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Do We Have Enough Pieces of the Jigsaw to Integrate CO_2 Fluxes in the Coastal Ocean?

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ABSTRACT: Annually integrated air-water CO_2 flux data in 44 coastal environments were compiled from literature. Data were gathered in 8 major ecosystems (inner estuaries, outer estuaries, whole estuarine systems, mangroves, salt marshes, coral reefs, upwelling systems, and open continental shelves), and up-scaled in the first attempt to integrate air-water CO_2 fluxes over the coastal ocean (26×10^6 km^2), taking into account its geographical and ecological diversity. Air-water CO_2 fluxes were then up-scaled in global ocean (362×10^6 km^2) using the present estimates for the coastal ocean and those from Takahashi et al. (2002) for the open ocean (336×10^6 km^2). If estuaries and salt marshes are not taken into consideration in the up-scaling, the coastal ocean behaves as a sink for atmospheric CO_2 (-1.17 mol C m^{-2} yr^{-1}) and the uptake of atmospheric CO_2 by the global ocean increases by 24% (-1.93 versus -1.56 Pg C yr^{-1}). The inclusion of the coastal ocean increases the estimates of CO_2 uptake by the global ocean by 57% for high latitude areas (-0.44 versus -0.28 Pg C yr^{-1}) and by 15% for temperate latitude areas (-2.36 versus -2.06 Pg C yr^{-1}). At subtropical and tropical latitudes, the contribution from the coastal ocean increases the CO_2 emission to the atmosphere from the global ocean by 13% (0.87 versus 0.77 Pg C yr^{-1}). If estuaries and salt marshes are taken into consideration in the up-scaling, the coastal ocean behaves as a source for atmospheric CO_2 (0.38 mol C m^{-2} yr^{-1}) and the uptake of atmospheric CO_2 from the global ocean decreases by 12% (-1.44 versus -1.56 Pg C yr^{-1}). At high and subtropical and tropical latitudes, the coastal ocean behaves as a source for atmospheric CO_2 but at temperate latitudes, it still behaves as a moderate CO_2 sink. A rigorous up-scaling of air-water CO_2 fluxes in the coastal ocean is hampered by the poorly constrained estimate of the surface area of inner estuaries. The present estimates clearly indicate the significance of this biogeochemically, highly active region of the biosphere in the global CO_2 cycle.

Introduction

The coastal ocean has been largely ignored in global carbon budgeting efforts, even if the related flows of carbon and nutrients are disproportionately high in comparison with its surface area (Smith and Hollibaugh 1993; Gattuso et al. 1998a; Wollast 1998; Liu et al. 2000; Chen et al. 2003). It receives massive inputs of organic matter and nutrients from land, exchanges large amounts of matter and energy with the open ocean across continental slopes, and constitutes one of the most biogeochemically active areas of the biosphere (Gattuso et al. 1998a). For instance, average primary production rates differ by a factor of 2 between open oceanic and coastal provinces (Wollast 1998). Although continental shelves only represent about 7% of the oceanic surface area, they account for about 20% of the total oceanic organic matter production, 80% of total oceanic organic matter burial, 90% of total oceanic sedimentary mineralization, and 30% and 50% of the total oceanic production and accumulation, respectively, of particulate inorganic carbon (Gattuso et al. 1998a; Wollast 1998). Intense air-water CO_2 exchanges can be expected from such significant carbon fluxes. Human activities are changing the continental water cycle and the flows of sediment, carbon, and nutrients to the coastal ocean with likely consequences for the sequestration or emission of anthropogenic CO_2 (Ver et al. 1999; Rabouille et al. 2001; Mackenzie et al. 2004a,b).

The cycle of CO_2 in the coastal ocean has recently been put under the spotlight by the work of Tsunogai et al. (1999). These authors reported in the East China Sea an air-water CO_2 flux of -2.92 mol C m^{-2} yr^{-1} that when extrapolated to the worldwide continental shelf area yields a sink for atmospheric CO_2 of -0.95 Pg C yr^{-1} that is designated as "the continental shelf pump" (note that Tsunogai et al. [1999, p. 701] used in their computation a continental shelf surface area of 27×10^6 km^2). It is driven by the cooling of surface coastal waters that leads to the formation of dense water as well as an enhancement of CO_2 absorption together with high primary production. In the dense bottom waters, sedimented organic matter is degraded into dissolved inorganic carbon (DIC) that is transported along isopycnals from the continental shelf to the adjacent deep ocean. The ex-

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port of particulate (POC) and dissolved (DOC) organic carbon from the shelf to the deep adjacent ocean across the continental shelf break is significant (e.g., Wollast 1998; Liu et al. 2000; Wollast and Chou 2001; Chen et al. 2003; Ducklow and McCallister 2004) and could in theory also drive a sink for atmospheric CO_2 over the shelf. Although the rate of final burial of organic matter on the continental slopes is recognized as relatively small (Wollast 1998; Wollast and Chou 2001 and references therein), the CO_2 produced in deep oceanic waters from the degradation of organic matter exported from continental shelves will to a large extent be ventilated back to the atmosphere in the open ocean. This leads to an underestimation of the sink of atmospheric CO_2 in the open ocean if the air-water CO_2 fluxes over continental shelves are not taken into account (Yool and Farsham 2001).

If the continental shelf CO_2 pump formulated by Tsunogai et al. (1999) is confirmed worldwide, it would have major implications on our understanding of the global carbon cycle and a significant revision of the estimate of the overall oceanic pump for atmospheric CO_2. It would imply an increase of 61% of the uptake of atmospheric CO_2 from the oceans, since open oceanic waters are estimated to absorb -1.56 Pg C yr^{-1} (Takahashi et al. [2002] revised climatology for reference year 1995 available from http://www.ldeo.columbia.edu/res/pi/CO2/).

It was established more than 30 years ago, by the pioneering studies of Park et al. (1969), Kelley and Hood (1971a), and Kelley et al. (1971), that some coastal ecosystems, such as estuaries and upwelling systems, behave (at least temporally) as strong sources of CO_2 to the atmosphere. A rigorous extrapolation of air-water CO_2 fluxes in the coastal ocean should take into account the potential latitudinal variability of air-water CO_2 fluxes (that has been documented in detail in open oceanic waters), and, more importantly, the diversity of coastal ecosystems with fundamentally contrasting carbon biogeochemical cycling.

This paper compiles current knowledge on air-water CO_2 fluxes in the major ecosystems of the coastal ocean and the main biogeochemical processes controlling them are briefly discussed. The first integration of CO_2 fluxes in the global ocean including coastal and open oceanic realms is also attempted. One of the aims of this tentative upscaling of air-water CO_2 fluxes in the coastal ocean is to identify the major pieces lacking from the jigsaw to allow a better constrained global integration in the future.

Synthesis

The coastal ocean is defined as the area extending from the shore to the continental shelf break, excluding continental slopes but including inner estuaries. The remaining oceanic waters are referred to as open ocean, the second component of what is referred to as global ocean. Data were gathered from literature in 8 main coastal ecosystems (inner estuaries, outer estuaries, whole estuarine systems, mangroves, salt marshes, coral reefs, upwelling systems, and open continental shelves). This list is not exhaustive but corresponds to a compromise between data availability and specificity of carbon cycling in these systems, and in particular air-water CO_2 fluxes. Table 1 summarizes partial pressure of CO_2 (pCO_2) and air-water CO_2 flux data in 44 coastal environments (also represented in Fig. 1). The majority of data in Table 1 are annually integrated CO_2 fluxes computed from field data (for a detailed literature survey of CO_2 data in coastal ecosystems excluding estuaries but including sites without a full annual coverage refer to Ducklow and McCallister [2004]). Air-water CO_2 fluxes derived from indirect approaches (mass balance calculations or numerical models) were not included in this compilation because they are prone to relatively large uncertainty. The net air-water CO_2 flux is the balance of numerous biogeochemical processes that in most coastal ecosystems are characterized by rates that are one order of magnitude higher than the net exchange of CO_2 across the air-water interface. The most straightforward and robust way to estimate air-water CO_2 fluxes relies on field pCO_2 data, although this approach also suffers from the reliability of gas transfer parameterizations and scaling problems. Mass balance calculations or numerical models are nevertheless essential to understand and evaluate the relative importance of the processes responsible for air-water CO_2 fluxes. Values for some study sites in Table 1 are not based on a full annual coverage, but from our understanding of carbon cycling and its seasonality in that given ecosystem, it was assumed that they give a reasonably good approximation of the direction and intensity of annual air-water CO_2 flux (in particular some sites in mangrove surrounding waters and inner estuaries). For some sites, pCO_2 field data were compiled from different publications and the annually integrated air-water CO_2 fluxes computed (as explained in the legend of Table 1).

Inner Estuaries

At the land-ocean interface, inner estuaries receive large amounts of dissolved and particulate matter, in particular organic and inorganic carbon,

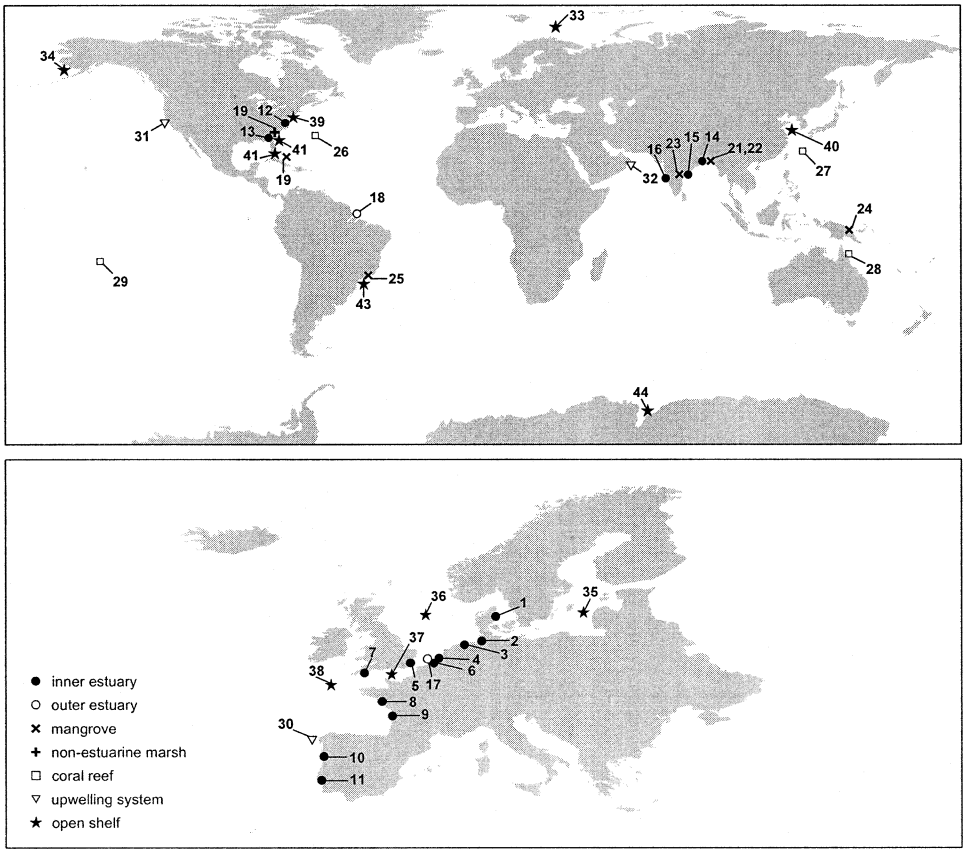

Fig. 1. Map showing location of coastal environments where air-water CO_2 fluxes have been satisfactorily integrated at annual scale. Numbers indicate locations named in first column of Table 1.

and nutrients carried by rivers. These are highly dynamic systems characterized by strong gradients of biogeochemical compounds, enhanced organic matter production and degradation processes, and intense sedimentation and resuspension. Terrestrial matter carried by rivers undergoes profound transformations in estuaries before reaching the adjacent coastal zone.

The relatively exhaustive definition of an inner estuary given by Cameron and Pritchard (1963, p. 306) was used: ''a semi-enclosed coastal body of water, which has free connection with the open sea, and within which seawater is measurably diluted with freshwater derived from land drainage.'' The upstream boundary of the inner estuary is the limit of the tidal influence (tidal river), where water currents and sedimentary processes become drastically different from those in the river. The lower boundary of the inner estuary is the geographic limit of the coast corresponding to the river mouth. Because inner estuaries exhibit a large diversity in terms of geomorphology, geochemistry and surface area of the drainage basin, freshwater discharge, and tidal influence, physical attributes are affected that strongly influence biogeochemical carbon and nutrient cycling, such as vertical stratification, longitudinal gradients, spatial extent, and residence time of freshwater.

Inner estuaries are net heterotrophic systems, where total respiration (R, sum of respiration by autotrophs and heterotrophs in both benthic and pelagic compartments) exceeds gross primary production (GPP), and where net ecosystem production (NEP = GPP − R) is <0. Gattuso et al. (1998a) reported an average NEP of -6 ± 2 mol C m^{-2} yr^{-1} in 21 estuaries worldwide. Caffrey (2004) reported an average NEP of -40 ± 24 mol C m^{-2} yr^{-1} in 42 United States estuaries. The ecosystem function of inner estuaries has been modified by human activities in a way that at present time is difficult to identify (Gattuso et al. 1998a; Smith et al. 2003; Gazeau et al. 2004a,b; Soetaert et al. 2004). Higher nutrient loadings due to human activities may have increased NEP, while degradation of anthropogenic organic carbon decreases NEP (Gattuso et al. 1998a). Overall, these ecosystems are sinks for organic matter, sources of inorganic nutrients and of CO_2 to the surrounding

TABLE 1. Range of pCO_2, air-water CO_2 fluxes, and gas transfer velocity parameterization (k) in coastal environments. The numbers in parentheses correspond to site identification in Fig. 1. Values in bold are for environments with full annual coverage. k wind parameterization after Carini et al. (1996) = C; Liss and Merlivat (1986) = LM; Nightingale et al. (2000) = N; Raymond et al. (2000) = R; Raymond and Cole (2001) = RC; Wanninkhof (1992) = W; Tans et al. (1990) = T; Wanninkhof and McGillis (1999) = WMcG. D denotes direct measurements with a floating dome.

Site	°E	°N	pCO_2 (ppm)	Air-Water CO_2 Fluxes (mol C m^{-2} yr^{-1})	k	Ref.
Inner estuaries						
Randers Fjord (1)	10.3	56.6	220–3400	4.4	D	Gazeau et al. (2004a)
Elbe (2)	8.8	53.9	580–1100	53.0	D	Frankignoulle et al. (1998)
Ems (3)	6.9	53.4	560–3755	67.3	D	Frankignoulle et al. (1998)
Rhine (4)	4.1	52.0	**545–1990**	**39.7**	D	Frankignoulle et al. (1998)
Thames (5)	0.9	51.5	**505–5200**	**73.6**	D	Frankignoulle et al. (1998)
Scheldt (6)	3.5	51.4	**125–9425**	**63.0**	D	Frankignoulle et al. (1998)
Tamar (7)	−4.2	50.4	**380–2200**	**74.8**	8.0 cm h^{-1}	Frankignoulle et al. (1998)
Loire (8)	−2.2	47.2	630–2910	64.4	13.0 cm h^{-1}/ D	Abril et al. (2003, 2004)
Gironde (9)	−1.1	45.6	**465–2860**	**30.8**	D	Frankignoulle et al. (1998)
Douro (10)	−8.7	41.1	1330–2200	76.0	D	Frankignoulle et al. (1998)
Sado (11)	−8.9	38.5	575–5700	31.3	D	Frankignoulle et al. (1998)
York River (12)	−76.4	37.2	350–1900	6.2	R	Raymond et al. (2000)
Satilla River (13)	−81.5	31.0	360–8200	42.5	12.5 cm h^{-1}	Cai and Wang (1998)
Hooghly (14)	88.0	22.0	**80–1520**	**5.1**	W	Mukhopadhyay et al. (2002)
Godavari (15)	82.3	16.7	220–500	5.5	RC	Bouillon et al. (2003)
Mandovi-Zuari (16)	73.5	15.3	**500–3500**	**14.2**	W	Sarma et al. (2001)
Outer estuaries						
Scheldt (17)	3.0	51.4	**50–700**	**1.1/1.9**	LM/W	Borges and Frankignoulle (2002a)
Amazon (18)	−50.0	1.0	**290–355**	**−0.5**	W	Körtzinger (2003)
Inner and outer estuaries (whole estuarine system)						
Scheldt	3.0	51.4	—	**7.3**	—	[1]Frankignoulle et al. (1998) and Borges and Frankignoulle (2002a)
Amazon	−50.0	1.0	—	**2.5**	—	[2]Richey et al. (1990) and Körtzinger (2003)
Non-estuarine salt marsh surrounding waters						
Duplin River (19)	−81.3	31.5	**500–3000**	**21.4/25.6**	W/RC	Wang and Cai (2004)
Mangrove surrounding waters						
Norman's Pond (20)	−76.1	23.8	385–750	5.0	C	Borges et al. (2003)
Mooringanga Creek (21)	89.0	22.0	800–1530	8.5	4.0 cm h^{-1}	Borges et al. (2003) based on Ghosh et al. (1987)
Saptamukhi Creek (22)	89.0	22.0	1080–4000	20.7	4.0 cm h^{-1}	Borges et al. (2003) based on Ghosh et al. (1987)
Gaderu Creek (23)	82.3	16.8	1380–4770	20.4	C	Borges et al. (2003)
Nagada Creek (24)	145.8	−5.2	540–1680	15.9	C	Borges et al. (2003)

TABLE 1. Continued.

Site	°E	°N	pCO_2 (ppm)	Air-Water CO_2 Fluxes (mol C m^{-2} yr^{-1})	k	Ref.
Itacuraçá Creek (25)	−44.0	−23.0	**660–7700**	**41.4**	4.0 cm h^{-1}	Borges et al. (2003) based on Ovalle et al. (1990)
Coral reefs						
Hog Reef (26)	−64.8	32.3	340–480	1.2	W	Bates et al. (2001)
Okinawa Reef (27)	127.5	26.0	95–950	1.8	LM	Ohde and van Woesik (1999)
Yonge Reef (28)	145.6	−14.6	250–700	1.5	D	Frankignoulle et al. (1996)
Moorea (29)	−149.8	−17.5	240–580	0.1	D	Gattuso et al. (1993, 1997) and Frankignoulle et al. (1996)
Upwelling systems						
Galician coast (30)	−9.2	42.5	**265–415**	**−1.3/−2.6**	LM/T	Borges and Frankignoulle (2002b)
California coast (31)	−122.0	36.8	**100–850**	**−0.5 (El Niño)/ 1.9 (La Niña)**	WMcG	Friederich et al. (2002)
Oman coast (32)	49.0	20.0	**365–660**	**0.9**	W	Goyet et al. (1998)
Open continental shelves						
Barents Sea (33)	30.0	75.0	**168–352**	**−2.8**	10.3	[3]Kaltin et al. (2002), Omar et al. (2003)
Bristol Bay (34)	−164	58.0	**111–450**	**−0.6**	10.3	[4]Kelly and Hood (1971b), Codispoti et al. (1986), Chen (1993), Murata and Takizawa (2002)
Baltic Sea (35)	20.0	57.0	**156–475**	**−1.5**	10.3	[5]Thomas and Schneider (1999), Schneier et al. (2003), and Kuss et al. (2004)
North Sea (36)	2.6	56.7	**145–495**	**−1.4**	WMcG	Thomas et al. (2004a)
English Channel (37)	−1.2	50.2	**200–500**	**0.0**	N	Borges and Frankignoulle (2003)
Gulf of Biscay (38)	−7.9	49.0	**260–460**	**−1.8/−2.9**	LM/W	Frankignoulle and Borges (2001)
U.S. Middle Atlantic Bight (39)	−74.5	38.5	**200–660**	**−0.7/−1.2**	LM/W	DeGranpre et al. (2002)
East China Sea (40)	125	32.0	**200–390**	**−1.2/−2.8**	LM/W	Wang et al. (2000)
U.S. South Atlantic Bight (41)	−80.6	31.0	**300–1200**	**2.5**	W	Cai et al. (2003)
Florida Bay (42)	−80.7	25.0	**325–725**	**1.7**	4.0 cm h^{-1}	Borges et al. (2003) based on Millero et al. (2001)
Southwest Brazilian coast (43)	−45.5	−25.0	**350–475**	**1.0**	10.3	[6]Ito et al. (2004)
Pryzd Bay (44)	78.9	−68.6	**50–325**	**−2.2**	W	[7]Gibson and Trull (1999)

[1] Using a flux of 63.0 mol C m^{-2} yr^{-1} and surface area of 220 km^2 for the inner estuary (Frankignoulle et al. 1998) and a flux of 1.5 mol C m^{-2} yr^{-1} and surface area of 2100 km^2 for the outer estuary (Borges and Frankignoulle 2002a).

[2] Using a flux of 164 mol C m^{-2} yr^{-1} (at Obidos, Richey et al. 1990) and surface area of 44,186 km^2 (from the river mouth to Obidos, based on Chapman et al. [2002], Seyler personal communication) for the inner estuary and a flux of −0.5 mol C m^{-2} yr^{-1} and surface area of 2.4×10^6 km^2 for the outer estuary (Körtzinger 2003).

[3] Using the average k value for continental shelves of 10.3 cm h^{-1} proposed by Tsunogai et al. (1999) and assuming a zero air-ice CO_2 flux (ice coverage based on data from the National Snow and Ice Data Center downloaded from http://nsidc.org/).

[4] Using the average k value for continental shelves of 10.3 cm h^{-1} proposed by Tsunogai et al. (1999) and assuming a zero air-ice CO_2 flux (ice coverage based on Walsh and Dieterle [1994]).

[5] Using the average k value for continental shelves of 10.3 cm h^{-1} proposed by Tsunogai et al. (1999).

[6] Using the average k value for continental shelves of 10.3 cm h^{-1} proposed by Tsunogai et al. (1999).

[7] Assuming a zero air-ice CO_2 flux during 297 d yr^{-1}.

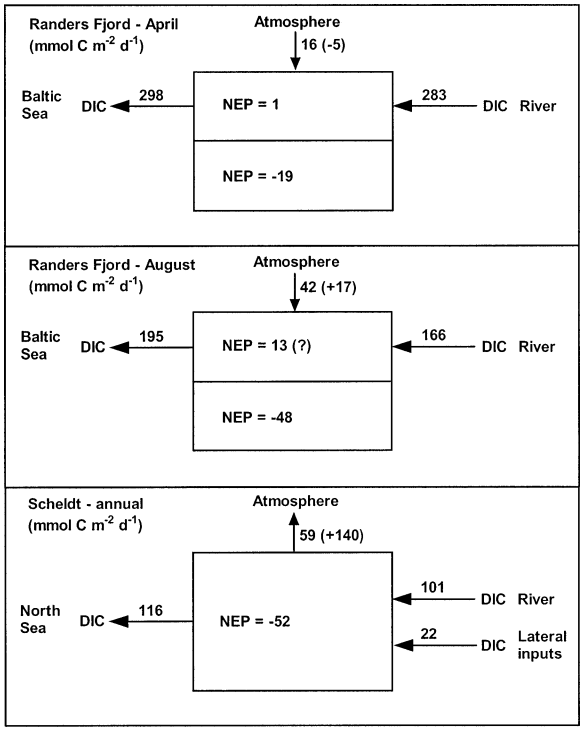

Fig. 2. Dissolved inorganic carbon (DIC) budgets for 2 cruises in the Randers Fjord and an annual budget in the Scheldt estuary, based on Gazeau et al. (2004a,b). Net ecosystem production (NEP) was estimated from up-scaled oxygen incubations in both estuaries. In the Randers fjord, NEP was up-scaled in the upper and bottom layers. Air-water CO_2 fluxes are computed as the closing term of the budget and compared with air-water CO_2 fluxes computed from pCO_2 measurements (numbers in brackets). Note that fluxes are expressed in mmol C m^{-2} d^{-1} unlike in other figures and tables.

water, and potential sources of CO_2 to the atmosphere.

All the estuaries listed in Table 1 are net sources of CO_2 to the atmosphere, so this behavior appears to be a general feature, although the range of reported air-water CO_2 fluxes encompasses one order of magnitude (in accordance with the recent review by Abril and Borges [2004] that also compiles studies in estuaries where pCO_2 was measured but air-water CO_2 fluxes were not reported). Highly polluted estuaries such as the Scheldt and relatively pristine ones such as the Satilla are oversaturated in CO_2 with respect to the atmosphere.

Among European estuaries, the Scheldt and Randers Fjord are at the higher and lower bounds, respectively, of reported air-water CO_2 fluxes. In both these estuaries a carbon budget was established from simultaneous and independent measurements of metabolic process rates and air-water CO_2 exchanges, based on the results from the recent European Union project EUROTROPH (Fig. 2). The Randers Fjord is a microtidal estuary characterized by a strong permanent stratification, while the Scheldt estuary is a macrotidal estuary characterized by a permanently well-mixed water column. Although on the whole the Randers Fjord is a net heterotrophic system, the mixed layer was net autotrophic while the bottom layer was strongly heterotrophic during both sampling cruises (Fig. 2). During the April cruise, the air-water CO_2 flux computed as the closing term of the carbon budget, agrees both in direction and order of magnitude with the air-water CO_2 flux computed from pCO_2 field data. This is not the case for the August cruise, but as discussed in detail by Gazeau et al. (2004b), the up-scaling of the pelagic O_2 incubations was probably unrealistic during this cruise. Other approaches applied by Gazeau et al. (2004b) give a mixed layer NEP of −48 and −61 mmol C m^{-2} d^{-1} for the Land-Ocean Interaction in the Coastal Zone (LOICZ) and Response Surface Difference approaches, respectively, that would correspond to a CO_2 emission of 77 and 90 mmol C m^{-2} d^{-1} to close the budget, in agreement both in direction and order of magnitude with the air-water CO_2 fluxes computed from pCO_2 field data. In the Scheldt estuary, the emission of CO_2 computed to close the annual carbon budget is in fair agreement with the air-water CO_2 fluxes computed from pCO_2 field data, both in terms of direction and order of magnitude. The emission of CO_2 from the Scheldt is almost 15 times higher than the one from the Randers Fjord (Table 1), although NEP is only 2 times lower in the Scheldt than in the Randers Fjord (Fig. 2). This can be attributed, at least partly, to the decoupling in the Randers Fjord of the production of organic matter in the mixed layer and its degradation in the bottom layer. In this way, the CO_2 produced by degradation processes will not be immediately available for exchange with the atmosphere in the Randers Fjord unlike the Scheldt estuary. The residence time of fresh water is much longer in the Scheldt (30–90 d) than in the Randers Fjord (5–10 d). For a similar NEP, the enrichment in DIC of estuarine waters and corresponding ventilation of CO_2 to the atmosphere will be more intense in the Scheldt than in the Randers Fjord. Ventilation of riverine CO_2 can contribute to the emission of CO_2 from inner estuaries but seems to be highly variable. It has been estimated by Abril et al. (2000) that the contribution is about 10% of the overall CO_2 emission from the Scheldt inner estuary. Based on the approach given by Abril et al. (2000), it can be estimated that in the Randers Fjord the ventilation of riverine CO_2 has a much larger contribution (more than 50%, 6.5 mmol C m^{-2} d^{-1}) to the average CO_2 emission from the estuary (12 mmol C m^{-2} d^{-1}). Note that lateral inputs of DIC in the

Scheldt estuary are significant when compared to the emission of CO_2 to the atmosphere. There is increasing evidence that this input term is highly significant in most estuaries (Cai and Wang 1998; Cai et al. 1999, 2000; Neubauer and Anderson 2003).

In inner estuaries, inputs of DIC, ecosystem metabolic rates, stratification of the water column, and residence time of water mass control the air-water gradient of pCO_2 (ΔpCO_2). The overall emission of CO_2 to the atmosphere is also strongly modulated by the gas transfer velocity (k). It was recently shown that k is site specific in inner estuaries (Kremer et al. 2003; Borges et al. 2004a). This is related to differences in the contribution of tidal currents to water turbulence at the interface and fetch limitation. The contribution to k from turbulence generated by tidal currents is negligible in microtidal inner estuaries but is substantial, at low to moderate wind speeds, in macrotidal inner estuaries (Zappa et al. 2003; Borges et al. 2004a). A given inner estuary is characterized by strong spatial gradients and seasonal variability of k related to differences in the relative contribution to turbulence at the air-water interface of wind speed, water currents, and topography (Borges et al. 2004b).

Outer Estuaries (River Plumes)

Ketchum (1983, p. 2) defines outer estuaries as ''plumes of freshened water which float on the more dense coastal sea water and they can be traced for many miles from the geographical mouth of the estuary.'' Some outer estuaries do not show either haline or thermal stratification, whatever the season, due to the combination of strong tidal currents and the shallowness of the area (e.g., Scheldt outer estuary). In this case, the outer estuary can be traced on the shelf by the gradient of salinity but also by the gradient of less conservative tracers such as water temperature, turbidity, chlorophyll *a,* inorganic nutrients, total alkalinity (TA), and chromophorid dissolved organic matter (Van Bennekom and Wetsteijn 1990; Hoppema 1991; Borges and Frankignoulle 1999; Del Vecchio and Subramaniam 2004). Outer estuaries are usually characterized by less intense carbon and nutrient cycling and air-water CO_2 areal fluxes than inner estuaries (Brasse et al. 1999, 2002; Reimer et al. 1999; Borges and Frankignoulle 2002a).

Undersaturation of CO_2 with respect to atmospheric equilibrium has been reported in various outer estuaries such as the plume of the Ganges, Mahanadi, Godavari, and Krishna rivers (Kumar et al. 1996), the Congo river (Bakker et al. 1999), the Yangtze and Yellow rivers (Chen and Wang 1999), and the Mississippi river (Cai 2003), although the low temporal coverage in these studies does not allow an annual integration of air-water CO_2 fluxes. Air-water CO_2 fluxes in outer estuaries are characterized by important spatial and seasonal variability, and in some cases with shifts between oversaturation and undersaturation of CO_2 (Hoppema 1991; Borges and Frankignoulle 1999, 2002a; Brasse et al. 2002). Significant interannual variability of DIC dynamics and air-water CO_2 fluxes has also been documented in the Scheldt outer estuary based on field (Borges and Frankignoulle 1999) and modeling (Gypens et al. 2004) approaches owing to changes in freshwater discharge and water temperature.

Air-water CO_2 fluxes have been satisfactorily integrated at an annual scale only in the Amazon and Scheldt outer estuaries (Table 1). In these two outer estuaries, the amplitude of the air-water CO_2 fluxes is similar but opposite in sign. The major difference between these two systems is that the Amazon outer estuary is a vertically haline stratified system that extends across the continental shelf break, while the Scheldt outer estuary is a permanently well-mixed system confined nearshore over the shelf. This difference is related to the huge freshwater discharge from the Amazon river (5520 $km^3\ yr^{-1}$) compared to the Scheldt river (4 $km^3\ yr^{-1}$), and to a lesser extent to the narrower shelf off the Brazilian coast than in the North Sea. In the Amazon outer estuary, stratification allows sedimentation of suspended particulate matter, and a lowering of light limitation of primary production. Production by photosynthesis of organic matter escapes the mixed (photic) layer by sedimentation across the pycnocline. The Amazon outer estuary efficiently exports organic matter to the deep ocean and acts as a sink for atmospheric CO_2 (Ternon et al. 2000; Körtzinger 2003). In the Scheldt outer estuary, the permanently well-mixed and turbulent water column prevents organic matter from escaping the surface layer by sedimentation and final carbon burial in the sediments is very low (Wollast 1983; de Haas et al. 2002). Although net lateral advective export of organic matter has not been estimated in the Scheldt outer plume, the input of organic and inorganic carbon from the Scheldt inner estuary and from the Belgian coast also contribute to the net annual emission of CO_2 to the atmosphere. Unlike the Amazon river plume, the Scheldt outer estuary is a net sink of organic matter and a source of atmospheric CO_2 (Borges and Frankignoulle 2002a).

Whole Estuarine Systems

Although outer estuaries are characterized by net annual air-water CO_2 areal fluxes that are usually one order of magnitude lower than inner es-

tuaries (Table 1), their surface area is much larger, and they have a significant effect on the overall budget of exchange of CO_2 with the atmosphere. The whole estuarine systems (outer and inner estuaries) of the Amazon and the Scheldt have relatively similar air-water CO_2 fluxes both in amplitude and direction (Table 1). In the case of the Scheldt, the emission of CO_2 to the atmosphere from the whole estuarine system is one order of magnitude lower than from the inner estuary (Table 1). This clearly shows that outer estuaries constitute a component of organic and inorganic carbon estuarine dynamics that cannot be neglected.

Mangrove and Salt Marsh Surrounding Waters

Mangrove and salt marsh surrounding waters are treated together because they occupy the same ecological niche and are fairly similar from the point of view of carbon cycling and air-water CO_2 exchanges. Salt marshes are intertidal habitats at temperate latitudes, whereas mangroves predominate in tropical and subtropical latitudes. Salt marshes are found in places where winter temperature is lower than 10°C, whereas mangroves occur where the minimal winter temperature is above 16°C (Chapman 1977). Salt marshes and mangrove forests co-occur at latitudes between 27° and 38° with marshes replacing mangroves as the dominant coastal intertidal vegetation at about 28° latitude (Alongi 1998).

Non-estuarine mangrove and salt marsh surrounding waters are significant sources of CO_2 to the atmosphere (Table 1). The overall ecosystem (aquatic, aboveground, and belowground compartments) is net autotrophic and a sink for atmospheric CO_2 due to large carbon fixation as plant biomass (Fig. 3). The air-water CO_2 fluxes are fueled by a net heterotrophy in aquatic and sediment compartments that receive large amounts of organic matter from the aboveground compartment, while aquatic primary production is usually low in most salt marsh and mangrove creeks, varying with geomorphology, water residence time, turbidity, and nutrient delivery (Alongi 1998; Gattuso et al. 1998a).

In both systems, water column DIC dynamics are significantly influenced by diagenetic degradation processes; during the ebb and at low tide, there is a strong influx of porewater (enriched in DIC, TA, and CO_2 and impoverished in oxygen) that mixes with the creek water, substantially affecting the chemical properties of the latter. During the flow, the migration of porewater towards the creek strongly decreases until it stops when the sediment surface is inundated at high tide (Ovalle et al. 1990; Borges et al. 2003; Wang and Cai 2004).

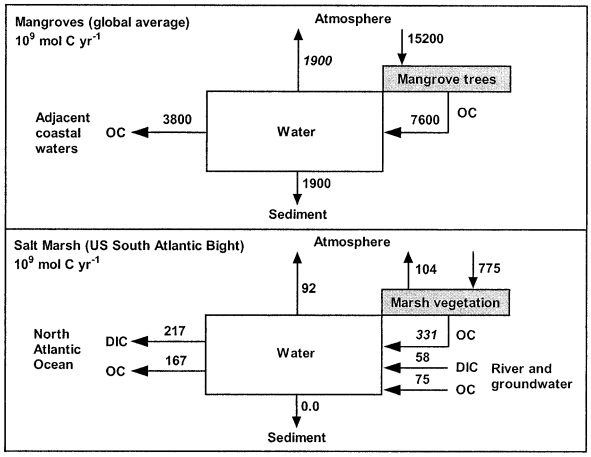

Fig. 3. Budgets of organic carbon (OC) and dissolved inorganic carbon (DIC) flows in mangroves (global budget given by Jennerjahn and Ittekkot [2002]) and the salt marshes of the U.S. South Atlantic Bight (based on Wang and Cai [2003] and Cai et al. [2003]). Values in italics are the closing terms for each budget. The values given by Jennerjahn and Ittekkot (2002) refer to the surface area of the intertidal region covered by mangroves and not the surface area of the waters surrounding mangrove forests. For the salt marshes of the U.S. South Atlantic Bight, the CO_2 emission from the water to the atmosphere was computed from the CO_2 fluxes for water above and surrounding the salt marshes, and using a total surface area of 4571 km^2 for salt marshes and a 1:5 ratio of water to marsh area (Wang and Cai 2003).

The air-water CO_2 flux is computed as the closing term in the global carbon budget of mangrove ecosystems proposed by Jennerjahn and Ittekkot (2002; Fig. 3). The export of organic matter to adjacent aquatic systems is prone to large uncertainty. If an air-water CO_2 flux of 18.7 mol C m^{-2} yr^{-1} is applied (mean of data from Table 1) then the export of organic matter to adjacent aquatic systems recomputed as the closing term is reduced by about 50% (1.98×10^{12} mol C yr^{-1}). In this calculation it is assumed that the air-water CO_2 flux is exclusively related to the degradation of mangrove-derived organic matter. This is not the case of most mangroves (if any) where the POC pool is a complex mixture with different origins (e.g., Bouillon et al. 2004a,b). Other carbon flows are not accounted for, such as the export of DIC to adjacent aquatic systems, the emission of CO_2 from air exposed sediments, and allochthonous inputs of DIC and organic matter that are highly significant in salt marshes (Fig. 3). This first order computation clearly illustrates the potential of air-water CO_2 fluxes as an important component in carbon cycling in mangrove ecosystems that has been so far overlooked.

In salt marshes the export of carbon as DIC to adjacent aquatic systems corresponds to more than twice the emission of CO_2 to the atmosphere (Fig.

3). There is no estimate of this term in mangroves, although it can be assumed to be significant since production of DIC in mangrove creeks has systematically been observed (Borges et al. 2003; Bouillon et al. 2003; Frankignoulle et al. 2003). The export of DIC from mangroves does not seem to significantly affect the air-water CO_2 fluxes in the adjacent aquatic ecosystem where the DIC is diluted. Bouillon et al. (2003) and Borges et al. (2003) observed in India and Papua New Guinea, respectively, that DIC and pCO_2 values are much higher in the mangrove creeks than in the adjacent aquatic systems. This is also confirmed by the work of Ovalle et al. (1999) who concluded that mangrove forests do not significantly affect the distribution of DIC over the shelf waters of Eastern Brazil, even at stations located 2 km away from the mangrove fringe. Biswas et al. (2004) reported pCO_2 values ranging from 154 to 796 ppm and an annual air-water CO_2 flux of 0.15 mol C m^{-2} yr^{-1} (computed with the Liss and Merlivat [1986] k parameterization) at the fringe of the Sundarban mangrove forest that are much lower than the values within two creeks (Mooringanga and Saptamukhi) in the same region (Table 1).

Coral Reefs

Coral reefs are carbonate structures dominated by scleractinian corals and algae, mostly distributed in the tropics (33.5°N, 31.5°S). Coral reefs thrive in low turbidity, oligotrophic waters with an annual minimum temperature of 18°C. They display high rates of organic carbon metabolism and calcification. Despite high rates of GPP and R, NEP is close to zero (Gattuso et al. 1998a). Coral reefs represent about 2% of the surface area of continental shelves but account for about 33% and 50% of the production and accumulation of particulate inorganic carbon over continental shelves (Milliman 1993). The CO_2 fixation by NEP is low, but the high rates of calcification lead to a release of CO_2 to the surrounding water according to: $Ca^{2+} + 2HCO_3^- \equiv CaCO_3 + CO_2 + H_2O$. As CO_2 interacts through thermodynamic equilibrium with the bases present in seawater (buffer effect), CO_2 increases by 0.6 mol for each mole of calcium carbonate ($CaCO_3$) precipitated in standard seawater (salinity = 35, temperature = 25°C, TA = 2370 μmol kg^{-1}, pCO_2 = 365 ppm). The ratio of CO_2 production to $CaCO_3$ precipitation depends in general on the thermodynamic equilibrium and in particular on temperature and salinity (Ware et al. 1992; Frankignoulle et al. 1994).

Based on global estimates of net calcification and NEP, Ware et al. (1992) computed a potential CO_2 release to the surrounding water from the balance of organic metabolism and calcification ranging from 3.0 to 11.3 mol C m^{-2} yr^{-1}. These estimates are higher than those reported in Table 1 because these systems are not closed and oceanic water permanently circulates across the reef system. The actual air-sea CO_2 flux will be strongly dependant on the residence time of the water mass, itself a function of the reef geomorphology (fringing, barrier, or atoll coral reef system), and water current patterns in the adjacent oceanic waters.

There has been a debate concerning the role of coral reef systems as sources or sinks of atmospheric CO_2 (Kayanne et al. 1995; Gattuso et al. 1996; Kawahata et al. 1999; Suzuki et al. 2001). Gattuso et al. (1996, 1999) have argued that fringing reefs under the influence of human pressure have shifted from a coral-dominated to a macroalgal-dominated state, as in the case of Shiraho reef, Ryukyu Islands, studied by Kayanne et al. (1995). This would lead to an increase of NEP and a decrease of calcification and possibly a shift from a source to a sink for atmospheric CO_2. Besides the metabolic processes occurring in the coral reef system and the residence time of the water mass, the actual flux of CO_2 across the air-water interface is further modulated by the ΔpCO_2 of the incoming oceanic water. The latter will be prone to seasonal variability due to biogeochemical processes independent from those occurring in the coral reef system.

On an annual scale, tropical and subtropical oceanic waters are sources of CO_2 (0.35 mol C m^{-2} yr^{-1}, ΔpCO_2 = 11 ppm, Takahashi et al. 2002 revised climatology). Based on the difference of pCO_2 between offshore and reef waters compiled by Suzuki and Kawahata (2003) in 9 coral reef systems and adding the data from Bates (2002) at Hog Reef, it can be estimated that incoming oceanic waters are enriched on average by 12 ppm during the transit through coral reef systems. A global emission of CO_2 from coral reef systems of about 0.73 mol C m^{-2} yr^{-1} can be roughly estimated, a value within the range of observations reported in Table 1.

Upwelling Systems

Upwelling systems are characterized by high primary production rates ranging from 5 to 170 mol C m^{-2} yr^{-1} off the Moroccan and Chilean coasts, respectively (Walsh 1988), making these areas sites of significant carbon fluxes across the continental shelf margin. During upwelling events, these systems are devoid of slope currents (a permanent feature of other marginal continental shelves) that hamper exchanges of matter from the continental shelf to the open ocean across the continental slope. These systems also usually develop upwelling

TABLE 2. Comparison in 3 upwelling systems of DIC and NO_3^- concentrations of upwelled water and upwelling index (UI). 1 = Sarma (2003); 2 = van Geen et al. (2000); 3 = Borges (unpublished, OMEX II data set); 4 = Chen et al. (2003); 5 = Álvarez-Salgado et al. (2002).

	Oman Coast	California Coast	Galician Coast
DIC (μmol kg^{-1})	2175 (1)	2160 (2)	2118 (3)
NO_3^- (μmol kg^{-1})	10 (4)	23 (4)	9 (5)
UI (m^3 s^{-1} km of coast^{-1})	5000 (4)	850 (4)	270 (5)
DIC input (mol d^{-1} km of coast^{-1})	9.7×10^8	1.6×10^8	5.1×10^7
NO_3^- input (mol d^{-1} km of coast^{-1})	4.4×10^6	1.7×10^6	2.2×10^5

filaments that are very efficient structures for the export of organic carbon as DOC and suspended POC to the adjacent deep ocean (Álvarez-Salgado et al. 2001, 2003).

Coastal upwelling areas are known to show oversaturation of CO_2 with respect to atmospheric equilibrium due to the input of CO_2-rich deep waters. The input of nutrients from upwelling fuels primary production that in turn lowers pCO_2 values. Each of these two processes has an opposing effect on the ΔpCO_2. In the Peruvian and Chilean coastal upwelling systems, which are known to be among the most productive oceanic areas worldwide, huge oversaturation of CO_2 with respect to the atmosphere has been reported with pCO_2 values up to 1,200 ppm, although low values down to 140 ppm have also been observed in relation to primary production (Kelley and Hood 1971a; Simpson and Zirino 1980; Copin-Montégut and Raimbault 1994; Torres et al. 2002, 2003). Other upwelling systems show a lesser range of variation, 100–850 ppm off the California coast (Simpson 1984; van Geen et al. 2000; Friederich et al. 2002), 300–450 ppm off the Mauritanian coast (Copin-Montégut and Avril 1995; Lefèvre et al. 1998; Bakker et al. 1999), and 365–750 ppm off the Oman coast (Körtzinger et al. 1997; Goyet et al. 1998; Lendt et al. 1999; Sabine et al. 2000; Lendt et al. 2003).

The distribution of DIC in upwelling systems is characterized by strong spatial heterogeneity as illustrated by high resolution surface mapping off the Portuguese, Californian, and Galician coasts (respectively, Pérez et al. 1999; van Geen et al. 2000; Borges and Frankignoulle 2002b). This spatial heterogeneity is usually related to topographic features that lead to enhanced upwelling at capes. The width of the continental shelf also determines the ratio of the volume of upwelled water to the volume of water on the shelf, which depends on the ratio between the surface area and the length of the shelf break. This has significant effects on temperature and DIC distributions over the shelf (Borges and Frankignoulle 2002c).

Biogeochemical cycling and air-water CO_2 fluxes vary at two distinct temporal scales. At a seasonal scale, the variability is related to the alternation of upwelling and non-upwelling (or downwelling) seasons. During the upwelling season, the variability is related to the oscillation between upwelling and upwelling-relaxation events, which have a periodicity ranging from 14 d off the Galician coast (Álvarez-Salgado et al. 1993) to 2 d off the Chilean coast (Torres et al. 1999).

Air-water CO_2 fluxes have been satisfactorily integrated in 3 coastal upwelling systems off the Galician, California, and Oman coasts (Table 1). The upwelling system off the Galician coast behaves as a sink for atmospheric CO_2, while the other 2 upwelling systems behave as sources for atmospheric CO_2. Concentrations of DIC and nitrate (NO_3^-) and Upwelling Index are significantly higher in the upwelling systems off the Oman and California coasts than the one off the Galician coast (Table 2). Off the Galician coast, at the end of an upwelling-relaxation event (end of the upwelling cycle), the surface water is depleted in nutrients and undersaturated with respect to atmospheric CO_2 (Álvarez-Salgado et al. 2001; Borges and Frankignoulle 2001, 2002b,c). In the upwelling systems off the Oman and California coasts, the input of DIC and NO_3^- are so intense (Table 2), that primary production probably does not deplete surface waters in nutrients and does not induce a significant undersaturation with respect to atmospheric CO_2.

Off the Galician coast, large upwelling filaments are characterized by stronger undersaturation with respect to atmospheric CO_2 than offshore waters, affecting significantly the overall budget of air-water CO_2 fluxes in noncoastal (offshore) waters (Borges and Frankignoulle 2001, 2002b,c). Off the Oman coast, upwelling filaments have been shown to be oversaturated in CO_2 with respect to atmospheric CO_2 (Lendt et al. 1999, 2003). These structures deserve further research since they actively link the coastal and open oceans and are efficient exporters of organic matter (Álvarez-Salgado et al. 2001).

Open Continental Shelves

Open continental shelves are defined as the coastal zones not comprised in the 7 ecosystems discussed above. Air-water CO_2 fluxes have been

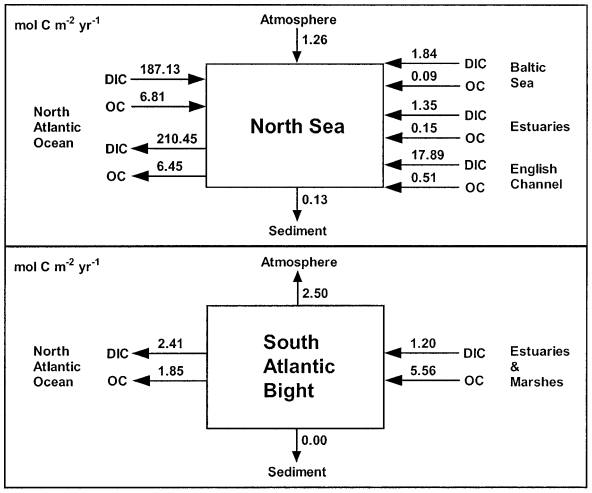

Fig. 4. Budgets of organic carbon (OC) and dissolved inorganic carbon (DIC) flows in the North Sea (Thomas et al. 2004b) and the U.S. South Atlantic Bight (Cai et al. 2003). Air-water CO_2 fluxes are computed as the closing term in the North Sea budget and are computed from pCO_2 measurements in the U.S. South Atlantic Bight budget. Thomas et al. (2004a) provide an estimate of air-water CO_2 fluxes of -1.38 mol C m^{-2} yr^{-1} for the North Sea based on pCO_2 measurements.

satisfactorily integrated in 12 open continental shelves, including a semi-enclosed sea (Baltic Sea) and marginal seas (Table 1). At high latitudes (Barents Sea, Bristol Bay, and Pryzd Bay) and at temperate latitudes (Baltic Sea, North Sea, Gulf of Biscay, and U.S. Middle Atlantic Bight), open continental shelves behave as sinks for atmospheric CO_2 at an annual rate similar to the one reported in the East China Sea. Subtropical and tropical open continental shelves (U.S. South Atlantic Bight, Florida Bay, and Southwest Brazilian coast) behave as significant sources for atmospheric CO_2. Oversaturation with respect to atmospheric CO_2 has also been reported at subtropical latitudes in the Southwest Florida shelf (Clark et al. 2004) and at tropical latitudes in the Eastern Brazil shelf (Ovalle et al. 1999), although the low temporal coverage in these studies does not allow an annual integration of air-water CO_2 fluxes.

Figure 4 compares DIC and organic carbon areal fluxes in the North Sea and the U.S. South Atlantic Bight. Both systems export carbon (DIC and organic carbon) to the adjacent deep ocean but behave differently from the point of view of air-water CO_2 exchange. River inputs of organic matter are 37 times higher in the U.S. South Atlantic Bight than in the North Sea. Total inputs of organic matter (rivers, Baltic Sea, and English Channel) are 7 times smaller in the North Sea than in the U.S. South Atlantic Bight. The net export of carbon (DIC and organic carbon) to the Atlantic Ocean is about 5 times higher in the North Sea (22.96 mol C m^{-2} yr^{-1}) than in the U.S. South Atlantic Bight (4.26 mol C m^{-2} yr^{-1}). On one hand the North Sea receives less organic carbon from external sources and on the other hand exports more efficiently carbon to the deep adjacent ocean. Note that according to the budgets in Fig. 4 both systems are net heterotrophic but organic carbon consumption is almost 4 times more intense in the U.S. South Atlantic Bight (3.71 mol C m^{-2} yr^{-1}) than in the North Sea (0.98 mol C m^{-2} yr^{-1}).

Another major difference between these two systems is that the North Sea is seasonally stratified while the U.S. South Atlantic Bight is permanently well mixed. In a seasonally stratified system, organic matter produced in the mixed layer can escape across the pycnocline and will be degraded in the bottom water column. The deep bottom water when circulating out of the system exports carbon as DIC to the adjacent deep ocean (this corresponds to the ''continental shelf pump'' as formulated by Tsunogai et al. 1999, p. 701). In a permanently well-mixed system the decoupling of production and degradation of organic carbon across the water column does not occur, and it will export DIC less efficiently. The CO_2 produced by degradation processes will also be to a large extent ventilated back to atmosphere over the continental shelf. This could also explain why the English Channel is not a significant sink for atmospheric CO_2 unlike other temperate continental shelves (Table 1), since it is also a permanently well-mixed system. In the English Channel, the amount of CO_2 fixed annually by pelagic new production is equivalent to the amount of CO_2 released by calcification from the extensive brittle star populations (Borges and Frankignoulle 2003).

High latitude continental shelves behave as significant sinks for atmospheric CO_2 (Table 1). The most comprehensive study in these regions is the annual cycle at Pryzd Bay, Antarctica, by Gibson and Trull (1999). In spring, pCO_2 decreases under the sea ice due to primary production occurring within or on the bottom of the ice, and can reach record low values of 46 ppm. When the sea ice breaks, surface waters are undersaturated in CO_2 and pCO_2 further decrease due to pelagic primary production. During the ice free periods, surface waters absorb atmospheric CO_2 at very high rates, on average -11.9 mol C m^{-2} yr^{-1}. When sea ice forms again, pCO_2 increases slowly due to degradation of organic matter and the input of CO_2-rich circumpolar deep water, according to Gibson and Trull (1999). In Brystol Bay, Western Bering Sea, during winter surface waters uncovered by sea ice are oversaturated in CO_2 in relation to the destratification of the water column and input to the surface of DIC rich deeper waters (Walsh and Dieterle

TABLE 3. Air-water CO_2 flux in open oceanic waters and major coastal ecosystems (excluding inner estuaries and salt marshes), by latitudinal bands of 30°. Surface areas of coastal ecosystems are based on Walsh (1988) and Gattuso et al. (1998a). 1 = Takahashi et al. (2002) revised climatology for year 1995 (downloaded from http://www.ldeo.columbia.edu/res/pi/CO2/); 2 = Average of fluxes in Barents Sea, Bristol Bay, and Pryzd Bay (Table 1); 3 = Surface area weighted average of fluxes off the Galician coast (90,000 km^2 = Iberian upwelling system), California coast (La Niña year, 336,000 km^2), and Oman coast (131,000 km^2; Table 1); 4 = Surface area weighted average of fluxes in Baltic Sea (128,727 km^2), North Sea (511,540 km^2), English Channel (82,600 km^2), Gulf of Biscay (270,000 km^2), U.S. Middle Atlantic Bight (63,100 km^2), and East China Sea (900,000 km^2; Table 1); 5 = Average of fluxes in Hog Reef, Okinawa Reef, Yonge Reef, and Moorea (Table 1); 6 = Average of fluxes in Norman's Pond, Mooringanga Creek, Saptamikhi Creek, Gaderu Creek, Nagada Creek, and Itauraça Creek (Table 1); 7 = Average of fluxes in U.S. South Atlantic Bight, Florida Bay, and Southwest Brazilian coast (Table 1). Fluxes were averaged when different gas transfer velocities were used. Small differences between total and subtotal values and the sum of individual fluxes are related to rounding of numbers.

	Surface (10^6 km^2)	Air-Water CO_2 Flux (mol C m^{-2} yr^{-1})		Air-Water CO_2 Flux (Pg C yr^{-1})	
60°–90°					
Open oceanic waters	30.77	−0.75 (1)		−0.28	
Open shelf	7.19	−1.88 (2)		−0.16	
Subtotal	37.96	−0.96		−0.44	
30°–60°					
Open oceanic waters	122.44	−1.40 (1)		−2.06	
Coastal upwelling systems	0.24	1.09 (3)	−1.69	0.003	−0.308
Open shelf	14.90	−1.74 (4)		−0.31	
Subtotal	137.58	−1.43		−2.36	
30°N–30°S					
Oceanic waters	182.77	0.35 (1)		0.77	
Coastal upwelling systems	1.25	1.09 (3)		0.02	
Coral reefs	0.62	1.52 (5)	2.40	0.01	0.10
Mangroves	0.20	18.66 (6)		0.04	
Open shelf	1.60	1.74 (7)		0.03	
Subtotal	186.44	0.39		0.7	
Coastal ocean	26	−1.170		−0.37	
Open ocean	336	−0.388		−1.56	
Global ocean	362	−0.444		−1.93	

1994). Sea ice coverage in Brystol Bay lasts about 32 d per year compared to 297 d in Pryzd Bay. Sea ice strongly affects air-water CO_2 exchange as well as the physical and biogeochemical processes of the underlying water, which in turn affect pCO_2. The duration of sea ice cover should have a critical influence on overall air-water CO_2 fluxes; at high latitudes, it is wise to distinguish between high and low sea ice cover over continental shelves. The effect on air-water CO_2 fluxes of sea ice and its interaction with the water column is more complex than the "seasonal rectification hypothesis" first introduced by Yager et al. (1995, p. 4389), as discussed later.

Tentative Up-scaling and Global Integration

To up-scale CO_2 fluxes in the coastal ocean, the fluxes from Table 1 were averaged as explained in the legends of Tables 3 and 4, to characterize 6 ecosystems: coastal upwelling systems, inner estuaries, non-estuarine salt marshes, coral reefs, mangroves, and open continental shelves. For a given ecosystem the air-water CO_2 fluxes were averaged unless reliable individual surface areas were available and a surface area weighted average was used instead (details in legends of Tables 3 and 4). Surface area estimates for each ecosystem, by latitudinal bands of 30°, were compiled from Woodwell et al. (1973), Walsh (1988), and Gattuso et al. (1998a). In absence of a global estimate of surface area for outer estuaries and whole estuarine systems, these two ecosystems were not included in the up-scaling. The choice of latitudinal bands is based on the natural delimitation of certain ecosystems, such as coral reefs, mangroves, and salt marshes, and also because in high-latitude continental shelves (60°–90°), light availability strongly limits primary production (phototrophic) and the presence of extensive sea ice has a significant effect on air-water CO_2 fluxes, as discussed above. Two up-scaling attempts were performed, one excluding inner estuaries and non-estuarine salt marshes (Table 3) and another including inner estuaries and non-estuarine salt marshes (Table 4), since there is considerable uncertainty regarding the surface area estimate of these two ecosystems, as discussed later.

Based on the up-scaling attempt that excludes inner estuaries and salt marshes (Table 3), the coastal ocean behaves as a sink for atmospheric

TABLE 4. Air-water CO_2 flux in open oceanic waters and major coastal ecosystems (including inner estuaries and salt marshes) by latitudinal bands of 30°. Surface areas of coastal ecosystems are based on Walsh (1988) and Gattuso et al. (1998a). Surface area of inner estuaries was computed using the total surface area of 0.9433×10^6 km^2 from Woodwell et al. (1973) that was distributed in latitudinal bands of 30° based on coastline length from World Vector Shoreline (Soluri and Woodson 1990) implemented in the LOICZ database, downloaded from http://hercules.kgs.ukans.edu/hexacoral/envirodata/main.htm. Surface area of non-estuarine salt marsh surrounding waters is arbitrarily estimated as 50% of the total salt marsh area of 0.2787×10^6 km^2 from Woodwell et al. (1973). 1 = Takahashi et al. (2002) revised climatology for year 1995 (downloaded from http://www.ldeo.columbia.edu/res/pi/CO2/); 2 = Surface area weighted average of fluxes in Randers Fjord (23 km^2), Elbe (327 km^2), Ems (140 km^2), Rhine (193 km^2), Thames (215 km^2), Scheldt (220 km^2), Tamar (19 km^2), Loire (110 km^2), Gironde (442 km^2), Douro (2 km^2), Sado (102 km^2), and York River (180 km^2); 3 = Average of fluxes in Barents Sea, Bristol Bay, and Pryzd Bay (Table 1); 4 = Duplin River (Table 1); 5 = Surface area weighted average of fluxes off the Galician coast (90,000 km^2 = Iberian upwelling system), California coast (La Niña year, 336,000 km^2), and Oman coast (131,000 km^2; Table 1); 6 = Surface area weight average of fluxes in Balic Sea (128,727 km^2), North Sea (511,540 km^2), English Channel (82,600 km^2), Gulf of Biscay (270,000 km^2), U.S. Middle Atlantic Bight (63,100 km^2), and East China Sea (900,000 km^2; Table 1); 7 = Average of fluxes in Satilla River, Hooghly, Godavari, and Mandovi-Zuari (Table 1); 8 = Average of fluxes in Hog Reef, Okinawa Reef, Yonge Reef, and Moorea (Table 1); 9 = Average of fluxes in Norman's Pond, Mooringanga Creek, Saptamikhi Creek, Gaderu Creek, Nagada Creek, and Itauraça Creek (Table 1); 10 = Average of fluxes in U.S. South Atlantic Bight, Florida Bay, and Southwest Brazilian coast (Table 1). Fluxes were averaged when different gas transfer velocities were used. Small differences between total and subtotal values and the sum of individual fluxes are related to rounding of numbers.

	Surface (10^6 km^2)	Air-Water CO_2 Flux (mol C m^{-2} yr^{-1})		Air-Water CO_2 Flux (Pg C yr^{-1})	
60°–90°					
Open oceanic waters	30.77	−0.75 (1)		−0.28	
Inner estuaries	0.40	46.00 (2)	0.78	0.22	0.7
Open shelf	6.79	−1.88 (3)		−0.15	
Subtotal	37.96	−0.46		−0.21	
30°–60°					
Open oceanic waters	122.44	−1.40 (1)		−2.05	
Inner estuaries	0.29	46.00 (2)		0.16	
Non-estuarine salt marshes	0.14	23.45 (4)	−0.55	0.04	−0.10
Coastal upwelling systems	0.24	1.09 (5)		0.003	
Open shelf	14.47	−1.74 (6)		−0.30	
Subtotal	137.58	−1.30		−2.15	
30°N–30°S					
Open oceanic waters	182.77	0.35 (1)		0.77	
Inner estuaries	0.25	16.83 (7)		0.05	
Coastal upwelling systems	1.25	1.09 (5)		0.02	
Coral reefs	0.62	1.52 (8)	3.45	0.01	0.15
Mangroves	0.20	18.66 (9)		0.04	
Open shelf	1.35	1.74 (10)		0.03	
Subtotal	186.44	0.41		0.92	
Coastal ocean	26	0.381		0.12	
Open ocean	336	−0.388		−1.56	
Global ocean	362	−0.331		−1.44	

CO_2 (−1.17 mol C m^{-2} yr^{-1}) and the uptake of atmospheric CO_2 by the global ocean increases by 24% (−1.93 versus −1.56 Pg C yr^{-1}). The inclusion of the coastal ocean increases the estimates of CO_2 uptake by the global ocean by 57% for high latitude areas (−0.44 versus −0.28 Pg C yr^{-1}) and by 15% for temperate latitude areas (−2.36 versus −2.06 Pg C yr^{-1}). At subtropical and tropical latitudes, the contribution from the coastal ocean increases the CO_2 emission from the global ocean by 13% (0.87 versus 0.77 Pg C yr^{-1}). At subtropical and tropical latitudes, the coastal environment that has the largest contribution to the increase of the CO_2 emission from the global ocean is mangrove surrounding waters (5%), followed by open continental shelves (4%), coastal upwelling systems (3%), and coral reefs (1%). Coastal upwelling systems have a moderate effect on air-water CO_2 budget of the coastal ocean and a low effect on the budget of the global ocean. Using the air-water CO_2 flux from the Galician coast (−2.0 mol C m^{-2} yr^{-1}) leads to an increase of the uptake of CO_2 from the coastal ocean of 14% (−0.42 Pg C yr^{-1}) but only of 3% from the global ocean (−1.98 Pg C yr^{-1}). Using the air-water CO_2 flux from the California coast (2.2 mol C m^{-2} yr^{-1}) leads to a decrease of the uptake of CO_2 from the coastal ocean of 6% (−0.35 Pg C yr^{-1}) but only 1% from the global ocean (−1.90 Pg C yr^{-1}).

Based on the up-scaling attempt that includes inner estuaries and non-estuarine salt marshes (Table 4), the coastal ocean behaves as a source for atmospheric CO_2 (0.38 mol C m^{-2} yr^{-1}) and the uptake of atmospheric CO_2 from the global ocean

decreases by 12% (−1.44 versus −1.56 Pg C yr^{-1}). The emission of CO_2 from non-estuarine salt marshes (0.04 Pg C yr^{-1}) is equivalent to the one from mangrove surrounding waters but remains modest compared to the emission of CO_2 from inner estuaries globally (0.43 Pg C yr^{-1}) or at temperate latitudes exclusively (0.16 Pg C yr^{-1}). At high and subtropical and tropical latitudes, the coastal ocean behaves as a source for atmospheric CO_2 but at temperate latitudes, it still behaves as a moderate sink for atmospheric CO_2. At temperate latitudes, the inclusion of coastal ocean increases the CO_2 uptake by the global ocean by 5% compared to 15% when estuaries and non-estuarine salt marshes are excluded (Table 3). At high latitudes, the inclusion of coastal ocean decreases the CO_2 uptake by the global ocean by 25%. At subtropical and tropical latitudes, the contribution from the coastal ocean increases by 20% the CO_2 emission from the global ocean, compared to 13% when estuaries and non-estuarine salt marshes are excluded (Table 3).

Concluding Remarks

At this point, the major pieces lacking from the jigsaw puzzle will be identified and can be separated into the detail of the up-scaling procedure (i.e., further classification within each given ecosystem) and lack of characterization (in space and time) of air-water CO_2 fluxes. Future changes of air-water CO_2 fluxes in the coastal ocean will also be briefly discussed.

Detail of the Up-scaling Procedure

Due to the relative paucity of available data, the up-scaling of air-water CO_2 fluxes in the coastal ocean was attempted based on a limited classification of ecosystems and simple surface area estimates divided in 30° latitudinal bands. The classification of continental shelves can be further detailed, based on the geometry (broad shelves: >100 km and narrow shelves: <50 km), the river discharge of sediments (high: >108 tons yr^{-1} and low: <106 tons yr^{-1}), and freshwater discharge (Wollast and Mackenzie 1989; Mackenzie 1991; Wollast 1998).

In inner and outer estuaries and open continental shelves, presence or absence of a seasonal or permanent stratification seems to be a critical factor controlling air-water CO_2 fluxes. In stratified systems the organic carbon produced by primary production can escape the surface layer across the pycnocline and the CO_2 produced by degradation processes in the bottom waters is not readily available for exchange with the atmosphere. Stratified (microtidal) estuaries are lower sources of atmospheric CO_2 than well-mixed (macrotidal) estuaries. In permanently well-mixed systems, the decoupling between production and degradation of organic matter can occur in time but does not occur across the water column. These systems are sources of CO_2 to the atmosphere or neutral, based on the data available to date. Shallow continental shelves are usually well-mixed systems and in these systems the overall effect of benthic calcification can be stronger than in deeper continental shelves, as illustrated by the neutral air-water CO_2 fluxes in the English Channel. In coral reefs, the data compiled by Suzuki and Kawatha (2003) suggest that fringing reefs are lower sources or even sinks for atmospheric CO_2 compared to barrier and atoll reefs systems. In coral reefs, residence time and volume of the water mass and calcification rates are the main controlling factors of air-water CO_2 fluxes. In mangrove and salt marsh surrounding waters, there are not enough data to determine the factors responsible for the intersite variability of air-water CO_2 fluxes, but the combination of residence time and volume of the water mass and organic carbon delivery to the creeks seems to be the most likely candidate.

In the future, up-scaling of CO_2 fluxes in the coastal ocean besides obvious latitudinal partitioning (high latitude, temperate, and subtropical-tropical) could be further detailed at least according to: macrotidal versus microtidal for estuaries; shallow versus deep and well-mixed versus (seasonally or permanently) stratified for temperate and subtropical-tropical open continental shelves; high versus low sea ice annual coverage for high latitude open continental shelves; high versus low Upwelling Index for upwelling systems; and fringing versus barrier-atoll for coral reefs.

Figure 5 shows that about 60% of freshwater discharge and an equivalent fraction of riverine total organic carbon (TOC = DOC + POC) delivery occur at subtropical and tropical latitudes. Counterintuitively, less than 12% of the CO_2 emission from inner estuaries occurs at these latitudes and the highest emission of CO_2 occurs at high latitudes, although characterized by the lowest freshwater discharge and riverine TOC delivery. There is also a counterintuitive anticorrelation between the latitudinal distribution of freshwater discharge and the surface area of inner estuaries. Although no data of air-water CO_2 fluxes are available in high latitude inner estuaries, the values used at temperate and subtropical and tropical latitudes can be considered as robust. Discrepancies revealed in Fig. 5 are probably due to the uncertainty on the estimate of the surface area of inner estuaries and on its partitioning by latitudinal bands, rather than on the air-water CO_2 areal fluxes. The estimate of surface area of inner estuaries given by

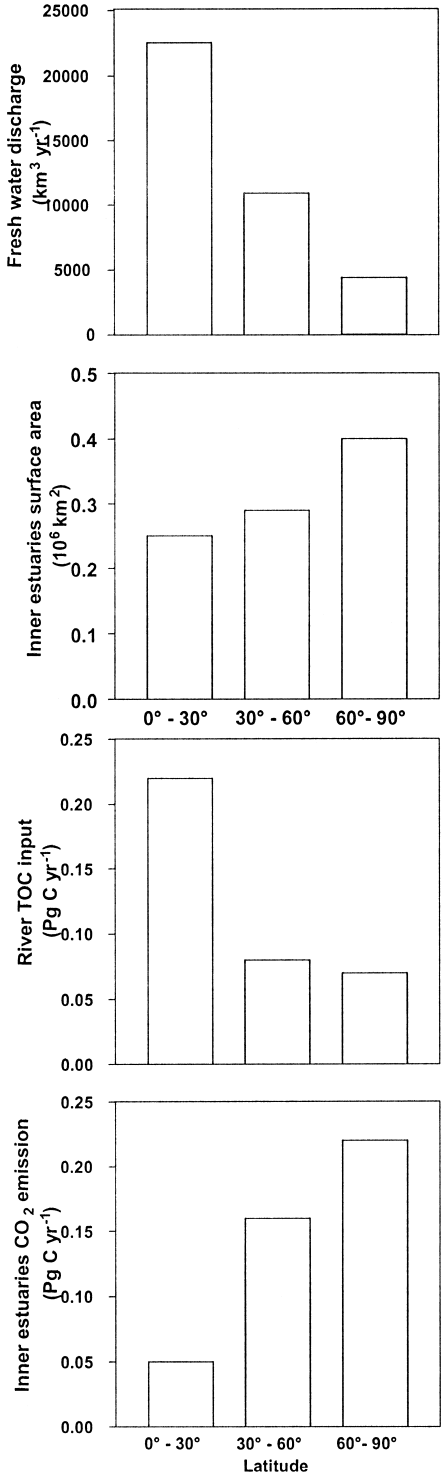

Fig. 5. Latitudinal distribution of the freshwater discharge (based on Dai and Trenberth [2002]), of the inner estuaries surface area, river total organic carbon (TOC) inputs (based on Ludwig et al. [1996]), and CO_2 emission from inner estuaries (Table 4). Surface area of inner estuaries was computed using the total surface area of 0.9433×10^6 km² from Woodwell et al. (1973) that was distributed in latitudinal bands of 30° based on coastline length from World Vector Shoreline (Soluri and Woodson 1990) implemented in the LOICZ database, downloaded from http://hercules.kgs.ukans.edu/hexacoral/envirodata/main.htm.

Woodwell et al. (1973, p. 225) has been widely used in literature although these authors caution their own estimate: "It would be surprising if estimates derived in this way were accurate within ± 50%." They estimated a ratio of inner estuary surface area to coast length for the U.S. that they extrapolated to the worldwide coastline.

Abril and Borges (2004) estimated that the global CO_2 emission from inner estuaries due to degradation of allochthonous riverine POC is around 0.09 Pg C yr^{-1}, assuming that about 50% of riverine POC is remineralized during estuarine transit (based on Abril et al. 2002) and using the global POC riverine input given by Ludwig et al. (1996). The fact that the present estimate is almost 5 times higher (0.43 Pg C yr^{-1}, Table 4) would confirm the idea that the inner estuary surface area given by Woodwell et al. (1973) is overestimated. At least four arguments can be raised that bring both estimates closer together. Based on more recent data Richey (2004) provides a higher value (0.50 versus 0.18 PgC yr^{-1}) of allochthonous riverine POC export to the coastal zone than Ludwig et al. (1996). This would bring the estimate of CO_2 emission due to the degradation of allochthonous riverine POC to 0.25 Pg C yr^{-1}. The assumption of a 50% remineralization of riverine POC of Abril et al. (2002) is based on the study of 9 European estuaries. Keil et al. (1997) estimated that in the Amazon delta more than 70% of riverine POC is remineralized during estuarine transit. This would bring the estimate of CO_2 emission due to the degradation of allochthonous riverine POC to 0.35 Pg C yr^{-1}. There is increasing evidence that lateral inputs of TOC and DIC in both polluted and pristine estuaries are highly significant compared to the riverine carbon inputs (Cai and Wang 1998; Cai et al. 1999, 2000; Neubauer and Anderson 2003; Gazeau et al. 2004a), although much less well constrained at the global scale. The contribution of the ventilation of river DIC to the overall emission of CO_2 from inner estuaries seems highly variable from one estuary to another but also highly significant, ranging from 10% to 50% in the Scheldt inner estuary and Randers fjord, respectively. This last point clearly highlights the importance of the concept that coastal ecosystems are not closed and constitute a continuum exchanging in both directions of carbon and nutrients with adjacent systems. The estimated overall emission of CO_2 from inner estuaries of 0.43 Pg C yr^{-1} based on the sur-

face area of Woodwell et al. (1973) could be a reasonable first-order estimate. The latitudinal partitioning of the emission from inner estuaries is most probably flawed based on the counterintuitive trends shown in Fig. 5.

The estimation of the role of estuaries in the budget of CO_2 exchanges in the coastal ocean is further complicated by the contribution from outer estuaries that is highly significant as discussed above for the Scheldt and Amazon whole estuarine systems. No global surface area estimate is available for outer estuaries for which there is also a lack of air-water CO_2 flux estimates. The actual computation of the air-water CO_2 fluxes is not straightforward in whole estuarine systems since the gas transfer velocity can be assumed to be mainly dependant on wind stress in outer estuaries and the contribution of tidal currents to water turbulence will increase upstream at least in macrotidal inner estuaries (Borges et al. 2004b).

In the present tentative up-scaling, the inclusion of inner estuaries leads to the reversal of the direction of air-water CO_2 fluxes in the coastal ocean and it seems critical to evaluate the surface area of inner and outer estuaries and its latitudinal partitioning with some accuracy. To achieve this, geographical information systems as those developed in the framework of LOICZ or sophisticated water mass analysis and classification schemes of satellite images (e.g., Oliver et al. 2004) seem to be promising approaches.

The relative contribution of the CO_2 emission from salt marsh surrounding waters compared to the one from inner estuaries is small in the present up-scaling but would increase if the surface area of inner estuaries would be revised to a lower value. Note that the surface area of salt marsh surrounding waters is also derived from Woodwell et al. (1973) and should also be used with caution. The estimation of the surface area of salt marsh and mangrove surrounding waters is very approximate and also requires a re-evaluation in the future. It was assumed that the surface area of surrounding waters is equivalent to the one of the corresponding intertidal zone covered by these habitats. Their overall role in the exchange of CO_2 with the atmosphere is further complicated by the fact that emerged intertidal sediments also emit CO_2 to the atmosphere at high rates (e.g., in the mangrove forests of Gazi Bay, Kenya, ranging between 4 and 165 mol C m^{-2} yr^{-1} [Middelburg et al. 1996] and in the salt marshes of Oyster Landing, U.S. South Atlantic Bight, ranging between 19 to 27 mol C m^{-2} yr^{-1} [Morris and Whiting 1986]).

Although there are not enough data to partition with confidence the up-scaling of air-water CO_2 fluxes in the coastal ocean into the two Hemispheres (since most data are available in the Northern Hemisphere, see Fig. 1), the relative distribution of the surface area of continental shelves clearly shows that the coastal ocean will have a much more marked effect on the global CO_2 fluxes in the Northern Hemisphere (Fig. 6). The relative contribution of the Northern Hemisphere to the uptake of atmospheric CO_2 and its partitioning into oceanic and terrestrial biospheres is the subject of a long lived debate initiated by the work of Tans et al. (1990). These authors attributed to the terrestrial biosphere a missing sink of CO_2 between -2.0 and -3.0 Pg C yr^{-1} at temperate latitudes required to balance the global CO_2 budget constrained with the North-South gradient of atmospheric CO_2. In the budget of Tans et al. (1990), the upper bound of the open ocean CO_2 sink was estimated to be -0.9 Pg C yr^{-1} but at present time it has been re-evaluated at -1.6 Pg C yr^{-1} (Takahashi et al. 2002). The missing sink of CO_2 at temperate latitudes to constrain the North–South gradient of atmospheric CO_2 can be roughly re-evaluated between -1.3 and -2.3 Pg C yr^{-1}. The higher bound of the sink for atmospheric CO_2 in the coastal ocean at temperate latitudes is -0.3 Pg C yr^{-1} (Table 3) and probably mostly located in the Northern Hemisphere (roughly -0.26 Pg C yr^{-1} based on Fig. 6), and is not negligible in relation to the missing CO_2 sink (contribution between 23% and 13%).

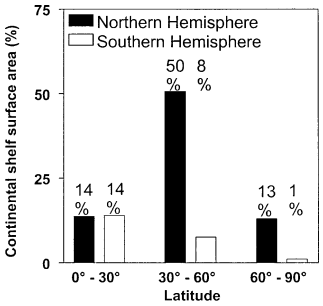

Fig. 6. Percentage of surface area of continental shelves by latitudinal bands in the Northern and Southern Hemisphere (based on data from Walsh [1988]).

Besides coastal and open oceanic waters, significant CO_2 exchanges are also associated with lakes (global CO_2 emission of 0.1 Pg C yr^{-1}, Cole et al. 1994), rivers (global CO_2 emission of 0.3 Pg C yr^{-1}, Cole and Caraco 2001), and freshwater wetlands (CO_2 emission of 0.5 Pg C yr^{-1} from central Amazon wetlands alone, Richey et al. 2002). In the context of a global evaluation of CO_2 fluxes, aquatic systems should be envisaged together since they constitute a continuum where carbon from the terrestrial biosphere and the atmosphere cascades.

Characterization of Air-water CO_2 Fluxes

To compute the exchange of CO_2 with the atmosphere in high-latitude open continental shelves a zero air-ice CO_2 flux was used, based on the assumption of Poisson and Chen (1987), which was also applied in the two Takahashi's climatologies (Takahashi et al. 1997, 2002). It has been established almost 30 years ago that above a threshold temperature of −7°C sea ice becomes permeable to CO_2 exchange with the atmosphere (Gosink et al. 1976). In the Southern Weddel Sea, DIC in brines has been reported to range between 840 and 4940 μmol kg^{-1} due to concentration of dissolved constituents during the formation of hypersaline brine, dilution of brine with meltwater, and biological uptake (Gleitz et al. 1995). Carbonate mineral precipitation and dissolution in brines has been evidenced in laboratory experiments (Papadimitriou et al. 2004) but to date has not been verified in the field (Anderson and Jones 1985; Gleitz et al. 1995). In accordance to such large shifts in DIC, Semiletov et al. (2004) reported at Barrow Point, Artic, in June 2002, air-ice CO_2 fluxes based on the eddy correlation technique ranging between −22 and 22 mol C m^{-2} yr^{-1}. Such large air-ice CO_2 fluxes can have a major effect on the annual budget of CO_2 exchanges but no further data on ice-air CO_2 fluxes are available in literature. Further research is required before air-ice CO_2 fluxes can be integrated with reasonable confidence in an up-scaling exercise.

In the present tentative up-scaling, the inclusion of inner estuaries leads to a reversal of the direction of air-water CO_2 fluxes in the coastal ocean at high latitudes. High latitude inner estuaries would contribute to about 51% of the total emission of CO_2 from inner estuaries (Table 4). No annually integrated air-water CO_2 fluxes have been reported in high latitude inner estuaries and, on first approximation, the value from inner estuaries at temperate latitudes was used.

Coastal upwelling systems can behave either as sinks or sources of atmospheric CO_2. Major upwelling systems, such as those off the California and Oman coasts, seem to be sources of CO_2 (Table 1). The coastal upwelling system off the Chilean coast also could be a source for atmospheric CO_2; Torres et al. (1999, 2003) computed a CO_2 efflux during two cruises in El Niño years (0.4–3.9 mol C m^{-2} yr^{-1} using the Wanninkhof and McGillis [1999] k parameterization) and it is hypothesized to be higher during La Niña years (Torres et al. 2003). Besides the coastal upwelling system off the Galician coast, other minor coastal upwelling systems could also be sinks for atmospheric CO_2. The coastal upwelling system off the west coast of Vancouver Island is simulated to act as a sink for atmospheric CO_2 according the biogeochemical model of Ianson and Allen (2002; ranging between −0.5 and −1.7 mol C m^{-2} yr^{-1} for La Niña and El Niño years, respectively, using the Wanninkhof [1992] k parameterization).

In highly productive macrophyte (seagrass and macroalgae) ecosystems, very little DIC data and no reliable annually integrated air-water CO_2 flux are available in literature. As shown by Gazeau et al. (2004c) in *Posidonia oceanica* phanerogam beds and by Delille et al. (1997, 2000) in *Macrocystis pyrifera* kelp beds, these ecosystems are at least during some seasons a net sink for CO_2 from the surrounding water. As for coral reef systems, the overall air-water CO_2 flux will be further modulated by the residence time of the incoming water mass and its original ΔpCO_2 (e.g., Gazeau et al. 2004c). Based on one cruise in Mallorca Island, Gazeau et al. (2004c) have estimated on first approximation that *P. oceanica* beds can only decrease the summertime CO_2 emission from the Mediterranean continental shelf by a modest 2.5%.

Interannual variability of air-water CO_2 fluxes has been documented in detail by field data in the open ocean in relation to large scale atmospheric oscillations acting at long (Pacific Decadal Oscillation, Takahashi et al. [2003]) or short (El Niño Southern Oscillation [ENSO], e.g., Feely et al. [2002]; North Atlantic Oscillation [NAO], e.g., Bates [2001]) time scales. Several studies based on global circulations models have shown that these oscillations induce a very significant interannual variation in the global uptake of atmospheric CO_2 from the open ocean, ranging from ±25% to ±100% (e.g., Le Quéré et al. 2003). El Niño events decrease Ekman pumping in coastal upwelling systems in the Eastern Pacific, reducing both DIC and nutrient delivery to the continental shelf. Recent research has also highlighted the effect of the NAO on the pelagic ecosystem functioning in the Southern Bight of the North Sea related to freshwater discharge and nutrient delivery to the coastal zone (Breton et al. 2004). It is then probable that such climatic and linked ecological oscillations affect air-water CO_2 fluxes in coastal areas, although a long high temporal resolution time series of measurements is needed to describe both the seasonal and interannual variability. In coastal ecosystems a very limited number of studies have investigated air-water CO_2 flux interannual variability based either on field (Bates 2002; Friederich et al. 2002) or modeling (Ianson and Allen 2002; Gypens et al. 2004) approaches. Friederich et al. (2002) showed that the California upwelling system shifts from a source for atmospheric CO_2 during La Niña years to a sink of atmospheric CO_2 during El Niño years

(Table 1). Ianson and Allen (2002) show that the upwelling system off the west coast of Vancouver Island shifts from a moderate sink to a significant sink for atmospheric CO_2 during La Niña and El Niño years, respectively. Torres et al. (1999, 2003) show that the Chilean upwelling system is a source for atmospheric CO_2 during El Niño years.

In the Southern Bight of the North Sea, Gypens et al. (2004) show, using a modeling approach, changes in intensity and direction of CO_2 fluxes related to interannual variability of freshwater discharge that changes nutrient delivery affecting GPP and temperature that changes pCO_2 in relation to thermodynamic effects but also to rates of metabolic processes (GPP and R).

The effect of extreme climate events on DIC chemistry and air-water CO_2 fluxes has to some extent been investigated in the open ocean (Bates et al. 1998), but to date has not been documented in the coastal ocean. In open continental shelves, storms can promote primary production by the replenishment of inorganic nutrients during stratified periods (Soetaert et al. 2001) and can be expected to affect ΔpCO_2 although this has not been investigated to date. In nearshore ecosystems, extreme climate-hydrological events can be expected to affect ΔpCO_2 and related air-water CO_2 fluxes. Suspended particulate matter and POC delivery from rivers are discharged in less than 25% of the time during flood events (e.g., Coynel et al. 2004). These hot spot POC flux events are particularly significant in rivers with a small to medium sized drainage basin ($< 1{,}000$–$10{,}000$ km^2) and are influenced by glaciermelt and snowmelt (Meybeck et al. 2003). In absence of long-term and high temporal resolution ΔpCO_2 monitoring it is difficult to speculate on the effect of such events on air-water CO_2 fluxes, since high floods will also affect DIC, DOC, and inorganic and organic nutrient delivery to inner and outer estuaries and other nearshore ecosystems.

Future Changes?

Future changes of the atmospheric CO_2 content and the inputs of carbon and nutrients from land and from mixing processes at ocean margins will affect air-water CO_2 fluxes in the coastal ocean, notably in relation to modifications of NEP and net ecosystem $CaCO_3$ production. Land use activities (agriculture and deforestation) have changed and are predicted to continue to change the fluxes of suspended sediments (Milliman 1991; Vörösmarty et al. 2003), organic carbon (Meybeck 1993), DIC (Raymond and Cole 2003), and nutrients (Smith et al. 2003) to the coastal ocean. These fluxes to the coastal ocean will be further modified by river discharge that is a function of the hydrological cycle (e.g., Manabe et al. 2004) and dam building and river diversion activities (Vörösmarty and Sahagian 2000). An increase of freshwater discharge to the Artic during the last 60 years has been recently reported (Peterson et al. 2002); future evolution of freshwater discharge is difficult to predict since spatial and temporal patterns of precipitation and evaporation are notoriously difficult to model (Allen and Ingram 2002). Nutrient delivery to the coastal ocean is predicted to continue to increase (Mackenzie et al. 2002) leading to an increase of GPP but also to potential shifts in phytoplanktonic communities and carbon flows through the entire ecosystem. The enhancement of NEP due to an increase of nutrient delivery will also depend on the evolution of the GGP:R ratio, e.g., in relation to enhanced carbon burial due to a higher riverine sediment delivery or to modifications of the ecosystem structure or to regression of certain ecosystems that are at present significant traps for organic matter (e.g., vegetated sediments, Duarte et al. 2004).

Specific coastal ecosystems are in most cases threatened by direct and indirect human effects. 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 effects 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). Some coastal habitats are predicted to adapt and survive with shifts in species composition, such as coral reef ecosystems (Hughes et al. 2003; Baker et al. 2004), but with probable loss of biodiversity and modifications of carbon flows.

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 with atmospheric CO_2 concentrations. This would have an effect on the contribution of coastal upwelling systems to the air-water CO_2 fluxes in the coastal ocean, although it is difficult to predict because of the increase of inputs to the shelf of both nutrients and DIC. It has also been hypothesized that the frequency, intensity, and duration of El Niño events during the last 30 years is related to global warming (Hunt 1999),

although the exact causes (natural versus anthropogenic) are debated (Kukla and Gavin 2004). El Niño events are known to strongly decrease primary production in coastal upwelling systems (Chavez et al. 2002) but the coastal marine ecosystems seem to recover within a few years (Fiedler 2002). Current projections show little change or a small increase in amplitude for El Niño events over the next 100 years (Houghton et al. 2001). As discussed above, shifts in the intensity or even in the direction of air-water CO_2 fluxes in coastal upwelling systems in relation to ENSO have been documented.

The increase of surface water DIC due to the invasion of anthropogenic CO_2 will decrease the $CaCO_3$ saturation state with potential decline of the $CaCO_3$ production in benthic (Gattuso et al. 1998b; Kleypas et al. 1999; McNeil et al. 2004) and planktonic (Riebesell et al. 2000; Zondervan et al. 2002) compartments and enhancement of shallow-water $CaCO_3$ dissolution (Andersson and Mackenzie 2004). The increase of seawater CO_2 concentration due to the invasion of anthropogenic CO_2 could also enhance primary production for at least some phytoplanktonic species, as reviewed by Wolf-Gladrow et al. (1999). It could also affect pelagic carbon export through increased production of transparent exopolymer particles or changes in the elemental stoichiometry of uptake, accumulation, and loss processes (Zondervan et al. 2002; Delille et al. 2004; Engel et al. 2004; Riebesell 2004).

Future changes of air-water CO_2 fluxes in the coastal ocean have been simulated, integrating some of these complex and diverse potential future effects on carbon cycling, using the TOTEM (Terrestrial Ocean Atmosphere Ecosystem Model; Ver et al. 1999; Mackenzie et al. 2000) or SOCM (Shallow-water Ocean Carbonate Model; Andersson and Mackenzie 2004; Mackenzie et al. 2004a,b) prognostic models. These models predict an enhancement of the sink for atmospheric CO_2 in the coastal ocean due to the increase of atmospheric CO_2 (increase of ΔpCO_2) and of NEP in relation to higher riverine inorganic nutrient inputs; the decrease of calcification and increase of benthic $CaCO_3$ dissolution are predicted to have a small overall effect on future air-water CO_2 fluxes in the coastal ocean (Andersson and Mackenzie 2004; Mackenzie et al. 2004a,b). The relative importance of the uptake of atmospheric CO_2 by the coastal ocean is also predicted to increase in comparison with the uptake by the open ocean that could decrease with the slowdown of the thermohaline circulation (Mackenzie et al. 2000).

To run such models it is required to reconstruct the pre-industrial NEP, net ecosystem calcification, and air-water CO_2 flux rates to set initial conditions. This gives insights into the anthropogenic signal associated to the present day air-water CO_2 fluxes. According to Andersson and Mackenzie (2004) and Mackenzie et al. (2004a,b), the pre-industrial (year 1700) and present-day (year 2000) air-water CO_2 fluxes simulated by SOCM are 0.69 and 0.15 mol C m^{-2} yr^{-1}, respectively. The latter value is in fair agreement with the one given in Table 4 (0.38 mol C m^{-2} yr^{-1}) and implies that the coastal ocean is at present-day a sink for anthropogenic CO_2 at a rate of -0.54 mol C m^{-2} yr^{-1} corresponding to a net absorption of -0.17 Pg C yr^{-1}. This value represents about 9% anthropogenic CO_2 absorption by the open ocean (-1.95 Pg C yr^{-1} based on the cumulated uptake for the 1980–1999 period reported by Sabine et al. 2004).

These models are relatively sensitive to the initial (pre-industrial) conditions (see Rabouille et al. 2001). Their performance may also be improved if the latitudinal and ecological diversity of air-water CO_2 fluxes in the coastal ocean is explicitly accounted for and with a robust validation with present-day air-water CO_2 fluxes based on more extensive field data.

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