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Distribution and air-water exchange of carbon dioxide in the Scheldt plume off the Belgian coast

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Abstract. In the present paper we report partial pressure of CO_2 (pCO_2) data obtained off the Belgian coast during 24 cruises. The temporal and spatial resolution of this data set allows us to discuss satisfactorily seasonal and inter-annual variability of pCO_2 in the study area. The dynamics of pCO_2 are described using two approaches: fixed reference stations and area survey cruises. The air-water fluxes of CO_2 in the Scheldt estuarine plume and in the outer-plume region are estimated quantitatively, showing that these areas correspond respectively to a net annual source and sink of atmospheric CO_2. The annually integrated air-water fluxes for the Scheldt estuarine plume range between +1.1 and +1.9 mol m^{-2} $year^{-1}$ as a function of the formulation of the exchange coefficient of CO_2. The annual net emission of CO_2 from the estuarine plume to the atmosphere is estimated to be between +2.3 to +4.0 Gmol $year^{-1}$ which represents 17 to 29% of the estimate reported in the literature for the Scheldt inner estuary.

Introduction

The role of the coastal ocean as a source or a sink of atmospheric CO_2 is the subject of a long-lived controversy that mainly originates from the paucity of data, their probable inadequate extrapolation and the diversity and complexity of this oceanic realm from the point of view of carbon cycling. The prevailing question is whether the coastal ocean is net autotrophic or net heterotrophic (e.g. Smith & Hollibaugh 1993; Wollast 1998). In an autotrophic system, the production of organic matter is higher than its total consumption, thus, such a system exports and/or stores organic matter and is then potentially a sink for atmospheric CO_2. However, the net exchange of CO_2 across the air-water interface will ultimately result from the integration of a variety of processes: the production/degradation/export of organic carbon, the production/dissolution/export of carbonates, the input of dissolved inorganic carbon

by vertical mixing processes and/or freshwater runoff and the thermodynamic effects related to both water temperature variations and water mass mixing.

The flux of CO_2 across the air-water interface can be estimated from the measurements of the air-water gradient of CO_2 that integrates all physical and biogeochemical processes at stake. This approach is the most direct one to assess the role of an ecosystem from the point of view of atmospheric coupling but has been only recently applied at large spatial and temporal scales in a limited number of coastal ecosystems. Based on a high resolution pCO_2 data-set in the Gulf of Biscay, Frankignoulle and Borges (2001) show that the European distal continental shelf (i.e. bordered by a continental margin) could absorb up to 45% of the estimated sink of atmospheric CO_2 reported in other studies for the North Atlantic Ocean. Moreover, the fluxes computed by Frankignoulle and Borges (2001) are of the same order of magnitude as those reported in the East China Sea by Tsunogai et al. (1999) and off the New Jersey coast by Boehme et al. (1998). On the other hand, based on the same approach, numerous studies have shown that estuaries are a net source of CO_2 to the atmosphere (e.g. Frankignoulle et al. 1996a; Cai & Wang 1998; Cai et al. 1999, 2000; Raymond et al. 2000). This apparent contradiction is related to the different trophic status of distal continental shelves (net autotrophic) and proximal continental shelves that are strongly influenced by terrestrial and anthropogenic carbon inputs and are thus net heterotrophic (Smith & Mackenzie 1987; Gattuso et al. 1998 and references therein).

Frankignoulle et al. (1998) have recently shown that European estuaries could release 5 to 10% of the present anthropogenic CO_2 emission from Western Europe. Based on field data from nine European estuaries, these authors show that the efflux from inner estuaries converges to +62.1 mol m^{-2} $year^{-1}$, while the efflux from outer estuaries (or estuarine plumes) converges to +3.7 mol m^{-2} $year^{-1}$. The integration of these atmospheric flux data ultimately depends on the ratio of the surface area and the respective flux values of inner and outer estuaries. However, atmospheric CO_2 fluxes in estuarine plumes are poorly constrained because dissolved inorganic carbon in these coastal areas shows marked seasonal and spatial variation (e.g. Hoppema 1991; Borges & Frankignoulle 1999; Reimer et al. 1999).

Ketchum (1983) defines estuarine plumes as ‘plumes of freshened water which float on the more dense coastal sea water and they can be traced for many miles from the geographical mouth of the estuary’. However, the Scheldt estuarine plume does not show either haline or thermal stratification, whatever the season, due to the combination of the strong tidal currents and the shallowness of the area (Nihoul & Ronday 1975). Furthermore, according to Ruddik (1996), the thermal signal of the Scheldt estuarine plume is poorly marked due to rapid and strong atmospheric heat exchange. Thus, the offshore

limit of the Scheldt estuarine plume cannot be easily determined from marked density gradients as commonly used in other systems (e.g. Officer 1983). According to Mommaerts (1991), the average value of salinity at the Scheldt mouth (3.6° E, Figure 1) was 28 for the 1977-1990 period. On the other hand, the characteristic value of salinity for the offshore end-member, i.e. the Channel Water, is 35 (Lee 1970). Thus, in the present study, we used salinity as a tracer for the Scheldt estuarine plume and we chose a salinity of 34 as the offshore boundary. In a previous study, conducted between 1995 and 1996, we suggested that the Scheldt estuarine plume was a net source of atmospheric CO_2 (Borges & Frankignoulle 1999). The aim of the present paper is to verify this preliminary hypothesis based on a new set of data obtained during the BIOGEST (BIOGas transfer in ESTuaries) project and evaluate quantitatively the atmospheric CO_2 flux in both the Scheldt estuarine plume and the offshore waters of the Southern Bight of the North Sea.

Materials and methods

Data presented in this paper were obtained from June 1995 to September 1999, on board the *R. V. Belgica* during 24 cruises (cruise number: 95/17, 95/30, 96/18, 96/27, 96/30, 97/02, 97/06, 97/12, 97/14, 97/15, 97/17, 97/22, 97/23, 97/25, 97/27, 97/29, 98/08, 98/12, 98/26, 99/04, 99/05, 99/11, 99/17, 99/19). Underway and discrete sampling were carried out as previously described in Borges and Frankignoulle (1999). In brief, the partial pressure of CO_2 (pCO_2) was measured by the equilibration technique (for details refer to Frankignoulle et al. 2001) using a non-dispersive infrared gas analyser (Li-Cor®, LI-6262), calibrated daily using pure nitrogen (*Air Liquide Belgium*) and two gas mixtures with a CO_2 molar fraction of 351.0 ppm (*Air Liquide Belgium*) and 360.5 ppm (*National Oceanic and Atmospheric Administration*). Underway dissolved oxygen was measured using a galvanic electrode (Kent®) calibrated, every 6 hours, from discrete samples analysed with the Winkler method using a potentiometric end-point determination. Oxygen saturation level ($\%O_2$) is computed from the observed oxygen concentration and the concentration of O_2 at saturation calculated according to Benson and Krause (1984). The concentration of chlorophyll-a and phaeopigments were determined from GF/F filtered samples by the fluorimetric method (Arar & Collins 1997). Salinity and *in-situ* temperature were measured using a SeaBird® SBE 21 thermosalinograph.

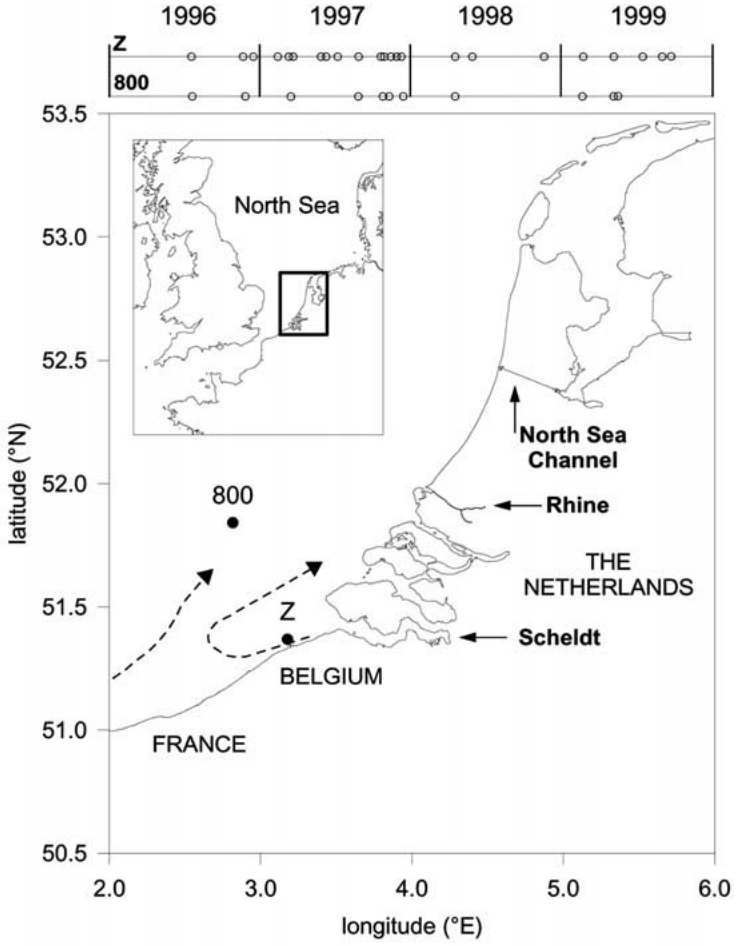

Figure 1. Map of the study site showing the locations of the Zeebrugge reference station (Z: 3.18° E 51.37° N) and the 800 reference station (2.87° E 51.84° N) and their sampling frequency. The pattern of residual currents is schematised by dotted arrows (based on Nihoul & Hecq 1984).

Results

Seasonal variability of pCO_2

Figure 1 shows the position of a coastal and an offshore reference station (Zeebrugge and 800, respectively) where pCO_2 data were obtained from July 1996 to September 1999. The Zeebrugge reference station is representative of the estuarine Scheldt plume with salinities below 33 while the 800 reference station is representative of offshore water (English Channel Water) with salin-

ities close to 35 (Figure 2(B)). Throughout the year significant over-saturation of CO_2 with respect to atmospheric equilibrium is observed at the Zeebrugge reference station (Figure 2(A)), except during the April and the May months that are characterised by a marked under-saturation of CO_2 related to the spring phytoplankton bloom as shown by the increase of chlorophyll-a concentration (Figure 2(F)) and oxygen saturation level (Figure 2(D)). At the 800 reference station, a marked decrease of pCO_2 values is also observed in relation to the spring phytoplankton bloom, although during the rest of the year pCO_2 values are relatively close to atmospheric equilibrium. Furthermore, the amplitude of the seasonal pCO_2 signal is higher at the Zeebrugge reference station ($\sim$570 μatm) than at the 800 reference station ($<$300 μatm).

Temperature affects the equilibrium constants of dissolved inorganic carbon and, in particular, the solubility coefficient of CO_2 so that pCO_2 rises of $\sim$4% when temperature increases of 1 °C. Figure 2(C) shows that in the sampled region water temperature has a strong seasonal signal and to filter the effect of temperature and focus on other potential factors affecting pCO_2, we computed pCO_2 values at an average temperature of 13 °C (Figure 2(E)). A constant decrease of pCO_2 (13 °C) is observed at the Zeebrugge reference station from mid-February to early May that could be related to primary production as suggested by the steady increase of $\%O_2$ and chlorophyll-a concentration values for the same period. There is a distinct increase of pCO_2 (13 °C) in June and July that would suggest a marked period of heterotrophy during this period as suggested by a noticeable decrease of $\%O_2$ values during the same period. Lastly, a steady increase of pCO_2 (13 °C) values is observed from early September to December that could be related to rising heterotrophy in the system and/or to enhanced inputs of inorganic carbon from the Scheldt (a more detailed discussion on the relative contribution of these processes is developed in section 'Provisional carbon budget in the Scheldt estuarine plume'). At the 800 reference station, pCO_2 (13 °C) values are relatively constant (except for the April–May period) suggesting that temperature variations are a major factor affecting pCO_2 seasonal variations except during the spring phytoplankton bloom.

Spatial variability of pCO_2

Figure 3 shows the distribution of pCO_2 off the Belgian coast from 5 cruises carried out during fall. The Scheldt estuarine plume during this season is systematically over-saturated in CO_2 (the offshore limit of the estuarine plume, i.e. the 34 isohaline, is shown in all maps as a dotted line). The range of variation of pCO_2 values are typically of $\sim$200 μatm and the overall distribution of pCO_2 follows the one of salinity (not shown) with pCO_2 decreasing offshoreward. However, the maximum of pCO_2 in the estuarine plume does

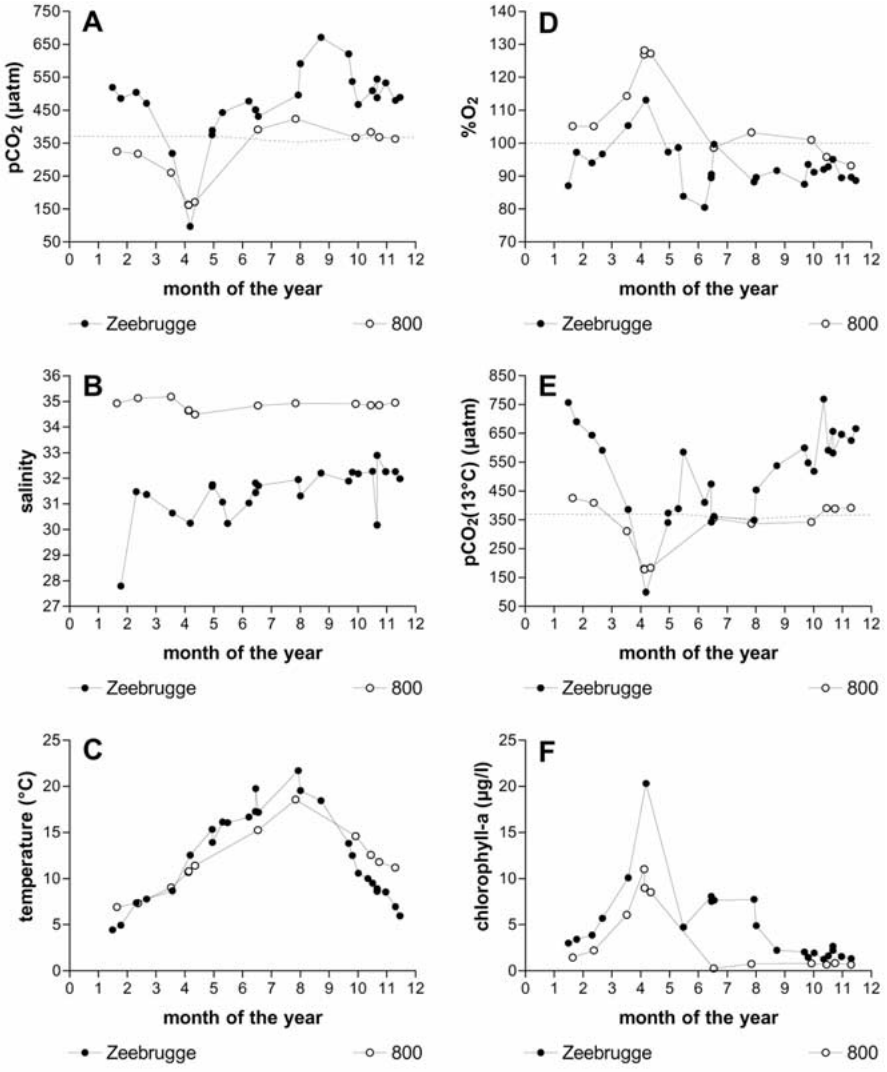

Figure 2. Composite seasonal evolution of pCO_2 (μatm), salinity, water temperature (°C), oxygen saturation level (%), chlorophyll-a concentration (μg l^{-1}) and pCO_2 normalized to a temperature of 13 °C, at the Zeebrugge and 800 reference stations, based on data from 22 cruises carried out from July 96 to September 99. The dotted horizontal line, in the pCO_2 plots, corresponds to atmospheric equilibrium based on the data from Weather Station Mike (NOAA/CMDL). In August, data at the same latitude but obtained 26 km west of the 800 station, were used.

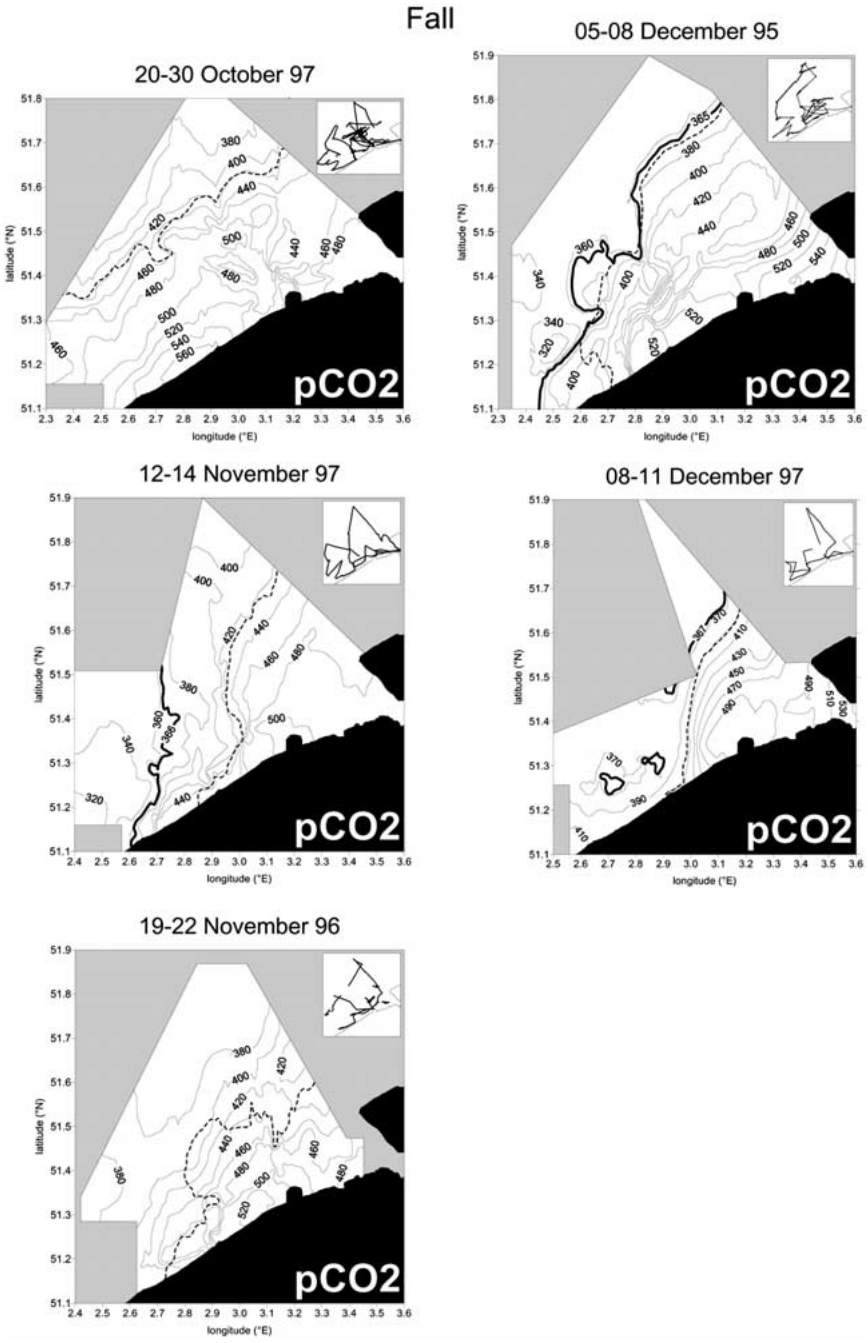

Figure 3. Spatial distribution of pCO_2 (μatm) off the Belgian coast in fall. The salinity 34 isopleth is represented by a dotted line. The bold isopleth corresponds to pCO_2 atmospheric equilibrium based on the data from Weather Station Mike (NOAA/CMDL).

not always coincide with the minimum of salinity (at the mouth of the Scheldt estuary) as would be expected if the input of over-saturated water from the Scheldt was the only process controlling the distribution of pCO_2. This is clear in the distribution of pCO_2 observed in October 97 and November 96. This cannot be explained by temperature variations (not shown) and interestingly the area where the maximum pCO_2 values are observed (between 2.7 and 3.2° E) corresponds to the area of the highest organic carbon content in the sediments off the Belgian coast (see Wollast 1976a). Possible explanations for this pattern in the pCO_2 distribution, such as the contribution from benthic respiration, based on a more detailed data analysis are developed in another publication (Borges & Frankignoulle in preparation). In October 97 and November 96, the outer-plume region (defined for salinities >34) is completely over-saturated in CO_2 while in November 97, December 95 and December 97 it is partly under-saturated in CO_2.

The distribution of pCO_2 observed during February follows the pattern described during fall (Figure 4). However, northernmost area of the sampled region shows higher chlorophyll-a values than during fall (not shown but typically <1 μg l^{-1}) and it seems to be related to the onset of the phytoplankton bloom as suggested by the $\%O_2$ values significantly above the saturation value ($\%O_2$ during fall typically $\leq 100\%$). In March, it is clear that the phytoplankton bloom controls the distributions of pCO_2 and $\%O_2$ in the outer-plume region. Strong under-saturation of CO_2 is observed close to the limit between the estuarine plume and outer-plume water. This area also shows higher chlorophyll-a concentrations. The chlorophyll-a concentrations in the estuarine plume are much lower and of the same order of magnitude as those observed during fall and early winter. This suggests that in March, the phytoplankton bloom is negligible in the estuarine plume compared to the outer-plume region.

During spring, the phytoplankton bloom controls the distribution of pCO_2 in both the estuarine plume and the outer-plume region (Figure 5). In April, under-saturation of CO_2 is observed throughout the sampled region except close to the mouth of the Scheldt estuary where pCO_2 values are slightly above saturation and $\%O_2$ values are below the saturation level. The lowest pCO_2 and highest $\%O_2$ values roughly coincide with the chlorophyll-a maximum and are observed as in March close to the limit between the estuarine plume and outer-plume region. During May, the under-saturation of CO_2 is very pronounced and generalised in the sampled region. The highest pCO_2 values are observed close to the coast and west of the Zeebrugge harbour, however they remain below atmospheric equilibrium. In this area, $\%O_2$ values are below the saturation level suggesting degradation of phytoplanktonic matter.

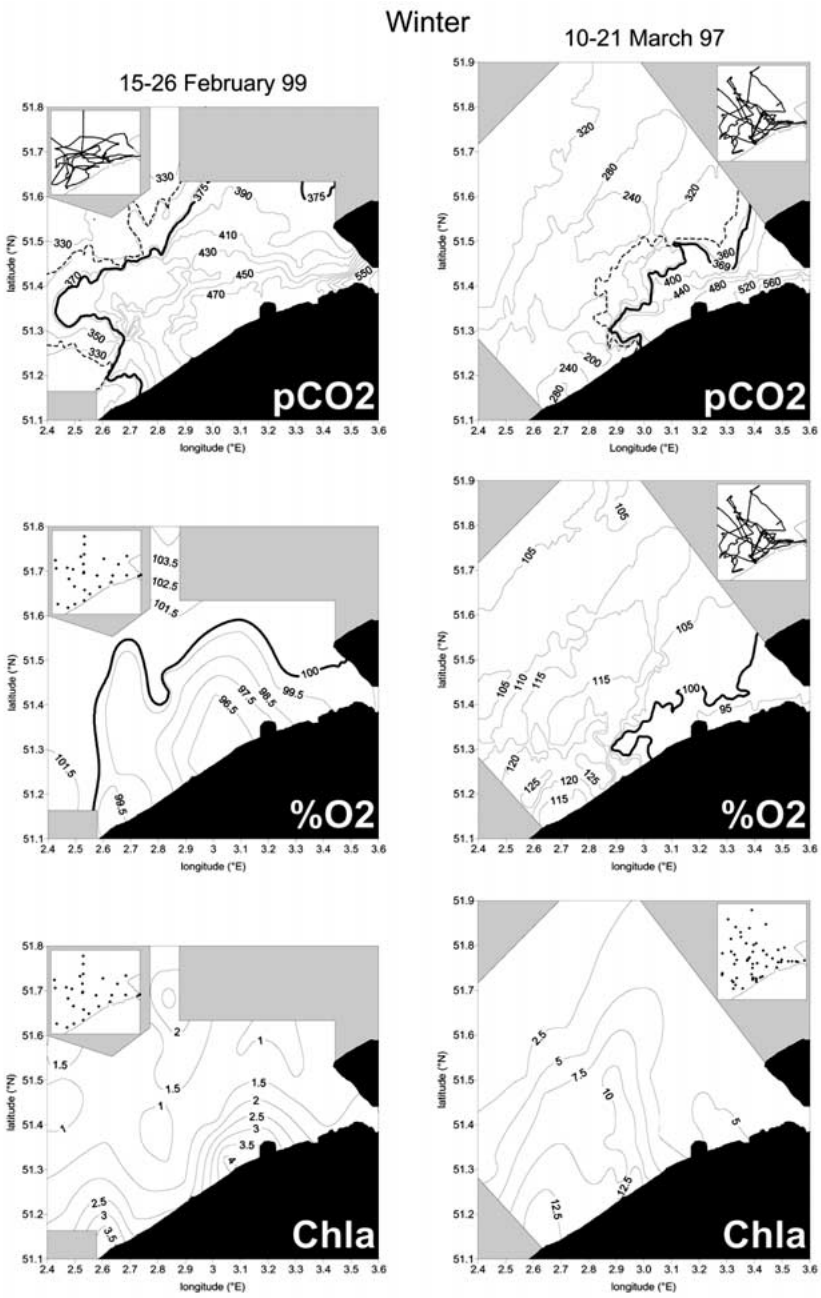

Figure 4. Spatial distribution of pCO_2 (μatm), oxygen saturation level (%) and chlorophyll-a concentration ($\mu g\, l^{-1}$) off the Belgian coast in winter. The salinity 34 isopleth is represented by a dotted line. The bold isopleth corresponds to pCO_2 atmospheric equilibrium based on the data from Weather Station Mike (NOAA/CMDL).

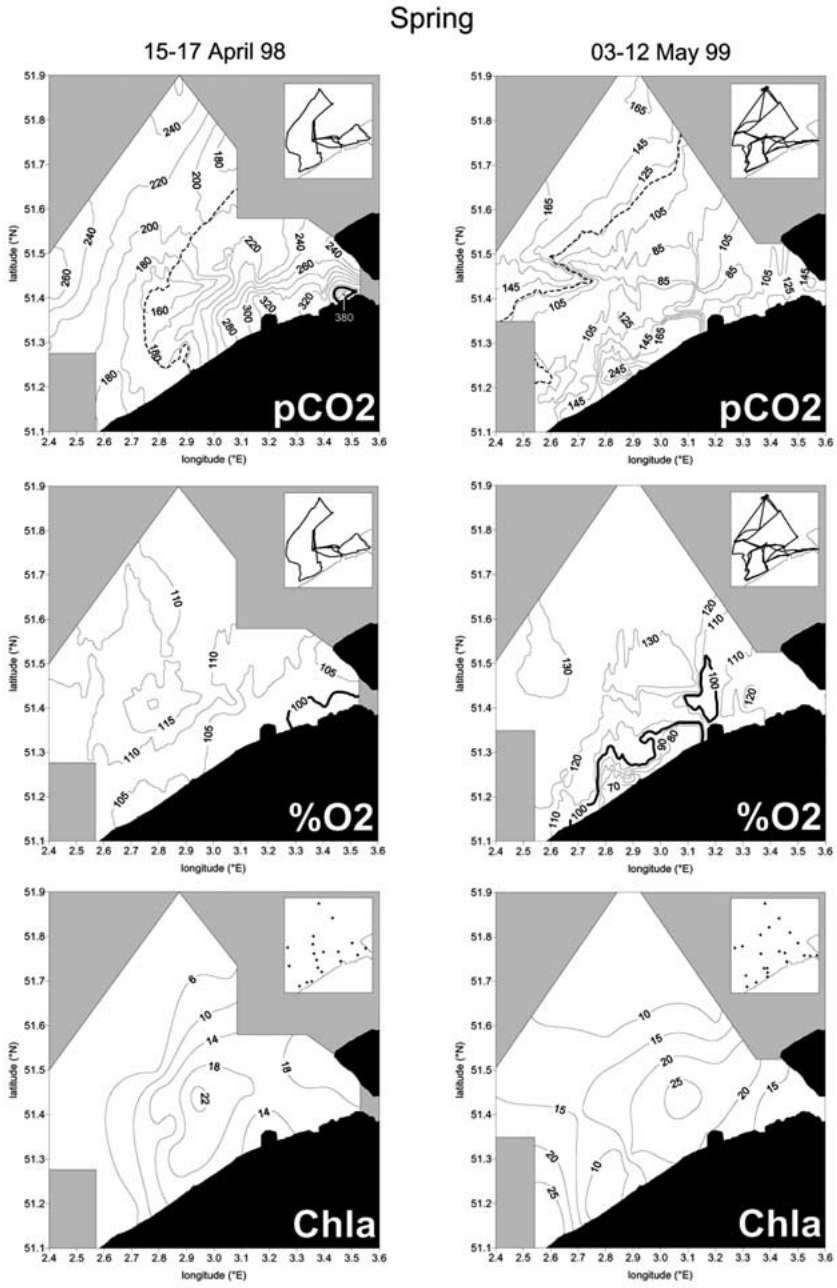

Figure 5. Spatial distribution of pCO_2 (μatm), oxygen saturation level (%) and chlorophyll-a concentration ($\mu g\, l^{-1}$) off the Belgian coast in spring. The salinity 34 isopleth is represented by a dotted line. The bold isopleth corresponds to pCO_2 atmospheric equilibrium based on the data from Weather Station Mike (NOAA/CMDL).

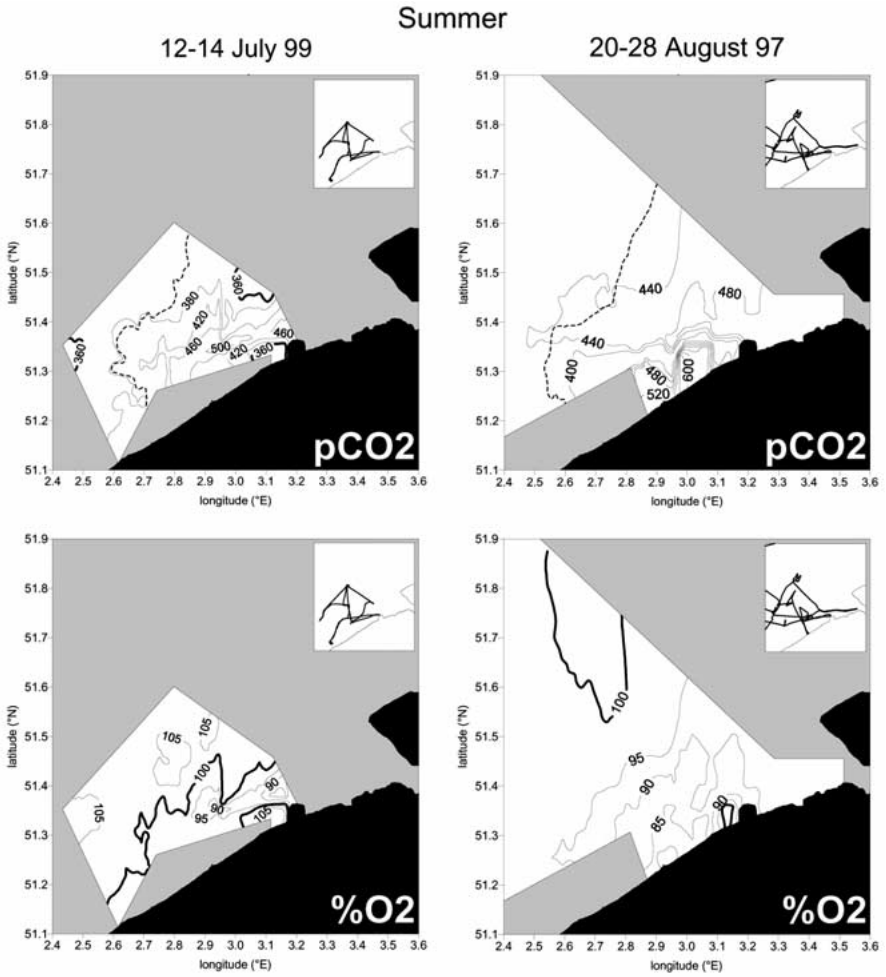

Figure 6. Spatial distribution of pCO_2 (μatm) and oxygen saturation level (%) off the Belgian coast in summer. The salinity 34 isopleth is represented by a dotted line. The bold isopleth corresponds to pCO_2 atmospheric equilibrium based on the data from Weather Station Mike (NOAA/CMDL).

For both summer cruises, the estuarine plume shows over-saturation of CO_2 related to degradation processes as shown by the distribution of $\%O_2$ (Figure 6). In August, it is clear that the maximum of pCO_2 is not located at the mouth of the Scheldt estuary but close to the coast and west of the Zeebrugge harbour.

Atmospheric CO_2 fluxes

Computation methods

One of the key issues of dissolved inorganic carbon dynamics is the flux of CO_2 across the air-water interface (F) that can be computed from the air-water gradient ($\Delta pCO_2 = pCO_{2water} - pCO_{2atmosphere}$) and the gas exchange coefficient (K) from equation:

$$F = \alpha.K.\Delta pCO_2$$

where α is the solubility coefficient of CO_2.

The air-water gradient of CO_2 dictates the direction of the flux and the magnitude of the flux is to a large extent imposed by the value of K that is function of various factors such as wind speed, air and water turbulence, waves, air bubbles, surface films, ... (e.g. Liss et al. 1997). However, wind speed is recognised as the main forcing factor on the K value and several algorithms have been proposed in literature. In our calculations, we applied the K-wind relationships proposed by Liss and Merlivat (1986), Wanninkhof (1992), Wanninkhof and McGillis (1999) and Nightingale et al. (2000a) that will be referred to as L&M, W, W&McG and N, respectively. We decided to use four formulations of the K-wind relationship to give a range of values for various reasons. Firstly, it is difficult to choose one relationship because there is no *consensus* in the relationships proposed in literature even in the light of experiments using the most recent tracer techniques (e.g. Wanninkhof & McGillis 1999; Nightingale et al. 2000a, b). Secondly, considering the strong non-linear characteristics of the K-wind relationships it is not possible to determine *a priori* the relative importance of the fluxes computed from one relationship in comparison to the fluxes computed from the other relationships. Thirdly, the fluxes reported in literature are usually computed using only one of the relationships mentioned above and thus, for a comparative purpose, it is useful to know the values calculated using the various available relationships. For the values of atmospheric pCO_2, we used the data from Weather Station Mike (66°00′ N 2°00′ E) from the NOAA/CMDL air samples network (available from the internet at http://www.cmdl.noaa.gov/). The atmospheric CO_2 molar ratio values were converted into pCO_2 values in wet air using the algorithms proposed in DOE (1994) and the flux data were computed using the Schmidt number formulation given by Wanninkhof (1992).

In the study area, pCO_2 values show intense seasonal variations but also important spatial heterogeneity. So, we attempted to budget air-water exchange using two approaches based the data from the reference stations

(Figure 2) and on the data from the area survey cruises (Figures 3 to 6). The first approach has the advantage of describing seasonal variations with a high resolution but does not take into account the spatial heterogeneity. The second approach could suffer from the lack of the temporal resolution, since only 9 months out of 12 were covered by the survey cruises. Both of these methods rely on the compilation of data obtained in different years and an important bias could be introduced in the computations from inter-annual variability.

Inter-annual variability of pCO_2

Borges and Frankignoulle (1999) compared data at the Zeebrugge reference station obtained in 1995 and 1996 and found a clear inter-annual variation. This variation was attributed to important differences in the fresh water discharge in winter. The re-analysis of these data shows that the difference in $p\mathrm{CO}_2$ for 95/96 during winter at the Zeebrugge reference station was between 10 to 20 μatm. In May, however, during the peak of the spring phytoplanktonic bloom, there is a significant inter-annual difference of about 170 μatm. The different river discharges in 95/96, induced important inter-annual differences in the salinity and temperature evolutions at the Zeebrugge reference station. However, Figures 2(B) and 2(C) show that the salinity and temperature evolutions for the 96/99 period are relatively consistent and we feel that in the data we report in the present paper, this inter-annual variability is relatively small. Firstly, most of the data points were obtained at the Zeebrugge reference station during one year: 54% of data points in 1997, 12% in 1996, 13% in 1998 and 21% in 1999 (see Figure 1). Secondly, when we compare data points relatively close in time from distinct years, the differences are much smaller than the seasonal signal of $\sim$570 μatm. Indeed, this difference is 34 μatm for late February 97/99, 13 μatm for late May 97/98, 20 μatm for mid July 96/99, 95 μatm for late August 97/99, 36 μatm for mid November 97/98, 45 μatm for late November 96/97 and 9 μatm for mid December 96/97.

Table 1 shows spatially integrated $p\mathrm{CO}_2$ values in the estuarine Scheldt plume, extracted from the area survey maps, for five months obtained in different years. This table shows that although the salinity in the estuarine plume is consistent from one year to another, $p\mathrm{CO}_2$ shows an inter-annual variability between 11 and 23 μatm except in May when the difference is 131 μatm. We estimate an inter-annual variability of $p\mathrm{CO}_2$ in the Scheldt estuarine plume of 20 μatm for all seasons except spring, a relatively small value compared to the seasonal signal.

Table 1. Comparison of spatially integrated pCO_2 (μatm) and salinity values in the Scheldt estuarine plume, for five months sampled in different years. The cruises with an asterisk are from Borges & Frankignoulle (1999)

	Salinity	pCO_2 (μatm)	pCO_2 difference (μatm)
February 96*	32.5	388	23
February 99	31.3	411	
March 96*	32.7	419	21
March 97	32.7	398	
May 96*	32.4	245	131
May 99	32.2	114	
November 96	33.5	463	11
November 97	32.8	473	
December 95	32.2	450	18
December 97	32.6	468	

Fixed station approach

Figure 7 shows the comparison of the pCO_2 values from the Zeebrugge reference station to the spatially integrated values for the estuarine plume extracted from the area survey maps (including the full salinity range up to 34 and for the same cruise). This shows that for $pCO_2 \geq 320$ μatm, the values at the Zeebrugge reference station are $\sim$50 μatm higher than the spatially averaged values but linearly correlated. We thus computed pCO_2 values that can be considered representative of the overall Scheldt estuarine plume by removing 50 μatm from the data of the Zeebrugge reference station for values $\geq$ 320 μatm.

The CO_2 air-water fluxes were then computed from daily averages of wind speed measured at the Zeebrugge harbour (not shown). The original data were obtained at 30 m above ground and were converted according to Smith (1985) to 10 m, the height of wind speed used in the various K formulations. The fluxes were computed from wind speed data-sets from 1996 to 1999, that cover the period of pCO_2 sampling and also allow us to assess the variability introduced by the choice of the wind speed data-set.

Using the fixed station approach, the estuarine Scheldt plume acts as net source of atmospheric CO_2 on an annual basis ranging from +1.10 to +1.89 mol m^{-2} $year^{-1}$ for the L&M and the W K-wind relationship, respectively (Table 2). The outer-plume acts as a sink of atmospheric CO_2 ranging from –0.33 to –0.58 mol m^{-2} $year^{-1}$ for the L&M and the W K-wind relationship,

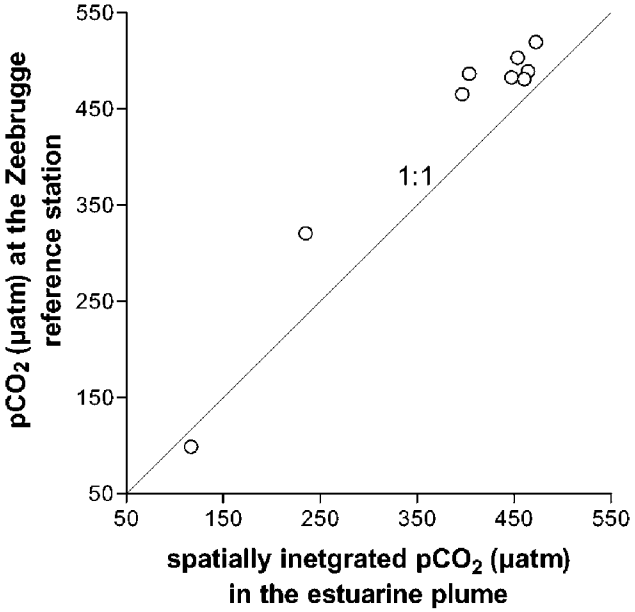

Figure 7. pCO_2 (μatm) at the Zeebrugge reference station *versus* spatially integrated pCO_2 values for the Scheldt estuarine plume, extracted from area survey maps.

respectively. The net annual fluxes are one order of magnitude lower than the extreme daily values computed. This is of course related to the important seasonal variability of the air-water gradient that ranges from –280 to +270 μatm at the Zeebrugge reference station and from –200 to +90 μatm at the 800 reference station. Lastly, the choice of year for the wind speed data-set introduces a relatively small difference in the results of the computations compared to difference due to the choice of the K-wind relationship, as illustrated by the relatively low standard error of the mean.

Survey area approach

The survey area approach is based on the computation of air-water CO_2 fluxes from interpolated fields of $\alpha.\Delta pCO_2$ and of water temperature that were separated into estuarine plume and outer-plume areas based on salinity. We assumed that the pCO_2 and temperature distributions remained unchanged during the duration of the cruise, meaning that the maps are considered synoptic. The wind speed field however was very variable for the duration of a cruise, typically 5 to 10 days. We can imagine, for instance, that when a CO_2 over-saturated region was sampled wind speed was very high and a few days later while sampling in a CO_2 under-saturated region wind speed was

Table 2. Annually integrated air-water CO_2 fluxes (mol m^{-2} $year^{-1}$) computed from the composite pCO_2 seasonal evolution at the Zeebrugge and at the 800 reference stations (Figure 2, see text for details) and the wind speed data obtained at the Zeebrugge harbour from 1996 to 1999. Numbers in brackets correspond to the maximum and minimum daily values computed during the annual cycle. L&M, W, W&McG and N stand for Liss & Merlivat (1986), Wanninkhof (1992), Wanninkhof & McGillis (1999) and Nightingale et al. (2000a), respectively

	L&M	W	W&McG	N
Zeebrugge reference station				
1996	1.00 (16.09; –20.06)	1.70 (27.11; –36.12)	1.06 (31.85; –39.07)	1.25 (20.01; –26.66)
1997	0.88 (15.33; –10.44)	1.65 (25.05; –15.84)	1.05 (22.79; –11.85)	1.22 (18.49; –11.69)
1998	1.34 (17.67; –11.59)	2.28 (30.66; –17.95)	1.62 (31.28; –14.30)	1.69 (22.63; –13.65)
1999	1.17 (11.65; –14.63)	1.95 (17.72; –23.72)	1.24 (13.51; –21.15)	1.44 (13.08; –17.51)
average	1.10	1.89	1.24	1.40
standard error	0.10	0.15	0.13	0.11
800 reference station				
1996	–0.31 (10.29; –14.11)	–0.55 (18.08; –25.44)	–0.33 (25.59; –27.51)	–0.41 (13.34; –18.78)
1997	–0.42 (2.68; –8.16)	–0.68 (3.94; –12.68)	–0.47 (2.60; –10.11)	–0.50 (2.91; –9.14)
1998	–0.29 (4.61; –9.05)	–0.52 (8.00; –14.03)	–0.31 (8.16; –11.18)	–0.38 (5.90; –10.36)
1999	–0.31 (2.74; –9.43)	–0.56 (4.17; –15.32)	–0.35 (3.19; –13.66)	–0.41 (3.08; –11.31)
average	–0.33	–0.58	–0.36	–0.43
standard error	0.03	0.04	0.03	0.03

much lower. If fluxes were calculated from immediate wind speed measurements an important bias could be introduced in the integration. On the other hand, if an average wind speed value for the cruise is used another bias is introduced in the integration because of the non-linear relationship between K and wind speed. Thus, we adopted a compromise solution by calculating the fluxes from a series of 3 hour averages of wind speed measured during the cruise and assuming that the sampled region is homogeneously submitted to that average wind. The fluxes are then spatially integrated. The final value of the flux for a cruise is the average of all of the spatially integrated values calculated from the series of 3 hour averages of wind speed.

Table 3 shows the air-water CO_2 fluxes computed for the estuarine plume and the outer-plume area, from 9 cruises covering the annual cycle. The annually integrated air-water CO_2 fluxes for the estuarine plume range from +1.08 to +2.81 mol m^{-2} $year^{-1}$ for the L&M and the W&McG K-wind relationships, respectively. These numbers are in very good agreement with those computed from the fixed station data approach based on the data from Zeebrugge reference station. The only apparent discrepancy is the CO_2 flux computed with the W&McG K-wind relationship that is significantly higher. This can be explained by very high efflux computed during the December 97 cruise that was characterized by 3hourly wind speed values ranging from 10.4 to 20.0 m s^{-1} with an average for the cruise of 14.7 m s^{-1}. The W&McG K-wind relationship is a cubic relationship that gives K values significantly higher than the other relationships for wind speeds $\geq$ 15 m s^{-1} but that for wind speeds $\leq$ 10 m s^{-1} lies between the L&M and the W K-wind relationships.

The fluxes computed for the outer-plume from the survey area approach range between –1.36 and –2.28 mol m^{-2} $year^{-1}$ for the L&M and the W K-wind relationship, respectively. They are significantly stronger than those computed from the fixed station approach using the data from 800 reference station. This is related to the fact that during the phytoplankton blooms (March, April and May) the CO_2 under-saturation in the outer-plume was more marked closer to the coast than at the 800 reference station (see Figures 4 and 5).

Provisional carbon budget in the Scheldt estuarine plume

The air-water CO_2 flux computations developed above show quantitatively that the Scheldt estuarine plume is annually a net source of atmospheric CO_2. In this section, we attempt to establish a carbon budget for the estuarine plume based in part on data from the literature to cross-check the flux computations and evaluate the major processes contributing to the CO_2 emission.

Table 3. Air-water CO_2 fluxes (mol m^{-2} $year^{-1}$) computed from interpolated plots of $\alpha.\Delta pCO_2$ and of temperature and the wind speed data measured during the cruise (see text for details) within the estuarine plume and in the outer-plume region. L&M, W, W&McG and N stand for Liss & Merlivat (1986), Wanninkhof (1992), Wanninkhof & McGillis (1999) and Nightingale et al. (2000a), respectively. The cruise with an asterisk is from Borges & Frankignoulle (1999)

	L&M	W	W&McG	N
Estuarine Plume (salinity <34)				
February 99	1.92	3.36	3.39	2.48
March 96	0.86	1.44	1.17	1.07
April 98	–6.39	–10.74	–9.92	–7.93
May 99	–11.18	–18.82	–17.67	–13.93
June 96*	–0.86	–1.37	–0.92	–1.01
August 97	2.21	3.64	2.41	2.69
October 97	7.02	12.17	13.96	8.98
November 97	1.52	2.64	1.29	1.95
December 97	10.68	19.23	27.64	14.20
Integrated	1.08	2.00	2.81	1.47
Outer-plume (salinity > 34)				
February 99	–1.67	–2.92	–2.94	–2.15
March 96	–2.17	–3.66	–2.96	–2.70
April 98	–7.52	–12.64	–11.67	–9.33
May 99	–9.54	–16.08	–15.10	–11.87
June 96*	–0.83	–1.33	–0.90	–0.98
August 97	1.47	2.43	1.61	1.79
October 97	2.08	3.60	4.14	2.66
November 97	0.17	0.30	0.14	0.22
December 97	1.25	2.25	3.23	1.66
Integrated	–1.36	–2.28	–2.01	–1.69

The first step is to estimate the net emission of CO_2 to the atmosphere that depends on the surface area of the estuarine plume. From the present data set and the one of Borges and Frankignoulle (1999), we estimated the surface area of the Scheldt estuarine plume. The easternmost 'boundary' of the estimation is the limit of the sampled region for all cruises, a line joining the mouth of Scheldt estuary (3.60° E 51.43° N) to the 800 station (2.87° E 51.84° N). The values are relatively variable (880–3800 km^2) since they depend on the combination of various factors such as the fresh water discharge, tidal and

residual currents and wind direction. Using an average value for the surface area of the estuarine plume of 2100 (±200) km^2, the fluxes from the fixed station approach (average value for the 1996–1999 wind speed data-sets) the net annual CO_2 emission is 2.3, 4.0, 2.6 and 2.9 10^9 mol of C per year (Gmol $year^{-1}$) for the K-wind relationships of L&M, W, W&McG and N, respectively.

These values of the net annual emission of CO_2 to the atmosphere represent between 17 to 29% of the net annual emission from the Scheldt inner estuary (13.9 Gmol $year^{-1}$) reported by Frankignoulle et al. (1998). The comparatively considerable net annual emission of CO_2 from the estuarine plume is unexpected since the net annual flux is much lower that the one of the inner estuary (63.1 mol m^{-2} $year^{-1}$, Frankignoulle et al. 1998). However, the estimated surface area of the estuarine plume (2100 km^2) is one order of magnitude higher than the one of the Scheldt inner estuary (220 km^2). The Scheldt estuarine plume is known to be deflected by the northwards residual current along the southern Dutch coast up to the mouth the river Rhine, so that the value of surface area of the estuarine plume we used is underestimated. For instance, Billen (1978) estimates the surface area of the region influenced by the terrestrial inputs of the Scheldt to 5300 km^2, so that our estimation of net annual emission of CO_2 from the estuarine plume would then increase by a factor of 2.5.

In Table 4, the fluxes of organic carbon available in the literature for the Belgian coast are summarized. We also estimated the flux of inorganic carbon from the Scheldt inner estuary to the estuarine plume. This calculation is based on the Apparent Zero End-member method (AZE, refer to Kaul & Froelich 1984) from inorganic carbon profiles from salinity 15 to 30 obtained during 19 cruises carried out in the Scheldt estuary from 1993 to 1999. This is not the flux of dissolved inorganic carbon (DIC) but the flux of the fraction of DIC that can be exchanged with the atmosphere (ΔDIC) and that can thus be compared to the air-water emission of CO_2. This fraction is calculated as the difference of observed DIC and the DIC value calculated if the sample was at equilibrium with the atmosphere. The ΔDIC profiles between salinities 15 and 30 were always linear (r^2 of 0.96 on average ranging between 0.85 and 0.99) and allowed us to compute by linear regression the value of ΔDIC at salinity 0 (ΔDIC_0). The transfer of ΔDIC from the Scheldt inner estuary to the estuarine plume (T) is then given by:

$$T = \Delta DIC_0 * Q$$

where Q is the flow of fresh water measured at Antwerp.

The flux value we calculated is probably underestimated due to the method used. Regnier and Steefel (1999) show that the flux of nitrogen from

Table 4. Budget of organic and inorganic carbon fluxes in the Scheldt estuarine plume. Organic carbon fluxes are compiled from the literature. The flux of inorganic carbon from the Scheldt inner estuary to the estuarine plume is calculated from the AZE method from 19 profiles in the Scheldt estuary from salinity 15 to 30, obtained from 1993 to 1999. The values of air-water exchange of CO_2 were computed with the K formulations, from left to right, of Liss and Merlivat (1986) and Wanninkhof (1992)

Inputs **(Gmol year^{-1})**		
Inorganic carbon from the Scheldt	1.0[a]	
Organic carbon from the Scheldt	0.5[b]–1.6[c]	
Organic carbon from the coast	1.4[c]	
Outputs **(Gmol year^{-1})**		
Preservation of organic carbon in sediments		1.9[c]
Air-sea exchange of CO_2		2.3–4.0[a]
Sum	2.9–4.0	4.2–5.9

[a]this work.
[b]Soetaert and Herman (1995).
[c]Wollast (1976b, 1983).

the Scheldt estuary to the North Sea could be strongly underestimated by the AZE method when compared to the flux calculated by these author's CONTRASTE model. To estimate inorganic carbon output from the Scheldt with this model, high temporal resolution and continuous data sets at both river and sea end-members are needed (Regnier et al. 1998). Such data sets are unfortunately not available so that our estimate from the AZE method is the only one possible at the present time. Keeping this in mind, Table 4 shows that the input of inorganic carbon from the Scheldt can only account for 25 to 44% of the net annual emission of CO_2 from the estuarine plume to the atmosphere. We can assume that the remaining fraction comes from the degradation within the estuarine plume itself of organic carbon originating from the Scheldt inner estuary and from the Belgian coast.

The net carbon output based on the CO_2 emission calculated from the K formulation of L&M is in good agreement with the net carbon input based on the organic carbon flux from Wollast (1976b, 1983). However, this net carbon output corresponds to 145% of the net carbon input based on the organic carbon flux from Soetaert and Herman (1995). These authors used an ecological model to estimate organic carbon consumption in the inner estuary and then derived the flux from the Scheldt to the North Sea. The flux proposed by Wollast (1976b, 1983) is based on organic carbon load data in the Scheldt from an intensive study of the Scheldt and Belgian coast during the late 1970s.

Using a 13 cruises data set of dissolved organic carbon (DOC) obtained from April 1997 to April 1998 by the NIOO in the Scheldt estuary (Jack Middelburg, personal communication), we estimated using the AZE method the flux of DOC from the Scheldt towards the North Sea to 1.3 Gmol year^{-1}. This flux could be underestimated as mentioned above but tends to support the higher organic carbon flux of Wollast (1976b, 1983). However, the net carbon output based on the CO_2 emission calculated from the K formulation of W correspond to 150% of the net input based on the organic carbon fluxes from Wollast (1976b, 1983). It should also be noted that only a fraction of the organic carbon brought into the estuarine plume from the Scheldt and from the coast is labile. For DOC, only 40% is labile according to Servais et al. (1987). An additional source of organic carbon should then be envisaged.

Discussion

The main problem associated with the two approaches we used to estimate and budget air-water CO_2 fluxes in the Scheldt estuarine plume is related to inter-annual variability of pCO_2. However, based on the comparison of data points from the Zeebrugge reference station and from area survey cruises from different years, we estimate inter-annual variability of pCO_2 to $\sim$20 μatm, except during the spring bloom conditions. The strong inter-annual variability of pCO_2 observed in spring ($\sim$100 μatm) could probably be related to the one of primary production as described for instance for the 1993-94-95 period by Lancelot et al. (1998). Moreover, this does not change the fact that the Scheldt estuarine plume is a net source of atmospheric CO_2. Indeed, the pCO_2 data from May 1999 used in the flux computations are the lowest ever reported in the area (see Frankignoulle et al. 1996b, c, 1998; Borges & Frankignoulle 1999) and for instance the higher pCO_2 values observed in spring of 1996 (Table 1) would increase our estimates of net annual CO_2 emission to the atmosphere. The net CO_2 efflux we computed for the Scheldt estuarine plume is in fair agreement with a simple budget based on organic carbon flux data reported in the literature. The fact that the input of dissolved inorganic carbon from the Scheldt inner estuary can only explain $<$50% of the emission of CO_2 by the estuarine plume strongly suggests that the rest of the emission is due to heterotrophic processes within the plume itself. This would in turn imply that on an annual basis the plume is net heterotrophic. This is consistent with the frequent observation, during all seasons (spring excepted) of a maximum of pCO_2 in the estuarine plume that did not correspond with the salinity minimum at the mouth of the Scheldt.

However, the net carbon output based on the flux computed with W K-wind relationship exceeds the net carbon input. Although this could be related

to the cumulated errors on the different estimates, it could also suggest an additional carbon input that was not accounted for. The sediments off the Belgian coast are known to accumulate important quantities of organic carbon as shown by Wollast (1976a). It is then probable that during the movements of the estuarine plume, organic carbon from the outer-plume waters accumulates in the sediments along the Belgian coast. It is also probable that at other moments, these sediments are covered by the estuarine plume and that the respiration of organic carbon increases the CO_2 content of the estuarine plume. For instance, the phytoplankton bloom of March 1997 in the outer-plume (Figure 4) developed in an area that was later in the year covered by the estuarine plume (plot of October 97 in Figure 3). The surface area covered by the March 97 phytoplankton bloom corresponded to $\sim$1500 km^2 and, if we assume that the primary production rate was 1 gC m^{-2} day^{-1} and that the bloom lasted 30 days, then 37.5 Gmol of carbon were produced. The complete degradation of this carbon pool during the rest of the year would produce a flux of 4.1 Gmol year^{-1}. It is not possible to estimate what fraction of this degradation could occur in the sediments and how much time these sediments were covered by the estuarine plume. However, this simple calculation shows that a fraction of the CO_2 emitted by the estuarine plume could come from the degradation of sedimented organic carbon originating from the outer plume.

All published dissolved inorganic carbon data in inner estuaries worldwide (Park et al. 1969; Kempe 1982; Frankignoulle et al. 1996a, 1998; Cai & Wang 1999; Cai et al. 1998, 2000; Semiletov 1999; Raymond et al. 2000; Sarma et al. 2001) show that these systems are a net source of CO_2 to the atmosphere due to their net heterotrophic status (Heip et al 1995; Gattuso et al 1998). However, the air-water CO_2 fluxes in estuarine plumes are poorly constrained due intense temporal and spatial variability. Data have been reported in various systems such as the plume of the Ganges, the Mahanadi, the Godavari and the Krishna (Kumar et al. 1996), of the Congo (Bakker et al. 1999), of the Yangtze and the Yellow river (Chen & Wang 1999; Tsunogai et al. 1999), of the Lena river (Semiletov 1999) and of the Amazon (Ternon et al. 2000). However, the most comprehensive studies from the point of view of both spatial and temporal coverage have been reported for the plume of the Rhine (Hoppema 1991) and the plume of the Elbe/Weser (Brasse et al. 1999, 2002; Reimer et al. 1999). Among the latter, air-water CO_2 fluxes were only computed by Reimer et al. (1999) using the W K-wind relationship and from their data we can estimate an annually integrated value of –4.6 mol m^{-2} year^{-1}. From the salinity distributions reported in Brasse et al. (1999, 2002) and Reimer et al. (1999), we estimate that the surface area of the plume of the Elbe/Weser (defined by salinities $<$34) to be $<$400 km^2. The net influx of

atmospheric CO_2 in the plume is then <–1.8 Gmol year^{-1} that is an order of magnitude lower than the net CO_2 efflux from the Elbe inner estuary (+17.3 Gmol year^{-1}) reported by Frankignoulle et al. (1998). Thus, although some estuarine plumes could be a net sink of CO_2 the overall estuarine system (inner and outer estuary) seems to be a net source of CO_2.

The air-water CO_2 fluxes computed from the 800 reference station and from the survey area approach show that the outer-plume is a net sink of CO_2. This confirms the hypothesis of Frankignoulle and Borges (2001) that the Southern Bight of the North Sea is a net sink, based on a series of transects that allow a detailed description of the spatial variability in the area although lacking in temporal resolution to give a meaningful annual integration. However, the two approaches we used in the present paper give air-water fluxes that differ by an order of magnitude due to stronger spring-time CO_2 under-saturation closer to the coast than at 800 reference station. A more extensive study of the Southern Bight of the North Sea is then needed before the air-water fluxes can be integrated in this area.

Conclusions

The data set reported in the present paper allowed us to confirm the conclusions concerning the dynamics of pCO_2 off the Belgian coast from an earlier work (Borges & Frankignoulle 1999): the distribution of pCO_2 in the Scheldt estuarine plume is dominated most of the year by heterotrophic processes occurring both in the inner estuary and in the estuarine plume itself that induce over-saturation of CO_2. Only during spring, under-saturation of CO_2 is observed related to important primary production. The net annual emission from the Scheldt estuarine plume represents an additional 17 to 29% of the annual net emission of CO_2 from the Scheldt inner estuary reported by Frankignoulle et al. (1998) in spite of the fact that the net fluxes of CO_2 in the estuarine plume are much lower than the one in the inner estuary. This unexpected result can be explained by the fact that the surface area of the estuarine plume is one order of magnitude higher that the one of the inner estuary. This shows that estuarine plumes constitute an aspect of the estuarine dynamics of organic and inorganic carbon that should not be neglected.

A budget of organic and inorganic carbon for the Scheldt estuarine plume was attempted from fluxes available in the literature. One interesting aspect is that the input of dissolved inorganic carbon from the Scheldt inner estuary can only account for 25 to 44% of the net annual emission of CO_2 from the estuarine plume, showing that the remaining fraction comes from heterotrophic processes within the plume itself.

The area off the Belgian coast outside the Scheldt plume was found to be a net sink of atmospheric CO_2. For the moment it is not possible to quantify the air-water CO_2 fluxes in the Southern Bight of the North Sea because of strong spatial heterogeneity in the pCO_2 distributions. However, this region seems to act as a sink for atmospheric CO_2 based on the fluxes computed from direct measurements of the air-water CO_2 gradient reported by Frankignoulle and Borges (2001) and based on an indirect carbon budgeting approach reported by Wollast (1998).

Thus, the present data confirm that the proximal continental shelf areas act as a net source of CO_2 due to their net heterotrophic status while distal continental shelf areas act a net sink due to their net autotrophic status. More high spatial and temporal resolution dissolved inorganic carbon data are then needed in the various shelf ecosystems to establish annual budgets of air-water CO_2 exchange, before a global integration can be achieved and the status of the overall continental shelf as a source or a sink of atmospheric CO_2 can be resolved.

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