

Shallow-water oceans: a source or sink of atmospheric CO₂?

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The shallow-water ocean environment is of great importance in the context of global change and is heavily impacted by human activity. This study evaluates the effects of human activity on the CO₂ exchange between the atmosphere and the surface water of shallow-water oceans. The evaluation is based on changes in net ecosystem metabolism, net ecosystem calcification, and atmospheric CO₂ concentrations, as seen in a process-driven biogeochemical box model. Numerical simulations show that this air–sea interface has probably served as a net source of CO₂ to the atmosphere for much of the past 300 years, but has recently switched, or will switch soon, to a net sink of CO₂, because of rising atmospheric CO₂ and increasing inorganic nutrient load.

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Little attention has been given to the role of the carbon (C) cycle of shallow-water oceans and their modeling in the context of global change, despite the fact that these regions are important on a global scale (Gattuso *et al.* 1998; Ver *et al.* 1999; Chen *et al.* 2003). The shallow-water ocean environment (ie bays, estuaries, lagoons, banks, and continental shelves) constitutes only 7% of global ocean surface area, but is the location where approximately 10–30% of the world's marine primary production occurs. Eighty percent of inputs from the land to the sea are deposited here, and 85% of organic C and 45% of inorganic C are buried in the sediments within this region (Figure 1; Gattuso *et al.* 1998; Wollast 1998; Chen *et al.* 2003).

The shallow-water ocean environment is also heavily impacted by human activities, as nearly 40% of the global population lives within 100 km of the coastline (Cohen *et al.* 1997). Since the onset of the industrial revolution, practices such as burning of fossil fuels and land-use changes have caused substantial increases in atmospheric CO₂ concentration and in the load of organic matter and nutrients transported via rivers and deposited in these shallow-water ecosystems (Mackenzie 2003). Such changes could alter the role of this system and considerably affect important processes such as air–sea CO₂ exchange in the region.

The net flux of CO₂ between the surface water and the atmosphere is dependent on the partial-pressure gradient of this gas between the surface water and the overlying air. The direction of the net flux is from high to low partial pressure. The partial pressure of CO₂ in the water column is strongly coupled to the processes of photosynthesis and respiration, but also to precipitation and dissolution of calcium carbonate minerals. CO₂ is consumed by primary production and released by respira-

tion/decay of organic matter according to the following generalized reaction:



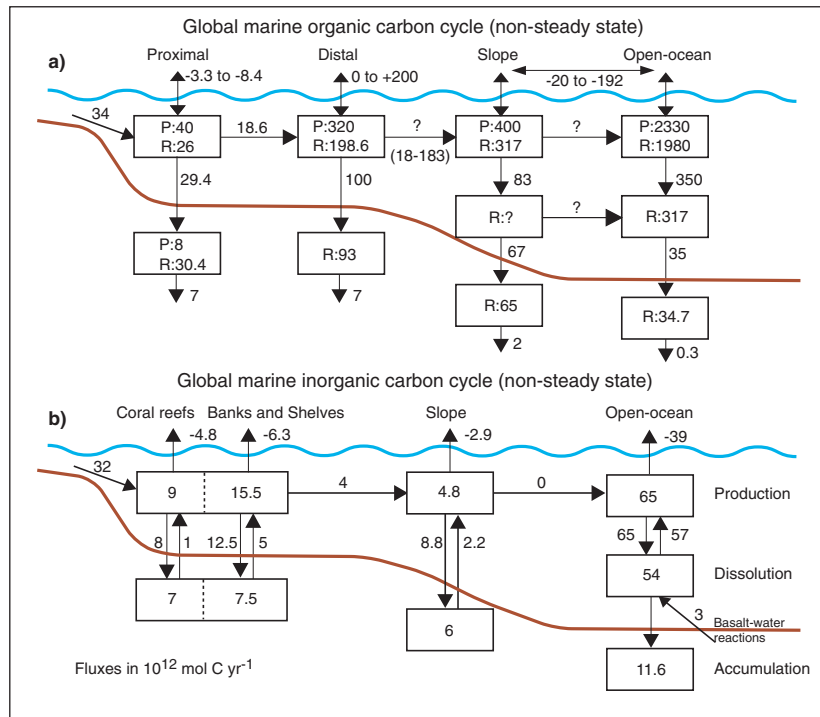
Depending on the imbalance between these two processes, which is referred to as the “net ecosystem metabolism” ($P - R$), CO₂ invasion into the surface water is favored if gross primary production (P) is greater than the total respiration for the entire ecosystem (R) (ignoring all other processes and assuming initial equilibrium with the atmosphere), and evasion from the surface water if R is greater than P . If $P - R > 0$ the system is referred to as “net autotrophic” and if $P - R < 0$ the system is referred to as “net heterotrophic”. CO₂ is also produced when carbonate minerals are precipitated abiotically as marine cements, or biotically by organisms producing shells, tests, or skeletons made of calcium carbonate, and consumed when these minerals dissolve:



Depending on the buffer capacity of surface seawater and the atmospheric partial pressure of CO₂, a certain fraction of the CO₂ released for every mole of calcium carbonate precipitated will escape into the atmosphere (Frankignoulle *et al.* 1994). As atmospheric CO₂ concentration increases due to the burning of fossil fuels, and additional anthropogenic CO₂ enters surface seawater, more CO₂ will be released to the atmosphere for every mole of calcium carbonate precipitated. In addition, the carbonate saturation state of the surface water will decrease owing to increased invasion of anthropogenic CO₂ (Gattuso *et al.* 1999; Kleypas *et al.* 1999; Andersson *et al.* 2003). Consequently, since numerous experimental investigations indicate that a direct relationship exists between the rate of calcification and the carbonate saturation state of surface water (Gattuso *et al.* 1999), calcium

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Figure 1. (a) Global marine organic and (b) inorganic C cycle, fluxes in units of 10¹² moles/year of C (1 gigaton of C is approximately 83×10¹² mole of C) (modified from Morse and Mackenzie 1990; Milliman 1993; Wollast 1994; Wollast 1998; Rabouille et al. 2001). Both cycles represent pre-industrial conditions and are not in steady state. Less well-known fluxes are denoted by a question mark and/or by a range of values. Negative values indicate a net flux of CO₂ from the surface ocean to the atmosphere. Air–sea exchange fluxes resulting from the imbalance between gross primary production and total respiration of organic matter and precipitation of CaCO₃ in the subdomains of the ocean are also shown. The precipitation of CaCO₃ always results in a flux of CO₂ out of the ocean (negative value). The air–sea CO₂ flux related to organic metabolism in the ocean or its subdomains may be negative or positive, depending on whether the region is a net source (net heterotrophic) or a net sink (net autotrophic) of atmospheric CO₂, respectively. During pre-industrial conditions the shallow-water ocean environment served as a net source of 18×10¹² moles/year of C to the atmosphere, owing to net heterotrophy (−7×10¹² moles/year of C; Smith and Hollibaugh 1993) and net ecosystem calcification (18.5×10¹² moles/year of C; causing a release of 11×10¹² moles/year of C to the atmosphere).



carbonate production could decline. A decreased carbonate saturation state may also lead to increased dissolution of calcium carbonate minerals (Andersson et al. 2003).

Changes in atmospheric CO₂ concentration, net ecosystem metabolism, and net ecosystem calcification (CaCO₃ precipitation - dissolution) will affect the partial pressure of CO₂ in the surface water of the shallow-water ocean environment and, consequently, the net air–sea CO₂ exchange. Here we use a process driven biogeochemical box model (Shallow-water Ocean Carbonate Model, SOCM) representative of this global region to evaluate changes in the air–sea CO₂ exchange between the atmosphere and the surface water, from the past to the present and extending into the future, based on human-induced changes in atmospheric CO₂ concentration, net ecosystem metabolism, and net ecosystem calcification.

Methods

Details of the biogeochemical box model used in the current study have been described elsewhere (Andersson et al. 2003), and we will focus here on the parts of the model directly pertinent to the air–sea CO₂ exchange flux (Figure 2). The major forcings (agents) of the model (Figure 3) were based on atmospheric CO₂ concentrations and temperatures projected by the International Panel on Climate Change “business-as-usual” (decadal to century timescale) emission scenario (IPCC IS92a; Enting et al. 1995). Inputs of organic and inorganic C and nutrients (nitrogen and phosphorus) via rivers and runoff

were based on observational data and model predictions from the Terrestrial Ocean Atmosphere Ecosystem Model (TOTEM; Ver et al. 1999). Net ecosystem metabolism (NEM; also known as net ecosystem production, NEP) was defined as the imbalance between P and R, and may be evaluated for any ecosystem using a mass balance approach, according to the following expression:

$$NEM^* = P - R = DIC_{in} + F_{CO_2a-s} - DIC_{out} - \frac{dC_{DIC}}{dt}$$

$$= Org C_{out} - Org C_{in} + \frac{dC_{org}}{dt} \tag{3}$$

where NEM* refers to a non-steady state situation, DIC_{in} and DIC_{out} are input and export of dissolved inorganic C, respectively, F_{CO₂a-s} is the air–sea CO₂ exchange, Org C_{in} and Org C_{out} are organic carbon input and export, respectively, and dC_{DIC}/dt and dC_{org}/dt refer to changes in the standing stock of dissolved inorganic carbon and organic carbon in the system, respectively. If the system is near a steady state (ie dC_{org}/dt ≈ 0), the expression simplifies to:

$$NEM = P - R = DIC_{in} + F_{CO_2a-s} - DIC_{out}$$

$$= Org C_{out} - Org C_{in} \tag{4}$$

Changes in net ecosystem calcification (NEC) were adopted from previous simulations, where calcium carbonate production and dissolution were expressed as functions of surface water and pore water carbonate satu-

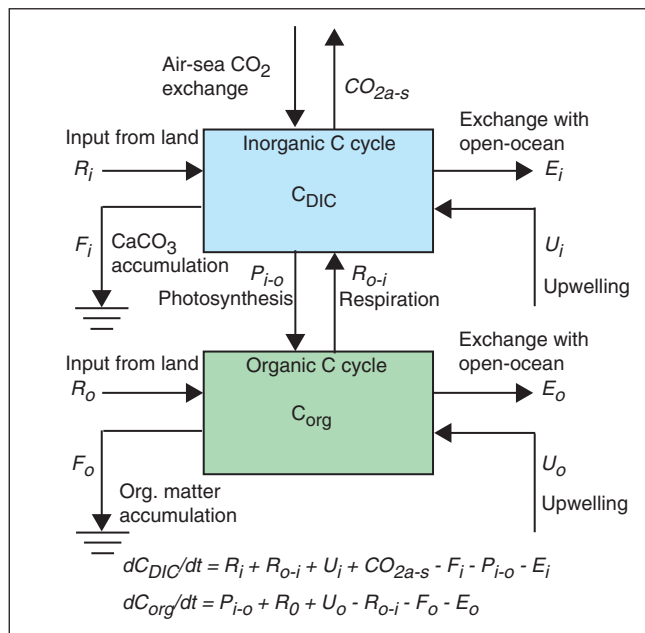


Figure 2. Simplified model schematic and mass balance equations for the inorganic and organic C cycle within the shallow-water ocean environment. The amount of carbon in the inorganic carbon reservoir (C_{DIC}) changes as a function of inputs of dissolved inorganic carbon from land via rivers, surface runoff and groundwater flow (R_i), respiration and decay of organic matter (R_{o-i}), upwelling (U_i), air-sea CO_2 exchange ($\pm CO_{2a-s}$), precipitation of calcium carbonate minerals (F_i), primary production (P_{i-o}), and physical exchange with the surface water of the open ocean (E_i). The organic C cycle is coupled to the inorganic C cycle via input of C from primary production (P_{i-o}) and output due to remineralization of organic matter (P_{o-i}). Furthermore, the organic C reservoir changes due to inputs of both dissolved and particulate organic C from land (R_o), upwelling (U_o), permanent burial of organic matter in the sediments (F_o), and exchange with the open ocean (E_o).

ration state based on experimentally derived kinetic rate equations (Andersson *et al.* 2003). Biogenic carbonate production was related to either a linear or a curvilinear saturation state dependence. Gas exchange of CO_2 between the surface water of the shallow-water ocean environment and the atmosphere was related to the above parameters and described by the following equation:

$$F_{CO_{2a-s}} = [-\Phi \times NEC] + NEM^* + [DIC_{out} - DIC_{in}] + \frac{dC_{DIC}}{dt} \quad (5)$$

where Φ is the fraction of CO_2 released to the atmosphere for each mole of $CaCO_3$ precipitated (Frankignoulle *et al.* 1994). Since instantaneous equilibrium with respect to CO_2 was assumed to be established between the atmosphere and the surface water at each time step (dt), the last term represents the flux of C between the surface water and the atmosphere, expressed as the time rate of change

of the surface water total dissolved inorganic C content (C_{DIC}) as a function of changes in the inorganic C content of the atmosphere (C_{ATM}). This equation is essentially a modification of the Revelle function and can be derived from the following expression:

$$\frac{dC_{DIC}}{dt} = \frac{d}{dt} \left[C_{DIC,t=0} \left\{ \frac{(C_{ATM} - C_{ATM,t=0})}{(R_0 \times C_{ATM,t=0} + D(C_{ATM} - C_{ATM,t=0}))} + 1 \right\} \right] \quad (6)$$

In the simulation, the Revelle constant (D) was set to four, and the initial Revelle factor (R_0) was assumed to be nine (ie the buffer mechanism of the seawater caused a fractional rise of CO_2 in the surface water that was one ninth of the increase in the atmosphere; Revelle and Munk 1977).

At the initial condition of the model simulation in the year 1700, the flux of carbon, nitrogen, and phosphorus did not change substantially, and the shallow-water ocean environment was assumed to be in a quasi-steady state. At that time, this region was assumed to serve as a net source of approximately 18×10^{12} moles/year of C to the atmosphere, owing to a net ecosystem metabolism of -7×10^{12} moles/year of C (Smith and Hollibaugh 1993) and a net ecosystem calcification of 18.5×10^{12} moles/year of $CaCO_3$ (Milliman 1993), which resulted in the release of 11×10^{12} moles/year of C to the atmosphere ($\Phi_{t=1700} \approx 0.6$). It is important to note that a great deal of uncertainty is associated with these initial boundary condition estimates.

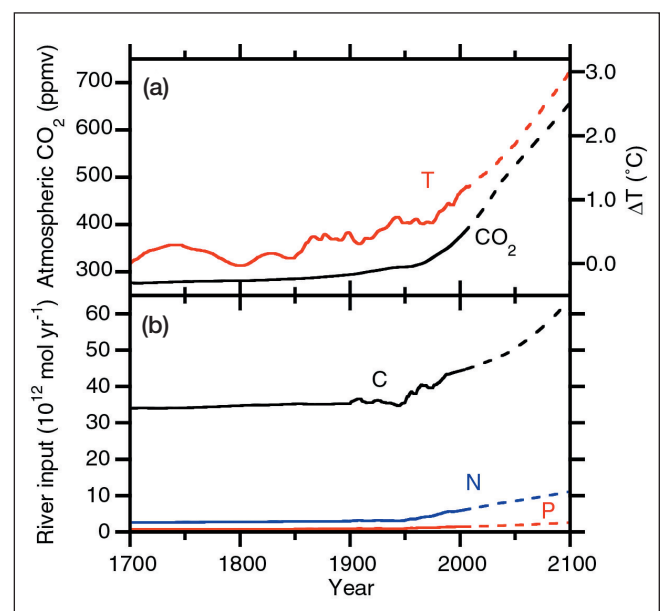


Figure 3. Major forcings (agents) of the model. (a) Atmospheric CO_2 concentration and temperature according to the International Panel on Climate Change “business-as-usual” emission scenario (IPCC IS92a; Enting *et al.* 1995) and (b) river input of organic C, nitrogen, and phosphorus based on observational data and model predictions using the Terrestrial Ocean Atmosphere Ecosystem Model (TOTEM; Ver *et al.* 1999).

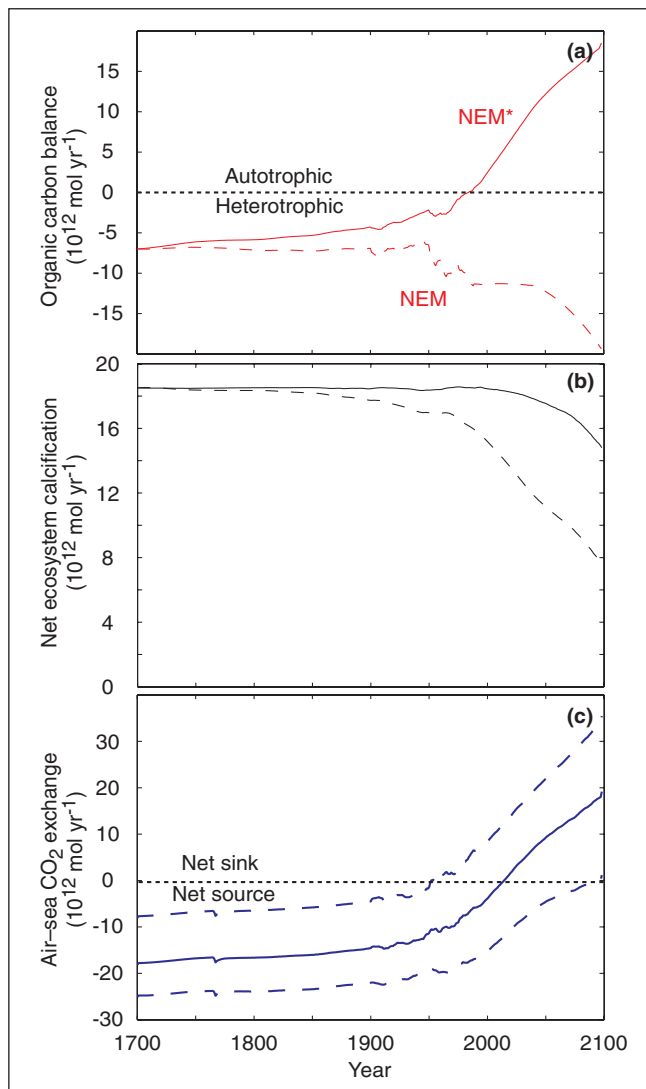


Figure 4. Numerical results of the model simulation between years 1700 and 2100. (a) Net ecosystem metabolism expressed as NEM* and NEM based on a mass balance approach (see text). The difference in result between the two curves represents changes in the organic C reservoir of the shallow-water ocean environment (ie $dC_{org}/dt \neq 0$). (b) Net ecosystem calcification: the two curves represent two scenarios adopting a linear (solid line) or a curvilinear (dashed line) biogenic carbonate saturation state dependence. (c) Air-sea exchange: the best estimate is illustrated by the solid blue line, whereas the dashed blue lines represent the range of results achieved, including a 50% uncertainty with respect to the organic C balance and the minimum and maximum estimates of calcification found in the literature.

Results and discussion

Net ecosystem metabolism

In determining the trophic status of a system it is commonly assumed that the amount of organic C present remains constant ($dC_{org}/dt = 0$), which could result in a spurious conclusion if not true. Based on a mass balance approach and assuming a steady state of the organic C

reservoir in the current simulation, the shallow-water ocean environment became increasingly net heterotrophic, owing to increased transport and deposition of organic matter to this region (Figure 4). However, the total mass of the organic matter reservoir was not in a steady state and increased throughout the simulation. Consequently, the region became increasingly net autotrophic if changes in organic C mass were incorporated in the calculation (Figure 4). The projected rise in autotrophy was driven by the substantial augmentation of riverine input of inorganic nutrients to the area (Mackenzie 2003), leading to amplified production (P) that increasingly exceeded the total ecosystem respiration (R).

Net ecosystem calcification

Net ecosystem calcification decreased owing to diminished biogenic precipitation of calcium carbonate (7–44%) and increased dissolution of calcium carbonate between year 1700 and the year 2100 (Figure 4; Andersson *et al.* 2003). The fraction of CO₂ released to the atmosphere for every mole of CaCO₃ precipitated changed from approximately 0.6 moles at the initial condition to 0.75 moles at the end of the simulation, when the partial pressure of CO₂ is approximately 700 ppm (Frankignoulle *et al.* 1994). Depending on whether biogenic CaCO₃ precipitation was related to a curvilinear or a linear saturation state dependence, the flux of CO₂ to the atmosphere owing to this process remained relatively unchanged or decreased by about 5×10^{12} moles/year of C. Although this decrease could be considered as a negative feedback to increasing atmospheric CO₂, the magnitude is unimportant relative to the total input of anthropogenic CO₂ into the ocean ($\sim 170 \times 10^{12}$ moles/year of C at present).

Air-sea CO₂ exchange

Based on the calculated changes in net ecosystem metabolism and calcification, and also on changes in atmospheric CO₂ content, the results of the numerical simulations suggest that the shallow-water ocean environment has served as a net source of CO₂ to the atmosphere throughout most of the past 300 years (Figure 4). However, its role as a source has substantially decreased and the net flux is expected to reverse at some point in time, if it has not already happened. Although much uncertainty is associated with the magnitude of the initial air-sea CO₂ exchange, the calculated trend is robust and representative of how this flux is changing direction and is likely to change in the future, owing to anthropogenic activities. Actual measurements of the air-sea CO₂ flux from various global shallow-water locations, based on CO₂ partial pressure and wind speed, can neither confirm nor refute these results, but they indicate that most regions where data are available act as sinks of atmospheric CO₂ today (Table 1). Nevertheless, some regions,

Table 1. *Estimates of measured air-sea CO₂ exchange from worldwide shallow-water locations (estuaries, reefs, shelves). Negative values denote CO₂ flux from ocean to atmosphere; positive values denote flux from atmosphere to ocean.

Location/Region	Net CO ₂ flux (g C m ⁻² yr ⁻¹)	Reference
Hog Reef flat, Bermuda	-14.4	Bates et al. 2001
New Jersey	+5.2 to +10.1	Boehme et al. 1998
Galician Coast	+7.9 to +14	Borges and Frankignoulle 2001
Scheldt Estuarine plume	-13.2 to -22.8	Borges and Frankignoulle 2002
South Atlantic Bight (SAB)	-30	Cai et al. 2003
Mid Atlantic Bight (MAB)	+12	DeGrandpre et al. 2002
Gulf of Calvi	-28	Frankignoulle 1988
Gulf of Biscay	+21 to +34.6	Frankignoulle and Borges 2001
European estuaries (Elbe, Ems, Rhine, Scheldt, Tamar, Thames, Gironde, Duoro, Sado)	-438 to -3330	Frankignoulle et al. 1998
Moorea, French polynesia	-6.6	Gattuso et al. 1993
Northern Arabian Sea	-5.5	Goyet et al. 1998
Cape Perpetua	+87.6	Hales et al. 2003
North Sea	+16.2	Kempe and Pegler 1991
Baltic Sea	+10.8	Thomas and Schneider 1999
East China Sea	+35	Tsunogai et al. 1999
East China Sea	+14.4 to +33.6	Wang et al. 2000

*It is important to realize that some of the estimates represent annual integrated flux measurements and others monthly or occasional measurements.

such as estuaries, coral reefs, and some upwelling regions, act as a source of CO₂ to the atmosphere. Estuaries, for instance, act as a source due to extensive deposition and remineralization of terrestrial organic matter. Coral reefs are considered to be slightly net autotrophic, but still act as a source of CO₂, due to the process of calcification. Globally, coral reefs are responsible for a net flux of C to the atmosphere, ranging from 2×10^{12} to 7×10^{12} moles per year (Ware *et al.* 1992).

Upwelling waters are colder and contain more dissolved inorganic C than surface waters, due to extensive remineralization of organic matter settling from the surface water to the deep ocean. As these waters upwell and reach the continental shelf, temperature and pressure change, and the solubility of CO₂ decreases, resulting in increased pCO₂ and, generally, a flux of CO₂ to the atmosphere. This CO₂ venting has been observed, for example, in the Northern Arabian Sea (Goyet *et al.* 1998). However, a recent study at Cape Perpetua, an area of substantial upwelling along the Oregon coast, indicated that this region, as opposed to other upwelling regions, acted as an important sink of CO₂ (Hales *et al.* 2003). The authors of the study suggest that production in the region was only limited by available nitrate, resulting in consumption of nitrate and CO₂ in stoichiometric proportions. In addition, the upwelling waters had very high total alkalinity and pre-formed nitrate relative to their total dissolved inorganic C content and were subject to only moderate warming and changes in CO₂ solubility, because of the relatively high latitude and mild temperatures of this region.

Results from the European continental shelf (Kempe and Pegler 1991; Frankignoulle and Borges 2001), the East

China Sea (Tsunogai *et al.* 1999; Wang *et al.* 2000), and certain parts of the US continental shelf (Boehme *et al.* 1998; DeGrandpre *et al.* 2002) strongly agree with one another and suggest that continental shelves act as a globally important sink of atmospheric CO₂. Based on observations from the East China Sea, Tsunogai *et al.* (1999) proposed the existence of a global continental shelf pump that theoretically could remove as much as one gigaton of C from the atmosphere per year, which roughly corresponds to about 15% of the CO₂ released annually from human activities. Chen *et al.* (2004) suggest that the marginal seas in the North Pacific alone may have taken up 1.6 gigatons of excess C (atmospheric C originating from anthropogenic sources). Opposed to these observations, a recent study from the South

Atlantic Bight indicates that this continental shelf region acts as a source of large amounts of CO₂ to the atmosphere (Cai *et al.* 2003). The authors suggest that extensive export and remineralization of organic matter from nearby salt marshes could account for this observed flux.

Based on the available current data, it is not possible to conclude unequivocally whether or not the global shallow-water ocean environment acts as a sink or a source of atmospheric CO₂, although most results point towards this region being a sink. Because biogeochemical processes are highly variable within this environment and few data exist, it is not possible to extrapolate the available results to the global situation. Similarly, it is not imprudent at this time to conclude whether this region is a sink or a source from a modeling perspective, and, because of the large heterogeneity observed in the natural environment, it is difficult to confirm the results of the model. Nevertheless, the calculated trend for coastal zone air-sea exchange of CO₂ as affected by human alterations of the environment from the past into the future is probably a rigorous and significant result derived from the model. In the context of global change, this result and the reasons for it are important, because of the role of the shallow-water ocean environment on a global scale and the disproportionate effect of human activities on this region.

■ Conclusions

In the past, the shallow-water ocean environment has apparently served as a net source of CO₂ to the atmosphere, but will switch to a net sink at some point in time, owing to human activities. However, it is not possible to

say when this transition will happen, or if it already has happened, because the timing is dependent on the magnitude of the flux estimate for pre-industrial time, which is not well constrained by the data available.

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