Carbon dioxide in European coastal waters

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Received 23 May 2006; accepted 30 May 2006
Available online 10 August 2006

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 \(67.0 \text{TgC yr}^{-1}\) 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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Keywords: carbon dioxide; fluxes; coastal ecosystems; estuaries

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 \(-1.0 \text{PgC yr}^{-1}\) 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 \(-1.6 \text{PgC yr}^{-1}\) (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 $-0.4$ Pg C 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 (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
regenerated primary production maintains during this period the low pCO2 at 15 °C values attained during the spring bloom (note however that pCO2 increases with temperature). However, in late summer and early fall, pCO2 at 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 at 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 at 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 in pCO2 and pCO2 at 15 °C that follows closely the spring bloom, suggesting a rapid remineralization of organic matter, followed by a steady increase of pCO2 at 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

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.

<table>
<thead>
<tr>
<th>Site (location in Fig. 2)</th>
<th>Characteristics</th>
<th>E</th>
<th>N</th>
<th>pCO2 (ppm)</th>
<th>Air—water CO2 fluxes (molC m−2 yr−1)</th>
<th>k</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner estuaries</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Randers Fjord (1)</td>
<td>MiT</td>
<td>10.3</td>
<td>56.6</td>
<td>220–3400</td>
<td>2.2</td>
<td>FC 1</td>
<td></td>
</tr>
<tr>
<td>Elbe (2)</td>
<td>MaT</td>
<td>8.8</td>
<td>53.9</td>
<td>580–1100</td>
<td>53.0</td>
<td>FC 2</td>
<td></td>
</tr>
<tr>
<td>Ems (3)</td>
<td>MaT</td>
<td>6.9</td>
<td>53.4</td>
<td>560–3755</td>
<td>67.3</td>
<td>FC 2</td>
<td></td>
</tr>
<tr>
<td>Rhine (4)</td>
<td>MaT; RD</td>
<td>4.1</td>
<td>52.0</td>
<td>545–1990</td>
<td>39.7</td>
<td>FC 2</td>
<td></td>
</tr>
<tr>
<td>Scheldt (5)</td>
<td>MaT</td>
<td>3.5</td>
<td>51.4</td>
<td>125–9425</td>
<td>63.0</td>
<td>FC 2</td>
<td></td>
</tr>
<tr>
<td>Thames (6)</td>
<td>MaT</td>
<td>0.9</td>
<td>51.5</td>
<td>505–5200</td>
<td>73.6</td>
<td>FC 2</td>
<td></td>
</tr>
<tr>
<td>Tamar (7)</td>
<td>MaT</td>
<td>–4.2</td>
<td>50.4</td>
<td>380–2200</td>
<td>74.8</td>
<td>C** 2</td>
<td></td>
</tr>
<tr>
<td>Loire (8)</td>
<td>MaT</td>
<td>–2.2</td>
<td>47.2</td>
<td>630–2910</td>
<td>64.4</td>
<td>C** 3</td>
<td></td>
</tr>
<tr>
<td>Gironde (9)</td>
<td>MaT</td>
<td>–1.1</td>
<td>45.6</td>
<td>465–2860</td>
<td>30.8</td>
<td>FC 2</td>
<td></td>
</tr>
<tr>
<td>Douro (10)</td>
<td>MaT; RD</td>
<td>–8.7</td>
<td>41.1</td>
<td>1330–2200</td>
<td>76.0</td>
<td>FC 2</td>
<td></td>
</tr>
<tr>
<td>Sado (11)</td>
<td>MaT</td>
<td>–8.9</td>
<td>38.5</td>
<td>575–5700</td>
<td>31.3</td>
<td>FC 2</td>
<td></td>
</tr>
<tr>
<td>Upwelling marginal seas</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Galician coast (12)</td>
<td>LUI</td>
<td>–9.2</td>
<td>42.5</td>
<td>265–415</td>
<td>–2.2</td>
<td>W 4</td>
<td></td>
</tr>
<tr>
<td>Gulf of Cadiz (13)</td>
<td>LUI</td>
<td>–7.0</td>
<td>37.0</td>
<td>125–700</td>
<td>–0.4</td>
<td>W 5</td>
<td></td>
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<tr>
<td>Non-upwelling marginal seas</td>
<td></td>
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</tr>
<tr>
<td>Barents Sea (14)</td>
<td>SS</td>
<td>30.0</td>
<td>75.0</td>
<td>168–352</td>
<td>–3.6</td>
<td>W 6</td>
<td></td>
</tr>
<tr>
<td>Bothnian Bay (15)</td>
<td>PS</td>
<td>21.0</td>
<td>63.0</td>
<td>150–550</td>
<td>+3.1</td>
<td>W 7</td>
<td></td>
</tr>
<tr>
<td>Baltic Proper (16)</td>
<td>PS</td>
<td>20.0</td>
<td>57.0</td>
<td>156–475</td>
<td>–0.8</td>
<td>W 8</td>
<td></td>
</tr>
<tr>
<td>North Sea (17)</td>
<td>SS</td>
<td>2.6</td>
<td>57.6</td>
<td>145–495</td>
<td>–1.4</td>
<td>W 9</td>
<td></td>
</tr>
<tr>
<td>English Channel (18)</td>
<td>WM</td>
<td>–1.2</td>
<td>50.2</td>
<td>200–500</td>
<td>0.0</td>
<td>W 10</td>
<td></td>
</tr>
<tr>
<td>Gulf of Biscay and Celtic Sea (19)</td>
<td>SS</td>
<td>–7.9</td>
<td>49.0</td>
<td>260–460</td>
<td>–0.8</td>
<td>W 11</td>
<td></td>
</tr>
<tr>
<td>Bay of Angels (20)</td>
<td>SS</td>
<td>7.4</td>
<td>43.6</td>
<td>345–450</td>
<td>–0.6</td>
<td>W 12</td>
<td></td>
</tr>
</tbody>
</table>
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, pCO₂ and pCO₂@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 pCO₂@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 N₂ 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 NO₃⁻ values are two to ten times lower. Note also that the much higher seasonal amplitude of pCO₂ and pCO₂@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 CO₂

Although a relatively abundant literature reporting data on CO₂ dynamics in coastal upwelling systems is available (see review by Borges, 2005), annually integrated air—water CO₂ 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 CO₂ 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 CO₂. The two systems that act as CO₂ sources (Oman and California coasts) are characterized by disproportionately higher upwelling indices that lead to much higher inputs of upwelled DIC and NO₃⁻ than in the systems that act as CO₂ 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 CO₂ 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 CO2 sinks, while systems at low-latitudes are CO2 sources (Cai and Dai, 2004). However, more data in other systems are required to validate this hypothesis. It has also been argued that the pCO2 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 CO2 fluxes and ecosystem metabolism

Net autotrophic ecosystems, where gross primary production (GPP) exceeds community respiration (CR) decrease CO2 in the surrounding waters, and conversely net heterotrophic systems (where GPP < CR) enrich the surrounding water in CO2. Nevertheless, in coastal environments the link between the exchange of CO2 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 CO2 flux between the water column and the atmosphere will be further modulated by other factors such as: additional biogeochemical processes (e.g. CaCO3 precipitation/dissolution); exchange of water with adjacent aquatic systems and the CO2 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 CO2 to the atmosphere. In certain shallow water temperate continental shelves, calcification can also be a major driver of the air—water CO2 fluxes. For instance, Borges and Frankignoulle (2003) hypothesized that the English Channel is not a significant sink for atmospheric CO2 unlike adjacent systems such as the Gulf of Biscay (Table 1) and the Southern Bight of the North Sea, due to the release of CO2 from extensive brittle star populations that on an annual scale balance the CO2 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 CO2 exchanges were carried out in 3 coastal ecosystems (Fig. 4). For some of the cruises and some of the sites, the CO2 fluxes and trophic status

Fig. 3. Comparison of the seasonal cycle of temperature, pCO2 and pCO2 normalized at a temperature of 15 °C (pCO2@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 pCO2, of pCO3 normalized to a constant temperature of 15 °C (pCO3@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))

<table>
<thead>
<tr>
<th></th>
<th>Gulf of Biscay</th>
<th>English Channel</th>
<th>SBNS</th>
<th>Gotland Sea</th>
<th>Bay of Angels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wintertime NO3 (μmol kg−1)</td>
<td>5−10^6</td>
<td>5−20^6</td>
<td>10−40^6</td>
<td>4^6</td>
<td>1^6</td>
</tr>
<tr>
<td>Salinity</td>
<td>35.4^d</td>
<td>35.1^e</td>
<td>34.6^f</td>
<td>7.0^i</td>
<td>38.0^j</td>
</tr>
<tr>
<td>pCO2 amplitude (ppm)</td>
<td>76^b</td>
<td>102^b</td>
<td>222^c</td>
<td>319^h</td>
<td>120^k</td>
</tr>
<tr>
<td>pCO3@15 °C amplitude (ppm)</td>
<td>122^b</td>
<td>55^g</td>
<td>283^h</td>
<td>589^i</td>
<td>68^k</td>
</tr>
<tr>
<td>DIC amplitude (μmol kg−1)</td>
<td>76^d</td>
<td>140^d</td>
<td>139^d</td>
<td>50^d</td>
<td></td>
</tr>
<tr>
<td>Total alkalinity (μmol kg−1)</td>
<td>233−234^f</td>
<td>2297−2334^f</td>
<td>2294−2353^h</td>
<td>1567−1593^i</td>
<td>2503−2550^m</td>
</tr>
<tr>
<td>Revelle factor</td>
<td>9.8−11.7^i</td>
<td>10.7−12.4^d</td>
<td>9.6−13.3^l</td>
<td>14.7−28.3^l</td>
<td>9.3−10.4^l</td>
</tr>
</tbody>
</table>

b From Pingree et al. (1977), Wafar et al. (1983), and Bentley et al. (1999).
c From Lenhart et al. (2004).
d From Lentz et al. (2005).
e From the nearby monitoring station B in the Villefranche roadstead (http://www.obs-vlfr.fr/Rade/).
f From Frankignoule and Borges (2001).
g From Borges and Frankignoule (2003).
h From Schiettecatte et al. (submitted for publication).
i From Schneider and Kuss (2004).
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. During the first Randers Fjord cruise a negative NEP (autotrophic status) is associated to a source of CO2 above; during the second cruise in the Bay of Palma a positive NEP (heterotrophic status) is related to a sink of atmospheric CO2. 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 mmolC m−2 d−1 is associated to a ML NCP of about 30 mmolC m−2 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 pCO3 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.
2.1.5. Conceptual frame of the biogeochemical controls of air–water CO₂ fluxes in coastal environments

Based on the above discussion and also based on the synthesis by Borges (2005) of CO₂ dynamics and exchanges with the atmosphere in other coastal environments (in particular at low latitudes), we propose a conceptual relationship of CO₂ fluxes and ML NCP, that summarises the drivers of CO₂ 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 latitude continental shelves act as sources of CO₂, 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 CO₂ oversaturated at low latitudes and CO₂ 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 CO₂. Microtidal estuaries due to their shorter freshwater residence time and stratification are less heterotrophic and lower sources of CO₂ than macrotidal estuaries. In the former the relative contribution of the ventilation of riverine CO₂ is higher than macrotidal estuaries. 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 CO₂. Note that there is increasing evidence that the emission of CO₂ from the aquatic compartment of these systems is indirectly linked to diagenetic organic carbon degradation, through the

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**Fig. 4.** Air–water CO₂ fluxes versus net ecosystem production (NEP) (A); and net community production in the mixed layer (ML NCP) (B). Air–water CO₂ fluxes were computed from field measurements of pCO₂ 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.

**Fig. 5.** Contribution of the ventilation of river CO₂ to the overall emission of CO₂ 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 CO₂ (RE in mmol m⁻² d⁻¹) was computed from ΔDIC (mmol m⁻³), average freshwater discharge (Q in m³ d⁻¹) and the inner estuary surface area (S in m²), 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 CO₂. El = Elbe; Em = Em; 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 Frankignoule et al. (1998); data for Sat from Cai and Wang (1998); data for YR from Raymond et al. (2000).
input of CO2 rich porewater (Borges et al., 2003; Bouillon et al., in press). Calcification is partly responsible for the emission of CO2 from coral reefs to the atmosphere, as it leads to an increase of CO2 in the oceanic waters circulating over these systems that are typically CO2 oversaturated. Finally, purely thermodynamic effects related to water cooling or warming will further modulate the exchange of CO2 between coastal aquatic environments and the atmosphere, at seasonal and annual timescales.

2.2. Scaling of CO2 fluxes in coastal environments and comparison at European scale with other aquatic and terrestrial compartments

Based on the air–water CO2 fluxes from Table 1, the continental shelf surface area estimates from Table 3, we scaled the CO2 fluxes in European coastal environments and compared them to CO2 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 CO2 fluxes from lakes and rivers must be considered as first order estimates. The sink of atmospheric CO2 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 CO2 over continental shelves could be almost fully balanced by the emission of CO2 from inner estuaries of about 67 TgC yr\(^{-1}\). 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 CO2 is emitted to the atmosphere within the inner estuary, then the potential emission of CO2 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 (Álesund to Svalbard)| 150          | Huthnance (2006) |
| Cape Wrath to Álesund       | 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    | 54           | Huthnance (2006) |
| and Clyde Sea               |              |                  |
| 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) |

Fig. 6. Conceptual diagram of the biogeochemical controls of air–water CO2 fluxes in coastal environments.
Table 4
Tentative budget of exchanges of atmospheric CO2 between aquatic, and terrestri cal compartments at European scale

<table>
<thead>
<tr>
<th></th>
<th>Surface area (10^3 km^2)</th>
<th>Atmospheric CO2 exchange (TgC yr^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continental shelf</td>
<td>3065^a</td>
<td>-68.1^a</td>
</tr>
<tr>
<td>Inner estuaries</td>
<td>112^a</td>
<td>67.0^a</td>
</tr>
<tr>
<td>Rivers</td>
<td>66^a</td>
<td>21.3^a</td>
</tr>
<tr>
<td>Lakes</td>
<td>165^g</td>
<td>15.2^a</td>
</tr>
<tr>
<td>Carbonate and silicate rock weathering</td>
<td>6996^d</td>
<td>-13.2^d</td>
</tr>
<tr>
<td>Export of POC from rivers to estuaries</td>
<td>6996^d</td>
<td>-8.5^d</td>
</tr>
<tr>
<td>Export of DOC from rivers to estuaries</td>
<td>6996^d</td>
<td>-11.2^d</td>
</tr>
<tr>
<td>Grasslands</td>
<td>832^l</td>
<td>-60.1^m</td>
</tr>
<tr>
<td>Croplands</td>
<td>1911^l</td>
<td>119.7^m</td>
</tr>
<tr>
<td>Peatlands</td>
<td>43^d</td>
<td>51.0^m</td>
</tr>
<tr>
<td>Forests</td>
<td>1665^d</td>
<td>-176.6^d</td>
</tr>
<tr>
<td>Fossil fuel emission</td>
<td>13 172^i</td>
<td>1462.5^k</td>
</tr>
</tbody>
</table>

^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 x 10^3 km^2 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 shelf, North Channel, Clyde Sea, Celtic Sea, Gulf of Biscay, and English Channel (1501 x 10^3 km^2 Table 3), air—water CO2 flux off the Galician coast (2.2 molC m^-2 yr^-1 Table 1) scaled to region from Cape Finsisterre to Cape Sagres (21 x 10^3 km^2 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 x 10^3 km^2 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 x 10^3 km^2 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 x 10^3 km^2 for countries listed in ^f).

^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 x 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^* 2^* grided fluxes from Amiott-Suchet and Probst (1995) extracted from the ISLSCP database for countries listed in ^l.

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

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

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

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

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 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; Vanderborght et al., submitted for publication). In the Satilla River estuary, lateral DIC inputs from the extensive saltmarshes 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 underrepresented 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 (Kremmer 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 x 10^3 km^2 based on the Coordination of information on the environment (CORINE) Land Cover program (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 x 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 x 10^3 km^2 given by Woodwell et al. (1973).
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; Siemtens, 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 Frankignoule, 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 (Semi-letov, 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, 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 CO2 fluxes is so far undocumented in any coastal environment.

Acknowledgements

For data and information, we thank Andreas Andersson, Wei-Jun Cai, Ioen Delille, Jean-Pierre Gattuso, Nathalie Gypens, Emma Huertas, John Huthnance, Ivan Janssens, Joachim Kuss, Christiane Lancelot, Wolfgang Ludwig, Jean-Claude Marty, Peter Raymond, and Sebastian Sobek. For fruitful and inspiring discussions, we thank the CARBOEUROPE working groups “Coastal Ecosystem Greenhouse Gas Budget”, and “River Carbon Fluxes and Greenhouse Gas emissions from continental waters”. Aida F. Ríos, Marion Gehlen and Fred T. Mackenzie reviewed a previous version of the paper. This is a contribution to CARBOEUROPE — GHG (EVK2-CT-2002-20014), CARBOOCEAN (511176-2), EUROTROPH (EVK3-CT-2000-00040), CANOPY (EV/12/20C), PEACE (SD/CS/03A), and SOLAS.BE (OA/00/025). AVB is a research associate at the Fonds National de la Recherche Scientifique. This is NIOO contribution n° 3818, and MARE contribution n° 080.

References


Leinweber, A., Neumann, T., Schneider, B., 2005. The role of N2-fixation to simulate the pCO2 observations from the Baltic Sea. Biogeosciences Discussions 1, 725–754.


