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Reconciling opposing views on carbon cycling in the coastal ocean: Continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO₂

Chen-Tung Arthur Chen^{a,*}, Alberto V. Borges^b^a Institute of Marine Geology and Chemistry, National Sun Yat-sen University, Kaohsiung 804, Taiwan, Republic of China^b Chemical Oceanography Unit, MARE University of Liège Allée du 6 Août, 17 (Bât B5), B-4000 Liège, Belgium

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ABSTRACT

Despite their moderately sized surface area, continental marginal seas play a significant role in the biogeochemical cycles of carbon, as they receive huge amounts of upwelled and riverine inputs of carbon and nutrients, sustaining a disproportionate large biological activity compared to their relative surface area. A synthesis of worldwide measurements of the partial pressure of CO₂ (pCO₂) indicates that most open shelves in the temperate and high-latitude regions are under-saturated with respect to atmospheric CO₂ during all seasons, although the low-latitude shelves seem to be over-saturated. Most inner estuaries and near-shore coastal areas on the other hand are over-saturated with respect to atmospheric CO₂. The scaling of air–sea CO₂ fluxes based on pCO₂ measurements and carbon mass-balance calculations indicate that the continental shelves absorb atmospheric CO₂ ranging between 0.33 and 0.36 Pg C yr⁻¹ that corresponds to an additional sink of 27% to ~30% of the CO₂ uptake by the open oceans based on the most recent pCO₂ climatology [Takahashi, T., Sutherland, S.C., Wanninkhof, R., Sweeney, C., Feely, R.A., Chipman, D., Hales, B., Friederich, G., Chavez, F., Watson, A., Bakker, D., Schuster, U., Metzl, N., Inoue, H.Y., Ishii, M., Midorikawa, T., Sabine, C., Hoppema, M., Olafsson, J., Amarasson, T., Tilbrook, B., Johannessen, T., Olsen, A., Bellerby, R., De Baar, H., Nojiri, Y., Wong, C.S., Delille, B., Bates, N., 2009. Climatological mean and decadal change in surface ocean pCO₂, and net sea–air CO₂ flux over the global oceans. *Deep-Sea Research II*, this issue [doi: 10.1016/j.dsr2.2008.12.009].]. Inner estuaries, salt marshes and mangroves emit up to 0.50 Pg C yr⁻¹, although these estimates are prone to large uncertainty due to poorly constrained ecosystem surface area estimates. Nevertheless, the view of continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO₂ allows reconciling long-lived opposing views on carbon cycling in the coastal ocean.

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1. Background

Land, rivers, open ocean, atmosphere, sediments and biota interact in coastal and shelf seas, leading to substantial spatial and temporal heterogeneity in carbon flows. Although the continental margins, considered here to extend from the coastline to a depth of 200 m, occupy only a little over 7% of the seafloor and less than 0.5% of the ocean volume, they play a major role in oceanic biogeochemical cycling. Significantly higher rates of new primary production occur in the continental margins than in the open oceans because of the higher supply of nutrients from cross-shelf break upwelling and riverine input, in addition to the rapid remineralization of organic matter due to enhanced pelagic and

benthic coupling (Walsh, 1988, 1991; Mackenzie et al., 1998a,b; Wollast, 1998; Liu et al., 2000; Muller-Karger et al., 2005).

Recognizing the importance of the continental margins in terms of the cycling of carbon and associated elements, the Joint Global Ocean Flux Study (JGOFS, established in 1988 as a core project under the International Geosphere Biosphere Program, IGBP) adopted continental margin studies as one of its operational elements. Five years later, another IGBP core project, the Land–Ocean Interaction in the Coastal Zone (LOICZ), was established to study in detail carbon and nutrient flows in coastal ecosystems. The first of four over-arching objectives of LOICZ was to determine the fluxes of materials between land, sea and atmosphere.

The first two of the six LOICZ foci were: Is the coastal zone a sink or source of CO₂ and What are mass balances of carbon, nitrogen and phosphorus in the coastal zone? (Crossland et al., 2005). The very first LOICZ report was entitled “Coastal seas: a net source or sink of atmosphere carbon dioxide?” (Kempe, 1995). These questions arise because it is not clear how much of the

* Corresponding author. Tel.: +886 7 525 5146; fax: +886 7 525 5346.
E-mail addresses: ctchen@mail.nsysu.edu.tw (C.-T.A. Chen),
alberto.borges@ulg.ac.be (A.V. Borges).

organic carbon transported to the coastal seas by rivers and new production on the continental shelves is permanently sequestered by export to the deep oceans or to sediments on the shelves and shallow marginal seas.

In order to determine the contribution of continental margins and seas to CO₂ sequestration and the horizontal fluxes of carbon, nitrogen and phosphorus across the ocean–continental margin boundary, the JGOFS/LOICZ Continental Margins Task Team (CMTT) was established (Chen et al., 1994).

Unfortunately, even now there is still a great deal of discussion about very basic questions on whether coastal waters are net sources or sinks of atmospheric CO₂, and whether primary production in coastal seas is exported or recycled. For instance, Smith and Mackenzie (1987) and Smith and Hollibaugh (1993) claimed that the oceans as a whole are net heterotrophic, and that they release more CO₂ into the atmosphere than they take up. Their argument was based on the imbalance between the total river transport of about 0.40 Pg C yr⁻¹ and the oceanic organic carbon burial rate of around 0.14 Pg C yr⁻¹. The difference of 0.26 Pg C yr⁻¹ would be most likely returned to the atmosphere. Ver et al. (1999a,b) and Mackenzie et al. (2000) also concluded that, in spite of an increased invasion of CO₂ from the atmosphere to the continental margins driven by the rise in atmospheric CO₂, continental margin waters are heterotrophic or, simply restated, sources of CO₂ to the atmosphere.

Upon the conclusion of the JGOFS project, Fasham et al. (2001) adopted the same view and reported a net CO₂ sea-to-air flux of 0.5 Pg C yr⁻¹ for continental margins. Noteworthy is that these authors, nevertheless, literally inserted a question mark alongside this value, which is larger than not only the value of 0.1 Pg C yr⁻¹ reported by Ver et al. (1999a,b) but also than the total river transport of 0.4 Pg C yr⁻¹ cited by Smith and Mackenzie (1987) and Smith and Hollibaugh (1993). As for LOICZ, the synthesis of first decade's activities ending in 2002 did not seem to answer properly the question as to whether the coastal zones are sources or sinks of carbon (Crossland et al., 2005). The chapter on “C, N, P fluxes in the coastal zone” did not provide any data on the atmosphere–marginal sea or on the shelf–open ocean fluxes of carbon but nevertheless concluded that “Smith and Hollibaugh (1993) estimated that there is about 7×10^{12} mol yr⁻¹ of net carbon oxidation in the coastal zone and 16×10^{12} mol yr⁻¹ in the open ocean. The LOICZ analysis does nothing to alter this essential picture”. And, the “Preface” of the synthesis volume simply states that “The question of whether the coastal zone is a source or sink of carbon is examined”.

Despite some uncertainties (Borges, 2005; Borges et al., 2005; Cai et al., 2006), mounting evidence based on pCO₂ measurements and mass-balance calculations (Chen et al., 2003; Chen, 2004) seems to indicate that the continental shelves are actually sinks of atmospheric CO₂. A chapter in the JGOFS synthesis volume concluded that the shelves take up 25×10^{12} mol yr⁻¹ of atmospheric CO₂ based mainly on the mass-balance approach (Chen et al., 2003). A chapter in the assessment organized by the Global Carbon Project gave an air-to-sea CO₂ flux of 30×10^{12} mol yr⁻¹ for the shelves (Chen, 2004). These fluxes, however, do not include inner estuaries, salt marshes or mangroves, which release CO₂ to the atmosphere (Borges, 2005; Borges et al., 2005). This emission of CO₂ is fuelled by inputs of terrestrial organic matter.

There is increasing evidence that a very large fraction of terrestrial/riverine organic matter is degraded and emitted as CO₂ to the atmosphere in these near-shore systems, and never reaches the continental shelves let alone the open ocean (e.g. Middelburg and Herman, 2007, and references therein). Hence, the “coastal” net heterotrophy postulated by Smith and Mackenzie (1987) and Smith and Hollibaugh (1993) is confined to these near-shore ecosystems, which allows one to reconcile their mass-balance

approach with the wealth of evidence showing that marginal seas are net autotrophic and net sinks for atmospheric CO₂.

It will be shown below that the available data of pCO₂ measurements in about 60 continental shelves of the world allows the conclusion that continental shelves are indeed sinks for atmospheric carbon. The present work updates previous compilations of pCO₂ measurements in coastal environments (Borges, 2005; Borges et al., 2005; Cai et al., 2006) and attempts to reconcile long-lived opposing views on C cycling in marginal seas, either as net heterotrophic and potential sources of CO₂ to the atmosphere (e.g. Smith and Mackenzie, 1987; Smith and Hollibaugh, 1993) or as autotrophic and potential sinks for atmospheric CO₂ (e.g. Gattuso et al., 1998; Wollast, 1998; Chen, 2004).

2. Air–sea CO₂ fluxes in inner estuaries, salt marshes and mangroves

Table 1 compiles available air–water CO₂ fluxes in near-shore ecosystems (inner estuaries, salt marshes and mangrove surrounding waters) and updates previous global compilations by Abril and Borges (2004), Borges (2005) and Borges et al. (2005), with an increase of almost 50% in available data. Notable differences with previous compilations are that data for some major inner estuaries are now available such as the Changjiang (ranked 4th river in the world in terms of freshwater discharge, Gao et al., 2005; Zhai et al., 2007) and the Mekong (ranked 10th river in the world in terms of freshwater discharge, Borges, unpublished), and for previously undocumented lagoons (four systems in The Ivory Coast (Koné et al., 2009) and Aveiro lagoon (Borges and Frankignoulle unpublished)). Also, information on the seasonality of CO₂ fluxes in mangrove surrounding waters is now available (Koné and Borges, 2008) and CO₂ fluxes in salt marshes are available at an additional site.

Inner estuaries act as sources of CO₂ to the atmosphere due to their heterotrophic ecosystem metabolic status (Odum and Hoskin, 1958; Odum and Wilson, 1962; Heip et al., 1995; Kemp et al., 1997; Gattuso et al., 1998; Gazeau et al., 2004; Hopkinson and Smith, 2005). The input of dissolved CO₂ from the upstream river contributes to about 10% of the emission of CO₂ from macrotidal inner estuaries, the remaining fraction of the emission of CO₂ is then due to heterotrophy or lateral inputs of CO₂ (Borges et al., 2006). The net heterotrophy of inner estuaries is sustained by terrestrial/riverine organic carbon inputs (freshwater phytoplankton and soil carbon), and in populated areas by waste water.

Mangroves surrounding waters act as CO₂ sources to the atmosphere also due to the heterotrophic nature of the water column and inter-tidal sediments. Heterotrophy is sustained by inputs of organic carbon that has several sources, either autochthonous (mangrove detritus and microphytobenthos) or allochthonous (phytoplankton, seagrass-derived material and terrestrial non-mangrove forests), and the relative contribution of these sources varies considerably from one site to another (Bouillon and Boschker, 2006). The emission of CO₂ from mangrove surrounding waters is also sustained by the input of CO₂-rich pore waters during ebbs (Ovalle et al., 1990; Borges et al., 2003; Bouillon et al., 2007c). Tidal pumping of pore water makes creeks waters act as conduits for the emission of CO₂ produced by diagenetic organic carbon degradation, leading to an under-estimate of traditional measurements of benthic metabolism (Bouillon et al., 2007c, 2008). The aquatic compartment of salt marshes is also a source of CO₂ to atmosphere due to its net heterotrophic status sustained by allochthonous and autochthonous organic carbon inputs (Cai et al., 2003; Wang and Cai, 2004), with a strong contribution of dissolved inorganic carbon (DIC) inputs

Table 1
Longitude, latitude, pCO₂ range (ppm), air–water CO₂ fluxes (FCO₂ in mol C m⁻² yr⁻¹) in near-shore ecosystems.

Site (country code)	°E	°N	pCO ₂ range	FCO ₂	References
<i>Inner estuaries</i>					
Aby lagoon (CI)	-3.3	4.4	60–325	3.9	Koné et al. (2009)
Altamaha Sound (US)	-81.3	31.3	390–3380	-32.4	Jiang et al. (2008a)
Aveiro lagoon (PT)	-8.7	40.7	143–11,335	-12.4	Borges and Frankignoulle (unpublished)
Betsiboka (MG)	46.3	-15.7	270–1530	-3.3	Ralison et al. (2008)
Bothnian Bay (FI)	21.0	63.0	150–550	-3.1	Algesten et al. (2004)
Changjiang (Yantze) (CN)	120.5	31.5	200–4600	-24.9	Gao et al. (2005), Zhai et al. (2007)
Chilka (IN)	85.5	19.1	70–6350	-25.0	Gupta et al. (2008)
Doboy Sound (US)	-81.3	31.4	390–2400	-13.9	Jiang et al. (2008a)
Douro (PT)	-8.7	41.1	1330–2200	-76.0	Frankignoulle et al. (1998)
Ebrié lagoon (CI)	-4.3	4.5	1365–3575	-31.1	Koné et al. (2009)
Elbe (DE)	8.8	53.9	580–1100	-53.0	Frankignoulle et al. (1998)
Ems (DE)	6.9	53.4	560–3755	-67.3	Frankignoulle et al. (1998)
Gironde (FR)	-1.1	45.6	465–2860	-30.8	Frankignoulle et al. (1998)
Godavari (IN)	82.3	16.7	220–500	-5.5	Bouillon et al. (2003)
Guadalquivir (ES)	-6.0	37.4	520–3606	-31.1	de la Paz et al. (2007)
Hooghly (IN)	88.0	22.0	80–1520	-5.1	Mukhopadhyay et al. (2002)
Loire (FR)	-2.2	47.2	630–2910	-64.4	Abril et al. (2003)
Mandovi-Zuari (IN)	73.5	15.3	500–3500	-14.2	Sarma et al. (2001)
Mekong (VN)	106.5	10.0	280–4105	-30.8	Borges (unpublished)
Potou lagoon (CI)	-3.8	4.6	1235–5120	-40.9	Koné et al. (2009)
Randers Fjord (DK)	10.3	56.6	220–3440	-2.2	Gazeau et al. (2005)
Rhine (NL)	4.1	52.0	545–1990	-39.7	Frankignoulle et al. (1998)
Sado (PT)	-8.9	38.5	575–5700	-31.3	Frankignoulle et al. (1998)
Sapelo Sound (US)	-81.3	31.6	390–2400	-13.5	Jiang et al. (2008a)
Saja-Besaya (ES)	-2.7	43.4	264–9728	-52.2	Ortega et al. (2005)
Satilla River (US)	-81.5	31.0	360–8200	-42.5	Cai and Wang (1998)
Scheldt (BE/NL)	3.5	51.4	125–9425	-63.0	Frankignoulle et al. (1998)
Tagba lagoon (CI)	-5.0	4.4	800–4250	-18.4	Koné et al. (2009)
Tamar (UK)	-4.2	50.4	380–2200	-74.8	Frankignoulle et al. (1998)
Tendo lagoon (CI)	-3.2	4.3	90–3600	-5.1	Koné et al. (2009)
Thames (UK)	0.9	51.5	505–5200	-73.6	Frankignoulle et al. (1998)
York River (US)	-76.4	37.2	350–1900	-6.2	Raymond et al. (2000)
<i>Non-estuarine marshes</i>					
Duplin River (US)	-81.3	31.5	500–3000	-21.4	Wang and Cai (2004)
Rio San Pedro (ES)	-5.7	36.6	380–3760	-39.4	Ferrón et al. (2007)
<i>Mangroves</i>					
Gaderu creek (IN)	82.3	16.8	1380–4770	-20.4	Borges et al. (2003)
Kidogoweni creek (KE)	39.5	-4.4	1480–6435	-23.7	Bouillon et al. (2007a)
Itacuraça creek (BR)	-44.0	-23.0	660–7700	-41.4	Ovalle et al. (1990), Borges et al. (2003)
Kiên Vãng creeks (dry season) (VN)	105.1	8.7	705–4605	-11.8	Koné and Borges (2008)
Kiên Vãng (wet season) (VN)	105.1	8.7	1435–8140	-56.5	Koné and Borges (2008)
Matolo/ndogwe/Kalota/Mto Tana creeks (KE)	40.1	-2.1	490–10,035	-25.8	Bouillon et al. (2007b)
Mooringanga creek (VN)	89.0	22.0	800–1530	-8.5	Ghosh et al. (1987), Borges et al. (2003)
Nagada creek (IN)	145.8	-5.2	540–1680	-15.9	Borges et al. (2003)
Norman's Pond (BS)	-76.1	23.8	385–750	-5.0	Borges et al. (2003)
Ras Dege creek (TZ)	39.5	-6.9	430–5050	-12.4	Bouillon et al. (2007c)
Saptamukhi creek (IN)	89.0	22.0	1080–4000	-20.7	Ghosh et al. (1987), Borges et al. (2003)
Shark River (US)	-81.1	25.2	920–2910	-18.4	Millero et al. (2001), Clark et al. (2004), Koné and Borges (2008)
Tam Giang creeks (dry season) (IN)	105.2	8.8	770–11,480	-51.6	Koné and Borges (2008)
Tam Giang creeks (wet season) (IN)	105.2	8.8	1210–7150	-46.9	Koné and Borges (2008)
Tana (KE)	40.1	-2.1	2240–5305	-47.9	Bouillon et al. (2007b)

Negative FCO₂ values indicate an emission of CO₂ from the water to the atmosphere.

BE: Belgium; BR: Brazil; BS: Bahamas; CI: Ivory Coast; CN: China; DE: Germany; DK: Denmark; ES: Spain; FI: Finland; FR: France; IN: India; KE: Kenya; MG: Madagascar; NL: The Netherlands; PT: Portugal; TZ: Tanzania; UK: United Kingdom; US: United States; VN: Vietnam.

from the inter-tidal and sub-tidal benthic compartments (Neubauer and Anderson, 2003; Ferrón et al., 2007).

It should be noted that mangrove and salt marsh ecosystems as a whole (including the aquatic compartment, the benthic compartment and above-ground biomass) act as sinks for atmospheric CO₂ due to the important above-ground primary production. A recent data compilation in mangrove ecosystems yields an above-ground net primary production (including litter fall, wood production and fine root production) of 114 mol C m⁻² yr⁻¹ (Bouillon et al., 2008), a sink for atmospheric CO₂ that is higher

than the emission of CO₂ to the atmosphere from the aquatic compartment of -27.1 mol C m⁻² yr⁻¹. Similarly, in the Duplin River salt marsh ecosystem, net primary production from above-ground vegetation is about 149.2 mol C m⁻² yr⁻¹ (Hopkinson, 1988), a sink of atmospheric CO₂ higher than the reported emission of CO₂ to the atmosphere from the aquatic compartment of -21.4 mol C m⁻² yr⁻¹ (Wang and Cai, 2004). However, we only envisage in the present paper the coastal ocean CO₂ fluxes, hence we only consider the CO₂ exchange between the atmosphere and the aquatic compartment.

Based on Table 1, average CO₂ emissions to the atmosphere are 32.1, 30.4 and 27.1 mol C m⁻² yr⁻¹ for inner estuaries, salt marsh waters and mangrove waters, respectively. Scaling of these average values yields CO₂ emissions of 0.36, 0.09 and 0.05 Pg C yr⁻¹ for inner estuaries, salt marsh waters and mangrove waters, respectively, using the Woodwell et al. (1973) estimate of surface area of inner estuarine surface area (0.943 × 10⁶ km²), total surface area of salt marshes and mangroves (0.384 × 10⁶ km²), and the FAO (2003) estimate of mangroves (0.147 × 10⁶ km²).

The potential emission of CO₂ from inner estuaries can be roughly estimated indirectly from a mass balance of terrestrial/riverine organic carbon. Assuming an input of terrestrial/riverine particulate organic carbon (POC) ranging from 0.17 Pg C yr⁻¹ (Ludwig et al., 1996) to 0.50 Pg C yr⁻¹ (Richey, 2004), and the degradation of POC during estuarine transit ranging from 50% (Abril et al., 2002) to 70% (Keil et al., 1997), we compute a potential emission of CO₂ from POC degradation by inner estuaries ranging from 0.09 to 0.35 Pg C yr⁻¹. Assuming a 10% removal of river dissolved organic carbon (DOC) during estuarine transit (Moran et al., 1999; Raymond and Bauer, 2000; Wiegner and Seitzinger, 2001), and the global DOC input of 0.21 Pg C yr⁻¹ (Ludwig et al., 1996) brings the potential emission of CO₂ from total organic carbon (TOC) removal by inner estuaries to a range between 0.11 and 0.37 Pg C yr⁻¹. If the emission of CO₂ due to ventilation of riverine CO₂ of 10% (Borges et al., 2006) is added, the overall potential emission of CO₂ by inner estuaries ranges from 0.12 to 0.41 Pg C yr⁻¹.

The CO₂ emission by inner estuaries based on pCO₂ measurements falls within the range of values estimated by mass balance, but is nevertheless 3-fold higher than the lowest estimate from the mass-balance computations. As discussed in detail by Abril and Borges (2004) and Borges (2005), the value of inner estuary surface area given by Woodwell et al. (1973) is probably overestimated. Also noteworthy is that most available data were obtained in macro-tidal estuaries, which have a vertically mixed water column and a long residence time. These physical characteristics promote TOC degradation with subsequent emission of CO₂ to the atmosphere compared to other ecotypes of estuaries such as micro-tidal estuaries (Borges, 2005). This is illustrated by the fact that the only system reported in Table 1 that behaves as a net annual sink for atmospheric CO₂ is the Aby lagoon, which is a permanently stratified system with a long residence time of the water mass, allowing the sedimentation of organic carbon across the pycnocline, making the upper mixed layer an effective carbon sink (Koné et al., 2009).

3. Air–sea CO₂ fluxes in continental shelves

Tsunogai et al. (1999) coined the term “continental shelf pump”, which would account for a net uptake of CO₂ of 1.0 Pg C yr⁻¹, if the world continental shelves would absorb atmospheric CO₂ at the same rate computed from data obtained from a single transect in the East China Sea. This value, however, is almost certainly an overestimate, as more recent studies in the East China Sea have yielded lower fluxes. Indeed, based on pCO₂ data from several cruises, Chen and Wang (1999) computed an air-to-sea flux of 2.0 mol C m⁻² yr⁻¹, lower than the value of 3.0 mol C m⁻² yr⁻¹ estimated by Chen and Tsunogai (1998) and Tsunogai et al. (1999). This points out the need for high-resolution coverage, both temporal and spatial, to provide robust and unbiased estimates of CO₂ air–sea fluxes in continental shelves.

Another example is the air–sea CO₂ flux estimates in the US South Atlantic Bight (SAB); based on five cruises Cai et al. (2003) estimated that the SAB was a strong source of CO₂ to the atmosphere at a rate of 2.5 mol C m⁻² yr⁻¹, but based on six

cruises, Jiang et al. (2008b) recently reported that the SAB is a sink for atmospheric CO₂ at a rate of 0.5 mol C m⁻² yr⁻¹. The difference between these two studies is that Cai et al. (2003) obtained their pCO₂ data along one single linear transect perpendicular to the coast, while Jiang et al. (2008b) surveyed the entire SAB, providing the necessary spatial coverage required to produce a robust estimate of air–sea CO₂ fluxes. Besides covering adequately the spatial heterogeneity, high temporal coverage is also required to estimate reliably air–sea CO₂ fluxes in highly dynamic coastal environments.

For instance, Thomas et al. (2004) reported that the Southern Bight of the North Sea (SBNS) was a source of CO₂ at a rate of 0.2 mol C m⁻² yr⁻¹. More recently, Schiettecatte et al. (2007) showed that the SBNS is actually a sink for atmospheric CO₂ at a rate of 0.7 mol C m⁻² yr⁻¹. Both the Thomas et al. (2004) and Schiettecatte et al. (2007) studies covered satisfactorily the spatial variability of the SBNS but the first estimate was based on only four cruises while the second was based on 10 cruises. The disagreement in net annual CO₂ flux estimates between the two studies is due to the fact that the “spring cruise” of the data set of Thomas et al. (2004) was carried out in May, during the declining phase of the phytoplankton bloom, implying that this data set did not adequately account for the strong CO₂ under-saturation in the SBNS typically observed in mid-April (Borges and Frankignoulle, 1999, 2002a) during the peak of the phytoplankton bloom.

In absence of long time-series of pCO₂ measurements in continental shelves, a not quantified potential bias in air–sea CO₂ flux estimates relates to inter-annual variability and long-term changes. In the California upwelling system, Friederich et al. (2002) reported a shift from an annual source to an annual sink of CO₂ due to the El Niño Southern Oscillation. Strong inter-annual variability in the sink of CO₂ in Tasman continental shelf has been recently reported due to changes in mixing related to the Southern Annular Mode (Borges et al., 2008). In coastal areas in the vicinity of the Bering and Okhotsk Seas a long-term increase in the sink of CO₂ has been reported (Takahashi et al., 2006), while in the North Sea a long-term decrease in the sink of CO₂ has been reported (Thomas et al., 2007). The causes of these long-term trends remain unclear.

During the past few years, the number of studies reporting air–sea CO₂ fluxes based on pCO₂ measurements worldwide has significantly increased, amounting to about 60 continental shelves listed in Table 2 according to the season, which also includes the annual average flux when available. The histogram of daily CO₂ fluxes during the different seasons is shown in Fig. 1. Although there is a large scatter, most studies report that the continental shelves are sinks for atmospheric CO₂ during most of the seasons. In spring, 14 studies reported that there is a net sink of CO₂ while only 4 reported a source of CO₂. In summer, a higher number of studies (25) reported a source of CO₂ to the atmosphere compared with 12 studies reporting otherwise. This is probably due to the thermodynamic increase of pCO₂ due to warming of surface waters, and due to the degradation of organic matter produced during the spring bloom. The surface seawater temperature starts to decrease in autumn, inducing a drop in pCO₂ values because of the change in the CO₂ solubility coefficient. As a result, marginal seas tend to be CO₂ sinks in autumn and winter.

Overall, the number of studies that reported continental shelves as CO₂ sinks outweigh those that reported continental shelves as CO₂ sources. Because of the small number of observations for each season, the distribution is not normal. The annually integrated CO₂ fluxes, however, show a more normal distribution, and the numerical average is ~1.1 mol C m⁻² yr⁻¹. This value, if scaled to the global surface area of continental shelves of 26 × 10⁶ km², yields an annual CO₂ uptake of about 29 × 10¹² mol C yr⁻¹ (0.35 Pg C yr⁻¹).

Table 2
Air–sea fluxes of CO₂ in various continental margins^a.

Area	Spring ^b (mmol m ⁻² d ⁻¹)	Summer (mmol m ⁻² d ⁻¹)	Fall (mmol m ⁻² d ⁻¹)	Winter (mmol m ⁻² d ⁻¹)	Annual (mol C m ⁻² yr ⁻¹)	References
Amazon River Plume					0.5–1.7	Ternon et al. (2000), Körtzinger (2003)
Antarctic Shelves		11–34 ¹			2.2 ²	1. Chen et al. (2004a, b); 2. Carrillo and Karl (1999)
Arabian Sea					–0.9	Goyet et al. (1998)
Arctic Sea					0.21 ¹ , 0.51 ²	1. Anderson and Jones (1981), Anderson et al. (1990); 2. Bates (2006)
Shelves					0.14	Anderson et al. (1998)
Atlantic Bight					0.5–1.3	DeGrandpre et al. (2002)
Baffin Bay	~0.3	0.45	~0.3	~0	0.43	Miller et al. (2002)
Baltic Sea					0.9 ¹ , 3.0 ²	1. Thomas et al. (2008); 2. Kuss et al. (2006)
Barrents Sea		2.7 ¹			0.55 ² , 3.6 ³	1. Kaltin et al. (2002); 2. Fransson et al. (2001); 3. Borges et al. (2005)
Bay of Bengal					–0.4	Goyet et al. (1998)
Beaufort Shelves		2.9 ¹			1.2 ²	1. Murata and Takizawa (2003); 2. Cai et al. (2006)
Benguela Current	11			5.5	0–1 ¹ , 1.62 ²	1. P. Monterio, personal communication (2007) 2. Santana-Casiano and González-Dávila (2009)
Bering Sea Basin					–4.7	Fransson et al. (2006)
Bering Sea Shelf	1.2 ¹	0.66 ²			4.3 ³	1. Nedashkovsky et al. (1995); 2. Codispoti et al. (1986); 3. Walsh and Dieterle (1994)
Black Sea		20				Goyet et al. (1991)
Brazil Shelf	–9.8 ¹	–4.2 ¹		–0.3 ¹	–1.8 ²	1. Ito et al. (2005); 2. Borges et al. (2005)
Bristol Bay					0.2	Borges et al. (2005)
California Coast					–2.2 to –0.7	Friederich et al. (2002)
Chukchi Sea	<0.1–1 ⁵	2.9 ¹ , 13–52 ^{2,3} , 30–90 ⁵	12 ⁴		4.8 ⁵ , 3.1 ⁶	1. Murata and Takizawa (2003); 2. Wang et al. (2003); 3. Li et al. (2004); 4. Pipko et al. (2002); 5. Bates (2006); 6. Kaltin and Anderson (2005)
E. China Sea	1.66 ¹ , 2.1 ± 2.8 ² , 1.8 ³ , 5.04 ± 1.59 ⁹	1.2 ³ , –2.52 ± 1.81 ⁹	–0.65 ¹ , 2.0 ³ , 1 ± 3 ⁹	3.1 ³	2.1 ³ , 3.3 ⁴ , 2 (1.1–2.5) ⁵ , 3 ⁶ , 1 ⁷ , 0.03 ⁸	1. Ma et al. (1999); 2. Peng et al. (1999); 3. Wang et al. (2000); 4. Tsunogai et al. (1997); 5. Chen and Wang (1999); 6. Tsunogai et al. (1999); 7. Zhang et al. (1999); 8. Zhang (1999); 9. Shim et al. (2007)
E. Mediterranean					0.78–4 × 10 ⁻⁴	de Madron et al. (2008)
Ecuador–Chile					–0.6	Cai et al. (2006)
English Channel					0 ¹ , –0.3 ²	1. Borges and Frankignoulle, 2003; 2. Thomas et al. (2008)
Funka Bay (Japan)					Mean ΔpCO ₂ = –75 μatm	Nakayama et al. (2000)
Galician Coast					2.2	Borges et al. (2005)
Gulf of Biscay	2.01	5.51	0.51	–0.31	1.7–2.91	Frankignoulle and Borges (2001)
Gulf of California		–5.4				Hidalgo-González et al. (1997)
Gulf of Cadiz		–18.6				Ait-Ameur and Goyet (2006)
Gulf of Lion					7.1	de Madron et al. (2008)
Gulf of Mexico Shelf		2–4.2 ¹			0.5 ²	1. Lohrenz and Cai, 2006; 2. Cai et al., 2006
Hudson Bay		3.9				Else et al. (2008)
Iberian	0.4 ¹	–0.07 ¹ , 4.5 ²	0.2 ¹ , 0.9 ²		1.6 (1.3–2.6) ²	1. Pérez et al. (1999); 2. Borges and Frankignoulle (2002a, b)
Japan Sea					3.8	Cai et al. (2006), Kang et al. (2008)

Jiaozhou Bay	-9.4	-22.2	-10.8	1.9	-3.7	Li et al. (2007)
Kara Sea					0.011	Fransson et al. (2001)
Laptev Sea					0.011	Fransson et al. (2001)
Mediterranean Sea					$0.52-2.8 \times 10^{-4}$	de Madron et al. (2008)
New Jersey Coast	> 0	< 0	< 0	≥ 0	0.44-0.84	Boehme et al. (1998)
NE Greenland		1.3				Yager et al. (1995)
North Sea	14 ¹	13 ¹ , 1.4 ²	-0.9 ¹		1.3 ³ , 1.5-2.2 ⁴ , 1.38 ⁵	1. Frankignoulle and Borges (2001); 2. Kempe and Pegler (1991); 3. Thomas et al. (2008); 4. Bozec et al. (2005); 5. Thomas et al. (2005)
Nova Scotia, Maine					0.7	Cai et al. (2006)
Okhotsk Sea		2.7-5.5 (May-Sept.) ¹			2.5 ² , 0.83 ³	1. Chen et al. (2003); 2. Otsuki et al. (2003); 3. Wakita et al. (2003)
Omani Coast					-2.5	Goyet et al. (1998)
Oregon Coast		20				Hales et al. (2005)
Patagenian Shelf					1.5	Bianchi et al. (2005)
Prydz Bay		75 ¹			2.2 ²	1. Wang et al. (1998); 2. Borges et al. (2005)
Ross Sea		25 ¹ , 4-10 ²			1.5 ³ , 0.07-1.55 ⁴	1. Wang et al. (1998); 2. Bates et al. (1998); 3. Borges et al. (2005); 4. Arrigo and Van Dijken (2007)
S. Atlantic Bight					-2.5	Cai et al. (2003)
S. China Sea		4.8 ¹ , -0.73 ²		0.5 ²	-0.18 ² , 1.0 ³ , -1.3 ⁴	1. Rehder and Suess (2001); 2. Chen et al. (2006a, b); 3. Chen et al. (2003); 4. Zhai et al. (2005)
Strait of Gibraltar	5.5 ± 2	-3 ± 8		19 ± 6	2.5	Santana-Casiano et al. (2002)
Sulu Sea		0				Chen et al. (2006b)
Taiwan St.	17.6					Ma et al. (1999)
Tasmania	7.14 ^c	7.09 ^c	6.21 ^c	5.14 ^c	2.3	Borges et al. (2008)
Vancouver Is. Coast					1.2	Borges et al. (2005)
W. European Shelves	1.1-18.3	3.4-24.4	0.4-2.4	-0.5~-0.9	4.8-7.9	Frankignoulle and Borges (2001)
Weddell Sea		-0.3 ^c				Stoll et al. (2002)
W. Florida Shelf					$\Delta pCO_2 = -43$ to $-64 \mu atm$	Wanninkhof et al. (1997)
W. Mediterranean	< 0	≥ 0	> 0	< 0	0.5 ± 0.18	Begovic and Copin-Montégut (2002)
					$1.5-8 \times 10^{-4}$	de Madron et al. (2008)
Yellow Sea	4.4 ¹	-1.8 ¹	4.4 ¹	4	2.4 ¹ , 2 ± 0.7 ²	Copin-Montégut and Bégovic (2002)
Global Coral Reefs (0.6 × 10 ⁶ km ²)	> 0 ¹ , < 0 ²	< 0 ³	~0 ²	> 0 ³	-0.1 to -3.2 ⁴ , -1.1 to -2.6 ⁵	1. Oh et al. (2000); 2. Wang et al. (2001)
Global Coastal (to ~40 m depth)						1. Smith (1973); 2. Kawahata et al. (1999); 3. Kayanne et al. (2005); 4. Borges et al. (2005); 5. Frankignoulle et al. (1996)
Global Shelves (~40 m-200 m depth)					-1.8	Rabouille et al. (2001)
GLOBAL					1.05	Rabouille et al. (2001)
					2.2 ¹ , 2.4 ² , 0.3 ³ , 1.9 ⁴ , 1 ⁵ , 1.8-2.0 ⁶ , 1.15 ⁷ , 1.17 ⁸ , 1.62 ⁹ , 0.72 ¹⁰	1. Sabine and Mackenzie (1991a, b); 2. Walsh and Dieterle (1994); 3. Liu et al. (2000); 4. Yool and Fasham (2001); 5. Chen et al. (2003); 6. Ducklow and McCallister (2004); 7. Chen (2004); 8. Borges (2005); 9. Borges et al. (2005); 10. Cai et al. (2006)

^a The most recent values are used, a positive flux is directed from air to sea, a negative flux is directed from sea to air.

^b Spring: March-May; Summer: June-August; Fall: September-November; Winter: December-February.

^c Austral seasons.

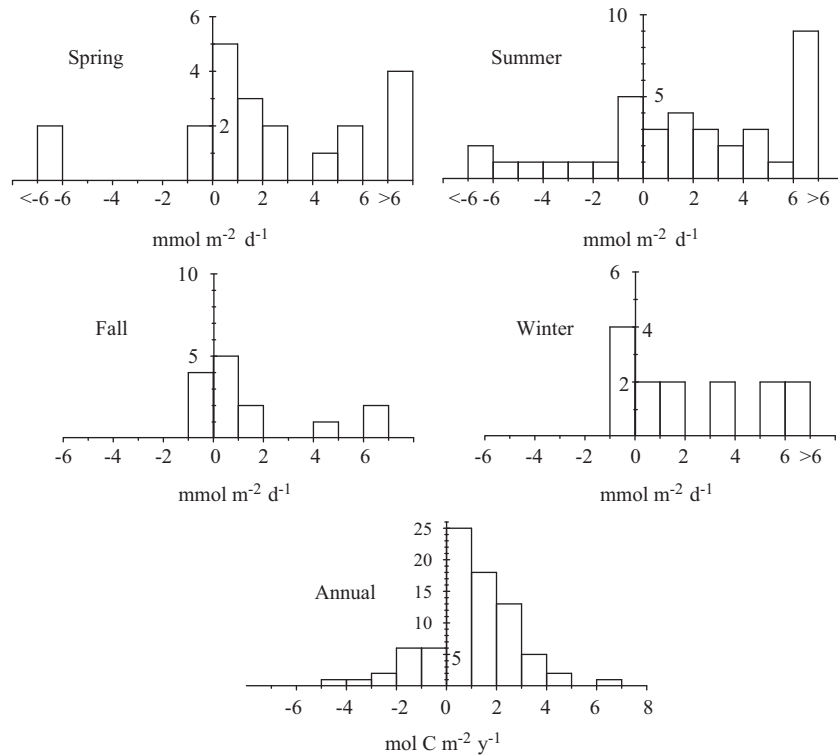


Fig. 1. Histogram of reported daily fluxes of CO₂ during different seasons as well as the annual flux.

Fig. 2 shows the histogram of reported daily fluxes of CO₂ by different latitude bands. High-latitude and temperate continental shelves are sinks for atmospheric CO₂, while tropical and sub-tropical shelves tend to act as sources of CO₂ to the atmosphere. This latitudinal variability in air–sea CO₂ fluxes is related to the fact that biological activity over continental shelves modulates a background CO₂ signal imposed by oceanic waters circulating over the continental shelf. Open oceanic waters are generally under-saturated in CO₂ at high- and mid-latitudes (Takahashi et al., 2002, 2009), where continental shelves are highly productive (e.g., Walsh, 1988), hence increasing the background open-ocean CO₂ under-saturation. At sub-tropical and tropical latitudes open oceanic waters are generally over-saturated in CO₂ (Takahashi et al., 2002, 2009), and non-upwelling continental margins are less productive, tending to be oligotrophic (e.g. Walsh, 1988), and receive massive inputs of terrestrial organic matter (up to 60% of the global TOC river inputs, e.g., Ludwig et al., 1996), leading to an enhancement of the background open ocean CO₂ over-saturation.

Continental shelves were divided into various biogeochemical regions (Polar, Subpolar, Western Boundary Current, Eastern Boundary Current, Tropical and Monsoonal) for each ocean basin following the classification of Jahnke (2009), and we scaled the air–sea CO₂ fluxes for the 27 regions (Table 3) based on the air–sea CO₂ fluxes compiled in Table 2. The scaled CO₂ fluxes by biogeochemical provinces yield a CO₂ sink of 27.3×10^{12} mol C yr⁻¹ (0.33 Pg C yr⁻¹ or 0.91 mol C m⁻² yr⁻¹) for a total continental shelf area of 30×10^6 km², in agreement with the CO₂ sink based on the scaled numerical average of 0.35 Pg C yr⁻¹ (or 1.1 mol C m⁻² yr⁻¹) given above for a smaller area. The largest contributions to this sink of CO₂ are from subpolar and polar biogeochemical provinces, respectively, 17.9 and 12.1×10^{12} mol C yr⁻¹. Monsoonal and tropical biogeochemical provinces act as moderate CO₂ sources of similar amount, respectively, 0.5 and 0.3×10^{12} mol C yr⁻¹. Eastern Boundary Current and Western Boundary Current biogeochemical provinces act, respectively, as a CO₂ sink (1.2×10^{12} mol C yr⁻¹) and as a CO₂ source (3.1×10^{12} mol C yr⁻¹).

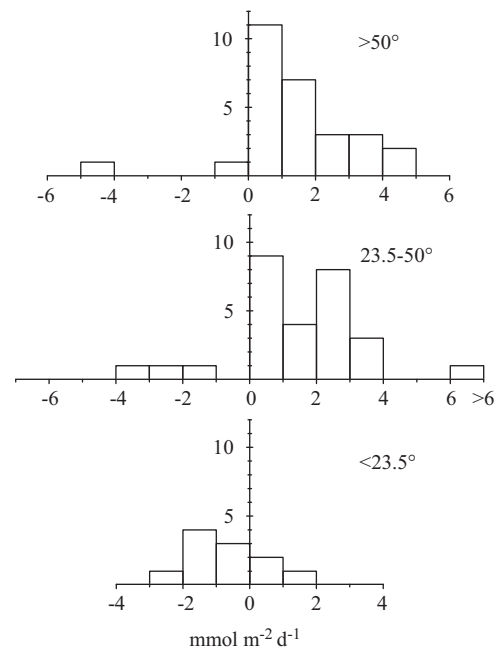


Fig. 2. Histogram of reported annual fluxes of CO₂ in different latitudinal bands.

Note that some western boundary current systems act as CO₂ sinks, namely those located in Atlantic Ocean basin (Aristegui et al., 2005) such as the Galician upwelling system (Borges and Frankignoulle, 2002b) and the Benguela upwelling system (Santana-Casiano and González-Dávila, 2009). Among the ocean basins, the largest coastal CO₂ sink is for the Atlantic Ocean (8.4×10^{12} mol C yr⁻¹) due to its large surface area (12.8×10^6 km², 42.6% of total continental shelf surface area), followed by the Arctic Ocean (7.7×10^{12} mol C yr⁻¹) due to large areal CO₂ fluxes (2.2 mol C m⁻² yr⁻¹ compared to 0.7 mol C m⁻² yr⁻¹ in the Atlantic

Table 3
Air–sea exchanges of CO₂ in continental shelves by biogeochemical provinces and ocean basins.

Region	Biogeochemical province	Area ^a (10 ⁶ km ²)	Air–sea flux (mol CO ₂ m ⁻² yr ⁻¹)	Total air–sea exchange (10 ¹² mol CO ₂ yr ⁻¹)
Arctic	Polar	3.51	2.2	7.72
Antarctic	Polar	2.19	2.0	4.38
NW Atlantic	Subpolar	2.25	1.0	2.25
NW Atlantic	Western Boundary Current	1.54	-0.5	-0.77
W Atlantic	Tropical	0.62	-0.1	-0.06
SW Atlantic	Western Boundary Current	1.68	-1.0	-1.68
SW Atlantic	Subpolar	2.33	1.5	3.50
NE Atlantic	Subpolar	2.34	1.6	3.74
NE Atlantic	Eastern Boundary Current	1.68	0.8	1.34
E Atlantic	Tropical	0.18	-0.1	-0.02
SE Atlantic	Eastern Boundary Current	0.22	0.5	0.11
Atlantic Subtotal		12.84	0.66 (ave.)	8.41
W Indian	Monsoonal	0.50	-1.4	-0.70
W Indian	Tropical	0.08	-0.1	-0.01
W Indian	Western Boundary Current	0.18	-1.0	-0.18
E Indian	Monsoonal	0.62	0.4	0.25
E Indian	Tropical	0.23	-0.1	-0.02
E Indian	Eastern Boundary Current	0.25	-0.1	-0.02
E Indian	Subpolar	0.38	1.8	0.68
Indian Subtotal		2.24	0.00 (ave.)	0.00
NW Pacific	Subpolar	2.91	2.5	7.28
NW Pacific	Western Boundary Current	1.36	1.1	1.50
W Pacific	Tropical	2.15	-0.1	-0.22
SW Pacific	Western Boundary Current	2.01	-1.0	-2.01
NE Pacific	Subpolar	0.22	1.8	0.40
NE Pacific	Eastern Boundary Current	0.40	-0.5	-0.20
E Pacific	Tropical	0.10	-0.1	-0.01
SE Pacific	Eastern Boundary Current	0.20	-0.1	-0.02
SE Pacific	Subpolar	0.03	1.8	0.05
Pacific subtotal		9.38	0.72 (ave.)	6.77
Grand totals		30.16	0.90 (ave.)	27.28

^a Taken from Jahnke (2009).

and Pacific Oceans). The Pacific Ocean and the Antarctic Ocean also significantly contribute 6.8 and 4.4×10^{12} mol C yr⁻¹, respectively, to the global continental shelf CO₂ sink, while the Indian Ocean continental shelf has a nearly neutral status with regards to the CO₂ exchange between the continental shelf and the atmosphere.

4. Carbon mass balance

The global carbon pools can be divided into several compartments, representing the atmosphere, rivers, shelf and slope waters, sediments, upper-ocean and deep-ocean organic carbon (both dissolved and particulate) as well as upper-ocean and deep-ocean inorganic carbon (Fig. 3). Fluxes among these compartments must balance each other out in order to conserve mass. In fact, the crux of the so-called Box Model is that the mass of various elements must be in balance even though the chemical forms of the elements under study may change, e.g., DOC may be oxidized to DIC.

As the amount of carbon entering the coastal ocean must equal the amount leaving it, values of C fluxes across the air–sea interface can thus be constrained based on various known inputs, offshore exports and burial across other boundaries on the

shelves. Most of these fluxes were tabulated in Chen et al. (2003) based on 27 studies. Chen (2004) made slight modifications to the box model of Chen et al. (2003) mainly because of a better quantification of new productivity on continental shelves taking into account DOC (Hansell and Carlson, 1998) in addition to POC production. Further, on account of the lower DOC values reported in subsurface waters in the open oceans in recent years, the flux of DOC from the open ocean to the shelves is reduced.

Fig. 3 is a schematic diagram summarizing the fluxes across boundaries, as indicated by various arrows. Values in the “shelves” box are for various species derived from primary and new production. There is a net off shelf transport of 50×10^{12} mol C yr⁻¹ of DOC, compared to a terrestrial input of 27×10^{12} mol C yr⁻¹. At least 23×10^{12} mol C yr⁻¹ of DOC is produced on the shelf, which represents 35% of new organic carbon production or 27% of the total new carbon production. A net air-to-sea flux of carbon is needed to support such an offshore transport of organic carbon. The net CO₂ sink in continental shelves computed to close the budget is 0.36 Pg C yr⁻¹, close to values of 0.33 and 0.35 Pg C yr⁻¹ based on scaled estimates from pCO₂ measurements given above.

As discussed earlier, some investigators have taken the view that the continental margins are net sources of CO₂ to the atmosphere (Smith and Mackenzie, 1987; Smith and Hollibaugh, 1993; Ver et al., 1999a, b; Mackenzie et al., 2000; Fasham et al.,

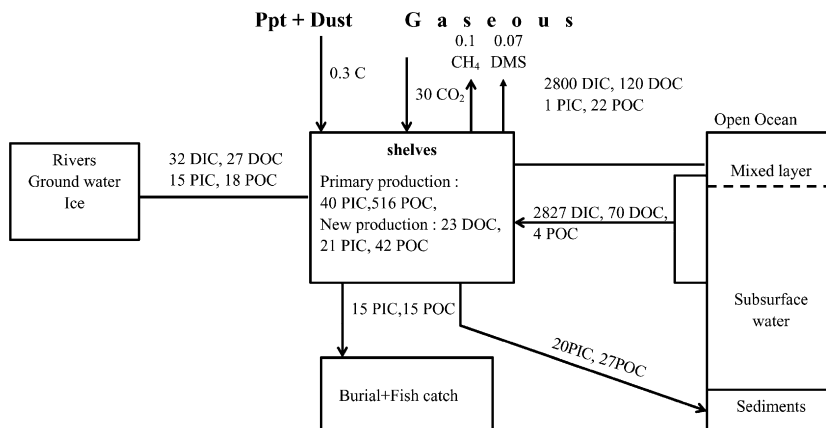


Fig. 3. Mass balance of carbon in continental shelves (flows are in 10^{12} mol C yr $^{-1}$; modified from Chen, 2004).

2001). This view is based on the simple global mass balance of terrestrial/riverine organic carbon inputs and carbon burial in sediments (Smith and Mackenzie, 1987). However, terrestrial/riverine organic carbon inputs are profoundly modified (and largely degraded) during estuarine transit based on the net heterotrophic ecosystem metabolic state of inner estuaries (Odum and Hoskin, 1958; Odum and Wilson, 1962; Heip et al., 1995; Kemp et al., 1997; Gattuso et al., 1998; Gazeau et al., 2004; Hopkinson and Smith, 2005), and based on organic carbon characterization both in the water column (e.g. Middelburg and Herman, 2007 and references therein) and sediments (Mayer et al., 2007 and references therein) of inner estuaries and near-shore coastal environments. Hence, inner estuaries and near-shore coastal ecosystems are effective filters for terrestrial/riverine organic inputs and impose a by-pass of carbon towards the atmosphere for the global carbon cycle. This is in agreement with the large CO $_2$ emission from inner estuaries we report and allows us to explain the apparent paradox that little terrestrial organic carbon can be accounted for in sediments or the water column of continental shelves and open oceanic waters based on tracer approaches (e.g. Hedges et al., 1997).

The view of a heterotrophic coastal ocean reported in earlier literature might have changed more recently. For instance, Yool and Fasham (2001) changed their view expressed in Fasham et al. (2001) and stated that, "...Results of simulations find modeled pump activity very variable between shelf regions, with the East China Sea shelf behaving very similarly to the global average", and "...should shelf regions absorb CO $_2$ at the rate of the East China Sea, the pump would account for a net oceanic uptake of 0.6 Pg C yr $^{-1}$ ". Mackenzie and colleagues also recently changed their view on net CO $_2$ fluxes in the coastal ocean. For instance, they stated in earlier papers that before anthropogenic activities, the global coastal ocean was a net autotrophic system with a net export of organic carbon to sediments and the open ocean of 20 T mol C yr $^{-1}$ (Ver et al., 1999a,b; Mackenzie et al., 2000). However, their later results (Rabouille et al., 2001) conclude that although the proximal coastal zones are CO $_2$ sources (8.4×10^{12} mol C yr $^{-1}$), the distal coastal zones are CO $_2$ sinks (28.4×10^{12} mol C yr $^{-1}$). As a result, the continental margins are found to be a net CO $_2$ sink of 20×10^{12} mol C yr $^{-1}$ (0.24 Pg C yr $^{-1}$) in the pre-anthropogenic state, which differs from the CO $_2$ source of 0.2 Pg C yr $^{-1}$ reported by Ver et al. (1999a,b) and Mackenzie et al. (2000).

In order to adjust the results of Ver et al. (1999a,b) and Mackenzie et al. (2000) with regard to the pre-anthropogenic CO $_2$ fluxes, a correction of 0.44 Pg C yr $^{-1}$ needs to be made (to correct

for a pre-anthropogenic source of CO $_2$ of 0.20 Pg C yr $^{-1}$ given by Ver et al. (1999a,b) and Mackenzie et al. (2000), and so also for a pre-anthropogenic sink of 0.24 Pg C yr $^{-1}$ given by Rabouille et al., 2001). As a consequence, this renders the continental margins as CO $_2$ sinks of 0.34 Pg C yr $^{-1}$ in the present time (year 2000).

The carbon flows through the land/ocean/atmospheric system are far more complicated and diverse than the above simple algebra would suggest, but it is nevertheless worth underscoring the fact that the corrected air–sea CO $_2$ flux of Ver et al. (1999a,b) and Mackenzie et al. (2000) of 0.34 Pg C yr $^{-1}$ agrees with the values reported here ranging from 0.33 to 0.36 Pg C yr $^{-1}$ based on scaled pCO $_2$ measurements and carbon mass balance in continental shelves.

5. Conclusions

The first LOICZ report asserted that whether coastal seas are net sinks or sources of CO $_2$ could not be determined (Kempe, 1995). Based on carbon mass-balance calculations as well as scaled estimates based on pCO $_2$ measurements, it is firmly established that most open shelf areas are sinks for atmospheric CO $_2$, although many inner estuaries, near-shore coastal waters and intensive upwelling areas are over-saturated in CO $_2$. On the whole, continental shelves are significant sinks for atmospheric CO $_2$, ranging from 0.33 to 0.36 Pg C yr $^{-1}$, which corresponds to an additional sink of 27% to ~30% of the CO $_2$ uptake by the open oceans based on the most recent pCO $_2$ climatology of Takahashi et al. (2009). On the other hand, inner estuaries, salt marshes and mangroves emit CO $_2$ to the atmosphere of ~0.50 Pg C yr $^{-1}$, although these estimates are prone to large uncertainty.

The concept of marginal seas as sinks and near-shore coastal ecosystems as sources of atmospheric CO $_2$ allows reconciling diverging views on carbon cycling in the coastal ocean. The fact that the inputs of terrestrial/riverine organic carbon would be in excess of carbon burial in marine sediments (Smith and Mackenzie, 1987) does not necessarily imply a net heterotrophy of marginal seas that is in contradiction with the high offshore export rates of POC and DOC consistently reported across continental margins (e.g. overview by Chen, 2003; Liu et al., 2000). Also, tracer-based analysis of water column and sediment organic carbon in inner estuaries, continental shelves and open ocean confirm high removal rates of terrestrial organic carbon. Hence, inner estuaries and near-shore ecosystems are effective filters for terrestrial/riverine organic inputs and impose a by-pass of carbon towards the atmosphere for the global carbon cycle.

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