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# Spatiotemporal variations of fCO<sub>2</sub> in the North Sea

A. M. Omar<sup>1,2</sup>, A. Olsen<sup>2,1</sup>, T. Johannessen<sup>1,2</sup>, M. Hoppema<sup>3</sup>, H. Thomas<sup>4,5</sup>, and A. V. Borges

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Correspondence to: A. M. Omar (abdirahman.omar@gfi.uib.no)

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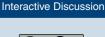
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<sup>&</sup>lt;sup>1</sup>Geophysical Institute, University of Bergen, Allégaten 70, 5007 Bergen, Norway

<sup>&</sup>lt;sup>2</sup>Bierknes Centre for Climate Research, University of Bergen, Allégaten 55, 5007 Bergen, Norway

<sup>&</sup>lt;sup>3</sup>Alfred Wegener Institute for Polar and Marine Research, Climate Sciences Department, P.O. Box 120161, 27515 Bremerhaven, Germany

<sup>&</sup>lt;sup>4</sup>Dalhousie University, Department of Oceanography, Halifax, Canada

<sup>&</sup>lt;sup>5</sup>Royal Netherlands Institute for Sea Research, Den Burg, Texel, The Netherlands

<sup>&</sup>lt;sup>6</sup>Chemical Oceanography Unit, University of Liège, Liège, Belgium

#### **Abstract**

Data from two Voluntary Observing Ship (VOS) (MS Trans Carrier and MV Nuka Arctica), acquired along one zonal and one meridional transect (2005–2007) augmented with data subsets from ten cruises (1987-2005) were used to investigate the spatiotemporal variations of the  $CO_2$  fugacity in seawater ( $fCO_2^{SW}$ ) in the North Sea at seasonal and inter-annual time scales. The observed seasonal  $fCO_2^{sw}$  variations were related to variations in sea surface temperature (SST), biology plus mixing, and air-sea  $CO_2$  exchange. Over the study period, the seasonal amplitude in  $fCO_2^{SW}$  induced by SST changes was 0.4-0.75 times those resulting from variations in biology plus mixing. Along the meridional transect,  $fCO_2^{sw}$  normally decreased northwards (-12  $\mu$ atm per degree latitude), but the gradient disappeared/reversed during spring as a consequence of an enhanced seasonal amplitude of  $fCO_2^{SW}$  in southern parts of the North Sea. Along the zonal transect, a weak gradient ( $-0.8\,\mu$ atm per degree longitude) was observed in the mean annual  $fCO_2^{SW}$ . Annually and averaged over the study area, surface waters of the North Sea were CO<sub>2</sub> undersaturated and thus a sink of atmospheric CO<sub>2</sub> throughout the year. However, during summer, surface waters in the region 55.5– 54.5° N were CO<sub>2</sub> supersaturated and, hence, a source for atmospheric CO<sub>2</sub>. Comparison of  $fCO_2^{sw}$  data acquired within two 1°×1° regions in the northern and southern North Sea during different years (1987, 2001, 2002, and 2005-2007) revealed large interannual variations, especially during spring and summer when year-to-year  $f CO_2^{SW}$ differences ( $\approx$ 160–200  $\mu$ atm) approached seasonal changes ( $\approx$ 200–250  $\mu$ atm). The springtime variations resulted from changes in magnitude and timing of the phytoplankton bloom, whereas changes in SST, wind speed, and total alkalinity may have contributed to the summertime interannual  $fCO_2^{SW}$  differences. The lowest interannual variation (10–50 μatm) was observed during fall and early winter. The comparison with data reported in October 1967 suggests that the  $fCO_2^{SW}$  growth rate in the central North Sea is similar to that in the atmosphere.

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#### 1 Introduction

The ocean takes up about 25% of the annual carbon emissions that result from fossil fuel burning and cement manufacturing (Canadell et al., 2007). So far, the oceanic sink has accounted for about half of the CO2 emitted from fossil-fuel consumption and cement-manufacturing since the onset of the industrial revolution (Sabine et al., 2004). Traditionally, marginal seas have been ignored when considering the exchange of carbon between atmosphere and ocean, due to their small surface area. Currently, however, these regions are receiving increased attention partly because uptake of atmospheric carbon dioxide (CO<sub>2</sub>) over shelf seas can be particularly effective. This is the case if subsequent formation of subsurface water and transport to the deep ocean takes place so that the absorbed carbon is isolated from the surface oceanatmosphere-system for a prolonged period of time. A number of studies (e.g. Tsunogai et al., 1999; Yool and Fasham, 2000; Thomas et al., 2004; Borges, 2005; Borges et al., 2005; Cai et al., 2006; Chen and Borges, 2009) have suggested that shelf seas may substantially contribute to the global ocean's uptake of atmospheric CO2 through the "continental shelf pump" - a term coined by Tsunogai et al. (1999), describing the mechanisms that transfer carbon from the atmosphere via the continental shelf to the deep ocean.

The North Sea (Fig. 1), as one of the best studied shelf seas, has been the subject of several basin wide and local investigations of the marine inorganic carbon cycle (Kelley, 1970; Kempe and Pegler, 1991; Hoppema, 1990, 1991; Borges and Frankignoulle, 1999, 2002; Brasse et al., 1999; Frankignoulle and Borges, 2001; Thomas et al., 2004, 2005, 2007, 2008; Bozec et al., 2005, 2006; Schiettecatte et al., 2006, 2007; Borges et al., 2008). Thomas et al. (2004) showed that the North Sea acts as a sink for atmospheric CO<sub>2</sub> and as a continental shelf pump, although the shallow southern part acts as a source during summer but an annual weak sink of atmospheric CO<sub>2</sub> (Schiettecatte et al., 2007). Furthermore, Thomas et al. (2007) suggested that the thermodynamic driving force of the sink (the gradient of fugacity of CO<sub>2</sub> (fCO<sub>2</sub>) at the air-sea inter-

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face  $\Delta f CO_2 = f CO_2^{sw} - f CO_2^{atm}$ ) has declined between 2001 and 2005 because  $f CO_2^{sw}$ increased faster than its atmospheric counterpart due to the invasion of anthropogenic carbon.

Despite being one of the best studied shelf seas, neither the seasonal  $fCO_2^{SW}$  cycle 5 nor its year-to-year variability is well documented in the North Sea. To improve this situation, the North Sea VOS (Voluntary Observing Ship) line has been initiated in 2005 funded by the EU Integrated Project CARBOOCEAN; http://www.carboocean. org/. Semi-continuous (ca. every 3 min) measurements for surface seawater f CO<sub>2</sub><sup>sw</sup> and sea surface temperature (SST) are made aboard the containership MS Trans Carrier which crosses the North Sea in a south-north direction on a weekly basis. Additionally, another CARBOOCEAN funded VOS line - the North Atlantic VOS line aboard MV Nuka Arctica - crosses the northern North Sea in a west-east direction ca. once every three weeks (Olsen et al., 2008).

Measurements from these two VOS lines constitute the first high frequency and season resolving  $fCO_2^{SW}$  dataset which cover most of the oceanographic regions in the North Sea. This work primarily analyses the above dataset with the focus on the spatiotemporal variations of  $fCO_2^{SW}$  in the North Sea, from seasonal to interannual time scales.

### Hydrographical regions and water masses in the North Sea

The North Sea (Fig. 1) is located on the north-western European continental shelf. In the east and southeast it is bounded by the European continent, by the British Isles in the west and south, and by the Norwegian west coast in the northeast. The circulation is anti-cyclonic and the sea receives warm water from the North Atlantic Current (NAC) through the north-west openings and fresh water mainly from Baltic Sea outflow and European rivers.

Generally, the deeper northern and central parts are stratified during summer while much of the shallow south is permanently mixed. Stratification in different areas can

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occur in salinity or (seasonally) in temperature. The VOS lines consistently cover six of the nine hydrographical regions and their corresponding water masses as identified by Lee (1980) (Fig. 1). The Continental Coastal Water (CCW) flows along the European continent from Dover Strait to about 56° N and is permanently mixed, except in some small places where freshwater plumes from major rivers e.g. Rhine and Elbe produce local salinity stratification. The low salinity Skagerrak Water (SW) flows along the Norwegian coast and is salinity stratified. The warm saline North Atlantic Water (NAW) enters from the north-west opening and extends as far south as about 55°N where during summer it is overlain by a combination of fresher coastal and/or SW. NAW is thermally stratified except around the Dogger Bank (centered ≈55° N, 3° E) where it is permanently mixed. The Scottish Coastal Water (SCW), English Coastal Water (ECW), and Channel Water (CW) all flow along the eastern coast of Britain and the track of MS Trans Carrier transect these waters only occasionally. Moreover, SCW is influenced by fresh river water and, thus, seasonally stratified by salinity whereas the ECW and CW are permanently mixed. The remaining three water masses (T1, T2, T3) are transition waters being mixtures of the adjacent water masses (Fig. 1).

#### Data and methods

#### VOS data and co-located parameters

Underway measurements of  $fCO_2^{SW}$  and sea surface temperature (SST) were obtained aboard two containerships MS Trans Carrier (operated by Seatrans AS, Norway www. seatrans.no) and MV Nuka Arctica (Royal Arctic Lines of Denmark). The route of MS Trans Carrier has changed overtime and today the ship crosses the North Sea along a transect roughly at 5° E (Fig. 1). At the start of the project, the ship track had a triangular shape as the ship also called the port of Immingham (UK) in addition to Bergen (Norway) and Amsterdam (The Netherlands). For the present analyses we use data exclusively from the line connecting Norway and Netherlands, since it has

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been the most persistent track. Note that even within this transect the ship track can change slightly, for example due to weather variations. Moreover, north of 58.5° N the ship has frequently stopped at several small ports before Bergen. For consistency, data acquired within the geographic rectangle 53.2° N–58.5° N and 4.4° E–5.5° E (henceforth the NS-transect) and during September 2005—December 2007 is used for the present analyses. Between February and December 2006 the VOS line was serviced by a sister ship MS *Norcliff* which was instrumented with the same measurement system.

The second ship, MV *Nuka Arctica*, crosses the North Sea approximately every three weeks along a transect (henceforth the WE-transect) between 59.5–57.7° N heading southeast until 7° E, and then continues east until 10° E, where it turns south and enters the port of Alborg, Denmark. The  $fCO_2^{sw}$  system was installed on board during 2004, but the data analyzed here are from 2005 through 2007.

The measurement method used aboard MS *Trans Carrier* is identical to that used aboard MV *Nuka Arctica* which was described in detail by Olsen et al. (2008). The instruments aboard the two ships are replicates and are a modified version of those described by Feely et al. (1998) and Wanninkhof and Thoning (1993). Briefly, for both ships, the *f* CO<sub>2</sub><sup>sw</sup> instrument uses a non-dispersive infrared (NDIR) CO<sub>2</sub>/H<sub>2</sub>O gas analyzer (LI-COR 6262) to determine the CO<sub>2</sub> concentration in a headspace air in equilibrium with a continuous stream of seawater. Every 3 min an analysis is done and the instrument is calibrated roughly every six hours with three reference gases with approximate concentrations of 200 ppm, 350 ppm, and 430 ppm, which are traceable to reference standards provided by National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL). The ZERO and SPAN of the NDIR response are determined once a day using a CO<sub>2</sub>-free gas (N<sub>2</sub>) and the reference standard with highest CO<sub>2</sub> concentration, respectively.

The seawater temperature in the equilibrator ( $T^{eq}$ ) and SST (measured at a dedicated seawater intake 2m below water level) were also recorded along with the raw mole fraction data ( $xCO_2$ ) from the NDIR. The temperature measurements were done using Hart Model 1521 digital thermometers from Hart Scientific, Inc.

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xCO<sub>2</sub> is converted to seawater fCO<sub>2</sub> in two steps. First, fCO<sub>2</sub> at the equilibrator temperature is computed according to (Körtzinger, 1999):

$$fCO_2^{eq} = xCO_2^{eq}(\rho^{eq} - \rho_{H_2O}) \exp(\rho^{eq} \frac{B + 2\delta}{BT^{eq}})$$
(1)

where  $p^{eq}$  is equilibrator pressure,  $p_{H2O}$  is the vapor pressure (Weiss and Price, 1980),  $_5$  R is the gas constant, and B and  $\delta$  are the first and second cross virial coefficients (Weiss, 1974).

Next, the  $CO_2$  fugacity at in situ temperature ( $fCO_2^{SW}$ ) was computed by taking into account the difference between equilibration and in situ temperatures (SST-T<sup>eq</sup><0.5°C) according to (Takahshi et al., 1993):

$$fCO_2^{SW} = fCO_2^{eq} \exp[0.0423(SST - T^{eq})]$$
 (2)

Data for sea surface salinity (SSS) and monthly mean sea level pressure (MSLP) were co-located with the VOS data from gridded fields obtained from different publicly accessible databases along the tracks of the ships. The SSS data are ocean analyses product of the Met Office's Forecasting Ocean Assimilation Model (Bell et al., 2006). The MSLP data were made available by Physical Science Division of NOAA/ERSL (http://www.cdc.noaa.gov/cdc/).

Monthly data for atmospheric xCO<sub>2</sub> were obtained from the NOAA/ESRL Global Monitoring Division (ftp://140.172.192.211/ccg/co2/flask/month/) for the two stations Mace Head, Ireland (53.33° N, 9.9° E) and station Mike (66° N, 2° E) for the years 2005 to 2007. In order to account for the latitudinal dependency, the monthly xCO<sub>2</sub> data have been fitted to linear functions of latitude. Hence, the atmospheric xCO2 value was determined for each fCO<sub>2</sub><sup>SW</sup> sample point. The resulting mole fractions were converted to atmospheric fugacity of CO<sub>2</sub>, fCO<sub>2</sub><sup>atm</sup>, using Eq. (1) except that SST and MSLP were used instead of  $T_{eq}$  and  $p_{eq}$ .

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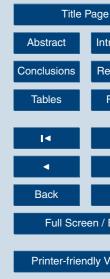
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#### 2.1.1 VOS data consistency and temporal coverage

The VOS data used in this study were acquired along the NS-transect during 4 months in 2005, 7 months in 2006 and 12 months in 2007, and along the WE-transect during 9 months in 2005, 7 months in 2006 and 11 months in 2007 (Fig. 2a). In late winter, MV Nuka Arctica sails on a track slightly different from the WE-transect and, thus, all data from March were excluded from the present analyses. Measurements from the two VOS lines coincided 3 months in 2005, 4 months in 2006, and 11 months for 2007 (Fig. 2a). Data from these 18 months were used to assess the consistency between measurements from the two ships within the crossover area (bounded by 57.944–58.3316° N; 4.996–5.594° E; see Fig. 1). For this purpose the data from each ship have been organized into 0.5° E×0.5° N×7 days bin averages. Linear regressions between the averaged data (Fig. 2b) resulted in residuals of 0±0.6°C for SST and  $1\pm13\,\mu$ atm for fCO<sub>2</sub><sup>SW</sup> meaning that there are no (or negligible) systematic differences between data acquired by the two measurement systems. Moreover, the large standard deviations of the residuals ( $\pm 0.6^{\circ}$ C and  $\pm 13 \mu$ atm) most probably reflect the weekly and mesoscale spatial variability.

#### Cruise data

Data acquired by scientific cruises and those measured aboard VOS ships are often complementary in the sense that the latter contains high frequency measurements but is limited in space and parameters while the former is limited in time but can be basin wide and normally contain a whole suit of parameters. In this work we take advantage of this typical complementarity by augmenting the VOS data with subsets of data from ten cruises. Five of the cruises were conducted in the North Sea aboard RV Pelagia (18 August-13 September 2001, 6-29 November 2001, 11 February-5 March 2002, 6-26 May 2002, and 17 August-6 September 2005). These data have been described in detail by others (Thomas et al., 2007, 2004; Bozec et al., 2005). Briefly, the RV Pelagia cruises covered the North Sea during all four seasons and obtained station data with

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a sampling resolution of 1° and underway data with one minute frequency sampling. During each cruise, water samples were collected for parameters including (but not limited to) dissolved inorganic carbon (DIC); total alkalinity ( $A_T$ ); salinity; and temperature. The DIC concentrations were determined by the coulometric method (e.g. Johnson et al., 1993) with a precision better than 1.5  $\mu$ mol kg<sup>-1</sup>. Underway  $\rho$ CO<sub>2</sub> has been measured semi-continuously (every minute) for surface water (pumped from 3 m below the sea surface) using a continuous flow system as described by Körtzinger et al. (1996). The water was pumped with a flow of 2–3 L min<sup>-1</sup> through the main equilibrator and the difference between in-situ and equilibrator temperature was typically less than 0.5°C. The system was calibrated against standards provided by the NOAA. Also, SST and SSS were determined in an underway mode in one-minute intervals. The underway  $\rho$ CO<sub>2</sub> data were converted to fCO<sub>2</sub><sup>sw</sup> by subtracting 0.3% (Weiss, 1974).

Five earlier cruises were conducted in the coastal North Sea along the Netherlands in 1987 (9–12 March, 13–16 April, 13–14 July, 3–4 August, and 23–25 November). Cruises in March, April and November were carried out with the research ship "Aurelia" of the Netherlands Institute for Sea Research. The two summer cruises were made with the research vessel "Holland" of the Ministry of Water Management of the Netherlands. Samples were taken from 2 m depth for the determination of  $A_T$ , and DIC in addition to SST and SSS. DIC and  $A_T$  were measured with a potentiometric titration with strong acid (HCI) with a measurement precision of 0.3%. A more detailed description of the surveys and measurement methods can be found in Hoppema (1990, 1991).

The 1987 cruise data for DIC and  $A_T$  were converted to  $fCO_2^{sw}$  values using the constants of Mehrbach et al. (1973) refit by Dickson and Millero (1987) and simultaneously acquired data for seawater temperature, salinity, phosphate and silicate. For few samples for which no nutrient data were available silicate and phosphate were set to 0, a choice that has negligible effects on the results. The random uncertainty associated with the computed  $fCO_2^{sw}$  values was estimated to be  $\pm 20\,\mu$ atm. It was difficult to assess the systematic errors since the measurements were done before the availability

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of any Certified Reference Material and the data is from highly variable coastal area.

#### Results and discussion

#### Seasonal and spatial variations

Figure 3 shows the seasonal and spatial variations of SST, SSS,  $fCO_2^{SW}$ , and  $\Delta fCO_2$ 5 along the two transects in the North Sea for a composite year.

For the NS-transect, SST shows seasonal changes with amplitude over 11°C being lowest during winter, increasing throughout spring, reaching maximum during summer, and decreasing throughout fall until reaching again minimum winter values (Fig. 3a). SST increases southwards along the transect (Fig. 3a), due to the solar radiation input which decreases with latitude in the North Sea (Otto et al., 1990). Linear regression between SST and latitude resulted in statistically significant and negative slopes (Table 1) throughout the year. The magnitude of the gradient, however, is smallest during winter and strongest during fall (Table 1).

The spatial variations of SSS (Fig. 3b) depict the different water masses; SW is located north of 58° N, but can extend southwards during summer; together with a diluted version of NAW (SSS>34 for most of the year), they dominate the central part of the transect (58° N-54.5° N), while CCW is confined south of 54° N, but extends northwards during summer (to ~54.5° N). Moreover, seasonality is evident for the former two water masses, being most fresh during summer and most saline during winter and early spring, and with increasing/decreasing salinity throughout fall/spring.

The most remarkable feature in the seasonal  $fCO_2^{SW}$  cycle along the N-S transect (Fig. 3c) is the decrease during spring when  $fCO_2^{SW}$  reaches values <320  $\mu$ atm everywhere due to biological carbon uptake during the spring phytoplankton bloom (Frankignoulle and Borges, 2001; Thomas et al., 2004). During the rest of the year, thermodynamic, remineralization and mixing processes take over the control of  $fCO_2^{SW}$  (the importance of the different controls for  $fCO_2^{sw}$  is discussed in Sect. 3.1.1) which shows

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values  $\geq$ 360  $\mu$ atm, except for areas north of 56° N where values <360  $\mu$ atm persist until October. Apart from the southern end of the transect (south of 54° N), fCO<sub>2</sub><sup>SW</sup> increases southwards (Fig. 3c and Table 1) throughout the year although the gradient is statistically insignificant during May (Table 1). The  $fCO_2^{SW}$  gradient is partly due to the abovementioned SST gradient (annual mean: -0.36°C °N-1, Table 1) which theoretically accounts for about half of the observed  $fCO_2^{SW}$  gradient (annual mean:  $-12.4 \mu$ atm °N<sup>-1</sup>, Table 1) beacuse  $fCO_2^{sw}$  increases by about 4.23% for every 1°C increase in temperature (Takahashi et al., 1993). The rest of the  $fCO_2^{sw}$  gradient is probably due to the fact that in the shallow southern parts of the North Sea permanent mixing brings up remineralized carbon into the surface and elevates  $f CO_2^{sw}$  whereas in the central and northern parts stratification prevents remineralized carbon from reaching the surface (Thomas et al., 2004). This hypothesis draws support from the fact that the gradient is strongest during summer and early fall (Table 1) when the majority of the organic matter formed during the productive season is remineralized. Approaching at the coast of the Netherlands (south of 54° N), however,  $fCO_2^{sw}$  decreases sharply southwards throughout the year (Fig. 3c and Table 1). Additionally, cruise data acquired along the NS-transect show that this region exhibit a surface  $A_T$ -SSS relationship (Table 2) that is almost identical to the one reported for the German Bight (Brasse et al., 1999) where the surface seawater receives excess total alkalinity due to river runoff from the central European rivers (Kempe and Pegler, 1991) and water-sediment interaction (Brasse et al., 1999; Thomas et al., 2009). Therefore, excess total alkalinity from the above mentioned processes conceivably results in the relatively lower  $fCO_2^{SW}$ in the southernmost part of the transect. Furthermore, a closer inspection of Fig. 3c reveals that the south is characterized by a stronger  $f CO_2^{sw}$  spring drawdown resulting in enhanced seasonal amplitude (≈230 μatm) compared to central (≈180 μatm) and northern regions ( $\approx 100 \,\mu atm$ ).

The seasonal cycle of  $\Delta f CO_2$  (Fig. 3d) resembles that of  $f CO_2^{sw}$  (Fig. 3c) because the seasonal amplitude of  $fCO_2^{atm}$  (~10  $\mu$ atm, not shown) is negligible compared to that of  $fCO_2^{sw}$  (above). The surface waters along the entire NS-transect are nearly at

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CO<sub>2</sub> equilibrium with the atmosphere during winter ( $\Delta f$ CO<sub>2</sub>≈ $-30-15 \mu$ atm). Strong CO<sub>2</sub> undersaturation ( $\Delta f$ CO<sub>2</sub>≈ $-50-170 \mu$ atm) is observed during spring, while during summer and early fall, surface waters in the southern area become supersaturated ( $\Delta f$ CO<sub>2</sub>>0). This seasonal cycle of  $\Delta f$ CO<sub>2</sub> is in good agreement with the one reported by Thomas et al. (2004) who constructed seasonal averages of fCO<sub>2</sub><sup>sw</sup> based on data from four basin-wide cruises in the North Sea.

Data from the WE-transect (Fig. 3e–h) confirm the seasonal variations reported above for the northernmost part of the NS-transect. Additionally, this data subset enable us to compare east-to-west and north-to-south gradients for SST and  $fCO_2^{SW}$ . SST shows seasonal change with amplitude of over 10°C, being coldest in February and March and warmest in August (Fig. 3e). Further, during winter and early spring, SST decreases eastwards (Table 3), but from late spring through fall the SST gradient reverses as a result of decreased mixed layer combined with solar radiation input that increase eastwards in the North Sea (Otto et al., 1990).

The spatial variations of SSS depict the water masses: the saline NAW (SSS>35) is usually encountered in the western part of the transect (Fig. 3f), the fresh SW in the east. Also evident from Fig. 3f is the seasonality for SW, being more fresh (SSS<31) during summer (July) and more saline (SSS>33) during winter (January). Additionally, the 35 isohaline retreats westwards during summer as also was reported by Lee (1980).

Values of  $fCO_2^{sw}$  are highest (360–380  $\mu$ atm) during late fall and winter and lowest ( $\approx$ 260  $\mu$ atm) during spring (Fig. 3g). Furthermore, the low  $fCO_2^{sw}$  values during spring seems to appear first in the eastern side around April and propagate westwards. In the region west of the Prime Meridian, the lowest  $fCO_2^{sw}$  values occur in June. Conversely, the recovery of  $fCO_2^{sw}$  towards maximum winter values seems to start in the west around August and propagate eastwards. Apart from these two features  $fCO_2^{sw}$  values do not show any systematic gradients along the WE-transect (Table 3). Nevertheless, a linear regression between annual  $fCO_2^{sw}$  data and longitude resulted in a statistically significant, but weak slope with poor statistics (Table 3, last column). The most im-

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portant feature in  $\Delta fCO_2$  (Fig. 3h) is that it is negative everywhere along the transect, showing that the area is a year-round sink for atmospheric  $CO_2$ .

# 3.1.1 The controls of $f CO_2^{SW}$

We decomposed the seasonal signal of  $fCO_2^{SW}$  data into individual components due to variations in SST, in air-sea  $CO_2$  exchange, in SSS, and in combined mixing and biology (a choice to be explained shortly), according to Olsen et al. (2008):

$$d_{\text{obs}}fCO_2^{sw} = d_{\text{sst}}fCO_2^{sw} + d_{\text{ase}}fCO_2^{sw} + d_{\text{sss}}fCO_2^{sw} + d_{m\&b}fCO_2^{sw}$$
(3)

where  $d_{\rm obs}f{\rm CO}_2^{\rm sw}$  is the observed monthly change in  $f{\rm CO}_2^{\rm sw}$ ,  $d_{\rm sst}f{\rm CO}_2^{\rm sw}$  is the change due to SST changes,  $d_{\rm ase}f{\rm CO}_2^{\rm sw}$  is the change due to air-sea gas exchange, and  $d_{\rm sss}f{\rm CO}_2^{\rm sw}$  and  $d_{m\&b}f{\rm CO}_2^{\rm sw}$  are the changes due to salinity variations and mixing plus biology, respectively. Details on the computations of each term are given by Olsen et al. (2008), here we only mention that (i) no nutrient data were acquired along the transects and, thus,  $d_{m\&b}f{\rm CO}_2^{\rm sw}$  is determined as a residual i.e. as the monthly change in  $f{\rm CO}_2^{\rm sw}$  that is left unexplained by the other processes. (ii) The determination of  $d_{\rm sss}f{\rm CO}_2^{\rm sw}$  requires the knowledge of  $A_T$  in the surface seawater, while  $d_{\rm ase}f{\rm CO}_2^{\rm sw}$  requires estimates of the air-sea  ${\rm CO}_2$  flux ( $F^{\rm ase}$ ). We used  $A_T$  versus SSS relationships observed along the NS- and WE-transects, based on data collected during the four RV *Pelagia* cruises conducted in 2001 and 2002. The  $A_T$ -SSS relationships and their statistics are given in Table 2. For the computation of  $F^{\rm ase}$  we used 6-hourly wind speed data from NCEP/NCAR (National Centers for Environmental Prediction/The National Center for Atmospheric Research). Gas transfer velocity was computed from wind speed using the relationship of Wanninkhof (1992).

Figure 4 shows the decomposition of various processes on the seasonal variations of  $fCO_2^{sw}$  obtained from Eq. (3) for the two transects (columns 1 and 5 starting from left), for the periods 2005/2006 and 2007 (columns 2 and 3) and for the southern and northern regions of the North Sea (columns 4 and 5). Generally, the largest monthly  $fCO_2^{sw}$  changes are observed from February to July. During this six month period,

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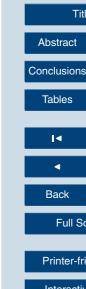
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fCO<sub>2</sub><sup>SW</sup> decreases during the first three months and increases during the last three (Fig. 4, row 1). During the rest of the year, both the magnitude and direction of monthly  $fCO_2^{SW}$  change is highly dependant on the region and on the year. For instance,  $fCO_2^{SW}$ increases from August to November in the north (panel u), while during the same period,  $fCO_2^{SW}$  decreases in the south (panel p). Similarly, data from 2005/2006 shows a marked  $fCO_2^{SW}$  decrease during August and September (panel f), whereas for the same period in 2007 a small increase was observed (panel k).

As to the importance of different  $fCO_2^{SW}$  drivers, monthly  $fCO_2^{SW}$  changes brought about by mixing and biology (row 5) dominate (-80 to  $40 \,\mu$ atm month<sup>-1</sup>) together with SST-induced changes (row 2, -40 to  $60 \,\mu$ atm month<sup>-1</sup>), whereas changes due to  $F^{\rm ase}$ (row 3) are of intermediate importance (-10 to 35  $\mu$ atm month<sup>-1</sup>) and changes from SSS (row 4) are negligible ( $<5 \,\mu$ atm month<sup>-1</sup>) (Fig. 4). Note that the changes from SSS are strongest on the WE-transect (≈10 µatm month<sup>-1</sup>) which is strongly influenced by SW, the water mass with most significant seasonal variation in SSS (Fig. 3f).

The combination of the second, third and last rows of Fig. 4 suggests that the increasing effect of warming on  $fCO_2^{SW}$  from March to July cannot completely compensate for the decreasing effect of biological uptake of carbon and shoaling of mixed layer depth. This imbalance induces CO2 undersaturation of surface waters which drives a CO<sub>2</sub> flux into the ocean (Fig. 4, row 3). Conversely, from August onwards, the decreasing effect of cooling on  $fCO_2^{SW}$  nearly equals the increasing effect of deepening mixed layer depth which entrains deeper water into the surface layer and thus brings regenerated and new nutrients and CO2 into the surface water. Consequently, the observed monthly  $fCO_2^{SW}$  change in this period is small, but variable from one year to another and from one region to another (Fig. 4, row 1). This in turn produces seawater  $fCO_2^{SW}$ values that are close to atmospheric equilibrium and, thus, monthly fCO<sub>2</sub><sup>SW</sup> changes resulting from air-sea exchange  $(d_{ase}fCO_2^{SW})$  are negligible from August to December on a basin scale (panel c), but variable from year to year and from region to region (panels h–w). Thus, in the north,  $d_{ase}fCO_2^{sw}$  is positive throughout the year (Fig. 4, panel w) while it reverses from July onwards for regions south of the 55.5° N (Fig. 4, panel r).

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Another difference between northern and southern regions is that the decreasing effect of shallow mixed layer and biological uptake seem to be more short-lived in the south lasting from February to May (panel t) compared to the north where this effect lasts from March to August (panel y).

The seasonal amplitudes of  $CO_2^{SW}$  due to the two most important drivers (changes in SST and biology plus mixing) can be estimated by integrating the monthly values of  $d_{\rm sst}fCO_2^{SW}$  and of  $d_{\rm m\&b}fCO_2^{SW}$ , respectively. Peak-to-peak values of the integrals give the magnitude of the seasonal amplitudes and were computed from data shown on rows 2 and 5 of Fig. 4. For the NS-transect and using data from all years (panels b and e), we obtained seasonal amplitudes of 144 and  $-185\,\mu$ atm due to changes of SST and biology plus mixing, respectively. However, the seasonal amplitudes due to changes of SST and biology plus mixing were, respectively, 195 and  $-169\,\mu$ atm for 2005/2006, and 119 and  $-210\,\mu$ atm for 2007. Thus, in the North Sea, the non-thermal control (biology plus mixing) dominated if either the whole study period or the single year 2007 were considered. During 2006, however, the SST control dominated, an inter-annual difference that resulted from greater seasonal SST amplitude in 2006 (below, Fig. 5c and g).

The above seasonal amplitudes were also variable from one region to another. For the region north of 57.5° N (Fig. 4, panels v and y), seasonal amplitudes due to changes of SST and biology plus mixing were 80 and  $-200\,\mu$ atm, respectively. For the region south of the 55.5° N (panels q and t), seasonal amplitudes due to changes of SST and biology plus mixing were 120 and  $-160\,\mu$ atm, respectively. While this confirms that the non-thermal control dominated in the North Sea over the study period, it also shows that in the southern region, the SST  $fCO_2^{sw}$  driver was stronger and the biological plus mixing driver was weaker compared to the northern region. The above finding agrees well with the results of Schiettecatte et al. (2007) who, based on data from monthly surveys in the Southern Bight of the North Sea, estimated the temperature and biological  $fCO_2^{sw}$  drivers using a calculation scheme proposed by Takahashi et al. (2002), and found that, over one annual cycle, the ratio of temperature control to the

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biological control is ≈0.70, in good agreement with our result, 120/160=0.75.

# 3.2 Interannual $fCO_2^{SW}$ variations and trends

The interannual variability of  $fCO_2^{SW}$  in the North Sea was investigated in two regions which were chosen on the basis of data availability (Fig. 1). The seasonal cycles for fCO<sub>2</sub><sup>SW</sup>, SST and co-located chlorophyll-a (chl-a) data from SeaWiFS (Sea-viewing Wide Field-of-view Sensor; http://oceancolor.gsfc.nasa.gov) in the two regions from different years is depicted on Fig. 5. In both regions, the VOS  $fCO_2^{SW}$  shows substantial year-to-year variations especially during spring and summer when interannual differences ( $\approx$ 160–200  $\mu$ atm) are comparable to the seasonal changes ( $\approx$ 200–250  $\mu$ atm) (Fig. 5a and e). Fall and early winter show the smallest interannual  $fCO_2^{SW}$  variations, 10-50  $\mu$ atm. Both seasonal and interannual variations appear to be somewhat larger in the southern site.

In order to apprehend the importance of the observed interannual  $fCO_2^{SW}$  changes for the air-sea  $CO_2$  flux ( $F^{ase}$ ) we used a linear relationship between monthly  $\Delta f CO_2$  and  $F^{\text{ase}}$  values  $(y=-0.0035(\pm 0.0003)^*x; R=0.95; p<0.0001)$  which was identified during the evaluation of Eq. (3) (above). The difference in annual mean  $\Delta f CO_2$  between 2005/2006 and 2007 is in the range of 15–25 μatm. Assuming this difference is representative for the whole NS-transect and using the aforementioned function, we estimated that observed  $fCO_2^{sw}$  changes have the potential to produce flux changes of  $0.6-1.1 \text{ mol C m}^{-2} \text{ yr}^{-1}$ , which is 50%–90% of mean  $F^{\text{ase}}$  computed for the NS-transect using data from all years (1.2 mol C m<sup>-2</sup> yr<sup>-1</sup>). However, interannual  $F^{ase}$  variations in the North Sea are most probably substantially less than 90% because (i) the southern region is characterized by enhanced seasonal  $fCO_2^{SW}$  changes (Fig. 5e-h) and, thus, it is not unlikely that this location is more susceptible to interannual changes than the rest of North Sea, and (ii) interannual  $fCO_2^{SW}$  variations can be accompanied by changes in wind speed with an opposing effect on  $F^{ase}$ . Indeed, when we computed  $F^{ase}$  for the whole NS-transect using first data from 2005/2006 and then data from 2007 we obtained a year-to-year  $F^{ase}$  variation of 0.6 (=1.5–0.9) mol C m<sup>-2</sup> yr<sup>-1</sup> i.e. 50% of the

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mean F<sup>ase</sup>

As to the cause of the observed interannual  $fCO_2^{SW}$  changes several features of Fig. 5 deserve attention. Firstly, a comparison between the curves for the years 2006 and 2007 (Fig. 5a and e) reveals that the springtime  $fCO_2^{SW}$  drawdown by phytoplankton blooms starts some weeks earlier in 2007. Additionally, chl-a (Fig. 5d and h) indicate that the phytoplankton bloom in 2007 was stronger. In the southern region, mean chl-a concentration from March to April was 21±6 mg m<sup>-3</sup> in 2007 and only  $4.3\pm2.1\,\mathrm{mg\,m}^{-3}$  in 2006 (Fig. 5h). In the northern region, mean chl-a in late March was  $13.7 \pm 1.5 \,\mathrm{mg}\,\mathrm{m}^{-3}$  in 2007 and only  $0.7 \pm 0.1 \,\mathrm{mg}\,\mathrm{m}^{-3}$  in 2006 (Fig. 5d). Hence, the interannual variations in springtime  $fCO_2^{SW}$  most probably result from changes in magnitude and timing of the spring phytoplankton bloom.

Secondly, interannual  $fCO_2^{SW}$  changes during summer can be partly accounted for by changes in SST. To verify this, we normalized  $fCO_2^{SW}$  values to a constant SST (12°C; Fig. 5b and f). A comparison between normalized fCO<sub>2</sub><sup>sw</sup> for 2006 and 2007 reveals that SST changes account for the differences in  $fCO_2^{SW^2}$  in the northern region during July and August (Fig. 5b). On the other hand,  $fCO_2^{sW}$  differences between 2005 and 2007 observed in the northern region during July and August cannot be attributed to SST changes since the 2005 summertime  $fCO_2^{SW}$  remained at elevated values even after temperature normalization (Fig. 5b). These elevated summertime  $fCO_2^{SW}$  values might be explained by changes in wind speed. High winds prevailed in the North Sea throughout 2005, with NCAR/NCEP wind speeds on average 2.4–2.7 m s<sup>-1</sup> higher than in 2006 and 2007. This would maintain enhanced carbon flux from the atmosphere into the ocean during spring and thus could result in higher summertime  $fCO_2^{SW}$  values. As to third possible cause,  $A_T$  variations were most probably not responsible for interannual summertime  $fCO_2^{SW}$  variations in the northern site because the mean value of salinity normalized surface  $A_T$  ( $A_{T35}$ ), computed from data acquired between 58.5° N-54° N during the RV *Pelagia cruises*, was  $2301\pm5 \mu$ mol kg<sup>-1</sup> and  $2303\pm14$  for August/September 2001 and August/September 2005, respectively. This indicates that essentially all  $A_T$  variations along this part of the NS-transect can be attributed to evap-

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oration/dilution, a process which has equal effects on  $C_T$  and  $A_T$  and, thus, a negligible effect on  $fCO_2^{SW}$ . For the southern region, the temperature normalization accounted for about half of the fCO<sub>2</sub><sup>sw</sup> differences between 2006 and 2007 observed during August (Fig. 5f). Additionally,  $A_T$  variations resulting from changes of river runoff and/or sediment-water interactions might play a significant role in the interannual  $fCO_2^{SW}$  variations at this site. Thomas et al. (2009) reported that in the shallow southeastern North Sea, anaerobic degradation of organic matter releases total alkalinity which buffers the fCO<sub>2</sub><sup>SW</sup> increase from decaying phytoplankton blooms. It is not unlikely that this alkalinity source varies between years due to the aforementioned variability in the biological productivity and, thus, produces some of the interannual  $fCO_2^{SW}$  variations observed in the southern site.

One particular implication of the observed high interannual variability is that it can conceal the trend in  $fCO_2^{SW}$  resulting from the equilibration of the surface waters with the increasing atmospheric CO<sub>2</sub>. For instance, a full equilibration with the atmospheric  $CO_2$  in the last two decades which would increase  $fCO_2^{SW}$  in the North Sea approximately by 30  $\mu$ atm (=1.6  $\mu$ atm yr<sup>-1</sup>×20 yr) would be indiscernible from the interannual variability since it is  $>30 \mu$ atm for most of the year (Fig. 5a and e). This is confirmed by the fact that the overlain older cruise data (squares, diamonds, and triangle) in Fig. 5a and e are not systematically lower than the VOS data. However, the VOS data acquired in January and February at the northern site showed the minimum observed year-to-year differences (±10 μatm, Fig. 5a) suggesting that only observations from these months may be appropriate for the determination of the trend. At present there are too few data from these months for a robust analysis on this matter. For periods much longer than 20 years, however, using winter/fall data might be able to discern the long-term trend. Kelley (1970) reported mean surface seawater xCO<sub>2</sub> value of ≈308±25 ppm in the North Sea. Kelley's samples were taken early October 1967 at locations approximately on the 4°E, most likely from the central North Sea as the ship sailed on the transatlantic route from Hamburg (Germany) to Boston (USA) which matched closely that of Buch (1939) (Kelley, 1970). Therefore, we converted the 1967

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mean  $xCO_2$  value to  $fCO_2^{SW}$  as described in Sect. 2.1, assuming equilibration pressure and temperature of 1 atmosphere and 14°C. The result was subtracted from the mean fCO<sub>2</sub><sup>sw</sup> value measured between 55° N-57° N on 1-15 October over the three years 2005, 2006, and 2007. We obtained an  $fCO_2^{SW}$  increase of  $61\pm33\,\mu$ atm (=364±22– 303±24) for the 40 years elapsed since 1967. This implies that the surface water in central North Sea has tracked more or less the atmospheric CO2 increase in agreement with the fCO<sub>2</sub><sup>SW</sup> growth rate recently reported for the North Atlantic (Takahashi et al., 2009). This finding is, however, somewhat surprising since rapid and marked changes at decadal time-scales have been reported in the whole North Sea for SST (Edwards et al., 2002), phytoplankton biomass (McQuatters-Gollop et al., 2007) and food-web structure (e.g. Beaugrand, 2004). Despite the above mentioned physical and biological decadal changes, it seems that the influence of water inputs from the North Atlantic, whose waters track more or less closely the atmospheric CO<sub>2</sub> increase (e.g. Lefèvre et al., 2004), governs the  $fCO_2^{SW}$  growth rate in the central North Sea. Thus, the above  $fCO_2^{SW}$  growth rate may be applicable in the northern North Sea as well since this region, too, receives large inputs of NAW. Conversely, the above estimated  $fCO_2^{SW}$ growth rate probably should not be extrapolated to the southern parts of the North Sea where  $A_T$  changes and eutrophication has stronger influence on  $fCO_2^{sw}$  (Thomas et al., 2009; Gypens et al., 2009).

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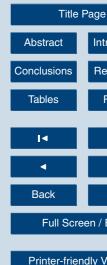
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**Figures** 







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**Table 1.** Monthly distribution of latitudinal gradients in  $fCO_2^{sw}$  and SST. Slopes (a, in  $\mu$ atm  $^{\circ}$  N<sup>-1</sup> or  $^{\circ}$  C  $^{\circ}$  N<sup>-1</sup>) and corresponding statistics obtained from linear regressions between  $fCO_2^{sw}$  or SST and latitude are shown. Positive values indicate properties increasing northwards and vice versa. For  $fCO_2^{sw}$  the gradient was determined for two regions, 54.5–58.5 N and 54.5–53.25 N. For clarity, p-values are shown only where these are >0.05.

_		Month Annua												
For:		1	2	3	4	5	6	7	8	9	10	11	12	mean
	а	-0.1	-0.1	-0.1	-0.3	-0.5	-0.3	-0.3	-0.3	-0.7	-0.7	-0.6	-0.3	-0.4
SST	R	0.4	0.4	0.4	0.9	0.9	0.9	0.8	0.8	1	0.9	0.9	0.8	1.0
	p													
	а	-4	-4	-9	-6	-2	-11	-23	-27	-27	-23	-10	-4	-12
fCO <sub>2</sub> <sup>sw</sup> (54.5–58.5° N)	R	0.6	0.8	0.7	0.5	0	0.5	0.9	0.9	0.9	0.9	0.8	0.5	0.9
7002 (04.0 00.0 14)	p					0.54								
	Α	13	14	81	106	41	29	80	55	66	43	24	23	48
fCO <sub>2</sub> <sup>SW</sup> (54.5–53.25° N)	R	0.9	0.8	0.9	0.9	0.9	0.9	0.9	0.9	0.8	0.8	0.7	0.8	0.9
	р													

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# Spatiotemporal variations of fCO $_2$ in the North Sea

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**Table 2.** Values of coefficients and statistical parameters for two relationships between  $A_T$  ( $\mu$ mol kg<sup>-1</sup>) and salinity ( $A_T = a^*$  salinity+b). The relationships were obtained by linear regressions using data acquired along the two transects (see Fig. 1) during four RV *Pelagia* cruises(in 2001 and 2002) and during the 1987 coastal cruises. Data from north of the 54° N have been de-spiked by binning it into  $0.5^\circ$  N× $0.5^\circ$  E grid prior to regressions.

Parameter	NS-tra	ansect	WE-transect		
а	13.3±3.2	-11.3±1.7	13.86±1.44		
b	1835±110	2698±54	1817.46±48.02		
Standard error of the estimate	±9	±28	±6		
R	0.75	0.74	0.95		
p	< 0.001	< 0.0001	< 0.0001		
Geographic limit	54–60° N	52.5–54° N	57.5–59° N		

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# Spatiotemporal variations of $f CO_2$ in the North Sea



**Table 3.** Monthly distribution of longitudinal gradients in  $fCO_2^{sw}$  and SST. Slopes (a, in  $\mu$ atm  $^{\circ}E^{-1}$  or  $^{\circ}C$   $^{\circ}E^{-1}$ ) and corresponding statistics obtained from linear regressions between  $fCO_2^{sw}$  or SST and longitude are shown. Positive values indicate properties increasing eastwards and vice versa. For clarity, p-values are shown only where these are >0.05.

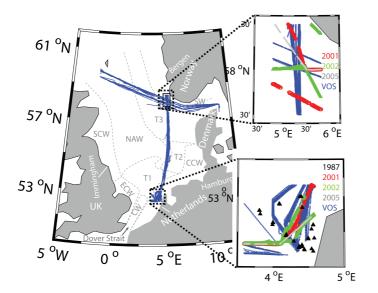
For:								Month						Annual
FOI.		1	2	3	4	5	6	7	8	9	10	11	12	mean
	а	-0.1	-0.3	0	-0.1	0.1	0.3	0.3	0.4	0.3	0.1	0	-0.1	0.1
SST	R	0.9	0.9	0	0.5	0.9	0.9	0.9	0.9	0.9	0.9	0	0.8	0.9
	p											0.4		
	а	-0.3	0.1	0	-4.1	1.2	2	1.6	-0.2	-1.3	-2.7	-3.4	-1.2	-0.8
$fCO_2^{sw}$	R	0	0	0	0.5	0.3	0.6	0.5	0	0.3	0.6	0.9	0.5	0.5
- 2	p	0.3	8.0			0.2			0.6	0.2				

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# Spatiotemporal variations of $fCO_2$ in the North Sea

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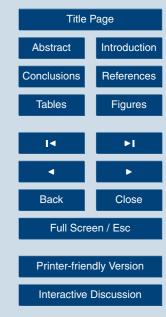
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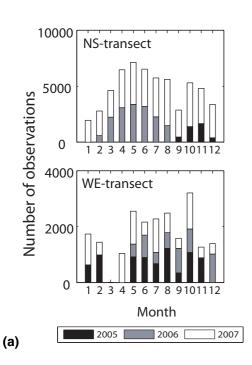


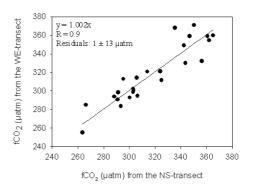
**Fig. 1.** Map of the North Sea, including the most persistent tracks (blue) of the VOS ships (*Nuka Arctica* and *Trans Carrier*) during 2005–2007, names of water masses and their corresponding hydrographic regions (dotted grey, after Lee, 1980). Solid rectangle (at the southern tip of Norway) indicates the area where the two VOS tracks crossover and from which data on Fig. 2b was acquired. Dashed rectangles indicate two sites at which the interannual variability is investigated using data from years and locations shown on the insets where blue indicates VOS tracks; red, green, and grey denote underway  $fCO_2^{sw}$  cruise tracks; black show stations. Water masses shown on the map are CCW: Continental Coastal Water; NAW: North Atlantic Water; SW: Skagerrak Water; SCW: Scottish Coastal Water; ECW: English Coastal Water; CW: Channel Water; T1–T3: transitional water 1–3.

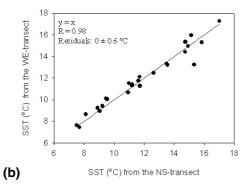
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# Spatiotemporal variations of fCO $_2$ in the North Sea









**Fig. 2.** (a) Number of  $fCO_2^{sw}$  observations per month made from 2005 to 2007 along the NS-and WE-transects. Note that only data used in this study is reported on the plot (other data were discarded due to various reasons detailed in section 2). (b) A comparison of  $fCO_2^{sw}$  (upper) and SST (lower) data acquired from the NS- and WE-transects in the crossover area  $(57.94-58.3^{\circ} \text{ N}, 5.23-5.5^{\circ} \text{ E}, \text{ see Fig. 1})$ . Data from each transect has been organized into  $0.5^{\circ} \text{ E} \times 0.5^{\circ} \text{ N} \times 7$  days bin averages in order to minimize differences due to spatial and/or temporal variations.

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# Spatiotemporal variations of fCO $_2$ in the North Sea

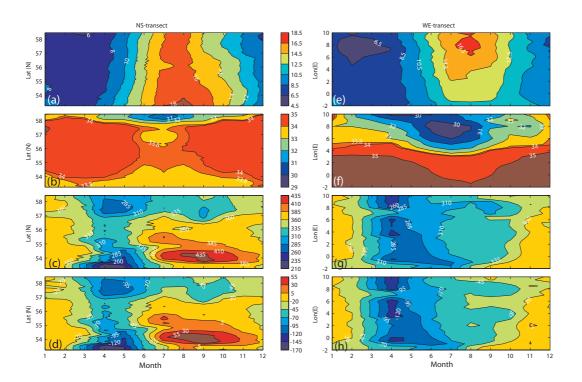
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Interactive Discussion





**Fig. 3.** Hovmöller diagrams of SST (**a** and **e**), SSS (**b** and **f**),  $fCO_2^{sw}$  (**c** and **g**), and  $\Delta fCO_2$  (**d** and **h**) along the NS-transect (left column) and WE-transect (right column). The seasonal cycles shown in the figure are for a composite year consisting of the months depicted on Fig. 2a (above).

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# Spatiotemporal variations of $fCO_2$ in the North Sea



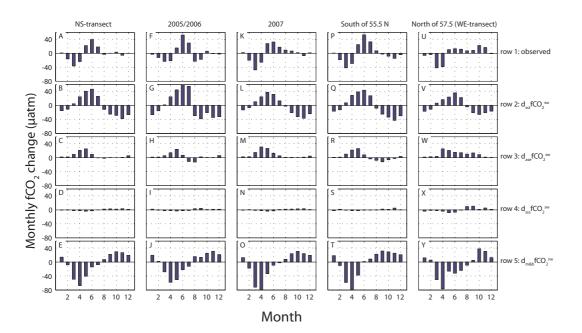
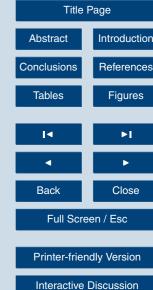


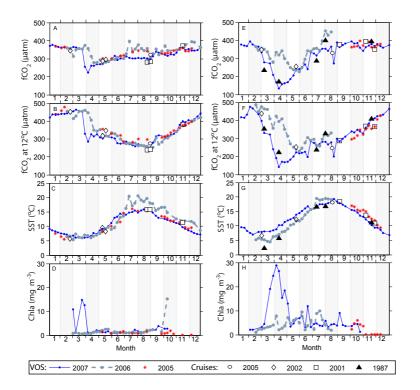
Fig. 4. Monthly changes in  $fCO_2^{SW}$  as observed (first row) and expected due to: SST changes (second row), air-sea CO<sub>2</sub> exchange (third row), SSS changes (fourth row), and biology plus mixing (last row). Negative values reflect a decrease in  $fCO_2^{SW}$  and vice versa. The changes are shown for five cases: along the NS-transect (first column starting from left), for the period 2005/2006 (2nd column), for the year 2007 (3rd column), for the region south of 55.5° N (4th column), and for the WE-transect (last column). The latter is referred to as north of the 57.5° N in Sect. 3.1.1 of the main text.

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**Fig. 5.** Seasonal cycles for  $fCO_2^{sw}$  (**a** and **e**), temperature normalized  $fCO_2^{sw}$  (**b** and **f**), SST (**c** and **g**), and co-located SeaWiFS Chlorophyll-a (**d** and **h**) for different years. All data was averaged weekly. For chl-a, only values between 0 and 30 mg m<sup>-3</sup> are considered realistic and plotted. Panels (a–d) show data acquired from a  $1.0^{\circ} \times 1.0^{\circ}$  site on the northern North Sea (57.5–58.5° N, 4.8–5.8° E; see Fig. 1) for which underway  $fCO_2^{sw}$  and SST data from 2001, 2002, and 2005–2007 are available. Panels (e–h) show data acquired from a  $0.6^{\circ} \times 1.0^{\circ}$  site in the southern North Sea (52.5–53.1° N, 3.6–4.6° E; see Fig. 1) for which also station data from 1987 are available in addition to underway data from 2001, 2002, and 2005–2007.

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