

Carbon dioxide in European coastal waters

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Abstract

We compiled from literature annually integrated air–water fluxes of carbon dioxide (CO₂) computed from field measurements, in 20 coastal European environments that were gathered into 3 main ecosystems: inner estuaries, upwelling continental shelves and non-upwelling continental shelves. The comparison of annual cycles of the partial pressure of CO₂ (pCO₂) in 5 contrasting continental shelves provided insights into the biogeochemical drivers of the CO₂ fluxes. The latter were also investigated by comparing CO₂ fluxes to net ecosystem (NEP) and net community production (NCP) in 3 contrasted coastal ecosystems. Air–water CO₂ fluxes were scaled at European regional level and compared to fluxes of atmospheric CO₂ in other aquatic and terrestrial compartments. Continental shelves are significant sinks for atmospheric CO₂ at an average rate of $-1.9 \text{ molC m}^{-2} \text{ yr}^{-1}$ that scaled at European level corresponds to an absorption of atmospheric CO₂ of $-68.1 \text{ TgC yr}^{-1}$. This sink is equivalent to the one reported for the terrestrial biosphere of $-66.1 \text{ TgC yr}^{-1}$, based on carbon-stock change models. Estuaries are significant sources of CO₂ to the atmosphere at an average rate of $49.9 \text{ molC m}^{-2} \text{ yr}^{-1}$ that is higher than the CO₂ emission to the atmosphere from rivers, streams and lakes. The scaled emission of CO₂ to the atmosphere from inner estuaries of about 67.0 TgC yr^{-1} would almost fully balance the sink of atmospheric CO₂ computed for continental shelves. However, the scaled emission of CO₂ from estuaries to the atmosphere is inconsistent with the potential emission of CO₂ based on the fate of river organic carbon during estuarine transit. This discrepancy is most probably due to the poorly constrained surface area estimate of inner estuaries.

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1. Introduction

Air–water fluxes of carbon dioxide (CO₂) in coastal environments are usually neglected in global carbon budgets because the coastal ocean only covers about 7% of the oceanic realm (e.g. Gattuso et al., 1998; Wollast, 1998). However, due to intense inputs of nutrients and carbon from land through rivers, and from the open ocean at continental margins, the coastal ocean is one of the most biogeochemically active regions of the biosphere. Inputs, production, degradation and export of organic matter in the coastal ocean are several

times higher than in the open ocean (e.g. Wollast, 1998). Consequently, it can be expected that the CO₂ fluxes between the atmosphere and coastal environments would be disproportionately more intense than their relative surface area, and significant for global carbon budgets.

The work of Tsunogai et al. (1999) put under the spotlight the CO₂ exchanges between the atmosphere and the coastal ocean, as these authors computed a sink of atmospheric CO₂ of -1.0 PgC yr^{-1} by scaling globally the air–sea CO₂ fluxes from East China Sea. Such a sink is comparable to the open ocean sink of atmospheric CO₂ estimated to -1.6 PgC yr^{-1} (Takahashi et al., 2002; Takahashi, 2003). More recent estimates of the global CO₂ sink over marginal seas based on scaled CO₂ fluxes computed from field measurements of the partial pressure of CO₂ (pCO₂) or from carbon mass balances

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range between -0.2 and -0.4 PgC yr^{-1} (Fig. 1), nevertheless still significant for the global CO_2 budget.

The coastal ocean is not solely composed of marginal seas and most near-shore coastal environments, such as estuaries, act as sources of CO_2 to the atmosphere (e.g. Frankignoulle et al., 1998; Abril and Borges, 2004) due to the degradation of riverine organic carbon (e.g. Gattuso et al., 1998; Abril et al., 2002; Hopkinson and Smith, 2005). If the CO_2 emission of near-shore ecosystems is scaled globally then it could almost fully balance the sink of CO_2 over marginal seas (Borges, 2005; Borges et al., 2005). Although the scaling of CO_2 fluxes in the coastal ocean is at present time prone to large uncertainties due to the scarcity of data and the unreliability of surface area estimates of some if not all near-shore ecosystems, a more or less balanced exchange of CO_2 between the atmosphere and the overall coastal ocean is consistent with the output of the Shallow-water Ocean Carbonate Model (SOCM; Fig. 1). SOCM simulates a decrease of the CO_2 emission from the coastal ocean to the atmosphere since pre-industrial

times and a neutral flux at present time (Andersson and Mackenzie, 2004; Mackenzie et al., 2004, 2005). This evolution is due to the rise of atmospheric CO_2 and the increase of net ecosystem production (NEP) related to the anthropogenic inputs of nutrients. Long term monitoring (e.g. Radach et al., 1990), and satellite imagery (Gregg et al., 2005) show an increase in coastal waters of phytoplankton biomass (chlorophyll-a), in agreement with the increase of NEP predicted by SOCM. SOCM predicts that during the next 100 years the coastal ocean will act as a sink for atmospheric CO_2 , due to the continued rise of atmospheric CO_2 and the increase of NEP, and to a much lesser extent to the decrease of calcium carbonate (CaCO_3) production and increase of CaCO_3 diagenetic dissolution (Andersson and Mackenzie, 2004; Mackenzie et al., 2004, 2005).

In the present paper, we discuss the biogeochemical controls of air–water CO_2 fluxes in European coastal environments. We also attempt a provisional scaling of these fluxes that are compared to the fluxes of atmospheric CO_2 in other aquatic and terrestrial compartments at European scale.

2. Results and discussion

2.1. Biogeochemical drivers of CO_2 dynamics

Annually integrated air–water CO_2 fluxes computed from pCO_2 field measurements were compiled from literature (Table 1; Fig. 2). Data in 20 coastal environments were gathered into 3 main ecosystems: inner estuaries, upwelling continental shelves and non-upwelling continental shelves. Inner estuaries are characterized by pCO_2 values well above atmospheric equilibrium and all the sites listed in Table 1 act as sources of CO_2 to the atmosphere. Upwelling and non-upwelling continental shelves act as moderate to strong sinks of atmospheric CO_2 .

2.1.1. Comparison of the pCO_2 seasonal cycle in five temperate continental shelves

The seasonal cycle of surface water temperature, pCO_2 , and pCO_2 normalized to a constant temperature of 15°C ($\text{pCO}_2@15^\circ\text{C}$) in 5 temperate European continental shelves are compared in Fig. 3. All the sites show a springtime decrease of pCO_2 except the Bay of Angels in the Mediterranean Sea, where the distinct increase of pCO_2 from early April to mid-August follows the one of temperature. On the contrary, during that period $\text{pCO}_2@15^\circ\text{C}$ shows a slight decrease probably due to a combination of biological uptake of CO_2 and emission of CO_2 to the atmosphere. Hence, the seasonal cycle of pCO_2 in the oligotrophic Mediterranean continental shelf (refer to wintertime nitrate (NO_3^-) concentrations in Table 2) is largely controlled by temperature change unlike the other meso- and eutrophic continental shelves of Fig. 3.

The Gulf of Biscay and the English Channel are characterized by a springtime decrease of pCO_2 and $\text{pCO}_2@15^\circ\text{C}$ similar in timing and amplitude. During summer, $\text{pCO}_2@15^\circ\text{C}$ remains relatively constant in both areas suggesting that

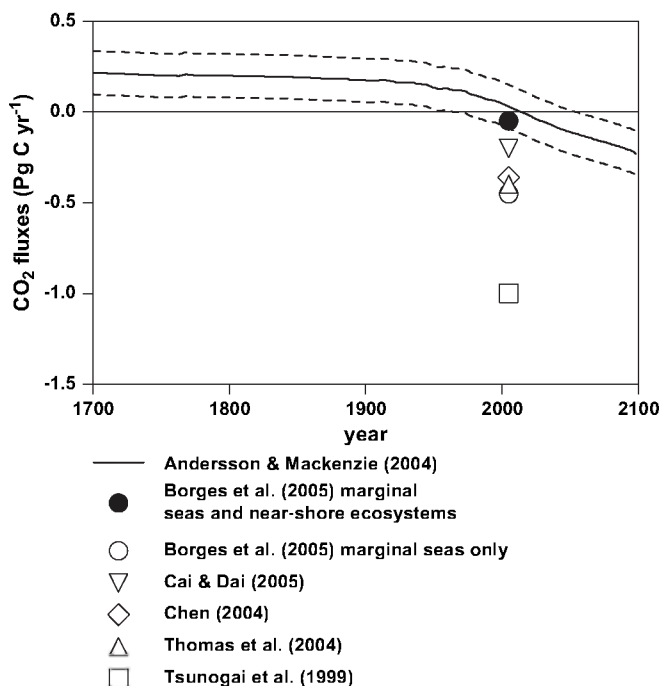


Fig. 1. Carbon dioxide fluxes between the coastal ocean and the atmosphere (PgC yr^{-1}) at global scale based on different approaches. The solid line corresponds to the output of the box model of Andersson and Mackenzie (2004) that accounts for organic and inorganic carbon fluxes (Shallow-water Ocean Carbonate Model, SOCM); dotted line corresponds to uncertainty estimate. The open diamond corresponds to mass balance computations of organic and inorganic carbon in several marginal seas (Chen, 2004). The open square and open up-triangle correspond to globally scaled fluxes computed from field pCO_2 measurements in, respectively, the East China Sea (Tsunogai et al., 1999), and the North Sea (Thomas et al., 2004). The open circle and open down-triangle correspond to globally scaled fluxes computed from field pCO_2 measurements in several marginal seas, by respectively, Borges et al. (2005), and Cai and Dai (2005). The full circle corresponds to globally scaled fluxes computed from field pCO_2 measurements in marginal seas and near-shore ecosystems (inner estuaries, saltmarsh and mangrove waters, coral reefs and coastal upwellings) by Borges et al. (2005).

Table 1

Range of pCO₂, air–water CO₂ fluxes, and corresponding gas transfer velocity (*k*) in European coastal environments. The numbers in parentheses correspond to site identification in Fig. 2. W denotes the *k*-wind parameterization given by Wanninkhof (1992), FC denotes direct measurements with a floating chamber, and C denotes a constant *k* value. *: *k* = 8.0 cm h⁻¹; **: *k* = 13.0 cm h⁻¹. MiT = micro-tidal; MaT = macro-tidal; RD = river dominated (i.e. most of the salinity mixing occurs in the outer-estuary); LUI = low Upwelling Index; SS = seasonally stratified; PS = permanently stratified; WM = permanently well-mixed. 1: Gazeau et al. (2005a); 2: Frankignoulle et al. (1998); 3: Abril et al. (2003, 2004); 4: Borges and Frankignoulle (2002a); 5: based on Huertas et al. (2005) but flux values converted to the *k* parameterization given by Wanninkhof (1992) using conversion factors determined from the Rayleigh frequency distribution from values originally computed from the *k* parameterization given by Woolf and Thorpe (1991); 6: based on data compiled from Kaltin et al. (2002) and Omar et al. (2003), using National Centers for Environmental Prediction (NCEP) daily wind speeds for the 1993–2003 period; 7: Algesten et al. (2004); 8: Thomas and Schneider (1999); 9: based on Thomas et al. (2004) but flux values converted to the *k* parameterization given by Wanninkhof (1992) using conversion factors determined from the Rayleigh frequency distribution from values originally computed from the *k* parameterization given by Wanninkhof and McGillis (1999); 10: Borges and Frankignoulle (2003); 11: based on pCO₂ data from Frankignoulle and Borges (2001) and additional data obtained in May 2001 and 2002, and June 2004, the atmospheric pCO₂ data from Mace Head, 6 hourly NCEP wind speeds from five grid points (–9.38°E 50.48°N; –7.50°E 50.48°N; –9.38°E 48.57°N; –7.50°E 48.57°N; –5.63°E 48.57°N), for the 1993–2004 period; 12: based on pCO₂ data from Copin-Montégut et al. (2004) extracted for the continental shelf (http://www.obs-vlfr.fr/cd_rom_dmtt/dyf_main.htm), the atmospheric pCO₂ data from Lampedusa Island, 6 hourly NCEP wind speeds (7.50°E 42.86°N) for the 1998–2000 period

Site (location in Fig. 2)	Characteristics	°E	°N	pCO ₂ (ppm)	Air–water CO ₂ fluxes (molC m ⁻² yr ⁻¹)	<i>k</i>	Ref.
<i>Inner estuaries</i>							
Randers Fjord (1)	MiT	10.3	56.6	220–3400	2.2	FC	1
Elbe (2)	MaT	8.8	53.9	580–1100	53.0	FC	2
Ems (3)	MaT	6.9	53.4	560–3755	67.3	FC	2
Rhine (4)	MaT; RD	4.1	52.0	545–1990	39.7	FC	2
Scheldt (5)	MaT	3.5	51.4	125–9425	63.0	FC	2
Thames (6)	MaT	0.9	51.5	505–5200	73.6	FC	2
Tamar (7)	MaT	–4.2	50.4	380–2200	74.8	C**	2
Loire (8)	MaT	–2.2	47.2	630–2910	64.4	C**	3
Gironde (9)	MaT	–1.1	45.6	465–2860	30.8	FC	2
Douro (10)	MaT; RD	–8.7	41.1	1330–2200	76.0	FC	2
Sado (11)	MaT	–8.9	38.5	575–5700	31.3	FC	2
<i>Upwelling marginal seas</i>							
Galician coast (12)	LUI	–9.2	42.5	265–415	–2.2	W	4
Gulf of Cadiz (13)	LUI	–7.0	37.0	125–700	–0.4	W	5
<i>Non-upwelling marginal seas</i>							
Barents Sea (14)	SS	30.0	75.0	168–352	–3.6	W	6
Bothnian Bay (15)	PS	21.0	63.0	150–550	+3.1	W	7
Baltic Proper (16)	PS	20.0	57.0	156–475	–0.8	W	8
North Sea (17)	SS	2.6	56.7	145–495	–1.4	W	9
English Channel (18)	WM	–1.2	50.2	200–500	0.0	W	10
Gulf of Biscay and Celtic Sea (19)	SS	–7.9	49.0	260–460	–0.8	W	11
Bay of Angels (20)	SS	7.4	43.6	315–450	–0.6	W	12

regenerated primary production maintains during this period the low pCO₂@15 °C values attained during the spring bloom (note however that pCO₂ increases with temperature). However, in late summer and early fall, pCO₂@15 °C further decreases in the Gulf of Biscay while it increases in the English Channel. This can be related to an early fall phytoplankton bloom in the Gulf of Biscay related to the input of nutrients as the water column starts to de-stratify (Joint et al., 2001). In the English Channel, the increase of pCO₂@15 °C probably results from heterotrophic processes related to the degradation of the organic matter accumulated during the earlier part of the seasonal cycle. Unfavorable light conditions to maintain regenerated primary production are probably responsible for the onset in the English Channel of this marked period of net heterotrophy in fall. Note that the English Channel is permanently well-mixed due to its shallowness while the Gulf of Biscay is characterized by a seasonal thermal stratification. This confirms the hypothesis that permanently well mixed systems are less efficient in exporting

organic matter and in absorbing atmospheric CO₂, than seasonally or permanently stratified systems (Borges, 2005).

The seasonal amplitude and in particular the spring decrease of pCO₂ and pCO₂@15 °C in the Southern Bight of the North Sea is much larger than in the English Channel and the Gulf of Biscay (Fig. 3, Table 2). This seems to be related to higher nutrient availability due to river inputs. Indeed, the salinity in the Gulf of Biscay is close to the baseline value of the adjacent North Atlantic waters, while it is significantly lower in the Southern Bight of the North Sea, also characterized by significantly higher wintertime NO₃⁻ concentrations (Table 2). Unlike the English Channel and the Gulf of Biscay, there is in the Southern Bight of the North Sea a sharp increase of pCO₂ and pCO₂@15 °C that follows closely the spring bloom, suggesting a rapid remineralization of organic matter, followed by a steady increase of pCO₂@15 °C from mid-June to early December. This in turn suggests the absence in the Southern Bight of the North Sea of a period of regenerated primary production that maintains pCO₂ at low levels during

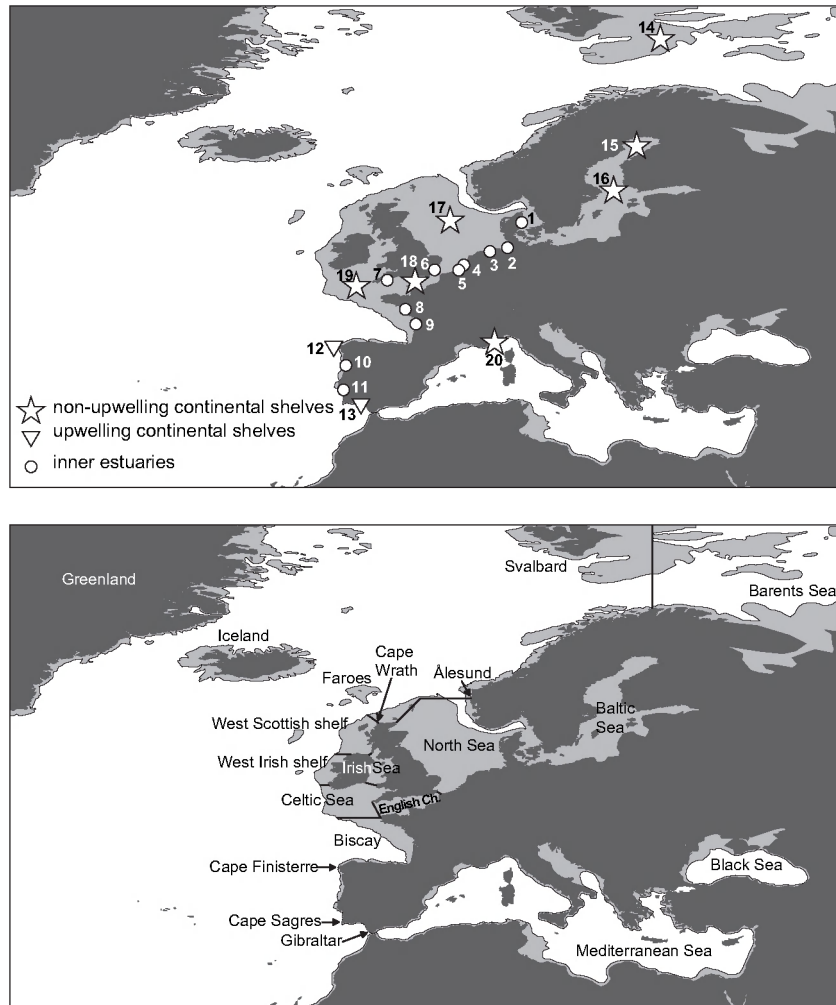


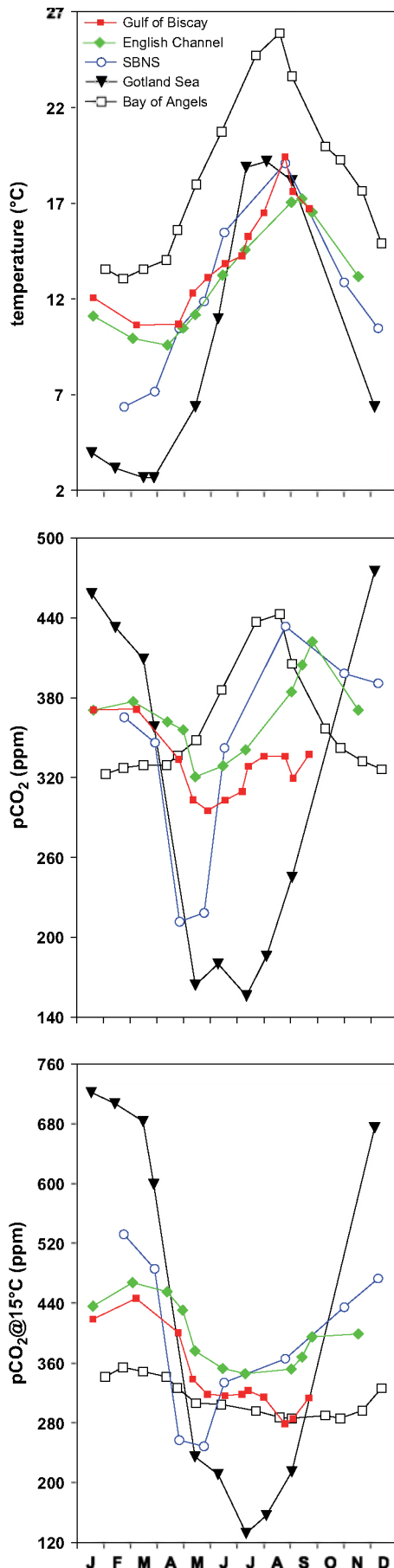
Fig. 2. Map showing the location of 20 European coastal environments where air–water CO_2 fluxes have been satisfactorily integrated at annual scale. Numbers indicate locations named in first column of Table 1. Light grey areas correspond to the continental shelf areas, delimited by the 200 m isobath (adapted from Gazeau et al., 2004 and Huthnance, 2006).

summer in the English Channel and the Gulf of Biscay. This is due to the strong top-down control of primary production by mesozooplankton that prevents any significant phytoplankton development in the Southern Bight of the North Sea, after the decline of the spring bloom (Lancelot et al., 2005).

In the Gotland Sea, pCO_2 and $\text{pCO}_2@15^\circ\text{C}$ sharply decrease from mid-March to mid-May due to the spring bloom. After the exhaustion of inorganic nutrients, a further decrease of $\text{pCO}_2@15^\circ\text{C}$ is observed in June and July that has been attributed to “luxury production” and related dissolved organic carbon (DOC) release (Thomas et al., 1999) and/or to N_2 fixation (Leinweber et al., 2005). This is consistent with an annual amplitude of dissolved inorganic carbon (DIC) in the Gotland Sea that is similar to the one in the Southern Bight of the North Sea although the wintertime NO_3^- values are two to ten times lower. Note also that the much higher seasonal amplitude of pCO_2 and $\text{pCO}_2@15^\circ\text{C}$ in the Gotland Sea than in the other four continental shelves is related to the higher Revelle factor due to lower salinity and total alkalinity (Table 2).

2.1.2. European coastal upwelling systems as sinks of atmospheric CO_2

Although a relatively abundant literature reporting data on CO_2 dynamics in coastal upwelling systems is available (see review by Borges, 2005), annually integrated air–water CO_2 fluxes have been calculated in 3 other coastal upwelling systems besides the Galician coast and the Gulf of Cadiz: off the Oman, California and Vancouver Island coasts. The coastal upwelling systems off the Oman and California coasts act as CO_2 sources to the atmosphere, while the coastal upwelling systems off the Vancouver Island coast, the Galician coast and the Gulf of Cadiz act as sinks for atmospheric CO_2 . The two systems that act as CO_2 sources (Oman and California coasts) are characterized by disproportionately higher upwelling indices that lead to much higher inputs of upwelled DIC and NO_3^- than in the systems that act as CO_2 sinks (Borges, 2005). This could be related to the fact that flushing rates are so high and the nutrients and DIC inputs so intense that exhaustion of nutrients and undersaturation of CO_2 do not occur over the continental shelf in high upwelling index systems, although probably occurring in upwelling filaments. It has also



been hypothesized that coastal upwelling systems located at high- and mid-latitudes are CO_2 sinks, while systems at low-latitudes are CO_2 sources (Cai and Dai, 2004). However, more data in other systems are required to validate this hypothesis. It has also been argued that the pCO_2 values of upwelled Eastern North Atlantic Central Water off the North Western Iberian coast are lower (about 400 ppm) compared to aged central waters of the South Atlantic, the Indian and the Pacific Ocean (Aristegui et al., 2004).

2.1.3. Relationship between air–water CO_2 fluxes and ecosystem metabolism

Net autotrophic ecosystems, where gross primary production (GPP) exceeds community respiration (CR) decrease CO_2 in the surrounding waters, and conversely net heterotrophic systems (where $\text{GPP} < \text{CR}$) enrich the surrounding water in CO_2 . Nevertheless, in coastal environments the link between the exchange of CO_2 with the atmosphere and the metabolic status of surface waters is not direct, as noted by Gattuso et al. (1998) among others. Besides NEP, the net CO_2 flux between the water column and the atmosphere will be further modulated by other factors such as: additional biogeochemical processes (e.g. CaCO_3 precipitation/dissolution); exchange of water with adjacent aquatic systems and the CO_2 content of the exchanged water mass; residence time of the water mass within the system; decoupling of organic carbon production and degradation across the water column related to the physical settings of the system. An extreme example is the case of coral reefs, where NEP is close to zero, but due to intense calcification rates these systems act as sources of CO_2 to the atmosphere. In certain shallow water temperate continental shelves, calcification can also be a major driver of the air–water CO_2 fluxes. For instance, Borges and Frankignoulle (2003) hypothesized that the English Channel is not a significant sink for atmospheric CO_2 unlike adjacent systems such as the Gulf of Biscay (Table 1) and the Southern Bight of the North Sea, due to the release of CO_2 from extensive brittle star populations that on an annual scale balance the CO_2 fixation by NEP.

In the course of the recent European project EUROTROPH (Nutrients Cycling and the Trophic Status of Coastal Ecosystems), simultaneous and independent measurements of metabolic process rates and air–water CO_2 exchanges were carried out in 3 coastal ecosystems (Fig. 4). For some of the cruises and some of the sites, the CO_2 fluxes and trophic status

Fig. 3. Comparison of the seasonal cycle of temperature, pCO_2 and pCO_2 normalized at a temperature of 15°C ($\text{pCO}_2@15^\circ\text{C}$) in 5 temperate European continental shelves. Data for the Gulf of Biscay (composite annual cycle compiled from data obtained from 1994 to 2004) from Frankignoulle and Borges (2001), for the English Channel (composite annual cycle compiled from data obtained from 1992 to 1999) from Borges and Frankignoulle (2003), for the Southern Bight of the North Sea (SBNS, continuous annual cycle from June 2003 to May 2004) from Schiettecatte et al. (submitted for publication), for the Gotland Sea (Baltic Sea, continuous annual cycle from December 1999 to September 2001) from Schneider et al. (2003) and Kuss et al. (2004), and for the Bay of Angels (dual continuous annual cycle from February 1998 to February 2000) from Copin-Montégut et al. (2004) extracted for the continental shelf from http://www.obs-vlfr.fr/cd_rom_dmtt/dyf_main.htm.

Table 2
Wintertime nitrate concentration, salinity, seasonal amplitude of pCO₂, of pCO₂ normalized to a constant temperature of 15 °C (pCO₂@15 °C), and of DIC, range of total alkalinity and of the Revelle factor, in 5 temperate European continental shelves (Gulf of Biscay, English Channel, Southern Bight of the North Sea (SBNS), Gotland Sea (Baltic Sea), and Bay of Angels (Mediterranean Sea))

	Gulf of Biscay	English Channel	SBNS	Gotland Sea	Bay of Angels
Wintertime NO ₃ ⁻ (μmol kg ⁻¹)	5–10 ^a	5–20 ^b	10–40 ^c	4 ^d	1 ^e
Salinity	35.4 ^f	35.1 ^g	34.6 ^h	7.0 ⁱ	38.0 ^j
pCO ₂ amplitude (ppm)	76 ^k	102 ^k	222 ^k	319 ^k	120 ^k
pCO ₂ @15°C amplitude (ppm)	167 ^k	122 ^k	283 ^k	589 ^k	68 ^k
DIC amplitude (μmol kg ⁻¹)	76 ^l	55 ^l	140 ^l	139 ^l	50 ^l
Total alkalinity (μmol kg ⁻¹)	2333–2345 ^f	2297–2334 ^g	2294–2353 ^h	1567–1593 ⁱ	2503–2550 ^m
Revelle factor	9.8–11.7 ^l	10.7–12.4 ^l	9.6–13.3 ^l	14.7–28.3 ^l	9.3–10.4 ^l

^a From Wollast and Chou (2001).

^b From Pingree et al. (1977), Wafar et al. (1983), and Bentley et al. (1999).

^c From Lenhart et al. (2004).

^d From Leinweber et al. (2005).

^e From the nearby monitoring station B in the Villefranche roadstead (<http://www.obs-vlfr.fr/Rade/>).

^f From Frankignoulle and Borges (2001).

^g From Borges and Frankignoulle (2003).

^h From Schiettecatte et al. (submitted for publication).

ⁱ From Schneider and Kuss (2004).

^j From Copin-Montégut et al. (2004) extracted for the continental shelf (http://www.obs-vlfr.fr/cd_rom_dmt/dyf_main.htm).

^k From Fig. 3.

^l Computed from salinity, temperature, pCO₂ and total alkalinity, using the carbonic acid dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987).

^m Computed from total alkalinity versus salinity relationship for the Mediterranean Sea from Copin-Montégut (1993).

are in contradiction with the conceptual relationship described above: during the second cruise in the Bay of Palma a positive NEP (autotrophic status) is associated to a source of CO₂ while during the first Randers Fjord cruise a negative NEP (heterotrophic status) is related to a sink of atmospheric CO₂ (Fig. 4A). This can be related to the fact that the air–water CO₂ fluxes are driven (at least partly) by the mixed layer metabolic processes, while NEP values reported in Fig. 4A are (by definition) integrated throughout the water column. The Randers Fjord and the Bay of Palma are, respectively, permanently haline stratified and seasonally thermally stratified systems. If the air–water CO₂ fluxes are compared to net community production in the mixed layer (ML NCP), then there is an agreement between the direction of the air–water CO₂ fluxes and the trophic status (Fig. 4B). Nevertheless, there is a quantitative disagreement between the intensity of the metabolic rates and the air–water CO₂ fluxes. In the case of the first Palma cruise, a modest sink of atmospheric CO₂ of about $-2 \text{ mmolC m}^{-2} \text{ d}^{-1}$ is associated to a ML NCP of about $30 \text{ mmolC m}^{-2} \text{ d}^{-1}$; conversely, the air–water CO₂ fluxes in the Scheldt estuary are 6 to 7 times higher than the ML NCP. This is most probably related to the residence time of the water mass, in the order of 5 d in the Bay of Palma, and ranging between 60 and 90 d (for freshwater) in the Scheldt estuary. Hence, in the Bay of Palma, the water mass is flushed rapidly and biological activity will have a small or undetectable effect on pCO₂ and related air–sea CO₂ fluxes (Gazeau et al., 2005b). On the contrary, in the Scheldt estuary the long residence time of the water mass will lead to a significant built up of DIC in the water column, and large emissions of CO₂ to the atmosphere.

2.1.4. Contribution of the ventilation of riverine CO₂ to estuarine CO₂ emission

The ventilation of riverine CO₂ can contribute to the emission of CO₂ from inner estuaries and could explain the larger CO₂ emission rates than those expected from ML NCP in the Scheldt estuary and the Randers Fjord. The ventilation of riverine CO₂ has been estimated by Abril et al. (2000) to contribute to about 10% of the overall CO₂ emission from the Scheldt inner estuary. Based on the approach given by Abril et al. (2000), the relative contribution of the ventilation of riverine CO₂ to the overall CO₂ emission was computed in several estuaries (Fig. 5). This contribution decreases with the increase of the freshwater residence time. In estuaries with a long freshwater residence time, the riverine CO₂ will be fully ventilated to the atmosphere within the estuary and the overall CO₂ emission from the estuary will be mostly related to ML NCP. In estuaries with very a short freshwater residence time, the enrichment of DIC from ML NCP will be less pronounced than in estuaries with a long freshwater residence time, and the contribution of the ventilation of riverine CO₂ will be larger. In the case of the Rhine estuary, the freshwater residence time is so short that all the riverine CO₂ is not ventilated to the atmosphere in the estuarine zone, and part of it is instead exported to the adjacent coastal ocean. Hence, the potential contribution of the ventilation of riverine CO₂ is higher than the actual observed emission from the estuary (Fig. 5). For the 11 estuaries in Fig. 5, the median of the potential emission from riverine CO₂ amounts to about 10%. Hence, about 90% of the emission of CO₂ from these inner estuaries could be attributed to heterotrophic activity.

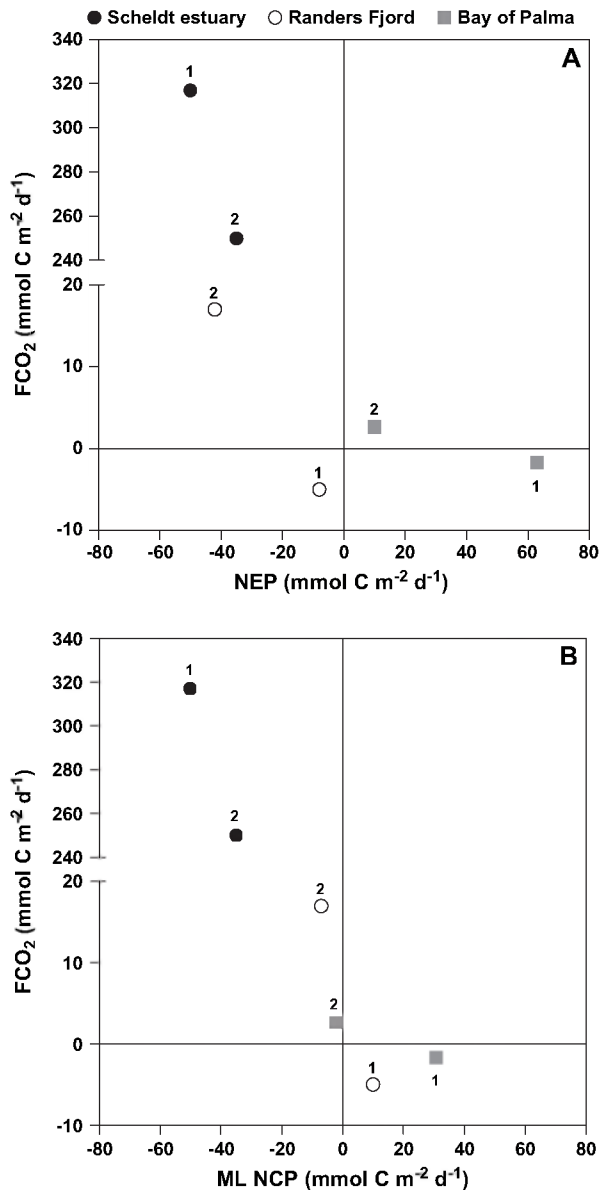


Fig. 4. Air–water CO_2 fluxes versus net ecosystem production (NEP) (A); and net community production in the mixed layer (ML NCP) (B). Air–water CO_2 fluxes were computed from field measurements of $p\text{CO}_2$ while ecosystem metabolic rates were scaled from oxygen incubations, as described in detail by Gazeau et al. (2005a,b,c). Numbers correspond to the following cruises; Scheldt estuary: 1 = 04/11–13/11/2002; 2 = 31/03–10/04/2003; Randers Fjord: 1 = 21/04–01/05/2001; 2 = 20/08–30/08/2001; Bay of Palma: 1 = 01/03–12/03/2002; 2 = 17/06–27/06/2002.

2.1.5. Conceptual frame of the biogeochemical controls of air–water CO_2 fluxes in coastal environments

Based on the above discussion and also based on the synthesis by Borges (2005) of CO_2 dynamics and exchanges with the atmosphere in other coastal environments (in particular at low latitudes), we propose a conceptual relationship of CO_2 fluxes and ML NCP, that summarises the drivers of CO_2 fluxes in coastal environments (Fig. 6). The trophic status of the mixed layer depends on the combination of inputs of inorganic nutrients and of allochthonous organic carbon, and is further modulated by light limitation and stratification. Low

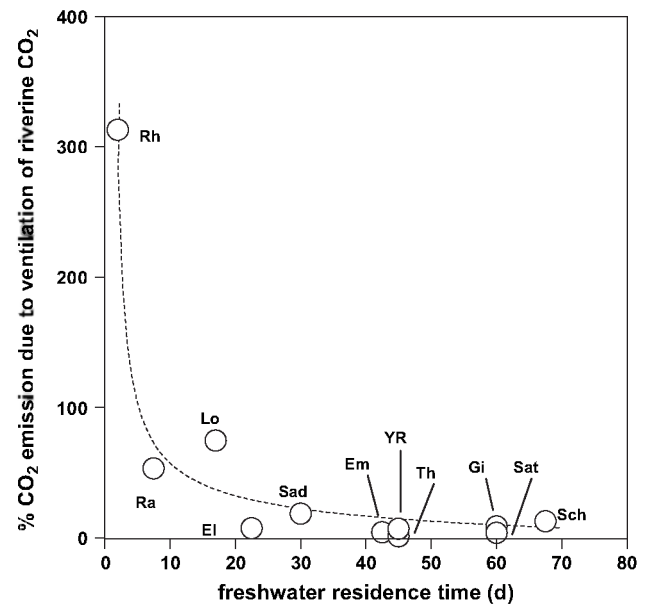


Fig. 5. Contribution of the ventilation of river CO_2 to the overall emission of CO_2 from different estuaries to the atmosphere versus average residence time of freshwater, based on nine European and two US estuaries. The potential emission of river CO_2 (RE in $\text{mmol m}^{-2} \text{d}^{-1}$) was computed from ΔDIC (mmol m^{-3}), average freshwater discharge (Q in $\text{m}^3 \text{d}^{-1}$) and the inner estuary surface area (S in m^2), according to $\text{RE} = \Delta\text{DIC} \times Q/S$, where ΔDIC is the difference between the observed DIC value at zero salinity and the DIC value calculated if the sample was at atmospheric equilibrium with respect to CO_2 . El = Elbe; Em = Ems; Gi = Gironde; Lo = Loire; Ra = Randers Fjord; Rh = Rhine; Sad = Sado; Sat = Satilla; Sch = Scheldt; Th = Thames; YR = York River. Data for El, Em, Gi, Lo, Rh, Sad, Sch and Th from Frankignoulle et al. (1998) and Frankignoulle and Middelburg (2002); data for Sat from Cai and Wang (1998); data for YR from Raymond et al. (2000).

latitude continental shelves act as sources of CO_2 , unlike high and mid latitude continental shelves. This is related to some extent to the background signal of oceanic waters that circulate over continental shelves that are typically CO_2 oversaturated at low latitudes and CO_2 undersaturated at mid and high latitudes. The metabolic status of the continental shelf will further modulate this baseline signal. While ML NCP is positive in mid latitude continental shelves such as the North Sea (Thomas et al., 2005a,b) this is not the case of low latitude continental shelves such as the South Atlantic Bight (Cai et al., 2003) due to larger inputs of terrestrial organic carbon (Borges, 2005). Coastal upwelling systems are net exporters of organic carbon (e.g. Álvarez-Salgado et al., 2001), but the upwelling index will modulate the inputs of nutrients and DIC, and the residence time of the water mass, and determine if the system acts as a source or a sink for atmospheric CO_2 . Microtidal estuaries due to their shorter freshwater residence time and stratification are less heterotrophic and lower sources of CO_2 than macrotidal estuaries. In the former the relative contribution of the ventilation of riverine CO_2 is higher than the in the latter. Mangrove and saltmarsh surrounding waters are net heterotrophic systems fuelled by the inputs of terrestrial intertidal vegetation and act as sources of CO_2 . Note that there is increasing evidence that the emission of CO_2 from the aquatic compartment of these systems is indirectly linked to diagenetic organic carbon degradation, through the

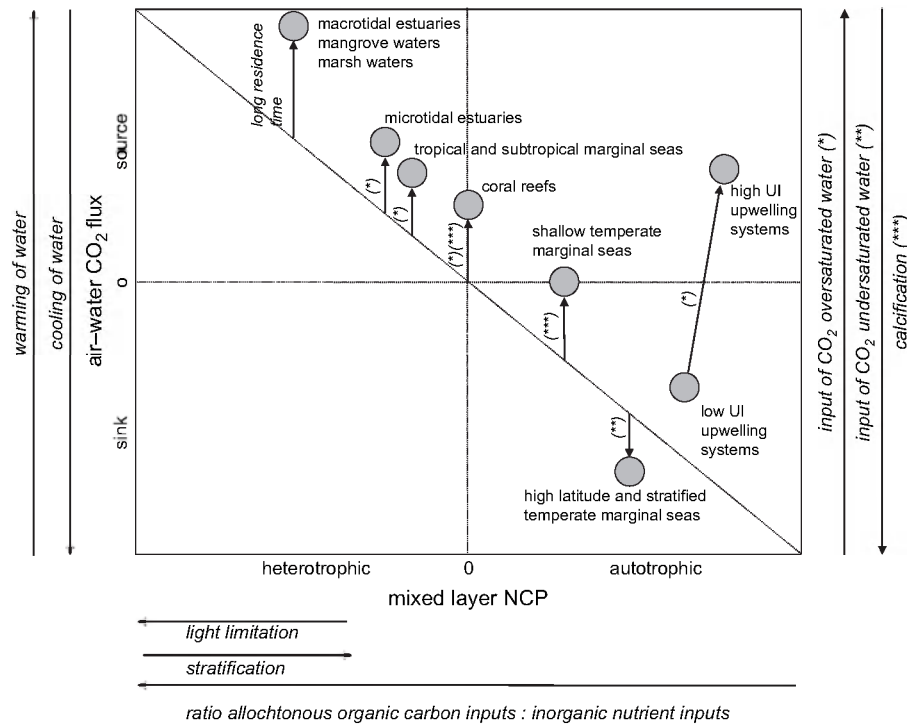


Fig. 6. Conceptual diagram of the biogeochemical controls of air–water CO_2 fluxes in coastal environments.

input of CO_2 rich porewater (Borges et al., 2003; Bouillon et al., *in press*). Calcification is partly responsible for the emission of CO_2 from coral reefs to the atmosphere, as it leads to an increase of CO_2 in the oceanic waters circulating over these systems that are typically CO_2 oversaturated. Finally, purely thermodynamic effects related to water cooling or warming will further modulate the exchange of CO_2 between coastal aquatic environments and the atmosphere, at seasonal and annual timescales.

2.2. Scaling of CO_2 fluxes in coastal environments and comparison at European scale with other aquatic and terrestrial compartments

Based on the air–water CO_2 fluxes from Table 1, the continental shelf surface area estimates from Table 3, we scaled the CO_2 fluxes in European coastal environments and compared them to CO_2 fluxes from other aquatic and terrestrial compartments gathered from literature (Table 4). The values reported in Table 4 were estimated with very different degrees of confidence, in particular, the CO_2 fluxes from lakes and rivers must be considered as first order estimates. The sink of atmospheric CO_2 over the continental shelf of about -68 TgC yr^{-1} is highly significant and for instance comparable to the sink associated to the terrestrial vegetation of -66 TgC yr^{-1} (sum of grasslands, croplands, peatlands and forests) based on a carbon-stock change modelling approach (Janssens et al., 2005). However, the sink of CO_2 over continental shelves could be almost fully balanced by the emission of CO_2 from inner estuaries of about 67 TgC yr^{-1} . However, this value should be considered with caution and most probably corresponds to an over-estimate. Indeed, assuming that during estuarine transit

50% of river particulate organic carbon (POC) (Abril et al., 2002) and that 10% of river DOC (Moran et al., 1999; Raymond and Bauer, 2000; Wiegner and Seitzinger, 2001) are degraded, and that the produced CO_2 is emitted to the atmosphere within the inner estuary, then the potential emission of CO_2 from estuaries would be about 5.4 TgC yr^{-1} at European scale

Table 3

Surface area estimates of European and Russian Republic continental shelves

	Surface area (10^3 km^2)	Reference
East Siberian Sea	890	Chen et al. (2003)
Laptev Sea	504	Chen et al. (2003)
Kara sea	880	Chen et al. (2003)
Barents Sea	600	Chen et al. (2003)
East Greenland	200	Huthnance (2006)
Iceland	107	Huthnance (2006)
Faroes	27	Huthnance (2006)
Norway (Ålesund to Svalbard)	150	Huthnance (2006)
Cape Wrath to Ålesund	51	Huthnance (2006)
English Channel	90	Huthnance (2006)
Baltic Sea	370	Gazeau et al. (2004)
North Sea	512	Gazeau et al. (2004)
West Scottish shelf	87	Huthnance (2006)
West Irish shelf	53	Huthnance (2006)
Irish Sea, North Channel and Clyde Sea	54	Huthnance (2006)
Celtic Sea	162	Huthnance (2006)
Gulf Biscay	122	Huthnance (2006)
Cape Finisterre to Cape Sagres	21	Based on Jones et al. (1997)
Cape Sagres to Gibraltar	9	Based on Jones et al. (1997)
Mediterranean Sea	450	Gazeau et al. (2004)
Black Sea	130	Gazeau et al. (2004)

Table 4
Tentative budget of exchanges of atmospheric CO₂ between aquatic, and terrestrial compartments at European scale

	Surface area (10 ³ km ²)	Atmospheric CO ₂ exchange (TgC yr ⁻¹)
Continental shelf	3065 ^a	-68.1 ^b
Inner estuaries	112 ^c	67.0 ^d
Rivers	66 ^e	21.3 ^f
Lakes	167 ^g	15.2 ^h
Carbonate and silicate rock weathering	6996 ⁱ	-13.2 ^j
Export of POC from rivers to estuaries	6996 ⁱ	-8.5 ^k
Export of DOC from rivers to estuaries	6996 ⁱ	-11.2 ^k
Grasslands	832 ^l	-60.1 ^m
Croplands	1911 ^l	119.7 ^m
Peatlands	43 ^l	51.0 ^m
Forests	1665 ^l	-176.6 ^m
Fossil fuel emission	13 172 ^l	1462.5 ⁿ

^a Sum of continental shelves in Table 3, excluding East Siberian, Laptev, Kara and Black Seas.

^b Based on air–water CO₂ flux in Barents Sea (-3.6 molC m⁻² yr⁻¹ Table 1) scaled to East Greenland, Iceland, Faroes, Norway (Ålesund to Svalbard), and Barents Sea (1084 × 10³ km² Table 3), surface area weighted average of CO₂ fluxes from the Baltic Sea, North Sea, English Channel and Gulf of Biscay (-1.0 molC m⁻² yr⁻¹ Table 1) scaled to Cape Wrath to Ålesund, North Sea, Baltic Sea, West Scottish shelf, West Irish shelf, Irish Sea, North Channel, Clyde Sea, Celtic Sea, Gulf of Biscay, and English Channel (1501 × 10³ km² Table 3), air–water CO₂ flux off the Galician coast (-2.2 molC m⁻² yr⁻¹ Table 1) scaled to region from Cape Finisterre to Cape Sagres (21 × 10³ km² Table 3), air–water CO₂ flux in the Gulf of Cadiz (-0.4 molC m⁻² yr⁻¹ Table 1) scaled to region from Cape Sagres to Gibraltar (9 × 10³ km² Table 3), and air–water CO₂ flux in the Bay of Angels (-0.8 molC m⁻² yr⁻¹ Table 1) scaled to the Mediterranean Sea continental shelf (450 × 10³ km² Table 3).

^c From Woodwell et al. (1973).

^d Based on surface area weighted average of CO₂ fluxes in all estuaries from Table 1.

^e Based on the assumption of Cole and Caraco (2001) that rivers cover 0.5% of total land (13 172 × 10³ km² for countries listed in ^l).

^f Based on CO₂ fluxes for European rivers compiled by Cole and Caraco (2001).

^g From Lehner and Döll (2004).

^h Based on average pCO₂ of 1350 ppm for European lakes from Sobek et al. (2005) and an average *k* value of 2 cm h⁻¹ for lakes given by Cole et al. (1994).

ⁱ Total drainage area for Albania, Austria, Belarus, Belgium, Bosnia-Herzegovina, Bulgaria, Croatia, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Irish Republic, Italy, Latvia, Lithuania, Luxembourg, Macedonia, Moldova, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Ukraine, United Kingdom, and Yugoslavia, from International Satellite Land-Surface Climatology Project (ISLSCP – <http://islsdp2.sesda.com/>).

^j Based on 2° × 2° gridded fluxes from Amiotte-Suchet and Probst (1995) extracted from the ISLSCP database for countries listed in ^l.

^k Based on 2° × 2° gridded fluxes from Ludwig et al. (1996) extracted from the ISLSCP database for countries listed in ^l.

^l For countries listed in ^l from Janssens et al. (2005).

^m For countries listed in ^e from Janssens et al. (2005).

ⁿ In 1995 for countries listed in ^e from Janssens et al. (2005).

based on the export fluxes of river DOC and POC (Table 4, from Ludwig et al., 1996). This value is more than ten times lower than the one scaled from the fluxes computed from pCO₂ field data (Table 4). There is growing evidence that lateral inputs of DIC and organic carbon in estuaries significantly contribute to overall CO₂ emission to the atmosphere (Cai and

Wang, 1998; Cai et al., 1999, 2000; Neubauer and Anderson, 2003; Gazeau et al., 2005c). In the Scheldt estuary, lateral inputs of freshwater, DIC and labile total organic carbon correspond to, respectively, 10%, 22% and 41% of the riverine inputs (respectively, Gazeau et al., 2005c; Soetaert et al., 2006; Vanderborgh et al., submitted for publication). In the Satilla River estuary, lateral DIC inputs from the extensive salt-marshes are 12 times higher than the river inputs (Cai and Wang, 1998). Hence, it seems unlikely that lateral inputs can explain the large discrepancy between the scaled air–water CO₂ fluxes and those computed from the fate of riverine organic carbon. This discrepancy can have several other origins. For instance, pCO₂ data in inner estuaries have been mostly obtained in macrotidal estuaries, and microtidal estuaries that seem to be characterized by lower CO₂ emissions are under-represented in the present compilation (only Randers Fjord). Most of the CO₂ flux values in inner estuaries from Table 1 were derived from floating chamber measurements. This method has been assumed to artificially enhance the exchange of CO₂ across the air–water interface (Raymond and Cole, 2001). However, there is a growing body of evidence that this method provides reasonable flux estimates (Kremer et al., 2003; Guérin et al., in press). Furthermore, it has been established that tidal currents significantly enhance gas transfer velocities in inner estuaries (Zappa et al., 2003; Borges et al., 2004) compared to other aquatic systems. As already noted by Abril and Borges (2004) and by Borges (2005), the surface area of inner estuaries given by Woodwell et al. (1973) is most probably an overestimate. For instance the surface area of the European estuaries, lagoons, salt marshes and mud flats has been estimated to 25 × 10³ km² based on the Coordination of information on the environment (CORINE) Land Cover programme (Uher, 2006). The total surface area of the European coastal wetlands (that aggregates lagoons, deltas, estuaries, coastal wetlands and tidal wetlands) from the Global Lakes and Wetlands Database (GLWD) is 36 × 10³ km² (Lehner and Döll, 2004). These estimates that aggregate various near-shore ecosystems are 3 to more than 4 times lower than the surface area of European estuaries alone of 112 × 10³ km² given by Woodwell et al. (1973).

Table 4 also shows that the emission of CO₂ to the atmosphere from continental aquatic compartments (streams, rivers and lakes), could be highly significant when compared to the absorption of CO₂ from the atmosphere due to carbonate and silicate rock weathering, and to the export of organic carbon from rivers to the coastal ocean. These high CO₂ emission rates result from net heterotrophy of the aquatic compartment, fuelled by terrestrial organic carbon inputs, and from the flux of dissolved CO₂ originating from soil respiration (Kling et al., 1991; Jones and Mulholland, 1998; Cole and Caraco, 2001; Jones et al., 2003; Duarte and Prairie, 2005). Importantly, the CO₂ fluxes from continental aquatic compartments are not accounted for in atmospheric CO₂ inversion models and will increase the gap with estimates of the terrestrial carbon sink based on carbon-stock change models. On the other hand, the export of organic matter from rivers to the coastal ocean, and the CO₂ absorption from rock weathering are typically

not accounted for in carbon-stock change models. Table 4 shows that these fluxes could be highly significant and could bridge the gap between estimates based carbon-stock change and inversion models (Janssens et al., 2003; Siemens, 2003). Note, however, that a significant portion of river POC export is due to freshwater phytoplankton and not soil carbon, unlike DOC.

Table 4 shows that the sink of atmospheric CO₂ over European continental shelves is negligible compared to the anthropogenic CO₂ emission. Furthermore, the flux of CO₂ based on field pCO₂ data is a mixed signal of the natural background signal and the anthropogenic perturbation signal. Current estimates of the anthropogenic CO₂ sink of the coastal ocean based on DIC inventory (Sabine et al., 2004) or modelling (Andersson and Mackenzie, 2004) approaches are roughly proportional to its relative surface area, unlike the overall atmospheric CO₂ sink that is disproportionately more intense than its relative surface area.

3. Conclusions and future challenges

Scaled air–water CO₂ fluxes at European level show that the sink of atmospheric CO₂ over continental shelves is highly significant and equivalent to the carbon sink of the terrestrial biosphere. This sink of CO₂ over continental shelves could be almost fully balanced by the emission of CO₂ from inner estuaries, that would be 2.5 times higher than the emission for continental aquatic systems (rivers, streams and lakes). However, the estimate of the potential emission of CO₂ from the fate in estuaries of river POC and DOC strongly suggests that the present scaled emission of CO₂ at European level is an overestimate. This is most probably related to the inadequate value of the surface area of inner estuaries used in the scaling. Nevertheless, the CO₂ fluxes from estuaries are significant (49.9 molC m⁻² yr⁻¹) compared to river and streams (26.9 molC m⁻² yr⁻¹) and lakes (7.6 molC m⁻² yr⁻¹) at European scale. The emission of CO₂ to the atmosphere from estuaries and their strongly heterotrophic nature implies that a large fraction of river POC and DOC is removed during estuarine transit and never reaches the adjacent continental shelf, let alone the open ocean. This is consistent with the fact 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). Hence, an important bias is introduced in global and regional carbon models that use as forcings the river carbon inputs directly into the open ocean basins.

Several challenges remain to better constrain the fluxes of CO₂ in coastal waters at European and global scales. The surface area of inner and outer estuaries could be evaluated based on satellite imagery approaches (e.g. Salisbury et al., 2004) in combination with geographical information system (GIS) approaches. More CO₂ data are required to scale air–water CO₂ fluxes in outer estuaries, that can be significant for the overall flux from estuarine systems (Borges and Frankignoulle, 2002b; Borges, 2005; Schiettecatte et al., 2006a). While data for other trace gases are available in several coastal

sites of the Mediterranean Sea (Uher, 2006; Bange, 2006), CO₂ flux data have only been satisfactorily integrated at annual scale in the Bay of Angels. It is most unlikely that data from this very narrow continental shelf (<10 km) are representative of wider continental shelves (off Tunisia, Alboran Sea) and influenced by river inputs (Gulf of Lyons, Adriatic Sea) of the Mediterranean Sea. Also, no CO₂ data are available in inner or outer Mediterranean non-tidal estuaries. Similarly, air–water CO₂ fluxes in high latitude continental shelves are only available for the Barents Sea, while little data have been reported in the Kara, East Siberian, Laptev Seas (Semiletov, 1999). No data are available over the continental shelf of the Black Sea, although influenced by the Danube, the largest European river (in terms of discharge, length and drainage area). Little or no CO₂ data are available in several biogeochemically important ecosystems (seagrass beds, lagoons, salt-marshes) for which surface area estimates would also require a careful (re)-analysis, based on satellite and/or GIS approaches. Finally, inter-annual and decadal variability of air–water CO₂ fluxes is so far undocumented in any coastal environment.

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