

Controls of the surface water partial pressure of CO₂ in the North Sea

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Abstract. The seasonal variability of the partial pressure of CO₂ (pCO₂) 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 CO₂-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-CO₂ removal from the surface layer due to the absence of seasonal stratification. The consequence is a reversal of the CO₂ sea-to-air flux during the spring bloom period, the only time, when CO₂ 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⁻² yr⁻¹ with higher values (4.3 mol C m⁻² yr⁻¹) in the northern part and lower values in the southern part (2.6 mol C m⁻² yr⁻¹).

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 CO₂, 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 CO₂. Recent studies however seem

to suggest that the ocean and the atmosphere entirely share the storage of the anthropogenic CO₂, 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 CO₂ fluxes between coastal ocean and atmosphere and the open ocean, respectively. Depending on the hydrodynamic and topographic conditions the biologically initiated CO₂-drawdown might finally supply the *continental shelf pump* (Tsunogai et al., 1999), a mechanism transferring atmospheric CO₂ 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).

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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 CO₂ 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 CO₂ 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 CO₂, most of which is exported to the North Atlantic Ocean. In detail, the smaller southern part releases CO₂ to the atmosphere ($-0.2 \text{ mol C m}^{-2} \text{ yr}^{-1}$), while the northern areas absorb CO₂ ($1.7 \text{ mol C m}^{-2} \text{ yr}^{-1}$).

Here, we investigate the variability of the partial pressure of CO₂ (pCO₂) in detail, which governs the CO₂ air-sea fluxes. Temperature effects will be unraveled from the biological processes controlling the pCO₂ applying the approach proposed by Takahashi et al. (2002). The consequences for the seasonal variability of the CO₂ air-sea fluxes are discussed. Finally, an estimate of the corresponding biological CO₂ 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 pCO₂ 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⁻¹. The main water flow through the equilibrator was 2–3 L min⁻¹ and the difference between in-situ and equilibrator temperature was typically less than 0.5°C. The atmospheric pCO₂ 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_T) 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⁻¹. The uncertainty of A_T was determined to 2–3 μmol kg⁻¹.

2.2 Calculations

2.2.1 Temperature vs. biological control

In order to identify and quantify the main factors controlling the variability of pCO₂ in the North Sea, we applied the calculation scheme proposed by Takahashi et al. (2002), which assumes the pCO₂ to be controlled solely by temperature and biological CO₂ drawdown. Other processes governing pCO₂ such as changes in A_T, riverine inputs, sediment/water column interaction and the air-sea exchange of CO₂ 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 pCO₂ and temperature data. In brief, the temperature effect can be removed by normalizing all pCO₂ 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_{mean} is the mean annual temperature and T_{obs} is the in-situ temperature at the time and location of the observation. The remaining variability of the pCO₂ is then controlled by the variations of DIC, assuming a constant A_T. The temperature signal can be obtained from the average annual pCO₂ and the difference between T_{obs} and T_{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 pCO₂ 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.

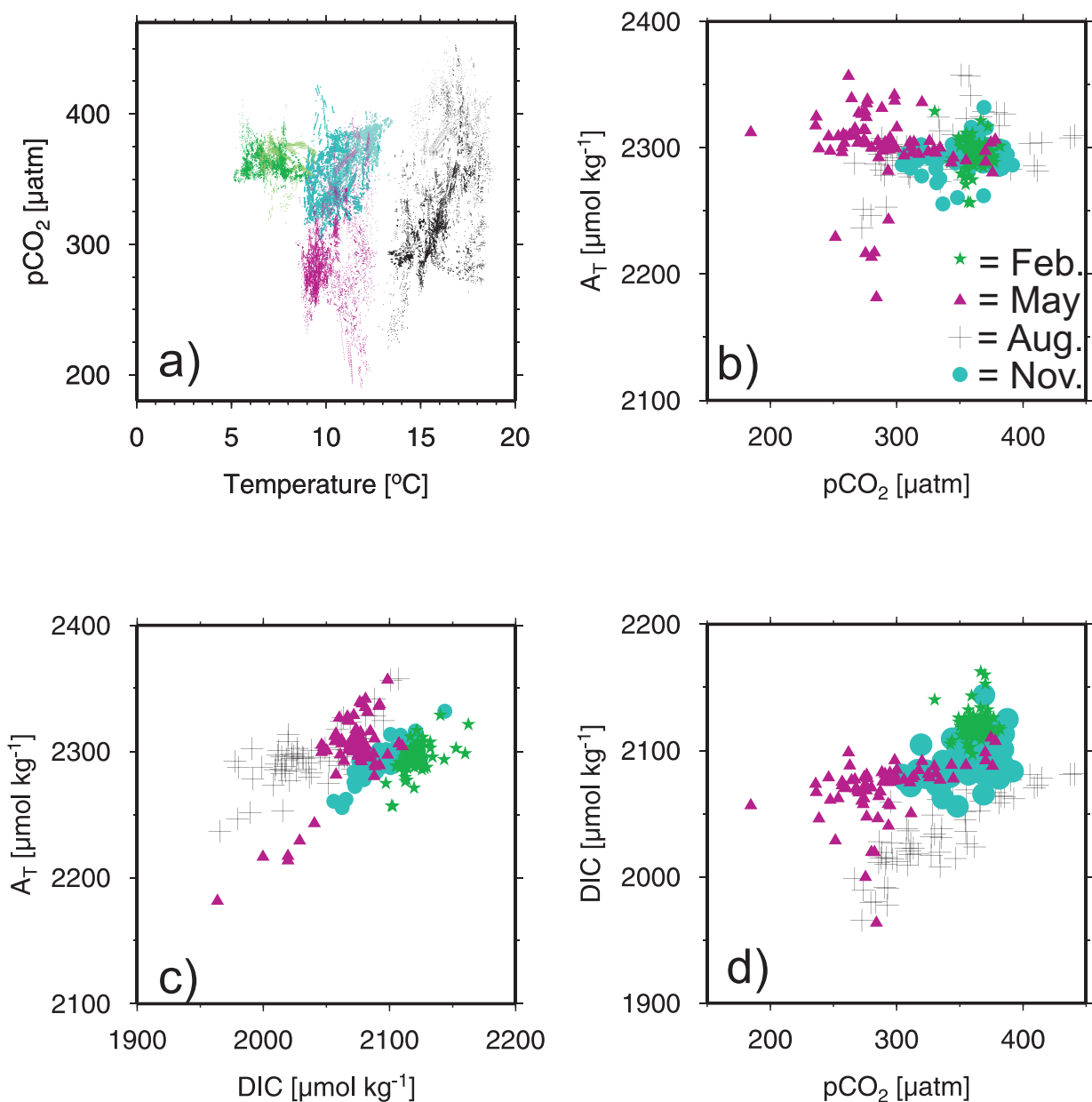


Fig. 1. Seasonal variability of the relationship between different surface water properties. (a) partial pressure of CO₂ (pCO₂) vs. Temperature. (b) Total alkalinity (A_T) vs. pCO₂. (c) A_T vs. dissolved inorganic carbon (DIC). (d) DIC vs. pCO₂. The green stars indicate February (winter) data, the purple 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 pCO₂ and temperature and salinity (Thomas and It-

tekkot, 2001; Thomas et al., 2001). This procedure, originally proposed for the determination of anthropogenic CO₂ 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):

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

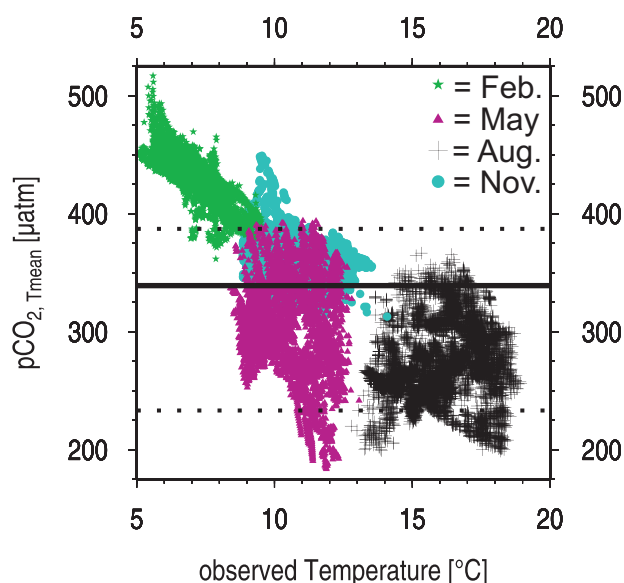


Fig. 2. pCO₂ values normalized to the average temperature of all observations (11.05°C) shown as function of their observational temperature. The lines indicate the observational, i.e., not normalized pCO₂ values at that temperature. The bold line shows the averaged observed pCO₂ for the temperature 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 pCO₂ 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 pCO₂ versus temperature relationship (Fig. 1a) reveals pCO₂ 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_T (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_T. Clearly, the maximum DIC draw-down is observed in summer, this in contrast to pCO₂ that shows minimal values during spring (Fig. 1a, d). The most pronounced seasonal and also regional signals can be observed in the pCO₂ 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 pCO₂ values than the northern and central parts, and in summer opposing directions of the CO₂ 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 pCO₂ values observed at the mean temperature with the values corrected to the mean temperature. In Fig. 2 the average pCO₂ (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 pCO₂ 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 pCO₂ because of DIC release to the water column by remineralization processes, while the spring and summer values show decreased pCO₂ 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 pCO₂ 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 CO₂ 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 pCO₂ 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 pCO₂ 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

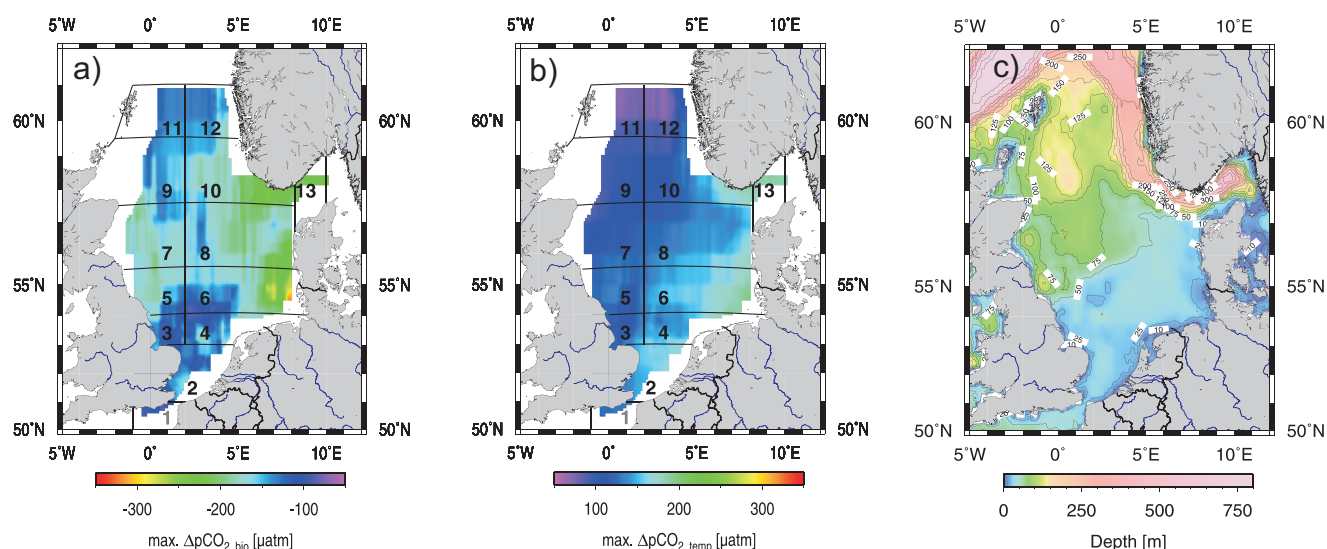


Fig. 3. Maximum changes in $\Delta p\text{CO}_{2, \text{bio}}$ (a) and $\Delta p\text{CO}_{2, \text{temp}}$ (b) calculated according to Takahashi et al. (2002). (c) Bottom topography of the North Sea using the ETOPO2 data set (National Geophysical Data Center: www.ngdc.noaa.gov). The grid structure is 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 CO₂ 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 CO₂ 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 pCO₂ maximum in summer (pCO_{2, temp} up to $135 \mu\text{atm}$, pCO_{2, bio} max: $-100 \mu\text{atm}$). Only during a very short period in spring the biological control dominates and causes a net reduction of the pCO₂ compared to the winter values. The highest seasonal pCO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ fluxes. With the onset of the spring bloom, all areas act as sinks for atmospheric CO₂, 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

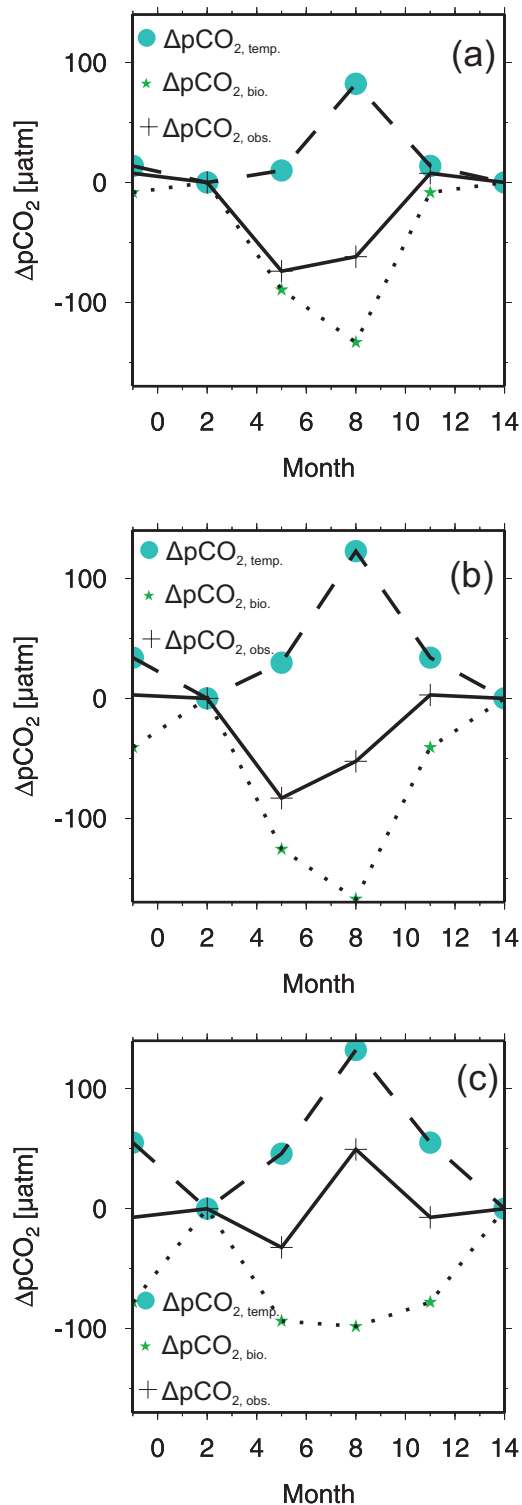


Fig. 4. Biological, temperature and observed $\Delta p\text{CO}_2$ signals for three different regions of the North Sea: (a) $60^\circ \text{N } 1^\circ \text{E}$, (b) $56^\circ \text{N } 1^\circ \text{E}$, and (c) $54^\circ \text{N } 3^\circ \text{E}$. The data are shown as difference to February.

CO_2 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_2 to the atmosphere (Fig. 5c). In autumn (Fig. 5d), primary production decreases in the North Sea enhancing the CO_2 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_2 .

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 $p\text{CO}_2$ in summer, while the northern part is clearly dominated by the biological processes with a summer decrease of $p\text{CO}_2$ typical for mid and high latitude waters.

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

The biological CO_2 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 $2.9 \text{ mol C m}^{-2} \text{ yr}^{-1}$ 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_2 also alters $p\text{CO}_2$ values next to the temperature and biological effects, the CO_2 uptake by the North Sea during the productive period needs to be considered. The CO_2 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 (NCP_{corr}). NCP_{corr} in the mixed layer amounts to $4 \text{ mol C m}^{-2} \text{ yr}^{-1}$ in the whole North Sea during the productive period, with values of $4.3 \text{ mol C m}^{-2} \text{ yr}^{-1}$ in the northern area and $2.6 \text{ mol C m}^{-2} \text{ yr}^{-1}$ 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 $p\text{CO}_2$ in open ocean regimes, attributes all non-temperature changes to biological processes. Several processes have been ignored

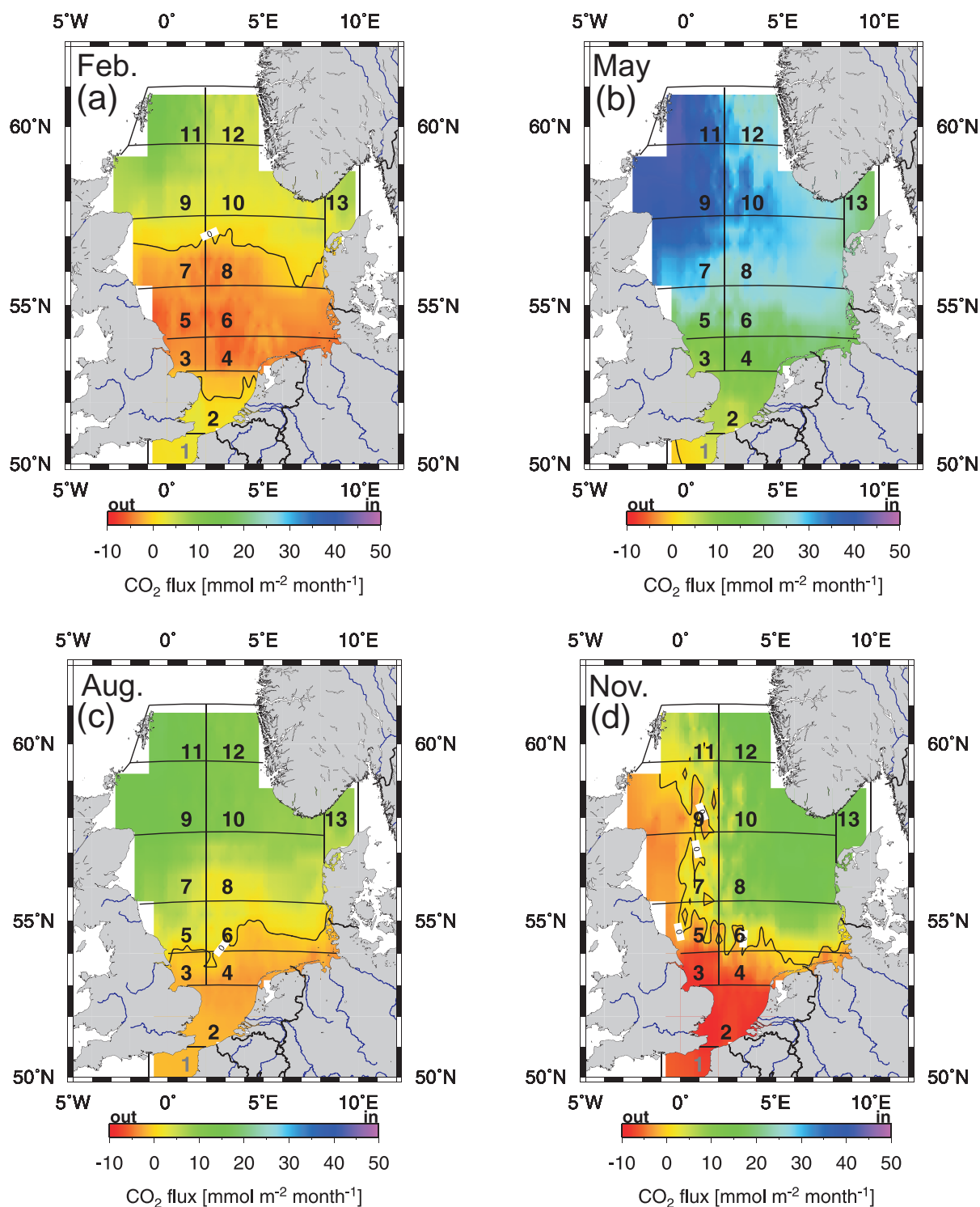


Fig. 5. Seasonal variability of the CO₂ air-sea fluxes. The monthly fluxes are taken from Thomas et al. (2004) and are shown for the months February (a), May (b), August (c) and November (d). The “zero” contour line has been indicated. The same color scale has been applied to all plots. The grid structure is according to Thomas et al. (2004).

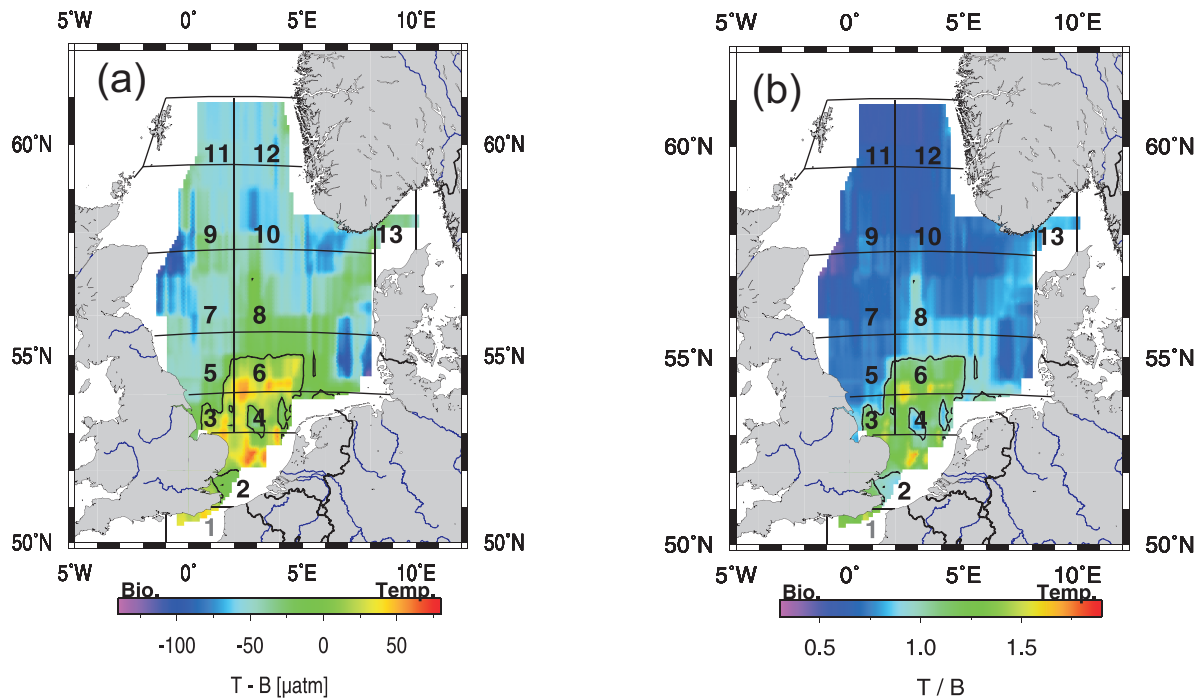


Fig. 6. Biological vs. temperature control of the pCO₂. (a) shows (T–B) and (b) shows (T/B) according to Fig. 3. The “0” (a) and “1” (b) contour lines are indicated, respectively, where both controls balance each other. The grid structure is according to Thomas et al. (2004).

Table 1. Seasonal and annual CO₂ air-sea fluxes, and net community production (NCP, in mol C m⁻² yr⁻¹) 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_{corr} denotes the NCP, which has been corrected for the CO₂ air-sea flux. See text for details. ΔDIC_{bio} and ΔDIC_{bio,corr} represent the DIC loss because of biological activity, i.e., NCP. Negative ΔDIC_{bio} 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 ⁻² yr ⁻¹]		Feb.=>Aug.		Sep.=>Jan.	Annual
	ΔDIC _{bio} [=-NCP] (uncorr.)	CO ₂ air-sea flux	ΔDIC _{bio,corr} [=-NCP _{corr}] (flux corr.)	CO ₂ air-sea flux	CO ₂ 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 CO₂. 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 CO₂ 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 CO₂ air-sea flux to the variability of the pCO₂, at least on a seasonal time scale.

Accordingly, in the North Sea the CO₂ air-sea flux substantially counteracts the ΔDIC_{bio} 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)¹ support the results presented here.

¹Bozec, 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.

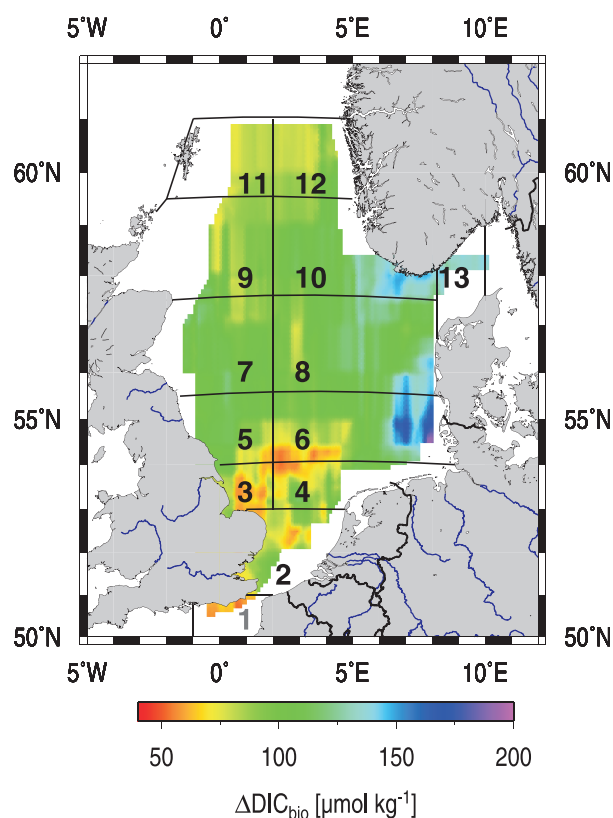


Fig. 7. Biological DIC uptake ($\Delta\text{DIC}_{\text{bio}}$) calculated from Fig. 3a according to Thomas et al. (2001). An average salinity of 34 and an average water column depth of 30 m were used for the calculations. The grid structure is according to Thomas et al. (2004).

Our approach here relies on the assumption that the observed field data cover the maximum amplitudes of the seasonal variations both in temperature and pCO₂. 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 pCO₂ 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 pCO₂ 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 pCO₂. These processes have been investigated for example by Thomas et al. (2005) and Bozec et al. (2005a), however their consider-

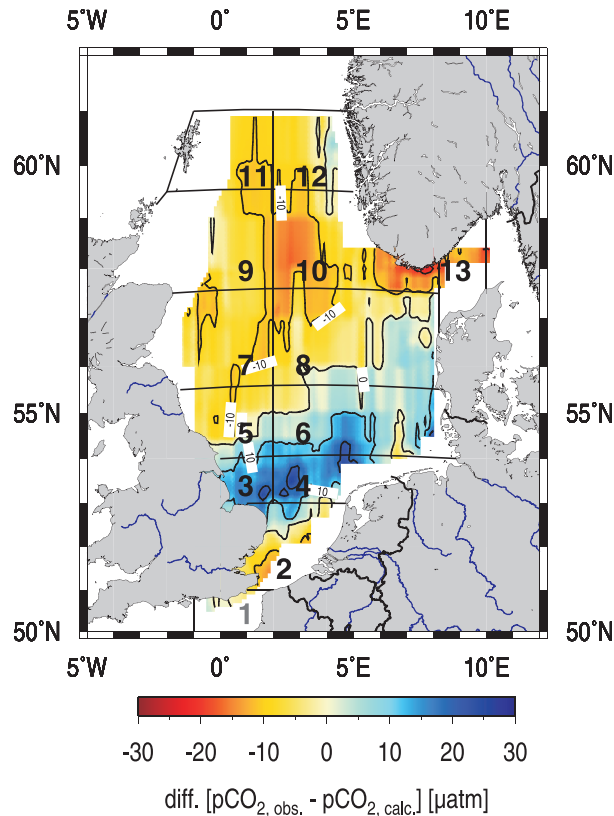


Fig. 8. Difference between the seasonal pCO₂ variations ($\text{pCO}_{2, \text{Feb}} - \text{pCO}_{2, \text{Aug}}$) from observations and the calculated according to Eqs. (3) and (4): ($\Delta\text{pCO}_{2, \text{temp}} - \Delta\text{pCO}_{2, \text{bio}}$) for the period from February to August.

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 pCO₂, 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 pCO₂ 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 pCO₂ 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 pCO₂ drawdown. Alkalinity release from the sediment surface or rivers would in contrast decrease the pCO₂ 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 pCO₂ decrease is less than the observed pCO₂ decrease implying further processes, which decrease the pCO₂. 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 pCO₂ 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 pCO₂ 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 pCO₂ 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)¹ shows that our straightforward approach does have the potential to reliably assess NCP and to identify and unravel the major controlling processes of the CO₂ 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)¹. 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)¹, which employ an alternative, more sophisticated approach with higher temporal and spatial resolution.

4.3 Summary

Based on pCO₂ 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 pCO₂ in the North Sea. The analysis focuses on temperature and biology as the major processes controlling pCO₂ in surface waters, while other processes influencing the variability of the pCO₂ 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 pCO₂ 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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References

- Bakker, D. C. E., de Baar, H. J. W., and de Wilde, H. P. J.: Dissolved carbon dioxide in Dutch coastal waters, *Mar. Chem.*, 55 (3–4), 247–263, 1996.
- Borges, A. V.: Do we have enough pieces of the jigsaw to integrate CO₂ fluxes in the coastal ocean?, *Estuaries*, 28 (1), 3–27, 2005.
- Borges, A. V., Delille, B., and Frankignoulle, M.: Budgeting sinks and sources of CO₂ in the coastal ocean: Diversity of ecosystems counts, *Geophys. Res. Lett.*, 32, L14601, doi:10.1029/2005GL023053, 2005.
- Borges, A. V. and Frankignoulle, M.: Distribution of surface carbon dioxide and air-sea exchange in the English Channel and adjacent areas, *J. Geophys. Res.*, 198 (C5), doi:10.1029/JC000571, 1–14, 2003.
- Borges, A. V. and Frankignoulle, M.: Distribution and air-water exchange of carbon dioxide in the Scheldt plume off the Belgian coast, *Biogeochem.*, 59 (1–2), 41–67, 2002.
- Borges, A. V. and Frankignoulle, M.: Daily and seasonal variations of the partial pressure of CO₂ in surface seawater along Belgian and southern Dutch coastal areas, *J. Mar. Syst.*, 19, 251–266, 1999.
- Bozec, Y., Thomas, H., Elkalay, K., and De Baar, H.: The continental shelf pump in the North Sea - evidence from summer observations, *Mar. Chem.*, 93, 131–147, 2005a.
- Chen, C.-A., Liu, K.-K., and MacDonald, R.: Continental margin exchanges, in: *Ocean Biogeochemistry: a JGOFS synthesis*, edited by: Fasham, M. J. R., Springer, 53–97, 2003.
- Frankignoulle, M. and Borges, A. V.: European continental shelf as a significant sink for atmospheric carbon dioxide, *Global Biogeochem. Cycles*, 15 (3), 569–576, 2001.
- Frankignoulle, M., Bourge, I., Canon, C., and Dauby, P.: Distribution of surface seawater partial CO₂ pressure in the English Channel and in the Southern Bight of the North Sea, *Cont. Shelf Res.*, 16 (3), 381–395, 1996.
- Gazeau, F., Smith, S. V., Gentili, B., Frankignoulle, M., and Gattuso, J.-P.: The European coastal zone: characterization and first assessment of ecosystem metabolism, *Estuarine, Coastal and Shelf Science*, 60, 673–694, 2004.
- IPCC: The scientific basis, in: *Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by: Johnson, C. A., Cambridge University Press, New York, 882pp., 2001.
- Johnson, K. M., Wills, K. D., Butler, D. B., Johnson, W. K., and Wong, C. S.: Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric detector, *Mar. Chem.*, 44, 167–187, 1993.
- Joint, I. R. and Pomroy, A. J.: Phytoplankton biomass and production in the southern North Sea, *Marine Ecology Progress Series*, 99, 169–182, 1993.
- Kempe, S. and Pegler, K.: Sinks and sources of CO₂ in coastal seas: the North Sea, *Tellus*, 43B, 224–235, 1991.
- Körtzinger, A., Thomas, H., Schneider, B., Gronau, N., Mintrop, L., and Duinker, J. C.: At-sea intercomparison of two newly designed underway pCO₂ systems – encouraging results, *Mar. Chem.*, 52, 133–145, 1996.
- Liu, K.-K., Atkinson, L., Chen, C. T. A., Gao, S., Hall, J., MacDonald, R., Talaue McManus, L., and Quinones, R.: Exploring continental margin carbon fluxes on a global scale, *EOS*, 81, 641–644, 2000a.
- Liu, K.-K., Iseki, K., and Chao, S.: Continental margin carbon fluxes, in: *The Changing Ocean Carbon Cycle: a midterm synthesis of the Joint Global Ocean Flux Study*, edited by: Field, J. G., Cambridge University Press, New York, 187–239, 2000b.
- Millero, F. J., Roche, P., and Lee, K.: The total alkalinity of Atlantic and Pacific Waters, *Mar. Chem.*, 60, 111–130, 1998.
- Pätsch, J. and Radach, G.: Long-term simulation of the eutrophication of the North Sea: temporal development of nutrients, chlorophyll and primary production in comparison to observations, *J. Sea Res.*, 38, 275–310, 1997.
- Pegler, K. and Kempe, S.: The carbonate system of the North Sea: determination of alkalinity and TCO₂ and calculation of PCO₂ and Si_{cal} (spring 1986), *Mitt. Geol.-Paläont. Inst. Univ. Hamburg*, 35–87, 1988.
- Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R., Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T.-H., Kozyr, A., Ono, T., and Rios, A. F.: The Oceanic Sink for Anthropogenic CO₂, *Science*, 305, 367–371, 2004.
- Sarmiento, J. L. and Gruber, N.: Sinks for anthropogenic carbon, *Phys. Today*, 8, 30–36, 2002.
- Takahashi, T., Sutherland, S. C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N. R., Wanninkhof, R., Feely, R. A., Sabine, C. L., Olafsson, J., and Nojiri, Y.: Global sea-air CO₂ flux based on climatological surface ocean pCO₂, and seasonal biological and temperature effects, *Deep-Sea Res. II*, 49, 1601–1622, 2002.
- Thomas, H., Bozec, Y., de Baar, H. J. W., Elkalay, K., Frankignoulle, M., Schiettecatte, L.-S., Kattner, G., and Borges, A. V.: The Carbon budget of the North Sea, *Biogeosciences*, 2, 87–96, 2005.

SRef-ID: 1726-4189/bg/2005-2-87.

Thomas, H., Bozec, Y., Elkalay, K., and De Baar, H.: Enhanced open ocean storage of CO₂ from shelf sea pumping, *Science*, 304, 1005–1008, 2004.

Thomas, H., Pempkowiak, J., Wulff, F., and Nagel, K.: Autotrophy, nitrogen accumulation and nitrogen limitation in the Baltic Sea: a paradox or a buffer for eutrophication?, *Geophys. Res. Lett.*, 30 (21), 2130, doi:10.1029/2003GL017937, 2003.

Thomas, H., England, M. H., and Ittekkot, V.: An off-line 3D model of anthropogenic CO₂ uptake by the oceans, *Geophys. Res. Lett.*,

- 28 (3), 547–550, 2001.
- Thomas, H. and Ittekkot, V.: Determination of anthropogenic CO₂ in the North Atlantic Ocean using water mass ages and CO₂ equilibrium chemistry, *J. Mar. Syst.*, 27, 325–336, 2001.
- Tsunogai, S., Watanabe, S., and Sato, T.: Is there a “continental shelf pump” for the absorption of atmospheric CO₂?, *Tellus*, 51B, 701–712, 1999.