

Variability of North Sea pH and CO₂ in response to North Atlantic Oscillation forcing

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[1] High biological activity causes a distinct seasonality of surface water pH in the North Sea, which is a strong sink for atmospheric CO₂ via an effective shelf pump. The intimate connection between the North Sea and the North Atlantic Ocean suggests that the variability of the CO₂ system of the North Atlantic Ocean may, in part, be responsible for the observed variability of pH and CO₂ in the North Sea. In this work, we demonstrate the role of the North Atlantic Oscillation (NAO), the dominant climate mode for the North Atlantic, in governing this variability. Based on three extensive observational records covering the relevant levels of the NAO index, we provide evidence that the North Sea pH and CO₂ system strongly responds to external and internal expressions of the NAO. Under positive NAO, the higher rates of inflow of water from the North Atlantic Ocean and the Baltic outflow lead to a strengthened north-south biogeochemical divide. The limited mixing between the north and south leads to a steeper gradient in pH and partial pressure of CO₂ (pCO₂) between the two regions in the productive period. This is exacerbated further when coinciding with higher sea surface temperature, which concentrates the net community production in the north through shallower stratification. These effects can be obscured by changing properties of the constituent North Sea water masses, which are also influenced by NAO. Our results highlight the importance of examining interannual trends in the North Sea CO₂ system with consideration of the NAO state.

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1. Introduction

[2] Coastal and marginal seas play an important role in the atmosphere-ocean carbon exchange, responsible for a disproportionately large amount of primary production relative to their surface area [Gattuso *et al.*, 1998], which is triggered by large inputs of nutrients and organic carbon from the adjacent ocean, land, and atmosphere [Wollast, 1998; Thomas *et al.*, 2005a; Thomas *et al.*, 2008b]. The export of this carbon into the adjacent open ocean, thus sequestering large quantities of anthropogenic CO₂, is known as the continental shelf pump [Tsunogai *et al.*, 1999; Thomas *et al.*, 2004]. The effectiveness of this pump is related to the physical and

biological conditions governing the CO₂ disequilibrium between the atmosphere and the sea surface, which in turn is thermodynamically responsible for the CO₂ uptake and the subsequent variation in pH and partial pressure of CO₂ (pCO₂). The codependence of this variability on physical and biological factors makes it difficult to discern the increase in CO₂ solely attributable to atmospheric pCO₂ increases [Santana-Casiano *et al.*, 2007].

[3] The North Sea is a shelf sea on the northwest European continent with links to the North Atlantic Ocean in the south and the north. The majority of water exchange with the North Atlantic occurs in the northern North Sea, where inflowing waters enter through the Orkneys-Shetland shelf, Shetland shelf, and the Norwegian channel, with the Norwegian Trench providing the main exit pathway of circulated water out of the North Sea [Otto *et al.*, 1990; Winther and Johannessen, 2006]. The total net carbon export to the North Atlantic via the Norwegian Trench has been estimated to be $6 \pm 1 \times 10^{12}$ mol C yr⁻¹ [Wakelin *et al.*, 2012], which includes more than 90% of the CO₂ drawn down from the atmosphere in the North Sea [Thomas *et al.*, 2005a]. The effectiveness of the North Sea CO₂ pump is determined principally by water mass exchange between the North Sea and the North Atlantic Ocean in combination with the export of carbon out of the surface layer, predominantly as sinking particulate organic matter [Thomas *et al.*, 2004; Bozec *et al.*, 2005]. The latter applies most significantly to the deeper

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(>50 m), seasonally stratified northern part of the North Sea (>56°N), where seasonality in pH is controlled by production of organic matter and its export [Thomas *et al.*, 2009]. The seasonality of pH and pCO₂ in the southern North Sea is also closely coupled to primary production; however, the export of organic matter is reduced by the rapid remineralization, which takes place in the shallow (<50 m) and well-mixed water column [Borges and Frankignoulle, 1999, 2002; Schiettecatte *et al.*, 2006, 2007].

[4] Over the North Atlantic Ocean, a number of atmospheric teleconnection patterns influence climate variability of which the North Atlantic Oscillation (NAO) is the most prominent. The NAO Index (NAOI) is defined as the difference of atmospheric sea level pressure (SLP) between the Icelandic low and the Azores high and accounts for the greatest proportion (>30%) of the observed SLP variance in the region from December to March [Hurrell, 2003]. The effects of the NAO control a number of large-scale processes at different timescales [e.g. Hurrell, 1995; Hurrell and van Loon, 1997; Greatbatch, 2000]. Since the atmospheric pressure anomalies are most pronounced during northern hemisphere winter [Greatbatch, 2000] and the ratio of signal to noise is the highest [Hurrell and van Loon, 1997], commonly (but not exclusively) the NAOI recorded during December, January, and February (DJF), has been referred to in the literature yielding the most accentuated NAOI variability. Thus, although the NAOI is commonly established for DJF consequences of the NAO have been identified at various timescales. While the atmospheric realm responds at immediate, shorter timescales, for example via variability of trajectory, direction and strength of winds, the oceanic system responds at times scales from seasons to decades, for example via altered circulation patterns at various spatial scales [e.g., Hurrell, 1995; Hurrell and van Loon, 1997; Greatbatch, 2000; Thomas *et al.*, 2008a]. Modeling studies [Thomas *et al.*, 2008b; Levine *et al.*, 2011; McKinley *et al.*, 2011] and long-term observations [Santana-Casiano *et al.*, 2007; Pérez *et al.*, 2010; Bates, 2001] suggest that NAO-driven changes exert significant control over the interannual variability of hydrographic properties and in turn the uptake of CO₂.

[5] Recently, observations from the North Sea [Thomas *et al.*, 2007] and the North Atlantic Ocean [Watson *et al.*, 2009] indicate that the surface water pCO₂ has risen faster than the atmospheric pCO₂, which has been linked to the effects of the NAO, with varying time scales of effect across the region [Santana-Casiano *et al.*, 2007; Thomas *et al.*, 2008a]. In-depth discussions of the role of the NAO in regulating the climate and weather go beyond the scope of the present paper, and can be found elsewhere, for example in Hurrell [1995], or Greatbatch [2000]. However, within the North Sea, many processes have demonstrated significant correlations with the wintertime (DJF) NAOI, which, as we later show, impact the carbonate system. The strength of the water mass exchange between the North Atlantic and the North Sea is regulated by the NAO, which in turn affects physical and chemical characteristics of the North Sea water column for the annual cycle. As a consequence of enhanced water mass exchange between North Atlantic and North Sea during years of positive NAOI (NAO+)[Winther and Johannessen, 2006; Kühn *et al.*, 2010], the corresponding increase of the North Sea's nutrient inventory leads to

higher productivity throughout the productive season from spring until the end of summer [Pätsch and Kühn, 2008]. Characteristic in the North Sea's response to NAO forcing can also be a hysteresis between cause and effect: In the North Sea, NAO+ has further been associated with higher precipitation across Scandinavia with drier conditions over central Europe [Jonita *et al.*, 2011]. Changes in precipitation patterns over the drainage area of the Baltic Sea during winter will affect the runoff from the Baltic Sea into the North Sea over the relevant (runoff) seasons. Additionally, stronger westerly winds during winter, correlated with a positive wintertime NAOI, push North Sea water into the Baltic Sea, a process that in turn leads to an enhanced outflow from the Baltic Sea into the North Sea during the subsequent spring and summer [Hordoir and Meier, 2010]. These patterns are generally reversed during a NAO negative (NAO−) state. From these few examples, it is evident that despite the fact that the NAOI is commonly established for winter (DJF), the consequences for the North Sea are complex, not restricted to the winter season, and can be (partly) masked or even overridden by local or regional weather. One of the primary aims of this paper is to unravel this complex situation and to understand the variability of the North Sea CO₂ system in front of this background.

[6] The intra-annual variability of pCO₂ and dissolved inorganic carbon (DIC) has been well documented in the North Sea [Frankignoulle and Borges, 2001; Thomas *et al.*, 2005b; Prowe *et al.*, 2009; Bozec *et al.*, 2006; Omar *et al.*, 2010; Artioli *et al.*, 2012]; however, on long time scales little work has been done [Thomas *et al.*, 2005a; Thomas *et al.*, 2007; Borges and Gypens, 2010] and despite the proximity of the North Atlantic, the drivers for interannual variability of the CO₂ system in relation to the North Atlantic variability have not yet been investigated from field observations. Further, the full scope of variations in pH and pCO₂ is still difficult to constrain when attempting to reproduce them in models [Prowe *et al.*, 2009; Gypens *et al.*, 2011; Lorkowski *et al.*, 2012; Artioli *et al.*, 2012]. Relying on a unique data set covering three basin-wide occupations of the North Sea during all relevant NAO phases, we are now able to examine the influences of NAO forcing on the North Sea carbonate system.

2. Materials and Methods

[7] The North Sea was sampled during August/September 2001, 2005, and 2008 using a station grid of approximately 90 identical stations each time [Bozec *et al.*, 2005, 2006]. These years experienced NAO (DJF) indices of −1.9, 0.12, and 2.1, respectively (<http://www.cgd.ucar.edu/cas/jhurrell/indices.html>, 2012). As we examine the influence of the NAO in the North Sea on different time scales, we assume that the wintertime NAO forcing will be responsible for producing the most prominent signal in the data on a basin-wide scale.

[8] Due to greater spatial coverage of DIC and pCO₂ data, in all three years, compared to that of total alkalinity (A_T) and pH, the latter two were calculated from the former two, as previously done in intercomparison studies [Thomas *et al.*, 2009]. Internal consistency studies from cruises with full carbonate parameter coverage in late summer indicate that A_T and pH can be predicted, using DIC and pCO₂, with an

Table 1. Dissolved Inorganic Carbon and Salinity End-Members^a

DIC ($\mu\text{mol kg}^{-1}$) and Salinity End-Members	2001	2005	2008
North Atlantic	2047 (35.06)	2078 (35.30)	2065 (35.13)
Baltic	1530 (8)	1530 (8)	1530 (8)
German Bight	2090 (30.36)	2012 (30.77)	2149 (32.28)

^aThe DIC end-members used for the water mass fraction calculation for the three years, with the corresponding salinity values in parentheses.

accuracy of $\pm 9 \mu\text{mol kg}^{-1}$ and ± 0.008 , respectively (L.A. Salt, manuscript in preparation, 2013). Only stations with valid values for DIC and pCO₂ for all of the three years were used, resulting in a total of 85 stations worth of data for comparison.

2.1. DIC and pCO₂

[9] Samples for the carbonate parameters were obtained following the operating procedures outlined in DOE [2007]. Carbonate system parameters, DIC, A_T, and pH (in 2005) were determined at 8–15 depths per station, yielding approximately 700 samples per cruise. All samples were analyzed within 12 h of sampling, and were verified for quality control using certified reference material (CRM) supplied by Prof. Andrew Dickson (Scripps Institute of Oceanography, USA). A single sample was obtained for both DIC and A_T and these were determined by coulometric and potentiometric titrations, respectively. For further details, please see Thomas *et al.* [2007].

[10] Surface water pCO₂ was measured every minute using a flow-through system with continuous equilibration and infrared detection [Körtzinger *et al.*, 1996], yielding approximately 20,000 measurements per cruise with an accuracy of $\pm 1 \mu\text{atm}$. A temperature normalization was applied to the pCO₂ data to obtain pCO_{2@16°C}, which is independent of temperature differences between the years [Takahashi *et al.*, 1993].

2.2. Calculations

2.2.1. Water Mass Analysis

[11] The North Sea surface waters (5 m depth) were separated into three simpler constituents using a mixing analysis of the dominant water masses in the North Sea [Kempe and Pegler, 1991; Shadwick *et al.*, 2011], with North Atlantic water, Baltic Sea water, and German Bight water as end-members. The latter two consist of a fraction of North Atlantic water; however, the large freshwater contribution makes both very distinct from North Atlantic water and allows us to track them into the central North Sea. In order to differentiate water mass fractions from n number of contributors, $n - 1$ end-member variables are required. As this

decomposition was done for the surface waters, temperature cannot be used, because due to seasonal heating and cooling it is not a conservative tracer as used in traditional multiparametric optimizations for analysis of deep waters. Salinity, DIC, and A_T all offer sufficiently distinct end-member concentrations to be used; however, the codependence of A_T on salinity makes DIC favorable. The DIC is nonconservative due to biological uptake/release of CO₂; however, the end-members used (Table 1) are sufficiently distinct that changes in DIC concentration affected by mixing are much greater than the potential interference of primary production/respiration. This was confirmed by similar results being obtained using salinity and A_T, which is more conservative with respect to primary production.

[12] The end-members for the North Atlantic and German Bight were determined individually for each year, with only the Baltic end-member remaining constant. As we lacked observations in the Baltic Proper, DIC and A_T values were taken from literature for a representative salinity of 8 [Thomas and Schneider, 1999; Hjalmarsson *et al.*, 2008] (Table 1). The North Atlantic end-member was determined by the maximum surface salinity found in the northwest North Sea (Latitudes $> 58^\circ\text{N}$ and Longitudes $< 0^\circ\text{E}$) and its corresponding DIC value. The German Bight end-member was determined by the salinity and DIC value found at the station closest to the Elbe river mouth (54.75°N , 8.25°E). By using annually determined end-members for the three years, we can rule out any change in water mass fractions occurring due to changes in the chemical signal of end-members, which we later show does occur in the North Sea. Statistics describing the calculated water mass fractions are shown in Table 2.

2.2.2. DIC Inventory Calculation of the North Sea

[13] To quantify the changes in DIC between years, differences in biological activity and remineralization must be accounted for. Here we use the apparent oxygen utilization ($\text{AOU} = [\text{O}_2]_{\text{sat}} - [\text{O}_2]_{\text{obs}}$) to account for production and remineralization, applying the Redfield ratio [Anderson and Sarmiento, 1994] in the following equation:

$$\text{DIC}^* = \text{DIC} - (\text{AOU} \times 0.7).$$

[14] These values were integrated throughout the water column to a common maximum depth per station, and then station totals were extrapolated over the entire North Sea basin. To help us better understand the changes, the International Council for the Exploration of the Sea (ICES) defined boxes [ICES, 1983] were used to examine the regional changes in DIC and salinity. Unless specified otherwise, boxes 1–5 refer to the entire water column, not just the upper 30 m, whereas boxes 11–15 refer to the deep (> 30 m) portion of these boxes, respectively.

Table 2. Statistics of the Different Water Mass Fractions Present in the North Sea in 2001, 2005, and 2008^a

Water Mass	2001			2005			2008		
	Range	Average	Median	Range	Average	Median	Range	Average	Median
North Atlantic	0–100	83	91	0–100	81	87	0–100	84	91
Baltic	0–16	2	0	0–15	3	1	0–20	3	7
German Bight	0–100	15	4	0–100	16	10	0–100	13	1

^aThe basin-wide range of values, average, and median are given with the units representing the % of the total water present in the North Sea.

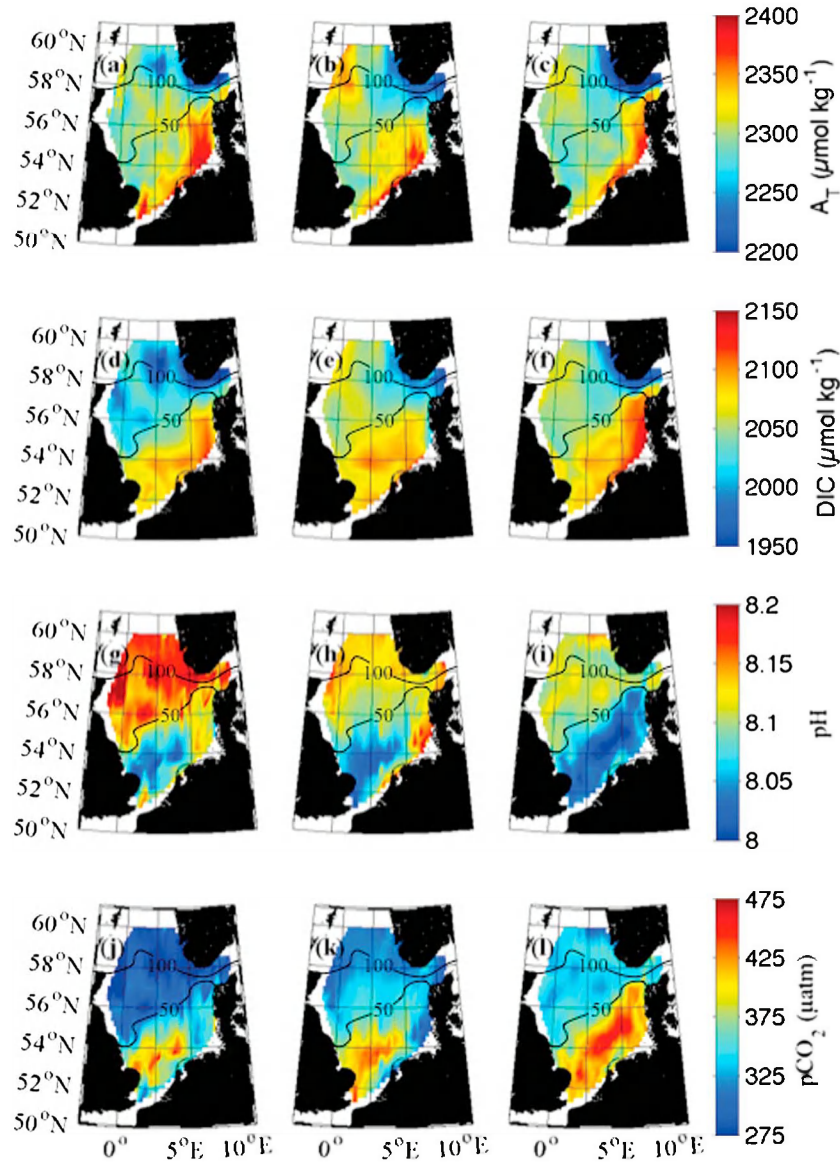


Figure 1. Surface layer distribution of carbonate parameters with 50 and 100 m depth contours. (a–c) Total alkalinity ($\mu\text{mol kg}^{-1}$) for the years 2001, 2005, and 2008, (d–f) dissolved inorganic carbon ($\mu\text{mol kg}^{-1}$) for the years 2001, 2005, and 2008, (g–i) pH for the years 2001, 2005, and 2008, and (j–l) partial pressure of CO₂ (pCO_2 ; μatm) for the years 2001, 2005, and 2008. The DIC and pCO_2 are observations, A_T and pH are calculated parameters from DIC and pCO_2 , using carbonic acid dissociation constants of *Mehrbach et al.*, 1973, refit by *Dickson and Millero* [1987], and pH is given on the Total scale. Average values for 2001, 2005, and 2008 are 2299, 2298, and 2291 $\mu\text{mol kg}^{-1}$ for A_T , respectively, 2034, 2052, and 2055 $\mu\text{mol kg}^{-1}$ for DIC, 8.129, 8.105, and 8.079 for pH, and 323, 344, and 369 μatm for pCO_2 .

2.2.3. Calculation of Brunt-Väisälä Frequency Squared

[15] To assess the vertical stability of the water column in the northern North Sea ($>56^\circ\text{N}$), we utilized the Brunt-Väisälä frequency squared:

$$N^2 = (-g/\rho) \cdot (\partial\rho/\partial z)$$

where z is the depth (m), ρ is density (kg m^{-3}) computed following the density equation of *Fofonoff and Millard* [1983], and g is the gravitational acceleration (9.807 m s^{-2}). The temperature and salinity data from the conductivity-temperature-depth (CTD) casts with a 1 m resolution were smoothed using

a cubic spline. The N^2 was calculated from the smoothed dataset and the depth at which the maximum N^2 occurs we defined as the mixed-layer depth.

3. Results

[16] The main distribution pattern of the carbonate parameters is relatively constant between years (Figure 1). The brackish Baltic outflow around the Norwegian headland has low A_T and DIC signals. The German Bight, in the southwest, is distinguished by its high A_T and high DIC content. The Shetland shelf represents the main North Atlantic inflow

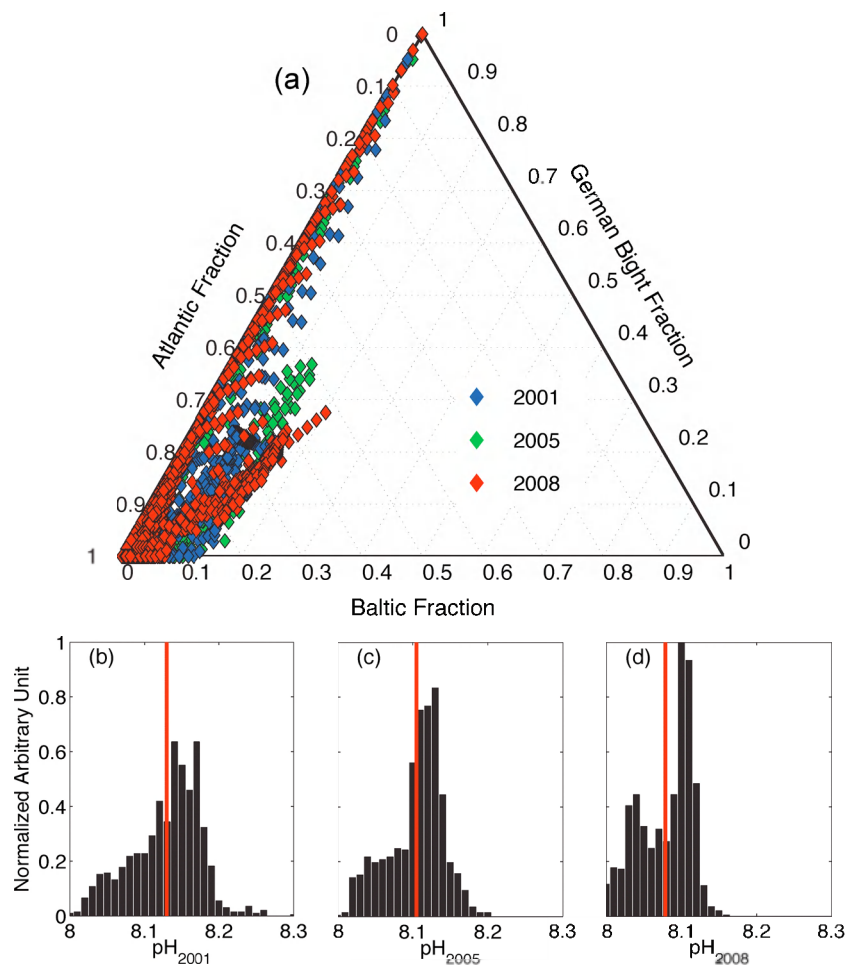


Figure 2. Water type contributions to the North Sea. (a) The fractions of North Atlantic water, Baltic water, and German Bight water in the North Sea in 2001 (blue), 2005 (green), and 2008 (red). (b–d) Histograms of the frequency of calculated pH values binned in 0.01 pH unit intervals with the mean value per year marked by the red line.

site, and is clearly identified by notably higher A_T values than the basin-wide average (Figure 1b). The anticorrelated pH and $p\text{CO}_2$ both show a strong gradient at the 50 m depth contour, representing the boundary at which the dominant control on $p\text{CO}_2$ changes from temperature, in the well-mixed south, to biology, in the stratified north [Prowse *et al.*, 2009; Thomas *et al.*, 2005b]. The gradient between the north and south is steepest in 2008, closely followed by 2001, and weakest in 2005. This pattern reflects the measured surface water temperatures in the North Sea, 2001 and 2008 being the warmest (mean surface temperatures of 16.2°C (± 1.3) and 16.1°C (± 1.1), respectively), and 2005 the coldest (15.4°C (± 1.0)). The highest northern pH values and lowest $p\text{CO}_2$ values are observed in the northern North Sea in 2001, with progressively decreasing mean pH and increasing mean $p\text{CO}_2$ trends over time. The average surface DIC increased by $21 \mu\text{mol kg}^{-1}$, although not uniformly, and the average surface A_T remained relatively constant, $\pm 4 \mu\text{mol kg}^{-1}$, throughout all three years.

[17] The North Sea CO_2 system is largely governed by the relative contribution of different water masses composing the North Sea water as well as the rate at which these are circulated within the North Sea shelf. The mixing analysis

(Figure 2a) clearly identifies the North Atlantic Ocean water as the dominant water mass, constituting an average 83% fraction throughout all three years (Table 2). The average, basin-wide fraction of Baltic water increases from 2% in 2001 to 3% in 2005 and 2008 (Table 2). The dominant North Atlantic inflow follows an anticlockwise circulation from the north, mixing in the south with German Bight water. In the northeastern areas, the Baltic Sea outflow plays an additional role where it is introduced to the circulation on its way out of the North Sea. This leads to the presence of two main mixing regimes, one consisting of North Atlantic and German Bight water, and the other of North Atlantic and Baltic water (Figure 2a). It can be seen that in 2008 these two regimes are most distinguishable, which corresponds to the year in which the maximum Baltic fraction was recorded (20%; Table 2). The formation of the two mixing environments is reflected in the formation of a dichotomy in pH measurements in 2008, which is absent in 2001 and 2005 (Figures 2b–2d). The dichotomy divides the North Sea, with more acidic waters in the south and higher pH values in the north. The divide is formed at, approximately, the 50 m depth contour accounting for the strong gradient visible in Figures 1i and 1l.

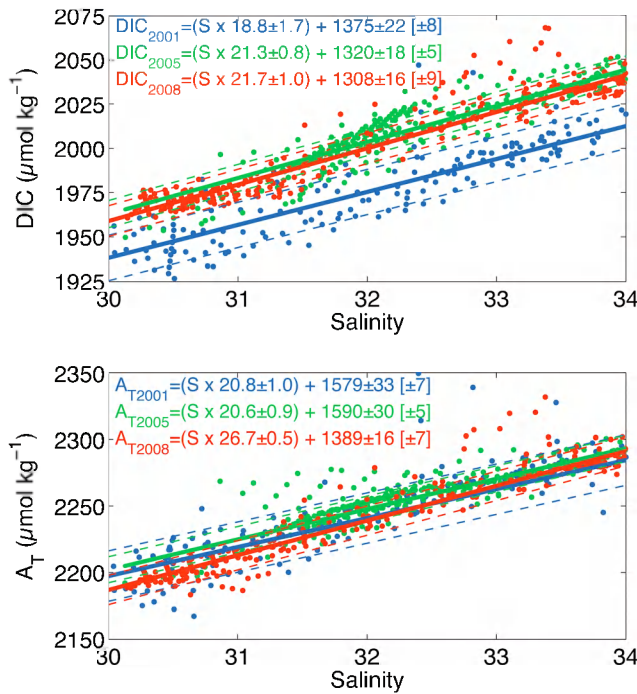


Figure 3. North Sea - Skagerrak mixing diagram. Linear fitted regressions for the mixing relationship between the Skagerrak and North Atlantic inflow in the northern North Sea. Upper graph shows DIC and lower graph shows A_T . Points were selected based on percentage of Baltic water mass fraction present ($>3\%$). Dashed lines represent one standard deviation ($\pm 1\sigma$) of the residuals for each fit, also given in parentheses.

[18] Examining the mixing relationship between the North Atlantic and Baltic water further reveals a change in the water mass end-members from 2001 to 2005. A linear regression was applied, for each year, to data with a Baltic water mass fraction greater than the three-year average of 3% (Figure 3) revealing three statistically significant relationships. The years 2005 and 2008 show a remarkably similar mixing line with the most notable difference being a general decrease in the salinities observed in the Skagerrak in 2008 compared to 2005. Such a shift is reflective of different proportions of the two water masses but indicates that the water masses remain constant in their properties. The difference

between these two years and 2001, however, is much greater. The slope of the regression line is shallower in 2001, indicative of a higher DIC Baltic end-member and a lower DIC North Atlantic end-member. The same relationship is reflected, between 2005 and 2008, in the A_T mixing diagram (Figure 3b).

[19] The inorganic carbon, after correction for metabolic DIC (calculations in section 2.2.2) and respective salinity inventories were used to quantify the changes (ΔS and ΔDIC) between the two time periods. The change in each ICES box for the two time periods showed a significant correlation coefficient of 0.903 and 0.839 (excluding Box 8) for the period 2001–2005 and 2005–2008, respectively. Box 8, heavily influenced by the German Bight, recorded very low salinities for 2008, coinciding with a larger Elbe discharge [<http://coast.gkss.de/staff/kappenberg/elbe/abfluss/elbe.abfluss>]. This box is likely to be more representative of local effects thus skewing the general pattern for the rest of the North Sea (including box 8 gives an $R^2 = 0.49$). Although the increase in DIC was basin-wide from 2001 to 2005, it did not occur evenly across the basin or throughout the water column.

[20] The greatest increases in average DIC concentration from 2001 to 2005 occurred in the central and northwestern North Sea. The latter region is significantly deeper than the southern North Sea; thus, the ICES boxes were further divided into a surface (30 m) and deep box. The surface boxes showed an increase of the same order of magnitude as the deep boxes; however, due to the greater DIC concentrations at depth, this constitutes a lower percentage of total increase. From 2005 to 2008, the changes in DIC were much smaller and demonstrated no clear pattern. The North Sea DIC inventory was 8.11 Pg C (1 Pg = 10^{15} g) in 2001, 8.17 Pg C in 2005, and 8.18 Pg C in 2008. Hence, it increased by approximately 0.8% ($+6 \times 10^{-2}$ Pg C) from 2001 to 2005, while the inventory remained almost stable ($+5 \times 10^{-3}$ Pg C, $<0.1\%$) between 2005 and 2008. The deep northern boxes demonstrated a greater inventory increase of 1.1% from 2001 to 2005, and a 0.0% change from 2005 to 2008. Of the entire observed change in these boxes, 97% occurred from 2001 to 2005.

[21] The changes in the DIC concentrations in the surface also manifest in the change in temperature-normalized $p\text{CO}_2$ ($p\text{CO}_2@16^\circ\text{C}$) distribution (Figure 4). The increase in the average North Sea $p\text{CO}_2@16^\circ\text{C}$ from 2001 to 2005 is 26 μatm , compared to 4 μatm from 2005 to 2008 (the increases for 2001 to 2005 and 2005 to 2008 for nontemperature

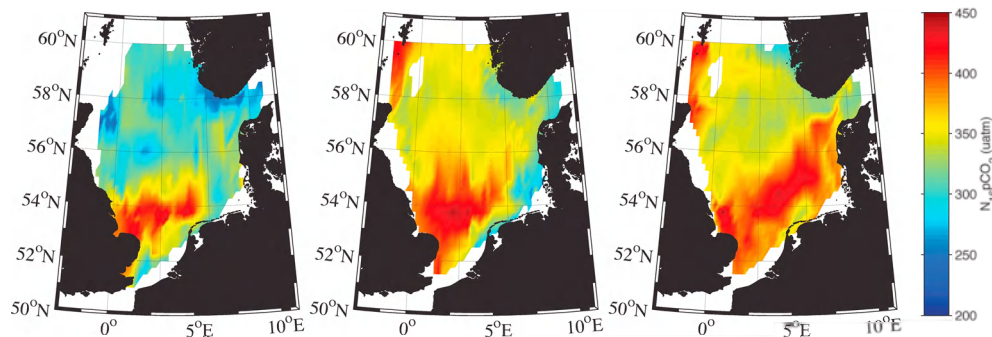


Figure 4. Distribution of temperature-normalized (16°C) $p\text{CO}_2$ in surface waters. In (a) 2001, (b) 2005, and (c) 2008.

normalized pCO₂ were 21 μatm and 25 μatm , respectively). Using an average basin-wide pCO₂@16°C from all three years (346 μatm), these increases correspond to 7.5% and 1.0% increases, which are proportional to the calculated increase in the North Sea DIC inventory. This agreement implies that the surface expression of pCO₂@16°C is, to a large extent, representative of the entire water column, which, due to the shallow depths of the majority of the North Sea is not surprising. Similar to the distribution of DIC increase, the majority of the increase in pCO₂@16°C occurs in the northern North Sea, namely, where the main inflow site is for North Atlantic water. In the north (>56°N), the average surface increase from 2001 to 2005 is 44 μatm , and from 2005 to 2008 the increase is 2 μatm . The southern North Sea shows much more stable increases, of 22 μatm and 18 μatm . At this time of year in the northern North Sea, pCO₂ without the effect of temperature is predominantly controlled by biology [Prowse *et al.*, 2009]. Using this parameter pCO₂@16°C to investigate the differences in production between the three years would indicate a drop in primary productivity from 2001 to 2005 and 2008. However, the AOU in subsurface waters in the northern North Sea show comparable values between all three years (36.4 $\mu\text{mol kg}^{-1}$ in 2001, 30.1 $\mu\text{mol kg}^{-1}$ in 2005, and 31.3 $\mu\text{mol kg}^{-1}$ in 2008), indicating that net community production (NCP) was similar.

4. Discussion

[22] Despite the similar fundamental patterns observed in 2001, 2005, and 2008, distinct differences occurred as a consequence of different DIC mixing patterns and proportions. In 2008, the year with the most positive NAO index (+2.1), the most pronounced front between the two mixing regimes occurs, where North Atlantic and German Bight waters were on the southern side and a mix of North Atlantic and Baltic Sea waters were on the northern side. This is caused by the fact that both the inflows of North Atlantic [Winther and Johannessen, 2006] and Baltic Sea [Hordoir and Meier, 2010] water into the North Sea are strongest under NAO+ conditions due to stronger westerly winds, strengthening the anticlockwise circulation [Lenhart *et al.*, 2004; Winther and Johannessen, 2006]. There is subsequently an increased flow from east to west along the isoclines at 50 m, (the Dooley current [Dooley, 1974]), in addition to increased flow down the west coast of the UK. When these inflows weaken during neutral (2005) or NAO− (2001) phases, there is a less pronounced mixing pattern and the contrast between the two regimes is diminished with more mixing occurring in the eastern central North Sea. The front between the north and south is thus less distinct or vanished, as for example, visible in the greater presence of Baltic Sea water (Figure 2) or in the distribution of A_T (Figure 1), which is unaffected by the anthropogenic CO₂ perturbation, in contrast to the remaining CO₂ system parameters.

[23] The biogeochemical divide along the 50 m contour, separating the northern and southern North Sea, is a well-documented feature in CO₂ distributions [Thomas *et al.*, 2004; Bozec *et al.*, 2005; Prowse *et al.*, 2009; Omar *et al.*, 2010]; however here, the manifestation of this divide is shown to be strongly influenced by the NAO. The observed mixing behavior has profound implications for the distribution of pH in the North Sea (Figures 1c–1e). The two

aforementioned mixing regimes lead to a higher pH in the stratified northern region, where Baltic Sea and North Atlantic inflows mix, and a lower, more acidic pH, in the shallower southern region. When these inflows weaken during NAO− years, evidently more thorough mixing between these regions occurs and the pH histogram reveals a more transitional pattern.

[24] In addition to NAO-driven changes in mixing ratios and rates, the North Sea CO₂ system is further affected by the biogeochemical properties of its composing water masses. This applies especially to the DIC concentrations of the inflowing North Atlantic Ocean waters, which have demonstrated substantial variability during the recent decade [Watson *et al.*, 2009; Thomas *et al.*, 2008a; Schuster and Watson, 2007]. The northern North Sea CO₂ system shows a substantial increase in DIC and temperature-normalized pCO₂ and decrease in pH between 2001 and 2005 (Figures 1 and 3) in comparison to that observed from 2005 to 2008. The concomitant change in salinity with the change in DIC throughout the water column reveals that the increase is water mass driven. Otto *et al.* [1990] state that changes in salinity in the North Sea stem from either changes in the salinity of inflowing water or changes in runoff. A shift in the salinity-DIC mixing diagram confirms that the DIC concentrations in the North Atlantic end-member have increased dramatically from 2001 to 2005, which we propose is a delayed response to NAO-driven changes in the North Atlantic [Thomas *et al.*, 2008b]. This accelerated the decrease in pH and increase in pCO₂ of the North Sea beyond that anticipated from the rise of atmospheric CO₂ concentrations alone [Thomas *et al.*, 2007]. The DIC and salinity changes between 2005 and 2008 also demonstrated a significant correlation, but were an order of magnitude smaller thus much less pronounced, yielding similar end-member DIC concentrations for 2005 and 2008, analogous to the variable behavior observed in surface pCO₂ in the North Atlantic Ocean [Schuster *et al.*, 2009].

[25] The same pattern was unsubstantial in the A_T-salinity mixing line. As the increase in DIC observed in the North Atlantic, and subsequently the North Sea, is driven by air-sea pCO₂ exchange, there is no concomitant change in A_T with DIC. However, there is still some variation in the A_T-salinity mixing lines, which could be associated with the noted change in salinity [Thomas *et al.*, 2008a]. The NAO also exerts large influence over precipitation patterns over Europe so that NAO+ leads to drier conditions across Europe but wetter conditions over Scandinavia [Hurrell and van Loon, 1997]. It follows that in 2008 we would expect more rainfall and runoff in the northern area of the Baltic drainage basin, which is associated with granite rocks and has lower A_T values compared to the south [Hjalmarsson *et al.*, 2008]. This would lead to lower A_T in 2008 compared to 2001, which is consistent with our computed A_T end-members (Figure 3b). These changes in precipitation patterns over Europe and thus riverine runoff into the North Sea may additionally alter salinity and DIC patterns in the southern North Sea, where the majority of riverine input enters the North Sea. However, the riverine contribution represents just 0.5% of the water budget and 0.7% of the carbon budget in the North Sea [Thomas *et al.*, 2005a], which is insufficient to cause the change recorded in DIC or pCO₂, although it may have contributed to the observed variability.

[26] The northern North Sea is sufficiently deep to develop a summer thermocline, thus facilitating phytoplankton blooms

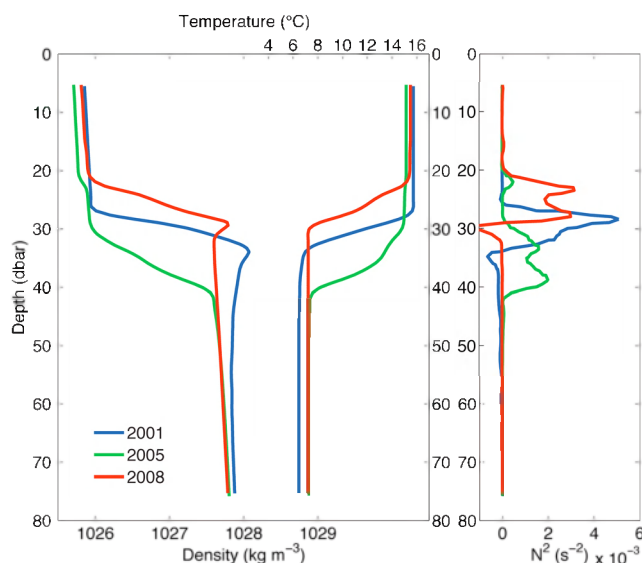


Figure 5. Stratification at 57°N, 2.25°E. (a) Vertical profiles of density and temperature for 2001 (blue), 2005 (green), and 2008 (red). (b) Brunt-Väisälä frequency squared profile for 2001 (blue), 2005 (green), and 2008 (red).

during the productive period, which are maintained in the surface mixed layer. Using the maximum water column value of a representative northern station of the Brunt-Väisälä frequency as an indicator of the mixed layer depth, we observe a very stable, but shallower stratification with a surface mixed layer of approximately 30 m in 2001 compared to 40 m in 2005 (Figure 5). Since the residence time of the waters in the North Sea is of less than one year, there is no accumulation of metabolic DIC (previous years' primary production has no effect on the current state of the North Sea). If the NCP were the same, as it was indicated in our datasets by AOU, a change in mixed-layer depth (MLD) would impact the observed pCO₂. While the biological pCO₂ drawdown was on the order of 300–330 μatm in 2001 [Thomas *et al.*, 2005b], a similar NCP would have caused a pCO₂ drawdown of 200–250 μatm in 2005, characterized by a mixed layer depth of 40 m. This would lead to a difference of 50–130 μatm between the two years, which is in line with the observed increase of 51 μatm of temperature-normalized pCO₂ (Figure 4) in the northern North Sea. Taking the observed salinity change into account, such an increase would correspond to a pH decrease of 0.056.

[27] Kühn *et al.* [2010] have modeled a greater CO₂ sink in the northern North Sea during years of NAO– (2001) compared to years of NAO+, which they attributed to weaker stratification facilitating greater upward transport of nutrients. The highest pH values and lowest pCO₂ values recorded are observed in the northern North Sea during years of NAO–; however, we cannot ascribe this to weaker stratification. The weaker stratification in 2005, associated with cooler temperatures, demonstrates that the expression of pH and CO₂ can be exaggerated or masked by physical conditions within the North Sea. The variability of the mixed layer depth in the North Sea is controlled by a combination of temperature and NAO [Lenhart *et al.*, 2004] and we propose the latter affects it through two possible processes. First, a stronger North Atlantic inflow weakens the thermocline in

years of neutral and positive NAO, leading to less stable stratification as found in 2005 and 2008. Alternatively, weaker winds may allow the thermocline to rise during more negative NAO conditions. In 2008, a stronger warming of the surface waters resulted in a more stable water column with a shallower mixed layer. This situation enhanced the NCP effect on the surface layer pCO₂. Simultaneously, the warmer waters experienced in 2008 raised the pCO₂, eventually leading to comparable pCO₂ conditions in 2005 and 2008, with 2008 showing the warmer and shallower surface layer.

[28] In summary, our results indicate that under conditions of NAO+, as in 2008, the North Sea shelf pump is more efficient than under NAO– due to increased rates of Atlantic and Baltic inflow into the North Sea and a strengthened anticlockwise circulation. The strengthened biogeochemical divide between the northern and southern North Sea means that more carbon is exported from the northern North Sea out of the Norwegian Trench without coming into contact with the atmosphere, which limits subsequent outgassing of remineralized CO₂ making the shelf pump more effective. When NAO+ occurs in conjunction with a year of higher SST, shoaling of the thermocline allows intense areas of primary production to develop. This causes lower pCO₂ and higher pH in surface waters of the northern North Sea; however, this is not shown to have any effect on total carbon uptake. In addition, any changes to the biogeochemical content or quantity of the source water masses contributing to the North Sea can intensify or diminish these expressions.

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