

# Controls of the surface water partial pressure of CO<sub>2</sub> in the North Sea

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**Abstract.** The seasonal variability of the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) has been investigated in the North Sea, a northwest European shelf sea. Based on a seasonal and high spatial resolution data set the main controlling factors – biological processes and temperature – have been identified and quantified. In the central and northern parts being a CO<sub>2</sub>-sink all year round, the biological control dominates the temperature control. In the southern part, the temperature control dominates the biological control at an annual scale, since the shallow water column prevents stronger net-CO<sub>2</sub> removal from the surface layer due to the absence of seasonal stratification. The consequence is a reversal of the CO<sub>2</sub> sea-to-air flux during the spring bloom period, the only time, when CO<sub>2</sub> is taken up from the atmosphere in the southern region. Net community production in the mixed layer has been estimated to 4 mol C m<sup>-2</sup> yr<sup>-1</sup> with higher values (4.3 mol C m<sup>-2</sup> yr<sup>-1</sup>) in the northern part and lower values in the southern part (2.6 mol C m<sup>-2</sup> yr<sup>-1</sup>).

## 1 Introduction

During the recent years many research efforts have been devoted to the understanding and quantification of the ocean carbon cycle, which plays a key role in the global carbon cycle and thus in controlling climate on earth (IPCC, 2001). The world ocean and the atmosphere have been identified as the major sinks for anthropogenic CO<sub>2</sub>, while the role of the terrestrial biosphere remains uncertain (IPCC, 2001; Sarmiento and Gruber, 2002). Part of this uncertainty can be attributed to the uncertainty in the assessment of the ocean sink for anthropogenic CO<sub>2</sub>. Recent studies however seem

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to suggest that the ocean and the atmosphere entirely share the storage of the anthropogenic CO<sub>2</sub>, while the terrestrial biosphere seems to play a neutral role (Thomas et al., 2001; Sabine et al., 2004). Sabine et al. (2004) relied their observational approach on a global data set, obtained in the framework of large national and international research efforts during the past decade such as the World Ocean Circulation Experiment (WOCE) or the Joint Global Ocean Flux Study (JGOFS). Complementarily to this refinement of the open ocean assessment intense research campaigns have been initiated during the last years in the coastal oceans, of which carbon cycle was investigated only barely before. Carbon fluxes have been investigated in several coastal regions (Liu et al., 2000a, b; Chen et al., 2003). In order to achieve an integrative global assessment, the available information yet appears to be too sparse and more site studies are required (Borges, 2005; Borges et al., 2005).

Coastal and marginal seas host a disproportionately large fraction of ocean productivity, in part fueled by terrestrial, anthropogenic or oceanic nutrient inputs. Coastal seas constitute the major link between the terrestrial and the open ocean environments and buffer terrestrial impacts before affecting the oceanic systems. The high biological activity causes high CO<sub>2</sub> fluxes between coastal ocean and atmosphere and the open ocean, respectively. Depending on the hydrodynamic and topographic conditions the biologically initiated CO<sub>2</sub>-drawdown might finally supply the *continental shelf pump* (Tsunogai et al., 1999), a mechanism transferring atmospheric CO<sub>2</sub> into the open ocean exploiting biological metabolism of coastal seas. For example, the continental shelf pump seems to be very efficient in the East China Sea (Tsunogai et al., 1999) or the North Sea (Thomas et al., 2004), while in the Baltic Sea it works less efficiently (Thomas et al., 2003, 2005).

The North Sea has been subject to intense investigations for the last decades and the foundation for carbon cycle investigations here was probably laid in the late 1980s by a basin-wide study (Pegler and Kempe, 1988; Kempe and Pegler, 1991). A variety of rather regional or local studies have been conducted in the following years (e.g. Bakker et al., 1996; Frankignoulle et al., 1996; Borges and Frankignoulle, 1999, 2002, 2003; Frankignoulle and Borges, 2001) most notably providing insight in near shore carbon and CO<sub>2</sub> fluxes. Recently a basin-wide field study has been carried out focusing on the understanding and quantification of internal and cross-boundary carbon (and related nutrient) fluxes in the North Sea. First investigations balanced the CO<sub>2</sub> air-sea fluxes, investigated the functioning of the *continental shelf pump* at a seasonal scale (Thomas et al., 2004; Bozec et al., 2005a) or reported on an initial 1-box carbon budget (Thomas et al., 2005). The North Sea has been shown to act as a sink for atmospheric CO<sub>2</sub>, most of which is exported to the North Atlantic Ocean. In detail, the smaller southern part releases CO<sub>2</sub> to the atmosphere ( $-0.2 \text{ mol C m}^{-2} \text{ yr}^{-1}$ ), while the northern areas absorb CO<sub>2</sub> ( $1.7 \text{ mol C m}^{-2} \text{ yr}^{-1}$ ).

Here, we investigate the variability of the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in detail, which governs the CO<sub>2</sub> air-sea fluxes. Temperature effects will be unraveled from the biological processes controlling the pCO<sub>2</sub> applying the approach proposed by Takahashi et al. (2002). The consequences for the seasonal variability of the CO<sub>2</sub> air-sea fluxes are discussed. Finally, an estimate of the corresponding biological CO<sub>2</sub> draw-down, which is a measure for net community production (NCP), will be provided.

## 2 Material and methods

### 2.1 Data

The data have been obtained during 4 cruises in the North Sea covering all seasons in a consecutive order (18.8.2001–13.9.2001, 6.11.2001–29.11.2001, 11.2.2002–5.3.2002 and 6.5.2002–26.5.2002). The pCO<sub>2</sub> has been determined continuously in one-minute intervals from the surface waters using a continuous flow system as described by Körtzinger et al. (1996). The water was pumped from approximately 3m below the sea surface at a rate of 60 L min<sup>-1</sup>. The main water flow through the equilibrator was 2–3 L min<sup>-1</sup> and the difference between in-situ and equilibrator temperature was typically less than 0.5°C. The atmospheric pCO<sub>2</sub> has been determined every 2 h and the system was calibrated against standards provided by the National Oceanic and Atmospheric Administration (NOAA). Temperature and salinity have been determined continuously from the surface water in one-minute intervals. From 97 stations per cruise, dissolved inorganic carbon (DIC) and total alkalinity (A<sub>T</sub>) have been determined using the coulometric method according to Johnson et al. (1993) and a Gran potentiometric open cell

titration, respectively. The DIC measurements were calibrated against certified reference material provided by Prof. Dickson, Scripps Institution of Oceanography, La Jolla, CA, USA. The uncertainty of the DIC is 1–2 μmol kg<sup>-1</sup>. The uncertainty of A<sub>T</sub> was determined to 2–3 μmol kg<sup>-1</sup>.

### 2.2 Calculations

#### 2.2.1 Temperature vs. biological control

In order to identify and quantify the main factors controlling the variability of pCO<sub>2</sub> in the North Sea, we applied the calculation scheme proposed by Takahashi et al. (2002), which assumes the pCO<sub>2</sub> to be controlled solely by temperature and biological CO<sub>2</sub> drawdown. Other processes governing to pCO<sub>2</sub> such as changes in A<sub>T</sub>, riverine inputs, sediment/water column interaction and the air-sea exchange of CO<sub>2</sub> are neglected by this procedure and are attributed inherently to the biological signal. Accordingly, the temperature and biological signals can be unraveled using the observed pCO<sub>2</sub> and temperature data. In brief, the temperature effect can be removed by normalizing all pCO<sub>2</sub> data to an average temperature for all seasons:

$$\text{pCO}_2 \text{ at } T_{\text{mean}} = \text{pCO}_2 \text{ at } T_{\text{obs}} * \exp[0.0423(T_{\text{mean}} - T_{\text{obs}})], \quad (1)$$

where  $T_{\text{mean}}$  is the mean annual temperature and  $T_{\text{obs}}$  is the in-situ temperature at the time and location of the observation. The remaining variability of the pCO<sub>2</sub> is then controlled by the variations of DIC, assuming a constant A<sub>T</sub>. The temperature signal can be obtained from the average annual pCO<sub>2</sub> and the difference between  $T_{\text{obs}}$  and  $T_{\text{mean}}$ :

$$\text{pCO}_2 \text{ at } T_{\text{obs}} = \text{annual mean pCO}_2 * \exp[0.0423(T_{\text{obs}} - T_{\text{mean}})]. \quad (2)$$

The changes in the pCO<sub>2</sub> related to biological ( $\Delta\text{pCO}_{2, \text{bio}}$ ) and to temperature ( $\Delta\text{pCO}_{2, \text{temp}}$ ) effects, respectively, follow then as:

$$\Delta\text{pCO}_{2, \text{bio}} = (\text{pCO}_2 \text{ at } T_{\text{mean}})_{\text{max}} - (\text{pCO}_2 \text{ at } T_{\text{mean}})_{\text{min}}, \quad (3)$$

$$\Delta\text{pCO}_{2, \text{temp}} = (\text{pCO}_2 \text{ at } T_{\text{obs}})_{\text{max}} - (\text{pCO}_2 \text{ at } T_{\text{obs}})_{\text{min}}, \quad (4)$$

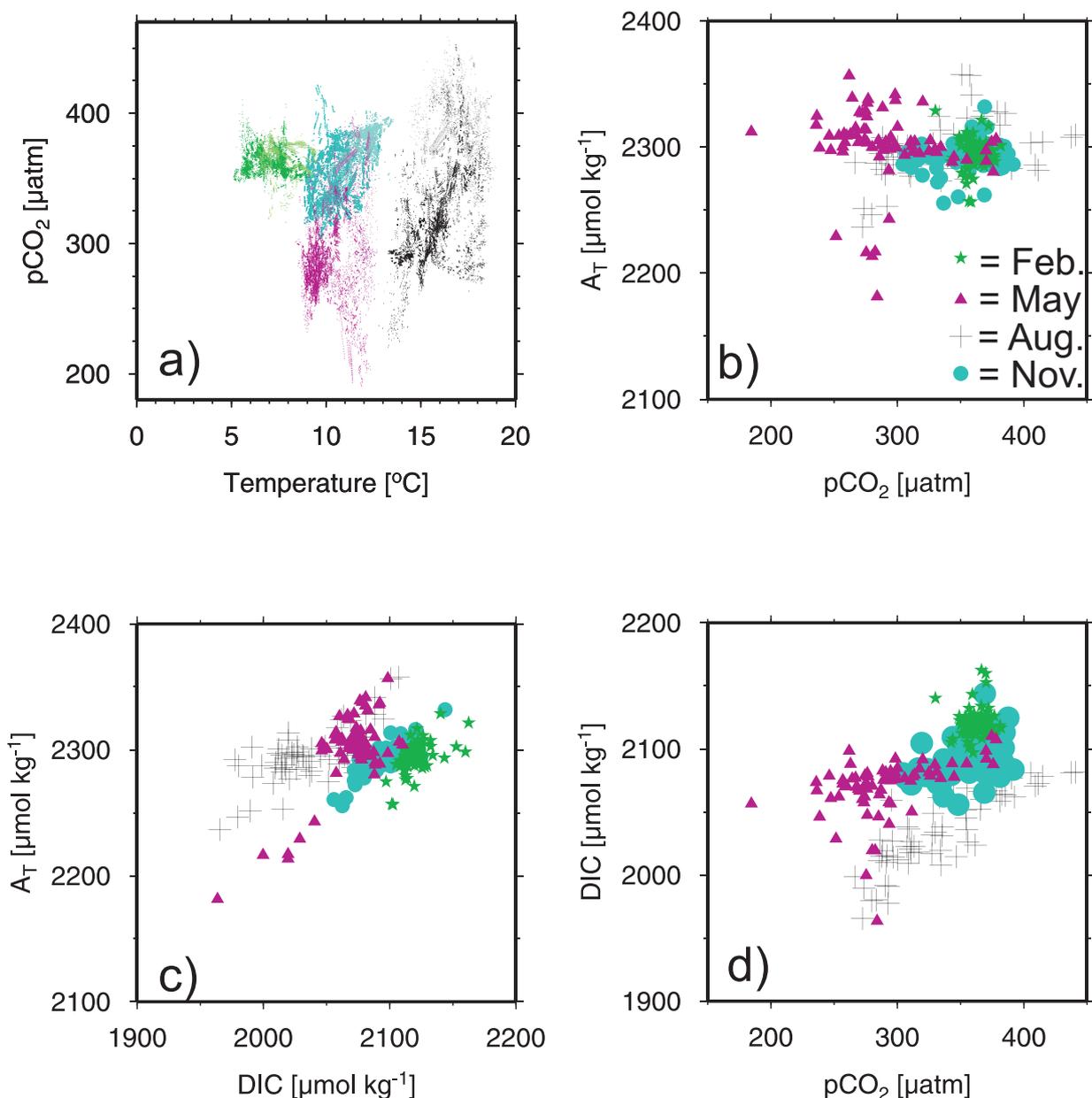
with the subscripts “max” and “min” indicating the annual maximum and minimum values.

In order to compare the magnitude of both temperature (T) and biological effects (B) either the ratio or the difference of the expressions  $\Delta\text{pCO}_{2, \text{bio}}$  and  $\Delta\text{pCO}_{2, \text{temp}}$  can be applied:

$$T - B = (\Delta\text{pCO}_{2, \text{temp}}) - (\Delta\text{pCO}_{2, \text{bio}}) \quad (5a)$$

$$T/B = (\Delta\text{pCO}_{2, \text{temp}}) / (\Delta\text{pCO}_{2, \text{bio}}) \quad (5b)$$

In areas with high seasonal variability of the biological activity the ratio (T/B) would be less than 1 or the difference (T-B) negative. In regions with weaker or annually rather constant biology, the (T/B) ratio would be larger than one or the difference positive, respectively.



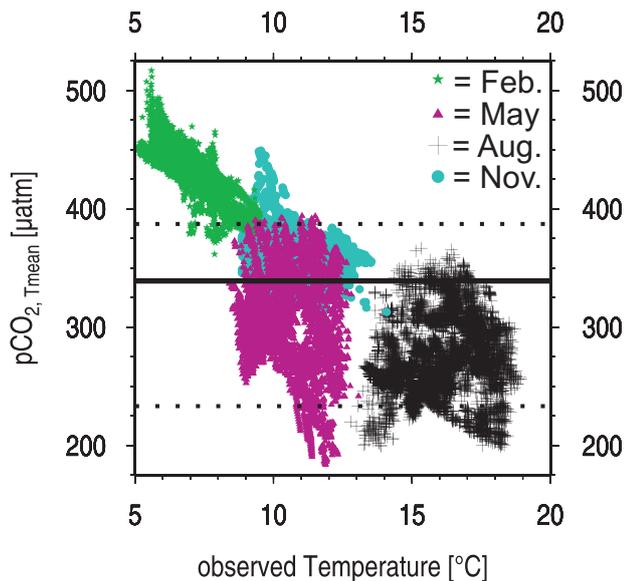
**Fig. 1.** Seasonal variability of the relationship between different surface water properties. (a) partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) vs. Temperature. (b) Total alkalinity (A<sub>T</sub>) vs. pCO<sub>2</sub>. (c) A<sub>T</sub> vs. dissolved inorganic carbon (DIC). (d) DIC vs. pCO<sub>2</sub>. The green stars indicate February (winter) data, the purple triangles May (spring) data, the black crosses the August (summer) data and the blue circle November (autumn) data, respectively. See inset in (b). The colors apply also to a) with the lighter colors indicating data south of 54° N and the darker colors data north of 54° N, respectively. All data have been projected onto the same grid.

### 2.2.2 Biological DIC uptake (net community production)

The above  $\Delta p\text{CO}_{2, \text{bio}}$  can be employed for the determination of the biological DIC uptake, i.e., the Net Community Production (NCP). Recently a procedure has been implemented to calculate any change in DIC as a function of a change in the pCO<sub>2</sub> and temperature and salinity (Thomas and It-

tekkot, 2001; Thomas et al., 2001). This procedure, originally proposed for the determination of anthropogenic CO<sub>2</sub> in the water column, is applied for the present purposes to obtain the biological DIC drawdown ( $\Delta\text{DIC}_{\text{bio}}$ ) as a function of  $\Delta p\text{CO}_{2, \text{bio}}$ , salinity ( $S$ ) and temperature ( $T$ , in °C):

$$\Delta\text{DIC}_{\text{bio}} = -199.6 + 0.89 * S + 0.42 * T + 0.6 * (\Delta p\text{CO}_{2, \text{bio}} + 276.8)$$



**Fig. 2.** pCO<sub>2</sub> values normalized to the average temperature of all observations (11.05°C) shown as function of their observational temperature. The lines indicate the observational, i.e., not normalized pCO<sub>2</sub> values at that temperature. The bold line shows the averaged observed pCO<sub>2</sub> for the temperature range 11.045°C–11.055°C, with the dotted lines showing the corresponding maximum and minimum values of that range, respectively. The remaining variability is attributed to biological changes.

(6)

For the calculations, an average salinity of 34 was assumed. In order to assess the corresponding NCP, an average depth of the mixed layer of 30 m was assumed.  $\Delta p\text{CO}_{2, \text{bio}}$  is obtained as the difference between the maximum and minimum pCO<sub>2</sub> at the annual mean temperature (3). The corresponding  $\Delta \text{DIC}_{\text{bio}}$  (6) allows us to compute NCP during the productive period February to August.

### 3 Results

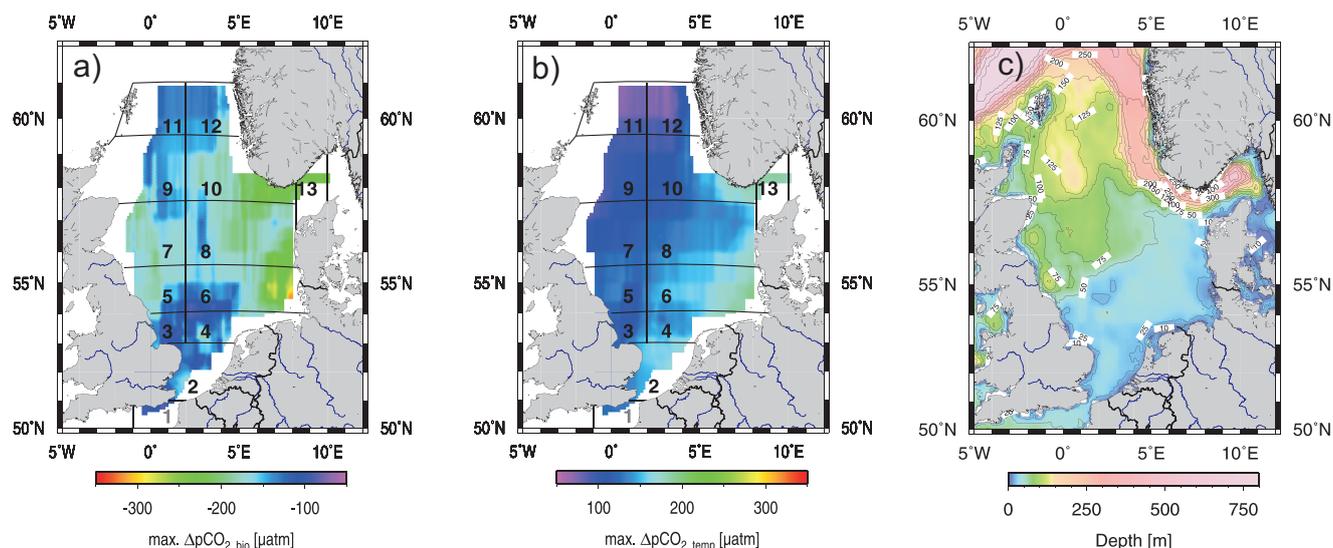
#### 3.1 Surface properties

The surface water properties of the North Sea (Fig. 1) during winter show a relatively homogenous behavior. The pCO<sub>2</sub> versus temperature relationship (Fig. 1a) reveals pCO<sub>2</sub> values between 360 µatm and 400 µatm throughout the entire North Sea. The temperatures range between 5°C and 10°C with slightly higher temperatures in the southern region of the North Sea. A<sub>T</sub> (Fig. 1b, c) shows homogenous behavior throughout the full annual cycle and only minor changes can be identified during spring, most likely as a consequence of fresh water inputs. In contrast, DIC shows a clear seasonal signal with highest values in winter and lowest values in summer (Fig. 1c, d). It is obvious that DIC undergoes

much more severe seasonal variations than A<sub>T</sub>. Clearly, the maximum DIC draw-down is observed in summer, this in contrast to pCO<sub>2</sub> that shows minimal values during spring (Fig. 1a, d). The most pronounced seasonal and also regional signals can be observed in the pCO<sub>2</sub> distributions with highest values during summer in the southern region (Fig. 1a, d) and lowest values in May throughout the North Sea. During all seasons the southern region shows higher pCO<sub>2</sub> values than the northern and central parts, and in summer opposing directions of the CO<sub>2</sub> air-sea flux are observed.

#### 3.2 Biological versus temperature controls

In order to give a brief overview, on how the method works, we compare the pCO<sub>2</sub> values observed at the mean temperature with the values corrected to the mean temperature. In Fig. 2 the average pCO<sub>2</sub> (339 µatm) observed at the mean temperature (11.05°C) is shown as well as the observed maximum (387 µatm) and minimum (233 µatm) at that temperature. The deviation from the average here can be seen as the variability of the biological effects on the pCO<sub>2</sub> at (uncorrected) mean temperature observations. Applying the correction according to (1) to all data then provides the variability of the biological effects for all seasons. Obviously the autumn and notably the winter data show an increase of the pCO<sub>2</sub> because of DIC release to the water column by remineralization processes, while the spring and summer values show decreased pCO<sub>2</sub> values as a consequence of biological DIC uptake, i.e., production of organic matter. The maximum values up to 330 µatm of the biologically induced pCO<sub>2</sub> changes ( $\Delta p\text{CO}_{2, \text{bio}}$ ), which reflects the net signal from production and respiration processes, are observed in the northern and central parts of the North Sea (Fig. 3a). Weaker effects of  $\Delta p\text{CO}_{2, \text{bio}}$  are observed in the southern part. The shallow (Fig. 3c), well mixed water column does not allow the spatial separation of organic carbon production in the surface waters from the degradation of organic carbon in the bottom waters that occurs in the stratified northern and central regions. The net biological signal is stronger in the northern region than in the southern region. The North-Sea-wide average biological CO<sub>2</sub> draw-down ( $\Delta p\text{CO}_{2, \text{bio}}$ ) is approximately 160 µatm indicating the North Sea as a highly productive area. This value is within the range observed in open oceanic waters from 50 µatm in the oligotrophic areas of the subtropics and tropics to 280 µatm in the highly productive upwelling regions of the Eastern equatorial Pacific (Takahashi et al., 2002). Temperature (Fig. 3b) shows a stronger control on pCO<sub>2</sub> in the southern and coastal, i.e., shallower regions. The shallow water column warms up faster and furthermore is not affected by the continuous inputs of large quantities of colder water from the North Atlantic Ocean (Thomas et al., 2005). Temperature increases the pCO<sub>2</sub> in the northern region by approximately 100 µatm, while in the south an increase of 200 µatm can be observed. The basin-wide maximum is approximately 200 µatm with



**Fig. 3.** Maximum changes in  $\Delta p\text{CO}_{2, \text{bio}}$  (a) and  $\Delta p\text{CO}_{2, \text{temp}}$  (b) calculated according to Takahashi et al. (2002). (c) Bottom topography of the North Sea using the ETOPO2 data set (National Geophysical Data Center: [www.ngdc.noaa.gov](http://www.ngdc.noaa.gov)). The grid structure is according to Thomas et al. (2004).

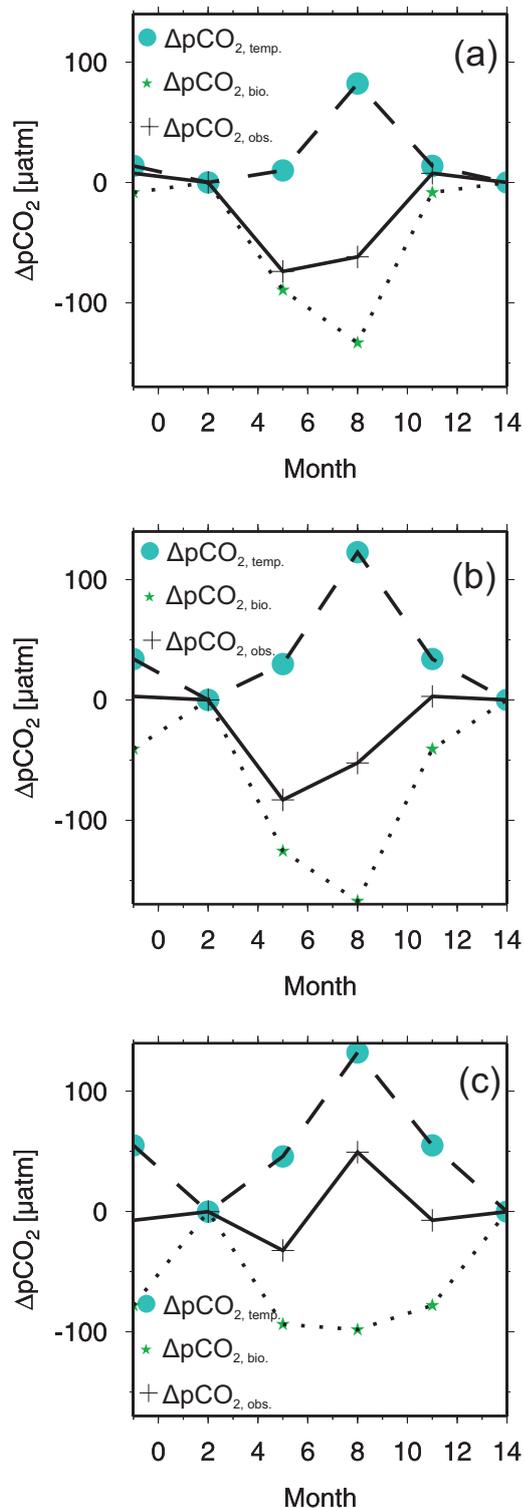
an average of  $130 \mu\text{atm}$ . This value is above the average of  $80 \mu\text{atm}$  observed in the open ocean at mid-latitudes, where maximum values of  $220 \mu\text{atm}$  are only observed in the confluence areas of the warm Kuroshio with the cold Oyashio current waters in the northwestern Pacific and of the warm Gulf Stream with the cold Labrador Current waters in the northwestern Atlantic (Takahashi et al., 2002).

A more detailed analysis allows us to identify and quantify the relevant regional features characterizing the CO<sub>2</sub> system in the North Sea. Three key areas are discussed: the deeper northern part of the North Sea (Fig. 4a), the central part (Fig. 4b), which still is stratified during summer, and the shallow continuously mixed southern part (Fig. 4c).

The northern region (Fig. 4a) shows the weakest temperature control, which is out competed by the biological CO<sub>2</sub> draw-down:  $60 \mu\text{atm}$  vs.  $-150 \mu\text{atm}$ , respectively. The annual cycle reveals lowest values in spring and summer, as expected for a high latitude sea. The opposite situation is found for the southern region, where the overall system appears to be temperature controlled with an observed pCO<sub>2</sub> maximum in summer (pCO<sub>2, temp</sub> up to  $135 \mu\text{atm}$ , pCO<sub>2, bio</sub> max:  $-100 \mu\text{atm}$ ). Only during a very short period in spring the biological control dominates and causes a net reduction of the pCO<sub>2</sub> compared to the winter values. The highest seasonal pCO<sub>2</sub> amplitude in the North Sea, observed in the central region, is generated by a synergistic coincidence of a somewhat lower temperature control compared to the southern region and of the presence of a thermocline, which permits the remineralization of the freshly produced and sunken organic matter below the surface layer. In the central region, the more rapid temperature rise during spring induces an ear-

lier establishment of the thermocline and thus a longer export pathway for the newly produced organic matter out of the surface layer leading to a higher biological signal compared to the northern region. The consequence is that the biological control is highest in the central region, while it is somewhat weaker in the northern areas, since the export of organic matter out of the surface layer is reduced compared to the central part because of the later onset of primary production and of the later rise of the thermocline. The stratification prevents the remineralization of the organic matter in the surface layer, which is the primary condition for the development of the biological net CO<sub>2</sub> drawdown over the entire productive period. This contrasted behavior is clearly visible by the summer maxima of  $\Delta p\text{CO}_{2, \text{bio}}$  in the northern and central region, since the stratification maintains the “accumulation” of the CO<sub>2</sub> drawdown until production decreases in later summer. In contrast, the absence of stratification in the south prevents this “accumulation”, showing the strongest  $\Delta p\text{CO}_{2, \text{bio}}$  only at its peak period during the bloom as compared to the other regions with the strongest  $\Delta p\text{CO}_{2, \text{bio}}$  at the accumulated maximum of the drawdown in late summer.

The consequences of the different controls on the CO<sub>2</sub> air-sea fluxes become evident when considering the seasonally resolved fluxes (Fig. 5). During winter (Fig. 5a) the North Sea appears to be a rather equilibrated system with regard to the CO<sub>2</sub> fluxes. With the onset of the spring bloom, all areas act as sinks for atmospheric CO<sub>2</sub>, even the shallower southern part, where the biological control out competes the temperature control as indicated in Fig. 4c. In summer, the central and northern parts continue absorbing



**Fig. 4.** Biological, temperature and observed  $\Delta p\text{CO}_2$  signals for three different regions of the North Sea: (a) 60° N 1° E, (b) 56° 1° E, and (c) 54° N 3° E. The data are shown as difference to February.

CO<sub>2</sub> from the atmosphere, but the increasing temperature and the remineralization of organic matter cause a flux reversal in the southern part that then emits CO<sub>2</sub> to the atmosphere (Fig. 5c). In autumn (Fig. 5d), primary production decreases in the North Sea enhancing the CO<sub>2</sub> release in the southern area; the northern area remains undersaturated, since the organic matter has been remineralized in bottom waters that are advected to the North Atlantic Ocean, which is subjected to water mass exchange with the Atlantic Ocean (Thomas et al., 2004). The decreasing temperature (Fig. 4a, b) and the weaker return of DIC into the surface layer due to destratification maintain the absorption of atmospheric CO<sub>2</sub>.

At an annual scale, the ratio between the maximum effects of temperature and biological activities or their respective difference indicate, which of the two processes is dominant (Fig. 6a, b). The southern part is clearly dominated by the temperature effects with an increase of pCO<sub>2</sub> in summer, while the northern part is clearly dominated by the biological processes with a summer decrease of pCO<sub>2</sub> typical for mid and high latitude waters.

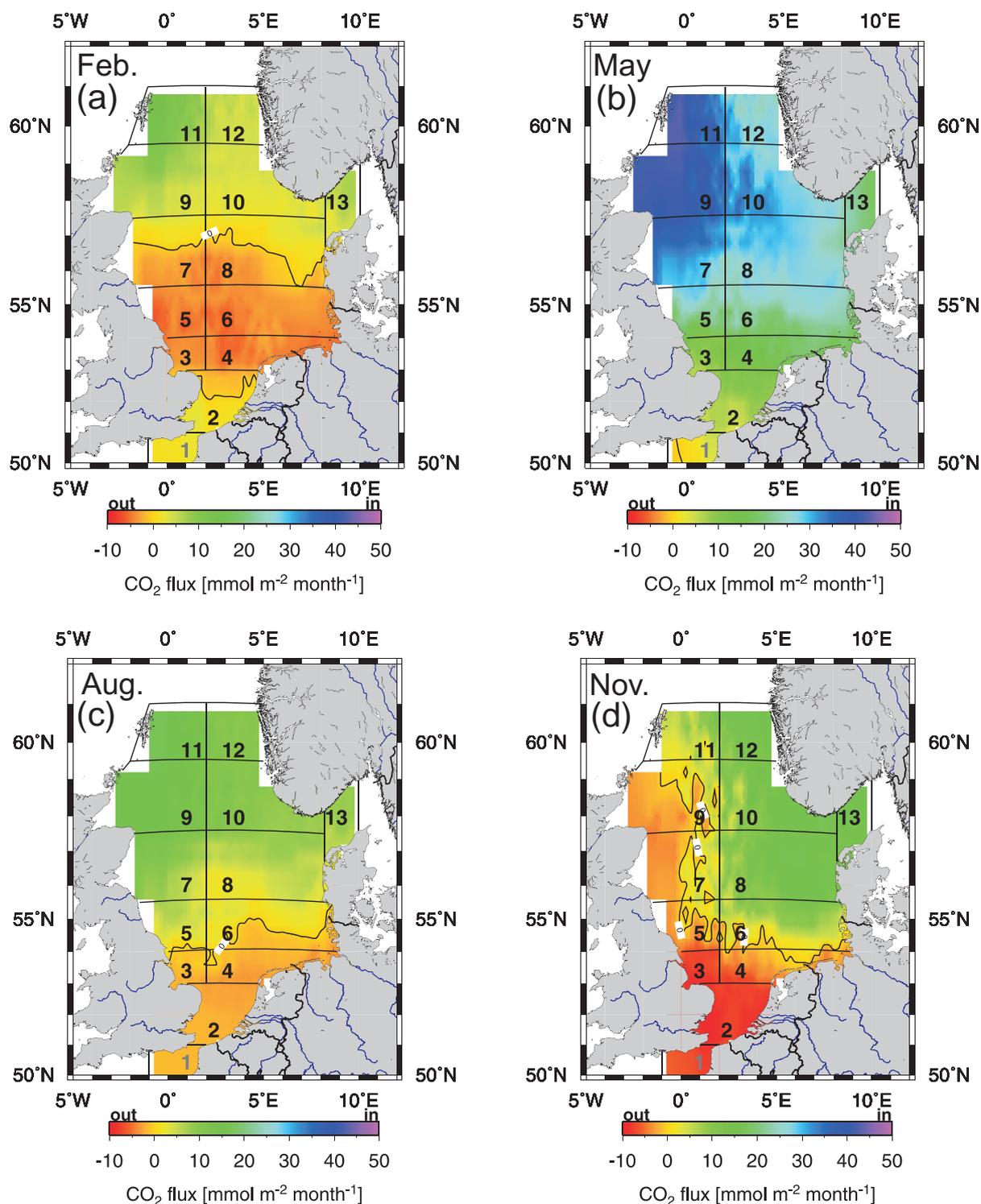
### 3.3 $\Delta\text{DIC}_{\text{bio}}$ and Net community production

The biological CO<sub>2</sub> drawdown ( $\Delta\text{DIC}_{\text{bio}}$ ), which has been computed from Eqs. (3) and (6), shows North-Sea-wide average of 100  $\mu\text{mol kg}^{-1}$ . The maximum values of 200  $\mu\text{mol kg}^{-1}$   $\Delta\text{DIC}_{\text{bio}}$  have been obtained for the German Bight area and the minimum values of 45  $\mu\text{mol kg}^{-1}$   $\Delta\text{DIC}_{\text{bio}}$  for the southern North Sea. The regional gradient of  $\Delta\text{DIC}_{\text{bio}}$  with high values in the central part, lower values in the northern part and lowest values in the southern part have already been discussed before (Fig. 4). Assuming a 30 m depth of the mixed layer, NCP amounts to 2.9 mol C m<sup>-2</sup> yr<sup>-1</sup> from February to August with higher values in the northern areas than in the southern area (Table 1). Since the air-sea exchange of CO<sub>2</sub> also alters pCO<sub>2</sub> values next to the temperature and biological effects, the CO<sub>2</sub> uptake by the North Sea during the productive period needs to be considered. The CO<sub>2</sub> air-sea fluxes for the period from February to August have been taken from Thomas et al. (2004) in order to establish a corrected term for NCP ( $\text{NCP}_{\text{corr}}$ ).  $\text{NCP}_{\text{corr}}$  in the mixed layer amounts to 4 mol C m<sup>-2</sup> yr<sup>-1</sup> in the whole North Sea during the productive period, with values of 4.3 mol C m<sup>-2</sup> yr<sup>-1</sup> in the northern area and 2.6 mol C m<sup>-2</sup> yr<sup>-1</sup> in the southern area, respectively.

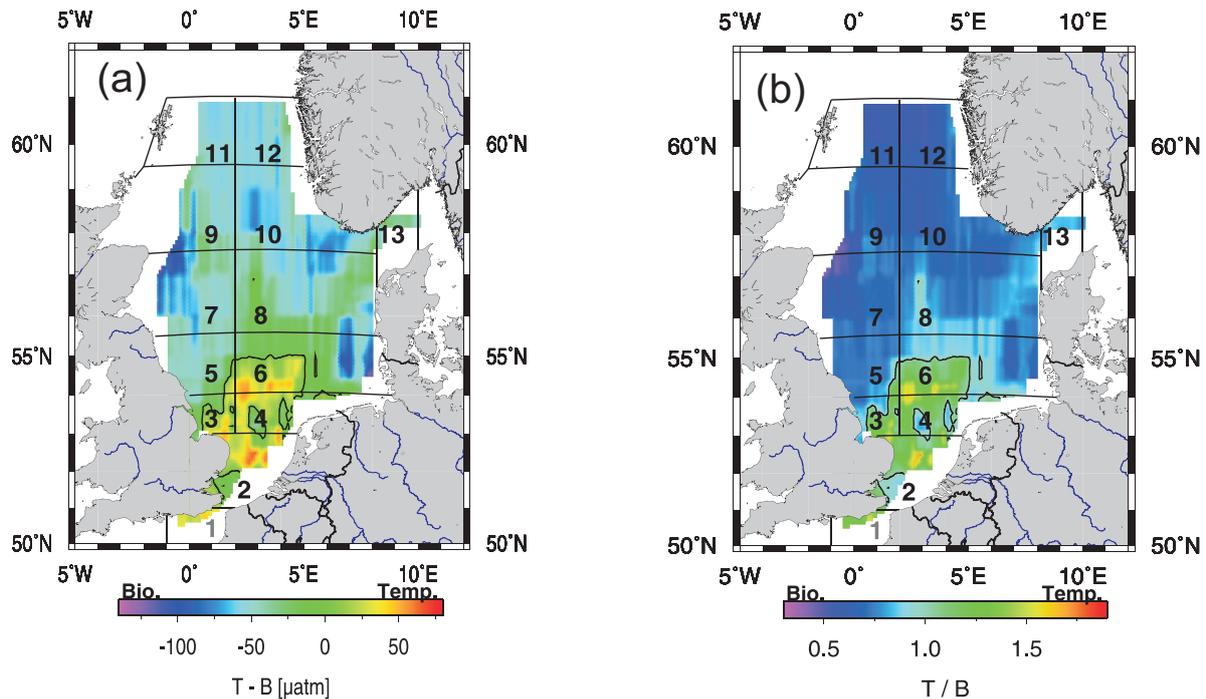
## 4 Discussion and summary

### 4.1 Methodological aspects

Obviously, the procedure by Takahashi et al. (2002), which has been developed to unravel the variability of the pCO<sub>2</sub> in open ocean regimes, attributes all non-temperature changes to biological processes. Several processes have been ignored



**Fig. 5.** Seasonal variability of the CO<sub>2</sub> air-sea fluxes. The monthly fluxes are taken from Thomas et al. (2004) and are shown for the months February (a), May (b), August (c) and November (d). The “zero” contour line has been indicated. The same color scale has been applied to all plots. The grid structure is according to Thomas et al. (2004).



**Fig. 6.** Biological vs. temperature control of the pCO<sub>2</sub>. (a) shows (T–B) and (b) shows (T/B) according to Fig. 3. The “0” (a) and “1” (b) contour lines are indicated, respectively, where both controls balance each other. The grid structure is according to Thomas et al. (2004).

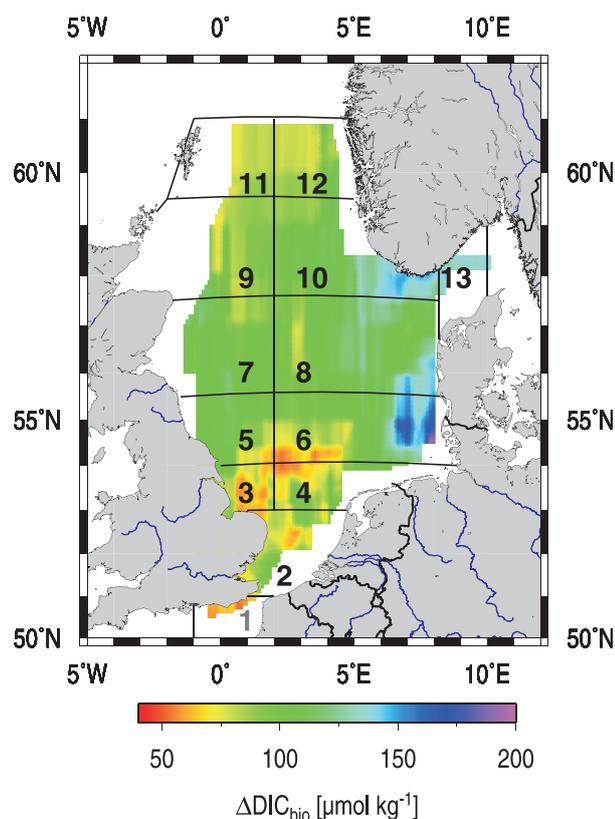
**Table 1.** Seasonal and annual CO<sub>2</sub> air-sea fluxes, and net community production (NCP, in mol C m<sup>-2</sup> yr<sup>-1</sup>) from February until August in the North Sea. Positive values indicate a flux into the marine area, i.e., an increase of the DIC pool. NCP<sub>corr</sub> denotes the NCP, which has been corrected for the CO<sub>2</sub> air-sea flux. See text for details. ΔDIC<sub>bio</sub> and ΔDIC<sub>bio,corr</sub> represent the DIC loss because of biological activity, i.e., NCP. Negative ΔDIC<sub>bio</sub> corresponds to positive NCP. For convenience, also the air-sea fluxes for the autumn period and the entire year have been given. The grid structure is according to Thomas et al. (2004): The Southern North Sea comprises the grid boxes 2–4, the Northern North Sea the grid boxes 5–13 and the entire North Sea grid boxes 2–13, respectively.

| [mol C m <sup>-2</sup> yr <sup>-1</sup> ] |   | Feb.=>Aug.                      |  | Sep.=>Jan.                      | Annual                          |
|---|---|---------------------------------|--|---------------------------------|---------------------------------|
|   | ΔDIC <sub>bio</sub><br>[=-NCP]<br>(uncorr.) | CO <sub>2</sub><br>air-sea flux | ΔDIC <sub>bio,corr</sub><br>[=-NCP <sub>corr</sub> ]<br>(flux corr.) | CO <sub>2</sub><br>air-sea flux | CO <sub>2</sub><br>air-sea flux |
| Southern North Sea                        | -2.36                                       | 0.19                            | -2.55  | -0.41                           | -0.22                           |
| Northern North Sea                        | -3.12                                       | 1.18                            | -4.30  | 0.47                            | 1.64                            |
| Entire North Sea                          | -2.94                                       | 1.04                            | -3.98  | 0.34                            | 1.38                            |

by this attribution, notably the air-sea exchange of CO<sub>2</sub>. The consideration of this process, intimately related to the biological DIC uptake, requires the consideration of factors such as wind speed and temporal development of the biological DIC uptake and brought this rather straight forward approach closer to a modeling approach. In awareness of this complication, we have considered the CO<sub>2</sub> air-sea fluxes reported by Thomas et al. (2004) in order to correct the later estimate of NCP (Table 1). This correction in turn can also be used to show the contribution of the CO<sub>2</sub> air-sea flux to the variability of the pCO<sub>2</sub>, at least on a seasonal time scale.

Accordingly, in the North Sea the CO<sub>2</sub> air-sea flux substantially counteracts the ΔDIC<sub>bio</sub> by 10–30%, which implies that these fluxes need to be considered in order to achieve a reliable estimate of NCP when applying the Takahashi et al. (2002) approach. The good agreement with the independent assessment of NCP by Bozec et al. (2005b)<sup>1</sup> support the results presented here.

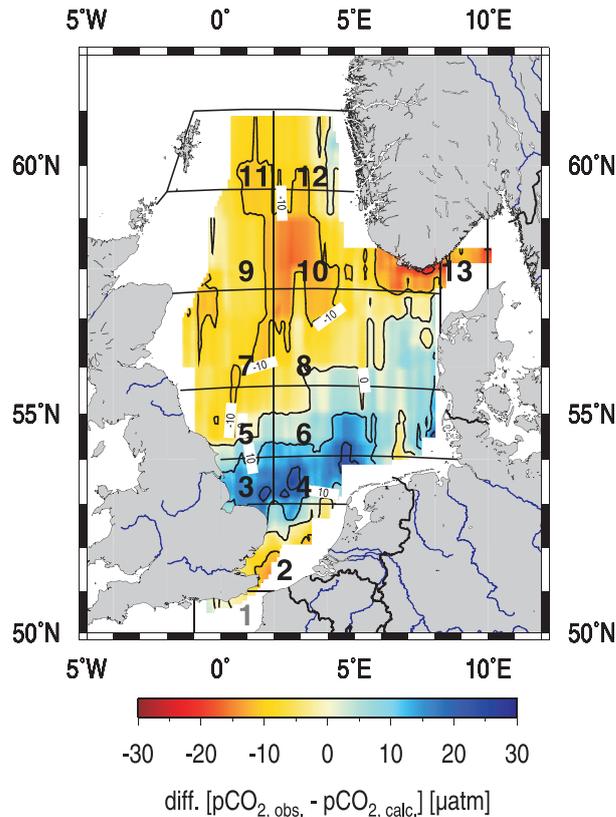
<sup>1</sup>Bozec, Y., Thomas, H., Schiettecatte, L.-S., Borges, A. V., Elkalay, K., and de Baar, H.: Assessment of the processes controlling the seasonal variations of dissolved inorganic carbon in the North Sea, *Limnol. Oceanogr.*, under revision, 2005b.



**Fig. 7.** Biological DIC uptake ( $\Delta\text{DIC}_{\text{bio}}$ ) calculated from Fig. 3a according to Thomas et al. (2001). An average salinity of 34 and an average water column depth of 30 m were used for the calculations. The grid structure is according to Thomas et al. (2004).

Our approach here relies on the assumption that the observed field data cover the maximum amplitudes of the seasonal variations both in temperature and pCO<sub>2</sub>. Our studies here relies on a data set with seasonal resolution, which was designed to cover both maximum amplitudes, which can be assumed to occur for temperature between winter and summer (February and August) and for pCO<sub>2</sub> between February and August or February and May, respectively. In highly variable system such as coastal systems, however it might be possible that on smaller spatial scales the pCO<sub>2</sub> minimum occurs at a different time. If this was the case, our approach was subject to some uncertainty. However, in basinwide studies, which show higher spatial variability, this problem is hardly to solve unless one would increase temporal coverage of a smaller region at the expense of the spatial coverage of the overall study.

Moreover, for the North Sea as a coastal area further processes such as inputs from rivers or the Baltic Sea, advection of water masses and interactions with the sediment are partly responsible for the variability of the pCO<sub>2</sub>. These processes have been investigated for example by Thomas et al. (2005) and Bozec et al. (2005a), however their consider-



**Fig. 8.** Difference between the seasonal pCO<sub>2</sub> variations ( $\text{pCO}_{2, \text{Feb}} - \text{pCO}_{2, \text{Aug}}$ ) from observations and the calculated according to Eqs. (3) and (4): ( $\Delta\text{pCO}_{2, \text{temp}} - \Delta\text{pCO}_{2, \text{bio}}$ ) for the period from February to August.

ation requires further information, mainly on the hydrodynamics. We have chosen here to apply the rather straightforward approach of Takahashi et al. (2002), which considers rather static snapshots of the North Sea. Obviously, above processes, which have been ignored here, contribute to the variability of pCO<sub>2</sub>, notably for near coast and the southern areas. These considerations also hold true for the assessment of the NCP, which might be seen as a lower bound, since additional carbon sources besides the atmosphere (e.g. rivers) have not been taken into account. In order to provide an estimate of the uncertainty related to the neglect of the above mentioned processes, the seasonal pCO<sub>2</sub> difference between February and August from observation has been compared with that from the calculations according to Eqs. (3) and (4) (Fig. 8). The difference between both provides a quantitative estimate of the corresponding uncertainty. The average difference over all data points is  $-2 \mu\text{atm}$ , however it appears to be a systematic pattern. Note the similarity in the pattern of the zero line in Fig. 8 and the 50 m depth contour shown in Fig. 3c. The shallower southern region, except for the areas close to English Channel, reveals a positive difference pointing toward a slight underestimation of  $\Delta\text{DIC}_{\text{bio}}$  and in turn

the computed NCP, or in other words, there are processes active in this region increasing the pCO<sub>2</sub> in summer other than temperature. Prime candidates for this were riverine inputs with high DIC concentrations for European continental rivers, which have been reported by Thomas et al. (2005). The neglect of these DIC inputs tends to underestimate NCP, since additional NCP was required to provide the corresponding pCO<sub>2</sub> drawdown. Alkalinity release from the sediment surface or rivers would in contrast decrease the pCO<sub>2</sub> during this time of the year, however here we can only state that these processes are not dominant compared to the apparent increase in DIC. In the northern region the predicted pCO<sub>2</sub> decrease is less than the observed pCO<sub>2</sub> decrease implying further processes, which decrease the pCO<sub>2</sub>. Prime candidates here were the inputs of lower DIC water from the Baltic Sea and Scandinavian Peninsula during spring and summer, which apparently cause a “dilution” of the DIC and pCO<sub>2</sub> in the northern area. The consequence here would be an overestimation of  $\Delta\text{DIC}_{\text{bio}}$  and in turn the computed NCP. The uncertainty of the NCP estimate related to the pCO<sub>2</sub> deviation (Fig. 8) could be assessed with regard to the average deviation of  $-2\ \mu\text{atm}$ , which corresponds to approximately  $1\ \mu\text{mol kg}^{-1}\ \Delta\text{DIC}_{\text{bio}}$ , which would most likely be too low, since both tend to cancel out each other. A more realistic description of the uncertainty can be obtained, when assessing the pCO<sub>2</sub> deviation individually for the shallower and deeper regions. Both regions show an average deviation of  $8\ \mu\text{atm}$ , which leads under consideration of (6) to an error of approximately 10% on  $\Delta\text{DIC}_{\text{bio}}$  and NCP, respectively.

The computation of NCP relies on the multiparameter linearization of the complex carbonate system equilibrium reactions (Thomas et al., 2001; Thomas and Ittekkot, 2001). The linearization is based on an open-ocean relationship between  $A_T$  and salinity according to Millero et al. (1998). It has been argued (Thomas and Ittekkot, 2001) that the computation of the DIC-change shows only a negligible dependence on the absolute values of  $A_T$ , since the multiparameter linearization has been established from differences. Still, in the near coastal areas the seasonal and regional variability in  $A_T$  and salinity might become a source of uncertainty. The average  $\Delta\text{DIC}_{\text{bio}}$  obtained here is  $98\ \mu\text{mol kg}^{-1}$  (max.:  $200\ \mu\text{mol kg}^{-1}$ , min.:  $45\ \mu\text{mol kg}^{-1}$ ) and according to (6) a change of salinity of 1 would approximately cause a change in  $\Delta\text{DIC}_{\text{bio}}$  of  $1\ \mu\text{mol kg}^{-1}$ .

A more detailed consideration of these features goes beyond the aim and capacity of the work presented here and would require more sophisticated tools such as coupled hydrodynamic ecosystem models, which on the other hand are subject to other uncertainties. Still, the good agreement with a sophisticated DIC mass balance by Bozec et al. (2005b)<sup>1</sup> shows that our straightforward approach does have the potential to reliably assess NCP and to identify and unravel the major controlling processes of the CO<sub>2</sub> system.

#### 4.2 Net community production vs. gross primary production

Although it is generally assumed that the southern North Sea reveals higher *gross* primary productivity (see for example Joint and Pomroy, 1993; Pätsch and Radach, 1997), *net* community production is lower here than in the central and northern areas because of the competing gross primary production and community respiration in the annually well mixed water column of the south. This finding is in good agreement with the results of the sophisticated DIC mass balance approach by Bozec et al. (2005b)<sup>1</sup>. Gazeau et al. (2004) reported a mean gross primary production (GPP) in the North Sea of approximately  $18\ \text{mol C m}^{-2}\ \text{yr}^{-1}$ , which appears to be on a similar order of magnitude as the values given by Pätsch and Radach (1997). The reverse spatial gradient of the GPP data by Pätsch and Radach (1997) and our NCP data can be explained by the different bottom topographical settings, discussed above. The separation of production and respiration processes into upper and lower water column permits higher net carbon fixation in the surface layer of the northern region, while the shallower mixed water column prevents higher NCP values despite of higher GPP. A more detailed discussion of the relation between GPP and NCP in the North Sea is given by Bozec et al. (2005b)<sup>1</sup>, which employ an alternative, more sophisticated approach with higher temporal and spatial resolution.

#### 4.3 Summary

Based on pCO<sub>2</sub> observations with high spatial and seasonal resolution, the approach by Takahashi et al. (2002) has been applied to evaluate the processes governing the variability of pCO<sub>2</sub> in the North Sea. The analysis focuses on temperature and biology as the major processes controlling pCO<sub>2</sub> in surface waters, while other processes influencing the variability of the pCO<sub>2</sub> have been neglected. The northern area shows a typical mid to high latitude behavior characterized by the strong seasonality of the biological processes. The southern part is a rather temperature controlled system, where biological net effects are vanished through near balanced production and respiration processes in the one-layered compartment. The highest seasonal amplitude of the pCO<sub>2</sub> is observed in the central part as a consequence of early stratification and high biological activity. The North Sea reveals a high NCP with higher values for the northern and central parts. Limitations of the approach proposed by Takahashi et al. (2002), when applied in coastal areas, are mainly related to additional DIC and  $A_T$  sinks and sources, which cannot be captured.

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