Carbon dioxide in European coastal waters

A.V. Borges[1,*], L.-S. Schiettecatte[1], G. Abril[2], B. Delille[1], F. Gazeau[1,3,4]

[1] University of Liège, Chemical Oceanography Unit, Institut de Physique (B5), B-4000 Liège, Belgium

[2] University of Bordeaux 1, Environnements et Paléoenvironnements OCéaniques (EPOC), CNRS-UMR 5805, Avenue des Facultés, F-33405 Talence, France

[3] Laboratoire d'Océanographie de Villefranche, CNRS-Université de Paris 6, B. P. 28, F-06234 Villefranche-sur-mer Cedex, France

[4] Netherlands Institute of Ecology, Centre for Estuarine and Marine Ecology, Postbus 140, NL-4400 AC Yerseke, The Netherlands

[*] corresponding author:
e-mail : alberto.borges@ulg.ac.be

Accepted in *Estuarine, Coastal and Shelf Science* - Special section on EU CarboEurope Concerted Action Synthesis of the European Greenhouse Gas budget

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.

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 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 yrs 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 Figure 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 Figure 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 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 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 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 Figure 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 mmol C m^{-2} d^{-1} is associated to a ML NCP of about 30 mmol C 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 Figure 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.

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 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 input of CO_2 rich porewater (Borges et al., 2003; Bouillon et al., 2006). 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 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, Soetaert et al., 2006; Gazeau et al., 2005c; Vanderborght et al., 2006). 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 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 under-represented 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., 2006). 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, 2005). 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 near-shore 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, 2005; Bange, 2005), 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.

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, Wolfang 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

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, 187-207.

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, L09316 (doi:10.1029/2004GL019714).

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., 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., 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.

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), GB4021 (doi:10.1029/2004GB002232).

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, 877-927.

Bange, H.W., 2005. Nitrous oxide and methane in European coastal waters. Estuarine Coastal and Shelf Science, this issue.

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., Delille, B., Frankignoulle, M., 2005. Budgeting sinks and sources of CO_2 in the coastal ocean: Diversity of ecosystems counts. Geophysical Research Letters 32, L14601 (doi:10.1029/2005GL023053).

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., 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).

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, submitted.

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., 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., 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., 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).

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., 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.

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, 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, 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., 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.

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.

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., 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.

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.

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

Guérin, F., Abril, G., Serça, D., Delon, C., Richard, S., Delmas, R., Tremblay, A., Varfalvy, L., 2006. 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, 123-147.

Huertas, I.E., Navarro, G., Rodríguez-Gálvez, S., Lubián, L.M., 2005. 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., 2006. 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, M.T., Tabor, A.R., Weatherall, P., 1997. General Bathymetric Chart of the Oceans, CD-ROM, British Oceanographic Data Centre, Proudman Oceanographic Laboratory.

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).

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.

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.

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.

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., 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, 193-225.

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

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., 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.

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

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, in press

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

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, GB2003 (doi:10.1029/2004GB002264).

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., 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.

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

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., 2005. Distribution and air-sea gas exchange of reduced sulphur gases in European coastal waters. Estuarine Coastal and Shelf Science, this issue

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

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

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

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.), In: The Global Coastal Ocean, John Wiley & Sons, 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, Springfield, Virginia, 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.

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 Figure 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.

Site (location in Fig.2)	Characteristics	°E	°N	pCO_2 (ppm)	Air-water CO_2 fluxes (mol C 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

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: Thomas and Schneider (1999); 8: Algesten et al. (2004); 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

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. (2006b); [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 Figure 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)

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 [g]
Inner estuaries	112 [b]	67.0 [h]
Rivers	66 [c]	21.3 [i]
Lakes	167 [d]	15.2 [j]
Carbonate and silicate rock weathering	6996 [e]	-13.2 [k]
Export of POC from rivers to estuaries	6996 [e]	-8.5 [l]
Export of DOC from rivers to estuaries	6996 [e]	-11.2 [l]
Grasslands	832 [f]	-60.1 [m]
Croplands	1911 [f]	119.7 [m]
Peatlands	43 [f]	51.0 [m]
Forests	1665 [f]	-176.6 [m]
Fossil fuel emission	13172 [e]	1462.5 [n]

[a] : Sum of continental shelves in Table 3, excluding East Siberian, Laptev, Kara and Black Seas; [b] : from Woodwell et al. (1973); [c] : based on the assumption of Cole and Caraco (2001) that rivers cover 0.5% of total land (13172 10^3 km^2 for countries listed in [e]); [d] : from Lehner and Döll (2004); [e] : 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/); [f] : for countries listed in [e] from Janssens et al. (2005); [g] : based on air-water CO_2 flux in Barents Sea (-3.6 mol C 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 mol C 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 mol C 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 mol C 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 mol C m^{-2} yr^{-1} Table 1) scaled to the Mediterranean Sea continental shelf (450 10^3 km^2 Table 3); [h] : based on surface area weighted average of CO_2 fluxes in all estuaries from Table 1; [i] : based on CO_2 fluxes for European rivers compiled by Cole and Caraco (2001); [j] : 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); [k] : based on 2°*2° gridded fluxes from Amiotte-Suchet and Probst (1995) extracted from the ISLSCP database for countries listed in [e]; [l] : based on 2°*2° gridded fluxes from from Ludwig et al. (1996) extracted from the ISLSCP database for countries listed in [e]; [m] : for countries listed in [e] from Janssens et al. (2005); [n] : in 1995 for countries listed in [e] from Janssens et al. (2005)

FIGURE CAPTIONS

Figure 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).

Figure 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)).

Figure 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. (2006b), 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

Figure 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.

Figure 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 x 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).

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

Fig. 1

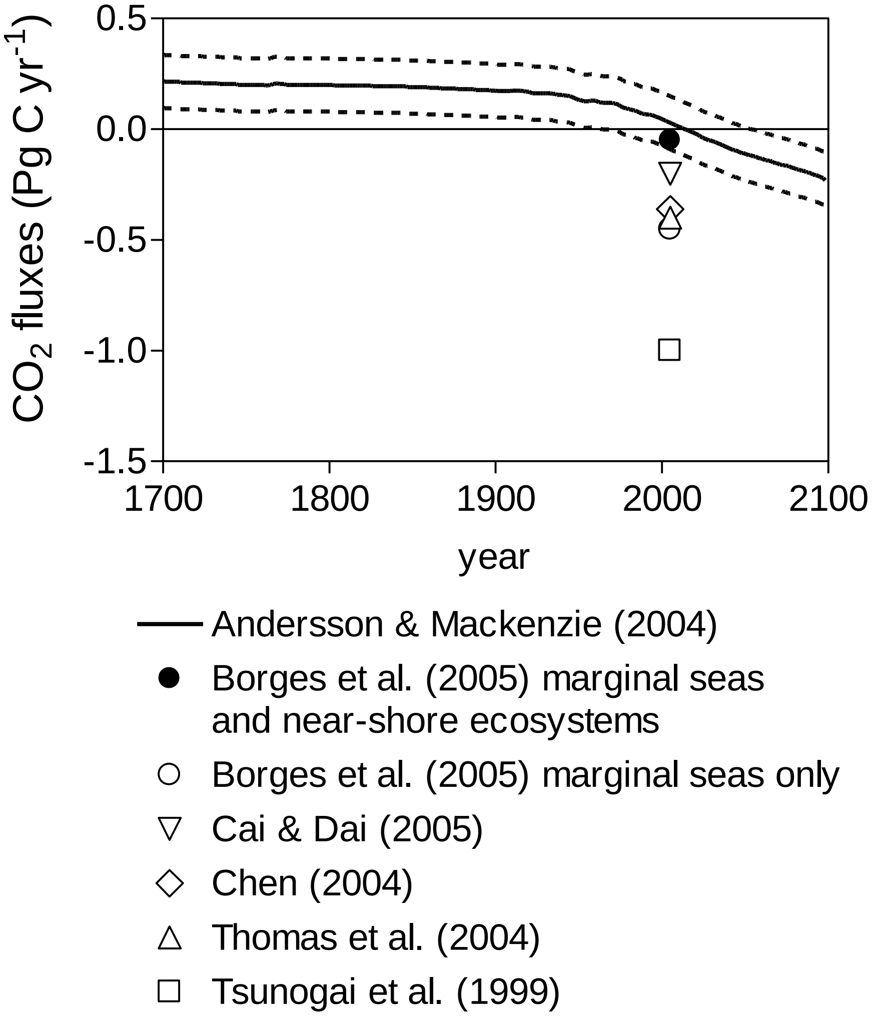

0.5
0.0
-0.5
-1.0
-1.5
CO_2 fluxes (Pg C yr^{-1})
1700
1800
1900
2000
2100
year
Andersson & Mackenzie (2004)
Borges et al. (2005) marginal seas and near-shore ecosystems
Borges et al. (2005) marginal seas only
Cai & Dai (2005)
Chen (2004)
Thomas et al. (2004)
Tsunogai et al. (1999)

Fig. 2

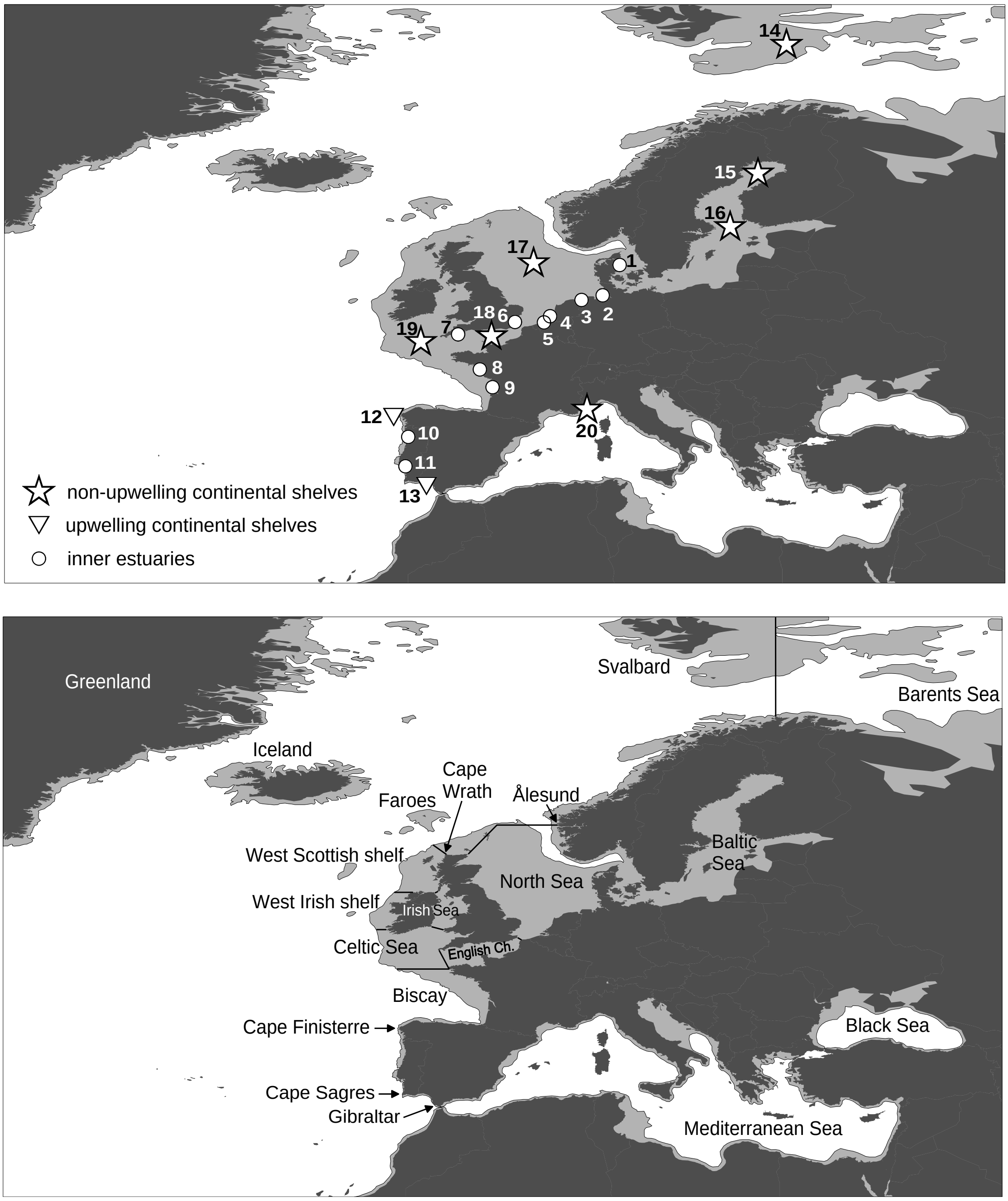

14
15
16
17
1
2
3
4
5
6
18
7
19
8
9
12
10
20
11
13
non-upwelling continental shelves
upwelling continental shelves
inner estuaries
Greenland
Svalbard
Barents Sea
Iceland
Faroes
Cape Wrath
Ålesund
West Scottish shelf
Baltic Sea
North Sea
West Irish shelf
Irish Sea
Celtic Sea
English Ch.
Biscay
Cape Finisterre
Black Sea
Cape Sagres
Gibraltar
Mediterranean Sea

Fig. 3 – *Color version for online version only*

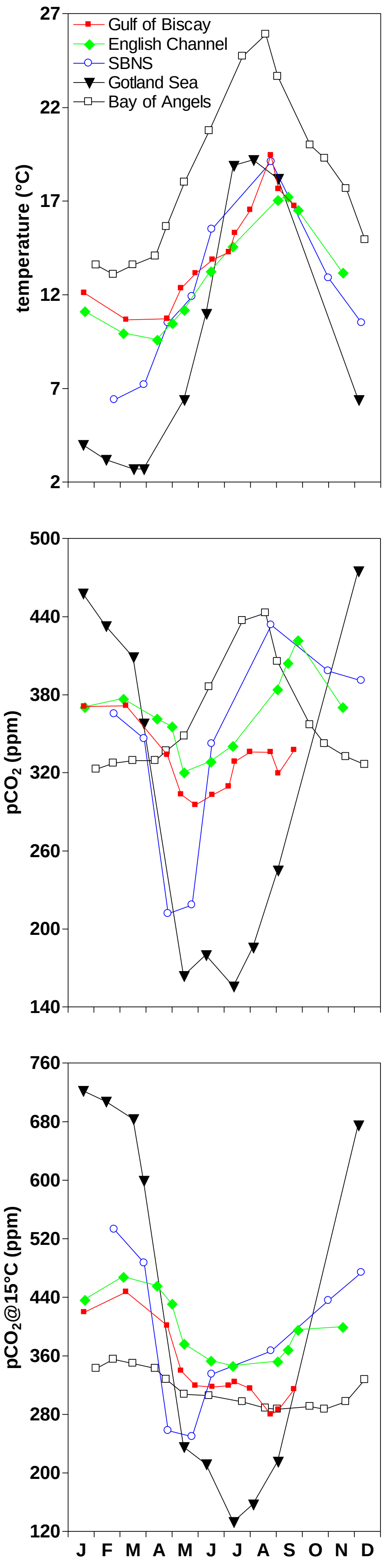
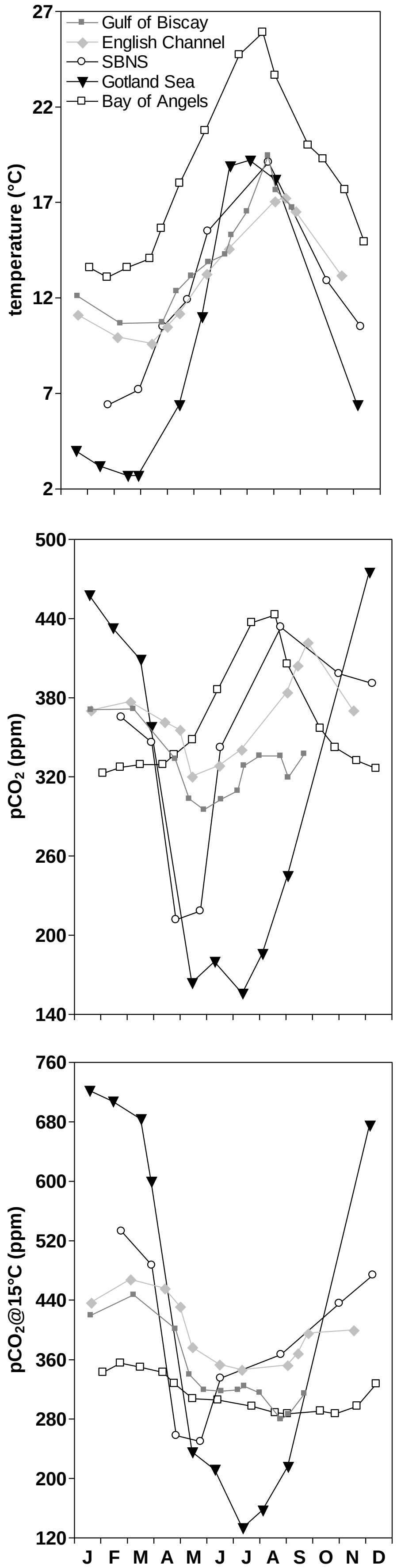
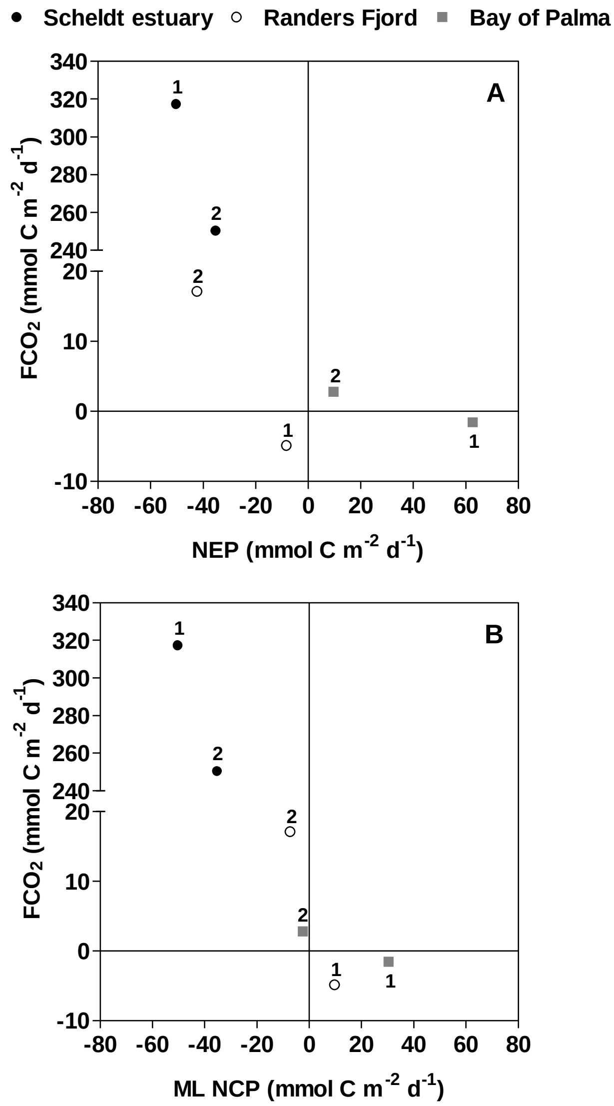


Fig. 3 – *BW version for print version*

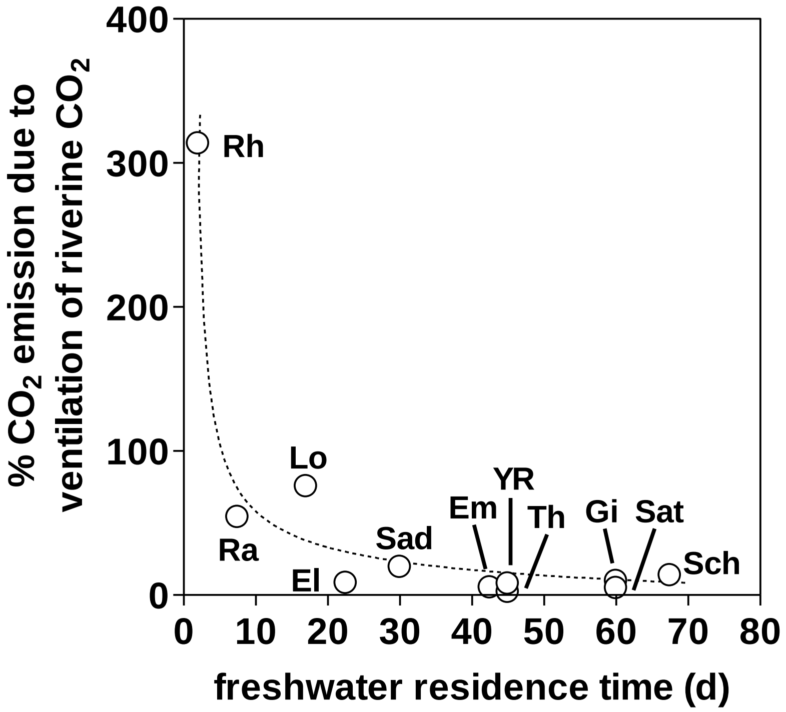


865 Fig. 4

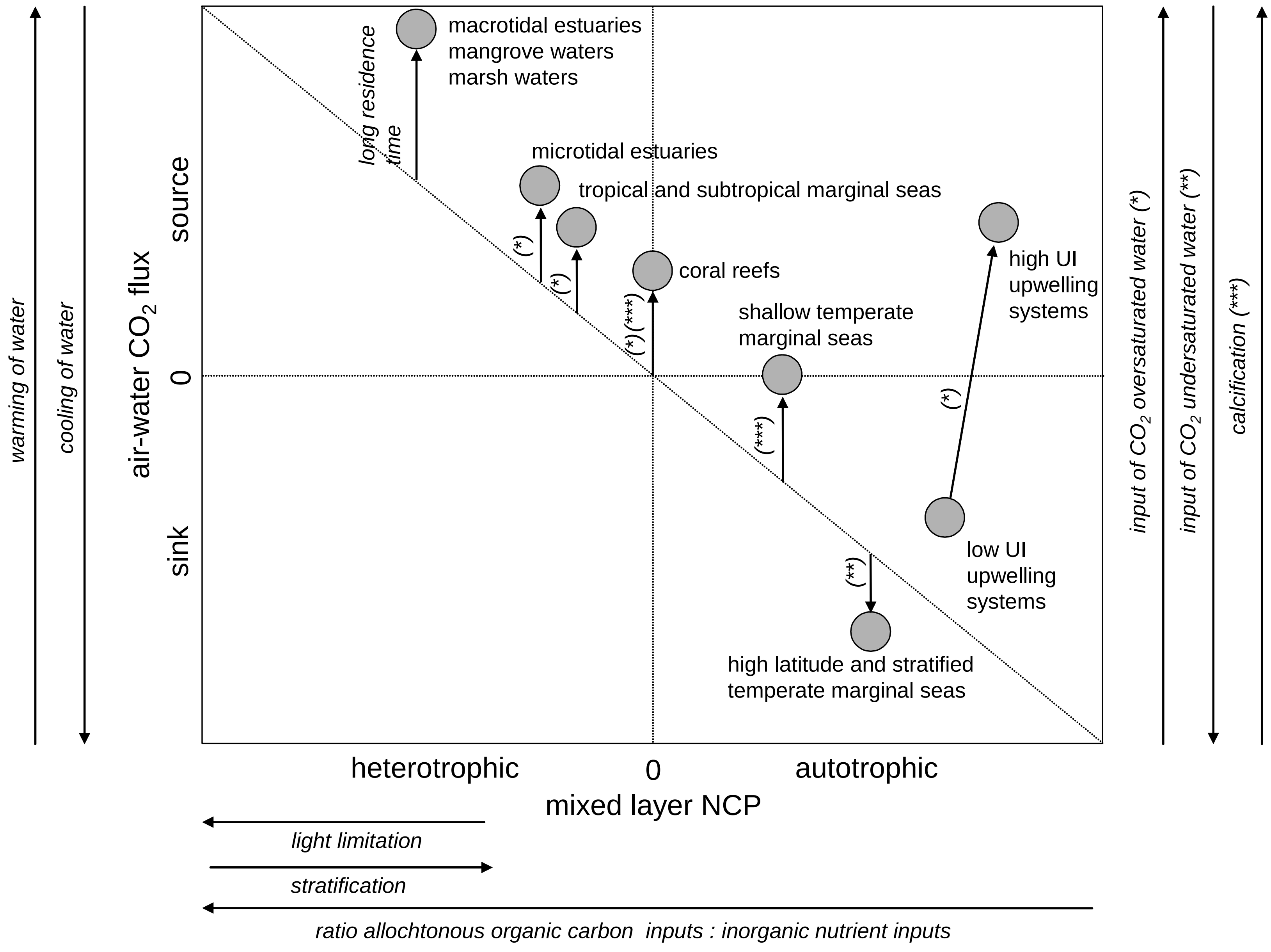
866


Scheldt estuary
Randers Fjord
Bay of Palma
A
B
FCO2 (mmol C m-2 d-1)
NEP (mmol C m-2 d-1)
ML NCP (mmol C m-2 d-1)
340
320
300
280
260
240
20
10
0
-10
-80
-60
-40
-20
0
20
40
60
80
1
2

867 Fig. 5


% CO_2 emission due to ventilation of riverine CO_2
freshwater residence time (d)
0
100
200
300
400
0
10
20
30
40
50
60
70
80
Rh
Lo
Ra
El
Sad
Em
YR
Th
Gi
Sat
Sch

868 Fig. 6



warming of water
cooling of water
air-water CO_2 flux
source
0
sink
macrotidal estuaries
mangrove waters
marsh waters
long residence time
microtidal estuaries
tropical and subtropical marginal seas
(*)
(*)
(*)(***)
coral reefs
shallow temperate marginal seas
high UI upwelling systems
(*)
(***)
low UI upwelling systems
(**)
high latitude and stratified temperate marginal seas
input of CO_2 oversaturated water (*)
input of CO_2 undersaturated water (**)
calcification (***)
heterotrophic
0
autotrophic
mixed layer NCP
light limitation
stratification
ratio allochtonous organic carbon inputs : inorganic nutrient inputs