



## 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<sub>2</sub> ( $p\text{CO}_2$ ) 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  $p\text{CO}_2$  in the study area. The dynamics of  $p\text{CO}_2$  are described using two approaches: fixed reference stations and area survey cruises. The air-water fluxes of CO<sub>2</sub> 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<sub>2</sub>. The annually integrated air-water fluxes for the Scheldt estuarine plume range between +1.1 and +1.9 mol m<sup>-2</sup> year<sup>-1</sup> as a function of the formulation of the exchange coefficient of CO<sub>2</sub>. The annual net emission of CO<sub>2</sub> from the estuarine plume to the atmosphere is estimated to be between +2.3 to +4.0 Gmol year<sup>-1</sup> 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<sub>2</sub> 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<sub>2</sub>. However, the net exchange of CO<sub>2</sub> 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<sub>2</sub> across the air-water interface can be estimated from the measurements of the air-water gradient of CO<sub>2</sub> 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 *p*CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sup>-2</sup> year<sup>-1</sup>, while the efflux from outer estuaries (or estuarine plumes) converges to +3.7 mol m<sup>-2</sup> year<sup>-1</sup>. 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<sub>2</sub> 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<sub>2</sub> (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<sub>2</sub> 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<sub>2</sub> ( $p\text{CO}_2$ ) was measured by the equilibration technique (for details refer to Frankignoulle et al. 2001) using a non-dispersive infrared gas analyser (Li-Cor<sup>®</sup>, LI-6262), calibrated daily using pure nitrogen (*Air Liquide Belgium*) and two gas mixtures with a CO<sub>2</sub> 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<sup>®</sup>) calibrated, every 6 hours, from discrete samples analysed with the Winkler method using a potentiometric end-point determination. Oxygen saturation level (%O<sub>2</sub>) is computed from the observed oxygen concentration and the concentration of O<sub>2</sub> 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<sup>®</sup> SBE 21 thermosalinograph.

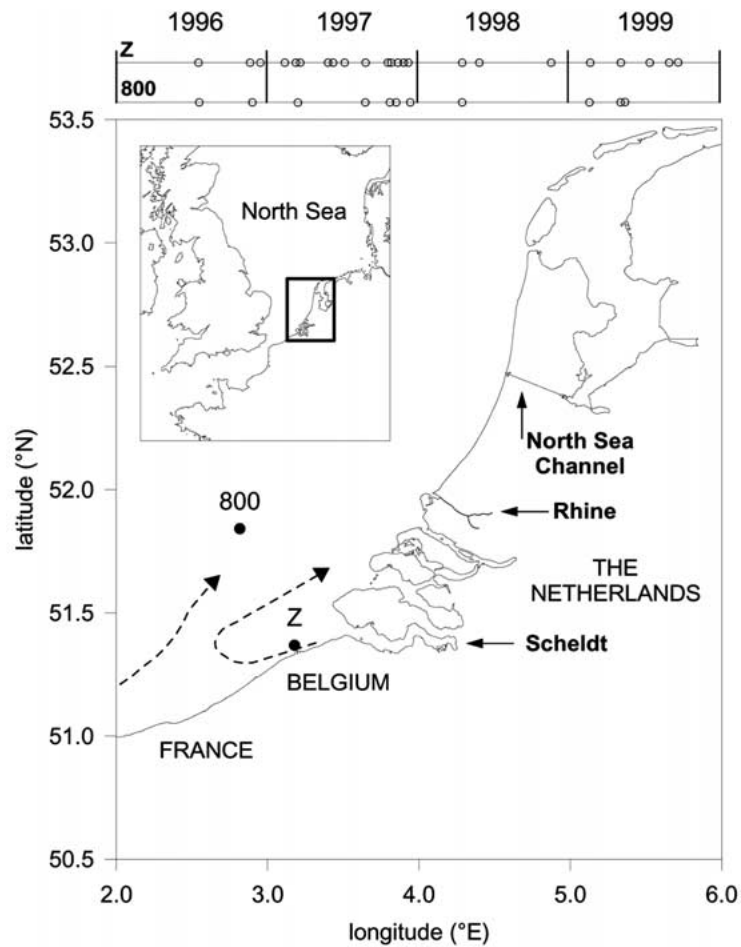


Figure 1. Map of the study site showing the locations of the Zeebrugge reference station (Z: 3.18° E 51.37° N) and the 800 reference station (2.87° E 51.84° N) and their sampling frequency. The pattern of residual currents is schematised by dotted arrows (based on Nihoul & Hecq 1984).

## Results

### *Seasonal variability of $p\text{CO}_2$*

Figure 1 shows the position of a coastal and an offshore reference station (Zeebrugge and 800, respectively) where  $p\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  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  $p\text{CO}_2$  values is also observed in relation to the spring phytoplankton bloom, although during the rest of the year  $p\text{CO}_2$  values are relatively close to atmospheric equilibrium. Furthermore, the amplitude of the seasonal  $p\text{CO}_2$  signal is higher at the Zeebrugge reference station ( $\sim 570 \mu\text{atm}$ ) than at the 800 reference station ( $< 300 \mu\text{atm}$ ).

Temperature affects the equilibrium constants of dissolved inorganic carbon and, in particular, the solubility coefficient of  $\text{CO}_2$  so that  $p\text{CO}_2$  rises of  $\sim 4\%$  when temperature increases of  $1^\circ\text{C}$ . 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  $p\text{CO}_2$ , we computed  $p\text{CO}_2$  values at an average temperature of  $13^\circ\text{C}$  (Figure 2(E)). A constant decrease of  $p\text{CO}_2$  ( $13^\circ\text{C}$ ) 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  $\%\text{O}_2$  and chlorophyll-a concentration values for the same period. There is a distinct increase of  $p\text{CO}_2$  ( $13^\circ\text{C}$ ) in June and July that would suggest a marked period of heterotrophy during this period as suggested by a noticeable decrease of  $\%\text{O}_2$  values during the same period. Lastly, a steady increase of  $p\text{CO}_2$  ( $13^\circ\text{C}$ ) 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,  $p\text{CO}_2$  ( $13^\circ\text{C}$ ) values are relatively constant (except for the April–May period) suggesting that temperature variations are a major factor affecting  $p\text{CO}_2$  seasonal variations except during the spring phytoplankton bloom.

#### *Spatial variability of $p\text{CO}_2$*

Figure 3 shows the distribution of  $p\text{CO}_2$  off the Belgian coast from 5 cruises carried out during fall. The Scheldt estuarine plume during this season is systematically over-saturated in  $\text{CO}_2$  (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  $p\text{CO}_2$  values are typically of  $\sim 200 \mu\text{atm}$  and the overall distribution of  $p\text{CO}_2$  follows the one of salinity (not shown) with  $p\text{CO}_2$  decreasing offshoreward. However, the maximum of  $p\text{CO}_2$  in the estuarine plume does

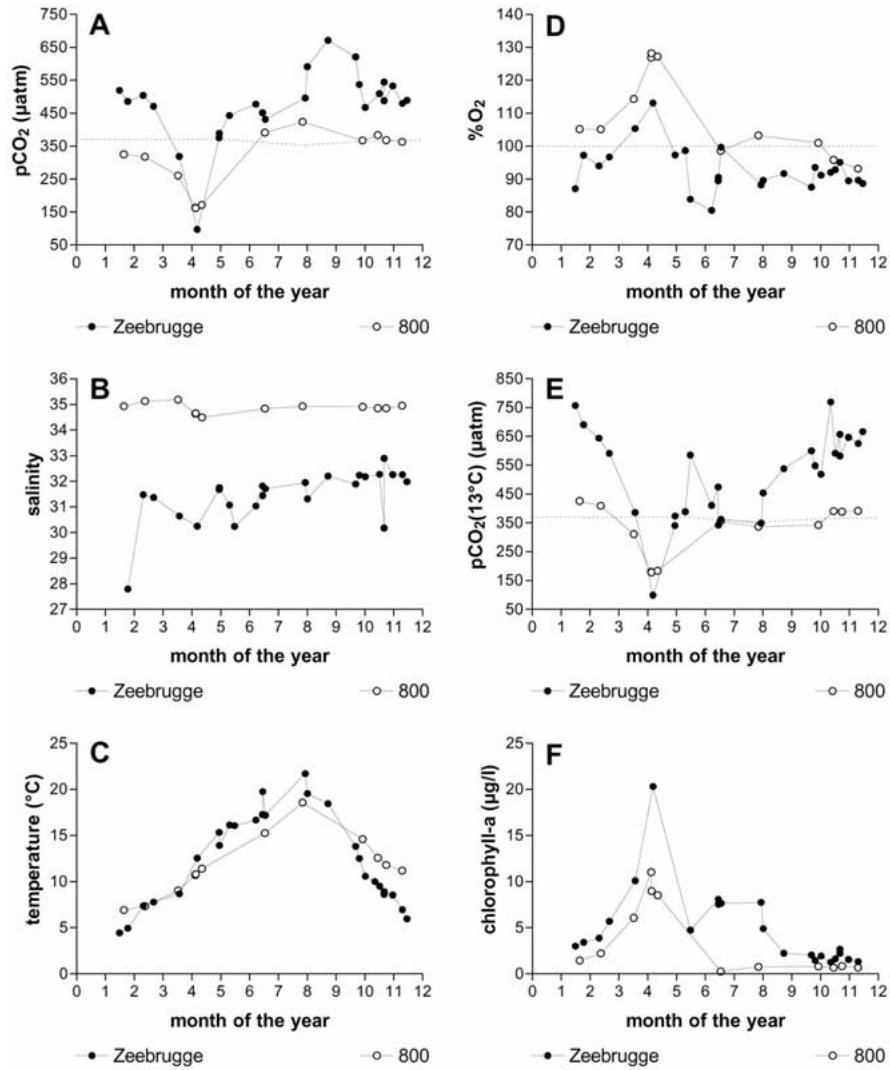


Figure 2. Composite seasonal evolution of  $p\text{CO}_2$  ( $\mu\text{atm}$ ), salinity, water temperature ( $^{\circ}\text{C}$ ), oxygen saturation level (%), chlorophyll-a concentration ( $\mu\text{g l}^{-1}$ ) and  $p\text{CO}_2$  normalized to a temperature of  $13^{\circ}\text{C}$ , at the Zeebrugge and 800 reference stations, based on data from 22 cruises carried out from July 96 to September 99. The dotted horizontal line, in the  $p\text{CO}_2$  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.

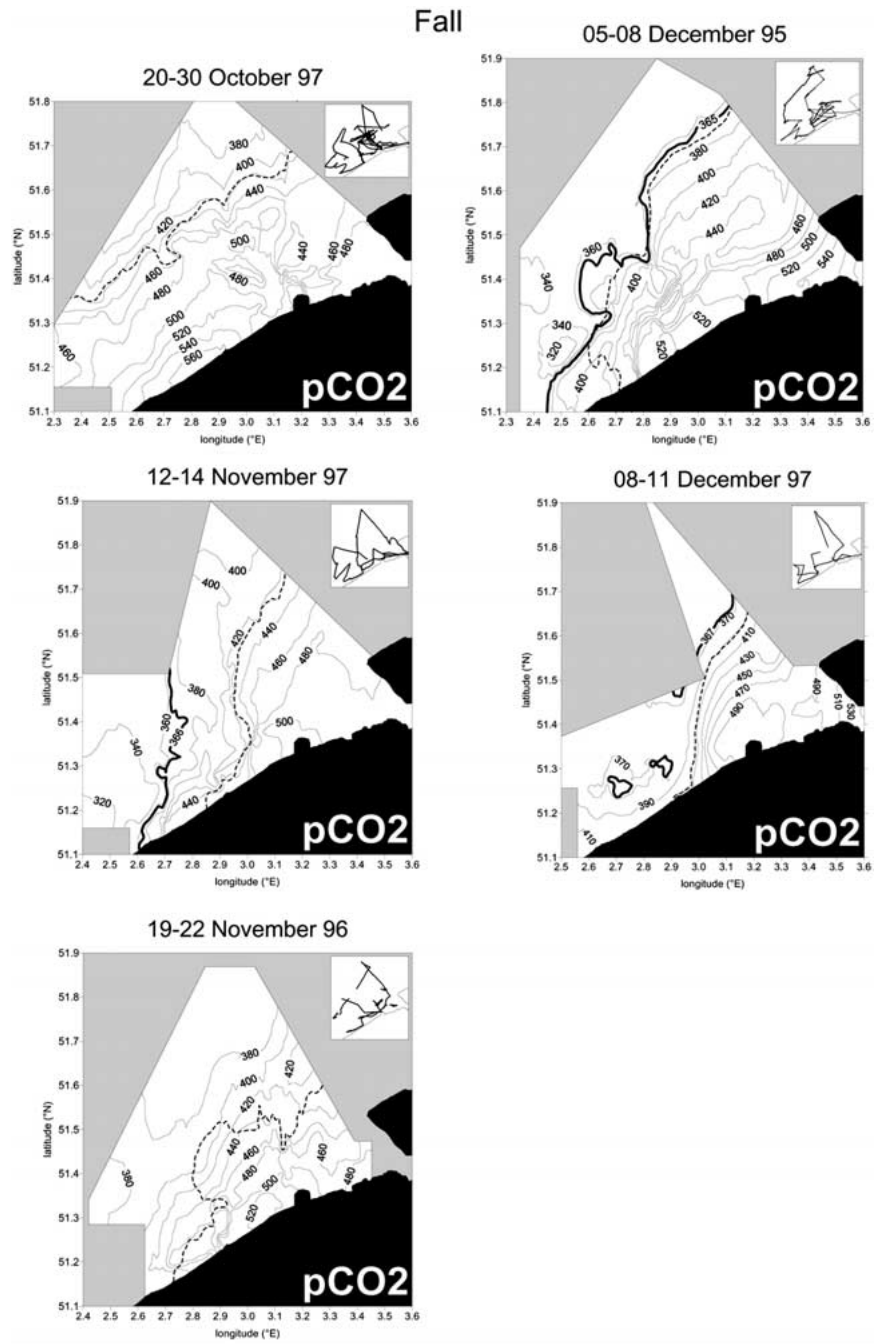


Figure 3. Spatial distribution of  $p\text{CO}_2$  ( $\mu\text{atm}$ ) off the Belgian coast in fall. The salinity 34 isopleth is represented by a dotted line. The bold isopleth corresponds to  $p\text{CO}_2$  atmospheric equilibrium based on the data from Weather Station Mike (NOAA/CMDL).

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  $p\text{CO}_2$ . This is clear in the distribution of  $p\text{CO}_2$  observed in October 97 and November 96. This cannot be explained by temperature variations (not shown) and interestingly the area where the maximum  $p\text{CO}_2$  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  $p\text{CO}_2$  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  $\text{CO}_2$  while in November 97, December 95 and December 97 it is partly under-saturated in  $\text{CO}_2$ .

The distribution of  $p\text{CO}_2$  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  $<1 \mu\text{g l}^{-1}$ ) and it seems to be related to the onset of the phytoplankton bloom as suggested by the  $\%\text{O}_2$  values significantly above the saturation value ( $\%\text{O}_2$  during fall typically  $\leq 100\%$ ). In March, it is clear that the phytoplankton bloom controls the distributions of  $p\text{CO}_2$  and  $\%\text{O}_2$  in the outer-plume region. Strong under-saturation of  $\text{CO}_2$  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  $p\text{CO}_2$  in both the estuarine plume and the outer-plume region (Figure 5). In April, under-saturation of  $\text{CO}_2$  is observed throughout the sampled region except close to the mouth of the Scheldt estuary where  $p\text{CO}_2$  values are slightly above saturation and  $\%\text{O}_2$  values are below the saturation level. The lowest  $p\text{CO}_2$  and highest  $\%\text{O}_2$  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  $\text{CO}_2$  is very pronounced and generalised in the sampled region. The highest  $p\text{CO}_2$  values are observed close to the coast and west of the Zeebrugge harbour, however they remain below atmospheric equilibrium. In this area,  $\%\text{O}_2$  values are below the saturation level suggesting degradation of phytoplanktonic matter.

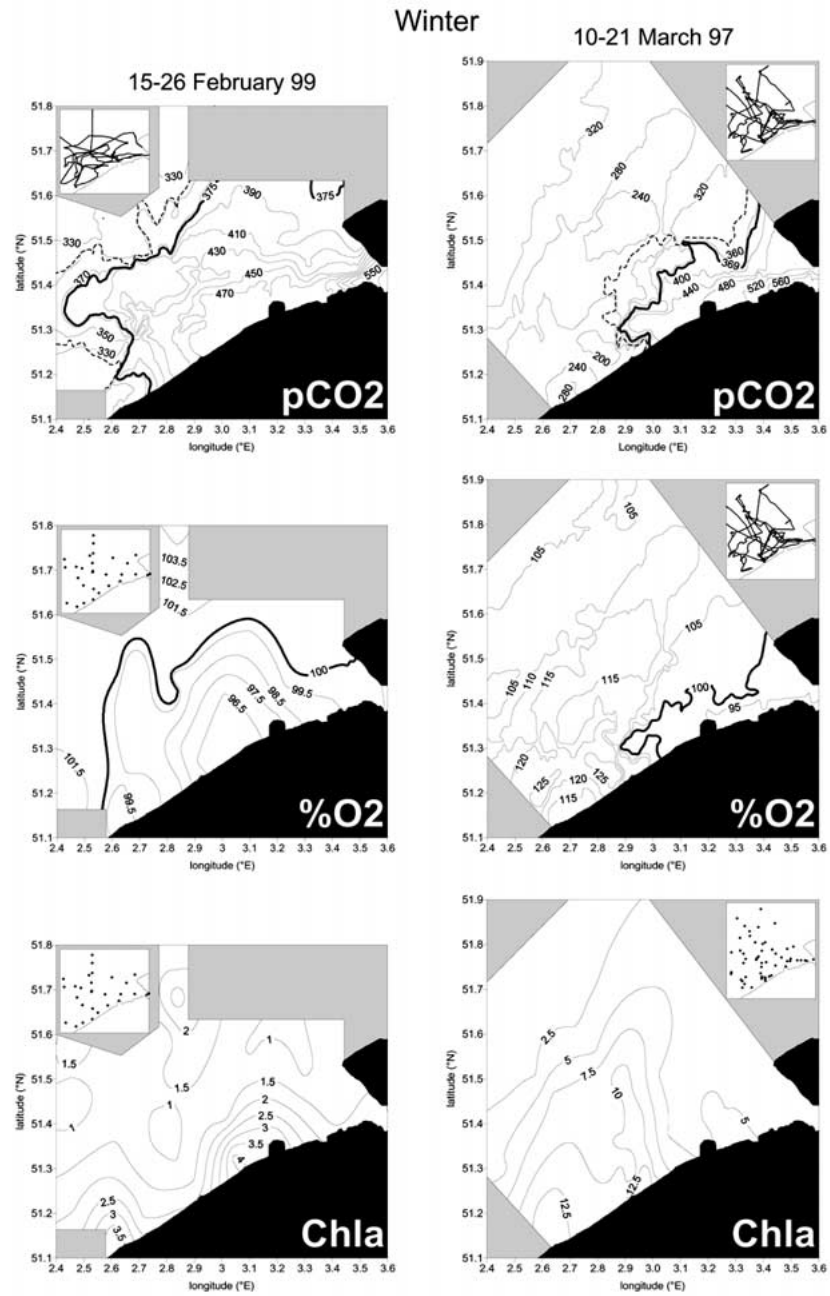


Figure 4. Spatial distribution of  $p\text{CO}_2$  ( $\mu\text{atm}$ ), oxygen saturation level (%) and chlorophyll-a concentration ( $\mu\text{g l}^{-1}$ ) off the Belgian coast in winter. The salinity 34 isopleth is represented by a dotted line. The bold isopleth corresponds to  $p\text{CO}_2$  atmospheric equilibrium based on the data from Weather Station Mike (NOAA/CMDL).

## Spring

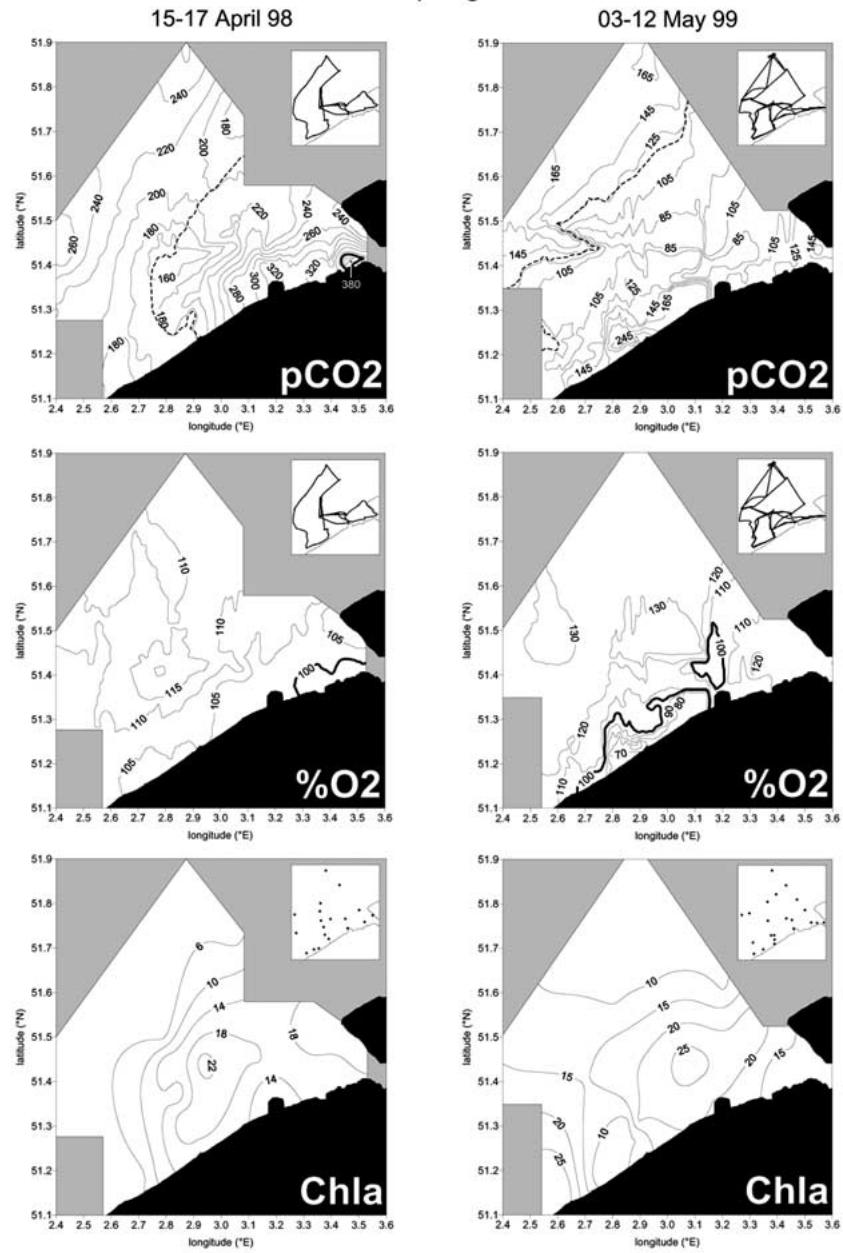


Figure 5. Spatial distribution of  $p\text{CO}_2$  ( $\mu\text{atm}$ ), oxygen saturation level (%) and chlorophyll-a concentration ( $\mu\text{g l}^{-1}$ ) off the Belgian coast in spring. The salinity 34 isopleth is represented by a dotted line. The bold isopleth corresponds to  $p\text{CO}_2$  atmospheric equilibrium based on the data from Weather Station Mike (NOAA/CMDL).

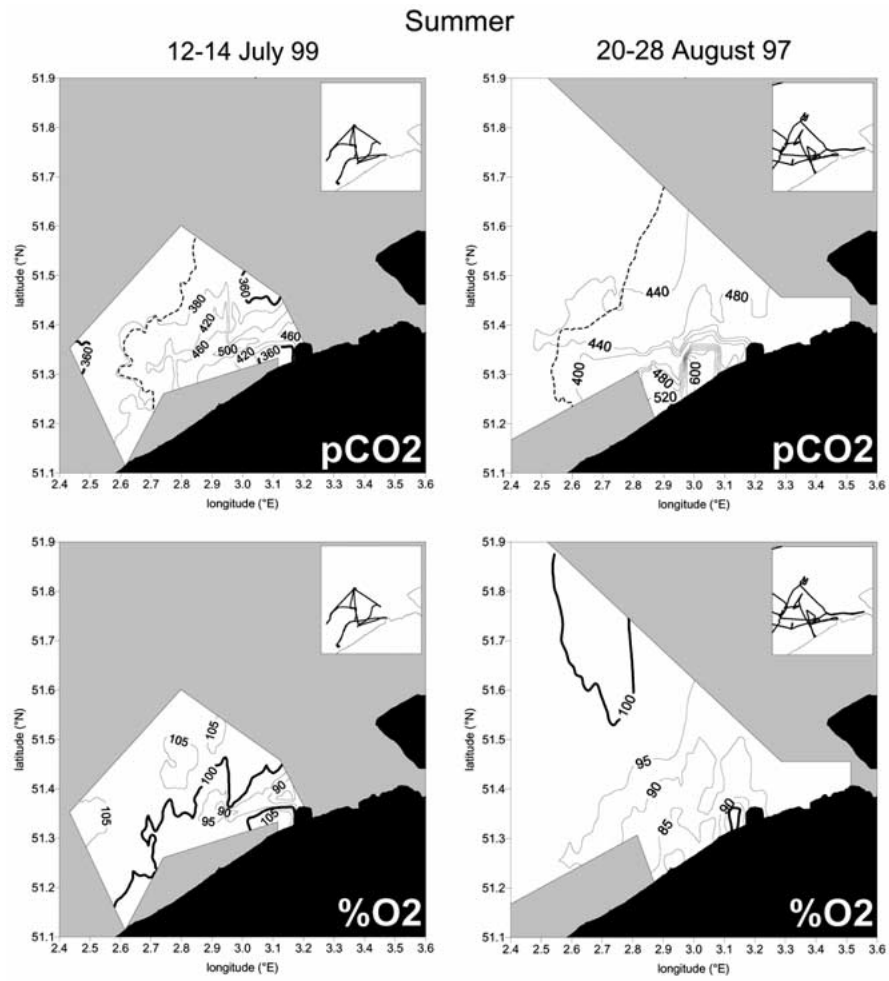


Figure 6. Spatial distribution of  $p\text{CO}_2$  ( $\mu\text{atm}$ ) and oxygen saturation level (%) off the Belgian coast in summer. The salinity 34 isopleth is represented by a dotted line. The bold isopleth corresponds to  $p\text{CO}_2$  atmospheric equilibrium based on the data from Weather Station Mike (NOAA/CMDL).

For both summer cruises, the estuarine plume shows over-saturation of  $\text{CO}_2$  related to degradation processes as shown by the distribution of  $\%\text{O}_2$  (Figure 6). In August, it is clear that the maximum of  $p\text{CO}_2$  is not located at the mouth of the Scheldt estuary but close to the coast and west of the Zeebrugge harbour.

## Atmospheric CO<sub>2</sub> fluxes

### *Computation methods*

One of the key issues of dissolved inorganic carbon dynamics is the flux of CO<sub>2</sub> across the air-water interface (F) that can be computed from the air-water gradient ( $\Delta p\text{CO}_2 = p\text{CO}_{2\text{water}} - p\text{CO}_{2\text{atmosphere}}$ ) and the gas exchange coefficient (K) from equation:

$$F = \alpha \cdot K \cdot \Delta p\text{CO}_2$$

where  $\alpha$  is the solubility coefficient of CO<sub>2</sub>.

The air-water gradient of CO<sub>2</sub> 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  $p\text{CO}_2$ , 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<sub>2</sub> molar ratio values were converted into  $p\text{CO}_2$  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,  $p\text{CO}_2$  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 $p\text{CO}_2$*

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  $p\text{CO}_2$  for 95/96 during winter at the Zeebrugge reference station was between 10 to 20  $\mu\text{atm}$ . In May, however, during the peak of the spring phytoplanktonic bloom, there is a significant inter-annual difference of about 170  $\mu\text{atm}$ . 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  $\sim 570$   $\mu\text{atm}$ . Indeed, this difference is 34  $\mu\text{atm}$  for late February 97/99, 13  $\mu\text{atm}$  for late May 97/98, 20  $\mu\text{atm}$  for mid July 96/99, 95  $\mu\text{atm}$  for late August 97/99, 36  $\mu\text{atm}$  for mid November 97/98, 45  $\mu\text{atm}$  for late November 96/97 and 9  $\mu\text{atm}$  for mid December 96/97.

Table 1 shows spatially integrated  $p\text{CO}_2$  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,  $p\text{CO}_2$  shows an inter-annual variability between 11 and 23  $\mu\text{atm}$  except in May when the difference is 131  $\mu\text{atm}$ . We estimate an inter-annual variability of  $p\text{CO}_2$  in the Scheldt estuarine plume of 20  $\mu\text{atm}$  for all seasons except spring, a relatively small value compared to the seasonal signal.

*Table 1.* Comparison of spatially integrated  $p\text{CO}_2$  ( $\mu\text{atm}$ ) 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 | $p\text{CO}_2$<br>( $\mu\text{atm}$ ) | $p\text{CO}_2$ difference<br>( $\mu\text{atm}$ ) |
|--------------|----------|---------------------------------------|--------------------------------------------------|
| 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  $p\text{CO}_2$  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  $p\text{CO}_2 \geq 320 \mu\text{atm}$ , the values at the Zeebrugge reference station are  $\sim 50 \mu\text{atm}$  higher than the spatially averaged values but linearly correlated. We thus computed  $p\text{CO}_2$  values that can be considered representative of the overall Scheldt estuarine plume by removing  $50 \mu\text{atm}$  from the data of the Zeebrugge reference station for values  $\geq 320 \mu\text{atm}$ .

The  $\text{CO}_2$  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  $p\text{CO}_2$  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  $\text{CO}_2$  on an annual basis ranging from  $+1.10$  to  $+1.89 \text{ mol m}^{-2} \text{ year}^{-1}$  for the L&M and the W K-wind relationship, respectively (Table 2). The outer-plume acts as a sink of atmospheric  $\text{CO}_2$  ranging from  $-0.33$  to  $-0.58 \text{ mol m}^{-2} \text{ year}^{-1}$  for the L&M and the W K-wind relationship,

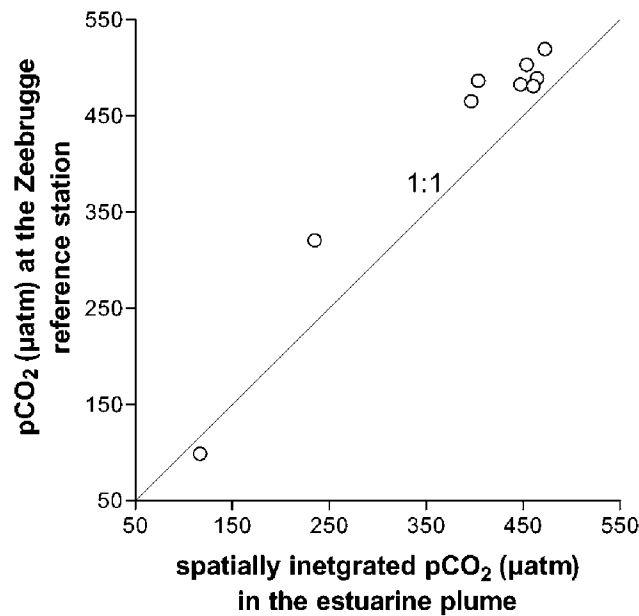


Figure 7.  $p\text{CO}_2$  ( $\mu\text{atm}$ ) at the Zeebrugge reference station versus spatially integrated  $p\text{CO}_2$  values for the Scheldt estuarine plume, extracted from area survey maps.

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  $+270$   $\mu\text{atm}$  at the Zeebrugge reference station and from  $-200$  to  $+90$   $\mu\text{atm}$  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  $\text{CO}_2$  fluxes from interpolated fields of  $\alpha \cdot \Delta p\text{CO}_2$  and of water temperature that were separated into estuarine plume and outer-plume areas based on salinity. We assumed that the  $p\text{CO}_2$  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  $\text{CO}_2$  over-saturated region was sampled wind speed was very high and a few days later while sampling in a  $\text{CO}_2$  under-saturated region wind speed was

Table 2. Annually integrated air-water CO<sub>2</sub> fluxes (mol m<sup>-2</sup> year<sup>-1</sup>) computed from the composite *p*CO<sub>2</sub> 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                     |
|------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| <b>Zeebrugge reference station</b> |                       |                       |                       |                       |
| 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)  |
| <b>average</b>                     | 1.10                  | 1.89                  | 1.24                  | 1.40                  |
| standard error                     | 0.10                  | 0.15                  | 0.13                  | 0.11                  |
| <b>800 reference station</b>       |                       |                       |                       |                       |
| 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)  |
| <b>average</b>                     | -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  $\text{CO}_2$  fluxes computed for the estuarine plume and the outer-plume area, from 9 cruises covering the annual cycle. The annually integrated air-water  $\text{CO}_2$  fluxes for the estuarine plume range from  $+1.08$  to  $+2.81 \text{ mol m}^{-2} \text{ year}^{-1}$  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  $\text{CO}_2$  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  $20.0 \text{ m s}^{-1}$  with an average for the cruise of  $14.7 \text{ m s}^{-1}$ . The W&McG K-wind relationship is a cubic relationship that gives  $K$  values significantly higher than the other relationships for wind speeds  $\geq 15 \text{ m s}^{-1}$  but that for wind speeds  $\leq 10 \text{ m s}^{-1}$  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  $-2.28 \text{ mol m}^{-2} \text{ year}^{-1}$  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  $\text{CO}_2$  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  $\text{CO}_2$  flux computations developed above show quantitatively that the Scheldt estuarine plume is annually a net source of atmospheric  $\text{CO}_2$ . 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  $\text{CO}_2$  emission.

Table 3. Air-water CO<sub>2</sub> fluxes (mol m<sup>-2</sup> year<sup>-1</sup>) computed from interpolated plots of  $\alpha \cdot \Delta p\text{CO}_2$  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      |
|------------------------------------------|--------|--------|--------|--------|
| <b>Estuarine Plume (salinity &lt;34)</b> |        |        |        |        |
| 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  |
| <b>Integrated</b>                        | 1.08   | 2.00   | 2.81   | 1.47   |
| <b>Outer-plume (salinity &gt; 34)</b>    |        |        |        |        |
| 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   |
| <b>Integrated</b>                        | -1.36  | -2.28  | -2.01  | -1.69  |

The first step is to estimate the net emission of CO<sub>2</sub> 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<sup>2</sup>) 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 ( $\pm 200$ ) km<sup>2</sup>, the fluxes from the fixed station approach (average value for the 1996–1999 wind speed data-sets) the net annual CO<sub>2</sub> emission is 2.3, 4.0, 2.6 and 2.9 10<sup>9</sup> mol of C per year (Gmol year<sup>-1</sup>) for the K-wind relationships of L&M, W, W&McG and N, respectively.

These values of the net annual emission of CO<sub>2</sub> to the atmosphere represent between 17 to 29% of the net annual emission from the Scheldt inner estuary (13.9 Gmol year<sup>-1</sup>) reported by Frankignoulle et al. (1998). The comparatively considerable net annual emission of CO<sub>2</sub> from the estuarine plume is unexpected since the net annual flux is much lower than the one of the inner estuary (63.1 mol m<sup>-2</sup> year<sup>-1</sup>, Frankignoulle et al. 1998). However, the estimated surface area of the estuarine plume (2100 km<sup>2</sup>) is one order of magnitude higher than the one of the Scheldt inner estuary (220 km<sup>2</sup>). The Scheldt estuarine plume is known to be deflected by the northwards residual current along the southern Dutch coast up to the mouth of 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<sup>2</sup>, so that our estimation of net annual emission of CO<sub>2</sub> 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 ( $\Delta$ DIC) and that can thus be compared to the air-water emission of CO<sub>2</sub>. 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  $\Delta$ DIC 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  $\Delta$ DIC at salinity 0 ( $\Delta$ DIC<sub>0</sub>). The transfer of  $\Delta$ DIC from the Scheldt inner estuary to the estuarine plume (T) is then given by:

$$T = \Delta \text{DIC}_0 * Q$$

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<sub>2</sub> were computed with the K formulations, from left to right, of Liss and Merlivat (1986) and Wanninkhof (1992)

|                                             |                                    |                      |
|---------------------------------------------|------------------------------------|----------------------|
| <b>Inputs (Gmol year<sup>-1</sup>)</b>      |                                    |                      |
| Inorganic carbon from the Scheldt           | 1.0 <sup>a</sup>                   |                      |
| Organic carbon from the Scheldt             | 0.5 <sup>b</sup> –1.6 <sup>c</sup> |                      |
| Organic carbon from the coast               | 1.4 <sup>c</sup>                   |                      |
| <b>Outputs (Gmol year<sup>-1</sup>)</b>     |                                    |                      |
| Preservation of organic carbon in sediments |                                    | 1.9 <sup>c</sup>     |
| Air-sea exchange of CO <sub>2</sub>         |                                    | 2.3–4.0 <sup>a</sup> |
| <b>Sum</b>                                  | 2.9–4.0                            | 4.2–5.9              |

<sup>a</sup>this work.

<sup>b</sup>Soetaert and Herman (1995).

<sup>c</sup>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<sub>2</sub> 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<sub>2</sub> 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  $1.3 \text{ Gmol year}^{-1}$ . 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  $\text{CO}_2$  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  $\text{CO}_2$  fluxes in the Scheldt estuarine plume is related to inter-annual variability of  $p\text{CO}_2$ . 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  $p\text{CO}_2$  to  $\sim 20 \mu\text{atm}$ , except during the spring bloom conditions. The strong inter-annual variability of  $p\text{CO}_2$  observed in spring ( $\sim 100 \mu\text{atm}$ ) 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  $\text{CO}_2$ . Indeed, the  $p\text{CO}_2$  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  $p\text{CO}_2$  values observed in spring of 1996 (Table 1) would increase our estimates of net annual  $\text{CO}_2$  emission to the atmosphere. The net  $\text{CO}_2$  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  $\text{CO}_2$  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  $p\text{CO}_2$  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<sub>2</sub> 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  $\sim 1500 \text{ km}^2$  and, if we assume that the primary production rate was  $1 \text{ gC m}^{-2} \text{ day}^{-1}$  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  $4.1 \text{ Gmol year}^{-1}$ . 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<sub>2</sub> 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<sub>2</sub> to the atmosphere due to their net heterotrophic status (Heip et al 1995; Gattuso et al 1998). However, the air-water CO<sub>2</sub> 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<sub>2</sub> 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  $-4.6 \text{ mol m}^{-2} \text{ year}^{-1}$ . 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  $<400 \text{ km}^2$ . The net influx of

atmospheric CO<sub>2</sub> in the plume is then  $<-1.8 \text{ Gmol year}^{-1}$  that is an order of magnitude lower than the net CO<sub>2</sub> efflux from the Elbe inner estuary ( $+17.3 \text{ Gmol year}^{-1}$ ) reported by Frankignoulle et al. (1998). Thus, although some estuarine plumes could be a net sink of CO<sub>2</sub> the overall estuarine system (inner and outer estuary) seems to be a net source of CO<sub>2</sub>.

The air-water CO<sub>2</sub> fluxes computed from the 800 reference station and from the survey area approach show that the outer-plume is a net sink of CO<sub>2</sub>. 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<sub>2</sub> 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  $p\text{CO}_2$  off the Belgian coast from an earlier work (Borges & Frankignoulle 1999): the distribution of  $p\text{CO}_2$  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<sub>2</sub>. Only during spring, under-saturation of CO<sub>2</sub> 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<sub>2</sub> from the Scheldt inner estuary reported by Frankignoulle et al. (1998) in spite of the fact that the net fluxes of CO<sub>2</sub> 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 than 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<sub>2</sub> 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<sub>2</sub>. For the moment it is not possible to quantify the air-water CO<sub>2</sub> fluxes in the Southern Bight of the North Sea because of strong spatial heterogeneity in the *p*CO<sub>2</sub> distributions. However, this region seems to act as a sink for atmospheric CO<sub>2</sub> based on the fluxes computed from direct measurements of the air-water CO<sub>2</sub> 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<sub>2</sub> due to their net heterotrophic status while distal continental shelf areas act as 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<sub>2</sub> 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<sub>2</sub> can be resolved.

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## References

- Arar EJ & Collins GB (1997) *In Vitro* Determination of Chlorophyll a and Pheophytin a in Marine and Freshwater Phytoplankton by Fluorescence. In: Methods for the determination of chemical substances in marine and estuarine environmental matrices (445.01-445.22). U.S. Environmental Protection Agency, Cincinnati
- Bakker DCE, de Baar HJW & de Jong E (1999) The dependence on temperature and salinity of dissolved inorganic carbon in East Atlantic surface waters. *Mar. Chem.* 65: 263–280
- Benson BB & Krause D (1984) The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere. *Limnol. Oceanogr.* 29: 620–632
- Billen G (1978) A budget of Nitrogen Recycling in the North Sea sediments off the Belgian coast. *Estuarine Coastal Shelf Sci.* 7: 127–146
- Boehme SE, Sabine CL & Reimers CE (1998) CO<sub>2</sub> fluxes from a coastal transect: a time series approach. *Mar. Chem.* 63: 49–67
- Borges AV & Frankignoulle M (1999) Daily and seasonal variations of the partial pressure of CO<sub>2</sub> in surface seawater along the Belgian and southern Dutch coastal areas. *J. Mar. Systems* 19: 251–266
- Brasse S, Reimer A, Seifert R & Michaelis W (1999) The influence of intertidal mudflats on the dissolved inorganic carbon and total alkalinity in the German Bight, southeastern North Sea. *J. Sea Res.* 42: 93–103
- Brasse S, Nellen M, Seifert R & Michaelis W (2002) The carbon dioxide system in the Elbe estuary. *Biogeochem.* 59: 25–40
- Cai W-J & Wang Y (1998) The chemistry, fluxes, and source of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnol. Oceanogr.* 43: 647–668
- Cai W-J, Pomeroy LR, Moran MA & Wang Y (1999) Oxygen and carbon dioxide mass balance for estuarine-intertidal marsh complex of five rivers in the southeastern U.S. *Limnol. Oceanogr.* 44: 639–649
- Cai W-J, Wiebe WJ, Wang Y & Sheldom JE (2000) Intertidal marsh as a source of dissolved inorganic carbon and a sink of nitrate in the Satilla River-estuarine complex in the southeastern U.S. *Limnol. Oceanogr.* 45: 1743–1752
- Chen T-A & Wang S-L (1999) Carbon, alkalinity and nutrient budgets on the East China Sea continental shelf. *Geophys. Res.* 104(C9): 20675–20686
- DOE (1994) Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water. In: Dickson AG & Goyet C (Eds) ORNL/CDIAC-74
- Frankignoulle M, Bourge I & Wollast (1996a) Atmospheric CO<sub>2</sub> fluxes in a highly polluted estuary (the Scheldt). *Limnol. Oceanogr.* 41: 365–369
- Frankignoulle M, Elskens M, Biondo R, Bourge I, Canon C, Desgain S & Dauby P (1996b) Distribution of inorganic carbon and related parameters in surface seawater of the English Channel during Spring 1994. *J. Mar. Syst.* 7: 427–434
- Frankignoulle M, Bourge I, Canon C & Dauby P (1996c) Distribution of surface seawater partial CO<sub>2</sub> pressure in the English Channel and in the Southern Bight of the North Sea. *Continental Shelf Res.* 16: 381–395
- 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: 434–436
- Frankignoulle M, Borges A & Biondo R (2001) A new design of equilibrator to monitor carbon dioxide in highly dynamic and turbid environments. *Water Res.* 35(5): 1344–1347
- Frankignoulle M & Borges AV (2001) European continental shelf as a significant sink for atmospheric CO<sub>2</sub>. *Global Biogeochem. Cycles* 15(3): 569–576

- Gattuso J-P, Frankignoulle M & Wollast R (1998) Carbon and carbonate metabolism in coastal aquatic ecosystems. *Annu. Rev. Ecol. Syst.* 29: 405–433
- Heip CHR, Goosen NK, Herman PMJ, Kromkamp J, Middelburg JJ & Soetaert K (1995) Production and consumption of biological particles in temperate tidal estuaries. *Oceanogr. Mar. Biol. Ann. Rev.* 33: 1–149
- Hoppema MJ (1991) The seasonal behaviour of carbon dioxide and oxygen in the coastal North Sea along the Netherlands. *Neth. J. Sea Res.* 28: 167–179
- Kaul L & Froelich P (1984) Modelling estuarine nutrient biogeochemistry in a simple system. *Geochim. Cosmochim. Acta* 48: 1417–1433
- Kempe S (1982) Valdivia cruise, October 1981: carbonate equilibria in the estuaries of Elbe, Weser, Ems and in the Southern German Bight. *Mitt. Geol.-Paläont. Inst. Univ. Hambourg, SCOPE/UNEP Sonderband* 52: 719–742
- Ketchum RH (1983) Estuarine characteristics In: Ketchum BH (Ed) *Ecosystems of the World*, Vol. 26 (pp 1–14). Elsevier
- Kumar MD, Naqvi SWA, George MD & Jayakumar DA (1996) A sink for atmospheric carbon dioxide in the northeast Indian Ocean. *J. Geophys. Res.* 101(C8): 18121–18125
- Lancelot C, Keller MD, Rousseau V, Smith Jr. WO & Mathot S (1998) Autecology of the Marine Haptophyte *Phaeocystis* sp. In: Anderson DM, Cembella AD & Hallegraeff GM (Eds) *Physiological Ecology of Harmful Algal Blooms*, NATO ASI Series, G41, 209–224
- Lee A (1970) The currents and water masses of the North Sea, *Oceanogr. Mar. Biol. Ann.* 8: 33–71
- Liss PS & Merlivat L (1986) Air-sea exchange rates: introduction and synthesis In: Buat-Ménard P (Ed) *The Role of Air-Sea Exchange in Geochemical Cycling* (pp 113–127). Utrecht, Reidel
- Liss PS, Watson AJ, Bock EJ, Jähne B, Asher WE, Frew NM, Hasse L, Korenowski GM, Merlivat L, Phillips LF, Schuessel PS & Woolf DK (1997) Physical processes in the microlayer and the air-sea exchange of trace gases, In: Liss PS & Duce RA (Eds) *The Sea Surface and Global Change* (pp 1–34). Cambridge University Press
- Mommaerts (1991) Distribution and trends of contaminants in seawater and sediments of the Southern Bight of the North Sea and the Western Scheldt Estuary, MUMM's data processing series, Vol. 2, 22 pp. Ministry of Public Health and Environment
- Nightingale PD, Liss PS & Schlosser P (2000a) Measurements of air-sea gas transfer during an open ocean algal bloom. *Geophys. Res. Lett.* 27: 2117–2120
- Nightingale PD, Malin G, Law CS, Watson AJ, Liss PS, Liddicoat MI, Boutin J & Upstill-Goddard RC (2000b) *In situ* evaluation of air-sea exchange parameterizations using novel conservative and volatile tracers. *Global Biogeochem. Cycles* 14: 373–387
- Nihoul JCJ & Ronday FC (1975) The influence of tidal stress on the residual circulation. *Tellus* 29: 484–490
- Nihoul JCJ & Hecq JH (1984) Influence of residual circulation on the physico-chemical characteristics of water masses and the dynamic of ecosystems in the Belgian coastal zone. *Contin. Shelf Res.* 3: 167–174
- Officer CB (1983) Physics of estuarine circulation In: Ketchum BH (Ed) *Ecosystems of the World*, Vol. 26 (pp 15–41). Elsevier
- Park PK, Gordon LI, Hager SW & Cissell MC (1969) Carbon dioxide partial pressure in the Columbia River. *Science* 166: 867–868
- Raymond PA, Bauer JE & Cole JC (2000) Atmospheric CO<sub>2</sub> evasion, dissolved inorganic carbon production, and net heterotrophy in the York River estuary. *Limnol. Oceanogr.* 45: 1707–1717

- Regnier P, Mouchet A, Wollast R & Ronday F (1998) A discussion of methods for estimating residual fluxes in strong tidal estuaries. *Continental Shelf Res.* 18: 1543–1571
- Regnier P & Steefel CI (1999) A high resolution estimate of the inorganic nitrogen flux from the Scheldt estuary to the coastal North Sea during a nitrogen-limited algal bloom, spring 1995. *Geochim. Cosmochim. Acta* 63: 1359–1374
- Reimer A, Brasse S, Doerffer R, Dürselen C-D, Kempe S, Michaelis W, Rick H-J & Seifert R (1999) Carbon cycling in the German Bight: an estimate of transformation processes and transport. *Dt. Hydrogr. Z.* 51: 311–327
- Ruddik K (1996) Study of the dispersion of fresh water (from the Scheldt and the Rhine/Meuse) by the interpretation of images from NOAA AVHRR, ERS-1/2 ATSR and ERS-1/2 SAR, Management Unit of the Mathematical Models of the North Sea and Scheldt Estuary (Ed), Bruxelles
- Sarma VVSS, Kumar MD & Manerikar M (2001) Emission of carbon dioxide from a tropical estuarine system, Goa, India. *Geophys. Res. Lett.* 28: 1239–1242
- Semiletov IP (1999) Aquatic sources and sinks of CO<sub>2</sub> and CH<sub>4</sub> in the polar regions. *J. Atmos. Sci.* 56: 286–306
- Servais P, Billen G & Hascoet M-C (1987) Determination of the biodegradable fraction of dissolved organic matter in waters. *Wat. Res.* 21: 445–450
- Smith SV (1985) Physical, chemical and biological characteristics of CO<sub>2</sub> gas flux across the air-water interface. *Plant, Cell and Environ.* 8: 387–398
- Smith SV & Mackenzie FT (1987) The ocean as a net heterotrophic system: implications from the carbon biogeochemical cycle. *Global Biogeochem. Cycles* 1: 187–198
- Smith SV & Hollibaugh JT (1993) Coastal metabolism and the oceanic organic carbon balance. *Rev. Geophys.* 31: 75–89
- Soetaert K & Herman PMJ (1995) Carbon flows in the Westerschelde estuary (The Netherlands) evaluated by means of an ecosystem model (MOSES). *Hydrobiologia* 311: 247–266
- Ternon JF, Oudot C, Dessier A & Diverres D (2000) A seasonal tropical sink for atmospheric CO<sub>2</sub> in the Atlantic ocean: the role of the Amazon River discharge. *Mar. Chem.* 68: 183–201
- Tsunogai S, Watanabe S & Sato T (1999) Is there a ‘continental shelf pump’ for the absorption of atmospheric CO<sub>2</sub>? *Tellus* 51B: 701–712
- Wanninkhof RH (1992) Relationship Between wind speed and gas exchange over the ocean. *J. Geophys. Res.* 97(C5): 7373–7382
- Wanninkhof R & McGillis WR (1999) A cubic relationship between air-sea CO<sub>2</sub> exchange and wind speed. *Geophys. Res. Lett.* 26: 1889–1892
- Wollast R (1976a) Propriétés physico-chimiques des sédiments et des suspensions de la Mer du Nord. In: Nihoul JCJ & Guillemin F (Eds) *Project Mer Rapport Final*, Vol 4 (pp 123–143). Services du premier Ministre Programmation de la politique scientifique, Belgium
- Wollast R (1976b) Transport et accumulation de polluants dans l’estuaire de l’Escaut. In: Nihoul JCJ & Wollast R (Eds) *Project Mer Rapport Final*, Vol 10 (pp 196–218). Services du premier Ministre Programmation de la politique scientifique, Belgium
- Wollast R (1983) Interactions in Estuaries and Coastal waters In: Bolin B & Cook RB (Eds) *The major Biogeochemical Cycles and their Interactions*, Wiley & Sons
- Wollast R (1998) The global coastal ocean. In: Brink KH & Robinson AR (Eds) *The Sea*, Vol. 10 (pp 213–252). Wiley & Sons

