Reconstructing the time history of the air-sea CO_2 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 CO_2 (pCO_2^{SW}) in the eastern subpolar North Atlantic (esNA) (50–64°N; 32–10°W) by using data of carbon-system parameters and chlorofluorocarbon-12 acquired in 1993. Wintertime pCO_2^{SW} 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 pCO_2^{SW} growth rate (3 µatm/yr) which is twice as large as that of atmospheric pCO_2, 1.47 µatm/yr. The sensitivity of the estimated pCO_2^{SW} 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 CO_2 is suggested as the process responsible for the excessive pCO_2^{SW} growth rate. **Citation:** Omar, A. M., and A. Olsen (2006), Reconstructing the time history of the air-sea CO_2 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 (CO_2). Assuming a constant wind field, the strength of the sink is proportional to the CO_2 disequilibrium across the air-sea interface $\Delta pCO_2 = pCO_2^{atm} - pCO_2^{SW}$, i.e., the difference between sea surface and atmospheric CO_2 partial pressures, pCO_2^{SW} and pCO_2^{atm}, respectively. In the subpolar NA, extensive heat loss and primary production lower pCO_2^{SW} so that a disequilibrium exists throughout most of the year and the flux of CO_2 is directed into the ocean. Additionally the pCO_2^{atm} is currently increasing so that an increasing air-sea CO_2 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 CO_2 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 CO_2 flux in the NA since pre-industrial times. For latitudes north of ∼50°N, their computation suggested a slightly decreasing ΔpCO_2.

Lefévre et al. [2004] analyzed pCO_2^{SW} data acquired in the region and showed that the disequilibrium decreased at an annual mean rate of −0.3 µatm yr^{-1} over the period 1982–1998. And *Friis et al.* [2005] provided measurement-based estimates of anthropogenic carbon (C_{ant}) accumulated in the subpolar NA over the period 1981–1999. For the surface water, they found that the increase of the C_{ant} was only reconcilable with a decreasing ΔpCO_2.

[3] In this paper, we reconstruct the time history of wintertime ΔpCO_2 in the eastern subpolar NA (50–64°N; 32–10°W) (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 [*McCartney 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) pCO_2^{SW} values for the eSPMW encountered during the cruise. The results are combined with data for the atmospheric mole fraction of CO_2 (xCO_2) to compute ΔpCO_2 and the temporal variability is analyzed.
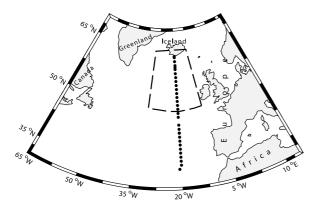
2. Data

[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 (C_T), total alkalinity (A_T), phosphate (P), silicate (Si), oxygen (O_2) 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 C_T, A_T, and O_2 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 substracted from the O_2 data because

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Figure 1. Map of the northern North Atlantic. The box show the eastern subpolar North Atlantic and the dots shown the sampling stations during the third leg of *Malcolm Baldrige* cruise (leg 2B, 18–29 August 1993).

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 = O$_2$ $_{saturation}$ − O$_2$ $_{measured}$) was recomputed.

3. Methods

[8] Wintertime climatological ranges of surface density (σ), 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 pCO$_2^{SW}$ values for the eSPMW were determined from preformed A$_T$ (A$_T^0$) and C$_T$ (C$_T^0$). The former was computed from the empirical relationship:

$$A_T^0 = 49.87 \times S + 566 \quad (1)$$

which was determined by regressing surface (depth < 200 m) salinity with alkalinity. The coefficient of determination (r^2) was 0.79 and the standard error of estimate was ±3 µmol kg^{-1}. C$_T^0$ was computed according to *Körtzinger et al.* [2003]:

$$C_T^0 = C_T - R_{C:O} \times AOU - \frac{1}{2}\left(A_T - A_T^0 + R_{N:O} \times AOU\right) \quad (2)$$

where C$_T$ and A$_T$ are the measured concentrations, R$_{C:O}$ and R$_{N:O}$ are the remineralization ratios between C$_T$ and O$_2$, and between NO$_3$ and O$_2$. We used the R$_{C:O}$ and R$_{N:O}$ 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 pCO$_2^{SW}$ was then computed from C$_T^0$, A$_T^0$, 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 pCO$_2^{SW}$ from C$_T$ and A$_T$. By propagating the uncertainties in C$_T^0$ (= 3.3 µmol kg^{-1}) and A$_T^0$(= ±3 µmol kg^{-1}) the maximum uncertainty in the computed pCO$_2^{SW}$ 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 pCO$_2^{atm}$ were calculated from xCO$_2$ 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 xCO$_2$ values were retrieved (ftp://ftp.cmdl.noaa.gov/ccg/co2/flask/month/), averaged over January to March, and converted to pCO$_2^{atm}$ according to:

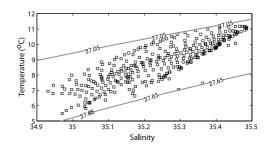$$pCO_2^{atm} = xCO_2(SLP - VP_{H_2O}) \quad (3)$$

where SLP is the monthly sea level pressure averaged over January to March for each year, VP$_{H_2}$O 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, ΔpCO$_2$ was computed for each sample as the difference between pCO$_2^{atm}$ and pCO$_2^{SW}$.
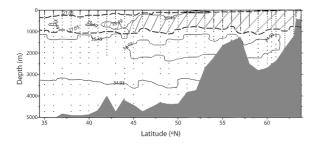
4. Results

[14] Figure 3 depicts the spatial distribution of eSPMW during the *Baldrige* 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 CO$_2$. This can be appreciated from Figure 4 which show wintertime pCO$_2^{atm}$

Figure 2. Wintertime (January–March) climatological temperature-salinity relationship for surface seawater in the eastern subpolar North Atlantic. Maximum and minimum density values are also shown (lines). These data were obtained from the World Ocean Atlas 2001 [*Conkright et al.*, 2002].

Figure 3. The distribution of 34.93 and 35.49 isohalines (solid contours) and 27.05 and 27.65 isopycnals (dashed contours) during the *Baldrige* 93 cruise. The hatched area shows the spatial distribution of eastern Subpolar Mode Water (eSPMW) as defined by salinity and potential density ranges of 34.93–35.49 and 27.05–27.65.

and the estimated values of pCO_2^{SW} and ΔpCO_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 $\mu atm\ yr^{-1}$ for pCO_2^{atm}, pCO_2^{SW} and ΔpCO_2, respectively.

5. Discussion

[16] Our computations suggest that the wintertime pCO_2^{SW} 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 *Lefévre et al.* [2004]. Quantitatively, however, the pCO_2^{SW} growth rate estimated in this study (3.00 $\mu atm\ yr^{-1}$) is larger than the ~1.8 $\mu atm\ yr^{-1}$ estimated by *Lefévre 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 $R_{C:O}$ and $R_{N:O}$ values as well as to the CFC-12 ages.

[17] If we were to use a lower value of $R_{C:O}$ then the estimated pCO_2^{SW} growth rate would decrease because the correction for remineralized carbon (= − $R_{C:O}$ × AOU, see equation (2)) would be reduced more for "older" eSPMW than for "younger" eSPMW. Changing $R_{N:O}$ has a similar effect on the estimated pCO_2^{SW} growth rate, but the effect is much smaller than that of $R_{C:O}$ because $R_{N:O}$ × AOU is an order of magnitude smaller than $R_{C:O}$ x 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 *Körtzinger et al.* [2001] and give a pCO_2^{SW} growth rate of 3.2 $\mu atm\ yr^{-1}$.

[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 Δ/Γ (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_2^{SW} growth rate is an upper limit. This is so because increasing the ages implies that the total pCO_2^{SW} increase of ≈50 μatm (Figure 4a) would be distributed over a longer time period and, thus, the growth rate would be reduced.
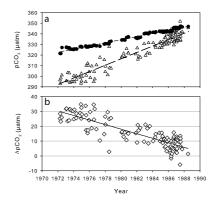
[19] In order to evaluate the combined effect of the loosely constrained remineralization quotients and the possible underestimation of water mass ages on the pCO_2^{SW} growth rate we (i) utilized the remineralization quotients of both *Körtzinger et al.* [2001] and *Redfield et al.* [1963] for the determination of pCO_2^{SW}, (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_2^{SW} growth rate. Important to mention is that, when the mean ages obtained by setting Δ/Γ equal to 0.75, 1, or 1.25 were used, the temporal trend of pCO_2^{SW} became quadric so that the data best fitted to equations of the form:

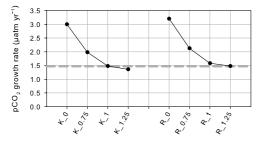$$pCO_2^{SW} = A \times (year)^2 + B \times (year) + C \qquad (4)$$

where year = 1993 – mean age and A, B, and C are constants. For these cases, therefore, the pCO_2^{SW} 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 $\mu atm\ yr^{-1}$ and 3.2 $\mu atm\ yr^{-1}$. This suggests that during 1972–1989 pCO_2^{SW} in the esNA increased at a rate around or above the atmospheric pCO_2 growth rate of 1.47 $\mu atm/yr$. Figure 5 also indicate that the 1.8 $\mu atm\ yr^{-1}$ growth rate estimated by *Lefévre et al.* [2004] would be obtained by using a Δ/Γ value between 0.75 and 1.

6. Conclusions and Further Remarks

[20] Using an extended back calculation approach we have shown that wintertime pCO_2^{SW} in the surface waters of

Figure 4. (a) Temporal changes of wintertime pCO_2^{atm} (dots) and pCO_2^{SW} (triangles), (b) Temporal changes of wintertime $\Delta pCO_2(= pCO_2^{atm} - pCO_2^{SW})$. Linear regressions of the data are also shown (lines).

Figure 5. Growth rates of reconstructed pCO_2^{SW} for the eastern subpolar North Atlantic during 1972–1989 for different combinations of remineralization quotients and transit times. On the x axis K_0.75 denotes that the quotients of *Körtzinger et al.* [2001] were used and CFC-12 ages were converted to mean transit times according to *Waugh et al.* [2004] by choosing $\Delta/\Gamma = 0.75$ (see sections 5 of the main text), R_1.25 denotes quotients of *Redfield et al.* [1963] and $\Delta/\Gamma = 1.25$, etc. The horizontal dashed line indicates the mean atmospheric pCO_2 growth rate during 1972–1989.

the eastern subpolar North Atlantic increased between 1972 and 1989. Our approach resulted at first hand in a pCO_2^{SW} growth rate estimate of 3 µatm 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 µatm yr^{-1}.

[21] With respect to the cause of the trend of increasing pCO_2^{SW}, no single process can be pointed out. The estimated pCO_2^{SW} depends mainly on preformed concentrations of total dissolved inorganic carbon (C_T^0) and alkalinity (A_T^0), potential temperature (θ), and salinity (S). Of these four parameters only C_T^0 exhibited a significant temporal trend (not shown) which, in turn, have caused the trend of increasing pCO_2^{SW}. There are several processes that may have caused the increase in C_T^0. 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 CO_2 flux into the study area increased C_T^0 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 ($P^0 = P - R_{C:O} \times AOU$) did not show any significant trend (not shown). We suggest that uptake of anthropogenic carbon is the main cause of the estimated pCO_2^{SW} increase. Especially, since this process can produce excessive pCO_2^{SW} 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 pCO_2^{SW} change will be amplified since the buffer capacity decreases due to cooling induced C_T uptake. Therefore if the pCO_2^{SW} 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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