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Contrasting effects of temperature and winter mixing on the seasonal and inter-annual variability of the carbonate system in the Northeast Atlantic Ocean

C. Dumousseaud[1], E. P. Achterberg[1], T. Tyrrell[1], A. Charalampopoulou[1], U. Schuster[2], M. Hartman[1], and D. J. Hydes[1]

[1]National Oceanography Centre, University of Southampton, European Way, Southampton, SO14 3ZH, UK
[2]School of Environmental Science, University of East Anglia, Norwich, NR4 7TJ, UK

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Correspondence to: E. P. Achterberg (eric@noc.soton.ac.uk)

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Abstract

Future climate change due to the increase in atmospheric CO_2 concentrations is expected to strongly affect the oceans, with shallower winter mixing and consequent reduction in primary productivity and oceanic carbon drawdown in low and mid-latitudinal oceanic regions. Here we test this hypothesis by examining the effects of cold and warm winters on the carbonate system in the surface waters of the Northeast Atlantic Ocean for the period between 2005 and 2007. Monthly observations were made between the English Channel and the Bay of Biscay using a ship of opportunity program. During the colder winter of 2005/2006, the maximum depth of the mixed layer reached 500 m in the Bay of Biscay, whilst during the warmer (by 2.6±0.5°C) winter of 2006/2007 the mixed layer depth reached only 300 m. The inter-annual differences in late winter concentrations of nitrate (2.8±1.1 μmol l^{-1}) and dissolved inorganic carbon (22±6 μmol l^{-1}), with higher concentrations at the end of the colder winter (2005/2006), led to differences in the dissolved oxygen anomaly and the fluorescence data for the subsequent growing season. In contrast to model predictions, the calculated air-sea CO_2 fluxes (ranging from +4.5 to −5.5 mmol m^{-2} d^{-1}) showed an increased oceanic CO_2 uptake in the Bay of Biscay following the warmer winter of 2006/2007 associated with wind speed and sea surface temperature differences.

1 Introduction

Since the late 1700s, the atmospheric concentration of CO_2 has increased from 280 to 380 ppm and the oceans have absorbed about half of the anthropogenic CO_2 emitted to the atmosphere (Sabine et al., 2004). While some oceanic regions act as a source of CO_2 to the atmosphere, the North Atlantic Ocean is reported as one of the strongest sinks in the world (Takahashi et al., 2009; Takahashi et al., 2002; Gruber et al., 2002). The uptake of atmospheric CO_2 by the oceans is however lowering oceanic pH and the saturation state of calcium carbonate (Orr et al., 2005; Feely et al., 2004; Caldeira and

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Wickett, 2003). Coccolithophores, coral reefs and other major calcifiers are expected to be affected by future changes in the oceanic carbonate chemistry and pH (Fabry, 2008).

Climate change is predicted to reduce the capacity of the oceans to absorb CO_2 through a decrease in winter mixing and a consequent reduced nutrient supply to surface layers and lower primary productivity during the following spring bloom (Sarmiento et al., 1998; Bopp et al., 2001; Doney et al., 2009). The North Atlantic sink of CO_2 has been in decline during the last few decades, related to changes in the North Atlantic Oscillation (NAO), surface circulation, vertical winter mixing, inorganic carbon chemistry, and/or sea surface warming (Schuster et al., 2009; Doney et al., 2009; Schuster and Watson, 2007; Corbière et al., 2007; Thomas et al., 2008).

However, the natural small-scale variability of the carbonate system observed in the oceans on a seasonal and inter-annual basis often makes the prediction of long-term impacts more difficult (Bates et al., 1996a), and highlights the importance of understanding the variability of the carbonate system on a regional and global scale. Time-series programs such as the Bermuda Atlantic Time-Series (BATS), the European Station for Time-series in the Ocean, Canary Islands (ESTOC), and the Hawaii Ocean Time-Series (HOTS) have improved our understanding of the processes affecting the carbonate system (e.g. Bates et al., 2007; González-Dávila et al., 2003; Dore et al., 2009). A significant number of other high-resolution observational programs are now operational (Doney et al., 2009), including observations from ships of opportunity as part of the FerryBox program and the CarboOcean project.

The FerryBox route presented in this study covers about 1000 km from the highly productive and shallow coastal waters of the English Channel, to the deep oligotrophic waters of the Bay of Biscay. Due to a complex physical context, the carbonate system and primary production in the English Channel and adjacent areas are subject to large seasonal and spatial variability (Frankignoulle et al., 1996a, b; Wollast and Chou, 2001; Bargeron et al., 2006). Michel et al. (2009) showed a continuous increase in sea surface temperature in the Bay of Biscay over the last 30 years, strongly correlated

with the NAO index. Furthermore, Padin et al. (2009) calculated a decrease in the net air-sea CO_2 flux between 1997 and 2004 for this oceanic region.

The observations made on a ship of opportunity, the MV *Pride of Bilbao*, constitute a unique dataset of carbonate chemistry measurements and coccolithophore abundances in the Northeast Atlantic Ocean surface waters, for two consecutive years. The aim of this work was to observe the seasonal and inter-annual variability of the carbonate system and the air-sea CO_2 flux in the English Channel and the Bay of Biscay. These observations, linked with the changes in winter mixing observed within the two years of our study, will provide a better understanding on how this ocean region may be affected by future climate change.

2 Methods

2.1 Area of study

The sample collection was undertaken on the ship of opportunity MV *Pride of Bilbao*, a passenger ferry undertaking weekly crossings between Portsmouth (UK) and Bilbao (Spain). The route covers the area between the Portsmouth harbour and the Iberian shelf (Fig. 1), crossing eight regions of different oceanographic characteristics (Bargeron et al., 2006). However, only the section between the Central English Channel and the Southern Bay of Biscay will be taken into account in this study (zones 2 to 7 in Fig. 1), as no samples were collected in the harbour regions. Thirteen crossings were occupied by researchers between September 2005 and July 2007 (Table 1).

2.2 Sampling

All samples were collected from the ship's underway supply (intake at about 5 m depth). Samples for Dissolved Inorganic Carbon (DIC) and Total Alkalinity (TA) were drawn in 250 ml borosilicate glass bottles (Schott Duran), with a head space of 1% (2.5 ml)

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allowed for water expansion, and immediately poisoned with 50 μl saturated solution of mercuric chloride to prevent further biological activity (Dickson et al., 2007). Samples were stored for later analysis in the laboratory.

Continuous temperature, conductivity and chlorophyll-*a*-fluorescence measurements were obtained from a MINIpack system (Chelsea Technologies Group, UK) installed on the ship (Hydes et al., 2003). The salinity data was calibrated using samples taken every two hours on each researcher-occupied crossing and analysed at the NOCS calibration laboratory using a salinometer (8400 B Autosal, Guildline, Canada). Nutrient samples were collected every half hour during the occupied crossings and analysed at NOCS using standard methods on an auto-analyser for silicate, nitrate and phosphate (Grasshoff, 1983). Dissolved oxygen concentrations were obtained using an optode (3930, Aanderaa, Norway) installed on the ship, and calibrated with discrete samples collected every hour and analysed on board by Winkler titration (Hydes et al., 2009).

2.3 DIC and TA measurements

The analysis of DIC and TA was undertaken using the VINDTA 3C (Marianda, Germany). The DIC samples were analysed using a coulometric titration (coulometer 5011, UIC, USA) and TA was determined using a closed-cell titration according to Dickson et al. (2007). The cell (100 ml) for the TA determination was equipped with a pH half cell electrode (glass bodied Orion 8101SC, Ross, USA) and an Ag/AgCl reference electrode (model 6.0729.100, Metrohm, Switzerland). The calculation of TA was based on a non-linear curve fitting (least-squares) approach (Dickson et al., 2007). All samples were analyzed at 25°C (±0.1°C) with temperature regulation using a water-bath (Julabo F12, Germany). Repeated measurements on the same batch of seawater ($n \geq 3$) were undertaken every day prior to sample analysis, in order to assess the precision of the method which was estimated for the whole dataset to be 1.1±0.5 μmol kg^{-1} for DIC and 1.1±0.6 μmol kg^{-1} for TA. The analytical precision hence was within the previously reported precision range for TA and DIC measurements (Bates et al., 1996a, b; Millero et al., 1998a). Certified Reference Materials (from A.G. Dickson, Scripps

Institution of Oceanography) were analysed as standards to calibrate the instrument at the beginning and end of each day of analysis. A daily correction factor was applied to all measured values according to Millero et al. (1998b), in order to standardize the results. To remove the influence of salinity on the distribution of DIC and TA, the data was normalized (nDIC and nTA) to a salinity of 35 (Millero et al., 1998a).

The fugacity of CO_2 (fCO_2) measurements available for the English Channel for the period 2006 and 2007 from the ship of opportunity MV *Santa Maria* (Schuster et al., 2009; Fig. 1) were used along with our TA, temperature, salinity and nutrient data to calculate values of DIC using the CO_2SYS program (Pierrot et al., 2006). The equilibrium constants of CO_2 from Mehrbach et al. (1973), refitted by Dickson and Millero (1987), were used for the calculation (Wanninkhof et al., 1999). The uncertainty in the calculation of DIC from TA and fCO_2 measurements was estimated to $\pm 3.4\,\mu mol\,kg^{-1}$ (Zeebe and Wolf-Gladrow, 2001). The calculated DIC values were compared against the measured values and showed good agreement (± 4–$6\,\mu mol\,kg^{-1}$), with the exception of the February, April, May and June 2007 data. From these comparisons it became apparent that, despite no evident problem with the analysis, some of the 2007 DIC data required correction. The calculated DIC concentrations for the English Channel were used where direct comparison with the MV *Santa Maria* data was possible and a monthly correction factor of 2% (calculated from the ratio between the measured and the calculated DIC concentrations) was applied to the 2007 data for the regions where no fCO_2 data were available.

2.4 Coccolithophore abundance

Seawater samples were pre-filtered through a 200 μm mesh to prevent zooplankton grazing during the filtration. The samples were filtered onto 0.4 μm membrane filters of 47 mm diameter (Isopore, Millipore, USA) using a vacuum of 400–500 mm Hg (reduced to 100 mm Hg towards the end of the filtration). A glass fibre filter (GF/F, Whatman, UK) was placed underneath the filters to ensure an even distribution of the material on the filter. Filters were rinsed with an ammonium hydroxide solution (approximate

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pH 9 to 10) to remove seawater salts, left to air-dry and stored in dark and dry conditions. Before analysis, a small piece of each filter was cut radially, placed on a stub and gold-coated. The number of coccospheres in each sample was counted under a Scanning Electron Microscope (Leo 1450VP, Carl Zeiss, Germany), using a computer-controlled stage and an automated image-capturing system. A meander-shaped transect was predefined on each filter at a 5000× magnification and the software SmartSEM (V05.01, Carl Zeiss, Germany) was used to capture and store all images. The image analysis was undertaken until 200–300 coccospheres were counted or 225 fields of view were analyzed (Tyrrell et al., 2008).

2.5 Air-sea CO_2 flux calculation

The air-sea CO_2 fluxes (F, in mmol m^{-2} d^{-1}) were calculated as follows (Wanninkhof 1992) for the three day period of each crossing:

$$F = k\alpha\Delta pCO_2 \quad (1)$$

Where ΔpCO_2 (μatm) is the difference between oceanic partial pressure of CO_2 (pCO_2) and atmospheric pCO_2 (a negative flux would hence correspond to a net transfer of CO_2 from the atmosphere to the ocean), k is the gas transfer velocity (m s^{-1}), and α is the solubility coefficient of CO_2 (mol atm^{-1} m^{-3}). The atmospheric pCO_2 data was obtained from the Mace Head (53.33° N; RAMCES/LSCE monitoring network) and the Azores meteorological stations (38.77° N; NOAA/ESRL Global monitoring division) and averaged for each crossing. The average difference in atmospheric pCO_2 observed between the two stations was 0.8 μatm. The oceanic pCO_2 data were calculated from the DIC and TA data obtained in this study and averaged for each crossing and each region. The solubility coefficient of CO_2 (α) was calculated according to Weiss (1974). The gas transfer velocity (k) was calculated according to the equations of Nightingale et al. (2000) and Sweeney et al. (2007). The fluxes calculated following these two equations agreed within ±0.05 mmol m^{-2} d^{-1}. The wind speed data used for the calculation of the gas transfer velocity was obtained from the MET Office Gascogne Buoy

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hourly data and averaged for each crossing. The wind speed was corrected from 3.5 m (height of the measurement) to 10 m above the surface according to Johnson (1999).

2.6 External sources of data

In addition to the fluorescence data obtained from the MINIpack, the SeaWIFS chlorophyll-*a* data (NASA Ocean Color Time-Series) from the Bay of Biscay and the English Channel for the period between 2005 and 2007 were used to investigate the interannual variability (http://reason.gsfc.nasa.gov/OPS/Giovanni/ocean.seawifs.shtml).

In order to determine the mixed layer depth (MLD) we used data from five Argo floats located in the Bay of Biscay for the period of our study (4900557, 6900359, 6900360, 6900362, and 6900365, http://www.coriolis.eu.org/cdc/argo.htm). The MLD was estimated according to the temperature-based criteria which defines the MLD as the shallowest depth corresponding to a temperature difference with the surface sea water temperature of more than $\Delta T = 0.5^{\circ}$C (Monterey and Levitus, 1997).

The North Atlantic Oscillation (NAO) time-series data were obtained from the Climate Prediction Center of the National Oceanic and Atmospheric Administration (NOAA) (http://www.cpc.noaa.gov/data/teledoc/nao_ts.shtml).

3 Results and discussion

3.1 Salinity, temperature and nitrate

A decrease in salinity and temperature with increasing latitude was observed for each crossing (Fig. 2a and b). The salinity distribution did not show a strong variation throughout the year and ranged for the whole study between 35.2 in the Central English Channel and 35.8 in the Southern Bay of Biscay. Lower salinities of approximately 34.8 were observed in the Ushant region in April 2006 due to freshwater inputs from the French rivers Loire and Gironde (Kelly-Gerreyn et al., 2006). Surface waters in Febru-

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ary 2007 were warmer than in February 2006 by 2.6±0.5°C for all regions; whereas July 2007 surface water temperatures were lower than July 2006 by 2.0±0.7°C.

Enhanced nitrate concentrations were observed during the winter months, with depleted levels in summer (Fig. 2c). Surface nitrate concentrations were higher during the 2005/2006 winter than during the 2006/2007 winter, whilst summer nitrate concentrations were below 0.05 μmol l^{-1} for both years and all regions. In the Bay of Biscay, surface nitrate concentrations were higher (up to 8.0 μmol l^{-1}) during the winter 2005/2006 than the values reported for the 2003/2004 winter (up to 4.5 μmol l^{-1} in February 2004) by Bargeron et al. (2006), whilst in winter 2006/2007 they were comparable (up to 4.1 μmol l^{-1}) to those of the 2003/2004 winter (Bargeron et al., 2006). From the English Channel to the Shelf Break, nitrate concentrations in the 2005/2006 winter were similar to the 2003/2004 winter (Bargeron et al., 2006) with an average winter concentration of 7.3 μmol l^{-1}, whilst during the 2006/2007 winter they were lower than during the winter 2003/2004 (Bargeron et al., 2006) with an average concentration of 5.4 μmol l^{-1}.

3.2 Dissolved oxygen anomaly and fluorescence

The dissolved oxygen anomaly at standard pressure ($\Delta[O_2]^o$) was calculated from the measured dissolved oxygen concentration ($[O_2]_{obs}$) and the saturation oxygen concentration ($[O_2]^o_{sat}$) according to Bargeron et al. (2006). The oxygen anomaly distribution (Fig. 2d) showed maxima during high primary productivity in spring times, and minima during the winter months when oxygen-depleted waters were brought to the surface due to winter mixing (Hydes et al., 2008), resulting in oxygen supersaturated surface waters in spring and undersaturated waters in winter. During spring 2006, dissolved oxygen anomalies were higher than in spring 2007 (up to 53.7 and 39.3 mmol m^{-3}, respectively), whilst during the 2005/2006 winter, they were lower than during the 2006/2007 winter (−2.8 and 3.9 mmol m^{-3}, respectively). This suggested a shallow winter mixing in 2006/2007, supported by the lower nitrate concentrations (Fig. 2c) observed in the winter of 2006/2007 compared to 2005/2006.

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The fluorescence data (Fig. 2e) provide an indication of the timing of peaks in primary production and of biomass present in the water. The data showed a similar temporal distribution to the oxygen anomaly, with maximum values during spring (23.4 and 13.6 arbitrary units for spring 2006 and 2007, respectively) and minimum values during winter. The spring fluorescence maximum in the Northern and Southern Bay of Biscay was almost twice as high (1.7 and 1.8 times higher, respectively) in 2006 compared to 2007 (23.4 and 20.9 arbitrary units in 2006 as opposed to 13.6 and 11.7 in 2007 for the two regions), in agreement with the SeaWIFS time-series chlorophyll-*a* distributions (Fig. 3). The fluorescence data for the Shelf Break and Ushant regions also indicated enhanced biomass (1.6 times higher) in 2006 compared to 2007 (20.9 and 13.4 arbitrary units in 2006 as opposed to 12.7 and 8.6 in 2007 for the two regions). The English Channel waters have been described as optically-complex case 2 waters (Vantrepotte et al., 2007; Morel and Prieur, 1977) and the interpretation of the optical signal can therefore be difficult and subject to errors. However, the SeaWIFS time-series chlorophyll-*a* distributions (Fig. 3) appeared to agree well with the temporal trend of the fluorescence data (Fig. 2e), with little or no inter-annual variability observed in the Central and Western English Channel regions between the two years of our study (12.8 and 13.9 arbitrary units in 2006 and 12.8 and 12.0 in 2007 for the two regions).

3.3 Total alkalinity

The TA concentrations ranged between 2319 μmol kg^{-1} and 2363 μmol kg^{-1} (Fig. 4a). The normalized TA ranged from 2286 μmol kg^{-1} to 2329 μmol kg^{-1} (Fig. 4b), with the exception of the Ushant anomaly in April 2006 (nTA=2354 μmol kg^{-1}) where a salinity anomaly was observed due to the influence of riverine inputs (Fig. 2a). Corbière et al. (2007) reported similar values of nTA ranging between 2327 μmol kg^{-1} (winter 2002) and 2289 μmol kg^{-1} (summer 2003) for the Northwest Atlantic subpolar gyre. A drawdown in nTA was observed in most of the regions during the crossings of May and July 2006 and corresponded with the highest cell abundances (up to 0.9×10^{6} cells l^{-1}

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and 0.4×10^6 cells l^{-1}, respectively) of *Emiliana huxleyi*, which was the dominant coccolithophore species observed on each crossing. All other crossings showed *E. huxleyi* abundances of less than 0.1×10^6 cells l^{-1}, which was about an order of magnitude lower than values reported during intense coccolithophore blooms in the North Atlantic (Holligan et al., 1993; Robertson et al., 1994).

In order to estimate the maximum TA drawdown (ΔTA) expected from the coccolithophore abundances (C) observed (on the basis of two moles of HCO_3^- consumed for each mole of $CaCO_3$ produced), we used an average value of 20 coccoliths per cell (Tyrrell and Young 2009), along with an average calcium content of 0.71 pg Ca per coccolith (Paasche 2002) and a molar mass of calcium (M_{Ca}) of 40.1 g mol^{-1}:

$$\Delta TA = (C * 20 * (0.71/M_{Ca}) * 10^{-6}) * 2$$

The maximum estimated TA drawdown due to the observed coccolithophore abundances was 1 μmol kg^{-1}, whilst the mean observed TA drawdown was 12 μmol kg^{-1}. Hence the estimated TA drawdown only accounted for a small fraction of the observed TA drawdown (between 3 and 10%), which suggests that the seasonal distribution of TA was not primarily controlled by production and dissolution of calcium carbonate (confirmed by the low coccolithophore abundances observed), but by uptake and supply of nitrate (Brewer and Goldman, 1976; Wolf-Gladrow et al., 2007), and freshwater inputs or removal such as mixing, precipitation, evaporation or river inputs (Tseng et al., 2007; Bates et al., 1996b).

The nTA distribution showed little variability, with the exception of the April 2006 data in the Ushant region, which indicated limitation of the normalization procedure when dealing with riverine inputs into coastal waters. In order to validate the TA data, the algorithm from Lee et al. (2006) for the North Atlantic Ocean was used for the winter months to calculate TA from sea surface salinity and sea surface temperature (SST) data. The measured TA showed good consistency with the calculated data, with a mean difference of 5.9±4.3 μmol kg^{-1} (n=128), in agreement with the uncertainty reported by Lee et al. (2006).

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3.4 Dissolved Inorganic Carbon

The DIC concentrations showed an overall increase with latitude for all crossings (Fig. 4c), ranging from 2058 μmol kg^{-1} (September 2005, Ushant) to 2142 μmol kg^{-1} (April 2006, Western English Channel). The salinity-normalized DIC (nDIC) concentrations (Fig. 4d) ranged from 2020 μmol kg^{-1} (July 2006, Southern Bay of Biscay) to 2122 μmol kg^{-1} (April 2006, Western English Channel). Our DIC observations were in agreement with values previously reported for the North Atlantic by Corbière et al. (2007) and Robertson et al. (1994), where DIC values ranged from 2070 μmol kg^{-1} in summer to 2140 μmol kg^{-1} in winter. This also agrees with the range reported for the Norwegian Sea, with DIC values ranging between 2140 μmol kg^{-1} in winter and 2050 μmol kg^{-1} to 2080 μmol kg^{-1} in summer (Findlay et al., 2008). The spring fluorescence maxima corresponded with periods of DIC drawdown (Figs. 2e and 4c). The DIC distribution showed an increase during the winter months corresponding to the decrease in the SST (Fig. 2b) and the minimum in O_2 anomaly (Fig. 2d). During the winter of 2006/2007, however, the nitrate concentrations and the O_2 anomaly suggested that the winter mixing was shallower than during the 2005/2006 winter for all regions except the Central and Western English Channel (Fig. 2c and d), leading to a smaller increase in the DIC concentration during the winter of 2006/2007 for the same regions.

3.5 Seasonal variability of DIC and nitrate

Surface DIC and nitrate concentrations were higher in winter than in summer as a result of carbon and nutrient enriched deep waters being brought to the surface due to deep winter mixing (Tseng et al., 2007; Bates et al., 1996b). The increase in biomass observed during spring and early summer (as indicated by the fluorescence data in Fig. 2e) resulted in a decrease in DIC concentrations (Fig. 4c), with a DIC minimum of 2063 μmol kg^{-1} observed in the Bay of Biscay in July 2006 and June 2007. The average seasonal amplitude for DIC and nitrate concentrations, respectively, from winter to spring was 62 μmol kg^{-1} and 7.4 μmol l^{-1} in 2005/2006, and 35 μmol kg^{-1} and

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4.7 μmol l^{-1} in 2006/2007. From late summer to early winter, an increase in surface water DIC was observed, resulting from the enhanced oceanic CO_2 uptake from the atmosphere due to increasing CO_2 solubility in seawater with decreasing air and sea surface temperature (Zeebe and Wolf-Gladrow, 2001). Entrainment by autumn storms of deep waters with higher DIC content also increased surface water DIC concentrations.

3.6 Influence of winter mixing on the carbonate system variability

The increase in atmospheric forcing observed over the winter of 2004/2005 in the Bay of Biscay had a strong effect on the surface layer characteristics due to a decrease in SST and enhanced winter mixing (Somavilla et al., 2009). This SST anomaly extended into the following winter (2005/2006), resulting in a second winter of deep winter mixing. The air temperature during the subsequent winter of 2006/2007 was however the warmest on record for about 500 years (Luterbacher et al., 2007), causing warming of the surface ocean and a reduction in winter mixing. The winter MLD in the Bay of Biscay was estimated from the Argo floats temperature data to be between 450 and 550 m in 2005/2006, and between 200 and 300 m in 2006/2007 (Fig. 5). The MLD observed for 2006/2007 corresponded to the average MLD observed between 2002 and 2004 (approximately 200 m) for the Bay of Biscay (Padin et al., 2008). The deeper MLD during the 2005/2006 winter resulted in higher surface winter concentrations of nutrients and DIC, and an enhancement of the spring bloom in the Bay of Biscay in 2006 (Figs. 2e and 3). The intensity of the spring bloom was reduced in 2007 as a result of a reduced winter mixing in 2006/2007. The inter-annual differences in DIC and nitrate concentrations were similarly affected by the difference in winter mixing in the Bay of Biscay, with winter nitrate concentrations 1.6 times higher in 2005/2006 compared with 2006/2007. This agreed with the differences in biomass, derived from the fluorescence data, observed between the two years (ratio of 1.7 between the two years).

We used a C:N ratio of 8.4 to estimate the seasonal DIC amplitude expected due

to seasonal nitrate drawdown (Table 2). This C:N ratio was shown to give a better estimate of the seasonal carbon consumption between winter and summer than the Redfield ratio of 6.6. This disagreement with the standard Redfield C:N ratio is often observed in coastal waters due to a more efficient recycling of nitrogen compared to carbon (Sambrotto et al., 1993). A similar discrepancy was previously observed in separate studies of the Northeast Atlantic (Körtzinger et al., 2001) and the Norwegian Sea (Findlay et al., 2008), where the use of data on nitrate consumption and a Redfield C:N ratio (6.6) was also shown to significantly underestimate the carbon consumption. A C:N ratio of 8.4 gave a close agreement in our study between the observed seasonal DIC drawdown and the C:N ratio-derived estimate (predicted/observed ratio of 1.08±0.18; Table 2).

The historical time-series of the monthly NAO index showed a dominant negative phase for the period between March 2005 and November 2006 (http://www.cpc.noaa.gov/data/teledoc/nao_ts.shtml), corresponding with the enhanced winter MLD observed in the Bay of Biscay during this period, and a positive phase during the winter of 2006/2007, corresponding with the shallower winter MLD during this period. The surface water nitrate concentration differences between the two winters were used along with a C:N ratio of 8.4 to estimate the influence of winter mixing on the DIC winter concentration (Table 3), and showed a good agreement with the measured winter to winter DIC variability (predicted/observed ratio of 1.07±0.16).

Inter-annual and seasonal variations in DIC concentrations in the North Atlantic Ocean have been reported to be dependent on the winter MLD and SST anomalies (Gruber et al., 2002; Bates, 2001). The NAO has been shown to relate to changes in the MLD associated with anomalies in SST and convection (Dickson et al., 1996; Gruber et al., 2002). In this region, a more negative phase of the NAO is associated with stronger winter mixing, negative SST anomalies, higher winter DIC concentrations (due to the deep supply from vertical mixing) and lower spring/summer DIC concentrations (due to increased primary productivity); whereas a more positive NAO phase is accompanied by warmer SSTs, less intense winter mixing, and a less pronounced

seasonal cycle of DIC (Gruber et al., 2002).

3.7 Air-sea CO_2 fluxes

The calculated air-sea CO_2 fluxes (F_{CO2}) showed significant differences between the various regions (Fig. 6). The English Channel acted as a seasonal source of CO_2 to the atmosphere during autumn and winter months and as a sink during spring and summer months (from +4.5 mmol m^{-2} d^{-1} in winter, to −3.3 mmol m^{-2} d^{-1} in summer). This is in agreement with other studies in this area (Frankignoulle et al., 1996a; Borges and Frankignoulle, 2003; Padin et al., 2007). In contrast, the Bay of Biscay acted as a sink of CO_2 during all seasons, with the exception of July 2006 for the Southern Bay of Biscay. Fluxes ranged between +0.2 and −4.7 mmol m^{-2} d^{-1}, consistent with the results of Padin et al. (2008, 2009) and Frankignoulle and Borges (2001).

Despite a few gaps in the monthly data available for the flux estimates, a good coverage of the seasonal cycle was available for the two years. The air-sea fluxes showed clear differences between similar months in 2005/2006 compared with 2006/2007 for all regions, apart from the Central English Channel and the Western English Channel. The latter regions did not show a significant difference between the two years (paired t-test, p=0.15, n=12). In all other regions, May, June and July 2007 showed an increase in the oceanic CO_2 sink, with the air-sea fluxes between 1.5 and 6.6 times larger compared with May, June and July 2006 (paired t-test, p=0.0002, n=12). The months of February and April however did not show statistical differences between the two years (paired t-test, p=0.06, n=12).

The wind speed (Fig. 7) was higher in May, June and July 2007 compared to 2006, which may have influenced the air-sea CO_2 flux differences observed in the Bay of Biscay, the Ushant front and the Shelf break regions between the two years. The winter 2005/2006 was colder than winter 2006/2007 by 2.6°C, while the summer of 2005/2006 was warmer than the summer of 2006/2007 by 2°C (Fig. 2b). This resulted in winter to summer SST differences of about 8°C in 2005/2006 and 3.4°C in 2006/2007, leading to enhanced solubility of CO_2 in the summer of 2007 compared to 2006. The oceanic

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pCO_2 and the CO_2 fluxes were fairly similar in the two winters (Figs. 6 and 7), which can be explained by the high DIC and low SST during the first winter and the low DIC and high SST during the following winter.

After the colder winter (2005/2006), the following seasonal changes occurred upon transition to summer (with their estimated impacts on the air-sea CO_2 flux, in $mmol\,m^{-2}\,d^{-1}$, given in brackets, see Table 4 for method of calculation): wind speed decreased by $4\,m\,s^{-1}$ (+0.9); temperature increased by 8°C (+5.7); and DIC decreased by $67\,\mu mol\,kg^{-1}$ (−6.2). After the warmer winter of 2006/2007 however, the following seasonal changes occurred: wind speed decreased by $3\,m\,s^{-1}$ (+0.7); temperature increased by 3.4°C (+2.5); and DIC decreased by $46\,\mu mol\,kg^{-1}$ (−4.0). The seasonal changes in DIC and SST both had important impacts on air-sea flux of CO_2 (Table 4). In terms of differences between years, it appears that the effects on air-sea CO_2 flux of the greater seasonal warming following the colder winter (+3.2) and lower wind speed (+0.2) outweighed the effect of stronger spring blooms in 2006 (−2.2). According to our analysis, the effect of the difference in winter mixing between the two years was therefore counteracted and in fact overwhelmed by the greater amount of warming of the surface waters. It was this latter factor, we calculate, which led to a stronger CO_2 sink in summer 2007 compared to summer 2006. Our observations for the Bay of Biscay are consequently in contrast to recent model results for the stratified northern North Sea, where biological productivity, and not temperature, was emphasized as the main driver for the air-sea flux of CO_2 (Prowe et al., 2009).

4 Conclusions

The changes in winter mixing and SST observed between the two consecutive years of our study period showed lower-amplitude seasonal cycles of nitrate and DIC and an associated decrease in primary productivity following the warmer winter of 2006/2007. While no particular changes were observed in the English Channel regions, elsewhere an enhanced carbon uptake from the atmosphere to the ocean was observed in the

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summer of 2007 compared to the summer of 2006. This occurred despite more intense phytoplankton blooms in spring 2006 compared with 2007. We attribute the surprisingly lower ocean carbon uptake in summer 2006 to a greater amount of warming from winter to summer (SST increase of 8°C between February and July in 2006, compared with only 3.4°C in 2007). This greater degree of warming tended to increase surface ocean pCO_2 towards higher values in summer 2006, and was sufficiently strong to offset the effects of the stronger phytoplankton blooms in that year. Stronger winds in summer 2007 compared with summer 2006 also contributed to an increased carbon uptake in summer 2007. While upper ocean stratification is expected to increase due to further CO_2 emissions, with the prediction that this will lead to decreased oceanic CO_2 uptake, we show in this study that a decrease in winter mixing can be followed by an increase in oceanic CO_2 uptake during the following summer. Our study highlights the importance of winter to summer temperature differences in controlling the annual CO_2 sink in temperate waters. Our results are in contrast with some model predictions and must be considered in the future in order to understand how the oceans will respond to future climate change and accompanying changes in stratification and storm frequency.

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Table 1. Crossing dates (Portsmouth to Bilbao) between 2005 and 2007.

Date	DIC and TA samples	Date	DIC and TA samples
26 Sep–29 Sep 2005	34 (DIC only)	18 Oct–19 Oct 2006	39
14 Dec–15 Dec 2005	33	10 Feb–11 Feb 2007	34
28 Feb–2 Mar 2006	40	4 Apr–5 Apr 2007	33
10 Apr–11 Apr 2006	21	10 May–11 May 2007	28
10 May–12 May 2006	15	4 Jun–6 Jun 2007	32
12 Jun–15 Jun 2006	27	10 Jul–12 Jul 2007	19
9 Jul–11 Jul 2006	16		

Table 2. Observed and estimated seasonal amplitude of DIC (differences based on the nitrate and DIC maximum in winter and the fluorescence and O_2 anomaly maximum in spring) for the periods September 2005 to July 2006 and October 2006 to July 2007.

Year	Region	ΔNitrate (μmol l^{-1})	ΔDIC (μmol kg^{-1})	ΔDIC (μmol kg^{-1}) from 8.4 C:N ratio	Predicted/observed ratio
2005/2006	Central English Channel	7.3	50	61	1.22
	Western English Channel	7.2	58	60	1.04
	Ushant	6.2	63	52	0.82
	Shelf Break	8.3	61	70	1.15
	Northern Bay of Biscay	8.0	71	67	0.95
	Southern Bay of Biscay	7.2	68	60	0.89
Average 2005/2006		7.4	62	62	
2006/2007	Central English Channel	5.2	36	44	1.21
	Western English Channel	5.3	45	44	0.99
	Ushant	5.4	39	45	1.16
	Shelf Break	4.5	25	38	1.48
	Northern Bay of Biscay	3.9	29	33	1.12
	Southern Bay of Biscay	4.0	36	34	0.94
Average 2006/2007		4.7	35	40	

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Table 3. Observed and estimated inter-annual differences of DIC (differences based on the nitrate maximum in winter) between the winters of 2005/2006 and 2006/2007.

Region	ΔNitrate (μmol l^{-1})	ΔDIC (μmol kg^{-1})	ΔDIC (μmol kg^{-1}) from 8.4 C:N ratio	Predicted/observed ratio
Central English Channel	1.4	12.7	11.6	0.92
Western English Channel	1.9	17.7	15.6	0.88
Ushant	2.7	20.7	22.9	1.11
Shelf Break	3.7	28.6	31.5	1.10
Northern Bay of Biscay	4.1	26.2	34.3	1.31
Southern Bay of Biscay	3.1	23.8	26.3	1.11

Table 4. Effect of varying wind speed ($m\,s^{-1}$), temperature (°C) and DIC concentration ($\mu mol\,kg^{-1}$) on the air-sea CO_2 flux calculation in $mmol\,m^{-2}\,d^{-1}$. Fluxes were calculated according to Eq. (1). The oceanic pCO_2 values were calculated from DIC, TA, salinity, and temperature data using the CO_2SYS program. The calculation considered only one varying parameter at a time while all other parameters were considered constant: TA=2350 $\mu mol\,kg^{-1}$; S=35; T=16; wind speed=8 $m\,s^{-1}$; DIC=2100 $\mu mol\,kg^{-1}$; and atmospheric pCO_2=380 μatm.

Varying parameter	Season	Value	Flux calculated	Seasonal difference	Flux difference
	Winter 2005/2006	10	−1.5		
Wind speed ($m\,s^{-1}$)	Summer 2006	6	−0.6	4	+0.9
	Winter 2006/2007	11	−1.8		
	Summer 2007	8	−1.0	3	+0.7
	Winter 2005/2006	10.6	−4.2		
Temperature (°C)	Summer 2006	18.6	+1.5	8.0	+5.7
	Winter 2006/2007	13.4	−2.4		
	Summer 2007	16.8	+0.1	3.4	+2.5
	Winter 2005/2006	2131	+2.7		
DIC ($\mu mol\,kg^{-1}$)	Summer 2006	2064	−3.5	67	−6.2
	Winter 2006/2007	2111	+0.5		
	Summer 2007	2065	−3.5	46	−4.0

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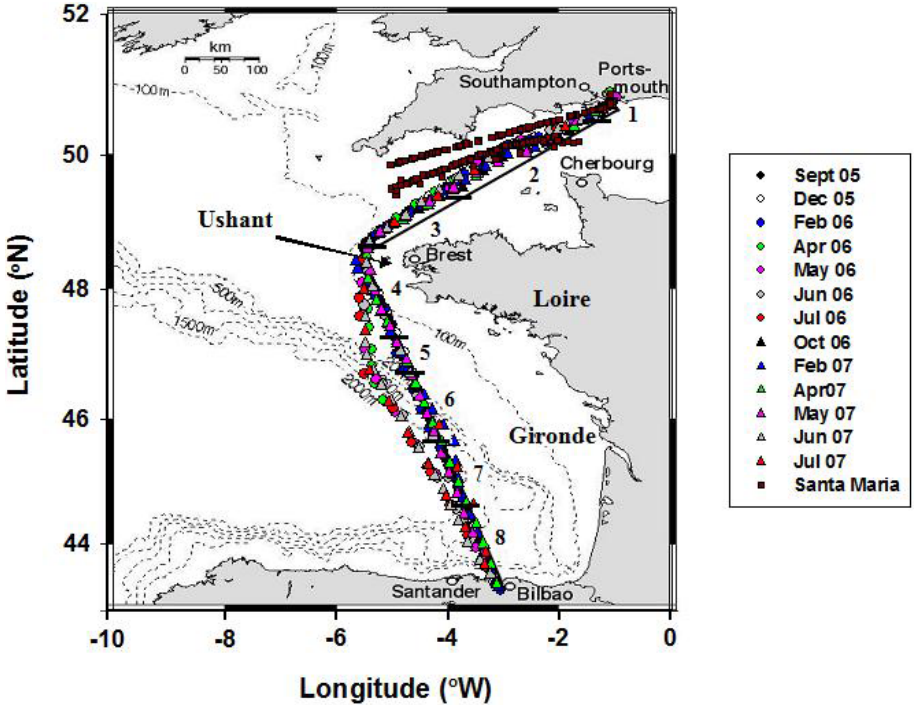

Fig. 1. Location of the FerryBox route and sub-regions associated: (1) Portsmouth Harbour; (2) Central English Channel; (3) Western English Channel; (4) Ushant tidal front; (5) Shelf break; (6) Northern Bay of Biscay; (7) Southern Bay of Biscay; (8) Iberian Shelf. The sampling positions for each crossing are shown as well as the MV *Santa Maria* track (figure adapted from Kelly-Gerreyn et al., 2006).

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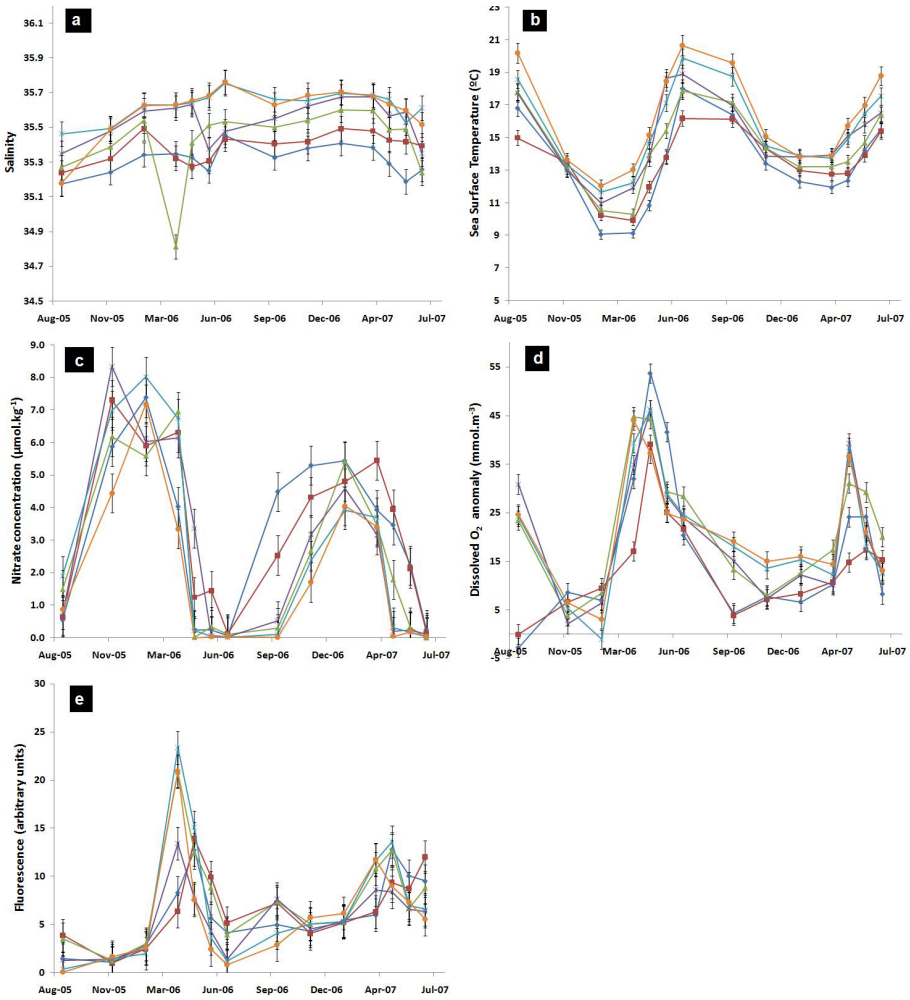

Fig. 2.

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Fig. 2. Monthly mean of **(a)** sea surface salinity, **(b)** sea surface temperature (°C), **(c)** surface nitrate concentration (μmol l^{-1}), **(d)** dissolved oxygen anomaly (mmol m^{-3}) and **(e)** fluorescence (arbitrary units) distribution averaged for each region: Central English Channel (dark blue); Western English Channel (red); Ushant (green); Shelf Break (purple); Northern Bay of Biscay (light blue); Southern Bay of Biscay (orange). The error bars represent the standard deviation for each mean. Data points are linearly interpolated between sampling points to allow a clear distinction of observations between regions. It should not be assumed that the interpolation provides an accurate estimate of the missing data.

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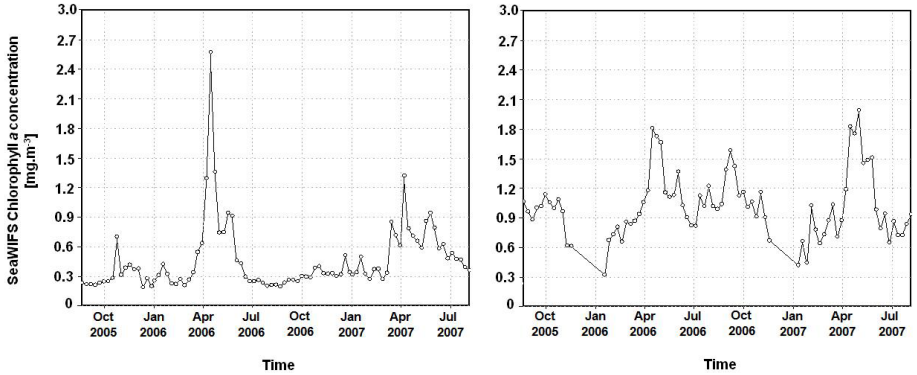

Fig. 3. Chlorophyll-*a* distribution (8-days average) for the Bay of Biscay area (left) and the English Channel area (right) between September 2005 and July 2007. Graphs generated by NASA's Giovanni (giovanni.gsfc.nasa.gov).

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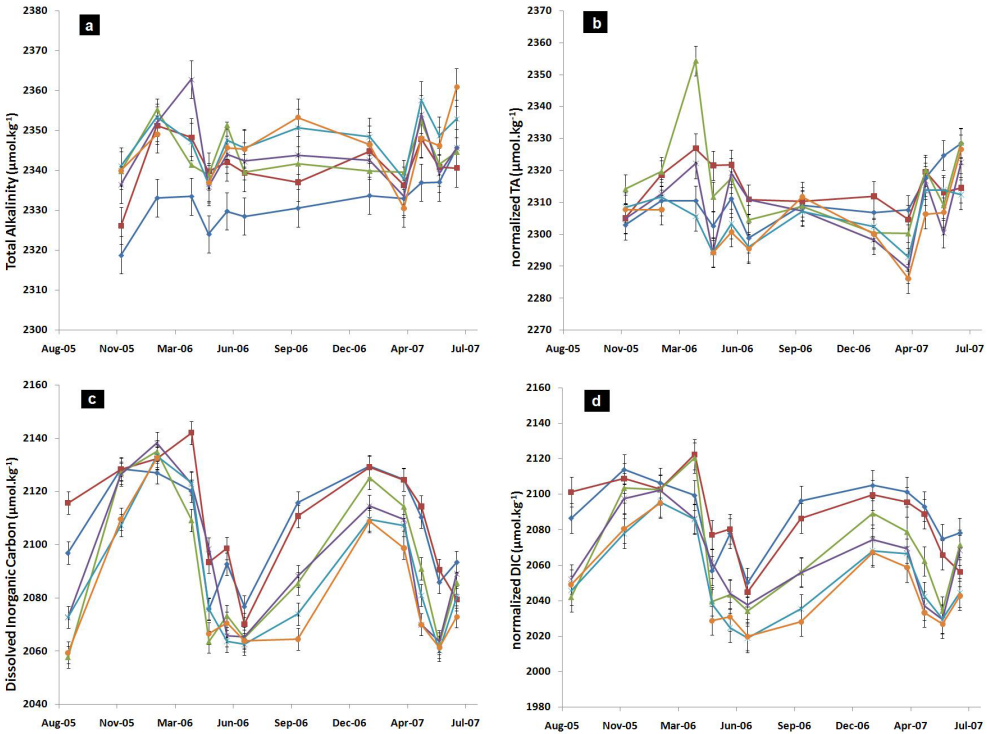

Fig. 4. Monthly mean concentrations (μmol kg^{-1}) of **(a)** TA, **(b)** nTA, **(c)** DIC and **(d)** nDIC: Central English Channel (dark blue); Western English Channel (red); Ushant (green); Shelf Break (purple); Northern Bay of Biscay (light blue); Southern Bay of Biscay (orange). Each data point represents the average of several measurements made within one part of the transect (Fig. 1). The error bars represent the standard deviation of each mean. Data points are linearly interpolated between sampling points to allow a clear distinction of observations between regions. It should not be assumed that the interpolation provides an accurate estimate of the missing data.

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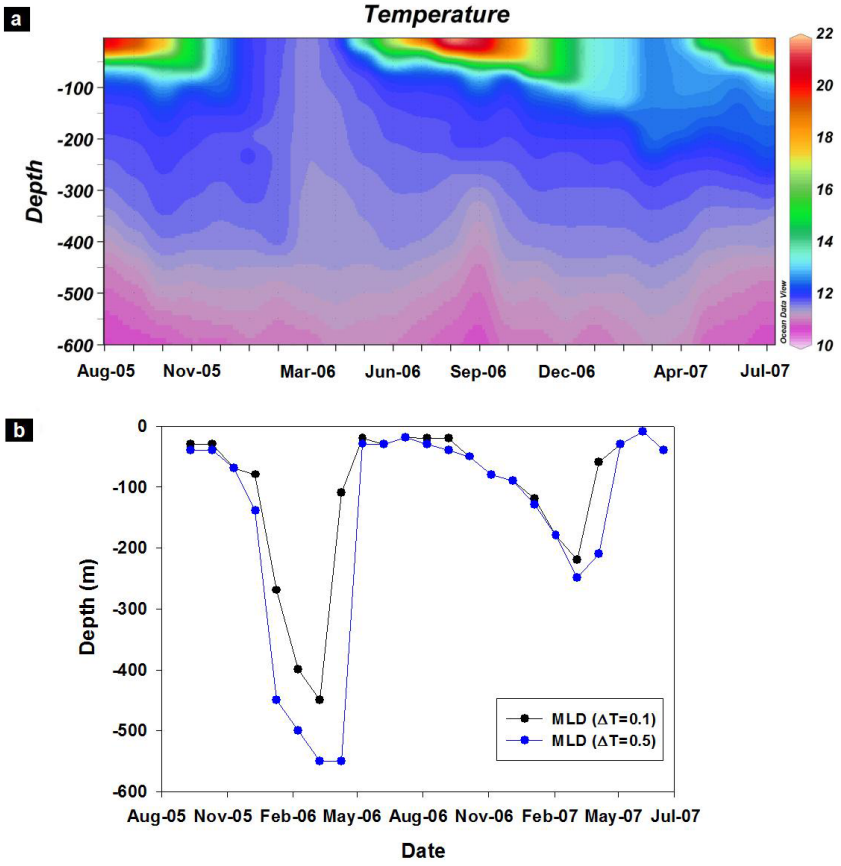

Fig. 5. **(a)** Argo float 6900362 temperature data for the Bay of Biscay for the period between July 2005 and April 2008 in the upper 600 m, **(b)** and mixed layer depths (MLD) calculated for the Argo float 6900362 data with ΔT (depth-surface) of −0.1°C and −0.5°C (http://www.coriolis.eu.org/cdc/argo.htm).

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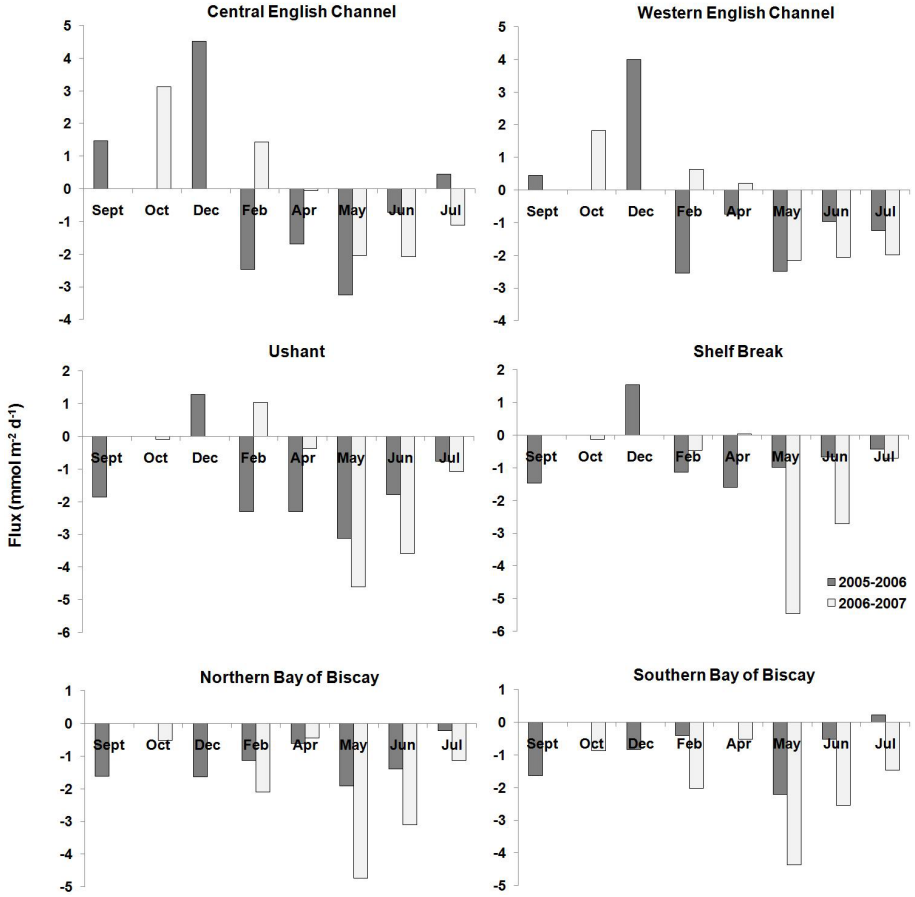

Fig. 6. Calculated air-sea CO_2 fluxes (mmol m^{-2} d^{-1}; negative values indicate a net flux into the sea) for each region in 2005/2006 (dark grey) and 2006/2007 (light grey).

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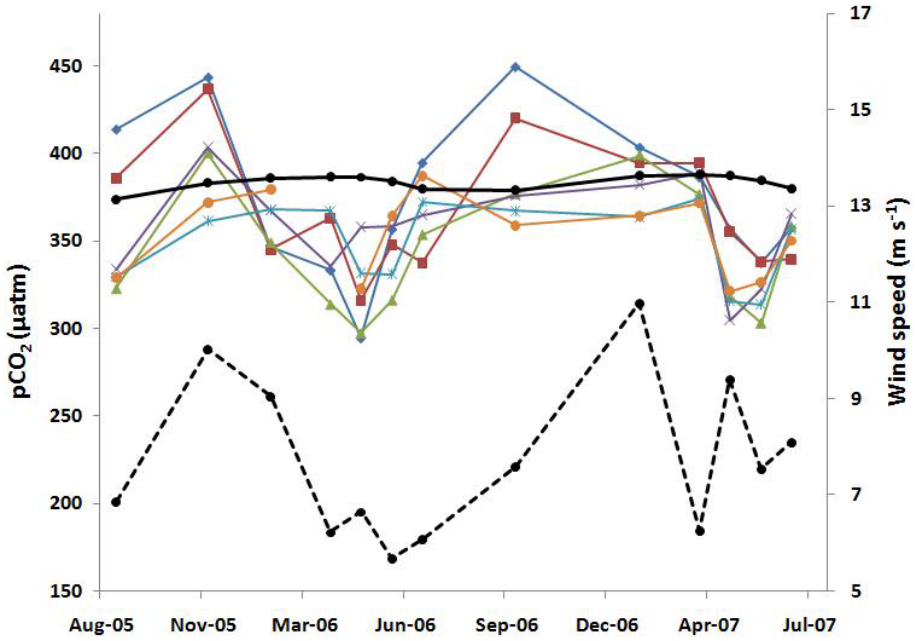

Fig. 7. Monthly mean calculated sea surface pCO_2 (μatm) for each region (colored in upper plot with left axis), atmospheric pCO_2 data (μatm; solid black line in upper plot with left axis), and wind speed data ($m\,s^{-1}$; dotted black line in lower plot with right axis). Colors used in the upper plot indicate: Central English Channel (dark blue); Western English Channel (red); Ushant (green); Shelf Break (purple); Northern Bay of Biscay (light blue); Southern Bay of Biscay (orange).

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