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HAL Id: hal-03334223

<https://hal.science/hal-03334223>

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Time series of the partial pressure of carbon dioxide (2001–2004) and preliminary inorganic carbon budget in the Scheldt plume (Belgian coastal waters)

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[1] A 4-year time series (2001–2004) of the partial pressure of CO₂ (pCO₂) and air-sea CO₂ fluxes is reported in the Scheldt estuarine plume. This system is oversaturated in CO₂ with respect to the atmosphere, except during the spring phytoplanktonic bloom, and acts as a net source of CO₂ to the atmosphere of 0.7 mol C m⁻² yr⁻¹ that represents 7 to 27% of the inner Scheldt estuary CO₂ emission. Results also highlight that a high spatial and temporal coverage of the surface pCO₂ in coastal ecosystems is crucial for reliable estimations of air-sea CO₂ fluxes. The seasonal variations of pCO₂ seem to be more dominated by biological activities (photosynthesis/respiration) than by temperature change. A stoichiometrically linked C/P mass balance budget failed to provide net ecosystem production estimates consistent with the pCO₂ dynamics in this area. It is hypothesized that this discrepancy is related to physiological characteristics of the dominant phytoplanktonic species (*Phaeocystis sp.*) within the studied area. On the basis of a preliminary dissolved inorganic carbon input/output budget, the annual emission of CO₂ toward the atmosphere seems to be largely due to the outgassing of the inputs of CO₂ from the inner Scheldt estuary, rather than due to organic carbon degradation.

Components: 9857 words, 8 figures, 3 tables.

Keywords: CO₂ air-sea fluxes; Belgian coastal water; Scheldt estuary.

Index Terms: 4806 Oceanography: Biological and Chemical: Carbon cycling (0428).

Received 10 October 2005; **Revised** 18 March 2006; **Accepted** 3 April 2006; **Published** 14 June 2006.

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

1. Introduction

[2] Coastal environments are important biogeochemical pathways between land and the open ocean that significantly modify the flows of matter and energy between the latter two systems. They receive and exchange considerable amounts of dissolved and particulate organic matter and nutrients, freshwater, energy and contaminants [Smith and Hollibaugh, 1993; Gattuso et al., 1998; Wollast, 1998]. Recent studies highlighted the significance of continental shelves in the global carbon cycle and in particular for the budgets of CO₂ [Tsunogai et al., 1999; Frankignoulle and Borges, 2001; Cai et al., 2003; Thomas et al., 2004, 2005a]. On the basis of an exhaustive literature survey, Borges et al. [2005] showed that marginal seas on the whole act as sinks of atmospheric CO₂ of about $-0.45 \text{ PgC yr}^{-1}$ that leads to a major revaluation of the oceanic sink for atmospheric CO₂, since open oceanic waters are a CO₂ sink of about -1.6 PgC yr^{-1} [Takahashi et al., 2002]. Nearshore coastal systems (estuaries, salt-marsh waters, mangrove waters, coral reefs, and coastal upwelling systems) act as sources of CO₂ and a preliminary upscaling suggests that the overall emission of CO₂ from these systems could be as high as 0.40 PgC yr^{-1} , thus balancing the CO₂ sink associated to marginal seas [Borges, 2005; Borges et al., 2005]. Estuaries are the largest contributors to this emission of CO₂, accounting for about 0.34 PgC yr^{-1} . However, due to an insufficient geographical coverage of the available data, the estimation of CO₂ air-water fluxes from coastal environments on a global scale remains highly uncertain, but potentially relevant.

[3] Estuaries can be divided into an inner part (extending from the geographical mouth to the uppermost limit of the tidal river) and an outer estuary defined by Ketchum [1983] as “a plume of freshened water which floats on the more dense coastal water and can be traced for many miles from the geographical mouth of the estuary”. According to Schettini et al. [1998], two types of outer estuaries can be distinguished depending on the degree of salinity mixing and intensity of the freshwater discharge: “In riverine plumes, freshwater discharge dominates over tidal and other effects, resulting in freshwater being directly injected over shelf waters (e.g., the Mississippi or the Rhine river plumes). In estuarine plume, much of the mixing takes place within an enclosed basin before being released to shelf waters”. In outer estuaries, intense biogeochemical transformations

(affecting both particulate and dissolved organic and inorganic materials) occur on short time (scale of days to week) and space scales [e.g., Dagg et al., 2004].

[4] The inner Scheldt estuary, located between Netherlands and Belgium (Figure 1), is a well-mixed macrotidal estuary, with a low freshwater discharge ($4 \text{ km}^3 \text{ yr}^{-1}$). The brackish part extends up to 100 km inland and drains a heavily populated and industrial basin [Wollast, 1988]. Lack of sewage treatment has led to a high content of organic matter and nutrients in these waters and a strong heterotrophic status with an estimated annual net ecosystem production (NEP) of -15 to $-40 \text{ mol C m}^{-2} \text{ yr}^{-1}$ in the inner estuary [Gazeau et al., 2005]. The estuarine plume is located along the Belgian coast deflected by the southwestward residual currents [Nihoul and Ronday, 1975; Yang, 1998]. The water column is well-mixed through the year due to its shallowness (mean depth of 20 m) and strong tidal currents. A high turbidity zone extends from the mouth of the Scheldt estuary and along the Belgian coast [Nihoul and Hecq, 1984; Wollast, 1988]. The suspended particulate matter mainly originates from the Dover Strait according to de Haas et al. [2002] and Fettweis and Van den Eynde [2003]. High nutrient inputs from the Scheldt have led to a dystrophization of the Belgian coast and recurrent spring blooms of *Phaeocystis* sp. The phytoplanktonic seasonal succession consists in consecutive blooms of diatoms and *Phaeocystis* occurring between February and May. A last diatom bloom occurs also in summer [Reid et al., 1990; Rousseau et al., 2002]. The spring bloom represents up to 77% of the annual net primary production with *Phaeocystis* sp. as the main contributor (55% [Lancelot et al., 2005]).

[5] The main objective of the present paper is to investigate partial pressure of CO₂ (pCO₂) dynamics in the surface waters of the Scheldt plume using a 4-year time series. Two data analysis approaches are presented. The first one is based on a high temporal data set of pCO₂ (frequency sampling twice a week) at a fixed station (Zeebrugge station) that allows to highlight the relative importance of temperature change and biological activities involved in the seasonal DIC dynamics. The second approach is a high spatial coverage of pCO₂ (the survey area approach, one to three surveys per month) that allows us to compute the air-sea CO₂ fluxes taking into account the strong spatial heterogeneity of the system. Moreover, the impact of biological activities on the carbon cycle in the

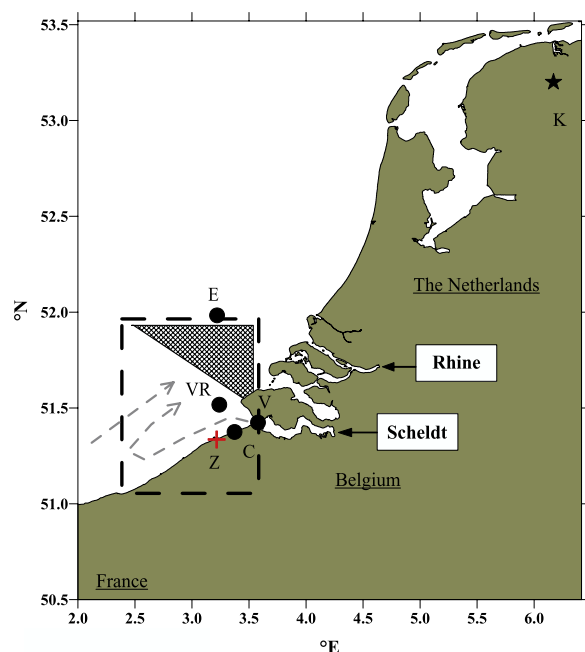


Figure 1. Map of the study site showing Zeebrugge station (Z, red cross), location of meteorological stations (E, Europlatform; V.R., Vlakte van de Raan; C, Cadzand; and V, Vlissingen; black circles) where wind speed data was acquired and atmospheric pCO₂ station (K, Kollumerwaard; black star). Hatched arrows represent the residual circulation off the Belgian coast. Hatched area represents the region not taken into account in the air-sea CO₂ flux computations.

Scheldt plume is assessed from NEP estimates based on a stoichiometrically linked C/P mass balance budget (Land-Ocean Interaction in the Coastal Zone; LOICZ). Finally, on the basis of these results and estimates of dissolved inorganic carbon (DIC) inputs from the Scheldt estuary, a tentative DIC budget is established to unravel the main processes controlling on an annual scale the air-sea CO₂ fluxes in the Scheldt estuarine plume.

2. Material and Methods

[6] Data were obtained from January 2001 to December 2004 on board the R/V *Belgica*. Figure 2 shows the sampling frequency for the fixed Zeebrugge station approach (red squares) and for the survey area approach (blue circles).

2.1. Partial Pressure of CO₂ and Air-Sea CO₂ Fluxes

[7] A nondispersive infrared gas analyzer (IRGA, Li-Cor[®], Li-6262) and an equilibrator were used to

measure the pCO₂ (for details on design and performance tests, refer to *Frankignoulle et al.* [2001]). The IRGA was calibrated weekly using pure nitrogen (Air Liquide Belgium) and two gas mixtures with a CO₂ molar fraction of 366 and 810 ppm (Air Liquide Belgium) that were calibrated against National Oceanic and Atmospheric Administration standards of a CO₂ molar fraction of 361 and 774 ppm. The temperature at the outlet of the equilibrator was monitored with a platinum resistance thermometer (PT100, METROHM[®]). The pCO₂ values were corrected for the temperature difference between in situ seawater and water in the equilibrator using the algorithm proposed by *Copin-Montégut* [1988]. Salinity, temperature and pCO₂ were sampled with a 1 minute frequency from the surface seawater supply of the ship (pump inlet at a depth of 2.5 m). Salinity and temperature were measured using a SeaBird[®] SBE21 thermosalinograph.

[8] pCO₂, salinity and temperature were interpolated using the Krigging method with Golden Software Surfer 8. Interpolated data were extracted for salinities up to 34 corresponding to the limit of the outer Scheldt plume used by *Borges and Frankignoulle* [2002]. The flux of CO₂ across the air-sea interface (F) was computed from the pCO₂ air-sea gradient ($\Delta p\text{CO}_2 = p\text{CO}_{2\text{sea}} - p\text{CO}_{2\text{air}}$), the solubility coefficient of CO₂ (α), and the gas transfer velocity (k) according to

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

A positive flux corresponds to a transfer of CO₂ from the water to the atmosphere.

[9] We used the k -wind parameterization given by *Nightingale et al.* [2000] (referred to hereafter as N&al), established in the Southern Bight of the North Sea (SBNS), close to our study area. Alternate k -wind parameterizations were also used to estimate the sensitivity of the computed fluxes to this parameter [*Liss and Merlivat*, 1986; *Wanninkhof*, 1992; *Wanninkhof and McGillis*, 1999; referred to as L&M, W, and W&McG, respectively] and to compare with previous studies carried out in this area. k values were computed using hourly wind speed values from 4 meteorological stations provided by the Royal Netherlands Meteorological Institute (<http://www.knmi.nl/samenw/hydra>): Cadzand (3.37°E 51.38°N), Vlissingen (3.58°E 51.42°N), Vlakte van de Raan (3.24°E 51.52°N) and Europlatform (3.22°E 51.98°N), shown in Figure 1. Vlakte van de Raan was chosen as the reference meteorological station,

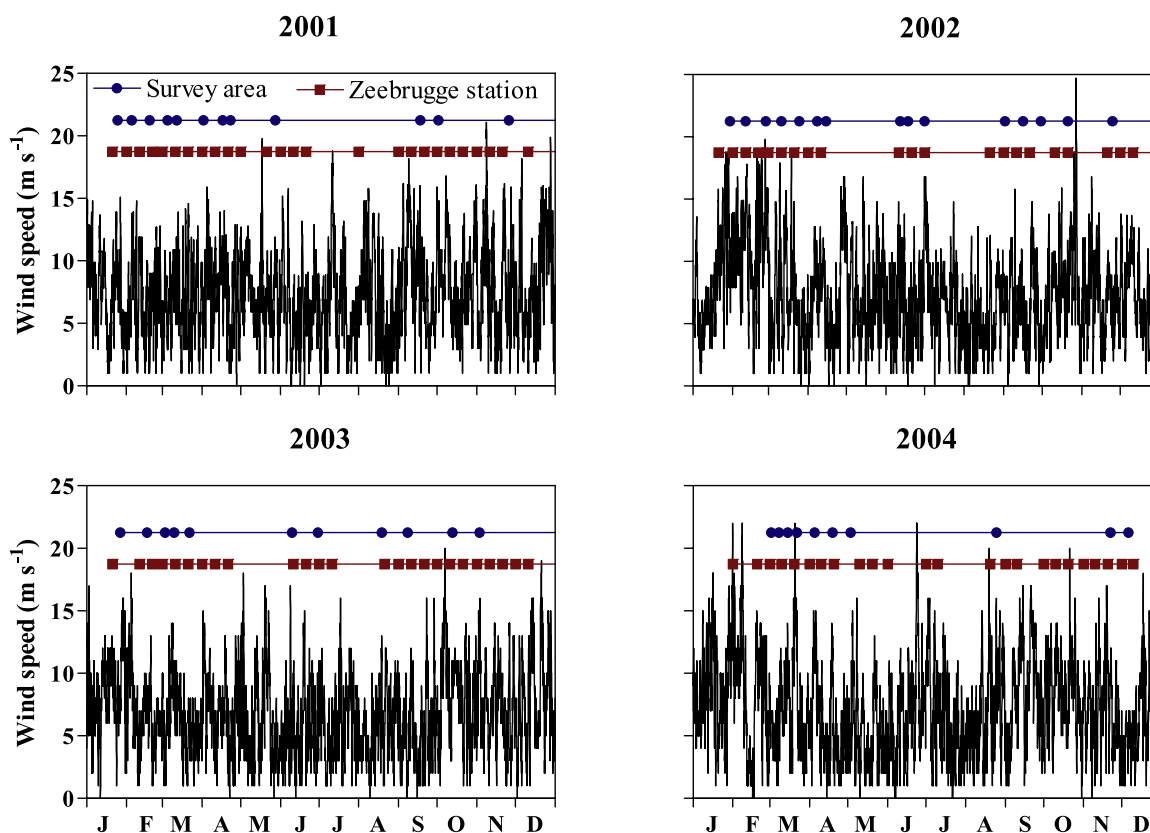


Figure 2. Wind speed data measured at station Vlakte van de Raan from 2001 to 2004 and temporal coverage for the survey area and Zeebrugge station approaches (blue circles and red squares, respectively).

being located in the plume. However, air-sea CO_2 fluxes were also computed using wind speed data from the 3 other stations (one offshore and two coastal referenced stations) in order to assess the sensitivity of the computed fluxes to this variable. Monthly values of atmospheric pCO_2 data used were measured at station Kollumerwaard in Netherlands (6.17°E 53.20°N) from the Dutch National Air Quality Monitoring Network supplied by the National Institute of Public Health and Environment. Atmospheric pCO_2 data were converted into pCO_2 in wet air ($\text{pCO}_{2\text{air}}$) according to *Dickson and Goyet* [1994].

2.2. Modeling Budget

[10] A dissolved inorganic phosphorus (DIP) budget in the Scheldt plume for year 2003 was carried on using the C/N/P stoichiometrically Land-Ocean Interaction in the Coastal Zone (LOICZ) method given by *Gordon et al.* [1996]. As the water column is well-mixed through the year, the Scheldt plume was considered as a one-layer box. Residual inputs and mixing fluxes from the inner Scheldt estuary as well as mixing fluxes with the open oceanic water (SBNS) were considered as shown

in Figure 3. *Lacroix et al.* [2004] reported that Belgian coastal waters could be influenced by inputs from the Rhine estuary. However, as the proportion of water masses coming from the Rhine is relatively small in this area based on total alkalinity (TA) distributions (*L.-S. Schiettecatte*, unpublished data) water and nutrient inputs from this estuary were neglected. Moreover, precipitation and evaporation were not taken into account, as these two quantities compensate each other [*OSPARCOM*, 2002]. Therefore the residual transport (V_{r1}) between the plume box and the SBNS was considered to be equivalent to the Scheldt discharge (V_{r2} ; Figure 3). Freshwater discharge data in the inner Scheldt estuary were provided by the Ministerie van de Vlaamse Gemeenschap Afdeling Waterbouwkundig Laboratorium en Hydrologisch Onderzoek. According to *Soetaert et al.* [2006], these data must be corrected for lateral inputs to estimate the discharge at the mouth. These lateral inputs represent on average 32% of the freshwater flow entering the estuary: 10% from the Antwerpen harbor, 12% from the Gent-Terneuzen channel and 10% from diffusive sources. The mixing transport between the plume

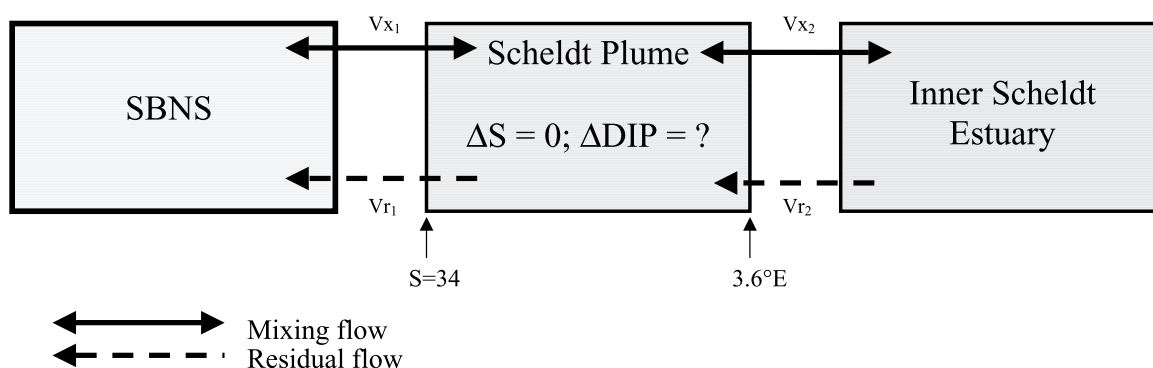


Figure 3. Land Ocean Interaction in the Coastal Zone (LOICZ) budgeting approach applied to dissolved inorganic phosphorus (DIP) in the Scheldt plume. Mixing exchange terms (V_{x1} and V_{x2}) were considered between the plume and the Southern Bight of the North Sea (SBNS) and between the plume and the inner Scheldt estuary. Residual fluxes (V_{r1} and V_{r2}) correspond to the water discharge from the inner Scheldt estuary (see text for details). Salinity 34 represents the outer limit of the Scheldt plume, and 3.6°E was considered as the limit between the inner Scheldt estuary and the plume.

and SBNS (V_{x1}) was estimated on the basis of salinity data which is a conservative parameter which is assumed to be at steady state in the plume over a tidal cycle ($dS/dt = 0$), following the equation

$$V_{x1} = \frac{[V_r(S_{r2} - S_{r1}) - V_{x2}(S_{\text{plume}} - S_{\text{Scheldt}})]}{(S_{\text{plume}} - S_{\text{SBNS}})} \quad (1)$$

where S_{plume} , S_{Scheldt} and S_{SBNS} are average salinities in the plume, Scheldt mouth and SBNS boxes, respectively. Monthly estimates of mixing fluxes between the plume and the inner Scheldt estuary (V_{x2}) were given by Gazeau *et al.* [2005] using the same procedure for year 2003. For more details on the calculation procedure, refer to Gordon *et al.* [1996].

[11] DIP data in 2003 for the Scheldt plume and SBNS boxes were acquired in the present study and completed with data from van der Zee and Chou [2005], from the Belgian Marine Data Center (BMDC, <http://www.mumm.ac.be/datacentre/>) and EUROTROPH (Nutrients Cycling and the Trophic Status of Coastal Ecosystems; <http://www.ulg.ac.be/oceanbio/eurotroph/>) and CANOPY (Carbon, Nitrogen and Phosphorus Cycling in the North Sea) projects. DIP data for the inner Scheldt estuary box were given by Gazeau *et al.* [2005]. Phosphorus atmospheric deposition represents less than 2% of the riverine inputs in the area [OSPAR-COM, 2002], so this term was neglected. Samples for DIP of the present study were collected with a frequency of 30 min from the seawater supply (depth of 2.5 m), filtered on cellulose acetate filters and kept frozen (-20°C) until analysis using the

spectrophotometric method given by Grasshoff *et al.* [1983].

[12] As DIP is not a conservative parameter and could be influenced by processes other than transport and dilution, nonconservative fluxes (basically, deviation from the dilution/mixing line) of DIP (ΔDIP) in the plume were estimated as the difference between DIP outputs and inputs in the plume box [Gordon *et al.*, 1996]. NEP (p-r in the LOICZ terminology) is the difference between gross primary production (GPP) and community respiration (CR) [Odum, 1956] and was calculated from the nonconservative fluxes of DIP, assuming that these fluxes are only related to biological activity, following the equation

$$\text{NEP} = -\Delta\text{DIP} \cdot (\text{C:P})_{\text{part}} \quad (2)$$

where NEP is expressed in $\text{mmol C m}^{-2} \text{d}^{-1}$, ΔDIP is the nonconservative flux of DIP ($\text{mmol P m}^{-2} \text{d}^{-1}$) and $(\text{C:P})_{\text{part}}$ is the particulate C:P ratio (a value of 106:1 was used according to the Redfield stoichiometry).

[13] Error propagations were performed on mean value of each parameter used for the DIP budget using a Monte Carlo procedure on Matlab 7. Mean values of salinity, freshwater discharge and DIP were randomly changed over one thousand iterations within 95% confidence interval.

2.3. Estimation of the DIC Inputs From the Inner Scheldt Estuary

[14] Inputs of DIC from the inner Scheldt estuary to the plume were calculated using the apparent

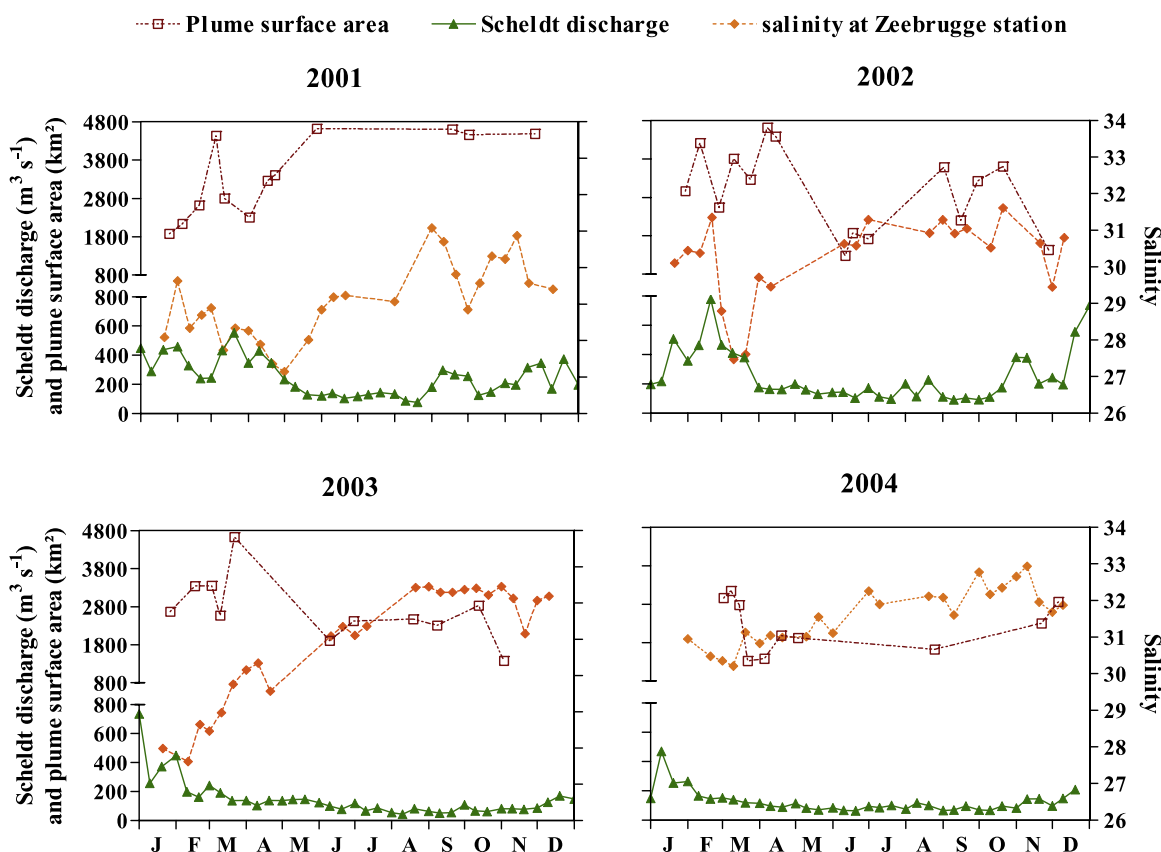


Figure 4. Water discharge from the inner Scheldt estuary in $\text{m}^3 \text{s}^{-1}$ (green triangles), surface area of the Scheldt plume in km^2 (red squares), and average salinity at the Zeebrugge station (orange diamonds) from 2001 to 2004.

zero end-member method (AZE) according to *Kaul and Froelich* [1984], from monthly DIC profiles from salinity 9 to 30 [*Gazeau et al.*, 2005], as DIC profiles show nonconservative behavior between salinities 0 to 9 due to strong heterotrophic processes. These fluxes correspond to fluxes of the DIC that can be exchanged with the atmosphere (excess DIC or ΔDIC) that is computed from the difference between the observed DIC and DIC calculated if the sample was at equilibrium with the atmosphere. ΔDIC profiles were linear in the inner Scheldt (r^2 ranging from 0.95 to 0.99 from salinities 9 to 30). Transfer of ΔDIC ($T\Delta\text{DIC}$) from the inner Scheldt was computed from the monthly Scheldt discharge and ΔDIC_0 corresponding to the ΔDIC value computed at salinity 0 from linear regression.

3. Results and Discussion

3.1. Dynamics of pCO_2 in Surface Waters

[15] Figure 4 shows the mean salinity observed at Zeebrugge, the surface area of the Scheldt plume and the water discharge from the inner Scheldt

estuary from 2001 to 2004. The surface area of the plume ranged between 800 and 4800 km^2 , with highest values observed from June to December 2001 and in spring of 2002 and 2003. Average salinity at Zeebrugge (ranging from 27 to 33) and the surface area of the plume showed no clear seasonal trends. Salinity increased and stabilized around 32 from August 2003 through 2004. The strongest freshwater discharges occurred during winter (up to $800 \text{ m}^3 \text{s}^{-1}$) in response to higher precipitation. During periods of high freshwater discharge, one would intuitively expect an increase of the surface area of the plume and a decrease of salinity. However, this was not always verified as shown in Figure 4. *Nihoul and Ronday* [1975] and *Yang* [1998] suggested that the water from the Scheldt mouth is deflected in a southwestward direction resulting from residual currents. *Yang* [1998] reported that changes of salinity in the Scheldt plume are mainly related to wind stress (intensity and direction). Along shore southeastward and on shore winds induce an increase of salinity, while along shore northeastward and offshore winds have the reverse effect. The surface area of the Scheldt plume results from a complex

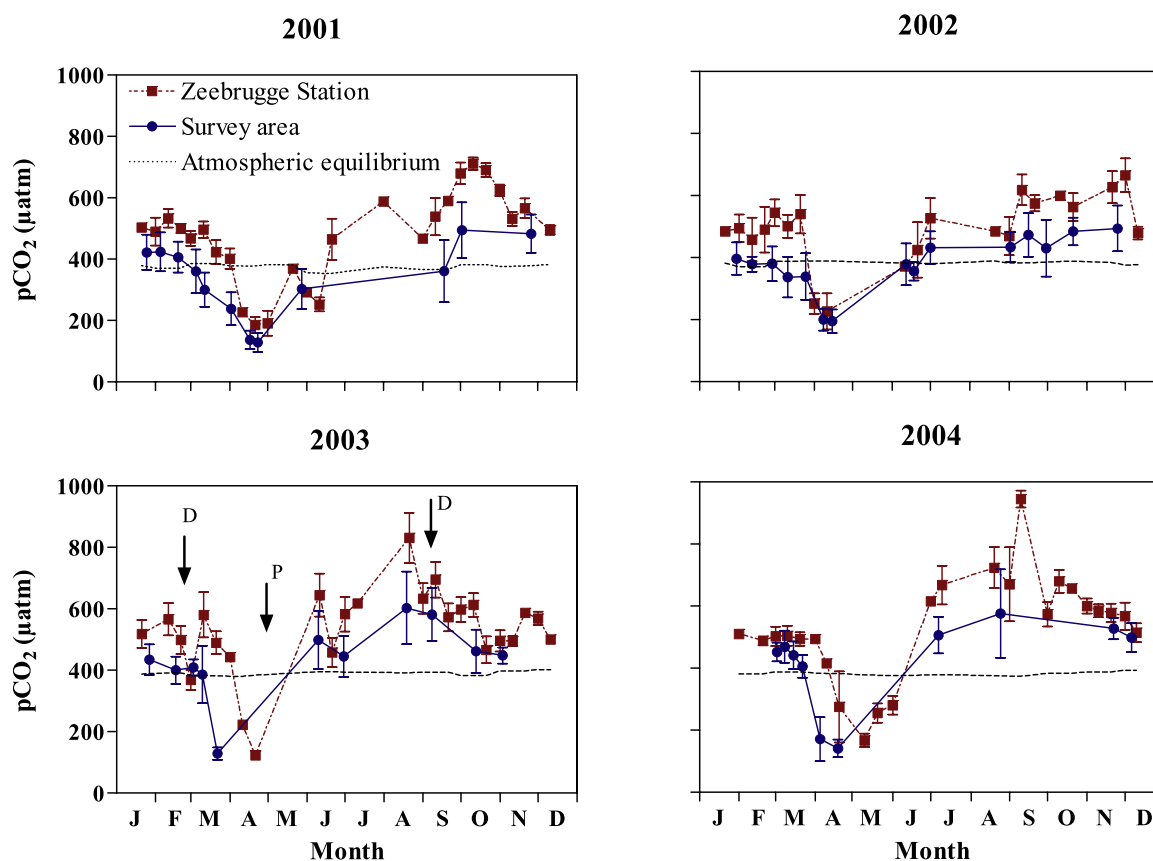


Figure 5. Averaged $p\text{CO}_2$ (μatm) on surface waters of the Scheldt plume (survey approach; blue circles) and at Zeebrugge station (red squares) from 2001 to 2004. Data are mean $\pm$ standard deviation (SD). The dotted line represents atmospheric $p\text{CO}_2$. P and D refer to *Phaeocystis* sp. and diatoms, respectively.

combination of residual currents (associated to tides), wind induced currents and freshwater discharge, so that no obvious correlations between salinity, surface area and freshwater discharge are apparent (Figure 4).

[16] Figure 5 shows the seasonal cycle of $p\text{CO}_2$ in surface seawaters at Zeebrugge station and from the survey area approach. The surface waters at Zeebrugge station show stronger CO_2 oversaturation with respect to the atmosphere than the whole Scheldt plume. The Zeebrugge station was characterized by rather low salinities (Figure 4), while the survey area approach values reflected the overall range of salinities (and mixing) in the Scheldt plume. Most of the time, the Scheldt plume showed a profile against salinity typical for estuarine environments with $p\text{CO}_2$ increasing with decreasing salinities (data not shown). Hence $p\text{CO}_2$ values at the Zeebrugge station tended to be higher than average values from the survey area approach. The range of $p\text{CO}_2$ values was similar from one year to another, with minimal values of around 100 μatm and maximal values of 600 and 900 μatm , for the

survey area approach and Zeebrugge station, respectively. In 2003 and 2004, a stronger decrease of $p\text{CO}_2$ during the spring phytoplanktonic bloom was observed in comparison to 2001 and 2002.

[17] The seasonal succession of phytoplanktonic blooms as described by Reid *et al.* [1990] and Rousseau *et al.* [2002], was apparent in the successive decreases of $p\text{CO}_2$ observed in 2003 (Figure 5). The diatom bloom started in February, followed by a bloom of diatoms-*Phaeocystis* sp. from March to May, and ended with a small diatom bloom in late August/early September. The increase of $p\text{CO}_2$ values observed during summer was due to heterotrophic processes (see hereafter). The $p\text{CO}_2$ decrease in the whole plume occurred earlier than at station Zeebrugge. This was related to the onset of the spring phytoplanktonic bloom in the offshore coastal waters, due to higher light penetration in the water column [Borges and Frankignoulle, 1999, 2002; van der Zee and Chou, 2005].

[18] The method developed by Takahashi *et al.* [2002] was used to separate the seasonal effect of

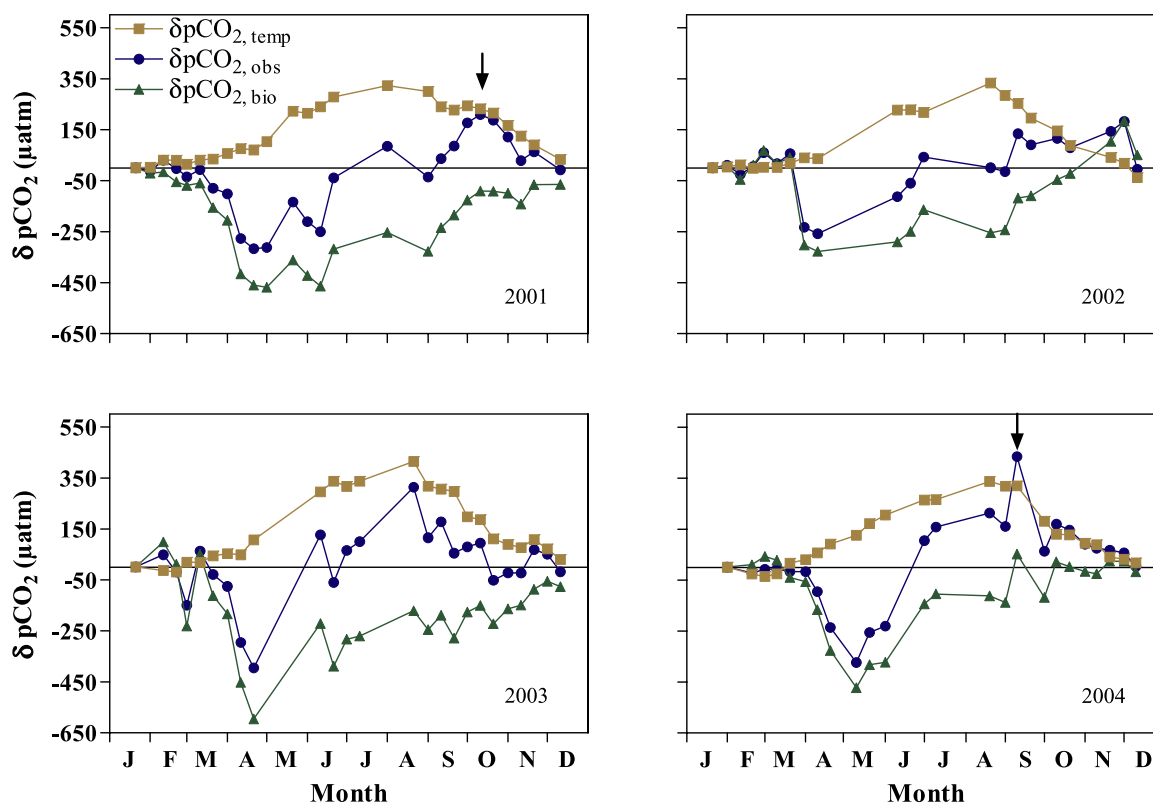


Figure 6. $\delta p\text{CO}_2$, obs (blue circles), $\delta p\text{CO}_2$, temp (brown squares), and $\delta p\text{CO}_2$, bio (green triangles) in μatm , from 2001 to 2004. See text for details on the calculations of $\delta p\text{CO}_2$. Arrows refer to low salinity events.

biological processes (B) and temperature (T) on $p\text{CO}_2$ dynamics over an annual cycle. A ratio of temperature over biology (T/B) greater than 1 implies the dominance of temperature effects over biological processes on $p\text{CO}_2$ dynamics. Biological and temperature effects were respectively calculated according to the following equations:

$$(B) \quad p\text{CO}_{2,\text{bio}} = p\text{CO}_2(T_{\text{mean}}) = p\text{CO}_2(\text{obs}) \cdot \exp[0.0423 \cdot (T_{\text{mean}} - T_{\text{obs}})] \quad (3)$$

$$(T) \quad p\text{CO}_{2,\text{temp}} = p\text{CO}_2(T_{\text{obs}}) = (\text{mean annual } p\text{CO}_2) \cdot \exp[0.0423 \cdot (T_{\text{obs}} - T_{\text{mean}})] \quad (4)$$

where T_{mean} is the mean annual temperature (10.7, 11.5, 12.8 and 10.6°C for 2001, 2002, 2003 and 2004, respectively) and T_{obs} is the in situ temperature.

[19] Seasonal effects of biological processes and temperature were determined, respectively, from the amplitude of $p\text{CO}_2$ (T_{mean}) and $p\text{CO}_2$ (T_{obs}) derived from equations (3) and (4). Figure 6 shows the seasonal variations of the $\delta p\text{CO}_2$, obs , $\delta p\text{CO}_2$, bio , $\delta p\text{CO}_2$, temp (calculated as the difference between $p\text{CO}_2$ monthly averaged values and a

reference, here $p\text{CO}_2$ averaged value for January of each year) from 2001 to 2004 at the Zeebrugge station. Maximum $|\delta p\text{CO}_2$, $\text{bio}|$ values were observed during spring phytoplanktonic blooms and were more pronounced in 2003. Generally, highest $|\delta p\text{CO}_2$, $\text{temp}|$ values were observed in August. From January to May, the $p\text{CO}_2$ dynamics was controlled by biological processes, as the increase of the $\delta p\text{CO}_2$, temp is not sufficient to counteract the drop of the $\delta p\text{CO}_2$, obs . From late spring to summer, the increase of $\delta p\text{CO}_2$, obs was due to the combination of heterotrophic activities and the increase of temperature, as both $\delta p\text{CO}_2$, bio and $\delta p\text{CO}_2$, temp increased. In early fall, the opposite trends were observed with a drop of temperature and a consecutive decrease of heterotrophic activities. However, during this period some values of $\delta p\text{CO}_2$, obs and $\delta p\text{CO}_2$, bio increased (as shown by arrows in September–October 2001 and 2004 in Figure 6), and could be explained by low salinity events with higher DIC content, and/or resuspension of sediments with subsequent degradation of fresh organic matter (see critics on this method below). In fall and winter, the decrease of temperature is the dominant factor controlling the $p\text{CO}_2$ dynamics.

Table 1. Amplitude in the $\delta p\text{CO}_2$, obs , $\delta p\text{CO}_2$, bio , and $\delta p\text{CO}_2$, temp Signals at Station Zeebrugge From 2001 to 2004 and Estimate of the T/B Ratio Computed According to *Takahashi et al.* [2002]

	$\delta p\text{CO}_2$, obs	$\delta p\text{CO}_2$, bio	$\delta p\text{CO}_2$, temp	T/B
2001	641	635	343	0.54
2002	562	670	382	0.57
2003	804	823	486	0.59
2004	884	650	373	0.57

[20] Table 1 shows the annual amplitudes in the $\delta p\text{CO}_2$, obs , $\delta p\text{CO}_2$, bio , $\delta p\text{CO}_2$, temp , and T/B ratio for Zeebrugge station. The amplitude in $\delta p\text{CO}_2$, bio was greater than $\delta p\text{CO}_2$, temp , and the T/B ratio was rather similar for the 4 years (~ 0.6) indicating that on an annual scale biological processes dominated over temperature effects. These results are in agreement with the output from the 1-D MIRO- CO_2 biogeochemical model for the Belgian coastal waters [*Gypens et al.*, 2004] that yields a T/B ratio of 0.66.

[21] As mentioned by *Thomas et al.* [2005b], the method developed by *Takahashi et al.* [2002] was designed for open oceanic systems and, in the case of coastal ecosystems, besides temperature and biology other physical/chemical processes can significantly affect the $p\text{CO}_2$ dynamics: freshwater discharge, exchange between different water masses, sediment/water column exchanges, variations of TA and air-sea CO_2 fluxes. In the present computations, these factors were inherently associated to the biological signal which can lead to misinterpretations of the results. Nevertheless, applying this method to the whole survey area for 2002 (highest temporal coverage among the 4 years), the different $\delta p\text{CO}_2$ (not shown) displayed the same relative variations than the ones for Zeebrugge station and therefore a similar T/B (~ 0.6) is estimated. As explained above, Zeebrugge station is shallow and close to the mouth of the Scheldt estuary and $p\text{CO}_2$ dynamics at this station is expected to be much more influenced by factors such as freshwater flow and sediment/water column exchanges than the whole plume area. Therefore these results indicate that the method of *Takahashi et al.* [2002] may be a reasonable approach to assess the qualitative relative importance of temperature and biological processes on the $p\text{CO}_2$ dynamics in this system.

[22] Recently, *Thomas et al.* [2005b] used the same computations for the whole North Sea. They found that biological processes dominate over tempera-

ture on the surface seawater $p\text{CO}_2$ dynamics in the northern part of the North Sea ($T/B < 1$), whereas it was the contrary ($T/B > 1$) in the SBNS. They concluded that for the SBNS biological net effects were vanished through near balanced production and respiration processes in the well-mixed water column, as the absence of a summer thermocline avoided export of spring synthesized organic matter. However, the data set (CANOBA cruises) of *Thomas et al.* [2005b] was based on 4 cruises in August and November 2001 and February and May 2002. During the last cruise, the SBNS was sampled at the end of May, when the bloom of *Phaeocystis sp.* was probably already declining, as also suggested by the modeling study of K. Elkalay et al. (Biogeochemical 1D ERSEM ecosystem model applied to recent carbon dioxide and nutrient data in the North Sea, submitted to *Journal of Marine Systems*, 2006). These results suggested then that the $p\text{CO}_2$, bio and therefore the T/B ratio were respectively underestimated and overestimated in their study. More recently, on the basis of a monthly survey carried on from June 2003 to May 2004, L.-S. Schiettecatte et al. (High temporal coverage of carbon dioxide measurements in the Southern Bight of the North Sea, submitted to *Marine Chemistry*, 2006) showed that the SBNS is a CO_2 sink where biological processes were dominant over temperature on the surface $p\text{CO}_2$ dynamics ($T/B \sim 0.8$), with a possible export of the newly synthesized organic matter to the adjacent system and/or smaller export to the sediments.

3.2. Net Ecosystem Production (NEP)

[23] A system is defined as autotrophic when GPP exceeds CR ($\text{NEP} > 0$) and heterotrophic when CR exceeds GPP ($\text{NEP} < 0$). NEP is relevant for $p\text{CO}_2$ dynamics since in an autotrophic system, there is a net removal of CO_2 from the water column, and conversely in a heterotrophic system there is a net release of CO_2 to the water column. The net CO_2 flux between the water column and the atmosphere will be further modulated by numerous other factors such as: other biogeochemical processes (CaCO_3 precipitation/dissolution), exchange of water with adjacent aquatic systems, residence time of the water mass within the system and decoupling of organic carbon production and degradation across the water column related to the physical settings of the system [e.g., *Borges*, 2005].

[24] Figure 7a shows computed monthly NEP values in 2003 estimated for the Scheldt plume using the LOICZ modeling procedure applied to

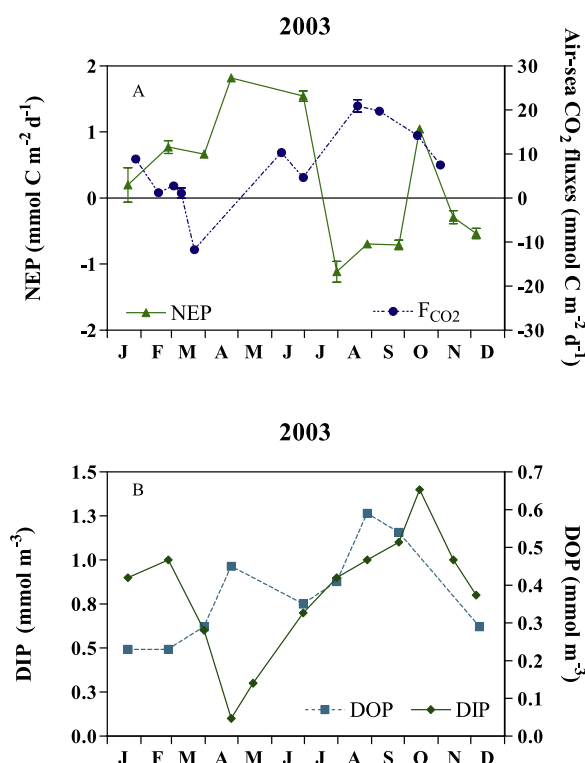


Figure 7. (a) Left axis: monthly net ecosystem production (NEP; mmol C m⁻² d⁻¹; green triangles) in 2003 estimated from the Land Ocean Interaction in the Coastal Zone (LOICZ) budgeting procedure applied to dissolved inorganic phosphorus (DIP). Errors bars refer to standard errors computed from a Monte Carlo procedure (see text for details). Right axis: Averaged air-sea CO₂ fluxes (F_{CO2} in mmol C m⁻² d⁻¹; blue circles) computed from pCO₂ data acquired in the whole plume (survey area approach), the gas transfer velocity parameterization as a function of wind speed given by Nightingale *et al.* [2000], and wind speed data from station Vlakte van de Raan. (b) Dissolved organic phosphorus (DOP) and DIP in mmol m⁻³ in the Scheldt plume.

DIP (10 months sampling coverage in 2003), and air-sea CO₂ fluxes from the survey area of the Scheldt plume (next section). From January to June and in October, the Scheldt plume was autotrophic (range 0.2 ± 3.0 to 1.8 ± 0.0 mmol C m⁻² d⁻¹) and heterotrophic the rest of the year (range -0.3 ± 0.1 to -1.1 ± 1.2 mmol C m⁻² d⁻¹; Table 2). The strongest autotrophy was computed for April (1.8 ± 0.0 mmol C m⁻² d⁻¹), in relation to the spring diatoms-*Phaeocystis* bloom when surface seawater were strongly undersaturated in CO₂ with respect to the atmosphere (Figure 5). Annually averaged NEP in the Scheldt plume was estimated to 0.2 ± 3.7 mmol C m⁻² d⁻¹, giving a metabolic status not significantly different from balance.

[25] Clearly, computed NEP values in spring during the phytoplanktonic bloom are too low to explain the decrease of pCO₂ during that period (Figure 5, survey area approach). If we assume a mean TA of the Scheldt plume of $2450 \mu\text{mol kg}^{-1}$, a decrease of about 300 μatm of the surface pCO₂ from early to mid March, and taking into account a mean air-sea CO₂ fluxes of about $-5 \text{ mmol C m}^{-2} \text{ d}^{-1}$, it would give an approximated NEP based on DIC of about $6 \text{ mmol C m}^{-2} \text{ d}^{-1}$. This rough estimate is higher than the one based on DIP budget of $1 \text{ mmol C m}^{-2} \text{ d}^{-1}$ for the same period. Several problems arise from the use of DIP in this procedure. The first one deals with the ability of *Phaeocystis sp.* to grow, under DIP depleted conditions, on dissolved organic phosphorus (DOP) by means of the alkaline phosphatase (AP). As *Phaeocystis sp.* is the third phytoplanktonic species to occur within this area after diatoms, the water column is depleted in DIP. In order to ensure their phosphate requirements, the *Phaeocystis* colonies de-repress (for DIP concentration below 0.5 mmol m^{-3}) the enzyme AP [Veldhuis and Admiraal, 1987; Van Boekel and Veldhuis, 1990]. The APs are located on the phytoplanktonic cell surface and mineralize DOP to DIP through the hydrolysis of the P-O-C bond. Chlorophyll-*a* (not shown) was highest during spring and consistent with the DIP decrease from February to end May due to photosynthetic activity whereas DOP increased during the same period (Figure 7b). The first peak of DOP (in April) is associated to a release from phytoplanktonic cells during primary production whereas the second one (August) should be associated to bacterial activities [van der Zee and Chou, 2005]. It is then possible that because of the physiological adaptation of *Phaeocystis sp.* to grow on DOP, our NEP computed for spring could be underestimated. However, it is also obvious that DOP concentrations were still important throughout summer suggesting a continued remineralization by bacteria. Therefore the NEP during summer, estimated from DIP alone, could have led to a significant underestimation of the heterotrophy. As no DOP data were available for the inner Scheldt estuary and the SBNS boxes, it was not possible to integrate DOP in the present LOICZ budget.

[26] The second problem encountered from the present budget comes from the use of the Redfield ratio in order to convert the NEP into carbon from DIP. We assumed a molar C/P ratio of 106:1. However, *Phaeocystis sp.* presents two life cycles. The first one is in the form of single flagellate cells evolving toward a colonial stage. These colonies

Table 2. Monthly Averaged Plume Surface Area, Scheldt Discharge, Salinity, and Dissolved Inorganic Phosphorus in the Estuary, Plume, and SBNS Boxes, and Δ DIP and computed NEP^a

Month	S	Q	Sal			DIP			Δ DIP	NEP
			Estuary	Plume	SBNS	Estuary	Plume	SBNS		
January	2974	37.6 (22.9)	22.5 (2.5)	32.5 (1.4)	34.5 (0.3)	3.1 (0.6)	0.9 (0.3)	0.6 (0.1)	1.9 [2.5]	0.2 [0.3]
February	3329	23.1 (13.6)	20.6 (3.3)	30.6 (2.6)	34.5 (0.4)	3.2 (0.5)	1.0 (0.3)	0.5 (0.1)	7.3 [0.9]	0.8 [0.1]
March	3535	15.4 (5.8)	21.3 (2.7)	31.4 (1.2)	34.3 (0.2)	2.8 (0.3)	0.6 (0.4)	0.1 (0.0)	6.3 [0.5]	0.7 [0.1]
April	4499	10.3 (3.1)	24.1(2.2)	31.0 (0.7)	34.5 (0.0)	2.1 (0.6)	0.1 (0.1)	0.1 (0.0)	17.2 [0.1]	1.8 [0.0]
June	1569	8.1 (2.8)	27.0 (2.4)	32.6 (0.7)	34.1 (0.0)	2.1 (0.5)	0.3 (0.2)	0.1 (0.0)	14.6 [0.7]	1.5 [0.1]
July	1716	7.5 (3.2)	29.3 (2.1)	32.8 (0.7)	34.2 (0.1)	2.1 (0.8)	0.7 (0.4)	0.1 (0.1)	−10.5 [1.5]	−1.1 [0.2]
August	3583	4.8 (3.7)	29.3 (1.1)	33.5 (0.4)	34.6 (0.2)	3.4 (0.5)	0.9 (0.5)	0.1 (0.1)	−6.6 [0.5]	−0.7 [0.1]
September	3389	4.4 (0.9)	28.9 (1.9)	33.3 (0.6)	34.3 (0.1)	3.5 (0.9)	1.0 (0.5)	0.4 (0.2)	−6.7 [0.7]	−0.7 [0.1]
October	2188	5.9 (2.3)	28.7 (2.0)	32.6 (0.1)	34.3 (0.1)	3.3 (0.8)	1.1 (0.1)	0.4 (0.1)	9.9 [0.4]	1.0 [0.0]
November	1408	6.1 (1.4)	29.5 (1.5)	32.5 (0.5)	34.6 (0.3)	2.8 (0.8)	1.4 (0.2)	0.5 (0.2)	−2.7 [0.9]	−0.3 [0.1]
December	2819	10.1 (4.8)	29.0 (1.2)	33.3 (0.5)	34.6 (0.2)	3.0 (0.6)	1.0 (0.2)	0.4 (0.1)	−5.1 [0.7]	−0.5 [0.1]
Mean	2819 (985)	12.0 (12.3)	25.8 (3.8)	32.4 (1.5)	34.4 (0.3)	2.5 (0.9)	0.8 (0.4)	0.3 (0.2)	2.3 [34.5]	0.2 [3.7]

^a Plume surface area, S, in km²; Scheldt discharge, Q, in 10⁶ m³ d^{−1}; dissolved inorganic phosphorus, DIP, in mmol m^{−3}; nonconservative fluxes of dissolved inorganic phosphorus, Δ DIP, in μ mol P m^{−2} d^{−1}; net ecosystem production, NEP, in mmol C m^{−2} d^{−1}. Numbers in parentheses refer to the standard deviations of the different averaged parameters, and numbers in brackets refer to the computed standard errors based on a Monte Carlo procedure (see text for details).

are characterized, under low nutrients concentration (probably nitrates), by the formation of an extracellular matrix rich in polysaccharides, leading to a C/P molar ratio higher than 106:1 [Lancelot and Mathot, 1987; Schoemann et al., 2005]. In culture experiments, Jahnke [1989] showed that the C/P molar ratio of *Phaeocystis* sp under DIP deficiency conditions ranged between 128:1 and 568:1. Using these two extreme values, the NEP computed for April 2003 would range between 2.2 and 9.7 mmol C m^{−2} d^{−1}.

[27] Finally, Gazeau et al. [2005] pointed out the fact that, due to abiotic processes such as DIP adsorption and desorption to and from suspended particles and/or sediment, the use of a C/P stoichiometrically linked budget to estimate NEP in the Scheldt inner estuary was strongly biased. These authors suggested net adsorption processes in the oligohaline part, while desorption processes could have introduced a bias in their results in the marine part of the estuary (due to an increase of pH; see Froelich [1988] for details). As suspended matter concentrations are of the same order of magnitude in the plume as the mouth of the estuary (L.-S. Schiettecatte, unpublished results), DIP desorption from suspended particles in the plume could be significant compared to DIP changes due to organic matter production and degradation. Indeed, Gazeau et al. [2005] estimated potential DIP desorption rates in the marine part of the inner Scheldt estuary ranging between 0.2 and 0.8 mmol P m^{−2} d^{−1}, which if applicable to our study site

would have lead to a strong underestimation of NEP.

3.3. Air-Sea CO₂ Fluxes in the Scheldt Plume

[28] Figure 8 shows the air-sea CO₂ fluxes computed for the Scheldt plume, from 2001 to 2004, from the survey area (blue circles) and Zeebrugge station (red squares) approaches using wind speed data from station Vlakte van de Raan and the *k*-wind parameterization of Nightingale et al. [2000]. The air-sea CO₂ fluxes computed at the Zeebrugge station were, most of the time, one order of magnitude higher than those computed from the survey area approach. This is related to the higher pCO₂ values at the Zeebrugge station as discussed above. For instance, both approaches showed that in 2002 the Scheldt plume was on average a net source of CO₂ to the atmosphere of 19 (±4) and 2 (±3.1) mmol C m^{−2} d^{−1} for, respectively, Zeebrugge station and survey area approaches. A sink of atmospheric CO₂ was only observed during the spring phytoplanktonic bloom for the area survey and Zeebrugge station approaches (up to −40 mmol C m^{−2} d^{−1}) in relation with the highest NEP observed in April (1.8 mmol C m^{−2} d^{−1}, Figure 7). During the rest of the year, surface waters were a source of CO₂ to the atmosphere, even during the late summer bloom when a positive NEP value was estimated (October). Strong wind speed short terms events (up to 20 m s^{−1}, Figure 2) were also responsible for high air-sea

CO₂ fluxes, up to 22 mmol C m⁻² d⁻¹ for the survey area approach (referred to as U₁₀ in Figure 8). Other events could be responsible for extreme air-sea CO₂ flux values at the Zeebrugge station, such as the presence of lower salinity with higher pCO₂ and/or remineralization of resuspended organic matter (referred to as S and DIC in Figure 8). These processes could be directly associated to storm events, although the presence of lower salinity waters was also dependent on the overall wind speed direction.

[29] Figure 7a shows that there was a general agreement in the trends of ecosystem metabolism and air-sea CO₂ fluxes. The sink of atmospheric CO₂ was observed during the autotrophic spring period while the highest emission of CO₂ to the atmosphere occurred during the strongly heterotrophic summer period. However, discrepancies were observed on a monthly basis: from early February to mid March, the Scheldt plume was a source of CO₂ to the atmosphere although characterized by a positive NEP. A similar situation was also observed in late May and October. Besides the potential problems associated with the use of a C/P stoichiometrically linked budget discussed above, processes other than organic carbon production and consumption can contribute to air-sea CO₂ fluxes, such as inputs of CO₂ from the inner Scheldt estuary, as discussed hereafter.

[30] Table 3 shows annually integrated air-sea CO₂ fluxes based on the survey area approach. On the basis of results from 2002, which was the year with the best temporal coverage, the plume of the Scheldt acted as a net source of CO₂ to the atmosphere of 0.7 (±1.1) mol C m⁻² yr⁻¹ (N&al). By contrast, in 2001, the plume of the Scheldt would be a sink for atmospheric CO₂ (-1.7 ± 1.8 mol C m⁻² yr⁻¹; N&al). In 2003 and 2004, CO₂ fluxes were higher than in 2002, respectively (2.6 ± 1.1 and 1.9 ± 1.7 mol C m⁻² yr⁻¹). As shown in Figure 8, there was a lack of data in 2001 during summer, when surface waters showed the highest CO₂ oversaturation and consequently high CO₂ emissions to the atmosphere. In 2003 and 2004, the lack of data during the spring phytoplanktonic bloom led to the overestimation of the annually integrated air-sea CO₂ flux. This clearly highlights the need of a strong temporal coverage in DIC dynamics studies for coastal environments.

[31] Air-sea CO₂ fluxes computed for 2002 from the survey area approach using wind speed data from the offshore station Europlatform (Figure 1)

gave values similar to the ones based on wind speed data from station Vlakte van de Raan, located in the plume (0.7 ± 1.0 mol C m⁻² yr⁻¹ for N&al, not shown in Table 3). The use of wind speed data from the two coastal meteorological stations (Cadzand and Vlissingen) gave lower air-sea CO₂ fluxes in 2002, respectively 0.2 (±0.8) and 0.4 (±0.6) mol C m⁻² yr⁻¹ using the N&al parameterization (not shown in Table 3). Wind speed measurements at Cadzand and Vlissingen are affected by orographic effects; hence the computed air-sea CO₂ fluxes are lower than those computed from data obtained at the other meteorological stations.

[32] The *k*-wind parameterization from L&M was determined from SF₆ mass balance budgets in lakes. According to Wanninkhof [1992], tracers experiments in lakes give *k* values that are underestimates for open ocean conditions at the same given wind speed due to fetch limitation. This could explain the lower CO₂ flux values computed using *k*-wind L&M relation, 0.5 (±0.9) mol C m⁻² yr⁻¹ for 2002 than those computed using the other parameterizations (Table 3). Fluxes computed from *k*-wind parameterization of W and W&McG gave higher values than those computed from the N&al parameterization, respectively 1 (±1.4) and 1.3 (±1.3) mol C m⁻² yr⁻¹, using wind speed data from station Vlakte van de Raan for 2002 (Table 3). The W, W&McG and N&alk-wind parameterizations were established for open ocean conditions but using different approaches. The W*k*-wind relationship is based on an ocean average gas transfer velocity derived from the global ocean inventory of bomb ¹⁴C of DIC given by Broecker *et al.* [1985]. The W&McG*k*-wind relationship is based on CO₂ covariance measurements in the North Atlantic and the fit to data was established to constrain the global ocean inventory of bomb ¹⁴C of DIC given by Broecker *et al.* [1985]. It has been claimed that the bomb radiocarbon ocean inventory of Broecker *et al.* [1985] is an overestimate; hence the W and W&McG parameterizations would overestimate *k* [Hesshaimer *et al.*, 1994; Peacock, 2004]. The N&alk-wind parameterization is based on two experiments with dual tracers (SF₆ and ³He) carried out in the SBNS.

[33] The annually integrated air-sea CO₂ fluxes we computed in this study for year 2002 are about 50% lower than of those computed by Borges and Frankignoulle [2002] (Table 3). These authors estimated annual air-sea CO₂ areal fluxes from a composite annual cycle based on campaigns car-

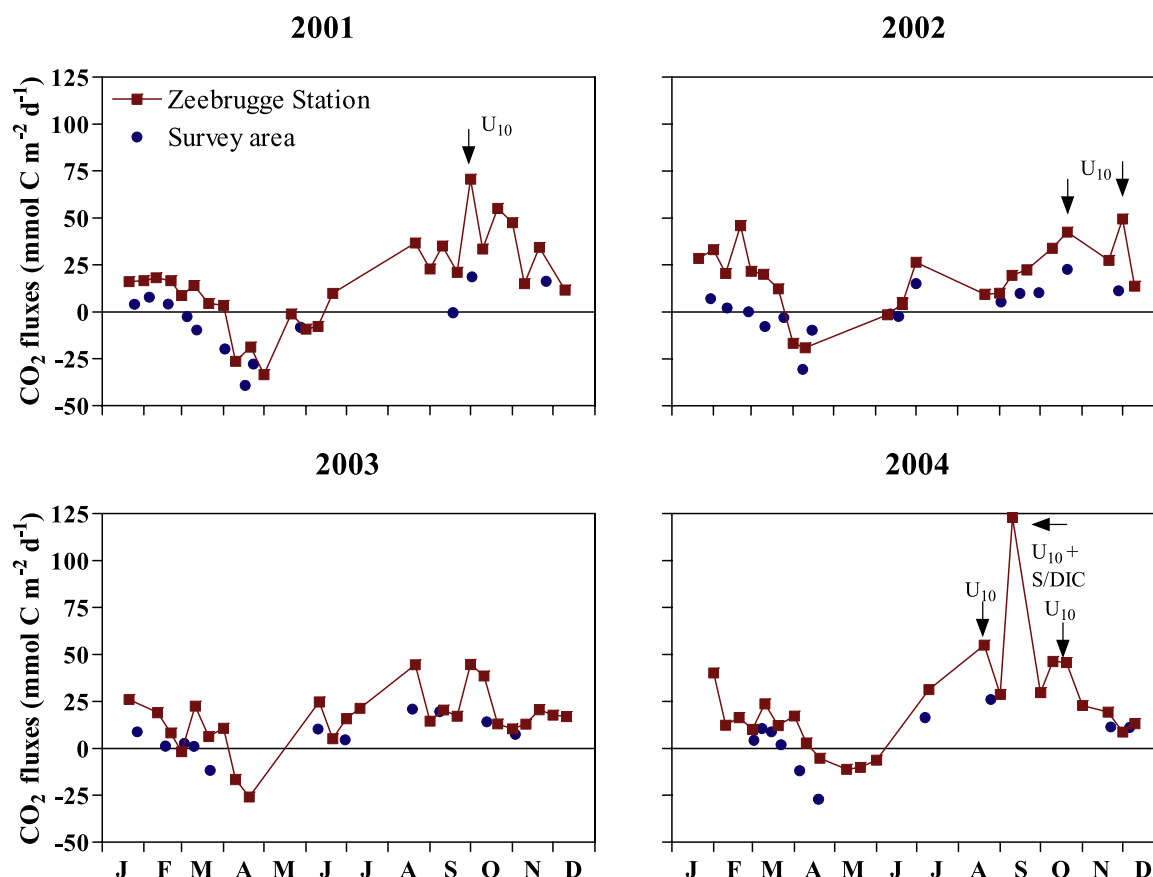


Figure 8. Air-sea CO₂ (mmol C m⁻² d⁻¹) fluxes from spatially integrated data (survey area approach; blue circles) and at Zeebrugge station (red squares) from 2001 to 2004. For air-sea CO₂ fluxes computation, the gas transfer velocity parameterization as a function of wind speed given by *Nightingale et al.* [2000] and wind speed data from station Vlakte van de Raan were used. U₁₀ refers to strong wind speed events, S refers to an observed decrease of salinity, and DIC refers to inputs of dissolved inorganic carbon from the sediments.

ried out over 4 years (1996 to 1999). This approach probably biased the air-sea CO₂ fluxes toward higher values, since the annual average $\Delta p\text{CO}_2$ value of *Borges and Frankignoulle* [2002] is more than two times higher than the one we obtained for 2002, 16 and 7 μatm , respectively.

[34] The net annual emission from the Scheldt plume (Table 3) ranges between 1.0 (± 3.7) and 3.1 (± 5.4) Gmol C yr⁻¹ depending on the gas transfer velocity parameterization. This represents between 7 and 22% of the emission of CO₂ from the inner Scheldt estuary of 141 Gmol C yr⁻¹ given by *Frankignoulle et al.* [1998] and between 9 and 27% of the emission of CO₂ from the inner Scheldt estuary of 112 Gmol C yr⁻¹ given by *Gazeau et al.* [2005]. These CO₂ emission estimates are below those given by *Borges and Frankignoulle* [2002] of 2.3 to 4.4 Gmol C yr⁻¹ because the latter values are derived from higher air-sea CO₂ flux estimates as discussed above, and to the use of a constant surface area for the plume

of 2100 km² (here we used plume surface area values on cruise by cruise basis).

3.4. DIC Budget in the Scheldt Plume: Preliminary Results

[35] Annually integrated, TΔDIC from the inner estuary represents 1.6 Gmol C yr⁻¹ (123% of the air-sea CO₂ fluxes in 2002; 1.3 Gmol C yr⁻¹, Table 3). Biological processes have been shown to be important drivers of pCO₂ seasonal variations within the Scheldt plume, but estimates of NEP based on a DIP budget suffer from several problems (see above). However, the estimated NEP (0.3 Gmol C yr⁻¹) allows to balance the DIC input/output budget. It could then suggest that an additional organic carbon input is not necessary to explain the CO₂ emission from the Scheldt plume as originally assumed by *Borges and Frankignoulle* [2002]. This assumption was based on an inorganic and organic carbon budget that suffered from a bias in the areal air-sea CO₂ flux

Table 3. Annually Integrated Air-Sea CO₂ Fluxes in the Scheldt Plume Computed Using Surface Water pCO₂ Data Acquired During the Survey Area, the Gas Transfer Velocity Parameterizations as a Function of Wind Speed, as Well as Wind Speed Data From Station Vlakte van de Raan^a

	Year	L&M	W	W&McG	N&al
<i>Fluxes, mol C m⁻² yr⁻¹</i>					
This study	2001	−1.3 (1.4)	−2.1 (2.3)	−1.7 (2.0)	−1.7(1.8)
	2002	0.5 (0.9)	1.0 (1.4)	1.3 (1.3)	0.7 (1.1)
	2003	2.0 (0.7)	3.3 (1.2)	2.9 (0.9)	2.6 (1.1)
	2004	1.4 (1.3)	2.4 (2.1)	2.0 (1.9)	1.9 (1.7)
Borges and Frankignoulle [2002]	1996–1999	1.1	2.0	2.8	1.5
<i>Emissions, Gmol C yr⁻¹</i>					
This study	2002	1.0 (3.7)	1.9 (6.2)	3.1 (5.4)	1.3 (5.0)
Borges and Frankignoulle [2002] ^b	1996–1999	2.3	4.2	4.4	3.1
% of the Scheldt estuary emission					
Frankignoulle et al. [1998]		7	13	22	9
Gazeau et al. [2005]		9	17	27	12

^a Air-sea CO₂ fluxes in mol C m⁻² yr⁻¹. Gas transfer velocity parameterizations as a function of wind speed given by Liss and Merlivat [1986] (L&M), Wanninkhof [1992] (W), Wanninkhof and McGillis [1999] (W&McG), and Nightingale et al. [2000] (N&al). Numbers in parentheses indicate standard errors of the computed fluxes. Annually integrated CO₂ emissions from the Scheldt plume were estimated from these computed fluxes and estimated surface areas of the plume during each survey. These CO₂ emissions are compared to the ones calculated by Frankignoulle et al. [1998] and Gazeau et al. [2005] in the inner Scheldt estuary.

^b CO₂ emission estimated from the annually integrated fluxes and a mean surface area of 2100 km².

estimates and from the use of a constant surface area of the plume, as discussed above. This is also consistent with the model of Soetaert and Herman [1995] that simulates an almost full consumption of river POC (90%) with the Scheldt inner estuary (i.e., only 10% is exported to the adjacent coastal zone). In the same way, carbon inputs of the Rhine/Meuse estuary and French estuaries (Seine and Somme) would have a negligible effect on the carbon dynamics off the Belgian coast. Another assumption that could emerge from this is that DIC mass balance budgets can be highly sensitive to the choice of the *k*-wind parameterization. The use of annually integrated air-sea CO₂ fluxes computed from other *k*-wind parameterizations also leads to inconsistencies in the present DIC mass balance budget, as also shown, for instance, in the Scheldt inner estuary [Gazeau et al., 2005].

4. Conclusions

[36] In the case of a heterogeneous and dynamic coastal ecosystem, such as an estuarine plume, a data set from a fixed station allows to describe qualitatively the dynamics of pCO₂ and its main biogeochemical drivers. However, the reliable computation of air-sea CO₂ fluxes requires a survey area approach with a high temporal and spatial resolution. Indeed, short-term events at daily to weekly scales related to strong winds and/or biological processes can generate high air-sea CO₂

fluxes and bias the direction and intensity of the net annual air-sea CO₂ flux in the case of low temporal sampling coverage.

[37] In the Scheldt estuarine plume, biological processes compared to temperature effects dominate the seasonal variations of pCO₂. A LOICZ mass balance budget of DIP showed an alternation of autotrophic and heterotrophic periods in accordance to previously described succession of phytoplankton species and biomass, and heterotrophic organisms. The patterns in the seasonal pCO₂ and air-sea CO₂ flux variations are consistent with the alternation of autotrophic and heterotrophic periods. However, the use of a LOICZ mass balance budget based on DIP is problematic because of physiological characteristics of *Phaeocystis* sp. that dominates the spring bloom biomass and production in the study area. Importantly, the polysaccharide-matrix characteristic of the *Phaeocystis* sp. colonies leads to significant variations in the carbon to phosphorous molar ratio. Also, *Phaeocystis* sp. can grow on dissolved organic phosphate during dissolved inorganic phosphate depletion. Gazeau et al. [2005] also attributed discrepancies in the inner Scheldt estuary between the NEP computed from the LOICZ modeling procedure based on DIP and the one from in situ oxygen incubations to DIP desorption from particles.

[38] The plume of the Scheldt is on an annual scale a net source of CO₂ to the atmosphere (0.7 mol C

$\text{m}^{-2} \text{yr}^{-1}$). On the basis of a preliminary DIC budget, we hypothesized that the inputs of CO_2 from the Scheldt inner estuary are largely responsible for the net annual CO_2 emission to the atmosphere from the plume.

Acknowledgments

[39] We thank the captains and crew of the R/V *Belgica* as well as Joan Backers (Management Unit of the North Sea Mathematical Models) for their help in running the underway pCO_2 system, Management Unit of the North Sea Mathematical Models for thermosalinograph data, S.V. Smith for its invaluable help for the implementation of the LOICZ budget, and two anonymous referees for pertinent and constructive comments on a previous version of the manuscript. This research was supported by the European Union in the framework of the EURO-TROPH project (contract EVK3-CT-2000-00040) and the CARBOOCEAN project (contract 511176-2), by the Belgian Federal Office for Scientific, Technical and Cultural Affairs (contract EV/12/20C) and by the Fonds National de la Recherche Scientifique (contract 2.4545.02), where A.V.B. is a research associate. This is MARE publication 83 and NIOO publication 3817. This work is dedicated to Michel Frankignoulle, former director of the Chemical Oceanography Unit, who left us on 13 March 2005.

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