

Rapid decline of the CO₂ buffering capacity in the North Sea and implications for the North Atlantic Ocean

Helmuth Thomas,^{1,2} A. E. Friederike Prowe,² Steven van Heuven,³ Yann Bozec,^{1,4} Hein J. W. de Baar,^{1,3} Laure-Sophie Schiettecatte,⁵ Kim Suykens,⁵ Mathieu Koné,⁵ Alberto V. Borges,⁵ Ivan D. Lima,⁶ and Scott C. Doney⁶

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[1] New observations from the North Sea, a NW European shelf sea, show that between 2001 and 2005 the CO₂ partial pressure ($p\text{CO}_2$) in surface waters rose by 22 μatm , thus faster than atmospheric $p\text{CO}_2$, which in the same period rose approximately 11 μatm . The surprisingly rapid decline in air-sea partial pressure difference ($\Delta p\text{CO}_2$) is primarily a response to an elevated water column inventory of dissolved inorganic carbon (DIC), which, in turn, reflects mostly anthropogenic CO₂ input rather than natural interannual variability. The resulting decline in the buffering capacity of the inorganic carbonate system (increasing Revelle factor) sets up a theoretically predicted feedback loop whereby the invasion of anthropogenic CO₂ reduces the ocean's ability to uptake additional CO₂. Model simulations for the North Atlantic Ocean and thermodynamic principles reveal that this feedback should be stronger, at present, in colder midlatitude and subpolar waters because of the lower present-day buffer capacity and elevated DIC levels driven either by northward advected surface water and/or excess local air-sea CO₂ uptake. This buffer capacity feedback mechanism helps to explain at least part of the observed trend of decreasing air-sea $\Delta p\text{CO}_2$ over time as reported in several other recent North Atlantic studies.

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1. Introduction

[2] Anthropogenic activities including fossil fuel combustion and land use have led to a substantial and accelerating increase of the partial pressure of carbon dioxide ($p\text{CO}_2$) in the atmosphere. The increased atmospheric $p\text{CO}_2$, in turn, leads to a net uptake of CO₂ by the oceans that partly attenuates the deleterious effects of anthropogenic CO₂ on climate [Intergovernmental Panel on Climate Change (IPCC), 2001; Fung et al., 2005]. Recent studies show that the ocean has served as a major sink for the anthropogenic CO₂, accounting for about half of the fossil fuel carbon emitted since the preindustrial era [Thomas et al., 2001; Sabine et al., 2004]. The North Atlantic Ocean [Takahashi et al., 1997] and its coastal [Thomas et al., 2004] and shelf

areas [Frankignoulle and Borges, 2001] play a key role in absorbing CO₂ from the atmosphere. The latter areas are thought to act as continental shelf pumps for CO₂ [Tsunogai et al., 1999; Thomas et al., 2004; Borges et al., 2005] supplementing substantially the CO₂ uptake by the open oceans. A pilot study in the North Sea, carried out in 2001/2002 with seasonal resolution, provided fundamental insight into the continental shelf pump mechanism and strength of the CO₂ uptake in coastal seas [Thomas et al., 2004, 2005a, 2005b; Bozec et al., 2005, 2006]. Chemical and biological activity, which are high in the surface of the world ocean and notably so in its shallower extensions [Wollast, 1998] such as the North Sea, partly mediate CO₂ uptake and introduce both positive and negative feedbacks with anthropogenic CO₂ uptake. For example, elevated CO₂ levels decrease benthic and pelagic calcification and increase CaCO₃ dissolution in sediments, both of which act to damp the growth of atmospheric CO₂ [Riebesell et al., 2000; Delille et al., 2005; Orr et al., 2005].

[3] The surface ocean constitutes the gateway for CO₂ into the ocean's interior, with the air-sea $p\text{CO}_2$ difference ($\Delta p\text{CO}_2$) being the thermodynamic driving force for surface gas exchange. Analysis of the raw observations at the Bermuda Atlantic Time-series Study station (BATS) [Bates, 2001] indicates that the surface water $p\text{CO}_2$ has risen faster than the atmospheric $p\text{CO}_2$, but if the data are seasonally detrended, surface water and atmospheric $p\text{CO}_2$ appear to

¹Royal Netherlands Institute of Sea Research, Den Burg, Netherlands.

²Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada.

³Department of Ocean Ecosystems, Rijksuniversiteit Groningen, Haren, Netherlands.

⁴Now at Scripps Institution of Oceanography, San Diego, California, USA.

⁵Chemical Oceanography Unit, University of Liège, Liège, Belgium.

⁶Marine Chemistry and Geochemistry Department, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA.

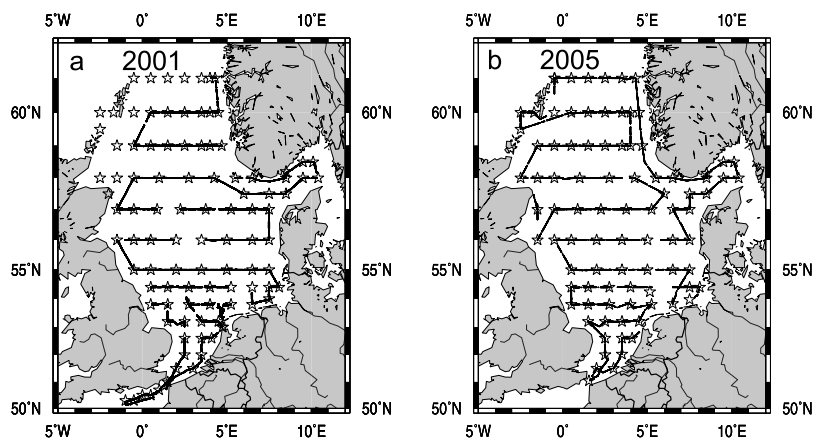


Figure 1. Underway surface water samples (line) and station locations (stars) in the North Sea are shown for (a) 2001 and (b) 2005. Ninety identical stations were sampled during both years.

rise at more comparable rates. At station ALOHA in the North Pacific subtropical gyre [Winn *et al.*, 1998] both surface water and atmospheric $p\text{CO}_2$ have been reported to rise at comparable rates during the 1990s, though a recent study suggests that changes in precipitation may be driving the surface water $p\text{CO}_2$ at ALOHA to rise faster than the atmospheric one [Dore *et al.*, 2003]. Similar rates of surface water and atmospheric $p\text{CO}_2$ increase have been confirmed in general for the North Pacific [Takahashi *et al.*, 2006], the equatorial Pacific [Feely *et al.*, 2006], and the Southern Ocean [Inoue and Ishii, 2005], though regional variability can be observed [Inoue and Ishii, 2005; Takahashi *et al.*, 2006]. In contrast, a series of studies of the northern North Atlantic Ocean [Lefèvre *et al.*, 2004; Omar and Olsen, 2006; Corbière *et al.*, 2007] also reported a faster increase of the surface ocean $p\text{CO}_2$ compared to that in the atmosphere. The observed decline in the air-sea $p\text{CO}_2$ difference in the northern North Atlantic could arise from a variety of biological, chemical, and physical factors and may reflect either natural interannual to decadal variability [e.g., Le Quéré *et al.*, 2000], the longer-term secular trend due to anthropogenic CO₂ transience, or some of both.

[4] A reliable understanding of the complex and regionally varying response of the surface ocean carbonate chemistry to increasing atmospheric $p\text{CO}_2$ is essential for predictions of the future evolution of the carbon cycle, the atmospheric CO₂ content, and ultimately climate [IPCC, 2001; Fung *et al.*, 2005]. Theoretical, laboratory, and modeling studies suggest that the buffer capacity of the seawater inorganic carbon system, reflected in the Revelle factor, decreases under high-CO₂ conditions: Seawater equilibrated with high- $p\text{CO}_2$ air holds less additional dissolved inorganic carbon (DIC) for the same size change in $p\text{CO}_2$, constituting a positive feedback on the atmospheric buildup of anthropogenic CO₂ [Revelle and Suess, 1957; Sarmiento *et al.*, 1995]. In the present study we employ a two-pronged strategy to deepen our understanding of the response of the North Sea and the North Atlantic Ocean to rising CO₂ conditions using new field data from the North Sea and numerical model simulations for the North Atlantic

Ocean. Supported by theoretical calculations, we demonstrate directly using the North Sea field observations that the efficiency of ocean carbon uptake is declining over time because of the oceanic uptake of anthropogenic CO₂. We propose that the regional patterns in the evolving surface water buffer capacity (Revelle factor), detected in the northern North Atlantic Ocean field data, may be a significant (on the order of 10–30%), though perhaps not dominant, factor in the observed decline in air-sea $\Delta p\text{CO}_2$. We investigate in detail temporal trends in the ocean inorganic carbon system and buffer capacity using two regional field data sets from 2001 and 2005 for the North Sea, which is intimately coupled to the North Atlantic Ocean [Thomas *et al.*, 2004, 2005a], and a global ocean carbon model [Moore *et al.*, 2004; Doney *et al.*, 2004].

2. Methods

[5] This study builds on previous work on CO₂ temporal trends in the North Atlantic [Bates, 2001; Lefèvre *et al.*, 2004; Omar and Olsen, 2006] but differs by providing a more comprehensive regional-scale analysis. We utilize two North Sea-wide field data sets from 2001 and 2005 comprising the full dissolved carbonate system and related data. The North Sea field data complement and enhance the ongoing tremendous efforts in using voluntary observing ships (VOS) to gather $p\text{CO}_2$ surface water data across the North Atlantic [e.g., Lefèvre *et al.*, 2004]. Our work here augments and moves beyond the VOS $p\text{CO}_2$ analysis because we can utilize additional essential observations of DIC, total alkalinity (A_T), and oxygen from both surface waters and throughout the entire water column. The cruises were carried out on R/V *Pelagia* at the same time of year from 16 August 2001 to 13 September 2001 and from 17 August 2005 to 6 September 2005. The entire North Sea was sampled by an adapted 1° by 1° grid of 90 identical stations during both years (Figure 1), resulting in high-resolution data sets for assessing the temporal changes between 2001 and 2005. Approximately 750 samples per cruise were analyzed for dissolved oxygen, A_T , and DIC,

Table 1. Changes of Selected Observed and Normalized CO₂ System Parameters, Apparent Oxygen Utilization (AOU), and Temperature in the North Sea Between Summer 2001 and Summer 2005 Given for the Entire, Northern, and Southern North Sea^a

	Atmospheric $p\text{CO}_2$, μatm	Surface Temperature, $^\circ\text{C}$	Surface Water $p\text{CO}_2$, μatm	$\Delta p\text{CO}_2$, μatm	Surface Water $p\text{CO}_2$ at $T = 16^\circ\text{C}$, μatm	$\Delta p\text{CO}_2$ at $T = 16^\circ\text{C}$, μatm	Surface DIC, μM	Normalized Surface DIC, μM
<i>Entire North Sea</i>								
2001	359	16.3 ± 1.2	327 ± 43	-31.2 ± 42	323 ± 36	-35.7 ± 37	2089 ± 36	2091 ± 41
2005	370	15.0 ± 1.4	349 ± 34	-20.0 ± 34	366 ± 29	-4.1 ± 31	2109 ± 27	2103 ± 27
<i>Northern North Sea (North of 54°N)</i>								
2001	359	16.0 ± 1.2	311 ± 33	-47.2 ± 33	311 ± 28	-48.5 ± 28	2079 ± 35	2080 ± 40
2005	370	14.8 ± 1.3	342 ± 27	-27.3 ± 27	361 ± 26	-8.0 ± 29	2107 ± 27	2099 ± 25
<i>Southern North Sea (South of 54°N)</i>								
2001	359	16.9 ± 1.0	378 ± 25	18.6 ± 25	366 ± 26	4.2 ± 29	2121 ± 11	2128 ± 17
2005	370	16.7 ± 0.8	405 ± 30	36.2 ± 30	403 ± 29	25.4 ± 34	2135 ± 6	2138 ± 9
	Water Column Mean DIC, μM	Normalized Water Column Mean DIC, μM	Change of DIC _{norm} Water Column Inventory, mol DIC m ⁻²		Water Column Mean AOU, μM	Water Column Mean A_T , μM	Revelle factor (Normalized)	
<i>Entire North Sea</i>								
2001	2153 ± 22	2106 ± 22			19.7 ± 9.9	2371 ± 13	10.1 ± 0.36	
2005	2166 ± 21	2117 ± 16	$+1.1 \pm 1.2$		18.9 ± 10.4	2375 ± 11	10.7 ± 0.33	
<i>Northern North Sea (North of 54°N)</i>								
2001	2160 ± 19	2101 ± 21			22.9 ± 7.9	2372 ± 13	10.0 ± 0.29	
2005	2169 ± 19	2114 ± 15	$+1.2 \pm 1.3$		20.9 ± 8.9	2376 ± 10	10.6 ± 0.29	
<i>Southern North Sea (South of 54°N)</i>								
2001	2127 ± 8	2125 ± 16			6.1 ± 4.1	2368 ± 17	10.5 ± 0.34	
2005	2137 ± 8	2140 ± 10	$+0.1 \pm 0.3$		0.8 ± 3.7	2367 ± 13	11.1 ± 0.34	

^aThe standard deviation reveals spatial variability of the averages which indicate general trends of the parameters between 2001 and 2005. The Revelle factor has been calculated from the station data (Figure 1) rather than from the basin-wide or regional averages. The atmospheric observations are in excellent agreement with observations from Ocean Station M (66°N , 2°E) (CO₂ Time Series data are available at <http://www.esrl.noaa.gov/gmd/ccgg/carbontracker/tseries.php?type=mr>). The water column mean concentrations are computed from the water column inventory divided by the water column depth.

using the coulometric method for the latter [Johnson *et al.*, 1993]. The uncertainties were estimated to be $2\text{--}3 \mu\text{mol kg}^{-1}$ ($\approx 0.1\%$) for A_T and $1.5 \mu\text{mol kg}^{-1}$ ($\approx 0.08\%$) for DIC. The surface water $p\text{CO}_2$ was determined continuously [Körtzinger *et al.*, 1996] with approximately 20,000 surface water $p\text{CO}_2$ data points per cruise; hourly measurements were also made for atmospheric $p\text{CO}_2$. The uncertainty of the $p\text{CO}_2$ data was estimated to be $1 \mu\text{atm}$ ($\approx 0.3\%$). Detailed descriptions of the methods are given elsewhere [Thomas *et al.*, 2005b; Bozec *et al.*, 2005]. The surface water $p\text{CO}_2$ data were normalized to a temperature (T) of 16°C according to Takahashi *et al.* [2002]:

$$[p\text{CO}_2]_{N16} = [p\text{CO}_2]_{\text{obs}} \exp[0.0423(16 - T_{\text{obs}}[^\circ\text{C}])]. \quad (1)$$

[6] Similar to the correction procedure proposed by Thomas [2002], the DIC concentrations were normalized for biological ($\Delta\text{DIC}_{\text{bio}}$) and solubility effects ($\Delta\text{DIC}_{\text{sol}}$);

$$\text{DIC}_{\text{norm}} = \text{DIC}_{\text{obs}} - \Delta\text{DIC}_{\text{sol}} - \Delta\text{DIC}_{\text{bio}}. \quad (2)$$

[7] Assuming the underlying assumptions are working well, the variability of the resultant DIC_{norm} term should be governed only by uptake or release of CO₂ from/to the atmosphere. The difference in DIC_{norm} between different times, given as the change in the average DIC concentration

and DIC inventory (Table 1), would then reflect the uptake of anthropogenic CO₂ and, to a lesser extent, variability in the natural level of DIC disequilibrium from the atmosphere. Apparent oxygen utilization (AOU) serves as a measure for biological effects, $\Delta\text{DIC}_{\text{bio}} = \text{AOU}$, since AOU integrates biological carbon release in the subsurface layer over a seasonal timescale. The $\Delta\text{DIC}_{\text{sol}}$ term accounts for effects of hydrographic variability in temperature and salinity (S) on equilibrium solubility. $\Delta\text{DIC}_{\text{sol}}$ is calculated in analogy to Thomas [2002] for the standard conditions $T = 16^\circ\text{C}$ and $S = 34.57$, which represent approximate observational averages from the two summer cruises in 2001 and 2005. We obtained a North Sea-specific A_T/S relationship from the 2001/2002 [Thomas *et al.*, 2005b] and 2005 field data:

$$A_T [\mu\text{mol kg}^{-1}] = 1949.6 + S(10.34) [\pm 23] \quad (3)$$

and computed $\Delta\text{DIC}_{\text{sol}}$ as

$$\Delta\text{DIC}_{\text{sol}} [\mu\text{mol kg}^{-1}] = S(3.53348) - T[^\circ\text{C}]8.10648 + 7.08289. \quad (4)$$

[8] The Revelle factor ($(\delta p\text{CO}_2/p\text{CO}_2)/(\delta\text{DIC}/\text{DIC})$) was calculated using standard thermodynamic relationships

applied to the observed and corrected data (T , S , DIC, A_T) with an estimated error of 0.04 units ($\approx 0.4\%$). The calculations have been carried out using the program CO₂SYS [Lewis and Wallace, 1998].

[9] Historical simulations using a global ocean carbon model are used to estimate the long-term trends of surface water $p\text{CO}_2$ and the Revelle factor over the North Atlantic. The ocean model includes the biogeochemical cycling of C, O, N, P, Fe, and Si and A_T and four phytoplankton functional groups (diazotrophs, diatoms, picoplankton, nanoplankton, and coccolithophores). The ecosystem module [Moore et al., 2004] coupled to a modified version of the Ocean Carbon-Cycle Model Intercomparison Project (OCMIP-2) biogeochemistry code [Doney et al., 2004] is embedded in the coarse-resolution Parallel Ocean Program ocean component of the Community Climate System Model [Yeager et al., 2006]. The historical ocean circulation simulations (1958–2004) are forced with interannually varying atmospheric physical data from the National Centers for Environmental Prediction/National Center for Atmospheric Research reanalysis and various satellite data products [Doney et al., 1998a, 2003, 2006]. Prior to 1958 the simulations are driven with a repeat annual cycle of physical forcing. The evolution of atmospheric CO₂ with time from 1820 to 2004 is prescribed using ice core and atmospheric observations.

3. Results and Discussion

[10] Observations from our cruises in the North Sea show that the atmospheric $p\text{CO}_2$ increased by 11 μatm between 2001 and 2005 (Table 1), which is similar to the atmospheric CO₂ rise recorded at the nearby Norwegian Sea Ocean Station M in the NOAA/CMDL atmospheric monitoring network (CO₂ Time Series, 2006, available at <http://www.esrl.noaa.gov/gmd/ccgg/carbontracker/tseries.php?type=mr>). While surface water $p\text{CO}_2$ and $\Delta p\text{CO}_2$ show the same general distribution patterns in both years [Thomas et al., 2004, 2005b] (Figure 2a), on a North Sea-wide scale the average $p\text{CO}_2$ increased from $327 \pm 43 \mu\text{atm}$ to $349 \pm 34 \mu\text{atm}$ between 2001 and 2005 (Table 1). The surface water $p\text{CO}_2$ rose faster than the atmospheric $p\text{CO}_2$ both in the supersaturated southern and the undersaturated northern parts, causing an overall decline of the $\Delta p\text{CO}_2$ of 11 μatm (from $-31 \mu\text{atm}$ in 2001 to $-20 \mu\text{atm}$ in 2005) on a North Sea-wide scale. The $\Delta p\text{CO}_2$ declined in the northern region, while supersaturation became more pronounced in the southern region. The decline of the $\Delta p\text{CO}_2$ in the undersaturated waters, similar to that observed in the North Atlantic Ocean [Lefèvre et al., 2004], is even more evident when the surface water $p\text{CO}_2$ is normalized to 16°C (Figures 2a and 2b), as the summer was colder in 2005 than in 2001 (Table 1). On a North Sea-wide scale the normalized surface water $p\text{CO}_2$ increased by 43 μatm , while the normalized $\Delta p\text{CO}_2$ declined by 32 μatm from $-36 \mu\text{atm}$ to $-4 \mu\text{atm}$ (Table 1). Note that this change would have brought the system almost to CO₂ equilibrium with the atmosphere if the temperature had been the same in 2001 and 2005.

[11] The water column mean DIC_{norm} (Table 1 and Figure 2c) increased over almost all of the North Sea by on average 11 μM from 2001 to 2005, with highest values up to 34 μM in the shallower, central and southern regions. This net water column DIC storage amounts to on average 1.1 mol C m⁻² (Figure 2d), or approximately 0.25 mol C m⁻² yr⁻¹, and complements the still evident CO₂ transfer from the atmosphere into the Atlantic Ocean by the North Sea's continental shelf pump. The increase of the mean DIC_{norm} in the southern region can be ascribed to a DIC increase of the waters imported from the Atlantic Ocean because of anthropogenic CO₂ uptake and constitutes one mechanism for the rise of the $p\text{CO}_2$ in supersaturated waters. Moreover, the supersaturation in the southern region reflects in part summer seasonal warming, yet the surface water undersaturation during winter and spring [Thomas et al., 2004, 2005b] also permits CO₂ uptake there. Previous studies [Thomas et al., 2004, 2005a] necessarily considered the North Sea to be in steady state over annual timescales and thus did not have the potential to identify the net water column DIC trend, which is close to the uncertainty of the derived annual carbon budgets.

[12] The North Sea consists of a shallower southern region showing classical characteristics of shelf seas, while the deeper, central and northern regions clearly represent oceanic conditions [Thomas et al., 2005b]. The flushing time for North Atlantic Ocean water circulating through the North Sea is on the order of 1 year [Lenhart et al., 1995], and seasonal stratification partly mimics open ocean conditions. Still, winter convection usually reaches the bottom, allowing anthropogenic CO₂ to penetrate the entire water column of the North Sea. The combination of ocean conditions in a relatively shallow, well-ventilated (on annual timescales) system accentuates temporal changes of the CO₂ system relative to the open ocean subpolar Atlantic at the same latitude where the anthropogenic CO₂ signal is spread over the vertical by deep convection. For example, an influx of CO₂ would cause higher near-surface DIC changes than in the open ocean because of the shallower mixed water column. On the other hand, the flushing timescale is short enough to prevent the North Sea from differing too greatly from the imported North Atlantic Ocean water on multi-annual timescales thus providing a window on the temporal evolution of the larger basin.

[13] The observed faster rise of surface water $p\text{CO}_2$ compared to atmospheric $p\text{CO}_2$ in the North Sea primarily reflects elevated surface DIC (Figures 2c and 2d) levels rather than changes in temperature or A_T (Table 1). Temperature normalization actually increases the temporal difference in $p\text{CO}_2$ and $\Delta p\text{CO}_2$. The A_T appears to be rather constant in the North Atlantic Ocean [Bates, 2001; Gruber et al., 2002], and in the North Sea, only a minor increase in A_T has been observed (Table 1), tending to counteract the measured $\Delta p\text{CO}_2$ decline.

[14] There are two further possible explanations for the North Sea $p\text{CO}_2$, $\Delta p\text{CO}_2$, and DIC temporal trends. First, for example, lower net community production and export over the summer of 2005, compared to 2001, would cause less subsurface DIC buildup, lower water column mean DIC, and lower AOU in the stratified subsurface waters.

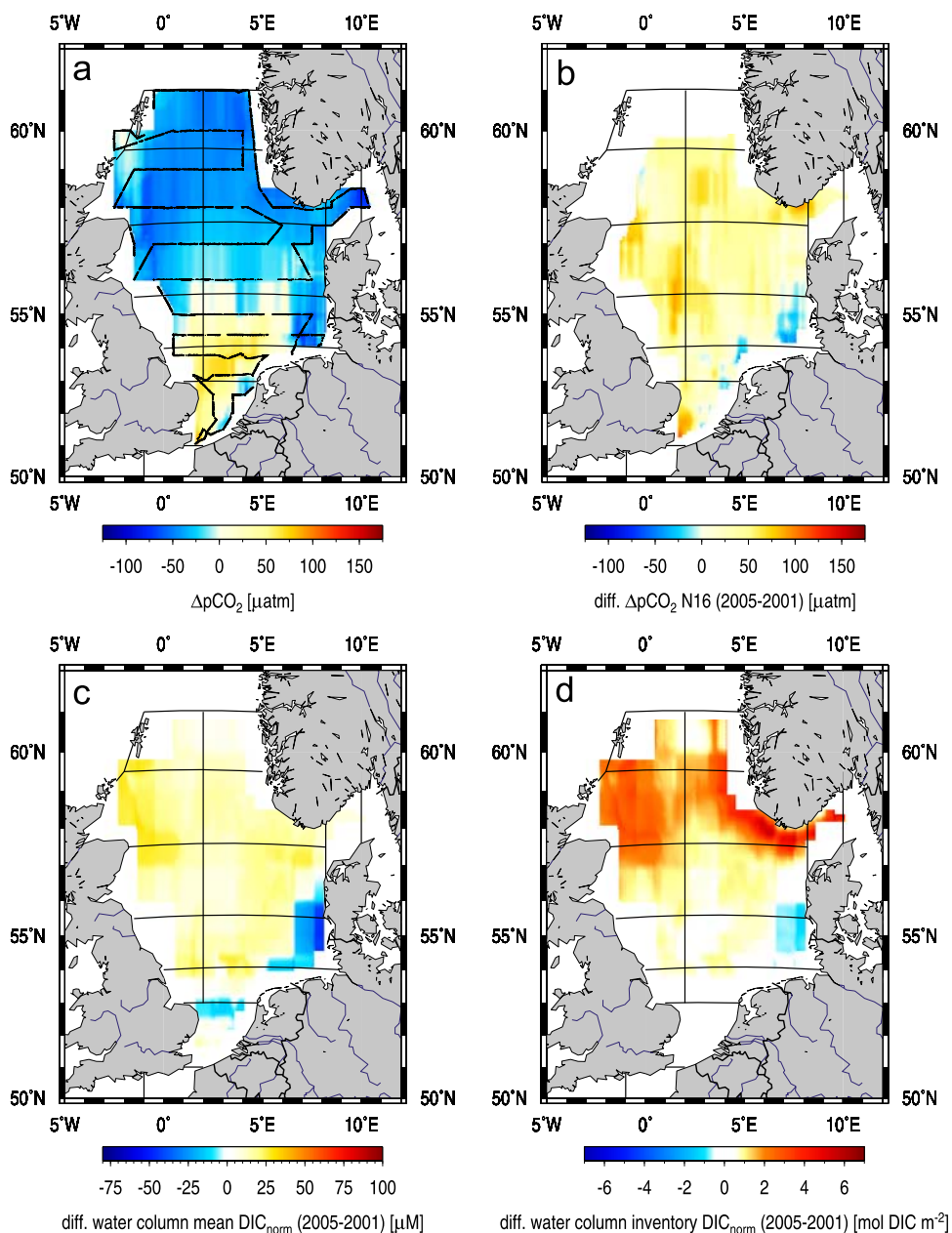


Figure 2. Changes of selected CO₂ system parameters in the North Sea between 2001 and 2005. (a) CO₂ partial pressure difference ($\Delta p\text{CO}_2$) recorded in the surface waters during the summer 2005 cruise. The cruise track is indicated by the black dots. (b) Changes in $\Delta p\text{CO}_2$ between the North Sea and atmosphere between 2005 and 2001 ($\Delta p\text{CO}_{2, 2005} - \Delta p\text{CO}_{2, 2001}$), normalized to a water temperature of 16°C. Positive values indicate declining $\Delta p\text{CO}_2$ in undersaturated areas and increasing $\Delta p\text{CO}_2$ in supersaturated areas. Positive values thus indicate a shift toward more CO₂ remaining or being released in/into the atmosphere. (c) Changes of the water column mean DIC concentrations and (d) the change of the DIC water column inventory after correction for biological and solubility effects (DIC_{norm}). See Table 1 for North Sea-wide averages.

Surface AOU is rapidly forced back to near zero through gas exchange and does not contribute significantly to interannual variability. Approximately 75% of the uptake of atmospheric CO₂ by the North Sea occurs between February and summer [Thomas *et al.*, 2004, 2005b], counteracting the effects of the biological DIC drawdown in the

surface waters. By late summer the water column mean DIC is thus dominated by seasonal organic matter degradation in the subsurface layer. On the basis of comparable water column average AOU in 2001 and 2005 (Table 1) one would also expect a comparable water column mean DIC in 2001 and 2005. However, an increase of the water column

mean DIC in 2005 is observed (Table 1). This discrepancy assigns biological variability a minor role in controlling the observed temporal differences. Further evidence of the minor role of biological activity on the interannual variability of DIC during summer is provided by the spatially restricted study of *Schiettecatte et al.* [2007] in the Southern Bight of the North Sea (SBNS). This multiyear study shows that interannual variability of $p\text{CO}_2$ due to biological activity is very low except during the spring phytoplanktonic bloom from March to April. During late August, as in the present study, interannual variations due to biology are negligible in the SBNS. Furthermore, effects of longer-term carbon removal to the sediments do not play a major role here, since the deposited organic matter is remineralized on short timescales [Thomas et al., 2004] and net carbon burial has not been observed on annual or longer timescales in the North Sea [de Haas et al., 2002].

[15] Second, a significant increase in wind speed and air-sea gas exchange would accelerate CO₂ equilibration of the surface ocean and lead to both an increase in DIC and a

decline in $\Delta p\text{CO}_2$. Wind data analyses [Swail et al., 2000; Lambert, 2004] suggest that wind distributions over the North Atlantic Ocean vary substantially on regional and interannual scales, attributable to storm track changes as well as changes in storm intensity and frequency. On a hemispheric scale, however, hardly any evidence can be derived for major changes in the wind strength during recent decades [Swail et al., 2000; Lambert, 2004; Lefèvre et al., 2004].

[16] Our observations from the North Sea support an alternative line of argument, namely, that the CO₂ saturation state is changing rapidly as a consequence of anthropogenic CO₂ additions. Seawater CO₂ system thermodynamics are such that $p\text{CO}_2$ increases with increasing DIC for fixed A_T , T , and S . For preindustrial and present ocean conditions the $p\text{CO}_2$ response grows nonlinearly for the same DIC increment as DIC and $p\text{CO}_2$ increase (Figure 3a) because of the depletion of carbonate anions. The common measure for this seawater buffer effect is the Revelle factor, which describes the fractional change of $p\text{CO}_2$ to changing DIC

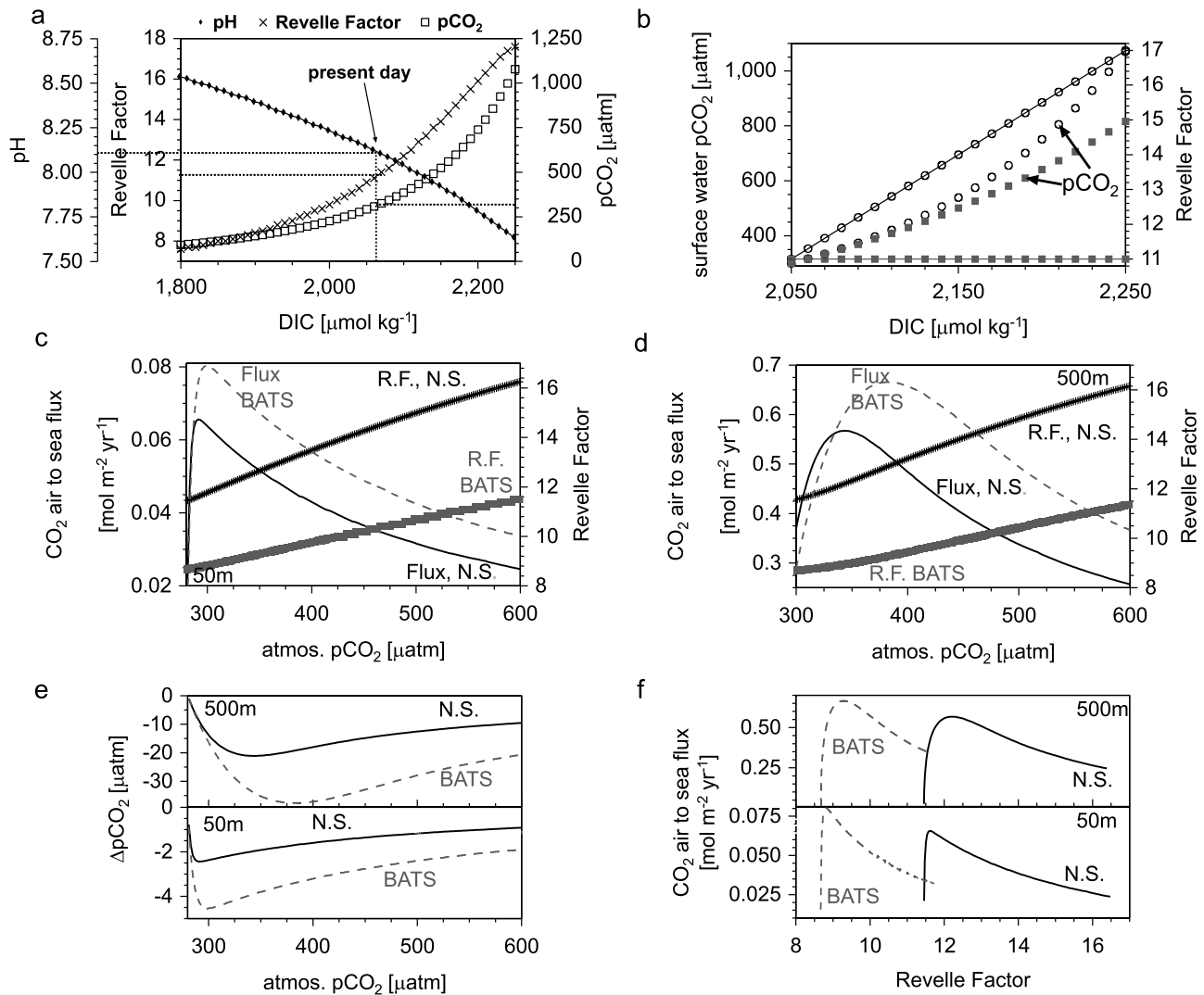


Figure 3

concentrations. The Revelle factor in surface waters is projected to be increasing with time because of ocean uptake of anthropogenic CO₂. This change of the Revelle factor is a direct response of the CO₂ system equilibria to these CO₂ additions [Revelle and Suess, 1957] and constitutes a feedback on ocean carbon uptake that, in turn, will accelerate the buildup of anthropogenic CO₂ in the atmosphere [Sarmiento *et al.*, 1995]. Purely thermodynamic considerations show that increasing surface water DIC with a (hypothetically) constant Revelle factor causes a much slower rise in surface water $p\text{CO}_2$ than is the case when full account is taken for CO₂ system thermodynamics and the effect of decreasing buffer capacity on $p\text{CO}_2$ (Figure 3b).

[17] We have relied on the normalized values of DIC and $p\text{CO}_2$ for the computations of the Revelle factor and its changes (Table 1 and Figure 4). This was done in order to prevent temperature and other interannual variability effects from masking or amplifying temporal changes in the Revelle factor. The computations of the Revelle factor change using the observations give consistent results (Figure 4) providing evidence both that other processes are less significant in governing the Revelle factor and that the additions of the CO₂ are the main processes driving the increase of the Revelle factor. In 2001 the normalized North Sea-wide average surface water Revelle factor was relatively high at 10.1, with higher values of 10.6 in the shallower southern North Sea and values of 10.0 in the northern North Sea. The Revelle factor baseline level is thus similar to North Atlantic values [Sabine *et al.*, 2004]. In only 4 years the Revelle factor increased by 0.6 units in the North Sea (Table 1 and Figure 4).

[18] As discussed previously, the large observed changes in the Revelle factor, like that of surface water $p\text{CO}_2$, result from elevated DIC. To what degree then is the change in

surface water Revelle factor responsible for the rapid decline in air-sea $\Delta p\text{CO}_2$? In order to explore this question and to provide mechanistic understanding of the underlying processes we computed idealized, i.e., abiotic and nonseasonal, annual CO₂ fluxes into an ocean environment solely as a function of increasing atmospheric CO₂ conditions (Figures 3c–3f). We have chosen two scenarios resembling the observed hydrochemical conditions of the North Sea and at BATS [Bates, 2001]. In order to account for different reservoir depths each scenario has been computed for mixed layer depths of 50 and 500 m. Seasonally and biologically driven fluxes [Thomas *et al.*, 2004, 2005b] as well as lateral processes have been ignored. Please note that the setup and choice of standard conditions are idealized (for details, see caption of Figure 3) and are not meant to represent the observed behavior in the North Sea or at BATS in a quantitative manner. Rather, they provide a mechanistic understanding of the governing processes under different environmental conditions.

[19] The computations show how rising atmospheric CO₂ causes the North Sea model box to fill with DIC and the Revelle factor to increase. At higher Revelle factor values a smaller increase in model DIC, and thus a smaller air-sea CO₂ flux, is required to equilibrate surface waters to the same incremental increase in atmospheric CO₂. As a result, air-sea CO₂ flux and $\Delta p\text{CO}_2$ decline even as the atmospheric CO₂ concentration continues to grow (Figures 3c–3f). The same computations relying on the hydrochemical conditions observed at BATS reveal that the lower baseline level of the Revelle factor (i.e., higher buffer capacity) causes a slower increase of the Revelle factor at BATS and allows initially higher fluxes into the ocean (Figures 3c and 3d), which is reflected by a more negative $\Delta p\text{CO}_2$ (Figure 3e). For each location the deep mixed layer scenar-

Figure 3. Equilibrium considerations of the CO₂ system for rising CO₂ concentrations. (a) Changes of the $p\text{CO}_2$, the Revelle factor, and pH as a function of increasing DIC concentrations because of continuing CO₂ additions. The calculations in Figure 3a assume the following standard conditions: $S = 35$, $T = 10^\circ\text{C}$, and $A_T = 2295 \mu\text{mol kg}^{-1}$, reflecting approximate annual average conditions observed in the North Sea. (b) A comparison of the responses of the carbonate system to CO₂ additions assuming a fixed or variable Revelle factor, respectively. DIC has been increased in $10 \mu\text{mol kg}^{-1}$ increments for a constant Revelle factor of 11 (grey line with grey squares). The resulting $p\text{CO}_2$ is shown by the grey squares. In the second computation the Revelle factor has been increased from 11 by 0.3 units per $10 \mu\text{mol kg}^{-1}$ DIC increase (black line and circles). The resulting $p\text{CO}_2$ is shown by the circles. (c–f) Results of idealized one-box computations revealing solely the changes and CO₂ fluxes as a function of rising atmospheric CO₂ conditions. The computations have been performed for two different systems resembling the hydrochemical conditions in the North Sea (solid lines and symbols) and at BATS (grey lines and symbols). For the North Sea we assumed as fixed standard conditions: $A_T = 2295 \mu\text{mol kg}^{-1}$, $T = 10^\circ\text{C}$, $S = 35$, and initial DIC = $2041.406 \mu\text{mol kg}^{-1}$. For BATS we assumed as fixed standard conditions: $A_T = 2388 \mu\text{mol kg}^{-1}$, $T = 24^\circ\text{C}$, $S = 36.6$, according to Bates [2001], and initial DIC = $1960 \mu\text{mol kg}^{-1}$. For both systems the following conditions have been assumed: gas transfer velocity equal to 7 cm hr^{-1} ; two mixed layer depth scenarios, 50 m and 500 m; and an increase of atmospheric CO₂, $2 \mu\text{atm yr}^{-1}$. The CO₂ fluxes into the DIC pool have been computed using an adaptive time step integrator technique and are shown once per year. The model runs have been started at equilibrium conditions; accordingly the first time steps reveal the buildup of the air-sea disequilibrium. The response of the CO₂ air to sea flux and the Revelle factor to rising atmospheric CO₂ conditions is shown for the 50 m (Figure 3c) and the 500 m (Figure 3d) scenarios. The corresponding response of the $\Delta p\text{CO}_2$ to rising CO₂ conditions for the 50 m (bottom) and 500 m (top) scenarios (Figure 3e) are shown. CO₂ air to sea fluxes are shown as a function of the Revelle factor for the 50 m (lower) and 500 m (upper) scenarios. Please note that the setup and choice of standard conditions are idealized and are not meant to represent the observed behavior in the North Sea or at BATS in a quantitative manner. The idealized model has been designed to provide mechanistic understanding of the governing processes under different environmental conditions.

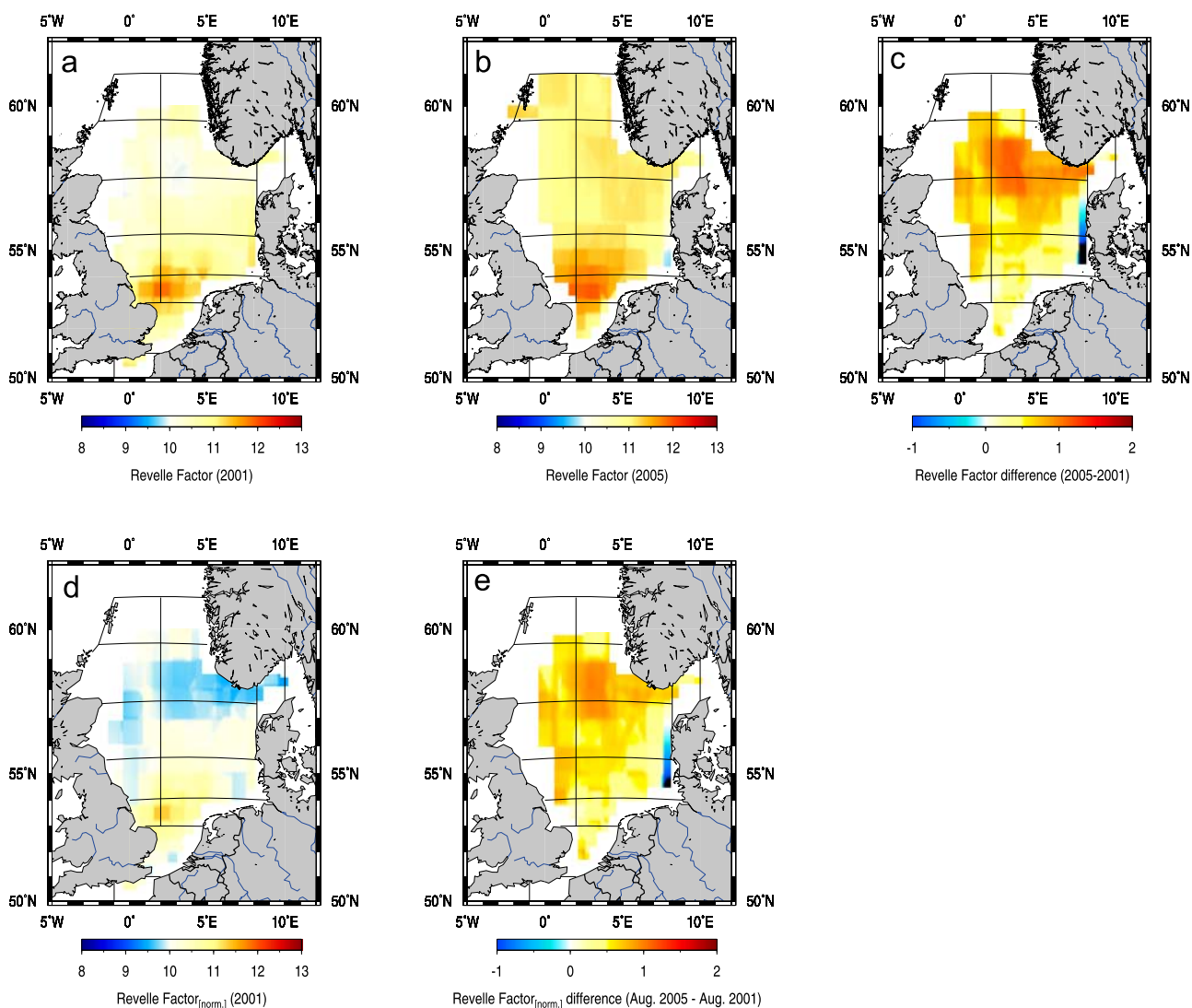


Figure 4. Revelle factor and its changes in the North Sea. The Revelle factor has been computed from (a–c) observed and (d and e) normalized data for the 90 stations for both 2001 and 2005 in order to eliminate effects on the CO₂ buffer capacity other than the invasion of CO₂. The Revelle factor, computed from the observed data, is shown for 2001 (Figure 4a) and 2005 (Figure 4b) as well as the difference between both years (Figure 4c). The North Sea-wide averages increase from 10.6 in 2001 to 11.1 in 2005. In 2001 the Revelle factor, computed from the normalized data, ranges from 9.4 to 11.3, with an average of 10.1 (Figure 4d). In 2005 the normalized Revelle factor ranges from 9.3 to 11.5, with an average of 10.7; that is, it is on average 0.6 units higher (Figure 4e). The computations of the Revelle factor difference using observed and normalized station data provide consistent results, while the normalization slightly lowers the absolute values of the Revelle factor.

ios reveal a slower equilibration and higher CO₂ fluxes compared to the shallower scenarios. The “deepwater” scenario for the North Sea conditions might represent the conditions of the North Atlantic Ocean waters before entering the North Sea. The high susceptibility of shallow water environments to rising atmospheric CO₂ conditions is emphasized by the fact that in shallower waters, surface water *p*CO₂ values track the rising atmospheric CO₂ closely, and the resulting anthropogenic CO₂ fluxes are smaller, reflecting the smaller reservoir size.

[20] A tentative quantitative evaluation of the idealized thermodynamic considerations shows that raising the surface water *p*CO₂ from 300 to 800 μatm requires approximately 200 μmol kg⁻¹ DIC, assuming a constant Revelle factor of 11. The more realistic computation, which considers the adjustment of the CO₂ system equilibria, requires approximately 20% less DIC (approximately 160 μmol kg⁻¹ DIC) for the same rise of the surface water *p*CO₂ (Figure 3b). The declining buffer capacity thus would cause a 20% reduction of the (accumulated) CO₂ air to sea fluxes

under the given conditions. Focusing on the deep ocean scenarios (Figures 3d–3f), the observed increase of the atmospheric $p\text{CO}_2$ from 359 to 370 μatm between 2001 and 2005 (Table 1) would correspond to a decline of the CO₂ air to sea flux by approximately 4%, a decrease in $\Delta p\text{CO}_2$ by 2 μatm , and an increase in the Revelle factor of 0.2 under “North Sea/northern North Atlantic” conditions. While in the same direction as the observed changes in the North Sea, the magnitude of the buffer feedback appears to be smaller. This suggests that local adjustments in air-sea flux due to the buffer factor may contribute, on the order of ~10–30%, but are probably not the dominant explanation for the observed signals.

[21] Interestingly, for the model “BATS” conditions with a 500 m deep reservoir the effect of the buffer feedback on CO₂ flux and $\Delta p\text{CO}_2$ is almost negligible for present-day $p\text{CO}_2$ levels and the change in Revelle factor with $p\text{CO}_2$ is smaller. Because the “BATS” computations start with a lower initial Revelle factor, the impact of the buffer feedback is not felt until higher atmospheric $p\text{CO}_2$ levels are reached. This is reflected in a positive shift of 40–60 μatm (20–30 years) with respect to atmospheric $p\text{CO}_2$ in the shape of the CO₂ flux curve in the deepwater case (Figure 3d). While the buffer feedback is universal, its impact will be observable regionally at different times.

[22] The North Sea is dominated by Atlantic Ocean water masses, and since the rapid rise of DIC and the Revelle factor do not appear to be explained by local North Sea buffer feedbacks alone, we must consider a remote source for the excess anthropogenic DIC that is advected laterally into the North Sea basin. If the rapid rise of the Revelle factor is also occurring in the North Atlantic source waters, the buffer feedback may also serve to explain, in part, the pattern of regional decreases in air-sea $\Delta p\text{CO}_2$ in parts of the North Atlantic Ocean [Lefèvre *et al.*, 2004; Omar and Olsen, 2006; Corbière *et al.*, 2007]. As a first step in addressing this question we examined numerical model results to assess the degree to which the observed Revelle factor changes in the North Sea extended over the North Atlantic Basin and the extent to which interannual variability affects the surface water Revelle factor distribution. We rely on a historical simulation (1958–2005) with a global ocean ecosystem, biogeochemistry circulation model, subsampling the simulation for the years 1995 until 2005 [Doney *et al.*, 2004, 2006; Moore *et al.*, 2004].

[23] In the historical simulation the northward flowing, midlatitude North Atlantic surface waters in the Gulf Stream/North Atlantic Current system show an increase of 0.2 to 0.3 units in the Revelle factor between 2000 and 2004 (Figures 5a and 5b) which may represent the state of the Atlantic Ocean water before entering the North Sea in 2001 and 2005, respectively. The baseline Revelle factor in the northern part of the North Atlantic Ocean (Figures 5d and 5e) is higher than in the south (11 compared to 9) [see also Sabine *et al.*, 2004], and as a result the response of the Revelle factor is an order of magnitude stronger than in the more southern regions (Figure 5c), revealing maximum values in the polar North Atlantic (Figure 5a) [Olsen *et al.*, 2006]. In recent years the Revelle factor has risen much faster compared to the rise of only one unit between the

onset of industrialization and 1995 [Sabine *et al.*, 2004]. The accelerated rise of the Revelle factor during recent years, which is evident in the North Atlantic simulations and North Sea observations, can be attributed to the higher baseline surface water DIC levels; because of nonlinearities in the seawater inorganic carbonate system the change in Revelle factor with respect to an increase in DIC is small at low DIC (low $p\text{CO}_2$) but then increases sharply under higher-CO₂ conditions (Figures 3a and 6).

[24] Model time series at specific locations (Figures 5c–5e) illustrate long-term trends of increasing Revelle factor and decreasing $\Delta p\text{CO}_2$ with time overlain by higher-frequency interannual variability associated with the North Atlantic Oscillation and other climate modes that alter ocean physics and biogeochemistry [Doney *et al.*, 1998b]. While the interannual variability in the simulated Revelle factor is substantial, it does not by itself explain the differences between 1995 and 2005, which appear to reflect longer-term, basin-wide trends. In conjunction with the DIC normalization calculations (equations (1)–(3)), the model simulation thus lends support to the contention that some fraction of the rise in Revelle factor between 2001 and 2005 observed in the North Sea field data reflects long-term secular trends. However, the model simulations also highlight the fact that there is substantial interannual variability in the Revelle factor in the source waters feeding the North Sea on top of the secular trend (Figures 5d and 5e) and that there is a strong need for more continuous monitoring of the system, rather than point-time sampling, to distinguish anthropogenic versus variability signals.

[25] The model simulations also reproduce the corresponding trend of decreasing $\Delta p\text{CO}_2$ (Figures 5d and 5e) evident from observational studies in the northern North Atlantic [Lefèvre *et al.*, 2004; Omar and Olsen, 2006; Corbière *et al.*, 2007] and the North Sea. For the more southern area (Figure 5c) our simulations yield a declining $\Delta p\text{CO}_2$ over time, which has been reported in the direct observations at BATS [Bates, 2001]. The seasonally detrended data from this location which have been derived in the Bates study, however, reveal a parallel development of the atmospheric and the surface water $p\text{CO}_2$ and thus no temporal trend in the $\Delta p\text{CO}_2$ (see also discussion of Figures 3d–3f). The verification of this feature goes beyond the scope of this paper. Theoretical considerations, however, imply that a decrease of the CO₂ buffer capacity (but simply at different intensities because of the baseline Revelle factor) may be contributing to the seemingly contradictory findings for $\Delta p\text{CO}_2$ in different regions of the North Atlantic Ocean.

[26] The response of the carbonate system has been calculated for the hydrochemical conditions observed at BATS [Bates, 2001] and in the North Sea, being comparable to the northern North Atlantic (Figure 6). The North Sea reveals a much stronger response of the Revelle factor and the $p\text{CO}_2$ to increasing DIC concentrations (Figure 6a). The change of the Revelle factor in the North Sea exceeds that at BATS by a factor of 2 because of the overall lower baseline level of the Revelle factor at BATS (Figures 6, 5b and 5c). The different responses are shown as function of DIC (Figure 6b) and of the equilibrated $p\text{CO}_2$ (Figure 6c).

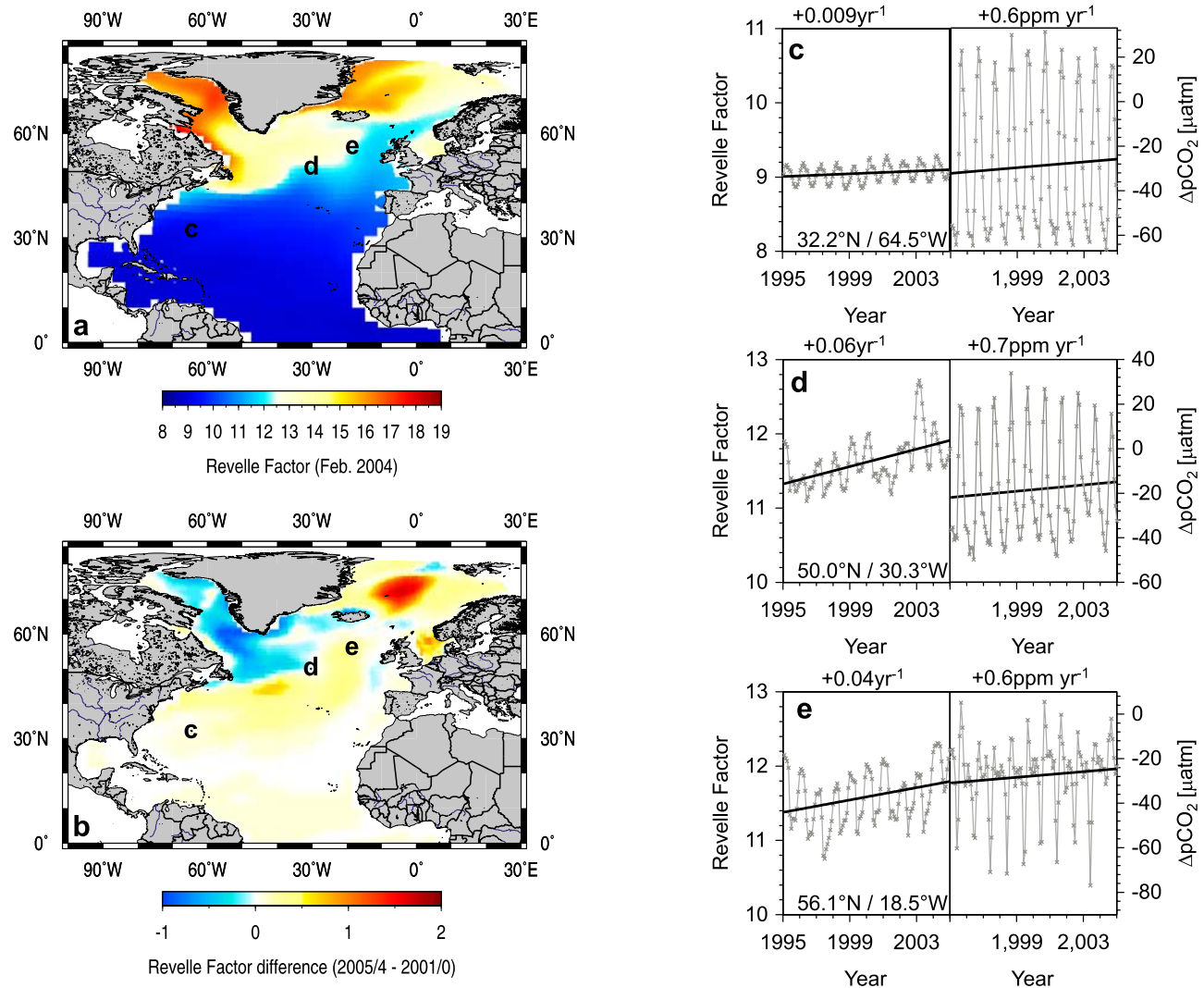


Figure 5. Simulations of the CO₂ system in the North Atlantic Ocean. (a) Simulated Revelle factor in the North Atlantic Ocean in February, 2004. The month of February has been chosen as a biologically inactive period. (b) Change of the Revelle factor between 2000 and 2004, which corresponds to the North Sea observations considering flushing times of the North Sea of approximately 1 year. The data are shown for February in order to yield a biologically inactive period. The color scale is the same as in Figures 2c and 2e. The decline of the $\Delta p\text{CO}_2$ and the rise of the Revelle factor between 1995 and 2004 for three locations in the North Atlantic Ocean: (c) 32.2°N/64.5°W (BATS), (d) 50.0°N/30.3°W, and (e) 56.1°N/18.5°W. The letters in Figures 5a and 5b indicate the locations of the three stations. For convenience, the changes of the observational, normalized Revelle factor in the North Sea (Figure 4e) are overlain. For convenience, the y scales span identical ranges: three Revelle factor units and 100 μatm for $\Delta p\text{CO}_2$.

[27] If the advection of North Atlantic Ocean water into the North Sea was the only process controlling the changes of the Revelle factor within the North Sea, the Revelle factor should rise in both environments similarly, assuming that the model is skillful. The long-term trend in the model of 0.2–0.3 units for the North Atlantic is smaller than the observed 0.6 units for the North Sea, but this difference could simply reflect the overlay of natural variability since we only have time samples from two years, 2005 and 2001.

Another possible explanation for the stronger rise of the Revelle factor in the North Sea could be additional “in situ” CO₂ uptake occurring in the North Sea, which is catalyzed by high biological activity [Thomas *et al.*, 2004], part of which accumulates and contributes to the DIC inventory increase of approximately 0.25 mol C m⁻² yr⁻¹ (Figures 2c and 2d). The theoretical considerations discussed above (Figures 3c–3f) show that in shallower-water environments such as the North Sea, smaller CO₂ fluxes are required to

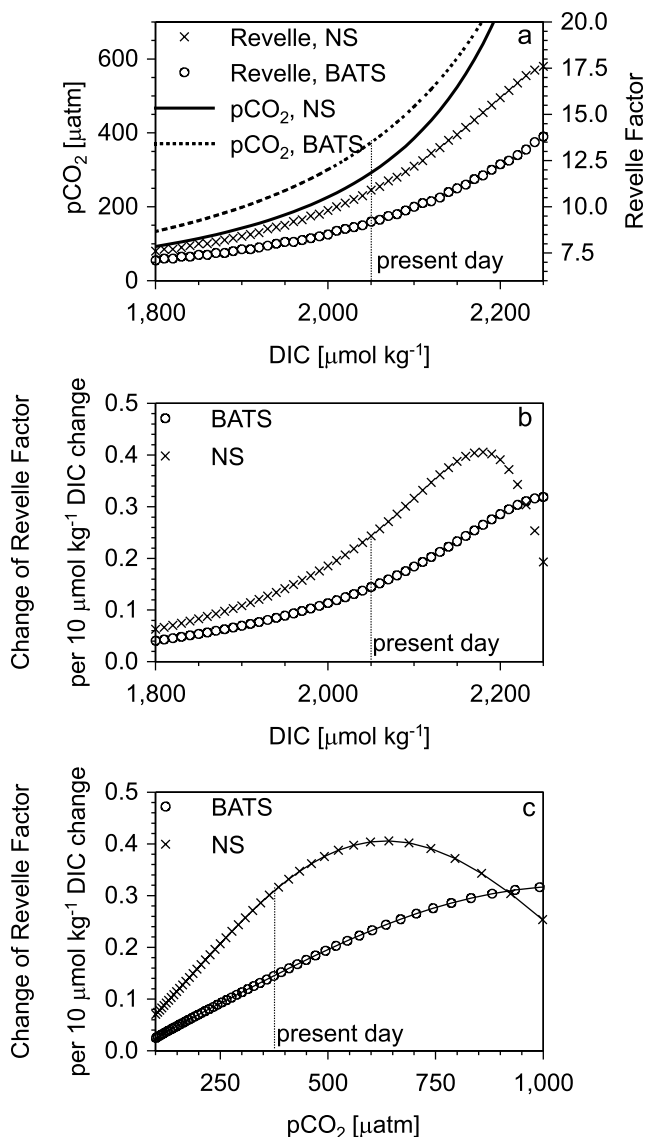


Figure 6. Equilibrium considerations of the CO₂ system for rising CO₂ concentrations for conditions observed at BATS and in the North Sea. The calculations assume the following standard conditions: $S = 35$, $T = 10^\circ\text{C}$, and $A_T = 2295 \mu\text{mol kg}^{-1}$, reflecting approximate annual average conditions observed in the North Sea. For BATS the following values have been assumed: $S = 36.6$, $T = 24^\circ\text{C}$, and $A_T = 2388 \mu\text{mol kg}^{-1}$. (a) Changes of the $p\text{CO}_2$ and Revelle factor as a function of incrementally increasing DIC concentrations. Changes of the slope of the Revelle factor per $10 \mu\text{mol kg}^{-1}$ DIC change calculated for BATS and in the North Sea as a function of (b) DIC and (c) the equilibrated $p\text{CO}_2$.

cause an accentuated response of the CO₂ equilibria because of the smaller reservoir size. Our study thus provides evidence that the observations from different locations in the North Atlantic [Bates, 2001; Lefèvre et al., 2004; Omar and Olsen, 2006] and the North Sea show complementary

views of the same process with regional fingerprints: the decrease of the ocean's CO₂ buffer capacity. The purely thermodynamic effect of the declining CO₂ buffer capacity might be amplified by further processes, which contribute to the observed higher DIC and declining $\Delta p\text{CO}_2$ levels. In the case of the North Sea such processes, which might not have been entirely accounted for by our normalization procedure, could be related to variability in quality or origin of the waters entering the North Sea in 2001 and 2005.

[28] It has been argued that the northward transport of the water masses in the North Atlantic contributes to the northward decline in $\Delta p\text{CO}_2$ and the rise in the baseline spatial patterns of the Revelle factor [Anderson and Olsen, 2002; Omar and Olsen, 2006]. This process alone, however, cannot serve to explain the temporal changes observed in the North Sea and Atlantic Ocean. We argue that the simulated temporal $\Delta p\text{CO}_2$ decline and Revelle factor rise, at least partly, constitute a direct response of the surface ocean to the uptake of anthropogenic CO₂ from the atmosphere. Here we do not differentiate between anthropogenic CO₂ uptake occurring locally versus uptake in remote locations whose signal is then advected to the northern North Atlantic [Olsen et al., 2006] and North Sea. In analogy with the baseline spatial patterns the effect of remote CO₂ uptake on the temporal trends in Revelle factor and $\Delta p\text{CO}_2$ in the North Atlantic depends upon the net heat and freshwater fluxes along the flow path from the uptake region as well as the initial hydrochemical state. Further, the changes in the surface water carbonate system due to anthropogenic CO₂ uptake alter the air-sea CO₂ flux downstream; increasing Revelle factor and the declining $\Delta p\text{CO}_2$ would constitute a (net) release of anthropogenic CO₂, a line of argument pursued, for example, by Anderson and Olsen [2002] or Mikaloff-Fletcher et al. [2006].

[29] Similar to the observations in the North Pacific Ocean [Takahashi et al., 2006], in some provinces of the North Atlantic Ocean the Revelle factor has decreased, for example, in southward flowing waters of polar origin (Figure 5b). These waters might be influenced by changes in the Arctic Ocean, which affect hydrography and carbon cycling in both Arctic and downstream waters [e.g., Anderson and Kaitin, 2001; Polyakov et al., 2005]. Corbière et al. [2007] argue in detail that the observed decline in $\Delta p\text{CO}_2$ south of Greenland has been caused by rising temperatures in this region. Rising temperatures would cause a lowering of the Revelle factor, which is indicated in our simulations (Figure 5b).

4. Conclusions

[30] Field observations demonstrate a significant recent decline in the buffering capacity of the inorganic carbonate system (increasing Revelle factor) in surface waters in the North Sea due to the uptake of anthropogenic CO₂. This effect, predicted by thermodynamic calculations as far back as the 1950s [Revelle and Suess, 1957; Sarmiento et al., 1992], sets up a negative feedback that decreases the ability of the surface ocean to take up additional anthropogenic CO₂. Simple idealized calculations suggest that the reduced buffer feedback could explain about 10–30% of the observed declines in the air-sea $\Delta p\text{CO}_2$ and net local CO₂

uptake flux in the North Sea and possibly, by analogy, the Gulf Stream/North Atlantic Drift regions of the North Atlantic Ocean [Lefèvre et al., 2004; Omar and Olsen, 2006].

[31] During the nineteenth and twentieth centuries the surface ocean's uptake capacity for CO₂ was large and allowed the ocean to absorb large amounts of CO₂ from the atmosphere without a proportional increase of the *p*CO₂ [Sabine et al., 2004]. In contrast, under current and future conditions the reduced buffer capacity causes the surface water *p*CO₂ to rise proportionally faster for the same incremental change in DIC and thus reduces the thermodynamic driving force for air-sea exchange of anthropogenic CO₂. Because of these thermodynamic effects a larger portion of future CO₂ emissions will remain in the atmosphere, thus enhancing the predicted, if not already observed [IPCC, 2001; Fung et al., 2005], global warming effects of CO₂ on climate on Earth. A reliable understanding of partitioning of future emissions of anthropogenic CO₂ between ocean, atmosphere, and land is not only essential for predicting climate on Earth. It is also of the highest relevance for current and future mitigation measures aiming for a reduction or stabilization of atmospheric CO₂ conditions [Dilling et al., 2003].

[32] This study was based on temporal trends from field data from two separate years. While the normalization procedure applied to the North Sea data is deemed to extract the effects of the anthropogenic CO₂ additions from any signal of natural variability, additional data are needed to confirm our findings. Routine ocean carbonate system data are needed for the North Sea and North Atlantic, the latter via, for example, the international Repeat Hydrography program. Complemented by in-depth analysis of the North Sea in regional models, the field data will likely further substantiate the observed trends of the rapidly decreasing CO₂ buffer capacity in the North Sea and the Gulf Stream/North Atlantic Drift regions.

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A. V. Borges, M. Koné, L.-S. Schiettecatte, and K. Suykens, Chemical Oceanography Unit, University of Liège, B-4000 Liège, Belgium.

Y. Bozec, Scripps Institution of Oceanography, San Diego, CA 92093-0244, USA.

H. J. W. de Baar, Royal Netherlands Institute of Sea Research, NL-1790 AB Den Burg, Texel, Netherlands.

S. C. Doney and I. D. Lima, Marine Chemistry and Geochemistry Department, Woods Hole Oceanographic Institution, 266 Woods Hole Road, Woods Hole, MA 02543-1050, USA.

A. E. Friederike Prowe and H. Thomas, Department of Oceanography, Dalhousie University, Halifax, NS, Canada B3H4J1. (helmuth.thomas@dal.ca)

S. van Heuven, Department of Ocean Ecosystems, Rijksuniversiteit Groningen, NL-9751 NN Haren, Netherlands.