 0.1 Pg C $year^{-1}$ scaled based on a fraction of the total $CaCO_3$ standing stock in the coastal ocean of 23% compared to the open ocean, based on remote sensing data (Balch et al. 2005). The decrease of global pelagic calcification for a doubling of atmospheric CO_2 has been evaluated to 7% using a general circulation ocean model (Gehlen et al. 2007). If we assume that this decrease also occurs in the coastal ocean, the negative feedback on increasing atmospheric CO_2 can be roughly evaluated to range between 0.013 and 0.019 PgC $year^{-1}$ (using a Ψ of 0.6).

The carboxylating enzyme Ribulose-1,5 bisphosphate-carboxylase/oxygenase (RUBISCO) relies exclusively on CO_2 as substrate and has a half saturation constant ranging between 20 and 70 μmol kg^{-1} (Badger et al. 1998). This can cause a rate limitation of phytoplankton photosynthesis, since [CO_2] in seawater at

Table 3.3 Minimum values of the partial pressure of CO_2 (pCO_2), pH, [CO_2] reported in various continental shelf seas

	pCO_2 (ppm)	pH(THIS)	[CO_2] (μmol kg^{-1})	Comment
Gotland Sea (Baltic)	160	8.413	6.2	1
Northern North Sea	225	8.261	10.9	2
Southern North Sea	125	8.459	5.7	2
English Channel	320	8.127	13.5	3
Celtic Sea	295	8.160	11.6	4
Bay of Angels (Mediterranean)	330	8.144	12.5	5
East China Sea	280	8.173	12.3	6
Chukchi Sea	70	8.647	4.7	7
US Middle Atlantic Bight	200	8.285	6.1	8

1. Based on Schneider et al. (2003) and Kuss et al. (2004)
2. Based on Omar et al. (2010)
3. Based on Borges and Frankignoulle (2003)
4. Based on Borges et al. (2006)
5. Based on Copin-Montégut et al. (2004)
6. Based on Wang et al. (2000)
7. Based on Bates (2006)
8. Based on DeGrandpre et al. (2002)

atmospheric equilibrium is typically ~10 μmol kg^{-1}. This can be a significant issue in near-shore environments where very low [CO_2] values can occur during the peak of the phytoplankton bloom. For instance, in Belgian coastal waters, at the peak of the *Phaeocystis* bloom extreme values of pCO_2 (72 ppm), pH (8.673 in the total hydrogen ion scale (THIS)) and [CO_2] (3 μmol kg^{-1}) were reported in May 1999 (Borges and Frankignoulle 2002b). However, in continental shelf seas with lesser influence from nutrient rich estuarine waters, values of the variables of carbonate system during phytoplankton blooms are not as extreme (Table 3.3).

Phytoplankton species have developed several carbon concentration mechanisms (CCMs) to overcome the potential CO_2 limitation of primary production (Raven 1991), leading to a specific sensitivity to CO_2 availability. Hence, photosynthesis by diatoms and the prymnesiophyte *Phaeocystis* (Burkhardt et al. 1999, 2001; Rost et al. 2003) is at or close to CO_2 saturation at typical actual marine CO_2 levels. On the other hand, photosynthesis of coccolithophorids is well below CO_2 saturation at typical actual marine CO_2 levels (Rost et al. 2003). However, these findings are mainly based on laboratory cultures with optimal light and nutrient conditions. In the real ocean, at the peak of phytoplankton bloom, nutrients are exhausted, and since CCMs rely in one way or another on enzymes, low nitrogen availability can lead to a down-regulation of CCMs. Since CO_2 levels are also low at the peak of the phytoplankton bloom, increasing levels of seawater CO_2 with global change could reduce the limitation of photosynthesis by CO_2 availability. In nutrient exhausted conditions, if light conditions remain favorable, phytoplankton continues to photosynthesize, and extracellular release of organic carbon allows regulation of the internal C:N:P ratios. This can lead to the formation of transparent

exopolymer particles that have strong aggregative properties and can enhance organic carbon export from surface to depth (Engel et al. 2004). Hence, increasing CO_2 levels with global change could lead to enhanced carbon export related to extracellular release of organic carbon in peak phytoplankton bloom conditions. Riebesell et al. (2007) have estimated that an increase of 27% of C export from mixed diatom and coccolithophorid assemblages would occur at an atmospheric pCO_2 of 750 ppm. Based on the present day estimates of export production from the coastal ocean ranging from 0.4 (Wollast 1998) to 0.8 PgC year^{-1} (Chen 2004), the potential negative feedback on increasing atmospheric CO_2 would range from 0.108 to 0.216 PgC year^{-1}.

Ocean acidification can also lead to changes in phytoplankton composition (Boyd and Doney 2002; Tortell et al. 2002), with potential impacts on C cycling and export, and ultimately on air–sea CO_2 fluxes. Further, the impact of ocean acidification will be modulated by the combined effect of other climate change impacts such as temperature increase and increased stratification. Temperature increase will directly impact metabolic rates of biota, while increased stratification will modulate vertical inputs of DIC and nutrients, and light conditions. The combined impact of temperature increase and acidification seems to lead to non-linear responses from phytoplankton (Feng et al. 2008). Temperature increase could also potentially modulate the response of coral reefs to ocean acidification (McNeil et al. 2004), although this has been strongly debated (Kleypas et al. 2005). Finally, increased stratification will favour phytoplankton communities that have a strong requirement for light availability and low inorganic nutrient requirements. Tyrrell and Merico (2004) reviewed the factors that favor the blooming of coccolithophorids and concluded that stratified and shallow mixed layers (inducing high light availability conditions) were one of the requisites for coccolithophorid blooming. Temperature increase and stratification could explain the appearance of not previously documented coccolithophorid blooms in some high latitude areas such as the Bering Sea (Merico et al. 2003) and the Barrents Sea (Smyth et al. 2004), the possible shift in the North Atlantic of phytoplankton communities towards coccolithophorids at the expense of diatoms based on the opal:$CaCO_3$ ratio of sedimenting particles (Antia et al. 2001), and the trend since the 1950s towards increasing pelagic calcification based on mass of $CaCO_3$ per coccolith from sediment cores (Iglesias-Rodriguez et al. 2008), in agreement with a global increase in stratification with strong impacts on marine productivity (Behrenfeld et al. 2006).

3.2.4 Anthropogenic Impacts on Specific Near-Shore Coastal Ecosystems

Specific near-shore coastal ecosystems are in most cases threatened by direct and indirect human impacts. For instance, losses in seagrass (Short and Neckles 1999;

Duarte 2002) and coral reef ecosystems (Hughes et al. 2003) are observed and predicted to continue due to mechanical damage (dredging and anchoring), eutrophication and siltation, the latter two leading in particular to light limitation. Negative indirect human impacts on seagrass and coral ecosystems include increases of erosion by the rise of sea level, frequency and intensity of extreme weather events, ultraviolet irradiance and water temperature. Other coastal ecosystems such as mangrove forests or salt-marshes are relatively resilient to the present and future alteration of hydrology, pollution or global warming, but in some parts of the world they are being cleared for urban development and aquaculture (Alongi 2002). Furthermore, some coastal habitats are predicted to adapt and survive with shifts in species composition, as coral reef ecosystems (Hughes et al. 2003; Baker et al. 2004) but with probable loss of biodiversity and modifications of carbon flows. It is unclear how these changes will affect carbon flows and ultimately air-sea CO_2 fluxes.

3.3 Conclusions

The present day contemporary CO_2 fluxes in shelf seas could be significant for the global carbon cycle, since available estimates converge to a value of 0.3 PgC $year^{-1}$ (Table 3.1) corresponding to 21% of the most recent estimate of contemporary sink of atmospheric CO_2 in open oceans of 1.4 PgC $year^{-1}$. However, these estimates are prone to large uncertainty, mainly due to inadequate representation of the spatial variability, and need to be improved based on more data, requiring a concerted global observational effort (Borges et al. 2009).

The potential feedbacks on increasing atmospheric CO_2 from changes in carbon flows in the coastal ocean could be disproportionately higher than in the open ocean. Yet, these potential feedbacks remain largely unquantified (Table 3.2) due to a poor understanding of the mechanisms, or lack of modelling to quantify them. Based on reported evaluations and back of the envelope calculations, it is suggested that changes of biological activity due to the increased nutrient delivery by rivers would provide by 2100 a negative feedback on increasing atmospheric CO_2 of the order of magnitude of the present day sink for atmospheric CO_2. This negative feedback on increasing atmospheric CO_2 would be one order of magnitude higher than negative feedback due to the decrease of either pelagic or benthic calcification related to ocean acidification, and than the negative feedback related to dissolution of $CaCO_3$ in sediments (Table 3.2). The increase of export production could also provide a significant feedback to increasing atmospheric CO_2, although based on the conclusions from a single perturbation experiment. Feedbacks on increasing atmospheric CO_2 due to effects of C cycling in continental shelf seas related to changes in circulation or stratification could be important but remain to be quantified.

Acknowledgments I'm grateful to Frédéric Gazeau for pointing out the availability of long pH time series in the Southern North Sea, to Nathalie Gypens for providing the GPP model outputs, and to Pedro Duarte for comments during manuscript elaboration. This is a contribution to Belgian Federal Science Policy Office PEACE project (SD/CS/03), EU IP CARBOOCEAN (511176), EU CSA COCOS (212196). The author is a research associate at the F.R.S.-F.N.R.S.

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