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# Carbon dioxide in European coastal waters

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**Abstract**

We compiled from literature annually integrated air–water fluxes of carbon dioxide ($CO_2$) 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 $CO_2$ ($pCO_2$) in 5 contrasting continental shelves provided insights into the biogeochemical drivers of the $CO_2$ fluxes. The latter were also investigated by comparing $CO_2$ fluxes to net ecosystem (NEP) and net community production (NCP) in 3 contrasted coastal ecosystems. Air–water $CO_2$ fluxes were scaled at European regional level and compared to fluxes of atmospheric $CO_2$ in other aquatic and terrestrial compartments. Continental shelves are significant sinks for atmospheric $CO_2$ at an average rate of $-1.9$ molC $m^{-2}$ $yr^{-1}$ that scaled at European level corresponds to an absorption of atmospheric $CO_2$ of $-68.1$ TgC $yr^{-1}$. This sink is equivalent to the one reported for the terrestrial biosphere of $-66.1$ TgC $yr^{-1}$, based on carbon-stock change models. Estuaries are significant sources of $CO_2$ to the atmosphere at an average rate of 49.9 molC $m^{-2}$ $yr^{-1}$ that is higher than the $CO_2$ emission to the atmosphere from rivers, streams and lakes. The scaled emission of $CO_2$ to the atmosphere from inner estuaries of about 67.0 TgC $yr^{-1}$ would almost fully balance the sink of atmospheric $CO_2$ computed for continental shelves. However, the scaled emission of $CO_2$ from estuaries to the atmosphere is inconsistent with the potential emission of $CO_2$ 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.


*Keywords:* carbon dioxide; fluxes; coastal ecosystems; estuaries

## 1. Introduction

Air–water fluxes of carbon dioxide ($CO_2$) 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 $CO_2$ 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 $CO_2$ exchanges between the atmosphere and the coastal ocean, as these authors computed a sink of atmospheric $CO_2$ of $-1.0$ PgC $yr^{-1}$ by scaling globally the air–sea $CO_2$ fluxes from East China Sea. Such a sink is comparable to the open ocean sink of atmospheric $CO_2$ estimated to $-1.6$ PgC $yr^{-1}$ (Takahashi et al., 2002; Takahashi, 2003). More recent estimates of the global $CO_2$ sink over marginal seas based on scaled $CO_2$ fluxes computed from field measurements of the partial pressure of $CO_2$ ($pCO_2$) 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.

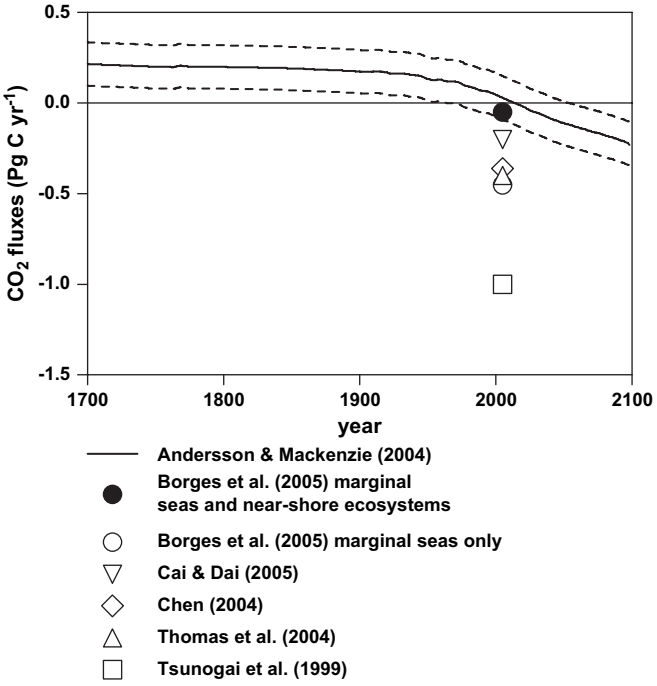



Fig. 1. Carbon dioxide fluxes between the coastal ocean and the atmosphere (PgC $yr^{-1}$) at global scale based on different approaches. The solid line corresponds to the output of the box model of Andersson and Mackenzie (2004) that accounts for organic and inorganic carbon fluxes (Shallow-water Ocean 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).

## 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 ($pCO_2$@15 °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 $pCO_2$@15 °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 $pCO_2$@15 °C similar in timing and amplitude. During summer, $pCO_2$@15 °C remains relatively constant in both areas suggesting that

Table 1
Range of $pCO_2$, air–water $CO_2$ 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 $pCO_2$ data from Frankignoulle and Borges (2001) and additional data obtained in May 2001 and 2002, and June 2004, the atmospheric $pCO_2$ 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 $pCO_2$ 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 $pCO_2$ 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 $m^{-2}$ $yr^{-1}$) | $k$ | Ref. |
|---|---|---|---|---|---|---|---|
| *Inner estuaries* | | | | | | | |
| 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 |
| *Upwelling marginal seas* | | | | | | | |
| 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 |
| *Non-upwelling marginal seas* | | | | | | | |
| 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 $pCO_2$@15 °C values attained during the spring bloom (note however that $pCO_2$ increases with temperature). However, in late summer and early fall, $pCO_2$@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 $pCO_2$@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 $CO_2$, than seasonally or permanently stratified systems (Borges, 2005).

The seasonal amplitude and in particular the spring decrease of $pCO_2$ and $pCO_2$@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 $NO_3^-$ 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 $pCO_2$ and $pCO_2$@15 °C that follows closely the spring bloom, suggesting a rapid remineralization of organic matter, followed by a steady increase of $pCO_2$@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 $pCO_2$ at low levels during

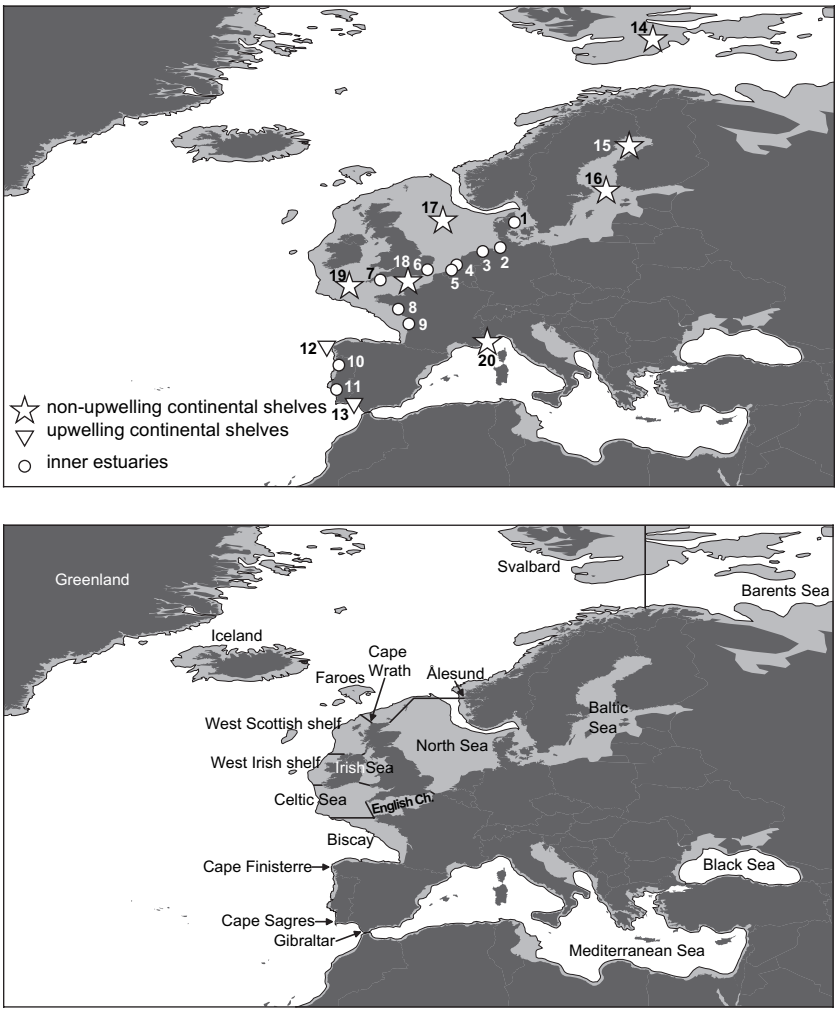


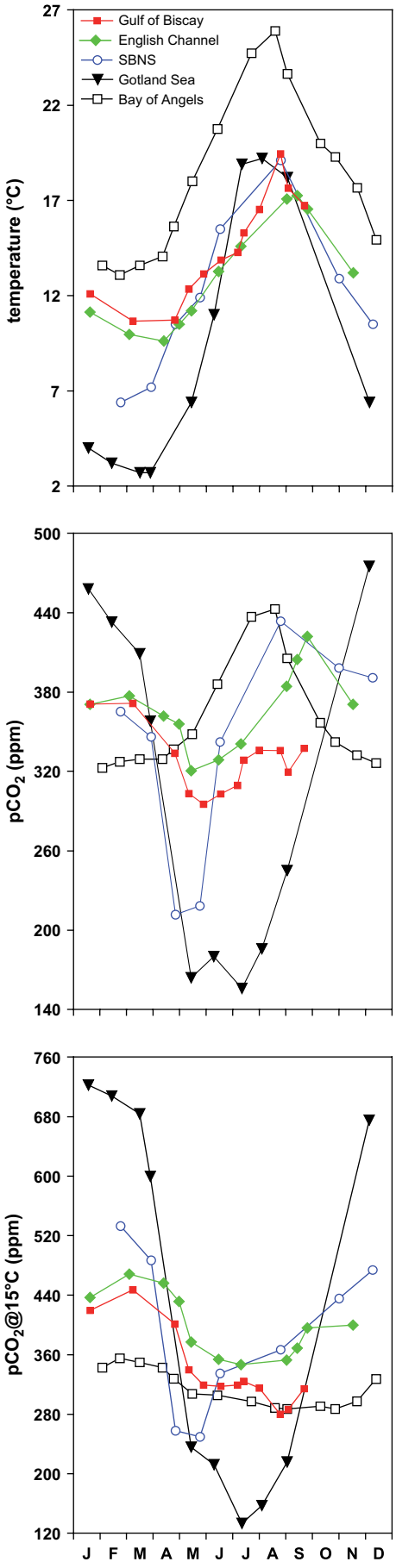

Fig. 2. Map showing the location of 20 European coastal environments where air–water $CO_2$ fluxes have been satisfactorily integrated at annual scale. Numbers indicate locations named in first column of Table 1. Light grey areas correspond to the continental shelf areas, delimited by the 200 m isobath (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 $pCO_2$@15 °C sharply decrease from mid-March to mid-May due to the spring bloom. After the exhaustion of inorganic nutrients, a further decrease of $pCO_2$@15 °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 $pCO_2$@15 °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 (Arístegui 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 GPP < 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 ($pCO_2$@15 °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 $pCO_2$, of $pCO_2$ normalized to a constant temperature of 15 °C ($pCO_2$@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_dmtt/dyf_main.htm).
[k] From Fig. 3.
[l] Computed from salinity, temperature, $pCO_2$ 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 $CO_2$ while during the first Randers Fjord cruise a negative NEP (heterotrophic status) is related to a sink of atmospheric $CO_2$ (Fig. 4A). This can be related to the fact that the air–water $CO_2$ 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 $CO_2$ 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 $CO_2$ fluxes and the trophic status (Fig. 4B). Nevertheless, there is a quantitative disagreement between the intensity of the metabolic rates and the air–water $CO_2$ fluxes. In the case of the first Palma cruise, a modest sink of atmospheric $CO_2$ of about $-2$ mmolC $m^{-2}$ $d^{-1}$ is associated to a ML NCP of about 30 mmolC $m^{-2}$ $d^{-1}$; conversely, the air–water $CO_2$ 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 $pCO_2$ and related air–sea $CO_2$ 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 $CO_2$ to the atmosphere.

### 2.1.4. Contribution of the ventilation of riverine $CO_2$ to estuarine $CO_2$ emission

The ventilation of riverine $CO_2$ can contribute to the emission of $CO_2$ from inner estuaries and could explain the larger $CO_2$ emission rates than those expected from ML NCP in the Scheldt estuary and the Randers Fjord. The ventilation of riverine $CO_2$ has been estimated by Abril et al. (2000) to contribute to about 10% of the overall $CO_2$ emission from the Scheldt inner estuary. Based on the approach given by Abril et al. (2000), the relative contribution of the ventilation of riverine $CO_2$ to the overall $CO_2$ 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 $CO_2$ will be fully ventilated to the atmosphere within the estuary and the overall $CO_2$ 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 $CO_2$ will be larger. In the case of the Rhine estuary, the freshwater residence time is so short that all the riverine $CO_2$ 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 $CO_2$ 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 $CO_2$ amounts to about 10%. Hence, about 90% of the emission of $CO_2$ from these inner estuaries could be attributed to heterotrophic activity.

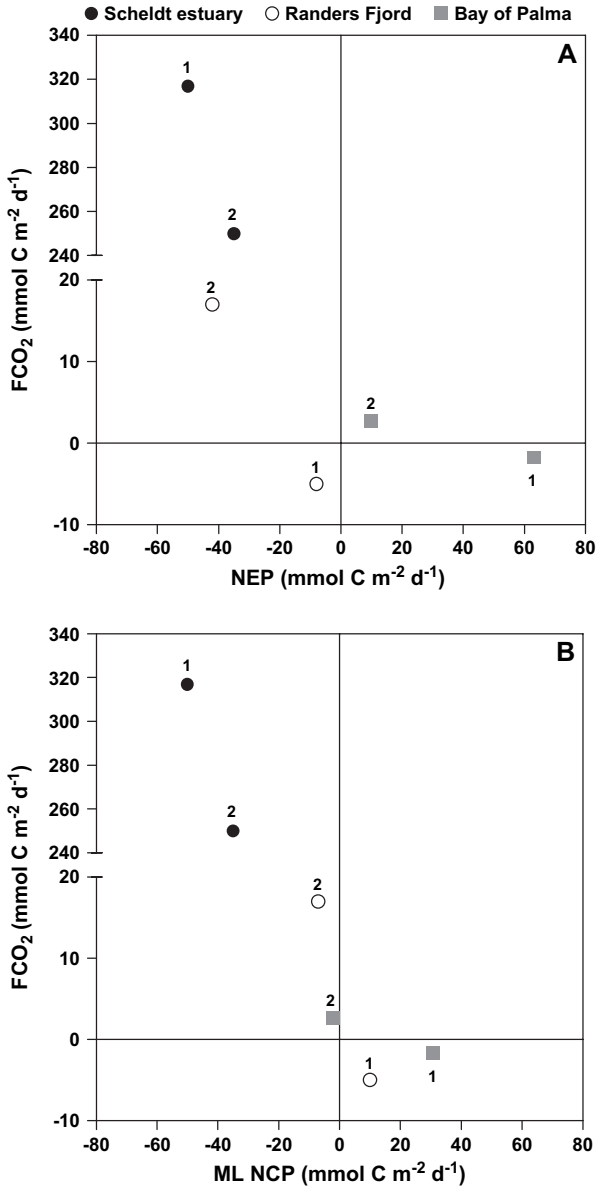



Fig. 4. Air–water $CO_2$ fluxes versus net ecosystem production (NEP) (A); and net community production in the mixed layer (ML NCP) (B). Air–water $CO_2$ fluxes were computed from field measurements of $pCO_2$ while ecosystem metabolic rates where scaled from oxygen incubations, as described in detail 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 allochtonous organic carbon, and is further modulated by light limitation and stratification. Low

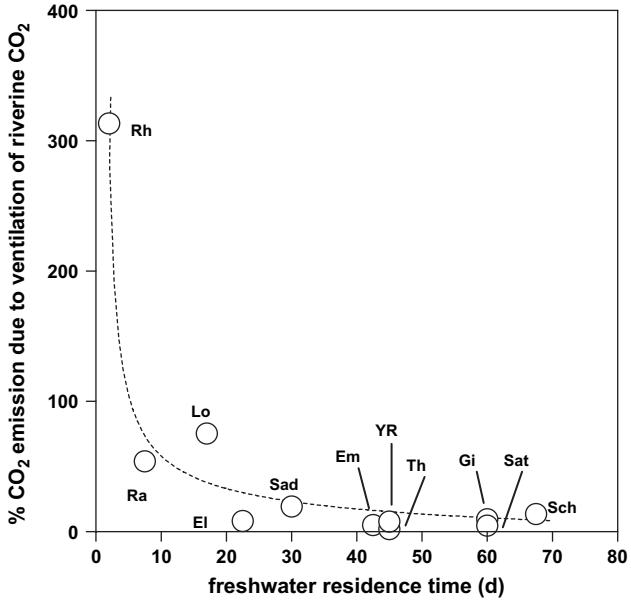



Fig. 5. Contribution of the ventilation of river $CO_2$ to the overall emission of $CO_2$ from different estuaries to the atmosphere versus average residence time of freshwater, based on nine European and two US estuaries. The potential emission of river $CO_2$ (RE in mmol $m^{-2}$ $d^{-1}$) was computed from ΔDIC (mmol $m^{-3}$), average freshwater discharge (Q in $m^3$ $d^{-1}$) and the inner estuary surface area (S in $m^2$), according to RE = ΔDIC × 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

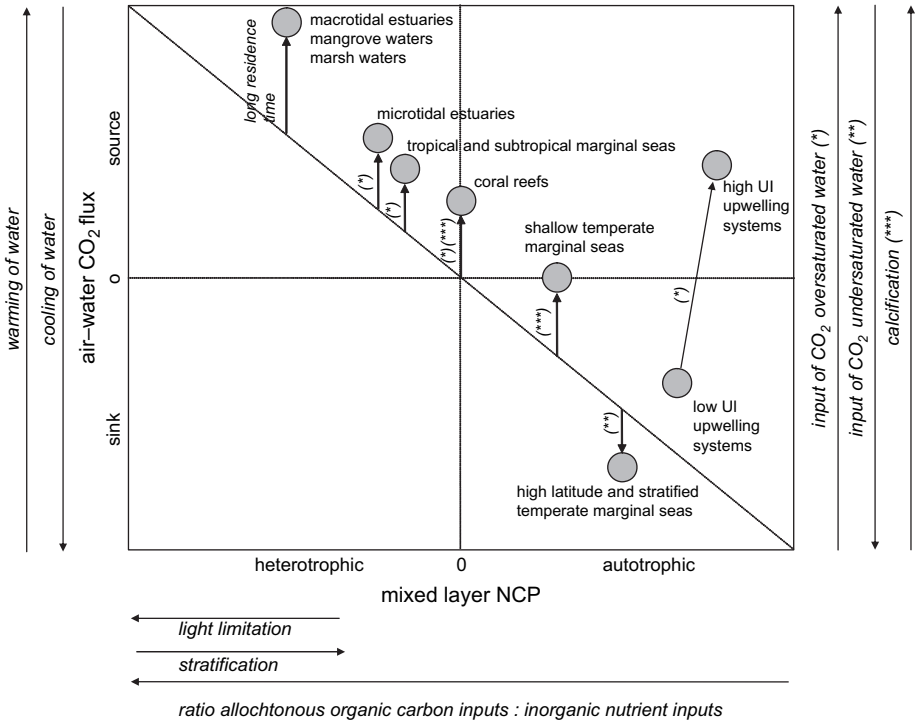



Fig. 6. Conceptual diagram of the biogeochemical controls of air–water $CO_2$ fluxes in coastal environments.

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 $CO_2$ 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[i] | 1462.5[n] |

[a] Sum of continental shelves in Table 3, excluding East Siberian, Laptev, Kara and Black Seas.
[b] Based on air–water $CO_2$ 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 × $10^3$ km$^2$ Table 3), surface area weighted average of $CO_2$ 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 × $10^3$ km$^2$ Table 3), air–water $CO_2$ flux off the Galician coast (−2.2 molC m$^{-2}$ yr$^{-1}$ Table 1) scaled to region from Cape Finisterre to Cape Sagres (21 × $10^3$ km$^2$ Table 3), air–water $CO_2$ flux in the Gulf of Cadiz (−0.4 molC m$^{-2}$ yr$^{-1}$ Table 1) scaled to region from Cape Sagres to Gibraltar (9 × $10^3$ km$^2$ Table 3), and air–water $CO_2$ flux in the Bay of Angels (−0.8 molC m$^{-2}$ yr$^{-1}$ Table 1) scaled to the Mediterranean Sea continental shelf (450 × $10^3$ km$^2$ Table 3).
[c] From Woodwell et al. (1973).
[d] Based on surface area weighted average of $CO_2$ 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 × $10^3$ km$^2$ for countries listed in [i]).
[f] Based on $CO_2$ fluxes for European rivers compiled by Cole and Caraco (2001).
[g] From Lehner and Döll (2004).
[h] Based on average $pCO_2$ 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-Hercegovina, 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://islscp2.sesda.com/).
[j] Based on 2° * 2° gridded fluxes from Amiotte-Suchet and Probst (1995) extracted from the ISLSCP database for countries listed in [i].
[k] Based on 2° * 2° gridded fluxes from Ludwig et al. (1996) extracted from the ISLSCP database for countries listed in [i].
[l] For countries listed in [i] 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 $pCO_2$ field data (Table 4). There is growing evidence that lateral inputs of DIC and organic carbon in estuaries significantly contribute to overall $CO_2$ 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; Vanderborght 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 $CO_2$ fluxes and those computed from the fate of riverine organic carbon. This discrepancy can have several other origins. For instance, $pCO_2$ data in inner estuaries have been mostly obtained in macrotidal estuaries, and microtidal estuaries that seem to be characterized by lower $CO_2$ emissions are underrepresented in the present compilation (only Randers Fjord). Most of the $CO_2$ 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 $CO_2$ 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 × $10^3$ km$^2$ 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 × $10^3$ km$^2$ (Lehner and Döll, 2004). These estimates that aggregate various nearshore ecosystems are 3 to more than 4 times lower than the surface area of European estuaries alone of 112 × $10^3$ km$^2$ given by Woodwell et al. (1973).

Table 4 also shows that the emission of $CO_2$ to the atmosphere from continental aquatic compartments (streams, rivers and lakes), could be highly significant when compared to the absorption of $CO_2$ 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 $CO_2$ emission rates result from net heterotrophy of the aquatic compartment, fuelled by terrestrial organic carbon inputs, and from the flux of dissolved $CO_2$ 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 $CO_2$ fluxes from continental aquatic compartments are not accounted for in atmospheric $CO_2$ 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 $CO_2$ 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 $CO_2$ over European continental shelves is negligible compared to the anthropogenic $CO_2$ emission. Furthermore, the flux of $CO_2$ based on field $pCO_2$ data is a mixed signal of the natural background signal and the anthropogenic perturbation signal. Current estimates of the anthropogenic $CO_2$ 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 $CO_2$ sink that is disproportionately more intense than its relative surface area.

## 3. Conclusions and future challenges

Scaled air–water $CO_2$ fluxes at European level show that the sink of atmospheric $CO_2$ over continental shelves is highly significant and equivalent to the carbon sink of the terrestrial biosphere. This sink of $CO_2$ over continental shelves could be almost fully balanced by the emission of $CO_2$ 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 $CO_2$ from the fate in estuaries of river POC and DOC strongly suggests that the present scaled emission of $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 $CO_2$ data are required to scale air–water $CO_2$ 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), $CO_2$ 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 $CO_2$ data are available in inner or outer Mediterranean non-tidal estuaries. Similarly, air–water $CO_2$ 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 $CO_2$ data are available in several biogeochemically important ecosystems (seagrass beds, lagoons, saltmarshes) 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 $CO_2$ fluxes is so far undocumented in any coastal environment.

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## References

Abril, G., Borges, A.V., 2004. Carbon dioxide and methane emissions from estuaries. In: Tremblay, A., Varfalvy, L., Roehm, C., Garneau, M. (Eds.), Greenhouse Gases Emissions from Natural Environments and Hydroelectric Reservoirs: Fluxes and Processes. Springer-Verlag, pp. 187–207.

Abril, G., Etcheber, H., Borges, A.V., Frankignoulle, M., 2000. Excess atmospheric carbon dioxide transported by rivers into the Scheldt estuary. Comptes Rendus de l'Académie des Sciences Série II Fascicule A-Sciences de la Terre et des Planètes 330 (11), 761–768.

Abril, G., Nogueira, E., Hetcheber, H., Cabeçadas, G., Lemaire, E., Brogueira, M.J., 2002. Behaviour of organic carbon in nine contrasting European estuaries. Estuarine, Coastal and Shelf Science 54, 241–262.

Abril, G., Etcheber, H., Delille, B., Frankignoulle, M., Borges, A.V., 2003. Carbonate dissolution in the turbid and eutrophic Loire estuary. Marine Ecology-Progress Series 259, 129–138.

Abril, G., Commarieu, M.-V., Maro, D., Fontugne, M., Guérin, F., Etcheber, H., 2004. A massive dissolved inorganic carbon release at spring tide in a highly turbid estuary. Geophysical Research Letters 31. doi:10.1029/2004GL019714. L09316.

Algesten, G., Wikner, J., Sobek, S., Tranvik, L.J., Jansson, M., 2004. Seasonal variation of $CO_2$ saturation in the Gulf of Bothnia: indications of marine net heterotrophy. Global Biogeochemical Cycles 18 (4). doi:10.1029/2004GB002232. GB4021.

Álvarez-Salgado, X.A., Doval, M.D., Borges, A.V., Joint, I., Frankignoulle, M., Woodward, E.M.S., Figueiras, F.G., 2001. Off-shelf fluxes of labile materials by an upwelling filament in the NW Iberian Upwelling System. Progress in Oceanography 51 (2–4), 321–337.

Amiotte-Suchet, P., Probst, J.L., 1995. A global model for present-day atmospheric/soil $CO_2$ consumption by chemical erosion of continental rocks (GEM-$CO_2$). Tellus B 47 (1–2), 273–280.

Andersson, A.J., Mackenzie, F.T., 2004. Shallow-water oceans: a source or sink of atmospheric $CO_2$? Frontiers in Ecology and the Environment 2 (7), 348–353.

Arístegui, J., Álvarez-Salgado, X.A., Barton, E.D., Figueiras, F.G., Hernández-Léon, S., Roy, C., Santos, A.M.P., 2004. Oceanography and fisheries of the Canary current/Iberian region of the Eastern North Atlantic. In: Robinson, A.R., Brink, K.H. (Eds.), The Sea 14. Harvard University Press, Cambridge, pp. 877–927.

Bange, H.W., 2006. Nitrous oxide and methane in European coastal waters. Estuarine, Coastal and Shelf Science 70 (3), 361–374.

Bentley, D., Hart, V., Guary, J.C., Statham, P.J., 1999. Dissolved nutrient distributions in the Central English Channel. Continental Shelf Research 19, 2083–2099.

Borges, A.V., 2005. Do we have enough pieces of the jigsaw to integrate $CO_2$ fluxes in the Coastal Ocean? Estuaries 28 (1), 3–27.

Borges, A.V., Frankignoulle, M., 2002a. Distribution of surface carbon dioxide and air–sea exchange in the upwelling system off the Galician coast. Global Biogeochemical Cycles 16 (2), 1020. doi:10.1029/2000GB001385.

Borges, A.V., Frankignoulle, M., 2002b. Distribution and air–water exchange of carbon dioxide in the Scheldt plume off the Belgian coast. Biogeochemistry 59 (1–2), 41–67.

Borges, A.V., Frankignoulle, M., 2003. Distribution of surface carbon dioxide and air–sea exchange in the English Channel and adjacent areas. Journal of Geophysical Research 108 (C8), 3140. doi:10.1029/2000JC000571.

Borges, A.V., Djenidi, S., Lacroix, G., Theate, J., Delille, B., Frankignoulle, M., 2003. Atmospheric $CO_2$ flux from mangrove surrounding waters. Geophysical Research Letters 30 (11), 1558. doi:10.1029/2003GL017143.

Borges, A.V., Delille, B., Schiettecatte, L.-S., Gazeau, F., Abril, G., Frankignoulle, M., 2004. Gas transfer velocities of $CO_2$ in three European estuaries (Randers Fjord, Scheldt, and Thames). Limnology and Oceanography 49 (5), 1630–1641.

Borges, A.V., Delille, B., Frankignoulle, M., 2005. Budgeting sinks and sources of $CO_2$ in the coastal ocean: diversity of ecosystems counts. Geophysical Research Letters 32. doi:10.1029/2005GL023053. L14601.

Bouillon, S., Dehairs, F., Korntheuer, M., Schiettecatte, L.-S., Borges, A.V., 2006. Sources and cycling of organic and inorganic carbon in the Tana estuary and delta (northern Kenya). Limnology and Oceanography, in press.

Cai, W.J., Dai, M., 2004. Comment on "enhanced open ocean storage of $CO_2$ from shelf sea pumping". Science 306 (5701), 1477. doi:10.1126/science.1102132.

Cai, W.J., Dai, M., 2005. How Significant is the Coastal Ocean Uptake of Atmospheric $CO_2$? – A Province-Based Approach, ASLO 2005 Summer Meeting, 14–24 June 2005, Santiago de Compostela, Spain.

Cai, W.-J., Wang, Y., 1998. The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. Limnology and Oceanography 43 (4), 657–668.

Cai, W.-J., Pomeroy, L.R., Moran, M.A., Wang, Y.C., 1999. Oxygen and carbon dioxide mass balance for the estuarine- intertidal marsh complex of five rivers in the southeastern US. Limnology and Oceanography 44 (3), 639–649.

Cai, W.-J., Wiebe, W.J., Wang, Y.C., Sheldon, J.E., 2000. Intertidal marsh as a source of dissolved inorganic carbon and a sink of nitrate in the Satilla River–estuarine complex in the southeastern US. Limnology and Oceanography 45 (8), 1743–1752.

Cai, W.-J., Wang, Z.H.A., Wang, Y.C., 2003. The role of marsh-dominated heterotrophic continental margins in transport of $CO_2$ between the atmosphere, the land–sea interface and the ocean. Geophysical Research Letters 30 (16), 1849. doi:10.1029/2003GL017633.

Chen, C.T.A., 2004. Exchanges of carbon in the coastal seas. In: Field, C.B., Raupach, M.R. (Eds.), The Global Carbon Cycle: Integrating Humans, Climate, and the Natural World, SCOPE. Island Press, Washington DC, pp. 341–350.

Chen, C.T.A., Liu, K.K., Macdonald, R., 2003. Continental margin exchanges. In: Fasham, M.J.R. (Ed.), Ocean Biogeochemistry: A Synthesis of the Joint Global Ocean Flux Study (JGOFS). Springer-Verlag, Berlin, pp. 53–97.

Cole, J.J., Caraco, N.F., 2001. Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism. Marine and Freshwater Research 52 (1), 101–110.

Cole, J.J., Caraco, N.F., Kling, G.W., Kratz, T.K., 1994. Carbon dioxide supersaturation in the surface waters of lakes. Science 265 (5178), 1568–1570.

Copin-Montégut, C., 1993. Alkalinity and carbon budgets in the Mediterranean Sea. Global Biogeochemical Cycles 7 (4), 915–925.

Copin-Montégut, C., Bégovic, M., Merlivat, L., 2004. Variability of the partial pressure of $CO_2$ on diel to annual time scales in the Northwestern Mediterranean Sea. Marine Chemistry 85 (3–4), 169–189.

Dickson, A.G., Millero, F.J., 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. Deep-Sea Research I 34, 1733–1743.

Duarte, C.M., Prairie, Y.T., 2005. Prevalence of heterotrophy and atmospheric $CO_2$ emissions from aquatic ecosystems. Ecosystems 8, 862–870.

Frankignoulle, M., Borges, A.V., 2001. European continental shelf as a significant sink for atmospheric carbon dioxide. Global Biogeochemical Cycles 15 (3), 569–576.

Frankignoulle, M., Middelburg, J.J., 2002. Biogases in tidal European estuaries: the BIOGEST project. Biogeochemistry 59 (1–2), 1–4.

Frankignoulle, M., Abril, G., Borges, A., Bourge, I., Canon, C., Delille, B., Libert, E., Théate, J.-M., 1998. Carbon dioxide emission from European estuaries. Science 282 (5388), 434–436.

Gattuso, J.-P., Frankignoulle, M., Wollast, R., 1998. Carbon and carbonate metabolism in coastal aquatic ecosystems. Annual Review Ecology Systematics 29, 405–433.

Gazeau, F., Smith, S.V., Gentili, B., Frankignoulle, M., Gattuso, J.-P., 2004. The European coastal zone: characterization and first assessment of ecosystem metabolism. Estuarine, Coastal and Shelf Science 60 (4), 673–694.

Gazeau, F., Borges, A.V., Barrón, C., Duarte, C.M., Iversen, N., Middelburg, J.J., Delille, B., Pizay, M.-D., Frankignoulle, M., Gattuso, J.-P., 2005a. Net ecosystem metabolism in a micro-tidal estuary (Randers Fjord, Denmark): evaluation of methods and interannual variability. Marine Ecology-Progress Series 301, 23–41.

Gazeau, F., Duarte, C.M., Gattuso, J.-P., Barrón, C., Navarro, N., Ruíz, S., Prairie, Y.T., Calleja, M., Delille, B., Frankignoulle, M., Borges, A.V., 2005b. Whole-system metabolism and $CO_2$ fluxes in a Mediterranean Bay dominated by seagrass beds (Palma Bay, NW Mediterranean). Biogeosciences 2 (1), 87–96.

Gazeau, F., Gattuso, J.-P., Middelburg, J.J., Brion, N., Schiettecatte, L.-S., Frankignoulle, M., Borges, A.V., 2005c. Planktonic and whole system metabolism in a nutrient-rich estuary (the Scheldt Estuary). Estuaries 28 (6), 868–883.

Gregg, W.W., Casey, N.W., McClain, C.R., 2005. Recent trends in global ocean chlorophyll. Geophysical Research Letters 32. doi:10.1029/2004GL021808. L03606.

Guérin, F., Abril, G., Serça, D., Delon, C., Richard, S., Delmas, R., Tremblay, A., Varfalvy, L. Gas transfer velocities of $CO_2$ and $CH_4$ in a tropical reservoir and its river downstream. Journal of Marine Systems, in press.

Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? Organic Geochemistry 27 (5–6), 195–212.

Hopkinson, C.S.J., Smith, E.M., 2005. Estuarine respiration: an overview of benthic, pelagic and whole system respiration. In: del Giorgio, P.A.,

Williams, P.J.L. (Eds.), Respiration in Aquatic Ecosystems. Oxford University Press, Oxford, pp. 123–147.

Huertas, I.E., Navarro, G., Rodríguez-Gálvez, S., Lubián, L.M. Temporal patterns of carbon dioxide in relation to hydrological conditions and primary production in the northeastern shelf of the Gulf of Cadiz (SW Spain). Deep-Sea Research II, in press.

Huthnance, J.M. North-East Atlantic margins. In: Atkinson, L., Liu, K.K., Quinones, R., Talaue-McManus, L. (Eds.), Carbon and Nutrient Fluxes in Global Continental Margins, in press.

Janssens, I.A., Freibauer, A., Ciais, P., Smith, P., Nabuurs, G.J., Folberth, G., Schlamadinger, B., Hutjes, R.W.A., Ceulemans, R., Schulze, E.D., Valentini, R., Dolman, A.J., 2003. Europe's terrestrial biosphere absorbs 7 to 12% of European anthropogenic $CO_2$ emissions. Science 300 (5625), 1538–1542.

Janssens, I.A., Freibauer, A., Schlamadinger, B., Ceulemans, R., Ciais, P., Dolman, A.J., Heimann, M., Nabuurs, G.-J., Smith, P., Valentini, R., Schulze, E.-D., 2005. The carbon budget of terrestrial ecosystems at country-scale – a European case study. Biogeosciences 2, 15–26.

Joint, I., Wollast, R., Chou, L., Batten, S., Elskens, M., Edwards, E., Hirst, A., Burkill, P., Groom, S., Gibb, S., Miller, A., Hydes, D., Dehairs, F., Antia, A., Barlow, R., Rees, A., Pomroy, A., Brockmann, U., Cummings, D., Lampitt, R., Loijens, M., Mantoura, F., Miller, P., Raabe, T., Alvarez-Salgado, X., Stelfox, C., Woolfenden, J., 2001. Pelagic production at the Celtic Sea shelf break. Deep-Sea Research II 48 (14–15), 3049–3081.

Jones Jr., J.B., Mulholland, P.J., 1998. Carbon dioxide variation in a hardwood forest stream: an integrative measure of whole catchment soil respiration. Ecosystems 1, 183–196.

Jones Jr., J.B., Stanley, E.H., Mulholland, P.J., 2003. Long-term decline in carbon dioxide supersaturation in rivers across the contiguous United States. Geophysical Research Letters 30 (10), 1495. doi:10.1029/2003GL017056.

Jones, M.T., Tabor, A.R., Weatherall, P., 1997. General Bathymetric Chart of the Oceans, CD-ROM, British Oceanographic Data Centre, Proudman Oceanographic Laboratory.

Kaltin, S., Anderson, L.G., Olsson, K., Fransson, A., Chierici, M., 2002. Uptake of atmospheric carbon dioxide in the Barents Sea. Journal of Marine Systems 38 (1–2), 31–45.

Kling, G.W., Kipphut, G.W., Miller, M.C., 1991. Arctic lakes and streams as gas conduits to the atmosphere: implications for tundra carbon budgets. Science 251, 298–301.

Kremer, J.N., Nixon, S.W., Buckley, B., Roques, P., 2003. Technical Note: conditions for using the floating chamber method to estimate air–water gas exchange. Estuaries 26 (4A), 985–990.

Kuss, J., Nagel, K., Schneider, B., 2004. Evidence from the Baltic Sea for an enhanced $CO_2$ air–sea transfer velocity. Tellus Series B 56 (2), 175–182.

Lancelot, C., Spitz, Y., Gypens, N., Ruddick, K., Becquevort, S., Rousseau, V., Lacroix, G., Billen, G., 2005. Modelling diatom and Phaeocystis blooms and nutrient cycles in the Southern Bight of the North Sea: the MIRO model. Marine Ecology-Progress Series 289, 63–78.

Lehner, B., Döll, P., 2004. Development and validation of a global database of lakes, reservoirs and wetlands. Journal of Hydrology 296 (1–4), 1–22.

Leinweber, A., Neumann, T., Schneider, B., 2005. The role of $N_2$-fixation to simulate the $pCO_2$ observations from the Baltic Sea. Biogeosciences Discussions 2, 609–636.

Lenhart, H.J., Pätsch, J., Kühn, W., Moll, A., Pohlmann, T., 2004. Investigation on the trophic state of the North Sea for three years (1994–1996) simulated with the ecosystem model ERSEM – the role of a sharp NAOI decline. Biogeosciences Discussions 1, 725–754.

Ludwig, W., Probst, J.L., Kempe, S., 1996. Predicting the oceanic input of organic carbon by continental erosion. Global Biogeochemical Cycles 10 (1), 23–41.

Mackenzie, F.T., Lerman, A., Andersson, A.J., 2004. Past and present of sediment and carbon biogeochemical cycling models. Biogeosciences 1 (1), 11–32.

Mackenzie, F.T., Andersson, A.J., Lerman, A., Ver, L.M., 2005. Boundary exchanges in the global coastal margin: implications for the organic and inorganic carbon cycles. In: Robinson, A.R., Brink, K.H. (Eds.), The Global Coastal Ocean- Multi-scale Interdisciplinary Processes. Harvard University Press, Cambridge, pp. 193–225.

Mehrbach, C., Culberson, C.H., Hawley, J.E., Pytkowicz, R.M., 1973. Measurements of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. Limnology and Oceanography 18, 897–907.

Moran, M.A., Sheldon, W.M., Sheldon, J.E., 1999. Biodegradation of riverine dissolved organic carbon in five estuaries of the southeastern United States. Estuaries 22 (1), 55–64.

Neubauer, S.C., Anderson, I.C., 2003. Transport of dissolved inorganic carbon from a tidal freshwater marsh to the York River estuary. Limnology and Oceanography 48 (1), 299–307.

Omar, A., Johannessen, T., Kaltin, S., Olsen, A., 2003. Anthropogenic increase of oceanic $pCO_2$ in the Barents Sea surface water. Journal of Geophysical Research 108 (C12), 3388. doi:10.1029/2002JC001628.

Pingree, R.D., Maddock, L., Butler, E.I., 1977. The influence of biological activity and physical stability in determining the chemical distributions of inorganic phosphate, silicate and nitrate. Journal of the Marine Biological Association of the UK 57, 1065–1073.

Radach, G., Berg, J., Hagmeier, E., 1990. Long-term changes of the annual cycles of meteorological, hydrographic, nutrient, and phytoplankton time series at Heligoland and at LV Elbe 1 in the German Bight. Continental Shelf Research 10, 305–328.

Raymond, P.A., Bauer, J.E., 2000. Bacterial consumption of DOC during transport through a temperate estuary. Aquatic Microbial Ecology 22 (1), 1–12.

Raymond, P.A., Cole, J.J., 2001. Gas exchange in rivers and estuaries: choosing a gas transfer velocity. Estuaries 24 (2), 312–317.

Raymond, P.A., Bauer, J.E., Cole, J.J., 2000. Atmospheric $CO_2$ evasion, dissolved inorganic carbon production, and net heterotrophy in the York River estuary. Limnology and Oceanography 45 (8), 1707–1717.

Sabine, C.L., Feely, R.A., Key, R.M., Lee, K., Bullister, J.L., Wanninkhof, R., Wong, C.S., Wallace, D.W.R., Tilbrook, B., Millero, F.J., Peng, T.H., Kozyr, A., Ono, T., Rios, A.F., 2004. The oceanic sink for anthropogenic $CO_2$. Science 305 (5682), 367–371.

Salisbury, J.E., Campbell, J.W., Linder, E., Meeker, L.D., Müller-Karger, F.E., Vörösmarty, C.J., 2004. On the seasonal correlation of surface particle fields with wind stress and Mississippi discharge in the northern Gulf of Mexico. Deep-Sea Research II 51, 1187–1203.

Schiettecatte, L.-S., Gazeau, F., van der Zee, C., Brion, N., Borges, A.V., 2006a. Time series of the partial pressure of carbon dioxide (2001–2004) and preliminary inorganic carbon budget in the Scheldt plume (Belgian coastal waters). Geochemistry, Geophysics, Geosystems (G3), 7, Q06009. doi:10.1029/2005GC001161.

Schiettecatte L.-S., Thomas, H., Bozec, Y., Borges, A.V., 2006b. High temporal coverage of carbon dioxide measurements in the Southern Bight of the North Sea. Marine Chemistry, submitted for publication.

Schneider, B., Kuss, J., 2004. Past and present productivity of the Baltic Sea as inferred from $pCO_2$ data. Continental Shelf Research 24 (15), 1611–1622.

Schneider, B., Nausch, G., Nagel, K., Wasmund, N., 2003. The surface water $CO_2$ budget for the Baltic Proper: a new way to determine nitrogen fixation. Journal of Marine Systems 42 (1–2), 53–64.

Semiletov, I.P., 1999. Aquatic sources and sinks of $CO_2$ and $CH_4$ in the polar regions. Journal of the Atmospheric Sciences 56 (2), 286–306.

Siemens, J., 2003. The European carbon budget: a gap. Science 302 (5651), 1681.

Sobek, S., Tranvik, L.J., Cole, J.J., 2005. Temperature independence of carbon dioxide supersaturation in global lakes. Global Biogeochemical Cycles 19. doi:10.1029/2004GB002264. GB2003.

Soetaert, K., Middelburg, J.J., Heip, C., Meire, P., Van Damme, S., Maris, T., 2006. Long-term change in dissolved inorganic nutrients in the heterotrophic Scheldt estuary (Belgium, The Netherlands). Limnology and Oceanography 51 (1), 409–423.

Takahashi, T., 2003. Ocean basin summations of sea–air flux computed using the 10 meter height winds. http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/text/10m_wind.prn.

Takahashi, T., Sutherland, S.C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N.R., Wanninkhof, R., Feely, R.A., Sabine, C., Olafsson, J., Nojiri, Y., 2002. Global sea–air $CO_2$ flux based on climatological surface ocean $pCO_2$, and seasonal biological and temperature effects. Deep-Sea Research II 49 (9–10), 1601–1622.

Thomas, H., Schneider, B., 1999. The seasonal cycle of carbon dioxide in Baltic Sea surface waters. Journal of Marine Systems 22 (1), 53–67.

Thomas, H., Ittekkot, V., Osterroht, C., Schneider, B., 1999. Preferential recycling of nutrients – the ocean's way to increase new production and to pass nutrient limitation? Limnology and Oceanography 44 (8), 1999–2004.

Thomas, H., Bozec, Y., Elkalay, K., De Baar, H.J.W., 2004. Enhanced open ocean storage of $CO_2$ from shelf sea pumping. Science 304 (5673), 1005–1008.

Thomas, H., Bozec, Y., De Baar, H.J.W., Elkalay, K., Frankignoulle, M., Schiettecatte, L.-S., Borges, A.V., 2005a. The carbon budget of the North Sea. Biogeosciences 2 (1), 87–96.

Thomas, H., Bozec, Y., Elkalay, K., De Baar, H.J.W., Borges, A.V., Schiettecatte, L.-S., 2005b. Controls of the surface water partial pressure of $CO_2$ in the North Sea. Biogeosciences 2 (4), 323–334.

Tsunogai, S., Watanabe, S., Sato, T., 1999. Is there a "continental shelf pump"- for the absorption of atmospheric $CO_2$? Tellus Series B 5 (3), 701–712.

Uher, G., 2006. Distribution and air–sea gas exchange of reduced sulphur gases in European coastal waters. Estuarine, Coastal and Shelf Science 70 (3), 338–360.

Vanderborght, J.-P., Folmer, I.M., Aguilera, D.R., Uhrenholdt, T., Regnier, P., 2006. Reactive-transport modelling of a river-estuarine-coastal zone system: application to the Scheldt estuary. Marine Chemistry, submitted for publication.

Wafar, M.V.M., Le Corre, P., Birrien, J.L., 1983. Nutrients and primary production in permanently well-mixed temperate coastal waters. Estuarine, Coastal and Shelf Science 17, 431–446.

Wanninkhof, R.H., 1992. Relationship between wind speed and gas exchange over the ocean. Journal of Geophysical Research 97 (C5), 7373–7382.

Wanninkhof, R., McGillis, W.R., 1999. A cubic relationship between air–sea $CO_2$ exchange and wind speed. Geophysical Research Letters 26 (13), 1889–1892.

Wiegner, T.N., Seitzinger, S.P., 2001. Photochemical and microbial degradation of external dissolved organic matter inputs to rivers. Aquatic Microbial Ecology 24, 27–40.

Wollast, R., 1998. Evaluation and comparison of the global carbon cycle in the coastal zone and in the open ocean. In: Brink, K.H., Robinson, A.R. (Eds.), The Global Coastal Ocean. John Wiley & Sons, pp. 213–252.

Wollast, R., Chou, L., 2001. The carbon cycle at the ocean margin in the northern Gulf of Biscay. Deep-Sea Research II 48 (14–15), 3265–3293.

Woodwell, G.M., Rich, P.H., Hall, C.A.S., 1973. Carbon in estuaries. In: Woodwell, G.M., Pecan, E.V. (Eds.), Carbon and the Biosphere. Virginia, Springfield, pp. 221–240.

Woolf, D.K., Thorpe, S.A., 1991. Bubbles and the air–sea exchange of gases in near saturation conditions. Journal of Marine Research 34, 435–466.

Zappa, C.J., Raymond, P.A., Terray, E.A., McGillis, W.R., 2003. Variation in surface turbulence and the gas transfer velocity over a tidal cycle in a macro-tidal estuary. Estuaries 26 (6), 1401–1415.