



Seasonal cycle of O₂ and pCO₂ in the central Labrador Sea: Atmospheric, biological, and physical implications

A. Körtzinger,¹ U. Send,² D. W. R. Wallace,¹ J. Karstensen,³ and M. DeGrandpre⁴

Received 4 June 2007; revised 12 October 2007; accepted 9 November 2007; published 14 February 2008.

[1] We present full 2004–2005 seasonal cycles of CO₂ partial pressure (pCO₂) and dissolved oxygen (O₂) in surface waters at a time series site in the central Labrador Sea (56.5°N, 52.6°W) and use these data to calculate annual net air-sea fluxes of CO₂ and O₂ as well as atmospheric potential oxygen (APO). The region is characterized by a net CO₂ sink (2.7 ± 0.8 mol CO₂ m⁻² yr⁻¹) that is mediated to a major extent by biological carbon drawdown during spring/summer. During wintertime, surface waters approach equilibrium with atmospheric CO₂. Oxygen changes from marked undersaturation of about 6% during wintertime to strong supersaturation by up to 10% during the spring/summer bloom. Overall, the central Labrador Sea acts as an O₂ sink of 10.0 ± 3.1 mol m⁻² yr⁻¹. The combined CO₂ and O₂ sink functions give rise to a sizable APO flux of 13.0 ± 4.0 mol m⁻² yr⁻¹ into surface waters of the central Labrador Sea. A mixed layer carbon budget yields a net community production of 4.0 ± 0.8 mol C m⁻² during the 2005 productive season about one third of which appears to undergo subsurface respiration in a depth range that is reventilated during the following winter. The timing of the spring bloom is discussed and eddies from the West Greenland Current are thought to be associated with the triggering of the bloom. Finally, we use CO₂ and O₂ mixed layer dynamics during the 2005 spring bloom to evaluate a suite of prominent wind speed-dependent parameterizations for the gas transfer coefficient. We find very good agreement with those parameterizations which yield higher transfer coefficients at wind speeds above 10 m s⁻¹.

Citation: Körtzinger, A., U. Send, D. W. R. Wallace, J. Kartensen, and M. DeGrandpre (2008), Seasonal cycle of O₂ and pCO₂ in the central Labrador Sea: Atmospheric, biological, and physical implications, *Global Biogeochem. Cycles*, 22, GB1014, doi:10.1029/2007GB003029.

1. Introduction

[2] The subpolar North Atlantic is characterized by large seasonal amplitudes of surface ocean carbon and oxygen dynamics and associated source/sink functions for atmospheric CO₂ and O₂ [Najjar and Keeling, 1997; Garcia and Keeling, 2001; Takahashi et al., 2002]. Key to this dynamic behavior is the combination of both strong physical and biological forcing of the subpolar gyre in the North Atlantic. The Labrador Sea is a region of particular interest, being one of the few regions of the world ocean where open ocean deep convection occurs, reaching depths between 700 and more than 2000 m [Lazier et al., 2002; Avsic et al., 2006]. The Labrador Sea is part of the Atlantic Arctic Province

(ARCT) of Longhurst [2007] which is characterized by large “spring bloom type” biological productivity in May–June fueled by vertical nutrient supply during winter convection. Seasonal variations of both physical factors (warming/cooling, deep convection and entrainment, wind speed etc.) and biological factors (productivity/respiration) drive air-sea exchanges of CO₂ and O₂. This seasonal forcing of gas exchange (e.g., warming simultaneous with primary production) is reinforcing in the case of O₂ exchange and self-compensating for CO₂. This complex forcing and high-amplitude seasonal variability coupled with the direct link to the vast ocean interior makes the region interesting, significant, and potentially vulnerable in the anthropocene era of global climate change.

[3] All major forcing factors (temperature [Levitus et al., 2005], salinity [Dickson et al., 2002], convection depth [Lazier et al., 2002; Avsic et al., 2006], and biological productivity [Behrenfeld et al., 2006]) are affected by subdecadal variability as well as longer-term climate-driven trends. These changes are bound to influence the CO₂ sink in the subpolar North Atlantic and may exert a significant control on the growth rate of CO₂ in the atmosphere as well as on our future climate. Temporal variability in the degree of surface seawater CO₂ saturation, and hence the

¹Leibniz Institute of Marine Sciences, Chemical Oceanography, University of Kiel, Kiel, Germany.

²Scripps Institution of Oceanography, University of California at San Diego, La Jolla, California, USA.

³Leibniz Institute of Marine Sciences, Physical Oceanography, University of Kiel, Kiel, Germany.

⁴Department of Chemistry, University of Montana, Missoula, Montana, USA.

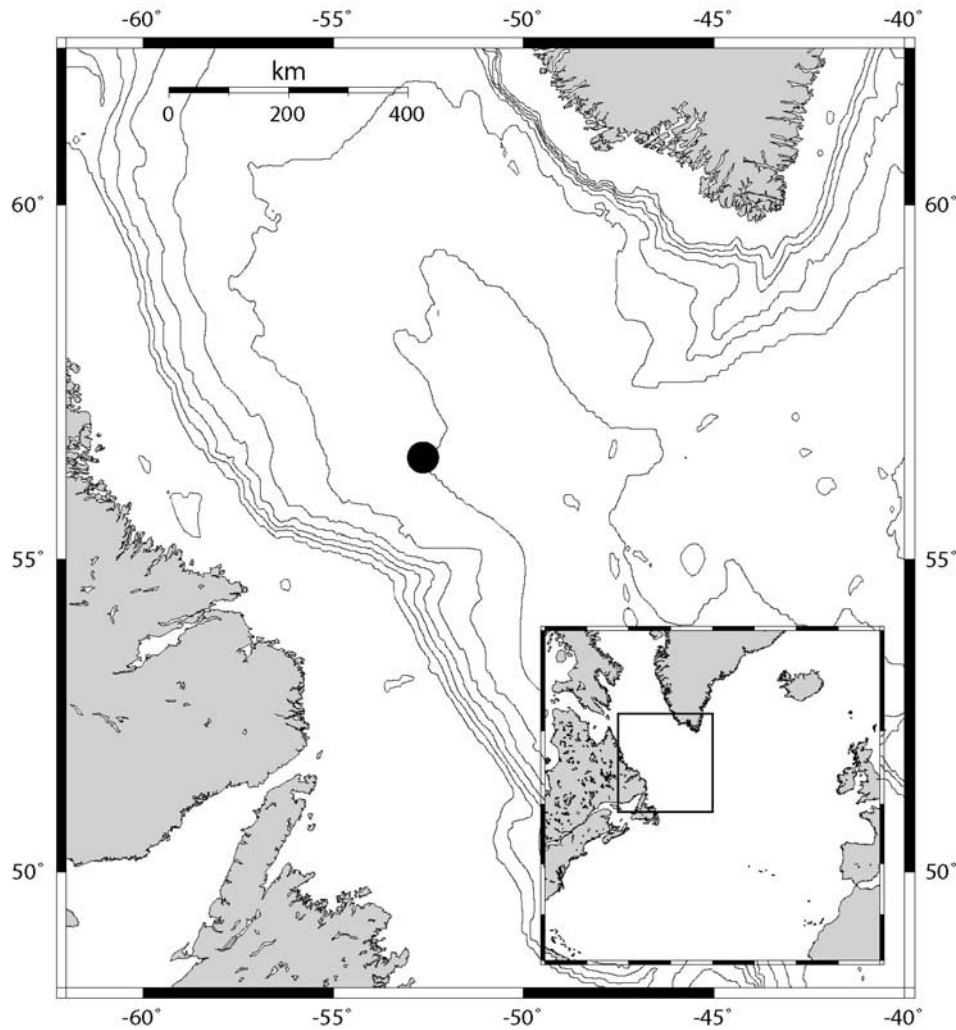


Figure 1. Map of the Labrador Sea in the subpolar northwest Atlantic Ocean with the location of the K1 mooring site at 56.5°N, 52.5°W. The bathymetry contour interval is 500 m.

corresponding sink for atmospheric CO₂, is starting to be observed [e.g., Lefèvre *et al.*, 2004; Omar and Olsen, 2006]. Measurement of such variability and attribution to variable forcing is critical for testing and improving models (including models of air-sea gas exchange) used to predict or explain future changes in atmospheric CO₂ and O₂. The main emphasis of this study is on the application of in situ measurement technology to examine the seasonal CO₂ and O₂ variability in the surface water of the Labrador Sea.

2. Methods and Data

2.1. Central Labrador Sea Mooring (K1)

[4] Since 1996 a long-term oceanographic mooring site has been operated continuously in the subpolar northwest Atlantic Ocean at the K1 location in the central Labrador Sea (56.5°N, 52.6°W (Figure 1)). The site, which is close to the location of the former Ocean Weather Station Bravo (56.5°N, 51°W), was chosen primarily to study trends and variability in deep convection activity [Avsic *et al.*, 2006].

Following a pilot study that took place in 2001 [DeGrandpre *et al.*, 2006], continuous mixed layer measurements of O₂ concentration and CO₂ partial pressure (pCO₂) have been made with autonomous instrumentation deployed at the K1 site from September 2004 to July 2005. Therein pCO₂ and O₂ sensors as well as a CTD sensor were deployed together at a nominal depth of about 38 m. Since the mooring featured a subsurface top flotation element instead of a surface buoy this was the closest the instrument package could be deployed to the surface, which has implications for the observability of mixed layer properties (see section 3.1).

2.2. Measurements

[5] A suite of physical (temperature, salinity, and pressure) and chemical parameters (pCO₂ and O₂) were measured successfully with autonomous instrumentation deployed at various depths at K1 (Table 1). Following is a brief description of the instrument used: The pCO₂ was

Table 1. Nominal Deployment Depths (Sampling Intervals) of Moored Instruments From Which Data Have Been Used in This Study

Parameter	Deployment Depths (Sampling Interval)
Temperature ^a	38 m, 92 m, 156 m, 246 m, 305 m, 422 m, 798 m (12 hour)
Salinity ^a	38 m, 92 m, 246 m, 798 m (12 hour)
Pressure	38 m, 92 m, 156 m, 246 m, 422 m, 798 m (12 hour)
Oxygen	38 m, 798 m (2 hour)
pCO ₂	38 m (1 hour)

^aT/S sensor at 10-m depth lost after a few days into the deployment.

measured with an autonomous sensor (SAMI-CO₂, Sunburst Sensors LLC, Missoula, Montana, United States) which is based on equilibration of a pH indicator solution contained in a gas permeable membrane with ambient pCO₂ and subsequent spectrophotometric pH determination in the equilibrated solution [DeGrandpre et al., 1995]. The sensor head was covered with a copper mesh to prevent biofouling. Oxygen measurements were made with a novel optode sensor (Model 3830, Aanderaa Data Instruments, Bergen, Norway) which senses O₂ partial pressure via its quenching effect on the fluorescence of a dye immobilized in a gas permeable sensing foil. This sensor has shown very good sensitivity and long-term stability [Körtzinger et al., 2005; Tengberg et al., 2006]. Measurements of temperature, salinity, and pressure were performed with SBE-37 MicroCAT recorders (Sea-Bird Electronics Inc., Bellevue, Washington, United States) and at some depths with RCM-8 current meters equipped with temperature sensors only (Aanderaa Data Instruments, Bergen, Norway).

2.3. Sources of Ancillary Data

[6] In the present analysis we made use of various other sources of information (Table 2) for the following parameters: sea surface temperature (SST), sea level barometric pressure (SLP), wind speed at 10 m height, atmospheric CO₂ concentration, climatological surface ocean pCO₂, and total alkalinity (A_T). Data were retrieved for the pixel (or average of pixels) that represents the location of the K1 site (56.5°N, 52.6°W).

[7] We used the extended CO₂ record derived from continuous measurements on Vestmannaeyjar, Iceland (ICE (63.25°N, 20.15°W)) to calculate atmospheric pCO₂ at barometric pressure (28-day running mean of SLP taken every 6 hours, Table 2) and 100% humidity (derived from 28-day running mean of Advanced Microwave Scanning Radiometer-EOS (AMSR-E) SST, Table 2).

[8] Climatological surface ocean pCO₂ data were retrieved for the K1 site from Takahashi et al.'s [2002] climatology. As the climatology's reference year is 1995, a correction to our 2004–2005 observation period was necessary. For this the increase of the annual mean atmospheric CO₂ mole fraction at the Mace Head Observatory relative to 1995 was added to the 1995 climatological pCO₂ for the K1 site pixel. This correction assumes that the ocean follows the atmospheric CO₂ increase with an air-sea

disequilibrium that is not changing with time. In reality this may not be exactly the case, but the currently available information does not provide a quantitatively consistent picture for an alternative correction.

[9] Mixed layer depths were estimated from vertical temperature, salinity, and (if available) oxygen profiles measured by Argo floats within ~100 km of the K1 site. Because of the region's weak vertical stratification during wintertime, classical mixed layer depth criteria such as the temperature ($\Delta T = 0.5^\circ\text{C}$) or density criterion ($\Delta\sigma = 0.125 \text{ kg m}^{-3}$) of *Monterey and Levitus* [1997] were not applicable. Weak vertical temperature and salinity gradients during periods of deeper mixing caused a strong overestimation of mixed layer depths using these criteria. Following *de Boyer Montégut et al.* [2004], we employed smaller but slightly variable criteria ($\Delta T \sim 0.2^\circ\text{C}$ and $\Delta\sigma \sim 0.03 \text{ kg m}^{-3}$) on the basis of visual inspection of individual profiles. Where oxygen data were available, an oxygen criterion ($\Delta\text{O}_2 = 5 \mu\text{mol L}^{-1}$) was applied for an independent estimate. The three estimates agreed on average to within 6% (0–33%, larger relative differences only for shallow mixed layers) and we herein use averages of the three estimates.

2.4. Calibration of O₂ and pCO₂ Data

[10] The oxygen optodes are provided with batch-calibrated sensor foils. The nominal sensor accuracy stated by

Table 2. Sources of Ancillary Data Used in the Present Study

Parameter	Source
Sea surface temperature	Advanced Microwave Scanning Radiometer-EOS on NASA EOS Aqua satellite, level 3 daily product in $0.25^\circ \times 0.25^\circ$ resolution [Wentz and Meissner, 2004]
Barometric pressure	Fleet Numerical Meteorology and Oceanography Center (FNMOC), sea level pressure on a $1^\circ \times 1^\circ$ grid every 6 hours, Pacific Fisheries Environmental Laboratory (PFEL) live access server (http://www.pfeg.noaa.gov/products/las.html)
Vertical T/S profiles	Argo float observatory, Argo Global Data Assembly Centers, Global Ocean Data Assimilation Experiment (http://www.usgodae.org/cgi-bin/argo_select.pl)
10 m wind speed	FNMOC, sea level pressure on a $1^\circ \times 1^\circ$ grid every 6 hours, PFEL live access server (http://www.pfeg.noaa.gov/products/las.html)
Atmospheric CO ₂	GLOBALVIEW-CO ₂ (2006). Cooperative Atmospheric Data Integration Project (http://www.esrl.noaa.gov/ccgg/globalview/)
Surface ocean pCO ₂	Climatology for reference year 1995 [Takahashi et al., 2002]
Surface ocean alkalinity	Global Surface Ocean Alkalinity Climatology, calculated using regional A _T relationships [Lee et al., 2006] and monthly mean sea surface temperature/sea surface salinity fields from the World Ocean Atlas 2001 (http://cdiac.ornl.gov/oceans/Lee_Surface_Alk_Climatol.html)
Chlorophyll <i>a</i>	Moderate Resolution Imaging Spectroradiometer, level 3 standard chlorophyll product (http://oceancolor.gsfc.nasa.gov/)
Net primary production	Ocean Productivity website with VGPM and CBPM products (http://web.science.oregonstate.edu/ocean.productivity/index.php)

the manufacturer is 8 $\mu\text{mol L}^{-1}$ or 5% whichever is greater. Results from field deployments have shown, however, that the stated accuracy is frequently not met when compared to oxygen data measured by classical Winkler titration [Körtzinger *et al.*, 2005]. Therefore a two-point laboratory calibration was carried out prior to deployment which allowed adjustment of the sensor's calibration coefficients. For this, two controlled O₂ concentrations were obtained, one in air and one in a zero-oxygen solution. When measuring in vapor-saturated air, the sensor reports O₂ concentrations as if submerged in freshwater equilibrated with air at the temperature of the measurement. The expected O₂ reading can then be calculated (at 100% humidity) using the dry air mole fraction of O₂ (0.20946), the temperature-dependent O₂ solubility in freshwater [Benson and Krause, 1984], and the barometric pressure at the time of the calibration. The zero-oxygen solution was prepared by addition of 5 g of sodium sulfite (Na₂SO₃) in 500 mL of water. The resulting accuracy of our O₂ measurements is estimated at 2 $\mu\text{mol L}^{-1}$.

[11] The SAMI-CO₂ sensor was calibrated by the manufacturer to the expected variability range in temperature and pCO₂ and should thus be calibration-free on the user side. Also, SAMI-CO₂ sensors have shown on various occasions to have good long-term stability [DeGrandpre *et al.*, 1995, 1999]. However, postcalibration of field data has sometimes turned out to be necessary to account for problems with the initial calibration (possibly due to changes occurring during sensor shipment) or from drift [Körtzinger *et al.*, 2008]. Postcalibration of the data was not possible for this study but several lines of evidence allow for plausibility checks on the data.

[12] First, underway pCO₂ measurements made onboard the research vessels used for deployment and recovery of the mooring were used. Of these the September 2004 data (R/V *Charles Darwin*, cruise 162b) are incorrect, probably due to undetected gas leakage in the equilibrator gas circuit and therefore cannot be used. The data from the recovery on 21 July 2005 (R/V *Thalassa*) are of good quality. Unfortunately, the SAMI pCO₂ sensor was sensing subsurface conditions during most of July as evidenced by the SST filter (described in section 3.1). Hence the surface pCO₂ and SST data of that cruise can only be used as plausibility check. Assuming a seasonal pCO₂ minimum associated with the SST maximum, mooring and ship-based pCO₂ agree reasonably well, however. Second, our pCO₂ measurements were compared to the climatological pCO₂ [Takahashi *et al.*, 2002] at this location, corrected to our measurement period (see section 2.3 for details) with a strikingly good agreement. Finally, a third line of evidence can be drawn from the fact that seawater pCO₂ levels approached the atmospheric pCO₂ in February 2005 and stayed very close to it for more than 3 months during which neither biological production nor warming/cooling were likely to have drawn it away from equilibrium. Seawater and atmosphere pCO₂ should thus have stayed at or near equilibrium which is what we observed with seawater pCO₂ ($376.8 \pm 3.1 \mu\text{atm}$) and atmospheric pCO₂ ($379.4 \pm 2.5 \mu\text{atm}$) being on average only 2.6 μatm apart.

Taking all this information together, we estimate an overall accuracy of our pCO₂ data of 5–10 μatm .

3. Results and Discussion

3.1. Seasonal Cycles of Surface Ocean pCO₂ and O₂

[13] The main goal of our study was to characterize full annual cycles of surface ocean pCO₂ and O₂ in terms of their physical and biological forcing. This was partly impaired by submergence of the sensor package from its normal deployment depths of 38 m (Table 1) to depths of up to 100 m during certain periods and events. Attempts to measure surface waters in direct contact with the atmosphere were also compromised when the mixed layer depth approached or shoaled above the instrument's deployment depth during some summer periods. Some of the data acquired during these times were collected from below the mixed layer and cannot be used to infer atmosphere-ocean exchanges.

[14] In order to exclude these data a filter based on SST was developed. Remotely sensed microwave SST data (AMSR-E, Table 2), which have been shown to agree very well with sea surface temperatures down to 10-m depth [Emery *et al.*, 2006], were compared with in situ temperatures measured at the pCO₂ sensor depth. The pCO₂ data were considered representative of the surface mixed layer when the in situ temperature differed by less than 0.8°C from the SST measured by the satellite-borne microwave instrument (Figure 2). This temperature criterion was adjusted to allow for small measurement error, small-scale variability in mixed layer temperature, and scatter associated with the AMSR-E temperature data (sensitivity is 0.3 K for an integration time of 2.6 ms). The filter proved very effective and mainly eliminated data from periods of high stratification and shallow mixing during summer 2005.

[15] The resulting picture of the seasonal pCO₂ cycle in the central Labrador Sea (Figure 3) shows a late winter maximum and a pronounced summer minimum. This pattern is caused by the counteracting effects of seasonal warming and spring/summer biological activity (see also DeGrandpre *et al.* [2006]). As has been shown for other subpolar regions [e.g., Takahashi *et al.*, 1993, 2002; Lüger *et al.*, 2004], the pCO₂ spring/summer drawdown due to net community production, as fueled by wintertime nutrient supply through deep vertical mixing, strongly exceeds the tendency for pCO₂ to increase as a result of the seasonal warming. Mixed layer pCO₂ levels approach atmospheric pCO₂ at a time when SST has reached its annual minimum where it remains for more than 3 months. Deep convection (Figure 2) already reached its maximum by mid-February but remained strong after that. With respiration presumably being rather small during this cold period of deep convection neither physical nor biological forcing on the surface pCO₂ appears strong enough to pull it away from near-atmospheric equilibrium.

[16] The situation changes drastically with the appearance of spring phytoplankton in early May which is associated with a pCO₂ drawdown of almost 100 μatm . Our ship-based survey in July 2005 suggests that the seasonal pCO₂ minimum coincides with the SST maximum in July–August.

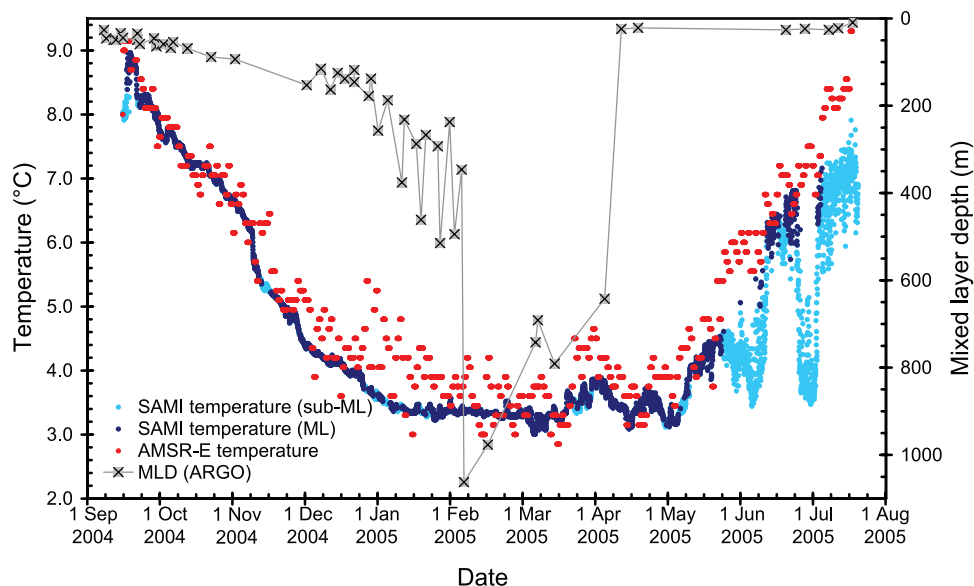


Figure 2. Comparison of temperature measurements made during the course of the K1 deployment by the SAMI pCO₂ sensor and the Advanced Microwave Scanning Radiometer-EOS on the NASA EOS satellite Aqua. The AMSR-E temperature data were used to distinguish mixed layer (ML) and submixed layer (sub-ML) location of the CO₂ sensor. Also shown is mixed layer depth estimated from Argo float profiles taken within ~100 km of the K1 mooring location.

After that, pCO₂ starts to rise continuously toward equilibrium despite the seasonal cooling. This cannot be explained by ongoing respiration and uptake of the atmospheric CO₂ alone, and we conclude that progressive deepening of the

mixed layer entrains wintertime dissolved inorganic carbon (DIC) levels to the surface plus respiratory CO₂ that has been accumulating in shallow sub-surface depths since last deep convection. This return flux of CO₂ represents the fraction of

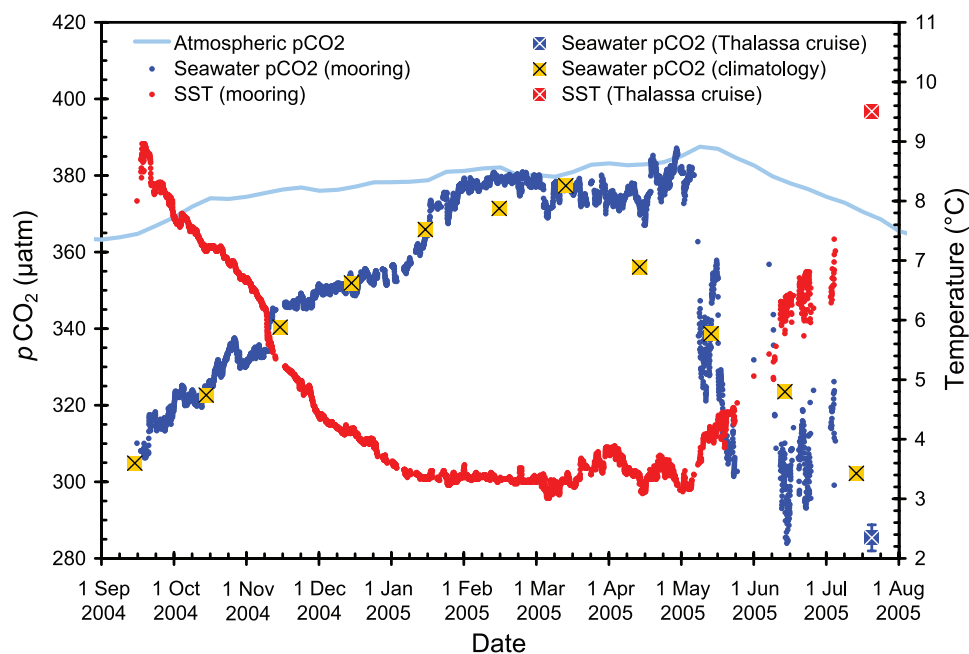


Figure 3. Mixed layer time series of pCO₂ and temperature measured during the course of the K1 deployment. For comparison, pCO₂ and temperature data from a ship-based survey in July 2005 are shown as is the climatological pCO₂ of Takahashi *et al.* [2002], corrected to the time and barometric pressure of the observational period. In addition, the atmospheric pCO₂ at barometric pressure is provided (from GLOBALVIEW-CO₂, 2006, <ftp.cmdl.noaa.gov/ccg/co2/GLOBALVIEW>).

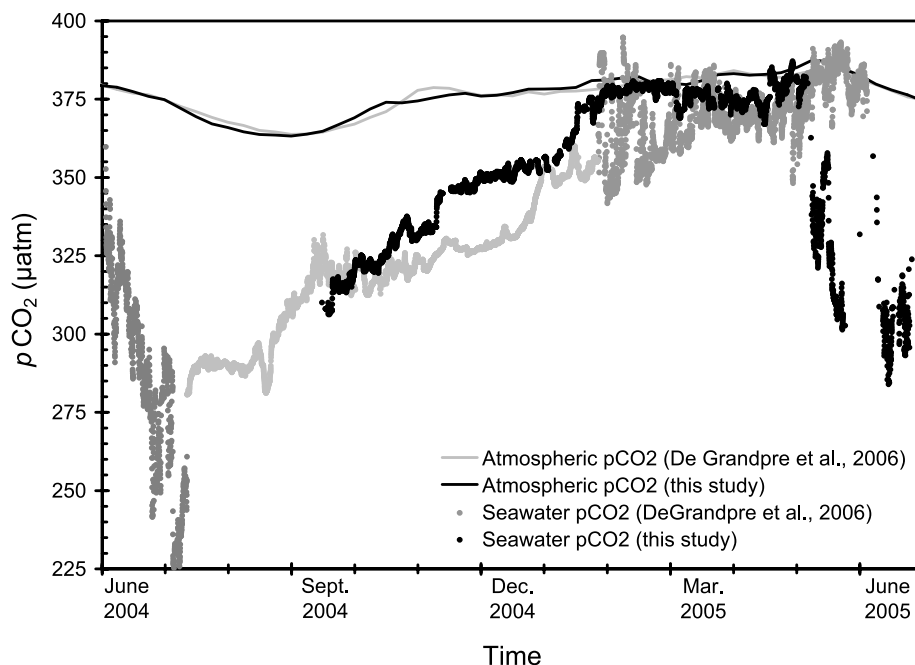


Figure 4. Comparison of $p\text{CO}_2$ time series at the K1 site from this study with a pilot study in 2000–2001 [DeGrandpre *et al.*, 2006] which combined mixed layer $p\text{CO}_2$ measurements (dark grey shade) with modeled $p\text{CO}_2$ data (light grey shade). The published earlier data were corrected upward by $8.0 \mu\text{atm}$ to account for the atmospheric CO_2 increase during this period.

the export production of the preceding spring/summer season which was respired above the base of the winter mixed layer. The net carbon drawdown observed during the spring bloom therefore does not represent the annual biological carbon sink from an atmospheric perspective. We will explore this in a more quantitative fashion in section 3.4.

[17] We compared our 2004–2005 data to the $p\text{CO}_2$ time series acquired during a pilot study in 2001–2002 [DeGrandpre *et al.*, 2006]. For this purpose the earlier data were adjusted upward by $8.0 \mu\text{atm}$ to account for the secular rise in atmospheric CO_2 concentrations that occurred over the 4 years separating the two times series (Figure 4). Note also that the time series of DeGrandpre *et al.* [2006] included the use of a one-dimensional biogeochemical model constrained by subsurface observations to estimate the surface $p\text{CO}_2$ time series for the period between 13 July 2000 and late January 2001 (indicated by the lighter shade of gray in Figure 4). Despite these adjustments and estimations the overall agreement between the two data sets is rather good. The earlier study captured the final stages of the 2000 spring bloom and the summer $p\text{CO}_2$ minimum very well. The (adjusted) minimum value of about $225 \mu\text{atm}$ in July–August 2000 is significantly lower, however, than the $p\text{CO}_2$ of about $285 \mu\text{atm}$ observed during the ship survey in July 2005. This could be due to interannual variability but we may also have simply missed the $p\text{CO}_2$ minimum in 2005. During late 2000–2001 winter, surface $p\text{CO}_2$ values also reached values at or near atmospheric equilibrium as was found for winter 2004–2005. Different from our study the onset of the spring bloom occurred about 3 weeks later in 2001 as compared to 2005.

[18] The seasonal O_2 cycle is shown in Figure 5. Here equilibrium with the atmosphere is reached in late summer/early fall when net community production has become small and the water column is still stratified. For some time (July–October) the various forcing factors for O_2 saturation, i.e., biogenic O_2 production and increasing O_2 solubility with seasonal cooling, appear either balanced or too weak to bring O_2 out of atmospheric equilibrium. This is only possible due to the roughly tenfold shorter-equilibration timescale of O_2 which is on the order of 1 month versus 1 year for CO_2 . After October the O_2 supply from the atmosphere can no longer keep up with cooling and vertical mixing which entrains oxygen-deficient waters, and the mixed layer becomes undersaturated by about 8% in February 2005. The fact that oxygen levels remain at undersaturation around 6% (0–12%) throughout the winter period can be explained by the deeply mixed water column which represents a huge oxygen deficit that is in contact with the atmosphere through a comparatively small surface area (1 m^2 per 1000 m^3 of water at a convection depth of 1000 m). Enhanced variability toward the end of the winter season points at lateral exchange under strongly elevated eddy activity with some indication of a small early spring bloom around mid-April. The associated strong and rapid (hours) vertical movements of the sensor package during this period contribute a vertical signal that is not always fully removed by the filtering algorithm which is based on daily microwave SST data. The onset of the proper spring bloom is as evident as in $p\text{CO}_2$ with O_2 levels soaring up by about $50 \mu\text{mol kg}^{-1}$ to a supersaturation of up to 10%. Reequilibration for O_2 does not occur before July.

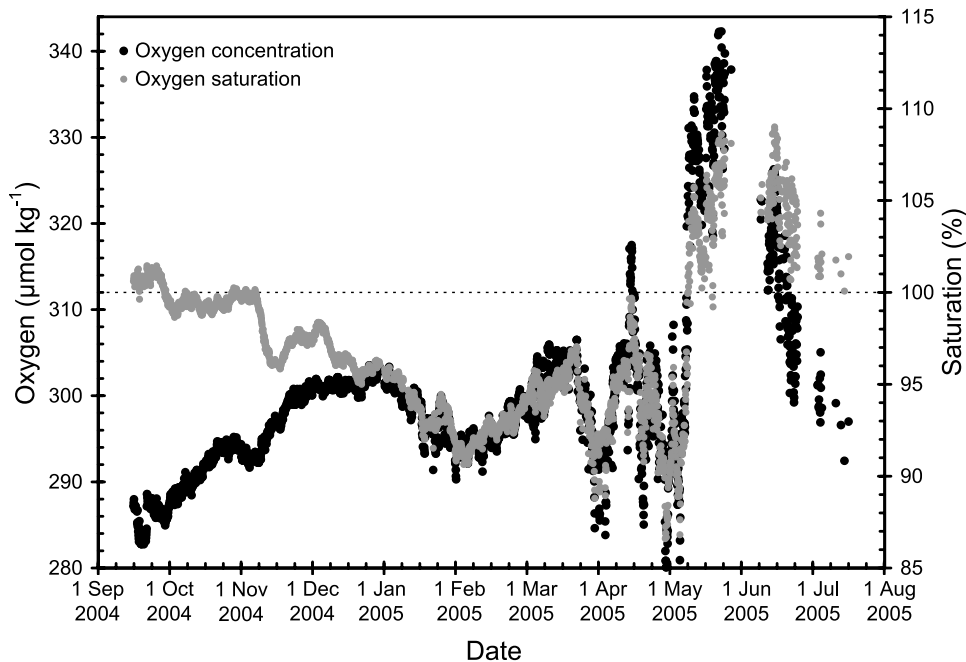


Figure 5. Mixed layer time series of oxygen concentration and saturation measured during the course of the K1 deployment. Oxygen saturation was calculated using the oxygen solubility after *Benson and Krause* [1984] at sea surface temperature, barometric pressure (Table 2), and 100% humidity.

[19] Overall, the observed seasonal cycles of CO₂ and O₂ agree rather well with the climatological situation as provided by *Takahashi et al.* [2002] for CO₂ and by *Najjar and Keeling* [1997, 2000] and *Keeling et al.* [1998] for O₂. For pCO₂ the peak-to-peak variation is very similar in data and climatology. It is obvious, however, that the space-time interpolation scheme involved in the construction of the pCO₂ climatology tends to smear out the sharp timing of the spring bloom (Figure 3). Our data show that the transition from the winter into the fully developed summer situation takes place in a matter of weeks, whereas the climatology shows a more gradual transition over 4 months. For O₂ the timing of the observed seasonal O₂ maximum in May 2005 is somewhat earlier than in the climatologies of *Najjar and Keeling* [1997] (i.e., 54–66°N zonal belt) and *Keeling et al.* [1998, Figure 1]. Also peak-to-peak variation in surface O₂ concentrations (~50 μmol kg⁻¹) is slightly larger than in the climatologies (35 and ~40 μmol kg⁻¹, respectively). Similar to the situation for CO₂, the annual harmonics used in the O₂ climatologies cannot fully reproduce the sudden occurrence of the spring bloom and the full variability as well as the rapid changes associated with it.

3.2. Evaluation of Air-Sea Gas Exchange Parameterizations

[20] Net air-sea gas exchange can be calculated with a bulk equation which for CO₂ takes the following form:

$$F_{\text{CO}_2} = k_{\text{CO}_2} K_0 (p\text{CO}_2^{\text{air}} - p\text{CO}_2^{\text{sea}}). \quad (1)$$

Herein k_{CO_2} is the transfer coefficient for CO₂, K_0 is the CO₂ solubility at in situ T and S after *Weiss* [1974], and

$p\text{CO}_2^{\text{air}}$ and $p\text{CO}_2^{\text{sea}}$ are the CO₂ partial pressures (at 100% humidity and SST) of air and seawater, respectively.

[21] Similarly, O₂ flux densities can be calculated from equation (2) where k_{O_2} is the transfer coefficient for O₂, and O₂^{sea} and O₂^{sat} are the measured and equilibrium O₂ concentrations of surface seawater, respectively. Here equilibrium O₂ concentrations O₂^{sat} were calculated at SST and barometric pressure (Table 2, 7-day running mean) using the solubility function of *Benson and Krause* [1984],

$$F_{\text{O}_2} = k_{\text{O}_2} (\text{O}_2^{\text{sat}} - \text{O}_2^{\text{sea}}). \quad (2)$$

[22] A variety of wind speed based parameterizations of the transfer coefficient k are available and the discussion about the best choice is still going on. We therefore explored the utility of our concomitant surface layer CO₂ and O₂ measurements to evaluate the most widely used parameterizations. We choose the following suite of parameterizations for short-term winds which essentially cover the full range and include linear, quadratic, and cubic wind speed dependencies: *Liss and Merlivat* [1986], *Wanninkhof* [1992], *Wanninkhof and McGillis* [1999], *Nightingale et al.* [2000], and *Sweeney et al.* [2007] (hereinafter referred to as LM86, W92, WM99, N2000, and S2007, respectively). Because of the strong nonlinearity of some of the parameterizations, transfer coefficients for CO₂ and O₂ were calculated on a 6-hour basis (rather than on the basis of weekly wind speed averages), thereby taking into account the observed wind speed distribution, and then averaged over the weekly calculation step. The resulting transfer coefficients were then scaled to observed SST using parameterizations of *Wanninkhof* [1992] for the temperature

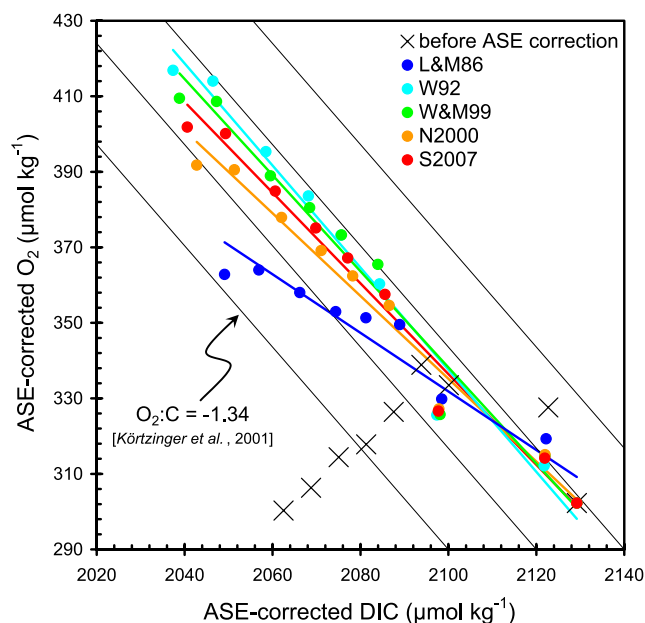


Figure 6. Correlation between mixed layer concentrations of DIC and O₂ before and after correction for the air-sea exchange component during a 9-week period in May–July 2005. Five different parameterizations for the gas transfer coefficient were used (see text for abbreviations). Also shown is the O₂:DIC relationship for biologically mediated changes with a stoichiometric O₂:C ratio of -1.34 [Körtzinger *et al.*, 2004].

dependence of the Schmidt numbers for CO₂ and O₂. By exploiting the tight stoichiometric constraint on biologically mediated DIC and O₂ changes we could test the validity of the various parameterizations.

[23] For the evaluation we tried to find a time period where (1) biologically mediated changes of DIC and O₂ were large, (2) as a consequence the CO₂ and O₂ disequilibria and hence the resulting fluxes were large too, and (3) the mixed layer was shallow so that changes in the DIC and O₂ inventories because of air-sea exchange and biological processes were also large. These criteria were only met during a 9-week period of the spring bloom (5 May to 7 July 2005) during which pCO₂ changed from near equilibrium to strong undersaturation and finally increasing pCO₂ levels toward the end while O₂ rose from strong undersaturation ($\sim 10\%$) to strong supersaturation ($\sim 10\%$) and near equilibrium toward the end. DIC was calculated from measured pCO₂ and climatological total alkalinity (Table 2) at in situ temperature and pressure using the CO2SYS software package [Lewis and Wallace, 1998] with the constants of Mehrbach *et al.* [1973] as refitted by Dickson and Millero [1987].

[24] O₂ release and CO₂ uptake during buildup and remineralization of organic matter in the ocean occur at a rather well-constrained O₂:C ratio. Körtzinger *et al.* [2001] found a value of -1.34 ± 0.06 for remineralization in the main thermocline. They were also able to show that the original value of -1.30 by Redfield *et al.* [1963] and the value of -1.45 ± 0.15 of Anderson and Sarmiento

[1994] were at the upper and lower end of the biochemically plausible range. We therefore use the O₂:C ratio of -1.34 ± 0.06 by Körtzinger *et al.* [2001] as stoichiometric constraint. Because of the concomitant large impact of biological fluxes and air-sea exchange, mixed layer O₂ and DIC concentrations during the 9-week period did not vary in an instructive way (Figure 6). When corrected for the influence of air-sea exchange using the four different parameterizations, however, rather tight linear relationships were found in all cases. If advective signals are assumed to be absent, the observed slope should within error agree with the known stoichiometric O₂:C ratio of net community production if the influence of air-sea fluxes had been fully removed, i.e., if a valid air-sea exchange model had been used. Below we will explore to what degree this was the case with the five different parameterizations.

[25] The five slopes (Figure 6, Table 3) range from -0.78 to -1.36 . Only when air-sea fluxes are corrected using the W92 and WM99 parameterizations the resulting slopes agree within error with the known stoichiometry. The agreement is borderline for the S2007 parameterization while air-sea fluxes estimated using the N2000 and especially the LM86 relationships are too weak to bring mixed layer O₂ and DIC values in line with the stoichiometric constraint. The wind speed measured every 6 hours during this period varied between 0.1 and 16.0 m s^{-1} with an average of 7.2 m s^{-1} (Figure 7). Interestingly, the transfer coefficients according to W92 and WM99 lie at the upper and lower end of the range (i.e., bracket the LM86, N2000, and S2007 estimates of k_{600} , the transfer coefficient for CO₂ in freshwater at 20°C) at wind speeds $< 8 \text{ m s}^{-1}$. At wind speed above about 10 m s^{-1} , however, W92 and WM99 yield transfer coefficients that are significantly higher than the other parameterization. The high wind speed range thus appears to be better represented by the stronger wind speed dependencies of W92 and WM99 causing the better agreement in this study.

[26] How does this reconcile with the results of Sweeney *et al.* [2007] who finally were able to close the gap between global-scale radiocarbon-based estimates and small-scale dual tracer studies by bringing down the bomb radiocarbon constraint by 25%? In the light of these findings the original bomb ¹⁴C constrained W92 and WM99 parameterizations should overestimate gas exchange which is not what we found here. The fact, however, that the W92 and WM99 parameterizations disagree most (and bracket all other parameterizations) in the wind speed range $< 8 \text{ m s}^{-1}$ indicates that it is not the lower end of the wind spectrum which causes the observed agreement or disagreement. In

Table 3. Observed O₂:DIC Slopes During 9-Week Spring Bloom Period After Correction of Mixed O₂ and DIC Concentrations for Net Air-Sea Fluxes of O₂ and CO₂, Respectively

Gas Exchange Parameterization	Resulting O ₂ :DIC Slope
Liss and Merlivat [1986]	-0.78 ± 0.10
Wanninkhof [1992]	-1.35 ± 0.06
Wanninkhof and McGillis [1999]	-1.27 ± 0.07
Nightingale <i>et al.</i> [2000]	-1.10 ± 0.06
Sweeney <i>et al.</i> [2007]	-1.20 ± 0.07

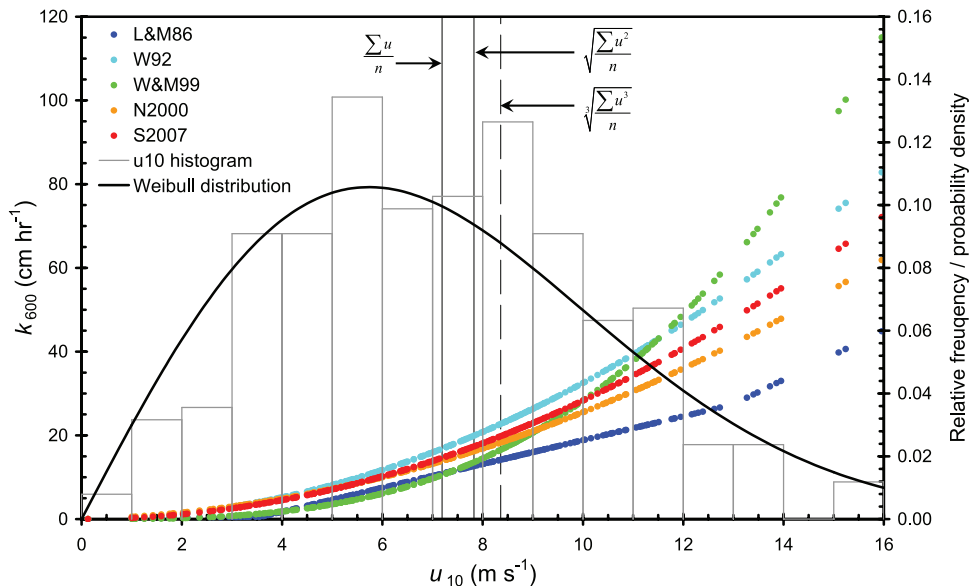


Figure 7. Transfer coefficients (normalized to a Schmidt number of 600) as calculated on the basis of wind speeds made every 6 hours during a 9-week period in May–July 2005 using five different parameterizations (see text for abbreviations). Also shown is a wind speed histogram as well as the probability distribution according to a Weibull function with a shape parameter $k = 2$.

contrast, it is the high wind speed range ($>10 \text{ m s}^{-1}$) where both W92 and WM99 yield significantly higher transfer coefficient than the other three parameterizations. The bottom line of this is that the new radiocarbon constraint is not in contradiction with our findings, but the parameterization may require a stronger than quadratic wind speed dependency to accommodate the impact of higher wind speeds as seen in our results.

3.3. Air-Sea Fluxes of CO₂, O₂, and APO

[27] We calculated CO₂ and O₂ fluxes during the entire period using equations (1) and (2) and the parameterization of Wanninkhof [1992]. All computations are based on weekly averages of $p\text{CO}_2^{\text{air}}$, $p\text{CO}_2^{\text{sea}}$, O_2^{sat} , O_2^{sea} , k_{CO_2} , k_{O_2} , and SST. Equations (1) and (2) are defined such that fluxes of CO₂ or O₂ into the ocean are positive, that is, represent a gain of substance from the ocean's perspective. CO₂ fluxes (Figure 8a) are always directed into the ocean peaking during summer and nearly vanishing during winter when air-sea equilibrium is established. O₂ fluxes on the contrary change sign across the seasonal cycle from oceanic uptake during winter to outgassing in summer. Applying data from September 2004 also for September 2005, we were able to close the seasonal cycle and derive cumulative oceanic sinks of $2.7 \pm 0.8 \text{ mol m}^{-2} \text{ yr}^{-1}$ (range, 2.0–2.9) for CO₂ and $10.0 \pm 3.1 \text{ mol m}^{-2} \text{ yr}^{-1}$ (range, 7.7–11.2) for O₂. The error margin corresponds to the propagation of uncertainty in the $p\text{CO}_2$ ($\leq 10 \text{ } \mu\text{atm}$) and O₂ ($\leq 2 \text{ } \mu\text{mol L}^{-1}$) measurements. In addition, each flux estimate includes in brackets the flux range spanned by the WM99 (upper bound) and N2000 parameterizations (lower bound). Note that we did not calculate fluxes on the basis of LM86.

[28] Interestingly, the CO₂ sink is mostly driven by the spring/summer bloom and early winter periods of high wind

speed whereas the O₂ sink occurs mostly during winter. The cumulative O₂ sink during the period of mixed layer deepening from end of October 2004 to early April 2005 amounts to $12.3 \text{ mol O}_2 \text{ m}^{-2}$ (range, 9.3–13.5) which is smaller than the value of Körtzinger *et al.* [2004] who estimated a buildup of the oxygen inventory during progressive mixed layer deepening of $17 \text{ mol O}_2 \text{ m}^{-2}$ in the preceding winter season, when the maximum convection depth was significantly deeper at $\sim 1400 \text{ m}$. Outgassing of O₂ during the spring bloom offsets the winter influx by less than 20%.

[29] During recent years, concurrent measurements of CO₂ and O₂ in the atmosphere have been used successfully to separate the terrestrial and oceanic sinks of atmospheric CO₂ [e.g., Keeling and Shertz, 1992]. In an attempt to further exploit the information contained in atmospheric CO₂ and O₂ data, Stephens *et al.* [1998] defined a new tracer, atmospheric potential oxygen, which is a linear combination of atmospheric CO₂ and O₂ concentrations ($\text{APO} = \text{O}_2 + 1.1 \text{ CO}_2$) that removes the terrestrial influence and most of the fossil fuel signal from atmospheric oxygen. Variations in APO therefore reflect mainly the air-sea exchange of O₂ and to a smaller extent also CO₂. Using our CO₂ and O₂ flux densities, we can calculate the APO flux density. Since APO is an atmospheric tracer, we use a different flux convention where oceanic uptake has a negative sign (i.e., a loss of matter from the atmosphere),

$$F_{\text{APO}} = -F_{\text{O}_2} - 1.1F_{\text{CO}_2}. \quad (3)$$

[30] As expected, the resulting APO flux densities (Figure 8b) are dominated by the O₂ fluxes. The annual flux of $-13.0 \pm 4.0 \text{ mol O}_2 \text{ m}^{-2}$ (range: -9.9 – -14.3) mostly occurs in the winter season. During summer time the opposite

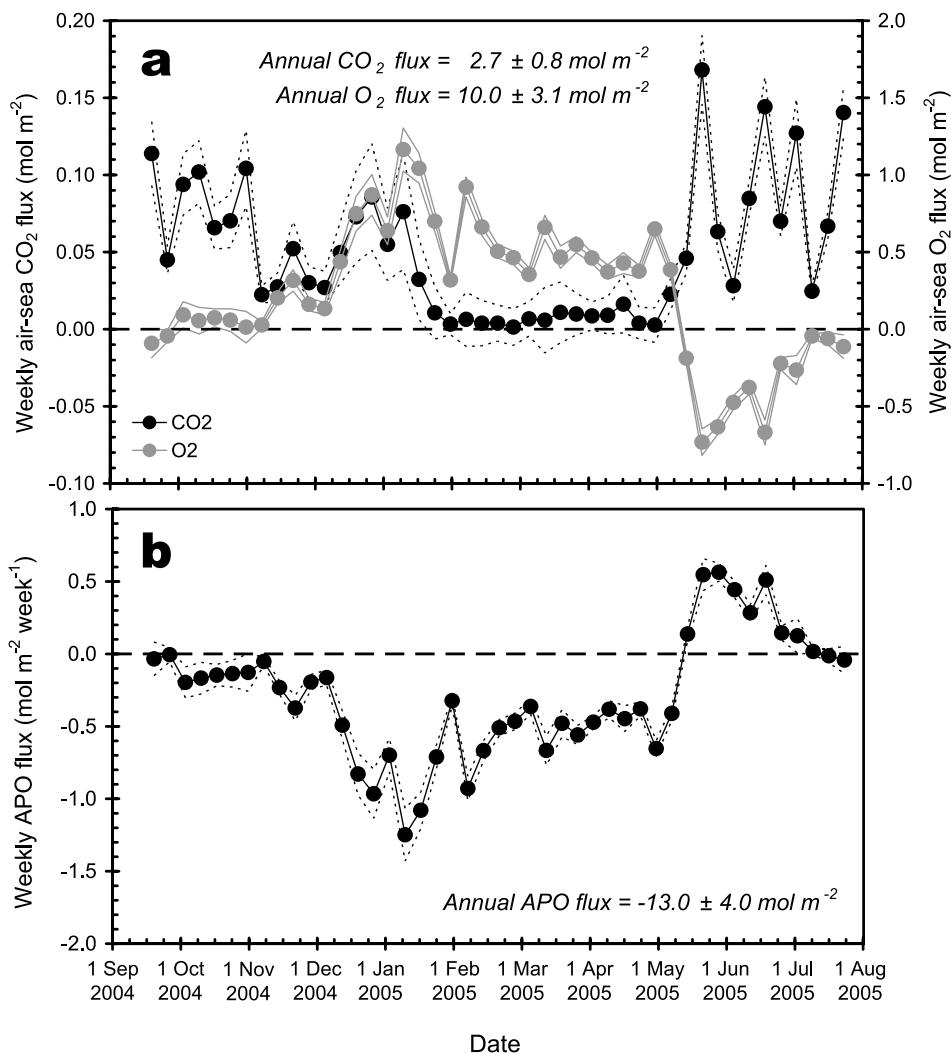


Figure 8. Weekly flux densities of (a) CO₂ and O₂ and (b) atmospheric potential oxygen (APO) at the K1 site during the course of the deployment. The error envelopes shown for each flux time series as well as the annual fluxes are a propagation of the maximum uncertainty in the pCO₂ ($\leq 10 \mu\text{atm}$) and O₂ ($\leq 2 \mu\text{mol L}^{-1}$) measurements. This error estimate does not include uncertainty associated with the choice among the available parameterizations of the transfer coefficient.

flux directions of CO₂ and O₂ partly compensate their APO influences with the oceanic uptake of CO₂ negating up to 25% of the oxygen-borne APO flux. The seasonal cycle of APO over the subpolar North Atlantic should therefore show a clear winter minimum and a rapid transition to the May–June summer maximum similar to what is observed at the atmospheric stations in Cold Bay, Alaska, USA (55.20°N, 162.72°W) or Sable Island, Nova Scotia, Canada (43.93°N, 60.02°W) [Battle *et al.*, 2006]. Unfortunately, no atmospheric site with high-quality measurements of CO₂ and O₂ exists downwind of the subpolar northwest Atlantic.

3.4. Physical and Biological Forcing of Surface Ocean pCO₂

[31] We follow a somewhat simplistic but nevertheless instructive way of separating thermal and biological (or more correctly nonthermal) forcing on the surface ocean

pCO₂ that has previously been used by Takahashi *et al.* [2002]. This approach makes use of the fact that the temperature dependence of pCO₂ under isochemical conditions (i.e., fixed DIC and A_T) is well constrained ($\partial \ln p\text{CO}_2 / \partial T = 0.04231^\circ\text{C}^{-1}$). This allows two measures: (1) construction of the thermally forced seasonal pCO₂ cycle ($p\text{CO}_{2,\text{therm}}$, equation (4)) and (2) removal of the thermal effect from observed pCO₂ ($p\text{CO}_{2,\text{nontherm}}$, equation (5)):

$$p\text{CO}_{2,\text{therm}} = \overline{p\text{CO}_2} e^{0.0423(T_{\text{obs}} - \bar{T})} \quad (4)$$

$$p\text{CO}_{2,\text{nontherm}} = p\text{CO}_{2,\text{obs}} e^{0.0423(\bar{T} - T_{\text{obs}})}. \quad (5)$$

[32] Herein overbars denote annual means and obs stands for observed. Equation (4) perturbs the annual mean pCO₂ in surface seawaters at K1 (353.2 μatm) with the deviation

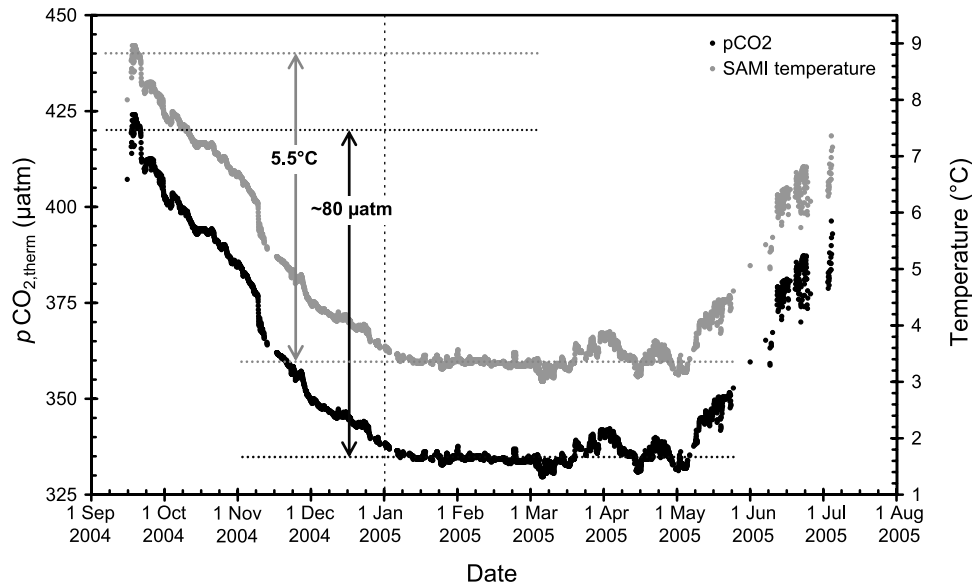


Figure 9. Perturbation of the mean $p\text{CO}_2$ during the observation period ($353.2 \mu\text{atm}$) with the deviation of observed SST from its annual mean. The resulting quantity $p\text{CO}_{2,\text{therm}}$ (equation (4)) is a measure of the (isochemical) thermal forcing of the seasonal $p\text{CO}_2$ cycle in the surface ocean.

of observed SST from its annual mean. The resulting $p\text{CO}_{2,\text{therm}}$ (Figure 9) can thus be looked at as the hypothetical $p\text{CO}_2$ that would be observed in an isochemical situation, i.e., no addition/removal of carbon by biological processes or air-sea exchange, which is characterized by the observed mean undersaturation. It is a realistic measure of the seasonal thermal forcing on surface ocean $p\text{CO}_2$. In contrast, equation (5) removes the thermal effect on the observed $p\text{CO}_2$ by correcting it to annual mean SST (5.96°C at the K1 site based on AMSR-E data from September 1, 2004 to August 31, 2005). The product $p\text{CO}_{2,\text{nontherm}}$ (Figure 10a) represents the observed $p\text{CO}_2$ variability that is not due to thermal effects and therefore must reflect chemical changes. These are biological carbon drawdown as well as DIC and/or A_T changes through advection, vertical entrainment, and diffusion as well as air-sea CO_2 exchange (DIC only).

[33] The seasonal peak-to-peak SST amplitude of $\sim 5.5^\circ\text{C}$ translates into a peak-to-peak variation of $p\text{CO}_{2,\text{therm}}$ of about $80 \mu\text{atm}$ (Figure 9). The summer-to-winter thermally driven $p\text{CO}_2$ decrease of $80 \mu\text{atm}$ is more than compensated by an increase of order $150 \mu\text{atm}$ due air-sea exchange and deepening of the mixed layer which brings CO_2 from wintertime DIC levels plus seasonal respiration back into the surface ocean (Figure 10b) causing the observed late winter maximum. Similarly, the winter-to-summer warming effect on $p\text{CO}_2$ is more than compensated by a counteractive consequence of net community production which explains the observed summer $p\text{CO}_2$ minimum.

[34] The seasonal DIC cycle (Figure 10b), as calculated from measured $p\text{CO}_2$ and climatological A_T (see section 3.2), shows a rapid decrease by $>100 \mu\text{mol kg}^{-1}$ during the spring bloom. The onset of the bloom, however, occurred well past the onset of stratification and is therefore restricted to a shallow mixed layer. Entrainment by definition must be

zero under conditions of stationary mixed layer depths. We furthermore assume that the diffusive flux is negligible in this context. The masking effect of uptake of atmospheric CO_2 on the biologically mediated DIC change can be calculated explicitly and removed. In contrast, the role of advection is generally more critical and cannot be corrected for easily.

[35] We therefore explored current velocities measured by current meters deployed at depths of 164, 308, and 1509 m in the same mooring (Figure 11a). These show high barotropicity and can therefore be used to infer advection at the sensor depth of ~ 38 m. The 164-m currents were separated into northward and eastward components and binned into 7-day averages (Figure 11b) which show rather low-advection activity until the end of March 2004 with average scalar current speeds of $\sim 0.05 \text{ m s}^{-1}$ that correspond to advection length scales of $\sim 30 \text{ km week}^{-1}$ (or $\sim 130 \text{ km month}^{-1}$). This is typical for the station's setting in the center of the deep convection region in the central Labrador Sea gyre. In fact, the mooring location had been chosen such that lateral signals would be small compared to the strong seasonal cycle of vertical mixing. In April the region is characterized by the crossing of a tongue of elevated eddy kinetic energy (EKE) which represents a marked maximum of the annual EKE cycle at K1 [Lilly *et al.*, 2003; Brandt *et al.*, 2004]. As we will show later this short period of strongly enhanced EKE coincides with, and may in fact be instrumental in, the triggering of the spring bloom. After this, peak advection activity is strongly reduced although the presence of mesoscale eddies is still visible. During the May–July period of strong carbon drawdown the average scalar current speed is 0.09 m s^{-1} . At advection length scales of $\sim 50 \text{ km week}^{-1}$ and a general southward flow direction we are confident that the observed temporal changes are representative of the central and

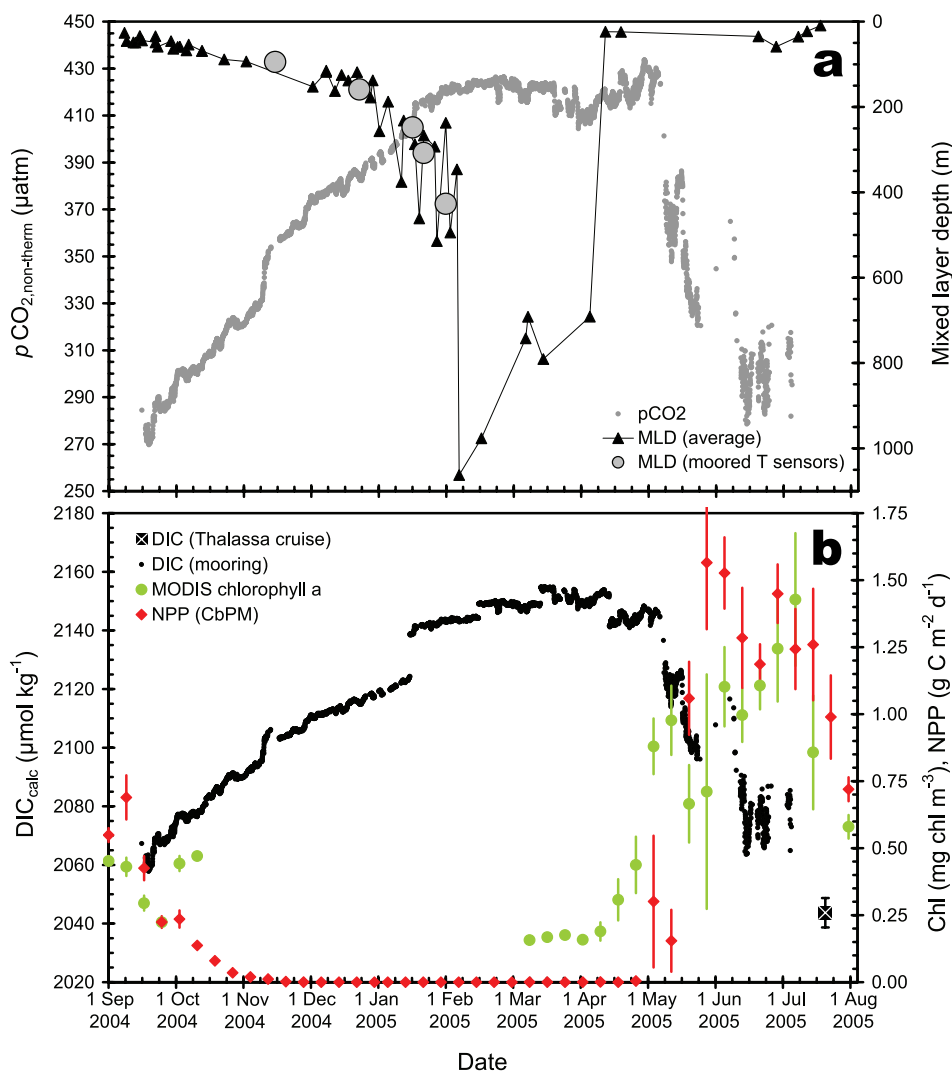


Figure 10. (a) Observed $p\text{CO}_2$ corrected to the annual mean SST (5.96°C based on AMSR-E data from September 1, 2004 to August 31, 2005). The resulting quantity $p\text{CO}_{2,\text{nontherm}}$ (equation (5)) is a measure of the chemically driven (isothermal) $p\text{CO}_2$ cycle in the surface ocean. Figure 10a also includes estimated mixed layer depths. (b) Mixed layer time series of dissolved inorganic carbon concentrations (DIC), calculated from observed $p\text{CO}_2$ and climatological total alkalinity (Table 2). Also shown for the K1 site are remotely sensed chlorophyll *a* concentrations from the Moderate Resolution Imaging Spectroradiometer sensor (NASA Aqua satellite, 8-day averages of 16 pixels from the 1080×2160 global grid) as well as net primary production estimates (CBPM, 8-day averages of 6 pixels from the 540×1080 global grid).

supposedly rather homogenous Labrador Sea convection region. Given the strength and direction of the flow field a significant influence from the boundary current can be ruled out.

[36] During this bloom period (mid-May to the third week of July) we found an integrated carbon drawdown (equal to net community production (NCP)) of $4.0 \pm 0.8 \text{ mol C m}^{-2}$ ($=48 \text{ g C m}^{-2}$) in the shallow mixed layer. We compared this to net primary production (NPP) estimated using two prominent methods: (1) remotely sensed chlorophyll concentrations and a light-dependent, depth-resolved model for carbon fixation (Vertically Generalized Production Model (VGPM) [Behrenfeld and Falkowski, 1997]) and (2) a new

approach based on remotely sensed chlorophyll concentrations and particulate backscattering coefficients (Carbon-Based Production Model (CBPM) [Behrenfeld *et al.*, 2006]). The two methods, which use the same chlorophyll data and parameterizations for the light dependence and euphotic depth, yield similar NPP values of 7.7 mol C m^{-2} (VGPM) and 8.0 mol C m^{-2} (CBPM) during the period from mid-May to the third week of July 2005. The comparison shows high synchronicity between carbon drawdown and the estimated NPP (Figure 10b). A quantitative comparison of NCP and NPP is not feasible as the former by necessity is restricted to the mixed layer while the latter is calculated across the photic zone. In the prevailing

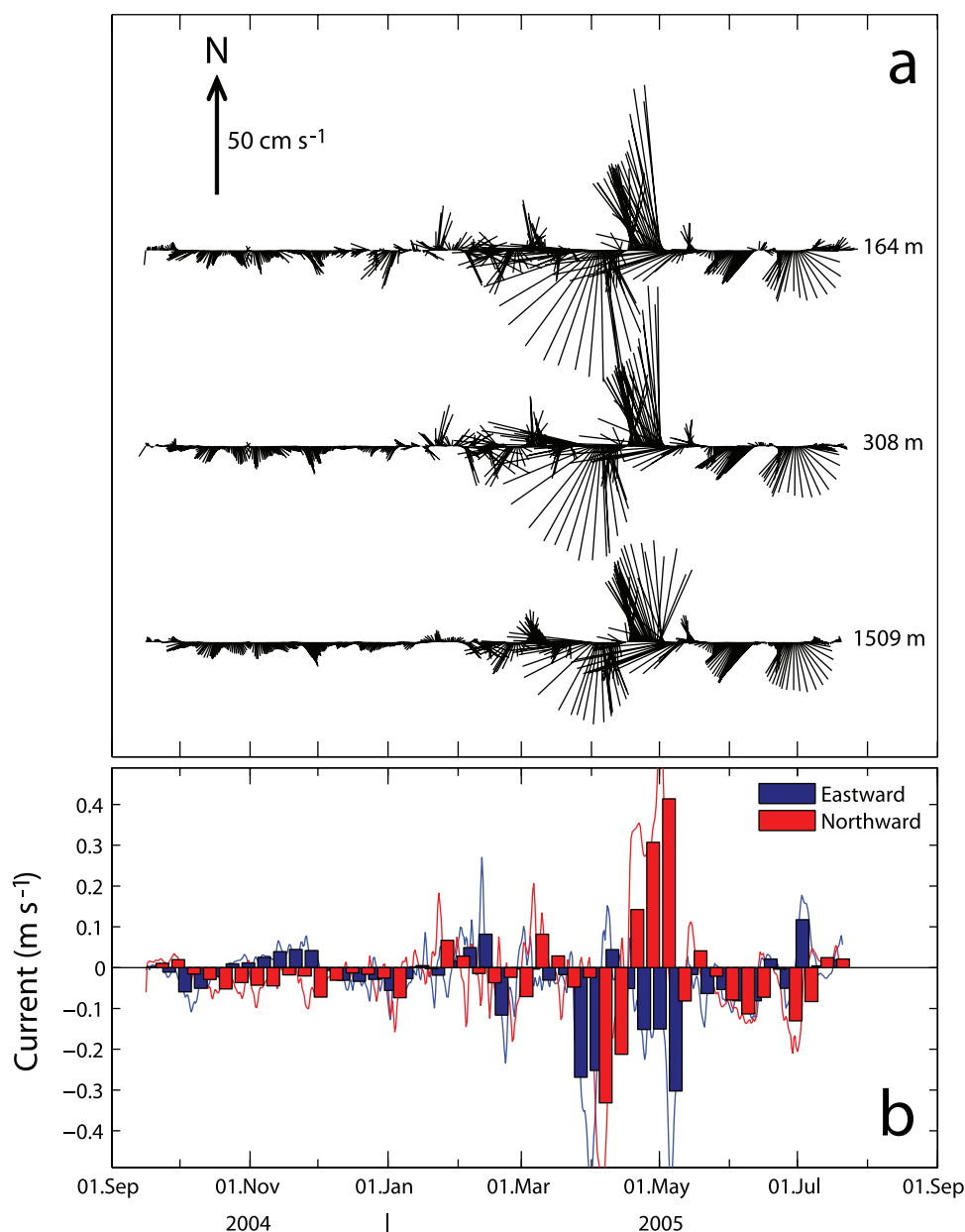


Figure 11. Current measurements during the 2004–2005 deployment at the K1 site: (a) stick vectors at three depths and (b) northward and eastward current speed with 7-day averages at 164 m depth.

situation of shallow mixing NPP that occurs below the mixed layer is not mirrored in our NCP estimate.

[37] We assume that most of the seasonal NCP is exported out of the mixed layer (as opposed to accumulation within it). Some of this material will undergo remineralization above the base of the winter mixed layer and the evolving respiratory CO₂ can thus be ventilated back to the surface ocean during the following winter. A simple budget calculation assuming repetition of the observed seasonal DIC cycle in the following 2005–2006 winter season and using mixed layer conditions at the end of deep mixing in March–April 2005 as well as the end of the productive season in

late July 2005 yields a reflux of 1.4 ± 0.5 mol C m⁻² of respiratory CO₂ back into the surface mixed layer. This accounts for about one third of the seasonal NCP of 4.0 ± 0.8 mol C m⁻² and leaves about 2.6 ± 1.3 mol C m⁻² yr⁻¹ which must have been exported to below the base of the winter mixed layer.

[38] The estimated seasonal NCP of 4.0 mol C m⁻² is only about 60% of the seasonal NCP found by Körtzinger *et al.* [2008] for the northeast Atlantic Ocean (49°N, 16.5°W) where wintertime nutrients levels are comparable. The major reason for this difference appears to be the different timing of the spring bloom which starts well in advance of

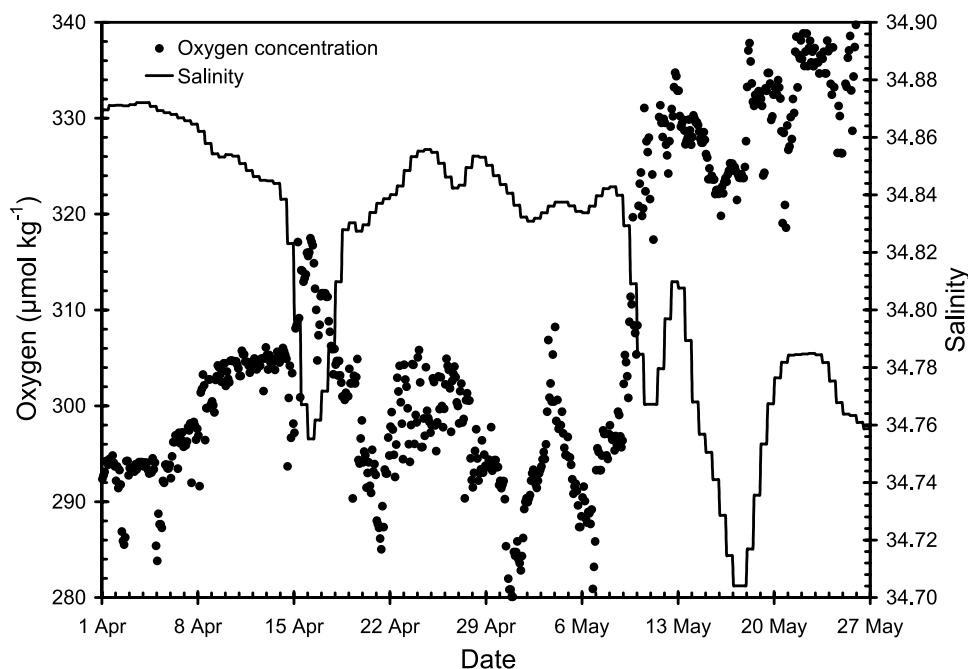


Figure 12. Observed oxygen concentration and salinity during the weeks before and after the onset of the spring bloom in early May 2005 highlighting the coincidence of fresher surface waters with higher-oxygen concentrations.

stratification in the northeast Atlantic and therefore, at similar nutrient concentrations, taps on a much larger nutrient reservoir in the mixed layer. At K1 in the Labrador Sea the available nutrient reservoir is already restricted to a very shallow summer mixed layer when the spring bloom starts. The timing of the bloom as evident in the CO₂ and O₂ data agrees very well with the sudden occurrence of enhanced chlorophyll levels as seen by the Moderate Resolution Imaging Spectroradiometer (MODIS) on the NASA Aqua satellite (Figure 10b). Similarly, the increase, peak, and decline of the CBPM NPP estimates (Figure 10b, 8-day averages of six pixels from the 540 × 1080 global grid) coincide very well with the chemical signatures observed during this study.

[39] It is an interesting question what might trigger the late spring bloom at the K1 site. There is no evidence that stratification itself plays an important role in the triggering of bloom. Solar irradiance is certainly a key variable but cannot explain the sharp onset of the spring bloom in May. It is noteworthy that the proper spring bloom, but also a brief transient period of elevated oxygen levels in the middle of April, coincide with negative spikes in the salinity record (Figure 12). The latter are most likely associated with eddies that spin off the West Greenland Current because of barotropic instability generated near Cape Desolation [Eden and Böning, 2002; Brandt et al., 2004; Hátún et al., 2007]. The regional EKE maximum in March–April [Lilly et al., 2003; Brandt et al., 2004] is clearly visible in the current record at K1 (Figure 11) which basically shows the passage of a single intense eddy the core of which passed around

mid-April, i.e., exactly when the low-salinity and high-oxygen patterns were observed (Figure 12).

[40] The eddy structures that were accompanied by elevated productivity in our observations are fresher than surrounding waters which points to their origin in the polar waters of the West Greenland Current. Such buoyant, anticyclonic eddies with low-salinity cores above 200 m have indeed been observed recently [Hátún et al., 2007] and appear to be important for rapid restratification of the Labrador Sea after winter convection. As we show here, they may also play a vital role in the triggering of the surface bloom in the central Labrador Sea. Our data provide no further insight into the driving mechanism(s), and we can only speculate that these fresher waters deliver an essential component such as iron necessary to alleviate a hypothetical iron limitation or a phytoplankton seed population from a neighboring biogeochemical province, the Boreal Polar Province, which thrives in a region that biogeographically is characterized by a dominance of Atlantic species [Longhurst, 2007].

4. Conclusions

[41] In this paper we present the first highly resolved annual cycles of pCO₂ and O₂ measured in the central Labrador Sea. The region is one of the few places in the world ocean where deep convection takes place during winter time. It further hosts sizable biological productivity confined to a short spring/summer period. On the basis of our analyses of the seasonal pCO₂ and O₂ cycles we can draw the following conclusions:

[42] 1. The seasonal pCO₂ cycle in the Labrador Sea is characterized by a marked summer minimum (winter maximum). The effect of summertime biological carbon draw-down on pCO₂ exceeds the counteractive effect of the seasonal SST cycle (hence the summer pCO₂ minimum). Close agreement with the climatological pCO₂ was found, with the exception that the sharp onset of the spring bloom is blurred in the climatology.

[43] 2. The central Labrador Sea acts as a sink for atmospheric CO₂. In 2004–2005 we estimated a CO₂ uptake of about $2.7 \pm 0.8 \text{ mol m}^{-2} \text{ yr}^{-1}$ which is 15% less than the climatological flux of $3.2 \text{ mol m}^{-2} \text{ yr}^{-1}$ for the pixel centered at 56°N, 52.5°W [Takahashi *et al.*, 2002] and 40% less than the estimate of DeGrandpre *et al.* [2006] for annual cycle 2000–2001. The observed CO₂ sink is mostly mediated by biological productivity during the summer period. During wintertime, surface seawater pCO₂ approaches atmospheric equilibrium as the effects of deep convection (reventilation of respiratory CO₂ that stems from a sizable fraction of the summertime biological carbon export) counteracts the cooling effect on surface pCO₂. During colder and hence more convective years, more respiration CO₂ will be entrained into the surface mixed layer that counteracts the effect of stronger cooling. Also stronger vertical entrainment of DIC (along with nutrients) should lead to enhanced net productivity in the next productive season. In contrast to oxygen these counteractive effects cause a damping of interannual variability in the net CO₂ sink [McKinley *et al.*, 2004].

[44] 3. The seasonal O₂ cycle features a marked period of undersaturation by around 6% during winter time when large volumes of oxygen-deficient waters are ventilated to the atmosphere. The brief period of supersaturation by up to 10% during spring/summer is driven by the phytoplankton that is confined to a rather shallow mixed layer.

[45] 4. The central Labrador Sea also acts as a sink for atmospheric oxygen. During our 2004–2005 observation period we estimated an annual O₂ sink of about $10.0 \pm 3.1 \text{ mol m}^{-2} \text{ yr}^{-1}$. The large O₂ uptake of 12.3 mol m^{-2} that occurs during the period of mixed layer deepening between October and April is partly offset by an O₂ source during the productive spring/summer season. This dominant role of deep convection supports the existence of a link between interannual variability in convection activity in the Labrador Sea [Avsic *et al.*, 2006] and interannual variability of air-sea O₂ fluxes [McKinley *et al.*, 2004].

[46] 5. In the Labrador Sea, annual CO₂ and O₂ fluxes are in the same direction and therefore reinforce each other in their influence on atmospheric potential oxygen. At an estimated APO flux of $-13.0 \pm 4.0 \text{ mol O}_2 \text{ yr}^{-1}$ the region should exert a noticeable imprint on regional APO patterns.

[47] 6. A mixed layer budget yielded a net community production (NCP) during the spring/summer bloom of 4.0 mol C m^{-2} the timing of which agrees very well with the timing of the net primary production during this period ($7.7\text{--}8.0 \text{ mol C m}^{-2}$) as estimated from remotely sensed products. A rough estimate indicates that about one third of the NCP is respired above the base of the winter mixed layer and returned to the atmosphere during the following convective season.

[48] 7. The surface ocean system shows a dramatic and rapid change from deep winter mixing to shallow summer stratification. This transition does not trigger, however, the onset of the spring bloom which occurred more than 1 month later in summer 2005. In contrast, enhanced productivity appears to be associated with lower salinity which is indicative of eddies importing waters of polar origin from the West Greenland Current that may bring in an essential component such as bioavailable iron or a phytoplankton seed population.

[49] 8. The parameterizations of the air-sea gas transfer coefficient by Wanninkhof [1992] and Wanninkhof and McGillis [1999] were found to be in best agreement with the observed mixed layer dynamics of CO₂ and O₂ during the spring bloom period. This points at a strong wind dependence at high wind speed ($>10 \text{ m s}^{-1}$).

[50] **Acknowledgments.** We would like to acknowledge the efforts and skills of the ship crews and scientific parties which prepared, deployed, recovered, and refurbished the multidisciplinary K1 mooring. We thank Cory Beatty (Department of Chemistry, University of Montana, Missoula, United States) for quality checks of the SAMI pCO₂ data. We also thank Robert O'Malley (Department of Botany and Plant Pathology, Oregon State University, Corvallis, Oregon, United States) for providing the VGPM and CBPM productivity estimates as well as MODIS chlorophyll data for the K1 site. Finally, we are grateful to two anonymous reviewers who helped to improve the manuscript. This paper was written during a sabbatical of the first author (A.K.) at the School of Oceanography, University of Washington, Seattle, United States, for which he is particularly grateful to his host Paul Quay. The present work was funded by the Collaborative Research Centre 460 (SFB 460) of the German Research Foundation.

References

- Anderson, L. A., and J. L. Sarmiento (1994), Redfield ratios of remineralization determined by nutrient data analysis, *Global Biogeochem. Cycles*, **8**, 65–80.
- Avsic, T., J. Karstensen, U. Send, and J. Fischer (2006), Interannual variability of newly formed Labrador Sea Water from 1994 to 2005, *Geophys. Res. Lett.*, **33**, L21S02, doi:10.1029/2006GL026913.
- Battle, M., et al. (2006), Atmospheric potential oxygen: New observations and their implications for some atmospheric and oceanic models, *Global Biogeochem. Cycles*, **20**, GB1010, doi:10.1029/2005GB002534.
- Behrenfeld, M. J., and P. G. Falkowski (1997), Photosynthetic rates derived from satellite-based chlorophyll concentration, *Limnol. Oceanogr.*, **42**, 1–20.
- Behrenfeld, M. J., R. T. O'Malley, D. A. Siegel, C. R. McClain, J. L. Sarmiento, G. C. Feldman, A. J. Milligan, P. G. Falkowski, R. M. Letelier, and E. S. Boss (2006), Climate-driven trends in contemporary ocean productivity, *Nature*, **444**, 752–755.
- Benson, B. B., and D. Krause Jr. (1984), The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater at equilibrium with the atmosphere, *Limnol. Oceanogr.*, **29**, 620–632.
- Brandt, P., F. A. Schott, A. Funk, and C. S. Martins (2004), Seasonal to interannual variability of the eddy field in the Labrador Sea from satellite altimetry, *J. Geophys. Res.*, **109**, C02028, doi:10.1029/2002JC001551.
- de Boyer Montégut, C., G. Madec, A. S. Fischer, A. Lazar, and D. Iudicone (2004), Mixed layer depth over the global ocean: An examination of profile data and a profile-based climatology, *J. Geophys. Res.*, **109**, C12003, doi:10.1029/2004JC002378.
- DeGrandpre, M. D., T. R. Hammar, S. P. Smith, and F. L. Sayles (1995), In situ measurements of seawater pCO₂, *Limnol. Oceanogr.*, **40**, 969–975.
- DeGrandpre, M. D., M. M. Baehr, and T. R. Hammar (1999), Calibration-free optical chemical sensors, *Anal. Chem.*, **71**, 1152–1159.
- DeGrandpre, M. D., A. Körtzinger, U. Send, D. W. R. Wallace, and R. G. J. Bellerby (2006), Uptake and sequestration of atmospheric CO₂ in the Labrador Sea deep convection region, *Geophys. Res. Lett.*, **33**, L21S03, doi:10.1029/2006GL026881.
- Dickson, A. G., and F. J. Millero (1987), A comparison of the equilibrium constants for the dissociation constants of carbonic acid in seawater media, *Deep Sea Res.*, **34**, 1733–1743.
- Dickson, B., I. Yashayaev, J. Meincke, B. Turrell, S. Dye, and J. Holfort (2002), Rapid freshening of the deep North Atlantic Ocean over the past four decades, *Nature*, **416**, 832–837.

- Eden, C., and C. Böning (2002), Sources of eddy kinetic energy in the Labrador Sea, *J. Phys. Oceanogr.*, **32**, 3346–3363.
- Emery, W. J., P. Brandt, A. Funk, and C. Böning (2006), A comparison of sea surface temperatures from microwave remote sensing of the Labrador Sea with in situ measurements and model simulations, *J. Geophys. Res.*, **111**, C12013, doi:10.1029/2006JC003578.
- Garcia, H. E., and R. F. Keeling (2001), On the global oxygen anomaly and air-sea flux, *J. Geophys. Res.*, **106**(C12), 31,155–31,166.
- Hátún, H., C. C. Eriksen, and P. B. Rhines (2007), Buoyant eddies entering the Labrador Sea observed with gliders and altimetry, *J. Phys. Oceanogr.*, **37**, 2838–2854.
- Keeling, R. F., and S. R. Shertz (1992), Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle, *Nature*, **358**, 723–727.
- Keeling, R. F., B. B. Stephens, R. G. Najjar, S. C. Doney, D. Archer, and M. Heimann (1998), Seasonal variations in the atmospheric O₂/N₂ ratio in relation to the kinetics of air-sea gas exchange, *Global Biogeochem. Cycles*, **12**(1), 141–164.
- Körtzinger, A., J. I. Hedges, and P. D. Quay (2001), Redfield ratios revisited: Removing the biasing effect of anthropogenic CO₂, *Limnol. Oceanogr.*, **46**, 964–970.
- Körtzinger, A., J. Schimanski, U. Send, and D. W. R. Wallace (2004), The ocean takes a deep breath, *Science*, **306**, 1337.
- Körtzinger, A., J. Schimanski, and U. Send (2005), High-quality oxygen measurements from profiling floats: A promising new technique, *J. Atmos. Oceanic Technol.*, **22**, 302–308.
- Körtzinger, A., U. Send, R. S. Lampitt, S. Hartman, D. W. R. Wallace, J. Karstensen, M. G. Villagarica, O. Llinas, and M. D. DeGrandpre (2008), Seasonal pCO₂ cycle at 49°N/16.5°W in the northeast Atlantic Ocean and what it tells us about biological productivity, *J. Geophys. Res.*, doi:10.1029/2007JC004347, in press.
- Lazier, J., R. Hendry, A. Clarke, I. Yashayaev, and P. Rhines (2002), Convection and restratification in the Labrador Sea, 1990–2000, *Deep Sea Res. Part I*, **49**, 1819–1835.
- Lee, K., L. T. Tong, F. J. Millero, C. L. Sabine, A. G. Dickson, C. Goyet, G.-H. Park, R. Wanninkhof, R. A. Feely, and R. M. Key (2006), Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans, *Geophys. Res. Lett.*, **33**, L19605, doi:10.1029/2006GL027207.
- Lefèvre, N., A. J. Watson, A. Olsen, A. F. Ríos, F. F. Pérez, and T. Johannessen (2004), A decrease in the sink for atmospheric CO₂ in the North Atlantic, *Geophys. Res. Lett.*, **31**, L07306, doi:10.1029/2003GL018957.
- Levitus, S., J. Antonov, and T. Boyer (2005), Warming of the world ocean, 1955–2003, *Geophys. Res. Lett.*, **32**, L02604, doi:10.1029/2004GL021592.
- Lewis, E., and D. W. R. Wallace (1998), Program Developed for CO₂ System Calculations, *ORNL/CDIAC-105*, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., U.S. Dep. of Energy, Oak Ridge, Tenn.
- Lilly, J. M., P. B. Rhines, F. Schott, K. Lavender, J. Lazier, U. Send, and E. D'Asaro (2003), Observations of the Labrador Sea eddy field, *Prog. Oceanogr.*, **59**, 75–176.
- Liss, P. S., and L. Merlivat (1986), Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Ménard, pp. 113–127, D. Reidel, Dordrecht, Netherlands.
- Longhurst, A. R. (2007), *Ecological Geography of the Sea*, 2nd ed., 542 pp., Academic, Amsterdam.
- Lüger, H., D. W. R. Wallace, A. Körtzinger, and Y. Nojiri (2004), The pCO₂ variability in the midlatitude North Atlantic Ocean during a full annual cycle, *Global Biogeochem. Cycles*, **18**, GB3023, doi:10.1029/2003GB002200.
- McKinley, G. A., M. J. Follows, and J. Marshall (2004), Mechanisms of air-sea CO₂ flux variability in the equatorial Pacific and the North Atlantic, *Global Biogeochem. Cycles*, **18**, GB2011, doi:10.1029/2003GB002179.
- Mehrbach, C., C. H. Culbertson, J. E. Hawley, and R. M. Pytkowicz (1973), Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr.*, **18**, 897–907.
- Monterey, G., and S. Levitus (1997), Seasonal variability of mixed layer depth for the World Ocean, *NOAA NESDIS Atlas 14*, 100 pp., Natl. Oceanic and Atmos. Admin., Washington, D.C.
- Najjar, R. G., and R. F. Keeling (1997), Analysis of the mean annual cycle of the dissolved oxygen anomaly in the World Ocean, *J. Mar. Res.*, **55**, 117–151.
- Najjar, R. G., and R. F. Keeling (2000), Mean annual cycle of the air-sea oxygen flux: A global view, *Global Biogeochem. Cycles*, **14**(2), 573–584.
- Nightingale, P. D., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard (2000), In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem. Cycles*, **14**(1), 373–388.
- Omar, A. M., and A. Olsen (2006), Reconstructing the time history of the air-sea CO₂ disequilibrium and its rate of change in the eastern subpolar North Atlantic, 1972–1989, *Geophys. Res. Lett.*, **33**, L04602, doi:10.1029/2005GL025425.
- Redfield, A. C., B. H. Ketchum, and F. A. Richards (1963), The influence of organisms on the composition of sea water, in *The Sea*, edited by M. N. Hill, pp. 26–77, Interscience, New York.
- Stephens, B. B., R. F. Keeling, M. Heimann, K. D. Six, R. Murnane, and K. Caldeira (1998), Testing global ocean carbon cycle models using measurements of atmospheric O₂ and CO₂ concentration, *Global Biogeochem. Cycles*, **12**, 213–230.
- Sweeney, C., E. Gloor, A. R. Jacobson, R. M. Key, G. McKinley, J. L. Sarmiento, and R. Wanninkhof (2007), Constraining global air-sea gas exchange for CO₂ with recent bomb ¹⁴C measurements, *Global Biogeochem. Cycles*, **21**, GB2015, doi:10.1029/2006GB002784.
- Takahashi, T., J. Olafsson, J. Goddard, D. W. Chipman, and S. C. Sutherland (1993), Seasonal variation of CO₂ and nutrients in the high-latitude surface oceans: A comparative study, *Global Biogeochem. Cycles*, **7**, 843–878.
- Takahashi, T., et al. (2002), Global air-sea CO₂ flux based on climatological surface ocean pCO₂, and seasonal biological and temperature effects, *Deep Sea Res. Part II*, **49**, 1601–1622.
- Tengberg, A., et al. (2006), Evaluation of a life time based optode to measure oxygen in aquatic systems, *Limnol. Oceanogr. Methods*, **4**, 7–17.
- Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, **97**, 7373–7382.
- Wanninkhof, R., and W. R. McGillis (1999), A cubic relationship between air-sea CO₂ exchange and wind speed, *Geophys. Res. Lett.*, **26**, 1889–1892.
- Weiss, R. F. (1974), Carbon dioxide in water and seawater: The solubility of a non-ideal gas, *Mar. Chem.*, **2**, 203–215.
- Wentz, F., and T. Meissner (2004), AMSR-E/Aqua Daily L3 Global Ascending/Descending 0.25° × 0.25° Ocean Grids V001, March to June 2004, http://www-nsidc.colorado.edu/data/amsre/data_summaries.html, Natl. Snow and Ice Data Center, Boulder, Colo.

M. DeGrandpre, Department of Chemistry, University of Montana, 32 Campus Drive, Missoula, MT 59812, USA.

J. Karstensen, Leibniz Institute of Marine Sciences, Physical Oceanography, University of Kiel, East Shore Campus, Wischhofstr. 1-3, D-24148 Kiel, Germany.

A. Körtzinger and D. W. R. Wallace, Leibniz Institute of Marine Sciences, Chemical Oceanography, University of Kiel, East Shore Campus, Wischhofstr. 1-3, D-24148 Kiel, Germany. (akoertzinger@ifm-geomar.de)

U. Send, Scripps Institution of Oceanography, University of California at San Diego, 8602 La Jolla Shores Drive, La Jolla, CA 92037, USA.