GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 15, NO. 3, PAGES 569-576, SEPTEMBER 2001

European continental shelf as a significant sink for atmospheric carbon dioxide

Michel Frankignoulle and Alberto V. Borges
Unité d'Océanographie Chimique, Université de Liège, Sart Tilman, Belgium

Abstract. The concentration of carbon dioxide was measured during 18 cruises in the surface waters of the North Atlantic European Shelf (Galician sea, Gulf of Biscay, Armorican Sea, Celtic Sea, English Channel, North Sea), covering all four seasons (9 out of 12 months) at interannual scale. This is the very first intensive field study of continental shelves, in terms of source/sink for atmospheric CO_2, which allows to integrate fluxes on an annual basis and over a large surface area. Here we show that European continental shelves are a sink of 90-170 million tons of carbon per year, which is an additional appreciable fraction to the presently proposed flux for the open North Atlantic Ocean (~ 45%). The air-sea fluxes of CO_2 we obtained are similar to those recently reported in the East China Sea, allowing us to conclude that the coastal ocean plays a considerable role in the global oceanic carbon cycle.

1. Introduction

Human activities presently release ~7.7 gigatons of carbon per year (Gt C yr^{-1}) to the atmosphere [*Mackenzie*, 1998], by fossil fuel burning and change in land use (e.g., deforestation). It is well established that 3.3 Gt C yr^{-1} remain in the atmosphere. The ocean behaves as a sink estimated to 2.0 Gt C yr^{-1}, and the terrestrial biosphere is often assumed to trap the remaining 2.4 Gt C yr^{-1} [*Sarmiento and Sundquist*, 1992; *Sundquist*, 1993; *Broecker and Peng*, 1998; *Mackenzie*, 1998]. However, this budget does not consider explicitly the fluxes in the coastal ocean because it is difficult to include this region in global circulation models and because of the lack of field data on the spatial distribution and temporal variability of pCO_2. The coastal ocean is known to house a large fraction of the oceanic primary production (15-30% [*Walsh*, 1988; 1991; *Wollast*, 1993; 1998]), a contribution by far larger than its surface area fraction (7%) of the total ocean. The role of continental shelves in the global carbon cycle has been the subject of a few major national and international research programmes (e.g., KEEP (Kuroshio Edge Exchange Processses), KUSTOS (Küstennahe Stoff-und Energieflüsse - der Übergang Land-Meer in der südöstlichen Nordsee), OMEX (Ocean Margin EXchange), SEEP (Shelf Edge Exchange Processes), SES (Shelf Edge Study), TROPICS (Tropical River-Ocean Processes in Coastal Settings),...) but it is not yet clear if these regions act as a sink or as a source of atmospheric CO_2 [*Garrels and Mackenzie*, 1971; *Smith and Mackenzie*, 1987; *Walsh*, 1988, 1989, 1991; *Smith and Hollibaugh*, 1993; *Ver et al.*, 1994, 1999a, b; *Kempe*, 1995; *Mackenzie et al.*, 1998; *Wollast*, 1998]. Indeed, the prevailing question is whether the continental shelves are net autotrophic or net heterotrophic [*Gattuso et al.*, 1998; *Mackenzie et al.*, 2000]. The coastal ocean is the site of intense physical and biological processes from which important air-sea gradients of CO_2 can be expected [*Mackenzie*, 1991], but the air-sea CO_2 exchanges are still poorly known. The causes of these uncertainties are multiple. First, these regions show high variability in time and in space that is usually not adequately monitored by sparse or incomplete data sets. Second, the budgets proposed in literature [*Garrels and Mackenzie*, 1971; *Walsh*, 1988; 1991; *Smith and Hollibaugh*, 1993; *Kempe*, 1995; *Gattuso et al.*, 1998; *Wollast*, 1993; 1998; *Mackenzie et al.*, 2000] are based on indirect calculations and use different approaches and a variety of experimentally determined processes that yield different conclusions from one author to another, even within the same research programme (SEEP I and II projects, [*Biscaye et al.*, 1994]).

The role of the shelves in the inorganic carbon cycle is uncertain because it results from the integration of production/degradation/export of organic carbon, burial/dissolution of carbonates in the shallow sediment and input of inorganic carbon from rivers and coastal upwellings. The best way to identify these areas as a global source or sink for atmospheric carbon dioxide is to integrate CO_2 fluxes over a complete year, an approach frequently used in open ocean studies [*Tans et al.*, 1990; *Takahashi et al.*, 1995, 1997; *Lefèvre et al.*, 1999].

Until recently, the distribution of surface water pCO_2 has been obtained either over large areas of the continental shelf but with a relatively poor temporal resolution as in the North Sea [*Kempe and Pegler*, 1991; *Schneider et al.*, 1992] or with a good temporal resolution but in very specific coastal ecosystems [*Codispoti et al.*, 1986; *Frankignoulle*, 1988; *Boehme et al.*, 1998; *Borges and Frankignoulle*, 1999; *Reimers et al.*, 1999; Thomas and Schneider, 1999; *Brasse*, 2000; *Delille et al.*, 2000]. Furthermore, the air-sea fluxes are not always computed in the above mentioned publications. A recent work carried out during five cruises in the East China Sea [*Tsunogai et al.*, 1999] suggests that continental shelves constitute a significant sink for atmospheric CO_2 and led the

Paper number 2000GB001307
0886-6236/01/2000GB1307$12.00

authors to formulate the "continental shelf pump" hypothesis that accounts for a sink in the range 0.5 to 1.0 Gt C yr^{-1}. This range is in good agreement with the value of 0.7 Gt C yr^{-1} proposed by *Sabine and Mackenzie* [1991] and based on budget calculations. In this work, we have monitored the partial pressure of carbon dioxide (pCO_2) over a large surface area of the European Atlantic continental shelf during 13 cruises in the Gulf of Biscay and adjacent areas (Plate 1) and during 5 cruises in the North Sea (Plate 2). Data from the Gulf of Biscay cover all four seasons over a period of several years. The studied area is influenced by most coastal particularities (shelf-edge discontinuity, vertical mixing, upwelling, slope current, sediment remineralization, tidal front, river input, eutrophication, etc.).

2. Material and Methods

Underway data of pCO_2 were obtained using a direct and an indirect method from the non toxic seawater supply of the ship (pump inlet at a depth of -2.5 m). Before 1995, pCO_2 was computed from the measurements of pH and total alkalinity using the constants of *Mehrbach et al.* [1973]. The measurement of pH was made using a Ross type combined electrode (ORION) calibrated on the National Bureau of Standards scale (NBS). Total alkalinity was determined using Gran electro-titration. From 1995, pCO_2 was directly measured using the equilibration technique, a general description of which is given by *Dickson and Goyet* [1994]. Our equilibrator consists of a Plexiglas cylinder (height, 80

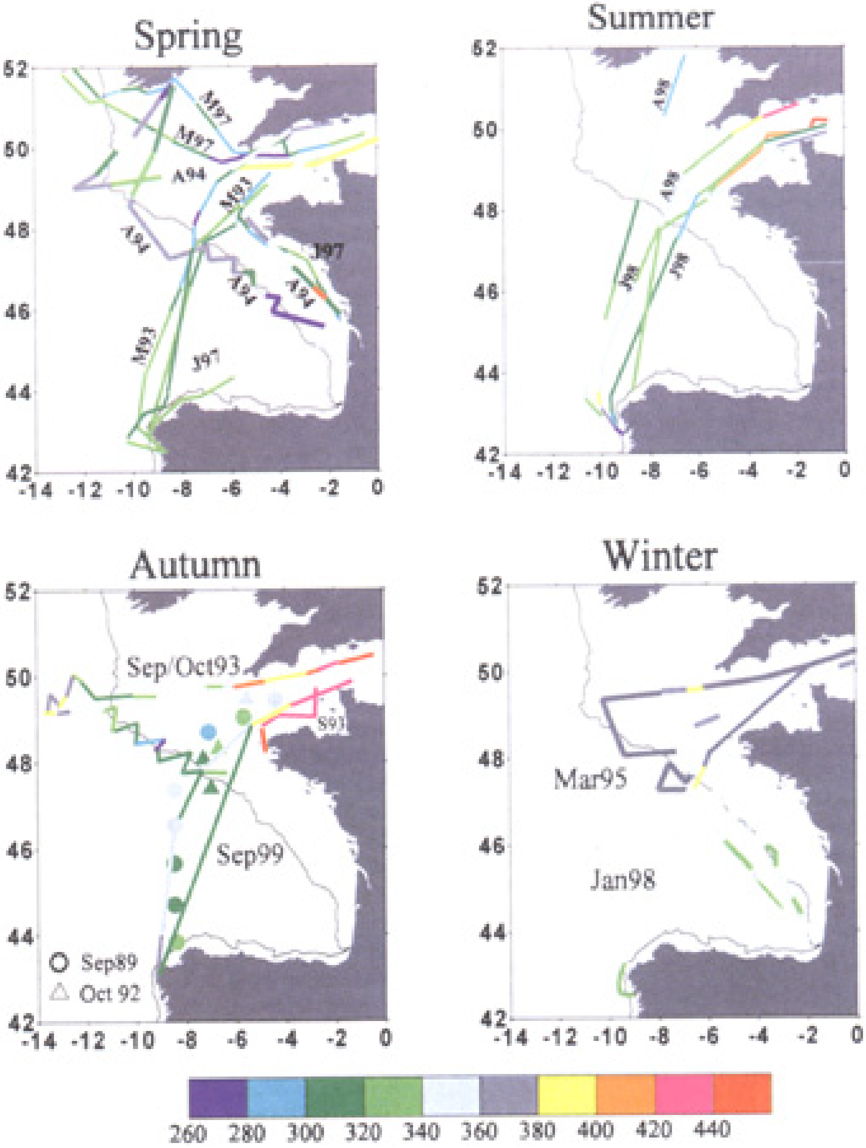

Plate 1. Surface water pCO_2 in the Gulf of Biscay and adjacent areas. Lines refer to ship tracks and their colors refer to the CO_2 partial pressure. The thin black line indicates the 200 m contour, i.e,. the shelf edge.

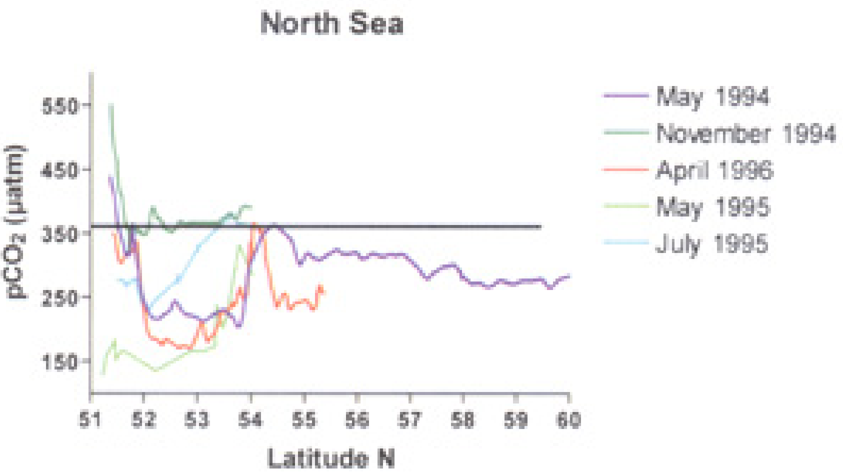

Plate 2. Surface water $p\text{CO}_2$ in the North Sea. Transects were carried out along the 3rd East meridian.

cm; diameter, 10 cm) filled with marbles to increase the exchange surface area [*Frankignoulle et al.*, 2001]. Seawater runs (3 L min^{-1}) from the top to the bottom of the equilibrator and air is pumped upwards (3 L min^{-1}). A non dispersive infrared gas analyser (Li-cor) was used to measure $p\text{CO}_2$ in wet air equilibrated with seawater. Before 1998, $p\text{CO}_2$ was measured in equilibrated air dried with Drierite and the data were converted into wet air using the algorithms proposed by *Dickson and Goyet* [1994]. The Li-cor was calibrated daily using three gas standards of 0 µatm (Air Liquide Belgium), 351.0 µatm (Air Liquide Belgium), 360.5 µatm (National Oceanic and Atmospheric Administration). The temperature at the outlet of the equilibrator was monitored and allowed to correct $p\text{CO}_2$ values for the temperature difference between in situ seawater and water in the equilibrator, using the algorithm proposed by *Copin-Montégut* [1988]. The concentration of chlorophyll a was determined from GF/F filtered samples by the fluorimetric method [*Arar and Collins*, 1997] and before 1997 by the spectrophotometric method [*Lorenzen and Jeffrey*, 1978].

The flux of CO_2 across the air-sea interface (F) can be computed from the air-sea gradient ($\Delta\, p\text{CO}_2$) and the gas exchange coefficient (K) using the equation: $F = \alpha.(K).(\Delta\, p\text{CO}_2)$, where α is the solubility coefficient of CO_2. The air-sea gradient of CO_2 imposes the direction of the flux and mainly depends on surface seawater $p\text{CO}_2$ since atmospheric $p\text{CO}_2$ is homogeneous and much less variable. The magnitude of the flux is mainly imposed by the value of K that is function of various parameters and processes such as wind speed, turbulence at the interface, air bubbles, surface films, etc. However, wind speed is recognized as the main forcing factor on the K value and several algorithms to derive K from wind speed have been proposed in the literature. In our calculations, we used the values of atmospheric $p\text{CO}_2$ from Barrow since they are considered to be representative for the Northern Hemisphere [*Keeling and Whorf*, 1999] and the three most commonly used algorithms for the exchange coefficient [*Liss and Merlivat*, 1986; *Tans et al.*, 1990; *Wanninkhof*, 1992]. We decided to use three formulations for the K-wind relationship to give a range of values for various reasons. First, it is difficult to select one single relationship because there is no consensus in the relationships proposed in literature even in the light of experiments using the most recent tracer techniques [*Wanninkhof and McGillis*, 1999; *Nightingale et al.*, 2000]. Second, considering the strong non-linear characteristics of the K-wind relationships, it is not possible to determine a priori the relative importance of the fluxes computed from one relationship in comparison to the fluxes computed from the other relationships. Third, the fluxes reported in literature are usually computed using only one of the three relationships mentioned above, and thus, for a comparative purpose, it is useful to have the values calculated using the various relationships.

3. Results and Discussion

3.1. $p\text{CO}_2$ Distribution

Except for winter, the whole Gulf of Biscay is strongly undersaturated with respect to the atmosphere (presently about 365 µatm), with most $p\text{CO}_2$ values below 340 µatm. During spring, large areas display $p\text{CO}_2$ values lower than 300 µatm. In winter, surface waters are close to atmospheric equilibrium, in the range of 340-380 µatm and the average value (367 µatm, Table 1) is at equilibrium.

In the western English Channel, over-saturation of CO_2 is observed during winter and autumn while spring and summer are characterized by undersaturation of variable intensity. A detailed study of the distribution of $p\text{CO}_2$ in the English Channel reported elsewhere (A. V. Borges and M. Frankignoulle, Distribution of surface carbon dioxide and air-sea exchange in the English Channel and adjacent areas, submitted to *Journal of Geophysical Research*, 2000, hereinafter cited as A. V. Borges, submitted manuscript, 2000a) shows that from the point of view of inorganic carbon dynamics, the difference between the Channel and the Gulf of Biscay is related to the fact that the former is a permanently well-mixed system while the latter shows strong seasonal stratification. This has two main consequences: first, the strong coupling with sediment remineralization induces strong oversaturation of CO_2 in the Channel, in particular during autumn; second, primary production in the Channel is light limited [*L'Helguen et al.*, 1996] rather than nutrient limited, as in the Gulf of Biscay, so that significant undersaturation of CO_2 is only observed from May to July, when light availability is maximum (A. V. Borges, submitted manuscript, 2000a).

Table 1. Average Values of Measured pCO_2 and Wind Speed Over the Shelf During 11 Cruises in the Gulf of Biscay and the 5 Cruises in the North Sea.

	Measured Parameters		Calculated Fluxes, mmole m^{-2} d^{-1}		
	pCO_2, μatm	Wind, m s^{-1}	L+M	W	T
Biscay					
Sept. 1999	355	4.6	-0.47	-0.44	-1.07
Aug. 1998	326	14.8	-11.10	-21.10	-17.40
July 1998	324	9.1	-4.78	-8.64	-10.07
June 1998	308	5.9	-3.37	-6.09	-7.60
Jan. 1998	367	19.0	+0.50	+0.94	+0.71
June 1997	315	14.4	-12.95	-24.37	-21.98
May 1997	306	9.4	-9.47	-17.71	-18.29
March 1995	348	8.7	-1.78	-3.21	-3.39
April 1994	340	6.3	-1.07	-2.21	-1.80
Sept. 1993	334	4.5	-1.27	-2.41	-2.22
May 1993	320	6.2	-3.1	-4.8	-6.2
Integrated	*332*		*-4.79*	*-7.89*	*-7.59*
Million tons of C per year			-88	-166	-162
North Sea					
April 1996	260	9.6	-36.16	-58.36	-71.18
May 1995	195	5.1	-16.44	-27.12	-40.27
Nov. 1994	370	5.2	+1.64	+2.47	+3.84
May 1994	287	8.3	-20.82	-31.78	-46.3
July 1995	306	7.0	-20.27	-36.44	-41.64

Fluxes are calculated using three different parameterizations of the exchange coefficient *versus* actual wind speed: L+M for *Liss and Merlivat* [1986], W for *Whaninkhof* [1992] and, T for *Tans* [1990]. Values of atmospheric pCO_2 at Barrow have been taken for flux computation. In the Gulf of Biscay, measurements and calculations have been integrated over the year and results obtained have been extrapolated to the European shelf area to estimate a global flux in million tons of carbon per year.

In the Southern Bight of the North Sea (latitude < 52.5°N), pCO_2 displays a wide range of values, from 150 to 550 μatm. This is due to both a variable discharge of highly oversaturated water from the Scheldt, the Thames, and the Rhine estuaries [*Frankignoulle et al.*, 1998] and an intense phytoplanktonic bloom which can induce severe undersaturation during spring [*Hoppema*, 1991; *Kempe and Pegler*, 1991; *Bakker et al.*, 1996; *Frankignoulle et al.*, 1996; *Frankignoulle et al.*, 1998; *Borges and Frankignoulle*, 1999]. The area between 52° and 54°N is most often strongly undersaturated (pCO_2 from 150 to 360 μatm) and the shallow area in the vicinity of the Dogger-Bank (54.5°N) is always close to saturation, whatever the season.

Our results show that the highest pCO_2 values are observed in the three following situations: (1) during winter when phytoplanktonic production is negligible, (2) in areas influenced by river input of oversaturated water, (3) when important vertical mixing occurs, which is during winter or in shallow areas situated close to a bathymetric change (western English Channel, Dogger-Bank in the North Sea). Oversaturation of CO_2 in shallow waters has also been mentioned by *Kempe and Pegler* [1991] over the Dogger Bank and by *Thomas and Schneider* [1999] in the Baltic Sea.

Coastal upwelling areas can also be sites of important oversaturation [*Simpson and Zirino*, 1980; *Körtzinger et al.*, 1997; *Goyet et al.*, 1998] owing to the high CO_2 content of upwelled deep water. Plate 1 shows that significant undersaturation was observed off the Galician coast, in June 1997, January 1998, July 1998, and August 1998. However, a detailed study of the Galician upwelling system we report elsewhere (A. V. Borges and M. Frankignoulle, Distribution of carbon dioxide and air-sea exchange in the upwelling system off the Galician coast, submitted to *Global Biogeochemical Cycles*, 2000b, hereinafter cited as A. V. Borges, submitted manuscript, 2000b) shows strong spatial variability and complex patterns in the surface distribution of pCO_2 as also reported off the Portuguese and the Californian coasts (*Pérez et al.* [1999] and van Green et al., [2000], respectively). Indeed, during a cruise carried out in the area in June 1992, pCO_2 values close to 450 μatm were observed, although associated with high primary production rate (1431 mg C m^{-2} d^{-1}) and chlorophyll a concentration (4.9 μg l^{-1}) [*Frankignoulle* *et al.*, 1993]. However, in spite of important spatial variability of pCO_2 over the continental shelf off the Galician coast, A. V. Borges (submitted manuscript, 2000b) concludes that the area is a net sink for atmospheric CO_2.

The daily variation of pCO_2 over the shelf has seldom been reported in the literature and one may enquiry about its magnitude compared to the spatial and seasonal variations presented above. Figure 1 shows some diel measurements we made both in the Gulf of Biscay and in the North Sea: pCO_2 presents a maximum value at dawn and a minimum at dusk, in good agreement with the daily metabolic processes (photosynthesis and respiration), however the daily variation does not exceed 20 µatm even in spring.

Our results also allow to discuss the major processes that control the distribution of pCO_2 in the Gulf of Biscay. Figure 2 shows the yearly evolution of the average measured values of pCO_2 and chlorophyll a concentration, as well as the expected pCO_2 according to the seasonal evolution of temperature. The variation of temperature affects the equilibrium constants of inorganic carbon and in particular the solubility coefficient of CO_2 (pCO_2 rises of ~4% for a temperature increase of 1°C). From January to March, when chlorophyll a concentration is low, the pCO_2 evolution is clearly in agreement with temperature change. From April, when chlorophyll a concentration significantly increases, the pCO_2 drastically decreases instead of increasing as expected from temperature change and is then mainly driven by primary production. Thus the observed seasonal variation of CO_2 in the Gulf of Biscay mainly results from net autotrophy over the shelf.

The dynamics of inorganic carbon resulting from photosynthesis is highly dependent upon the types of organisms present and whether they are calcifying or not. Calcification is known to induce an increase of pCO_2 due to the chemical equilibrium involved in solid carbonate production (i.e., $Ca^{2+} + 2HCO_3^- = CO_2 + CaCO_3 + H_2O$). Photosynthesis and calcification thus have opposite effects on pCO_2 change, and the final result of their concomitance depends on their relative importance. For instance, oversaturation of pCO_2 with respect to the atmosphere during a coccolithophore bloom has been reported in the North Atlantic [*Holligan et al.*, 1993]. A convenient parameter to study the importance of calcification is the homogenous buffer factor β, defined as the relative variation of the partial CO_2 pressure to the one of total dissolved inorganic carbon ($\beta = d\ln(pCO_2)/d\ln(DIC)$, where DIC is the total dissolved inorganic carbon, i.e., the summation of dissolved CO_2, bicarbonate and carbonate concentrations). The value of β ranges from ~12, when dissolved CO_2 is the only species involved (no calcification), to about -7, when precipitation/dissolution of calcium carbonate is the only occurring process [*Frankignoulle*, 1994]. We have computed β values at La Chapelle Bank, a reference station frequently sampled and situated at the shelf edge. Figure 3 shows that β values range between 0 and 12 and are well correlated (r^2 = 0.79, p = 0.0006) to the normalized alkalinity. Calcification or carbonate dissolution appears to occur for each sampled period, except in April 1994, and with a maximum in May 1993. The production of calcium carbonate by calcifying organisms (e.g., coccolithophorides) is then an important

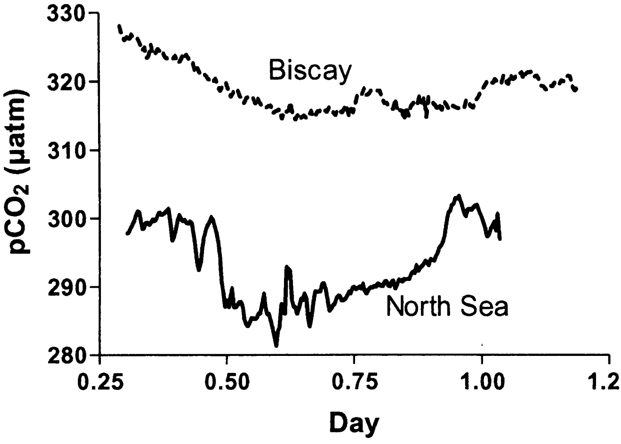

Figure 1. Diel cycles measurement of pCO_2 carried out in the Gulf of Biscay (April 21 1993, La Chapelle Bank, 47°24'N 07°16'W) and in the North Sea (May 31 1994, 54°00'N 3°00'E).

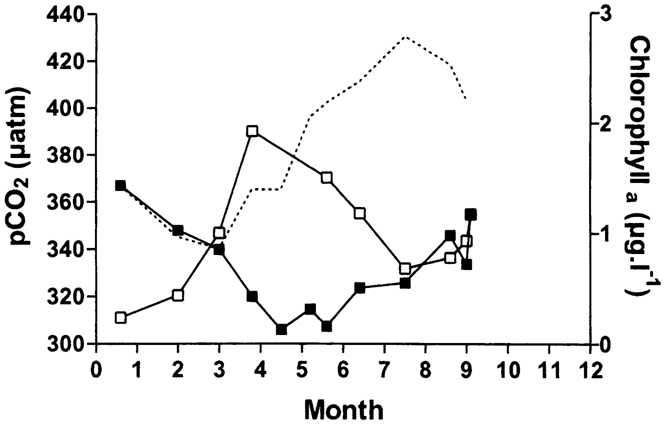

Figure 2. Evolution of average measured pCO_2 (solid squares) and chlorophyll a concentration (open squares) over the shelf in the Gulf of Biscay and adjacent areas. The dotted line shows the theoretical evolution of pCO_2 as calculated from seasonal temperature evolution and the pCO_2 measured in January.

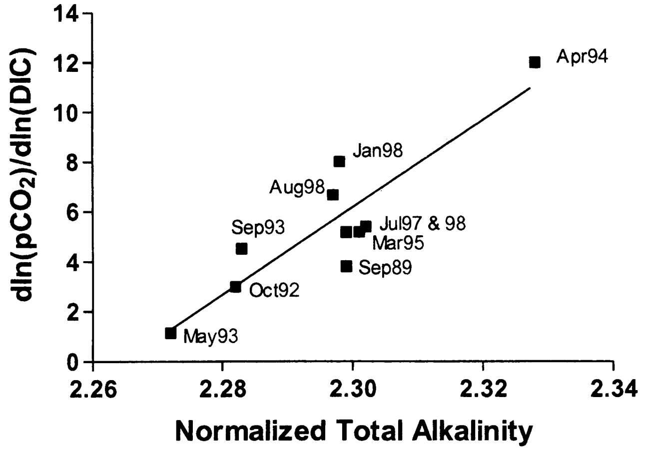

Figure 3. The homogeneous buffer factor β versus total alkalinity normalized to salinity 35, obtained at La Chapelle bank. β is calculated by plotting the natural logarithm of pCO_2 versus the one of DIC, calculated from pH and total alkalinity data obtained in the surface layer (0-50 m). Regression of β *versus* normalized alkalinity yields r^2=0.79, p<0.001.

feature of the carbon cycle in the investigated area, as already suggested by a previous suspended matter study [*Wollast and Chou*, 1998], but undersaturation of CO_2 nevertheless prevails.

3.2. Air-Sea CO_2 Exchanges

Table 1 summarizes averaged values of pCO_2, wind speed, and calculated air-sea CO_2 fluxes that we have obtained above shelves during the various cruises. The data obtained in offshore and deep waters have not been taken into account for the calculations presented in Table 1. The direction of the CO_2 flux is always from air to sea, both in the Gulf of Biscay and in the North Sea, except during some winter cruises (January 1998 and November 1994, respectively). Both in the western English Channel and in the Southern Bight of the North Sea, oversaturation is often observed (Plates 1 and 2), but the surface areas of these sites are small compared to the Gulf of Biscay and the whole North Sea, respectively.

Results shown in Table 1 clearly illustrate the respective effects of both wind speed and CO_2 gradient on the calculated flux. During summer 1998, in July and August, the pCO_2 is unchanged, but the influx is multiplied by 2.5 due to the increase of wind speed from 9 to 15 m s^{-1}. In September 1993 and September 1999, the same wind speed was observed but the influx is divided by 5.5 according to the respective values of the CO_2 gradient.

In the Gulf of Biscay and adjacent seas, where our 10 years data set covers the four seasons, the air-sea CO_2 flux was integrated over the complete annual cycle. Results are in the range of -4.8 to -7.9 mmol m^{-2} d^{-1}, depending on which gas exchange coefficient is used (*Liss and Merlivat* [1986] and *Wanninkhof* [1992], respectively). The data in the Southern Bight of the North Sea were not annually integrated because they do not cover sufficiently well the very important temporal and spatial variability. As an example, *Kempe and Pegler* [1991] calculated an influx of -7.5 mmol m^{-2} d^{-1} for the entire North Sea in May-June 1986, and for the same season and the same exchange coefficient [*Liss and Merlivat,* 1986], we report here an influx of -16.44 mmol m^{-2} d^{-1}. Moreover, the North Sea is a semi enclosed sea which is not representative of a typical continental shelf system bordered by a margin. However, our data strongly suggest that the North Sea behaves globally as a relatively important net sink for atmospheric CO_2. In the same manner, *Thomas and Schneider* [1999] have shown, using the *Wanninkhof* [1992] exchange coefficient, that the Baltic Sea is a net annual sink of -2.5 mmol m^{-2} d^{-1}.

If one extrapolates our values obtained in the Gulf of Biscay to the surface area of the European continental shelf (5 million square kilometres [*Walsh*, 1988]), one obtains a net influx in the range 0.09-0.17 Gt C yr-1. The North Atlantic sink for latitudes included between 42° and 78°N has been estimated to be 0.23-0.34 Gt C yr-1 [*Takahashi et al.*, 1995; *Sarmiento et al.*, 1995], again depending on the *K* formulation (*Liss and Merlivat* [1986] and *Wanninkhof* [1992], respectively) and the European shelf is thus an additional sink that amounts to about 45% of this value. We consider this sink as "additional" to the one in the open North Atlantic ocean, since we applied the same approach as the one used by *Takahashi et al.* [1995] to estimate the CO_2 influx. Whether or not it is a sink of anthropogenic CO_2 will be discussed hereafter. Such an additional and significant flux is of particular importance in the context of the controversy introduced by *Tans et al.* [1990] concerning the terrestrial versus oceanic sink of CO_2 in the Northern Hemisphere. Furthermore, it should be noted that the Atlantic Ocean (north of 50°S) alone represents ~60% of the total uptake of atmospheric CO_2 by the global open ocean [*Takahashi et al.*, 1997].

Our results are also in agreement with the direction and magnitude of CO_2 fluxes reported in other continental shelf areas. For instance, *Chen and Wang* [1999], *Tsunogai et al.* [1999], and *Wang et al.* [2000] have recently reported in the East China Sea, a net annual CO_2 flux of -3.3 and -7.7 mmol m^{-2} d^{-1} for the *Liss and Merlivat* [1986] and the *Wanninkhof* [1992] *K* formulations, respectively. *Boehme et al.* [1998] report, in a coastal transect off the New Jersey coast, an annually integrated air-sea flux in the range of -1.2 to -2.3 mmol m^{-2} d^{-1} for the *K* formulation of *Liss and Merlivat* [1986] and *Tans et al.* [1990], respectively. In the light of the fact that the surface area of both our sampling region and the East China Sea represents 9.4% of the total surface area of the shelves worldwide and 13.2% of the shelf surface area in the Northern Hemisphere, we can hypothesise that middle- and high-latitude continental shelves in the Northern Hemisphere are a significant net sink of atmospheric CO_2. This hypothesis is corroborated by the sparse pCO_2 data available in the literature over other continental shelves in the Northern Hemisphere that show low values in spite of high variability, as 125 μatm in the Bering Sea [*Codispoti et al.*, 1986], 130 μatm along the Californian coast [*Simpson*, 1984], 225 μatm in the Bay of Bengal [*Kumar et al.*, 1996].

The hypothesis of an important sink for atmospheric CO_2 over the continental shelf of the Northern Hemisphere contributes to debate on the trophic status of continental shelves but of course does not allow to solve it. The debate comes mainly from the paucity of data and probable inadequate extrapolation of available measurements of gross primary production and ecosystem respiration. *Gattuso et al.* [1998] have recently compiled all available data for coastal ecosystems, and they conclude that the proximal continental shelf that is directly influenced by the inputs of terrestrial organic matter is net heterotrophic. However, the distal continental shelf is net autotrophic due to the low influence of terrestrial inputs and important export of carbon to the sediments and across the continental shelf break. Our pCO_2 data in the Gulf of Biscay allows to confirm the latter statement.

Whether or not the influx we computed corresponds to a flux of anthropogenic CO_2 is difficult to establish. Such a "perturbation flux" in the coastal sea can be related either to the increase of the atmospheric CO_2 content that modifies the air-sea gradient or to enhanced carbon export due to anthropogenic input of nutrients (i.e., eutrophication). Making such an estimation is a very challenging task and has been attempted with a global modeling approach by the group at the University of Hawaii [see *Ver et al.*, 1994, 1999a, b; *Mackenzie et al.*, 1998, 2000]. These authors conclude that the additional carbon preservation related to eutrophication does not compensate the degradation of organic carbon introduced by human activity. However, still according to these authors, the increase of atmospheric CO_2 content has modified the status of the proximal continental shelf from a preindustrial source of atmospheric CO_2 [*Wollast and Mackenzie*, 1989] to a present-day near equilibrium state [*Mackenzie et al.*, 1998].

4. Conclusions

In the present work we show, using a direct and observational approach and with a high-temporal and spatial resolution, that the Gulf of Biscay, a distal continental shelf area, acts as a significant sink for atmospheric CO_2. Data reported in literature in various other study sites allow to hypothesise that this could the case in middle- and high-latitude continental shelf areas of the Northern Hemisphere. However, more field data on carbon fluxes are needed to constrain a worldwide extrapolation. The global integration of air-sea fluxes should then allow to determine whether or not the continental shelves as a whole (both proximal and distal) act as a net sink or a net source of CO_2 and to which extent it corresponds to a perturbation flux. In particular, little data is available in the Southern Hemisphere, in high northern latitudes, but also in coastal upwelling systems, wet tropical continental shelves and river plumes that could act as sources of atmospheric CO_2, as reported by *Goyet et al.* [1998], *Brunskill et al.* [2000], and A. V. Borges and M. Frankignoulle, Carbon dioxide in the Scheldt plume off the Belgian coast., I., Air-sea exchange, submitted to *Biogeochemistry*, 2000c), respectively. The latter regions but also subtropical regions in general although undersampled could be an significant component of the coastal ocean carbon cycle because of the important accumulation of carbonate phases in shallow water environments that induces a release of dissolved CO_2 with possible further transfer to the atmosphere [*Frankignoulle et al.*, 1995].

Acknowledgments. We thank officers and crew of the *R. V. Belgica* (Belgium) and the *R. R. S. Charles Darwin* (United Kingdom) for the welcome received on board, the Unité de Gestion de Modèle Mathématique de la Mer du Nord (Belgium) for providing thermosalinograph and meteorological data, numerous colleagues for fruitful discussions and field assistance, as well as Roland Wollast and two other anonymous referees for pertinent comments on a previous version of the manuscript. This work has been funded by the Fonds National de la Recherche Scientifique (Belgium), with which Michel Frankignoulle is a research associate and Alberto Vieira Borges a doctoral fellowship, by the European Union (Marine Science and Technology programme, OMEX project contract MAS3-CT97-0076, Environment and Climate programme, BIOGEST project ENV4-CT96-0213) and the Service de la Politique Scientifique de Belgique (Programme d'implulsion Global Change, convention GC/12/011). This is ELOISE contribution 197.

References

Arar, E.J., and G.B. Collins, *In vitro* determination of chlorophyll a and pheophytin a in marine and freshwater phytoplankton by fluorescence, in *Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices*, vol. 445, pp. 1-22, U.S. Environ. Prot. Agency, Cincinnati, Ohio, 1997.

Bakker, D.C.E., H.J.W. de Barr, and H.P.J. de Wilde, Dissolved carbon dioxide in Dutch coastal waters, *Mar. Chem.*, *55*, 247-263, 1996.

Biscaye, P.E., C.N. Flagg, and P.G. Falkowski, The Shelf Edge Exchange Processes experiment, SEEP-II: An introduction to hypotheses, results and conclusions, *Deep Sea Res., Part II*, *41*, 231-252, 1994.

Boehme, S.E., C.L. Sabine, and C.E. Reimers, CO_2 fluxes from a coastal transect: A time series approach, *Mar. Chem.*, *63*, 49-67, 1998.

Borges, A.V., and M. Frankignoulle, Daily and seasonal variations of the partial pressure of CO_2 in surface seawater along the Belgian and southern Dutch coastal areas, *J. Mar. Syst.*, *19*, 251-266, 1999.

Brasse, S., Kohlenstoffumsaetze in der Deutschen Bucht, suedoestliche Nordsee: Saisonale Transformationsprozesse und Transporte,Ph. D. thesis, 112 pp., Univ. of Hamburg, Hambourg, Germany, 2000.

Broecker, W.S., and T.-H. Peng, in *Greenhouse Puzzles*, 284 pp., Lamont-Doherty Earth Observatory, Palisades, New York, 1998.

Brunskill, G.J., K.A. Burns, D. Alongi, I. Zagorskis, and J. Pfitzner, Preliminary carbon mass balance in the Gulf of Papua, Papua New Guinea, Project TROPICS, 1991-1999, paper presented at the International Liège Colloquium on Ocean Hydrodynamics, Univ. of Liège, Liège, Belgium, May 8-12, 2000.

Chen, C.-T.A., and S.-L. Wang, Carbon, alkalinity, and nutrient budgets on the East China Sea continental shelf, *J. Geophys. Res.*, *104*, 20,675-20,686, 1999.

Codispoti, L.A., G.E. Friederich, and D.W. Hood, Variability in the inorganic carbon system over the Bering Sea shelf during spring 1980 and spring-summer 1981, *Cont. Shelf Res.*, *5*, 133-160, 1986.

Copin-Montégut, C., A new formula for the effect of temperature on the partial pressure of carbon dioxide in seawater, *Mar. Chem.*, *25*, 29-37, 1988.

Dellile, B., D. Dellile, M. Fiala, C. Prevost, and M. Frankignoulle, Seasonal changes of pCO$_2$ over a subantartic *Macrocystis* kelp bed, *Polar Biol.*, *23*, 706-716, 2000.

Dickson, A., and C. Coyet (Eds), *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water*, Carbon Dioxide Information Analysis Center, Oak Ridge, Tenn., 1994.

Frankignoulle, M., Field measurements of air-sea CO_2 exchange, *Limnol. Oceanogr.*, *33*, 313-322, 1988.

Frankignoulle, M., A complete set of buffer factors for acid/base CO_2 system in seawater, *J. Mar Syst.*, *5*, 111-118, 1994.

Frankignoulle, M., M. Elskens, M. Loijens, and P. Dauby, Seawater pCO$_2$ distribution and air-sea CO_2 exchanges on the Atlantic European Shelf, in *Proceedings of Progress in Belgian Oceanographic Research*, Brussels, Royal Academy of Belgium, pp.159-170, 1993.

Frankignoulle, M., M. Pichon, and J. P. Gattuso, Aquatic calcification as a source of carbon dioxide, in *Carbon Sequestration in the Biosphere*, NATO ASI Ser. Vol.133, edited by M. Beran,, vol. 133, pp. 265-271, Springer-Verlag, New York, 1995.

Frankignoulle, M., I. Bourge, C. Canon, and P. Dauby, Distribution of surface seawater partial CO_2 pressure in the English Channel and in the Southern Bight of the North Sea, *Cont. Shelf Res.*, *16*, 381-395, 1996.

Frankignoulle, M., G. Abril, A. Borges, I. Bourge, C. Canon, B. Delille, E. Libert, and J.-M. Théate, Carbon dioxide emission from European estuaries, *Science*, *282*, 434-*436*, 1998.

Frankignoulle, M.,A. Borges, and R. Biondo, A new design of equilibrator to monitor carbon dioxide in highly dynamic and turbid environments, *Wat. Res.*,*35* (5), 1344-1347, 2001.

Garrels, R.M., and F.T. Mackenzie (Eds.), *Evolution of Sedimentary Rocks*, 397 pp., W.W. Norton, New York, 1971.

Gattuso, J.-P., M. Frankignoulle, and R. Wollast, Carbon and carbonate metabolism in coastal aquatic ecosystems, *Annu. Rev. Ecol. Syst.*, *29*, 405-433, 1998.

Goyet, C., F.J Millero, D.W. O'Sullivan, G. Eischeid, S.J. McCue, and R.G.J. Bellerby, Temporal variations of pCO$_2$ in surface seawater of the Arabian Sea in 1995, *Deep Sea Res.*, *45*, 609-623, 1998.

Holligan, P.M.et al. A biogeochemical study of the coccolithophore, *Emiliana huxley*, in the North Atlantic, *Global Biogeochem. Cycles*, *4*, 879-900, 1993.

Hoppema, J.M.J., The seasonal behaviour of carbon dioxide and oxygen in the coastal North Sea along the Netherlands, *Neth. J. Sea Res.*, *28*, 167-179, 1991.

Keeling, C.D., and T.P. Whorf, in *Trends: A Compendium of Data on Global Change*, Carbon Dioxide Information Analysis Center, Oak Ridge, Tenn., 1999.

Kempe, S., Coastal Seas: A net source or sink of atmospheric carbon dioxide?, *Rep. and Stud.*, *95*, pp. 1-27, (LOICZ) Texel, 1995.

Kempe, S., and K. Pegler, Sinks and sources of CO_2 in coastal seas: The North Sea, *Tellus Ser. B*, *43*, 224-235, 1991.

Körtzinger, A., J.C. Duinker, and L.

Mintrop, Strong CO_2 emissions from the Arabian Sea during South-West Monsoon, *Geophys. Res. Let.*, *24*, 1763-1766, 1997.

Kumar, M.D., S.W.A. Naqvi, M.D. George, and D.A. Jayakumar, A sink for atmospheric carbon dioxide in the northeast Indian Ocean, *J. Geophys. Res.*, *101(C8)*, 18,121-18,125, 1996.

Lefèvre, N., A.J. Watson, D.J. Cooper, R.F. Weiss, T. Takahashi, and S.C. Sutherland, Assessing the seasonality of the oceanic sink for CO_2 in the northern hemisphere, *Global Biogeochem. Cycles*, *13*, 273-286, 1999.

L'Helguen, S., C. Madec, and P. Le Corre, Nitrogen uptake in permanently well-mixed temperate coastal waters, *Estuarine Coastal Shelf Sci.*, *42*, 803-818, 1996.

Liss, P., and L. Merlivat, Air-sea exchange rates: introduction and synthesis, in *The Role of Air-Sea Exchanges in Geochemical Cycling, NATO ASI Ser. C185*, edited by P. Buat-Ménard, pp. 113-118, Reidel, Norwell, Mass., 1986.

Lorenzen, C.J., and S.W. Jeffrey, Determination of chlorophyll a in seawater, *UNESCO Tech. Pap. Mar. Sci.*, *35*, 1-21, 1978.

Mackenzie, F.T., What is the importance of ocean margin processes in Global Change?, in *Ocean Margin Processes in Global Change*, edited by R.F.C Mantoura, J.M. Martin, and R. Wollast, pp. 433-454, J. Wiley, N. Y., 1991.

Mackenzie, F.T. (Ed.), in *Our Changing Planet*, 486 pp., Prentice-Hall, Englewood Cliffs, N. Y., 1998.

Mackenzie, F.T., A. Lerman, and L.M. Ver, Role of the continental margin in the global carbon balance during the past three centuries, *Geology*, *26*, 423-426, 1998.

Mackenzie, F.T.,L.M. Ver, and A. Lerman, Coastal-zone biogeochemical dynamics under global warming, *Int. Geol. Rev.*, *42*, 193-206, 2000.

Mehrbach, C., C.H. Culberson, J.E. Hawley, and P.M. Pytowicz, Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr.*, *18*, 897-907, 1973.

Nightingale, P.D., G. Malin, C.S. Law, A.J. Watson, P.S. Liss, M.I. Liddicoat, J. Boutin, and R.C. Upstill-Goddard, In situ evaluation of air-sea exchange parameterizations using novel conservative and volatile tracer, *Global Biogeochem. Cycles*, *14*, 373-387, 2000.

Pérez, F.F, A.F. Ríos, and G. Rosón, Sea surface carbon dioxide off the Iberian Peninsula (North Eastern Atlantic Ocean), *J. Mar. Sys.*, *19*, 27-46, 1999.

Reimer, A., S. Brasse,R. Doerffer, C.-D. Dürselen, S. Kempe, W. Michaelis, H.-J. Rick, and R. Seifert, Carbon cycling in the German Bight: An estimate of transformation processes and transport, *Dtsch. Hydrogr. Z.*, *51*, 311-327, 1999.

Sabine, C.L., and F.T. Mackenzie, Oceanic sinks for anthropogenic CO_2, *Int. J. Energy Env. Econ.*, *1*, 119-127, 1991.

Sarmiento, J.L., and E.T. Sundquist, Revised budget for the oceanic uptake of anthropogenic carbon dioxide, *Nature*, *356*, 589-593, 1992.

Sarmiento, J.L., R. Murnane, and C. Le Quéré, Air-sea CO_2 transfer and the carbon budget of the North Atlantic, *Philos. Trans. R. Soc. London, Ser. B*, *348*, 211-219, 1995.

Schneider, B., K. Kremling, and J.C. Duinker, CO_2 partial pressure in the Northeast Atlantic and adjacent shelf waters: processes and seasonal variability, *J. Mar. Syst.*, *3*, 453-463, 1992.

Simpson, J.J., On the exchange of oxygen and carbon dioxide between ocean and atmosphere in an eastern boundary current, in *Gas Transfer at Water Surfaces*, edited by W. Brutsaert and G.H. Jirka, pp. 505-514, D. Reidel, Norwell, Mass., 1984.

Simpson, J.J., and A. Zirino, Biological control of pH in the Peruvian coastal upwelling area, *Deep Sea Res.*, *27*, 234-248, 1980.

Smith, S.V., and J.T. Hollibaugh, ,Coastal metabolism and the oceanic organic carbon balance, *Rev. Geophys.*, *31*, 75-89, 1993.

Smith, S.V., and F.T. Mackenzie, The ocean as a net heterotrophic system: implications from the carbon biogeochemical cycle, *Global Biogeochem. Cycles*, *1*, 187-198, 1987.

Sundquist, E.T., The global carbon dioxide budget, *Science*, *259*, 934-941, 1993.

Takahashi, T., T.T. Takahashi, and S.C. Sutherland, An assessment of the role of the North Atlantic as a CO_2 sink, *Philos. Trans. R. Soc. London, Ser. B*, *348*, 143-152, 1995.

Takahashi, T., R.A. Feely, R.F. Weiss, R.H. Wanninkhof, D.W. Chipman, S.C. Sutherland, and T.T. Takahashi, Global air-sea flux of CO_2: An estimate based on measurements of sea-air pCO_2 difference, *Proc. Natl. Acad. Sci. U.S.A.*, *94*, 8292-8299, 1997.

Tans, P.P., I.Y. Fung, and T. Takahashi, Observational constraints on the global atmospheric CO_2 budget, *Science*, *247*, 1431-1438, 1990.

Thomas, H., and B. Schneider, The seasonal cycle of carbon dioxide in Baltic Sea surface waters, *J. Mar. Syst.*, *22*, 53-67, 1999.

Tsunogai, S., S. Watanabe, and T. Sato, Is there a "continental shelf pump" for the absorption of atmospheric CO_2?, *Tellus Ser.B*, *51*, 701-712, 1999.

van Green, A., R.K. Takesue, J. Goddard, T. Takahashi, J.A. Barth, and R.L. Smith, Carbon and nutrient dynamics during coastal upwelling off Cape Blanco, Oregon, *Deep Sea Res. Part II*, *47*, 975-1002, 2000.

Ver, L.M., F.T. Mackenzie, and A. Lerman, Modeling pre-industrial C-N-P-S biogeochemical cycling in the land-coastal margin system, *Chemosphere*, *29*, 855-887, 1994.

Ver, L.M., F.T. Mackenzie, and A. Lerman, Biogeochemical responses of the carbon cycle to natural and human perturbations: past, present, and future, *Am. J. Sci.*, *299*, 762-801, 1999a.

Ver, L.M., F.T. Mackenzie, and A. Lerman, Carbon cycle in the coastal zone: Effects of global perturbations and change in the past three centuries, *Chem. Geol.*, *159*, 283-304, 1999b.

Walsh, J.J. (Ed.), in *On the Nature of Continental Shelves*, 520 pp., Academic Pr., San Diego, Calif., 1988.

Walsh, J.J., How much shelf production reaches the deep sea?, in *Productivity of the Ocean: Present and Past*, edited by W.H. Berger, V.S. Smetacek, and G. Wefer, pp. 175-191, J. Wiley, New York, 1989.

Walsh, J.J., Importance of continental margins in the marine biogeochemical cycling of carbon and nitrogen, *Nature*, *350*, 53-55, 1991.

Wang, S.-L., C.-T.A. Chen, G.-H. Hong, and C.-S. Chung, Carbon dioxide and related parameters in the East China Sea, *Cont. Shelf Res.*, *20*, 525-544, 2000.

Wanninkhof, R., Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, *97*, 7373-7382, 1992.

Wanninkhof, R., and W.R. McGillis, A cubic relationship between air-sea CO_2 exchange and wind speed, *Geophys. Res. Let.*, *26*, 1889-1892, 1999.

Wollast, R., and F.T. Mackenzie, Global biogeochemical cycles and climate, in *Climate and Geo-Sciences*, edited by A. Berger, S. Schneider, and J.-C. Duplessy, pp. 453-473, Kluwer Acad., Norwell, Mass., 1989.

Wollast, R., Interactions of carbon and nitrogen cycles in the coastal zone, in *Interactions of C, N, P and S Biogeochemical Cycles and Global Change*, edited by R. Wollast, F.T. Mackenzie, and L. Chou, pp. 195-210, D. Reidel, Norwell, Mass., 1993.

Wollast, R., Evaluation and comparison of the global carbon cycle in the coastal zone and in the open ocean, in *The Sea*, vol. 10, edited by K.H. Brink, and A.R. Robinson, pp. 213-252, J. Wiley, New york, 1998.

Wollast, R., and L. Chou, Distribution and fluxes of calcium carbonate along the continental Margin in the Gulf of Biscay, *Aquat. Geochem.*, *4*, 369-393, 1998.

A.V. Borges and M. Frankignoulle. Unité d'Océanographie Chimique, Institut de Physique B5, B4000 Sart Tilman, Belgium (Michel.Frankignoulle@ulg.ac.be; Alberto.Borges@ulg.ac.be)

(Received May 31, 2000, revised October 16, 2000;
accepted October 31, 2000)