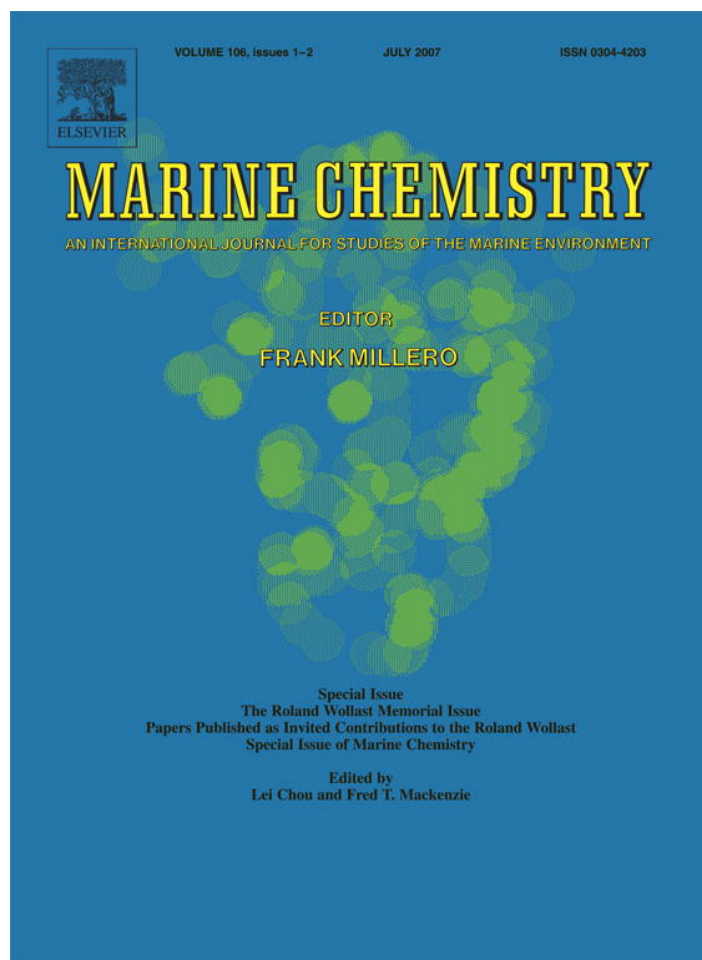


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High temporal coverage of carbon dioxide measurements in the Southern Bight of the North Sea

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Abstract

A monthly survey of the partial pressure of CO₂ (pCO₂) was carried in the Southern Bight of the North Sea (SBNS) from June 2003 to May 2004. The spatial variability of the surface distribution of the pCO₂ was relatively small (within a range of 10–70 μatm) compared to the amplitude in the seasonal signal (~260 μatm). On an annual scale, the pCO₂ dynamics appeared to be controlled by biological processes (primary production in springtime and respiratory processes in summer), rather than temperature (in summer). The comparison with measurements carried out in 2001 and 2002 (13 cruises) shows that the inter-annual variability of pCO₂ was close to the range of the spatial variability and mostly observed in spring, associated to biological processes (primary production). Net ecosystem production estimated from dissolved inorganic carbon (DIC) temporal variations showed that the SBNS is autotrophic, at an annual rate of 6.3 mol C m⁻² yr⁻¹. The decoupling in time between autotrophy in spring and heterotrophy in summer, associated to the relatively rapid flushing time of the water mass in the area (~70 days), might allow the export of a fraction of the springtime synthesized organic matter to the adjacent areas of the North Sea. The SBNS was on a yearly basis a sink of atmospheric CO₂ at a rate of -0.7 mol C m⁻² yr⁻¹.

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Keywords: North Sea; Scheldt estuary; Air–sea CO₂ fluxes; Dissolved inorganic carbon; Net ecosystem production; Biological pump

1. Introduction

The representation of the present-day CO₂ fluxes and the understanding of their biogeochemical drivers are essential requirements to reliably validate numerical models, as well as to strengthen their predictive capabilities on future increase of atmospheric CO₂. It is well established that open oceanic waters are a major sink for anthropogenic CO₂, absorbing about 48% of the CO₂

emissions related fossil fuels burning and cement production (Sabine et al., 2004). However, coastal ecosystems remain grossly under-represented in global present-day CO₂ budgets. Estimates of the global CO₂ sink over marginal seas based on scaled CO₂ fluxes (F_{CO_2}) computed from field measurements of the partial pressure of CO₂ (pCO₂) or from carbon mass balances range between -0.2 and -1.0 PgC yr⁻¹ (Tsunogai et al., 1999; Chen, 2004; Thomas et al., 2004; Borges, 2005; Borges et al., 2005). This wide range of estimates reflects to some extent the latitudinal and ecosystem variability of coastal environments, but also to a large extent the insufficient data coverage in these heterogeneous and

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dynamic environments. Nevertheless, such values are comparable to the open ocean sink of atmospheric CO_2 estimated to -1.6 PgC yr^{-1} (Takahashi et al., 2002).

The Southern Bight of the North Sea (SBNS from the Dover Strait to 53°N , Fig. 1) is a permanently well-mixed coastal zone that receives high inputs of nutrients and organic and inorganic carbon from the Scheldt, Rhine/Meuse and Thames estuaries, and indirectly from the Seine through inputs from the English Channel. Previous studies in the SBNS reported measurements of pCO_2 along transects or survey approaches at seasonal or annual scales (Kempe and Pegler, 1991; Hoppema, 1991; Bakker et al., 1996; Frankignoulle and Borges, 2001; Borges and Frankignoulle, 2003; Thomas et al., 2004). These studies based on different temporal and spatial coverages of pCO_2 in surface waters of the SBNS report a broad range of pCO_2 and F_{CO_2} values. Indeed, in dynamic and heterogeneous coastal ecosystems, the two sampling approaches (high spatial coverage with low temporal resolution versus high temporal resolution at a fixed station) can lead to uncertainties regarding the pCO_2 dynamics and the direction and amplitude of F_{CO_2} (e.g. Schiettecatte et al., 2006).

In the present study, the spatial distribution and temporal variability of surface water pCO_2 in the SBNS are investigated based on 23 cruises from 2001 to 2004, with a monthly dataset from June 2003 to May 2004. We

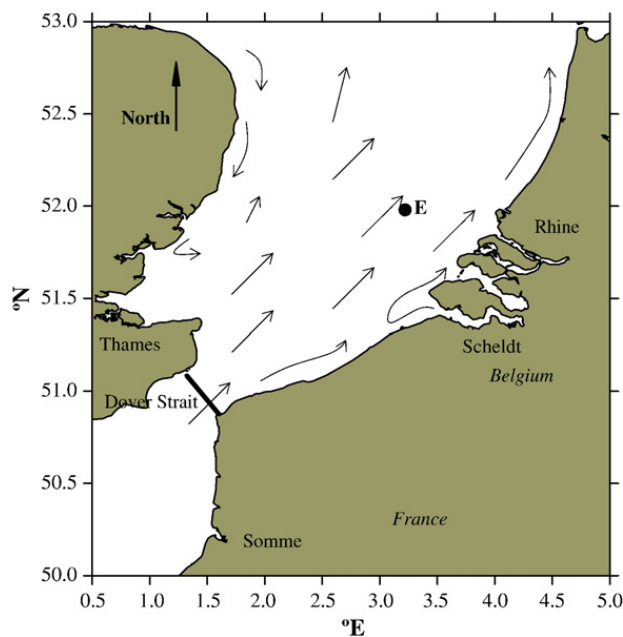


Fig. 1. Map of the studied area. Arrows represent general pattern of surface currents within the area. Black line shows the limit of the English Channel. The filled circle shows the location of the wind speed station (Europlatform, E) used for the computation of air–sea CO_2 fluxes.

attempt to address the biogeochemical drivers of the seasonal pCO_2 dynamics and some of the factors involved in the inter-annual pCO_2 variability. Net ecosystem production (NEP) is estimated from the temporal variation of dissolved inorganic carbon (DIC), and F_{CO_2} . The latter estimates allow us to characterize the SBNS as a source or a sink for atmospheric CO_2 .

2. Materials and methods

Data were obtained from 2001 to 2004 from 23 cruises on board of the *R.V. Belgica*. The ship tracks are shown in Figs. 2 and 3. Cruises always started from Zeebrugge harbour, close to the mouth of the Scheldt estuary (3.18°E 51.3°N), and data were collected to a longitude of 0.5°E and to latitude of 53°N , when possible (Fig. 1). Underway parameters (salinity, temperature and pCO_2) were sampled with a 1 min 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. pCO_2 was measured by means of a non-dispersive infrared gas analyzer (IRGA, Li-Cor®, Li-6262) and an equilibrator (Frankignoulle et al., 2001). For further details on the equilibrator 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 of a CO_2 molar fraction of 366 and 810 ppm (Air Liquide Belgium), calibrated against two National Oceanic and Atmospheric Administration (NOAA) standards with a CO_2 molar fraction of 361 and 774 ppm. The temperature at the outlet of the equilibrator was monitored with a platinum resistance thermometer (PT100, METROHM®), with an estimated accuracy of $\pm 0.05^\circ\text{C}$. The pCO_2 values were corrected for the temperature difference between *in-situ* seawater and water in the equilibrator using the algorithm proposed by Copin-Montégut (1988, 1989) and then corrected to the local barometric pressure. The accuracy of the pCO_2 measurement by equilibration was estimated to $\pm 2 \mu\text{atm}$ (cumulated errors on temperature correction and instrument calibration). Oxygen (O_2) concentrations were measured in 2003 with a 1 min frequency using a galvanic electrode calibrated daily against discrete samples, and every 30 min by discrete sampling in 2004. In parallel of O_2 sampling, total alkalinity (TA) discrete surface samples were also taken. O_2 and TA were measured using respectively the Winkler method and the Gran electrotitration method. The accuracy of TA measurements was $\pm 3 \mu\text{mol kg}^{-1}$. The oxygen saturation level ($\%\text{O}_2$) was computed from the observed concentration of dissolved O_2 and the concentration of

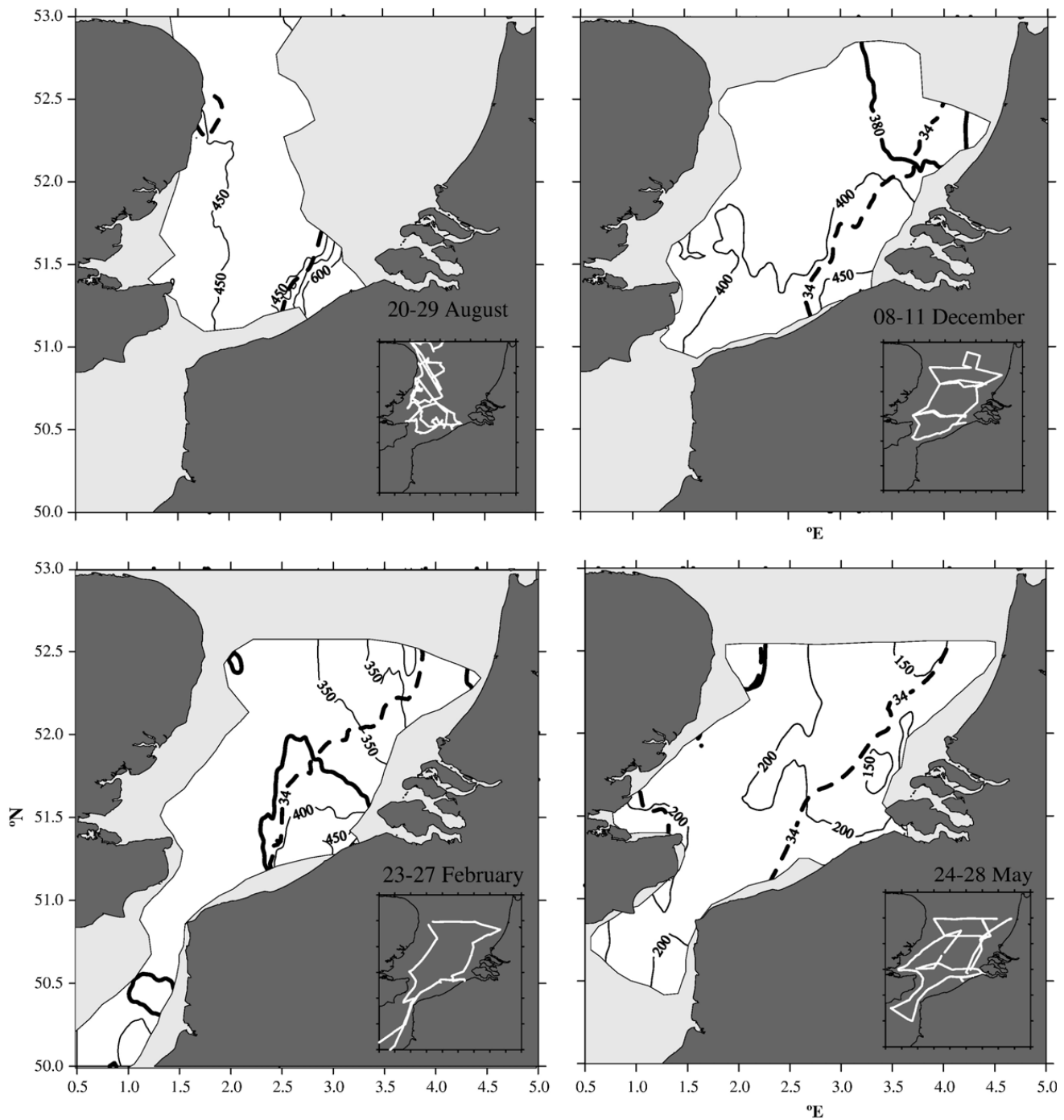


Fig. 2. Surface distribution of the partial pressure of CO_2 (pCO_2) in the Southern Bight of the North Sea (SBNS) and adjacent areas (English Channel) in August and December 2003, and in February and May 2004. The black line shows the limit of estuarine plumes defined by the 34 isohaline. The black bold line shows the atmospheric equilibrium. Inserts show the ship tracks.

O_2 at saturation calculated according to Benson and Krause (1984). The accuracy of O_2 measurements was $\pm 0.5 \mu\text{mol kg}^{-1}$ (0.2% of level of saturation). DIC was computed from pCO_2 and TA measurements using carbonic acid constants given by Roy et al. (1993), dissociation constants of boric acid given by Dickson (1990) and the CO_2 solubility coefficient (α) given by Weiss (1974). The accuracy of DIC computed from TA

and pCO_2 were estimated to be $\pm 5 \mu\text{mol kg}^{-1}$ (cumulated errors on TA and pCO_2).

F_{CO_2} was computed from the pCO_2 air–sea gradient ($\Delta\text{pCO}_2 = \text{pCO}_2 - \text{pCO}_{2\text{atm}}$, where $\text{pCO}_{2\text{atm}}$ refers to values in the atmosphere), α , and the gas transfer velocity (k) according to:

$$F_{\text{CO}_2} = \alpha k \Delta\text{pCO}_2 \quad (1)$$

We used nominally the k parameterization as function of wind speed given by Nightingale et al. (2000), established in the North Sea. For comparative purposes with previous studies, computations were also carried out with the k parameterizations as function of wind speed given by Wanninkhof (1992), and Wanninkhof and McGillis (1999). We used the wind speed (u_{10}) data measured at the meteorological station Europlatform (3°22'E 51°98'N) provided by the Royal Netherlands Meteorological Institute (<http://www.knmi.nl/samenw/hydra>).

As the SBNS is bordered by industrialized countries, the atmospheric CO₂ signal is expected to be increased by continental CO₂ (e.g. Bakker et al., 1996; Borges and Frankignoulle, 2003). As there is no apparent trend in wind direction in this area (OSPARCOM, 2002) and as pCO_{2atm} was not measured during the cruises, 2 stations located in the North Sea were chosen as (1) continentally influenced (Kollumerwaard, 6.17°E 53.20°N, referred as K hereafter), and (2) free of continental CO₂ contamination (Shetland station, 1.15°W 60.10°N,

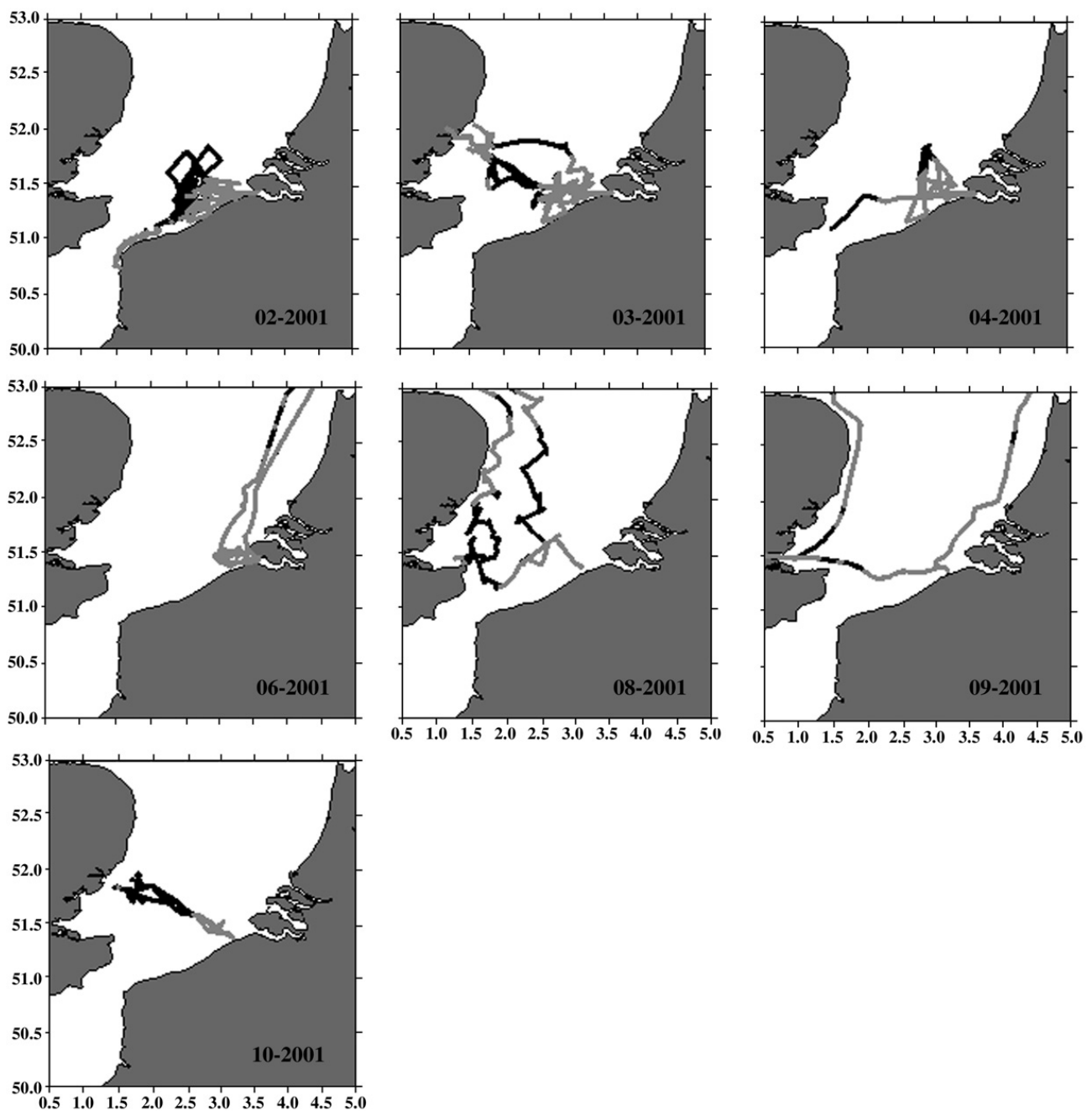


Fig. 3. Ship track for cruises from 2001 to 2002 (MM-YY). Grey tracks show surface area covered by the estuarine plumes. Left axis: Latitude (50 to 53 °N), right axis (0.5 to 5 °E).

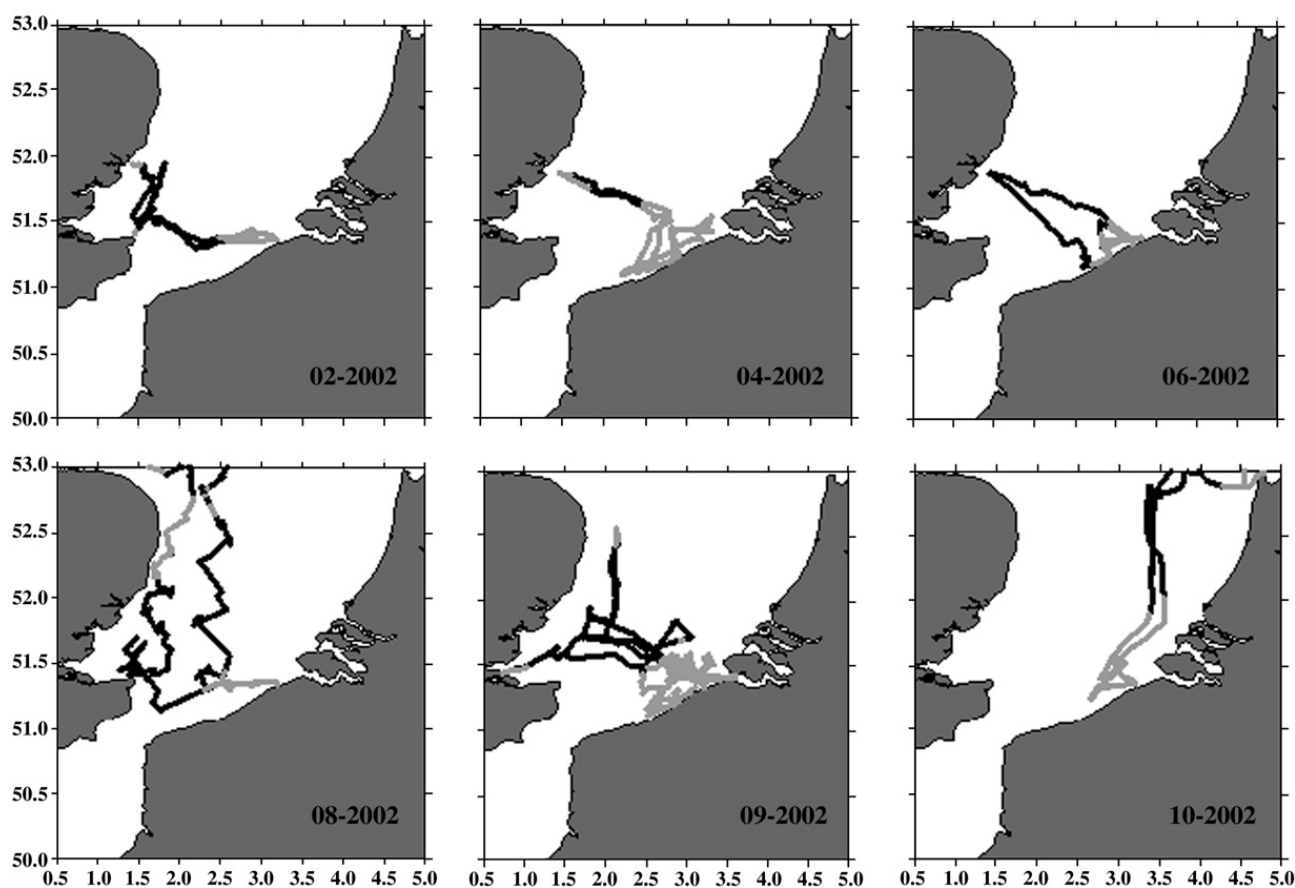


Fig. 3 (continued).

referred as S hereafter). Data from K were provided by the Dutch National Air Quality Monitoring Network supplied by the National Institute of Public Health and Environment and data from S were provided by the GLOBALVIEW-CO₂ (2006) (<ftp.cmdl.noaa.gov>, Path: <cog/co2/GLOBALVIEW>). Monthly pCO_{2atm} (in dry air) were compared with pCO_{2atm} measurements obtained in the SBNS during 4 cruises in 2001 and 2002 (September and November 2001, March and May 2002) during a carbon and nutrient cycling study in the same area of the North Sea (Thomas et al., 2004) (Table 1). As the measurements of pCO_{2atm} from the latter study were in between those from K and S (Table 1), monthly means of pCO_{2atm} from the 2 stations were used to compute ΔpCO_2 . Values of pCO_{2atm} in dry air were converted into pCO_{2atm} in wet air according to Dickson and Goyet (1994).

The net ecosystem production (NEP, in mmol C m⁻² day⁻¹) was computed from the temporal DIC variations from August 2003 to May 2004, according to the following equation:

$$NEP = \frac{(DIC_1 - DIC_2) \times d}{\Delta t} - F_{CO_2} \quad (2)$$

where DIC₁ and DIC₂ are the mean values in mmol m⁻³ during two consecutive cruises, F_{CO_2} in mmol C m⁻² day⁻¹ is the mean F_{CO_2} for the two cruises, Δt is the time interval in days between the two cruises, and d is depth in m. The computations were carried out using a mean depth of 30 m (based on measurements on board of the *R.V. Belgica*), and when Δt did not exceed the average flushing time in the area of about 73 days (OSPARCOM, 2002).

This method is suitable for permanently well-mixed and shallow systems such as the SBNS since it does not require the determination of seasonally variable mixed layer depths and provides an integrated signal

Table 1

Monthly atmospheric pCO₂ (in ppm, in dry air) for stations Kollumerwaard (K) and Shetland (S) in 2001 and 2002, and the mean pCO_{2atm} measurements (in ppm, in dry air) from Thomas et al. (2004) in the Southern Bight of the North Sea

Month	K	S	Mean K and S	Thomas et al. (2004)
September 2001	373	363	368	364
November 2001	381	373	377	383
March 2002	392	378	385	383
May 2002	395	378	386	383

for the pelagic and benthic compartments. We assume that the DIC dynamics is only driven by air–sea CO_2 exchange and production/degradation of organic matter. Calcium carbonate production/dissolution is assumed to be negligible based on the current knowledge of this area (Borges and Frankignoulle, 1999, 2002; Frankignoulle and Borges, 2001; Gypens et al., 2004; Schiettecatte et al., 2006). The major caveat of this method is that the advective inputs/outputs of DIC must be assumed to be constant during two cruises. This uncertainty can be assumed minimal as long as the time step (time interval between two cruises) is lower than the flushing time (~ 73 days, OSPARCOM, 2002).

3. Results and discussion

3.1. Spatial distribution and seasonal cycle of $p\text{CO}_2$

Fig. 2 shows for the annual cycle 2003–2004 the seasonal variations of the spatial distribution of $p\text{CO}_2$ in the surface waters of the SBNS and adjacent areas (eastern English Channel), while Fig. 4 show the monthly averages of $p\text{CO}_2$, $\% \text{O}_2$, TA and DIC for the SBNS excluding the eastern English Channel. For a given cruise, the $p\text{CO}_2$ distribution in the SBNS was quite homogeneous, as the amplitude of spatial variations ranged between 10 and 70 μatm (at most 50 μatm when estuarine plumes are excluded, e.g. for the area with salinities > 34), which was relatively small compared to the amplitude of the seasonal signal (~ 260 μatm , Table 2). Maximum and minimum $p\text{CO}_2$ values in the SBNS were observed in August and April 455 ± 36 and 192 ± 35 μatm , respectively, Table 2). Higher $p\text{CO}_2$ values were observed along the Belgian coastal zone (BCZ e.g. eastern part of the SBNS including the Scheldt plume; up to 900 μatm in August) related to the discharge of DIC rich waters from the heterotrophic inner Scheldt estuary (for details on the $p\text{CO}_2$ dynamics in the BCZ refer to Borges and Frankignoulle, 1999, 2002; Schiettecatte et al., 2006). During winter, the SBNS was oversaturated in CO_2 with respect to the atmosphere, when temperature ($\sim 6.3 \pm 0.3$ $^\circ\text{C}$ in February) and biological activities (O_2 close to atmospheric equilibrium, Fig. 4A) were at the lowest. According to the spatial distribution of $\% \text{O}_2$ (data not shown) the onset of the diatom phytoplanktonic bloom was in March (Rousseau et al., 2002), outside of the Scheldt and Rhine/Meuse plumes, due to better light penetration outside the plumes (Van bennekomp and Wetsteijn, 1990). The phytoplanktonic bloom then spread within 3 weeks to the entire studied region as shown by the

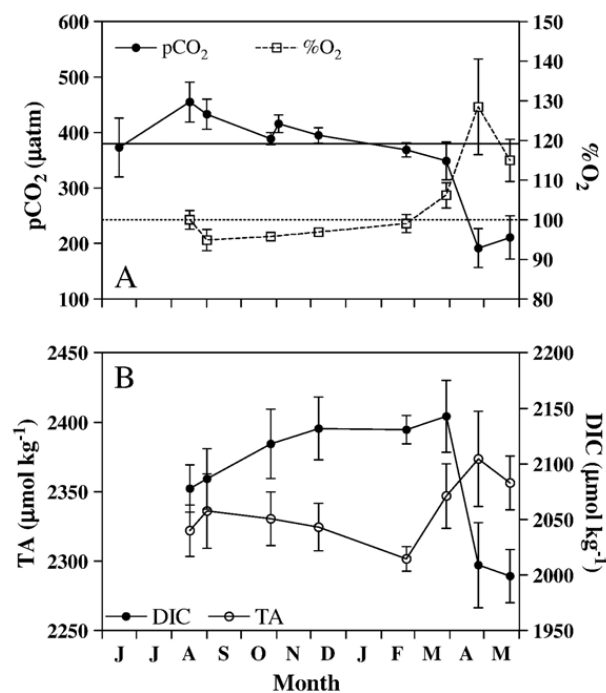


Fig. 4. Monthly averaged values for the Southern Bight of the North Sea (SBNS) from June 2003 to May 2004 of: (A) partial pressure of CO_2 ($p\text{CO}_2$, in μatm filled circles) and percentage of oxygen saturation ($\% \text{O}_2$, empty squares) and (B) Total alkalinity (TA, empty circles) and dissolved inorganic carbon (DIC, filled circles) in $\mu\text{mol kg}^{-1}$. Error bars represent standard errors of the means. Average atmospheric equilibrium of $p\text{CO}_2$ and O_2 are shown as solid and dotted lines, respectively.

strong CO_2 undersaturation in April–May ($p\text{CO}_2 \sim 190$ μatm ; Figs. 2 and 4A) and high $\% \text{O}_2$ (120% for the SBNS, and up to 180% for the Scheldt plume, data not shown). The $p\text{CO}_2$ decrease in the SBNS was also mirrored by a DIC decrease between February and May of about 150 $\mu\text{mol kg}^{-1}$, whereas TA increased by about 70 $\mu\text{mol kg}^{-1}$ (Fig. 4B). The mean nitrate concentration within the BCZ from a 7 years survey (1993–2000) is about 31 μM with maximum values of 140 μM for salinities < 33 and about 50 μM for salinities > 33 (De Galan et al., 2004). High nitrate concentrations were also reported in the BCZ by van Der Zee and Chou (2005) and Lancelot et al. (2005), respectively 80 and 50 μM . The TA increase should then be related to the assimilation of nitrate by phytoplankton as the uptake of 1 mole of nitrate causes an increase of 1 mole of TA (Brewer and Goldman, 1976).

During early summer (June 2003, data not shown), two contrasting patterns were observed: while the most of the SBNS remained CO_2 undersaturated, the Scheldt plume was strongly CO_2 oversaturated. Strong heterotrophic activities had already started in June 2003 in the Scheldt plume, unlike the rest of the SBNS.

Table 2
Means of the partial pressure of CO₂ (pCO₂, in μatm), pCO₂ normalized at 12.6 °C (pCO_{2@12.6 °C}), salinity and temperature (°C) in the Southern Bight of the North Sea (SBNS), for years 2001, 2002 and annual cycle 2003–2004

	2001			2002			2003–2004					
	pCO ₂	pCO _{2@12.6 °C}	Salinity	Temperature	pCO ₂	pCO _{2@12.6 °C}	Salinity	Temperature	pCO ₂	pCO _{2@12.6 °C}	Salinity	Temperature
January	385 (±44)	502 (±75)	33.0 (±1.7)	6.7 (±0.8)	369 (±15)	454 (±25)	34.2 (±0.6)	8 (±0.3)	369 (±13)	490 (±23)	34.3 (±0.5)	6.3 (±0.3)
February	344 (±40)	450 (±56)	32.5 (±1.4)	6.6 (±0.4)	230 (±45)	266 (±53)	32.1 (±0.9)	9.3 (±0.1)	349 (±34)	443 (±44)	34.3 (±0.6)	7.3 (±0.4)
March	149 (±30)	178 (±35)	30.7 (±2.4)	8.6 (±0.2)	364 (±30)	316 (±21)	33.7 (±0.7)	15.9 (±0.6)	192 (±35)	210 (±39)	34.2 (±0.8)	10.7 (±0.4)
April	260 (±24)	230 (±20)	30.8 (±1.2)	15.3 (±0.7)	479 (±38)	370 (±30)	34.3 (±0.4)	18.9 (±0.5)	211 (±39)	216 (±42)	34.2 (±0.6)	12.2 (±0.6)
May	423 (±47)	328 (±33)	34.0 (±0.3)	18.7 (±0.5)	477 (±40)	377 (±33)	33.1 (±0.8)	18.5 (±0.3)	373 (±53)	324 (±34)	34.2 (±0.7)	15.8 (±1.0)
June	436 (±60)	381 (±57)	33.0 (±0.9)	15.9 (±0.5)	432 (±47)	378 (±49)	32.9 (±1.2)	16 (±0.6)	455 (±36)	343 (±23)	34.4 (±0.3)	19.4 (±0.4)
July	422 (±31)	374 (±31)	34.1 (±0.5)	15.5 (±0.6)	416 (±16)	427 (±32)	34.4 (±0.5)	12.1 (±0.9)	433 (±27)	332 (±20)	34.3 (±0.3)	19.0 (±0.2)
August					395 (±14)	440 (±27)	34.5 (±0.4)	10.2 (±0.7)	389 (±11)	384 (±19)	34.3 (±0.4)	12.9 (±0.6)
September									416 (±16)	427 (±32)	34.4 (±0.5)	12.1 (±0.9)
October									395 (±14)	440 (±27)	34.5 (±0.4)	10.2 (±0.7)
November												
December												

Numbers in brackets refer to the standard errors.

3.2. Biological effects versus temperature

In order to separate and assess the seasonal effects of biological processes and temperature on the pCO₂ dynamics over an annual cycle, the method developed by Takahashi et al. (2002) was applied on the data from June 2003 to May 2004. This method gives a qualitative information on the effect of temperature and the “net biology effect” on the pCO₂ dynamics. As defined by Takahashi et al. (2002), the “net biology effect” (Eq. (3)) includes all the biogeochemical processes acting on net CO₂ utilization (primary production, respiration), changes of TA by nitrate consumption, air–sea CO₂ exchange and changes of DIC by advection of different waters and freshwaters discharges. Following the Takahashi et al. (2002) method, the temperature effect was removed from the observed pCO₂ by normalizing the pCO₂ data at the annual mean temperature (12.6 °C for 2003–2004), Eq. (3). The effect of temperature is assessed by perturbing the mean annual pCO₂ (358 μatm) with the difference between annual mean temperature and observed temperature, Eq. (4). Biological (*B*) and thermal (*T*) effects on the pCO₂ (pCO_{2B} and pCO_{2T}) were thus calculated for each month from June 2003 to May 2004 according to the following equations:

$$(B) \quad pCO_{2B} = pCO_2(T_{\text{mean}}) \\ = pCO_2 \cdot \exp(0.0423 \cdot (T_{\text{mean}} - T_{\text{obs}})) \quad (3)$$

$$(T) \quad pCO_{2T} = pCO_2(T_{\text{obs}}) = (\text{mean annual } pCO_2) \\ \times \exp(0.0423 \cdot (T_{\text{obs}} - T_{\text{mean}})) \quad (4)$$

where T_{mean} is the mean annual temperature (12.6 °C) and T_{obs} is the *in-situ* temperature.

The effect of *B* and *T* on the amplitude of the seasonal variations of pCO₂ are determined, respectively, from the amplitude of pCO_{2B} and pCO_{2T}. A *T/B* ratio greater than 1 implies the dominance of temperature effects over biological processes on the pCO₂ dynamics. Fig. 5 shows the seasonal variations of the δpCO₂, δpCO_{2B}, δpCO_{2T} (differences calculated using the February values, which have the lowest temperatures and biological activities). Maximum |δpCO_{2B}| values were observed during the spring phytoplanktonic bloom (April–May; ~270 μatm) while maximum δpCO_{2T} values were observed in August (~200 μatm). From February to May, biological CO₂ draw down, *i.e.*, photosynthesis, was the main driver of the surface waters pCO₂ dynamics, as *T/B* ~ 0.29 (*T*–*B* = –195), whereas from June to December temperature was the main driver of pCO₂ dynamics (*T/B* = 1.34; *T*–*B* = 39). Over an

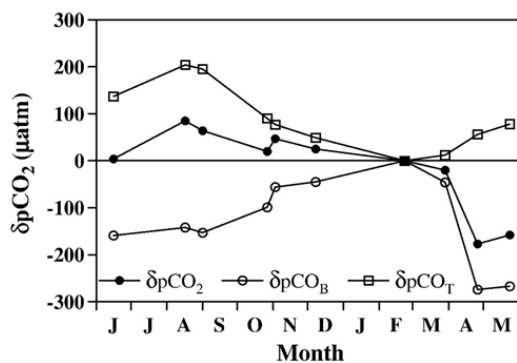


Fig. 5. $\delta p\text{CO}_2$ (filled circles) $\delta p\text{CO}_{2T}$ (filled squares) and $\delta p\text{CO}_{2B}$ (empty circles) for the Southern Bight of the North Sea (SBNS), calculated as the difference with February, from June 2003 to May 2004.

annual cycle, the dynamics of the surface $p\text{CO}_2$ in the SBNS was mainly controlled by biological activities, with a T/B ratio of 0.74 ($T-B=-70$). As stated above, all biogeochemical processes such as estuarine inputs are inherently included in the term “Biological” in the $p\text{CO}_{2B}$ computations. However, when estuarine plumes are excluded in the computations (data with salinity ≥ 34 , data not shown) the annual T/B ratio is rather similar (0.79).

These results differ from those reported by Thomas et al. (2005a) who suggested that the surface $p\text{CO}_2$ dynamics in the SBNS was seasonally controlled by temperature rather than by biology with maximum $|\delta p\text{CO}_{2B}|$ and $\delta p\text{CO}_{2T}$ of 100 and 135 μatm , respec-

tively, and a T/B of 1.35. Fig. 7 shows that the late May 2002 cruise from the Thomas et al. (2005a) study was carried out during the declining phase of the phytoplankton bloom, and that this data-set does not adequately account for the strong CO_2 under-saturation in the SBNS typically observed in mid-April during the peak of the phytoplankton bloom (Reid et al., 1990; Borges and Frankignoulle, 1999, 2002, 2003; Frankignoulle and Borges, 2001; Rousseau et al., 2002; Gypens et al., 2004; Schiettecatte et al., 2006).

3.3. Net ecosystem production

An ecosystem is defined as autotrophic if NEP is positive, *i.e.* when gross primary production (GPP) exceeds community respiration (CR), and as heterotrophic when CR exceeds GPP (Odum, 1956). There are several ways to appraise the metabolic status of an ecosystem, as reviewed by Gazeau et al. (2004) for European coastal zones. Here, we used a simple approach to compute NEP ($\text{mmol C m}^{-2} \text{ day}^{-1}$) based on the temporal DIC variations according to the Eq. (2), from August 2003 to May 2004 (Table 3 and Fig. 6).

The SBNS was heterotrophic from mid-August to March (-6.0 to $-23.9 \text{ mmol C m}^{-2} \text{ day}^{-1}$), and was autotrophic from April to May, with strongest NEP value in April ($161.3 \text{ mmol C m}^{-2} \text{ day}^{-1}$). At an annual scale the SBNS was strongly autotrophic at a rate of $\sim 17.3 \text{ mmol C m}^{-2} \text{ day}^{-1}$. When estuarine plumes were excluded from the computations (data not shown),

Table 3

Monthly averaged dissolved inorganic carbon (DIC in mmol m^{-3}), density (in kg m^{-3}), air–sea CO_2 fluxes (F_{CO_2} in $\text{mmol C m}^{-2} \text{ day}^{-1}$) computed with the k parameterization given by Nightingale et al. (2000), time interval between cruises (Δt in days) and net ecosystem production (NEP in $\text{mmol C m}^{-2} \text{ day}^{-1}$) in the Southern Bight of the North Sea (SBNS), calculated for a mean depth of 30 m from the annual cycle from August 2003 to May 2004

Cruise	DIC (mmol m^{-3})	Density (kg m^{-3})	F_{CO_2} ($\text{mmol C m}^{-2} \text{ day}^{-1}$)	$\Delta t(d)$	NEP ($\text{mmol C m}^{-2} \text{ day}^{-1}$)
August	2128 (21)	1024.4 (0.2)	6.8 (0.2)	15	-23.9
September	2137 (27)	1024.3 (0.4)	4.2 (0.2)	56	-23.5
October	2173 (31)	1025.9 (0.3)	4.5 (0.0)	42	-14.2
December	2189 (29)	1026.6 (0.2)	1.4 (0.1)	77	0.4
February	2188 (13)	1026.8 (0.3)	-2.1 (0.1)	35	-6.0
March	2200 (32)	1026.5 (0.5)	-5.3 (0.3)	28	161.3
April	2061 (39)	1025.9 (0.7)	-19.1 (0.1)	28	27.2
May	2050 (24)	1025.8 (0.5)	-13.1 (0.0)		17.3
Mean					17.3

Numbers in parenthesis refer to standard error.

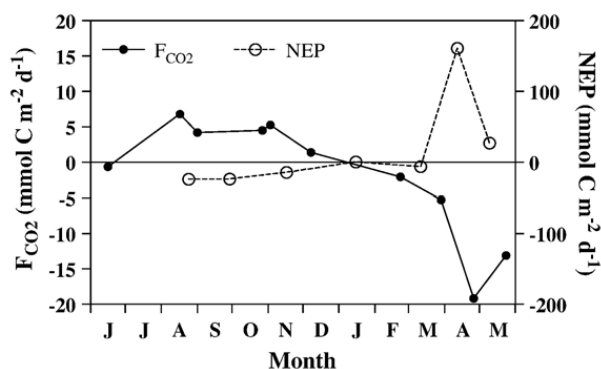


Fig. 6. Estimated net ecosystem production (NEP in $\text{mmol C m}^{-2} \text{ day}^{-1}$, empty circles) and monthly air–sea CO_2 fluxes (F_{CO_2} , $\text{mmol C m}^{-2} \text{ day}^{-1}$, filled circles) computed using the gas transfer velocity parameterization given by Nightingale et al. (2000) for the Southern Bight of the North Sea (SBNS) from June 2003 to May 2004.

annually integrated NEP remained relatively unchanged ($17.2 \text{ mmol C m}^{-2} \text{ day}^{-1}$). However, the SBNS (excluding the estuarine plumes) was autotrophic from mid-February to May (14.7 to $139.7 \text{ mmol C m}^{-2} \text{ day}^{-1}$), with strongest values in April ($139.7 \text{ mmol C m}^{-2} \text{ day}^{-1}$). Heterotrophy was lower from August to mid-January (-12.9 versus $-20.5 \text{ mmol C m}^{-2} \text{ day}^{-1}$, mean NEP values for that period when excluding and including estuarine plumes, respectively). Estuarine plumes receive nutrient inputs that can support higher GPP, but during summer heterotrophy is also stronger due to the higher organic matter availability from the spring phytoplankton blooms, and to a lesser extent due to the inputs of organic matter from inner estuaries. These trends in NEP are in agreement with previous studies in the BCZ and the Scheldt estuarine plume (Gypens et al., 2004; Schiettecatte et al., 2006).

These NEP values at annual scale and for the productive period (from February to August, $39.6 \text{ mmol C m}^{-2} \text{ day}^{-1}$, including estuarine plumes) are slightly higher but in fair agreement with those reported in the SBNS by Bozec et al. (2006), respectively, 10.1 and

$33.3 \text{ mmol C m}^{-2} \text{ day}^{-1}$. These authors estimated NEP from the data-sets of Thomas et al. (2004, 2005a,b), with a DIC mass balance at the scale of the whole North Sea, based on the water flows from European Regional Seas Ecosystem Model (Lenhart and Pohlmann, 1997) and using International Council for the Exploration of the Sea (ICES) boxes (the SBNS is divided into 2 ICES boxes). As mentioned above, the peak of phytoplanktonic bloom was not fully captured by the underlying data-sets, which can explain the slightly higher NEP values from our study, although the differences could also be due the methodological approaches or inter-annual variability. Our annual integrated NEP value is also in good agreement with the NEP value of $15.3 \text{ mmol C m}^{-2} \text{ day}^{-1}$ computed for the SBNS by Gattuso et al. (1998) based on the GPP and CR incubation based measurements of Joiris et al. (1982).

3.4. Air–sea CO_2 fluxes

From February to June, the SNBS was a sink of atmospheric CO_2 ranging from -0.6 to $-19.1 \text{ mmol C m}^{-2} \text{ day}^{-1}$ (respectively, in June and April), using the Nightingale et al. (2000) k parameterization, in agreement with its trophic status (Fig. 6). From August to December, the SNBS was a source of CO_2 to the atmosphere ranging from 1.4 to $6.8 \text{ mmol C m}^{-2} \text{ day}^{-1}$, also in agreement with its trophic status. On an annual scale, the SBNS was a net sink for atmospheric CO_2 at a rate of $-0.65 \text{ mol C m}^{-2} \text{ yr}^{-1}$. When estuarine plumes are excluded from the computations, annually integrated F_{CO_2} increased by about 20% (annual sink for atmospheric CO_2 at a rate of $-0.83 \text{ mol C m}^{-2} \text{ yr}^{-1}$; data not shown).

Previous studies carried out in the SBNS which attempted to assess its role as a sink or source of CO_2 on an annual scale are presented in Table 4. Although the dataset from Frankignoulle and Borges (2001) did not cover a complete annual cycle, these authors hypothesized that

Table 4

Comparison of air–sea CO_2 fluxes (F_{CO_2} in $\text{mmol C m}^{-2} \text{ day}^{-1}$) in the Southern Bight of the North Sea (SBNS), from the present study and literature, computed using the gas transfer velocity parameterization from Wanninkhof (1992), and Wanninkhof and McGillis (1999), referred, respectively, as W and W and McG

Month	This study			Frankignoulle and Borges (2001)		Thomas et al. (2004)	
	$\Delta p\text{CO}_2$	F_{CO_2} [W]	F_{CO_2} [W and McG]	$\Delta p\text{CO}_2$	F_{CO_2} [W]	$\Delta p\text{CO}_2$	F_{CO_2} [W and McG]
September	55	5.1	3.8			17.7	1.2
November	31	6.7	6.8	5	2.5	16.5	2.4
April	-182	-23.7	-20.7	-105	-58.4		
May	-170	-15.7	-12.2	-170	-27.1	-17.3	-2.4

the SBNS was an annual CO_2 sink. The F_{CO_2} values for April 1996 and May 1995 computed by Frankignoulle and Borges (2001) are about 2 times stronger than those computed in this study, due to differences in wind speed. Frankignoulle and Borges (2001) used in their computations a mean u_{10} of 9.6 m s^{-1} in April 1996 against 6.2 m s^{-1} in April 2004. In May 1995 and 2004, average u_{10} were respectively 5.1 and 5.3 m s^{-1} and $\Delta p\text{CO}_2$ values were similar. Frankignoulle and Borges (2001) computed F_{CO_2} with instantaneous u_{10} (1 min frequency) obtained during the 2 days transect, whereas F_{CO_2} in this study was computed with hourly u_{10} data measured during the full duration of the cruise. The differences in F_{CO_2} are due to the strong non-linear relationship between k and u_{10} , which can lead to significant differences due to the wind speed frequency distribution and the averaging methods used (e.g. Bates and Merlivat, 2001; Lüger et al., 2006).

The high temporal resolution of the present study allows us to provide evidence that the recent seasonal study by Thomas et al. (2004) did not capture the maximum extent of the $p\text{CO}_2$ minimum during spring in the SBNS. According to this study the SBNS (corresponding to the box 2 in their study) was an annual source of CO_2 at a rate of $0.2 \text{ mol C m}^{-2} \text{ yr}^{-1}$, while the present study identifies the SBNS as a CO_2 sink on an annual scale of $-0.7 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (Table 3).

3.5. Inter-annual variability of $p\text{CO}_2$

Fig. 7 shows for the SBNS the annual cycle of mean surface $p\text{CO}_2$ and $p\text{CO}_2@12.6^\circ\text{C}$ based on data obtained from June 2003 to May 2004, with additional data from 2001 to 2002. Table 2 gives the means (and standard errors) of the surface $p\text{CO}_2$, $p\text{CO}_2@12.6^\circ\text{C}$, salinity and temperature for data gathered from 2001 to 2004. Clear inter-annual variability was observed which in some cases can be explained by temperature, biological activities and mean salinity (e.g. estuaries discharges with higher DIC content). Temperature effect on the $p\text{CO}_2$ dynamics from one year to another is shown by the comparison of $p\text{CO}_2$ and $p\text{CO}_2@12.6^\circ\text{C}$ during summer (e.g. mid-August 2001–2003; mid-September 2001–2002). In other cases inter-annual variability of mean $p\text{CO}_2$ was related to differences in biological activity. The largest differences occurred during the spring bloom when mean $p\text{CO}_2$ values in April 2001 and 2002 were, respectively, $\sim 40 \mu\text{atm}$ lower and higher than in 2004. Inter-annual differences among the mean $p\text{CO}_2$ are consistent with Sea-viewing Wide Field-of-view Sensor (SeaWiFS) level-3 chlorophyll-a data (<http://reason.gsfc.nasa.gov/Giovanni/>). Concentration

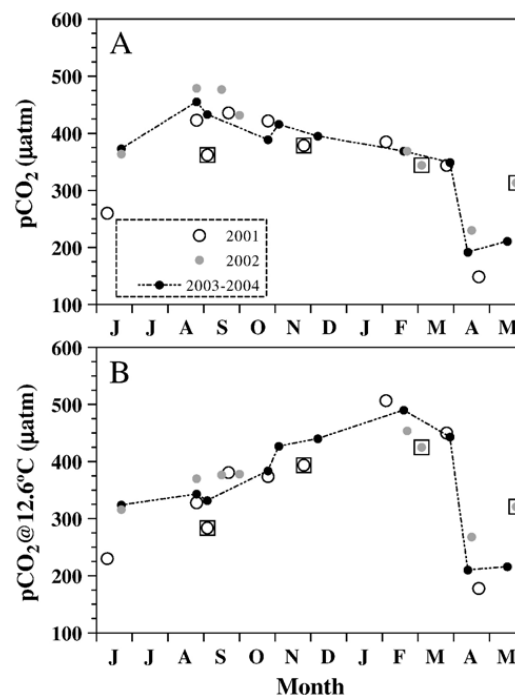


Fig. 7. Mean surface partial pressure of CO_2 ($p\text{CO}_2$) and $p\text{CO}_2$ normalized to a temperature of 12.6°C ($p\text{CO}_2@12.6^\circ\text{C}$) in the Southern Bight of the North Sea (SBNS), gathered from 2001 to 2004. Annual cycle from June 2003 to May 2004 is shown as black circles, $p\text{CO}_2$ measured during 2001 and 2002 are represented respectively by empty and grey circles. Data from Thomas et al. (2004) are identified with a square.

in chlorophyll-a (data not shown) was higher in April 2001 (up to $25 \mu\text{g l}^{-1}$), than in 2002 and 2004 for the same month (around $10 \mu\text{g l}^{-1}$), in agreement with the observed mean $p\text{CO}_2$ in April between the different years. From 2001 to 2004, phytoplankton biomass as shown by chlorophyll-a was variable from year to year in amplitude, but with a recurrent maximum during April. During spring 2004, chlorophyll-a increased from mid February and fluctuated around $10 \mu\text{g l}^{-1}$ until late June, whereas the phytoplanktonic bloom in 2002 last from March to May, with a moderate bloom during summer. Differences in mean $p\text{CO}_2$ for spring 2002 and 2004 could be related to both concentration in chlorophyll-a, mean salinity and/or temperature. Lower salinity (as it is the case for April 2002 compared to April 2004) would imply higher concentrations of nutrients and suspended matter.

The decrease of $p\text{CO}_2$ between mid-and late August 2001 could be due to a moderate summer bloom of diatoms (Reid et al., 1990; Gypens et al., 2004 from observations from 1996–1999), as suggested by oxygen concentrations slightly above atmospheric equilibrium for stations close to estuarine mouths in late August 2001 (Bozec et al., 2005). The increase of $p\text{CO}_2$ from

late August to mid-September 2001 might be related to a decrease of the mean salinity in the whole area from 34 to 33, respectively (Table 2), and related increase of DIC content in the estuarine plumes and/or to the degradation of organic matter produced by the bloom in late August.

Based on the MIRO biogeochemical model (Lancelot et al., 2005) constrained by global solar radiation, sea-water temperature and riverine nutrients loads, over the period 1989–2003, Gypens et al. (2007) suggested that inter-annual variability in diatom biomass depends on both meteorological conditions (light and temperature) and nutrient loads, whereas *Phaeocystis* sp. blooms are mainly controlled by nutrient availability. A CO₂ module was coupled to the MIRO model by Gypens et al. (2004) and validated at a single fixed station in the BCZ. This study showed that inter-annual variations of the pCO₂ in the Belgian coastal waters are strongly driven by nutrient availability and amplitude and timing of biological activity, owing to inter-annual variations of freshwater discharge and temperature.

4. Summary and conclusions

A monthly survey from June 2003 to May 2004 in the SBNS shows that the seasonal variations of the surface distribution of pCO₂ are mainly controlled by biological activity rather than by temperature. Comparison with data obtained in 2001 and 2002 shows that a relatively important inter-annual variability of pCO₂ occurs in the SBNS. This inter-annual variability is partly due to temperature but also to biological activity, in particular during the periods of the phytoplankton blooms in April and May. The SBNS is a sink for atmospheric CO₂ ($-0.7 \text{ mol C m}^{-2} \text{ yr}^{-1}$) mainly driven by autotrophic processes, as shown from the simple computation of NEP based on the temporal variation of DIC.

These results are in disagreement with the conclusions on air–sea CO₂ exchange based on the Thomas et al. (2004, 2005a) data-set that consists in 4 cruises in the whole North Sea. This disagreement is due to the fact that the May 2002 cruise in the data-set of Thomas et al. (2004, 2005a) was carried out during the declining phase of the phytoplankton bloom, implying that this data-set does not adequately account for the strong CO₂ under-saturation in the SBNS typically observed in mid-April during the peak of the phytoplankton bloom. The study by Thomas et al. (2004, 2005a) aimed at a basin wide study of the North Sea with a high vertical and horizontal resolution of dissolved inorganic carbon variables and nutrients. This brings to the fore the difficulty of reconciling high spatial and temporal

resolution for field based studies of biogeochemical variables and processes in coastal ecosystems.

High temporal resolution of measurements of pCO₂ is clearly a master key to provide reliable annually integrated air–sea CO₂ fluxes, and to assess the different drivers of pCO₂, particularly in highly dynamic and heterogeneous coastal environments, such as estuarine plumes or proximal continental shelves (e.g. Boehme et al., 1998; DeGrandpre et al., 2002; Friederich et al., 2002; Schiettecatte et al., 2006). On the other hand, basin wide regional coverage is required to quantify and understand large scale carbon cycling. Thus, Thomas et al. (2004) showed that the northern part of the North Sea followed the paradigm of the “continental shelf pump” as proposed by Tsunogai et al. (1999). This is due to the sequestration below the thermocline of the spring synthesized organic matter, which by respiratory processes enriches the deeper waters in DIC, that are subsequently transported to the adjacent North Atlantic. In contrast, DeGrandpre et al. (2002) showed that the Middle Atlantic Bight owed its potential to absorb CO₂ to wind-thermodynamic effects. As suggested by Thomas et al. (2004, 2005a) the permanently well-mixed SBNS does not follow either of these conceptual schemes of carbon sequestration. However, it seems to be an efficient biological pump for CO₂ due to the decoupling in time of biological processes (primary production at springtime and respiration processes in summer) combined to the relatively rapid flushing time in the area (~70 days). This combination might allow for a fraction of the organic matter synthesized during spring to escape remineralization within the area, and to be exported towards the German Bight.

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