Reconstructing the time history of the air-sea CO₂ disequilibrium and its rate of change in the eastern subpolar North Atlantic, 1972–1989

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[1] This study determines the temporal changes of wintertime surface ocean partial pressure of CO₂ (pCO₂SW) in the eastern subpolar North Atlantic (esNA) (50–64⁰N; 32–10⁰W) by using data of carbon-system parameters and chlorofluorocarbon-12 acquired in 1993. Wintertime pCO₂SW and its temporal trend from early 1970s through to the late 1980s were reconstructed through the application of a back-calculation method that isolates surface variations which have been transmitted to the ocean interior during the formation of Subpolar Mode Water. Our computations suggest a pCO₂SW growth rate (3 μatm/yr) which is twice as large as that of atmospheric pCO₂, 1.47 μatm/yr. The sensitivity of the estimated pCO₂SW growth rate to remineralization ratios as well as to the CFC-12-derived ages is discussed. Cooling and northward advection of surface water equilibrated with the increasing atmospheric CO₂ is suggested as the process responsible for the excessive pCO₂SW growth rate. Citation: 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.

1. Introduction

[2] It is generally accepted that the North Atlantic (NA) is an important sink region for atmospheric carbon dioxide (CO₂). Assuming a constant wind field, the strength of the sink is proportional to the CO₂ disequilibrium across the air-sea interface ∆pCO₂ = pCO₂SW – pCO₂atm, i.e., the difference between sea surface and atmospheric CO₂ partial pressures, pCO₂SW and pCO₂atm, respectively. In the subpolar NA, extensive heat loss and primary production lower pCO₂SW so that a disequilibrium exists throughout most of the year and the flux of CO₂ is directed into the ocean. Additionally the pCO₂SW is currently increasing so that an increasing air-sea CO₂ disequilibrium is expected, and this is often indicated by ocean carbon models [e.g., Wetzel et al., 2005], and has been an underlying assumption employed when compiling the global air-sea CO₂ flux climatology [Takahashi et al., 2002]. However, the contrary has been suggested in a number of recent studies. Anderson and Olsen [2002] employed a conceptual advective model to calculate the change of the air-sea CO₂ flux in the NA since pre-industrial times. For latitudes north of ~50⁰N, their computation suggested a slightly decreasing ∆pCO₂.

[3] In this paper, we reconstruct the time history of wintertime ∆pCO₂ in the eastern subpolar NA (50–64⁰N; 32–10⁰W) (Figure 1) over the time period 1972–1989.

[4] Our approach takes advantage by the fact that mode water characteristics in the interior of the ocean reflect variations of wintertime sea surface properties in the formation region [e.g., Hanawa and Talley, 2001]. The winter mixed layer in the eastern subpolar NA (esNA) is dominated by a type of Subpolar Mode Water (SPMW) and during summer this is isolated from the surface by a seasonal pycnocline [McCaffrey and Talley, 1982]. We assume that climatological wintertime (January–March) surface seawater properties can be used to define the SPMW that forms in the esNA during winter. This water type is henceforth referred to as eastern Subpolar Mode Water (eSPMW) in order to differentiate it from the broader term SPMW.

[5] By using data acquired during the third leg of the 1993 Ocean Atmosphere Carbon Exchange Study (OACES) cruise of the R/V Malcolm Baldrige (18–29 August 1993) (Figure 1) we identify eSPMW that formed in the esNA at times determined from their apparent CFC-12 ages. We then extend the back-calculation approach of Brewer [1978] to estimate preformed (i.e., wintertime) pCO₂SW values for the eSPMW encountered during the cruise. The results are combined with data for the atmospheric mole fraction of CO₂ (xCO₂) to compute ∆pCO₂ and the temporal variability is analyzed.

2. Data

[6] The Baldrige data have been described in detail by others [Körtzinger et al., 2003, and references therein] and were made available by the Global Ocean Data Analysis Project (GLODAP) [Key et al., 2004]. Data for salinity (S), temperature (T), total dissolved inorganic carbon (CT), total alkalinity (AT), phosphate (P), silicate (Si), oxygen (O₂) and CFC-12 ages (see Key et al. [2004] for the computation of these ages) were retrieved from the database (http://cdiac.esd.ornl.gov/oceans/home.html, accessed on March 4, 2005).

[7] The accuracy of the CT, AT, and O₂ data have been determined to 1.5, 2.5, and 1 μmol kg⁻¹, respectively [Körtzinger et al., 2003, and references therein]. A value of 7.5 μmol kg⁻¹ were substraction from the O₂ data because...
these data have been double corrected (first after Wanninkhof et al. [1999] and then after Gouretski and Jancke [2001]) (R. Key, personal communication, 2005). After this re-correction, apparent oxygen utilization (AOU = O2 saturation − O2 measured) was recomputed.

3. Methods

[8] Wintertime climatological ranges of surface density (ρ), salinity, and temperature for the esNA were determined using data from the World Ocean Atlas 2001 [Conkright et al., 2002]. The resulting ranges (Figure 2) of temperature (5.5–11.2°C), salinity (34.93–35.49), and density (27.06–27.65 kg m–3) agree well with those reported by McCartney and Talley [1982], for the winter mixed layer of the esNA and were used to define eSPMW. All water samples with properties falling within the climatological ranges were identified in the cruise data and assumed to be remnants of eSPMW that formed in the esNA at times given by their apparent CFC-12 ages.

[9] The preformed pCO2 values for the eSPMW were determined from preformed AT (AT0) and CT (C0). The former was computed from the empirical relationship:

\[ A_0^T = 49.87 \times S + 566 \]  

which was determined by regressing surface (depth < 200 m) salinity with alkalinity. The coefficient of determination (r2) was 0.79 and the standard error of estimate was ±3 μmol kg–1. C0T was computed according to Körtzinger et al. [2003]:

\[ C_T^0 = C_T - R_{CO} \times AOU - \frac{1}{2} (A_T - A_0^T + R_{NO3} \times AOU) \]  

where CT and AT are the measured concentrations, RC0 and RNO3 are the remineralization ratios between CT and O2, and between NO3 and O2. We used the RC0 and RNO3 values which were estimated by Körtzinger et al. [2001] for the North Atlantic. Alternative values will affect our results as discussed in section 5.

[10] Preformed pCO2 was then computed from CT0, AT0, P, Si, S, and potential temperature (θ), using the constants of Merbach et al. [1973] refitted by Dickson and Millero [1987]. These constants have been recommended by Lueker et al. [2000] for the computation of pCO2 from CT and AT. By propagating the uncertainties in C0T ( = 3.3 μmol kg–1) and A0T (±3 μmol kg–1) the maximum uncertainty in the computed pCO2 values was obtained to be ±7 μatm (or 2 %).

[11] The Baldridge cruise was carried out during August and, in order to limit seasonal biasing effects, only data from deeper than 200 m were used for the temporal analysis.

[12] Values of pCO2 were calculated from xCO2 data measured at Niwot Ridge, Colorado, USA which have been made available by the Carbon Cycle Greenhouse Gases Group at the National Oceanic and Atmospheric Administration (NOAA), USA. Monthly xCO2 values were retrieved (ftp://ftp.cmdl.noaa.gov/ccg/co2/flask/month/), averaged over January to March, and converted to pCO2 according to:

\[ pCO2_{am} = xCO2 (SLP - VP_{H2O}) \]  

where SLP is the monthly sea level pressure averaged over January to March for each year, VPH2O is the wintertime water vapor pressure and was computed from θ according to Cooper et al. [1998]. The SLP data originate from the NCEP/NCAR reanalysis project [Kalnay et al., 1996] and were obtained from the IRI/LDEO Climate Data Library (http://ingrid.ldeo.columbia.edu/).

[13] Finally, ΔpCO2 was computed for each sample as the difference between pCO2 and pCO2SW.

4. Results

[14] Figure 3 depicts the spatial distribution of eSPMW during the Baldridge cruise. From 46°N and northward, eSPMW was found at each station throughout the 200–1000 m layer. South of 45°N the presence of eSPMW was sporadic both with respect to station and depth, indicating that eSPMW indeed forms in the subpolar region.

[15] There were no trends in wind speed (not shown) so over the study period, the waters embodying the winter mixed layer of the esNA (i.e., eSPMW) changed from being strong sink to weak sink of atmospheric CO2. This can be appreciated from Figure 4 which show wintertime pCO2 values.
and the estimated values of $pCO_{SW}^{\text{CO}_2}$ and $\Delta pCO_2$ as a function of formation year ($= 1993 - $ CFC-12 age) of eSPMW. Evidently, the eSPMW was undersaturated with respect to atmospheric $CO_2$ throughout the study period (Figure 4a). However, this disequilibrium decreased consistently over the years and nearly vanished at the end of the study period (Figure 4b). Straight lines fitted to the data (Figures 4a and 4b) suggest linear trends of 1.47, 3.00, and $-1.53 \text{ mm} \text{yr}^{-1}$ for $pCO_{\text{interior}}^{\text{CO}_2}$, $pCO_{SW}^{\text{CO}_2}$ and $\Delta pCO_2$, respectively.

5. Discussion

[16] Our computations suggest that the wintertime $pCO_{SW}^{\text{CO}_2}$ in the eastern subpolar North Atlantic increased at a greater rate than the atmospheric $pCO_2$ so that the disequilibrium decreased between 1972 and 1989. This is in qualitative agreement with Lefèvre et al. [2004]. Quantitatively, however, the $pCO_{SW}^{\text{CO}_2}$ growth rate estimated in this study (3.00 $\text{mm} \text{yr}^{-1}$) is larger than the ~1.8 $\text{mm} \text{yr}^{-1}$ estimated by Lefèvre et al. [2004] for the months January–March. The difference in growth rates can be reconciled as our estimate, being based on reconstructions rather than observations, is sensitive to the choice of $R_{CO}$ and $R_{NO}$ values as well as to the CFC-12 ages.

[17] If we were to use a lower value of $R_{CO}$ then the estimated $pCO_{SW}^{\text{CO}_2}$ growth rate would decrease because the correction for remineralized carbon ($= - R_{CO} \times \text{AOU}$, see equation (2)) would be reduced more for “older” eSPMW than for “younger” eSPMW. Changing $R_{NO}$ has a similar effect on the estimated $pCO_{SW}^{\text{CO}_2}$ growth rate, but the effect is much smaller than that of $R_{CO}$ because $R_{NO} \times \text{AOU}$ is an order of magnitude smaller than $R_{CO} \times \text{AOU}$. There are several alternative remineralization quotients available [e.g., Redfield et al., 1963; Takahashi et al., 1985; Anderson and Sarmiento, 1994], but only those of Redfield et al. [1963] are applicable to our study area and at the same time free from known biases. These latter quotients, however, are higher than those of Körting et al. [2001] and give a $pCO_{SW}^{\text{CO}_2}$ growth rate of $3.2 \text{ mm} \text{yr}^{-1}$.

[18] The use of apparent CFC-12 ages implicitly assumes that the surface-to-interior spreading of water can be estimated from a single transit time. This assumption is strictly only valid for the limiting case of no mixing and, in order to account for mixing, Waugh et al. [2004] applied the concept of transit time distribution (TTD) in the subpolar North Atlantic. They found that CFC-12 ages are smaller than the mean transit times (mean ages, henceforth) for much of the gyre. Being unable to constrain by how much CFC-12 ages underestimate the mean ages they provided several possible relationships between CFC-12 ages and mean ages [Waugh et al., 2004, Figure 6b] by choosing the ratio $\Delta T$ (which denotes the width of the TTD divided by the mean age) equal to either 0, 0.75, 1, and 1.25. Thus, the only certain consequence for our results is that since the CFC-12 ages are a lower limit of a range of possible ages the estimated $pCO_{SW}^{\text{CO}_2}$ growth rate is an upper limit. This is so because increasing the ages implies that the total $pCO_{SW}^{\text{CO}_2}$ increase of $\approx 50 \mu \text{m} \text{yr}^{-1}$ (Figure 4a) would be distributed over a longer time period and, thus, the growth rate would be reduced.

[19] In order to evaluate the combined effect of the loosely constrained remineralization quotients and the possible underestimation of water mass ages on the $pCO_{SW}^{\text{CO}_2}$ growth rate we (i) utilized the remineralization quotients of both Körtzinger et al. [2001] and Redfield et al. [1963] for the determination of $pCO_{SW}^{\text{CO}_2}$, (ii) replaced the CFC-12 ages with mean ages obtained through employing the relationships of Waugh et al. [2004] and (iii) re-estimated the $pCO_{SW}^{\text{CO}_2}$ growth rate. Important to mention is that, when the mean ages obtained by setting $\Delta T$ equal to 0.75, 1, or 1.25 were used, the temporal trend of $pCO_{SW}^{\text{CO}_2}$ became quadric so that the data best fitted to equations of the form:

$$pCO_{SW}^{\text{CO}_2} = A \times (\text{year})^2 + B \times (\text{year}) + C \quad (4)$$

where $\text{year} = 1993 - $ mean age and $A$, $B$, and $C$ are constants. For these cases, therefore, the $pCO_{SW}^{\text{CO}_2}$ growth rate was determined as the mean value of the time derivative of equation (4) evaluated for the years 1972 through to 1989. The re-estimated growth rates are depicted in Figure 5 and fall between 1.36 $\mu \text{m} \text{yr}^{-1}$ and 3.2 $\mu \text{m} \text{yr}^{-1}$. This suggests that during 1972–1989 $pCO_{SW}^{\text{CO}_2}$ in the eSNA increased at a rate around or above the atmospheric $pCO_2$ growth rate of 1.47 $\mu \text{m} \text{yr}^{-1}$. Figure 5 also indicate that the 1.8 $\mu \text{m} \text{yr}^{-1}$ growth rate estimated by Lefèvre et al. [2004] would be obtained by using a $\Delta T$ value between 0.75 and 1.

6. Conclusions and Further Remarks

[20] Using an extended back calculation approach we have shown that wintertime $pCO_{SW}^{\text{CO}_2}$ in the surface waters of
the eastern subpolar North Atlantic increased between 1972 and 1989. Our approach resulted at first hand in a $\text{pCO}_2$ growth rate estimate of 3 $\mu$atm yr$^{-1}$. After taking the caveats of the analysis into account we have shown that this is an upper limit, and a lower limit is close to the atmospheric growth rate of 1.47 $\mu$atm yr$^{-1}$.

[21] With respect to the cause of the trend of increasing $\text{pCO}_2$, no single process can be pointed out. The estimated $\text{pCO}_2$ depends mainly on preformed concentrations of total dissolved inorganic carbon ($C_T$) and alkalinity ($A$), potential temperature ($\theta$), and salinity ($S$). Of these four parameters only $C_T$ exhibited a significant temporal trend (not shown) which, in turn, have caused the trend of increasing $\text{pCO}_2$. There are several processes that may have caused the increase in $C_T$. Analysis of NCEP/NCAR reanalysis data reveal no increase in the mean wind speed during the winter season so it is unlikely that enhanced air-sea $\text{CO}_2$ flux into the study area increased $C_T$ during the study period. Similarly, a long term decrease in the amount of carbon fixed into organic matter and/or increased remineralization is also unlikely because the preformed phosphate ($P_\text{pre} = P - R_{\text{pCO}_2} \times AOU$) did not show any significant trend (not shown). We suggest that uptake of anthropogenic carbon is the main cause of the estimated $\text{pCO}_2$ increase. Especially, since this process can produce excessive $\text{pCO}_2$ growth rates in the North Atlantic as shown by Wallace [2001] and Anderson and Olsen [2002]. The reason for this is that the surface water feeding this region originates mainly further south where temperatures are higher and buffer capacities larger. As water with any given $C_T$ change are moved northward the corresponding $\text{pCO}_2$ change will be amplified since the buffer capacity decreases due to cooling induced $C_T$ uptake. Therefore if the $\text{pCO}_2$ in the south changed at the same rate as the atmosphere, greater than atmospheric increases can take place in the north.

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References


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