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Variability of the surface water partial pressure of CO_2 in the North Sea

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Abstract

The seasonal variability of the partial pressure of CO_2 (pCO_2) has been investigated in the North Sea, a northwest European shelf sea. Based on a seasonal, high 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_2-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_2 removal from the surface layer due to the absence of seasonal stratification. The consequence is a reversal of the CO_2 sea-to-air flux during the spring bloom period, the only time, when CO_2 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 CO_2, 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_2. Recent studies however seem to suggest that the ocean and the atmosphere entirely share the storage of the anthropogenic CO_2, 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

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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; Liu et al., 2000b; 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).

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_2 fluxes between coastal ocean and atmosphere and the open ocean, respectively. Depending on the hydrodynamic and topographic conditions the biologically initiated CO_2-drawdown might finally supply the continental shelf pump (Tsunogai et al., 1999), a mechanism transferring atmospheric CO_2 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 (Frankignoulle et al., 1996; Borges and Frankignoulle, 1999, 2002, 2003; Frankignoulle and Borges, 2001) most notably enabling insight in near shore carbon and CO_2 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_2 air-sea fluxes, investigated the functioning of the continental shelf pump at a seasonal scale (Thomas et al., 2004;

Bozec et al., 2005) 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_2, most of which is exported to the North Atlantic Ocean. In detail, the smaller southern part releases CO_2 to the atmosphere ($-0.2\,mol\,C\,m^{-2}\,yr^{-1}$), while the northern areas absorb CO_2 ($1.7\,mol\,C\,m^{-2}\,yr^{-1}$).

Here, we investigate the variability of the partial pressure of CO_2 (pCO_2) in detail, which governs the CO_2 air-sea fluxes. Temperature effects will be unraveled from the biological processes controlling the pCO_2 applying the approach proposed by Takahashi et al. (2002). The consequences for the seasonal variability of the CO_2 air-sea fluxes are discussed. Finally, an estimate of the corresponding biological CO_2 drawdown, 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 onboard R.V. Pelagia covering all seasons in a consecutive order (18.8.2001–13.9.2001, 6.1.2001–29.11.2001, 11.2.2002–5.3.2002 and 6.5.2002–26.5.2002). The pCO_2 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 pCO_2 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 pCO_2 in the North Sea, we applied the calculation scheme proposed by Takahashi et al. (2002). Accordingly, the temperature and biological signals can be unraveled using the observed pCO_2 and temperature data. In brief, the temperature effect can be removed by normalizing all pCO_2 data to an average temperature for all seasons:

$$pCO_2 \text{ at } T_{mean} = pCO_2 \text{ at } T_{obs} * \exp[0.0423(T_{mean} - T_{obs})], \quad (1)$$

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 pCO_2 is then controlled by the variations of DIC, assuming a constant A_T. The temperature signal can be obtained from the average annual pCO_2 and the difference between T_{obs} and T_{mean}:

$$pCO_2 \text{ at } T_{obs} = \textit{annual mean} pCO_2 * \exp[0.0423(T_{obs} - T_{mean})]. \quad (2)$$

The changes in the pCO_2 related to biological ($\Delta pCO_{2,bio}$) and to temperature changes ($\Delta pCO_{2,temp}$) effects, respectively, follow then as:

$$\Delta pCO_{2,bio} = (pCO_2 \text{ at } T_{mean})_{max} - (pCO_2 \text{ at } T_{mean})_{min}, \quad (3)$$

$$\Delta pCO_{2,temp} = (pCO_2 \text{ at } T_{obs})_{max} - (pCO_2 \text{ at } T_{obs})_{min}, \quad (4)$$

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 $\Delta pCO_{2,bio}$ and $\Delta pCO_{2,temp}$ can be applied:

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

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

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

2.2.2. Biological DIC uptake (net community production)

The above $\Delta pCO_{2,bio}$ 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_2 and temperature and salinity (Thomas and Ittekkot, 2001; Thomas et al., 2001). This procedure, originally proposed for the determination of anthropogenic CO_2 in the water column, is applied for the present purposes to obtain the biological DIC drawdown (ΔDIC_{bio}) as a function of $\Delta pCO_{2,bio}$, salinity (S) and temperature (T, in °C):

$$\Delta DIC_{bio}=-199.6+0.89*S+0.42*T+0.6*(\Delta pCO_{2,bio}+276.8) \quad (6)$$

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 30m was assumed. $\Delta pCO_{2,bio}$ is obtained as the difference between the maximum and minimum pCO_2 at the annual mean temperature (3). The corresponding ΔDIC_{bio} (6) allows deriving NCP during the productive period February to August.

3. Results and discussion

3.1. Surface properties

The surface water properties of the North Sea (Fig. 1) during winter show a relatively homogenous behavior. The pCO_2 versus temperature relationship (Fig. 1a) reveals pCO_2 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 pCO_2 that shows minimal values during spring (Fig. 1a, d). The most pronounced seasonal and also regional signals can be observed in the pCO_2 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_2 values than the northern and central parts, and in summer opposing directions of the CO_2 air-sea flux are observed.

3.2. Biological versus temperature controls

The maximum values up to 330 μatm of the biologically induced pCO_2 changes ($\Delta pCO_{2,bio}$) are observed in the northern and central parts of the North Sea (Fig. 2a). Weaker effects are observed in the southern part, because the shallow (Fig. 2c), 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 North-Sea-wide average biological CO_2 draw-down ($\Delta pCO_{2,bio}$) 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. 2b) shows a stronger control on pCO_2 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_2 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 an average of 130 μatm. This value is above the average of 80 μatm observed in the open ocean at mid-latitudes, where maximum values of 220 μatm 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 identifying and quantifying the relevant regional features characterizing the CO_2 system in the North Sea. Three key areas are discussed: the deeper northern part of the North Sea (Fig. 3a), the central part (Fig. 3b), which still is stratified during summer, and the shallow continuously mixed southern part (Fig. 3c).

The northern region (Fig. 3a) shows the weakest temperature control, which is out competed by the biological CO_2 draw-down: 60 μatm vs. −150 μatm, 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_2 maximum in summer ($pCO_{2,temp}$ up to 135 μatm, $pCO_{2,bio}$ max: −100 μatm). Only during a very short period in spring the biological control dominates and causes a net reduction of the ΔpCO_2 compared to the winter values. The highest seasonal ΔpCO_2 amplitude in the North Sea, observed in the central region, is generated by a synergistic coincidence of somewhat a lower temperature control compared to the southern region and of the presence of a thermocline, which enables 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 earlier establishment of the thermocline and thus a longer export of 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_2 drawdown over the entire productive period. This contrasted behavior is clearly visible by the summer maxima of $\Delta pCO_{2,bio}$ in the northern and central region, since the stratification maintains the "accumulation" of the CO_2 drawdown until production deceases in later summer. In contrast, the absence of stratification in the south prevents this "accumulation", showing the strongest $\Delta pCO_{2,bio}$ only at its peak period during the bloom as compared to the other regions with the strongest $\Delta pCO_{2,bio}$ at the accumulated maximum of the drawdown in late summer.

The consequences of the different controls on the CO_2 air-sea fluxes become evident, when considering the seasonally resolved fluxes (Fig. 4). During winter (Fig. 4a) the North Sea appears to be a rather equilibrated system with regard to the CO_2 fluxes. With the onset of the spring bloom, all areas act as sinks for atmospheric CO_2, even the shallower southern part, where the biological control out competes the temperature control as indicated in Fig. 3c. In summer, the central and northern parts continue absorbing 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. In autumn, primary production deceases 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 (Thomas et al., 2004). The decreasing temperatures (Fig. 3a, 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 activity or the respective difference indicate, which of the two processes is dominant (Fig. 5a, b). The southern part is clearly dominated by the temperature effects with an increase of pCO_2 in summer, while the northern part is clearly dominated by the biological processes with a summer decrease of pCO_2 typical for mid and high latitude waters.

3.3. Net community production

NCP in the mixed layer (Fig. 6, Table 1) amounts to 2.9 mol C m^{-2} from February to August with higher values in the northern areas than in the southern area. Since the air-sea exchange of CO_2 also alters pCO_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 mol C m^{-2} in the whole North Sea during the productive period, with values of 4.3 mol C m^{-2} in the northern area and 2.6 mol C m^{-2} in the southern area, respectively. Although it is generally assumed that the southern North Sea reveals higher gross primary productivity, 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.

4. Discussion and summary

Based on pCO_2 observations with high spatial and seasonal resolution, the approach by Takahashi et al. (2002) has been applied to evaluate temperature and biological processes governing the variability of pCO_2 in the North Sea. The analysis is focused

on temperature and biology as the major processes controlling pCO_2 in surface waters. 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_2 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.

Obviously, further processes such as inputs from rivers or the Baltic Sea, and advection of water masses are partly responsible for the variability of the pCO_2. These processes have been investigated for example by Thomas et al. (2005) and Bozec et al. (2005), however their consideration requires further information, mainly on the hydrodynamics. We have chosen here to apply the rather straight forward 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_2, notably for near coast and the southern areas. The ignorance of these processes points to the limits of our approach. 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. Accounting for additional carbon sources would potentially lead to a somewhat higher estimate of NCP. However, the good agreement with a sophisticated DIC mass balance by Bozec et al. (2005[1]) shows that our straightforward approach does have the potential to reliably assess NCP and to identify and to unravel the major controlling processes of the CO_2 system.

[1]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, Limnology and Oceanography, submitted, 2005.

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Table 1. Seasonal and annual CO_2 air-sea fluxes, and net community production (NCP) from February until August in the North Sea. Positive values indicate a flux into the marine area, i.e., and increase of the DIC pool. NCP_{corr} denotes the NCP, which has been corrected for the CO_2 air-sea flux. See text for details. For convenience, also the air-sea fluxes for the autumn period and the entire year have been given. The southern North Sea comprises the gird boxes 2–4 and the northern North Sea the boxes 5–13, respectively. The grid structure is shown in Fig. 2.

[mol CO_2 m^{-2} yr^{-1}]	NCP (uncorr.)	Feb.=>Aug. CO_2 air-sea flux	NCP_{corr} (flux corr.)	Sep.=>Jan. CO_2 air-sea flux	Annual 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

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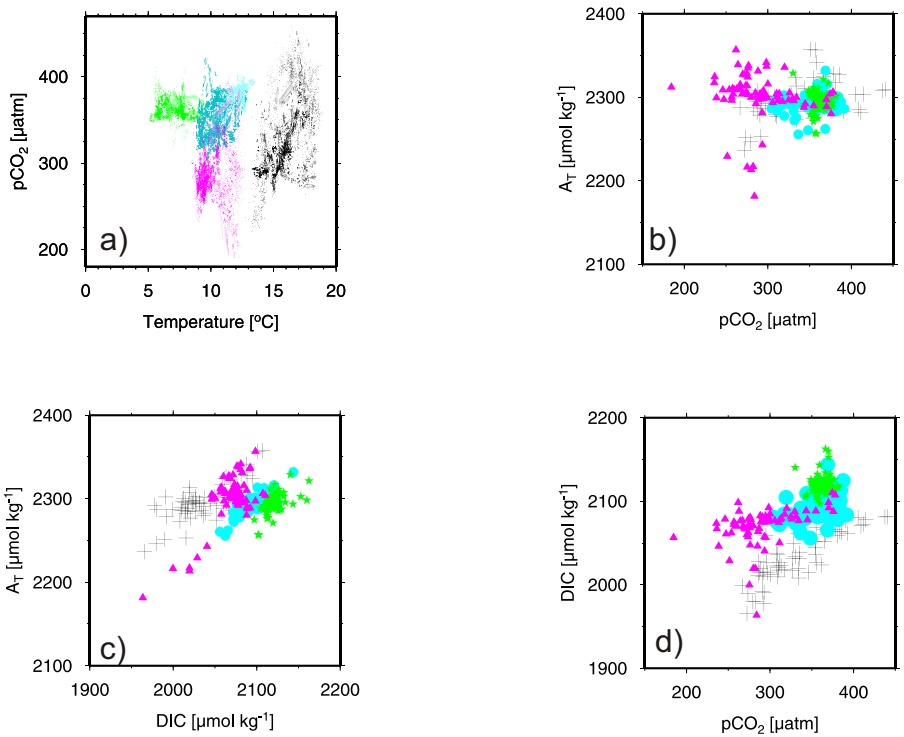

Fig. 1. Seasonal variability of the relationship between different surface water properties. **(a)** partial pressure (pCO_2) vs. Temperature. **(b)** Total alkalinity (A_T) vs. pCO_2. **(c)** A_T vs. dissolved inorganic carbon (DIC). **(c)** DIC vs. pCO_2. In a) the lighter colors indicate data south of 54° N and the darker colors data north of 54° N, respectively. All data have been projected onto the same grid.

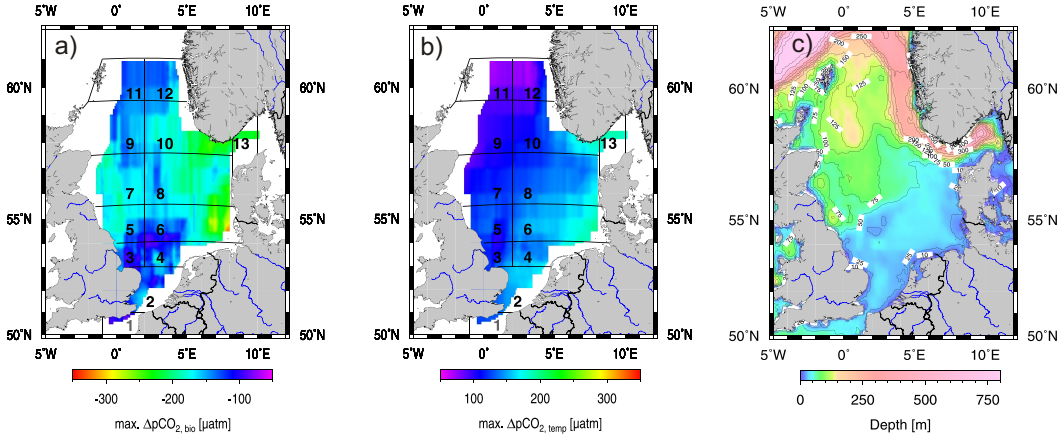

Fig. 2. Maximum changes in $\Delta pCO_{2,bio}$ **(a)** and $\Delta pCO_{2,temp}$ **(b)** calculated according to Takahashi et al. (2002). **(c)** Bottom topography of the North Sea using the ETOPO2 data set (National Geophysical Data Center: http://www.ngdc.noaa.gov). The grid structure is according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

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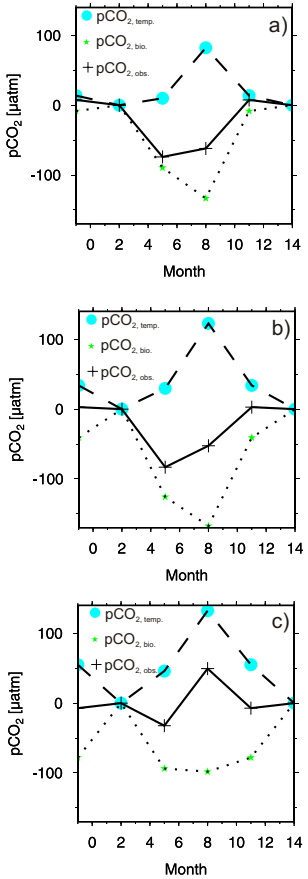

Fig. 3. Biological, temperature and observed ΔpCO_2 signals for three different regions of the North Sea: **(a)** 60° N 1° E, **(b)** 56° 1° E, and **(c)** 54° N 3° E. The data are shown as difference to February.

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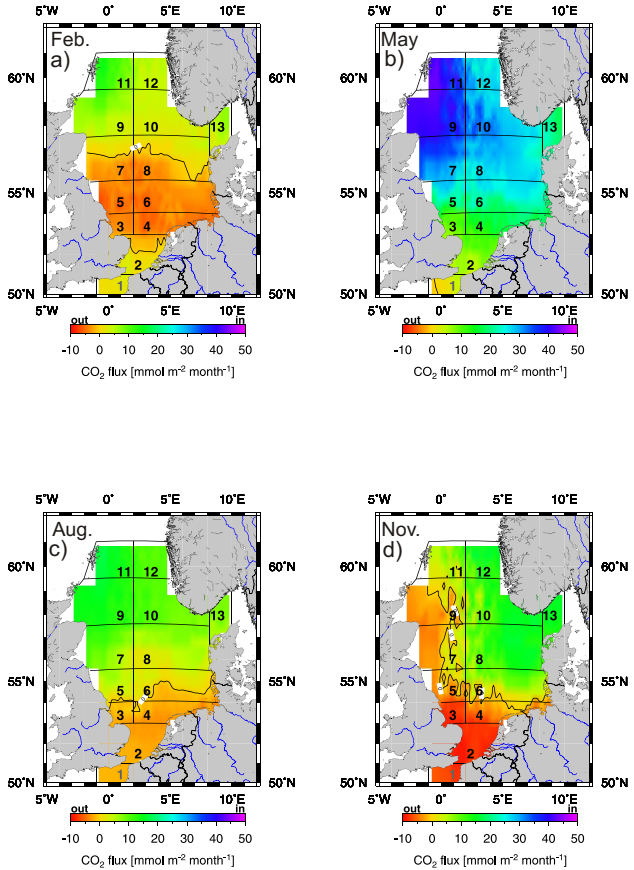

Fig. 4. Seasonal variability of the CO_2 air-sea fluxes. The monthly fluxes are taken from Thomas et al. (2004) and are shown for the months February **(a)**, May **(b)**, August **(c)** and November **(d)**. The "zero" contour line has been indicated. The same color scale has been applied to all plots. The grid structure is according to Thomas et al. (2004).

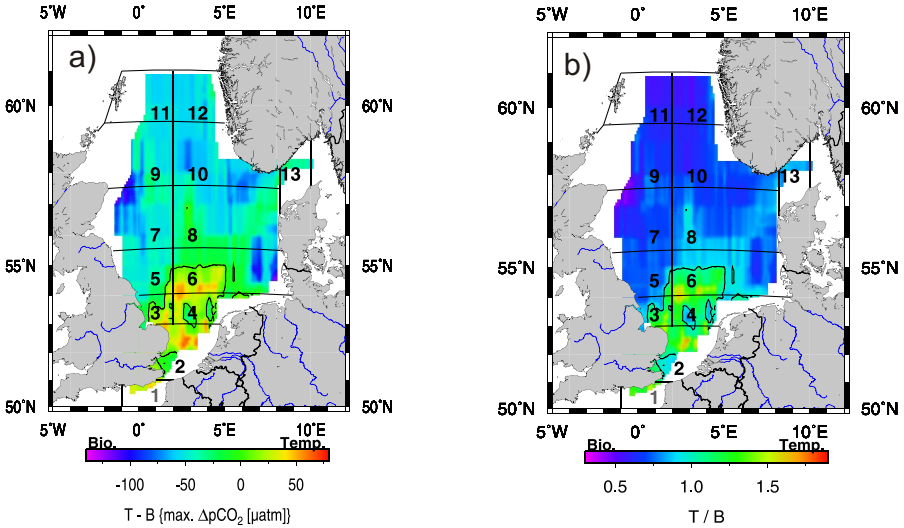

Fig. 5. Biological vs. temperature control of the pCO_2. **(a)** shows (T–B) and **(b)** shows (T/B) according to Fig. 3. The "0" (a) and "1" (b) contour lines are indicated, respectively, where both controls balance each other. The grid structure is according to Thomas et al. (2004).

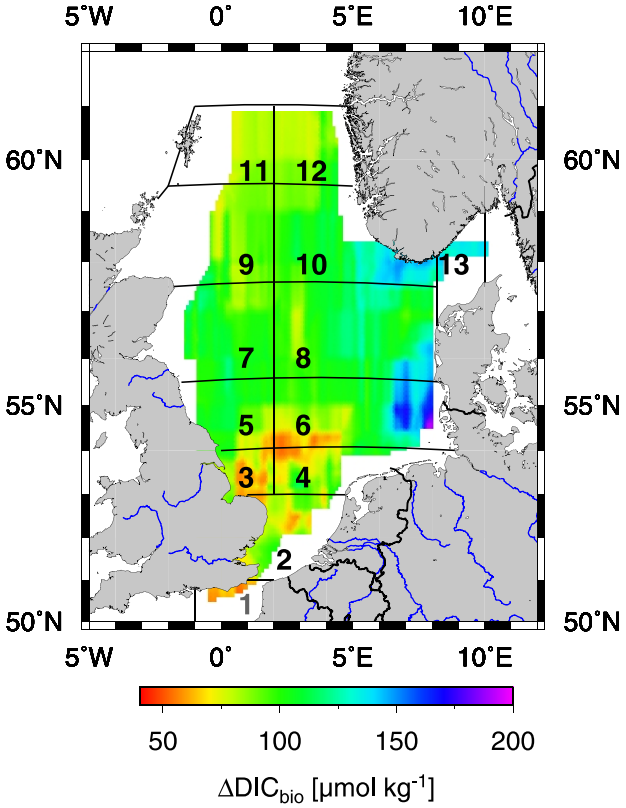

Fig. 6. Biological DIC uptake (ΔDIC_{bio}) calculated from Fig. 3a according to Thomas et al. (2001). An average salinity of 34 and an average water column depth of 30 m were used for the calculations. The grid structure is according to Thomas et al. (2004).