

Anthropogenic increase of oceanic $p\text{CO}_2$ in the Barents Sea surface water

Abdirahman Omar,^{1,2} Truls Johannessen,^{3,4} Staffan Kaltin,⁵ and Are Olsen^{3,4}

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[1] We evaluate the change of surface water CO_2 partial pressure ($p\text{CO}_2^{\text{sw}}$) in the Barents Sea (BS) between 1967 and 2000–2001. We use temperature (T) data collected during a survey in the BS in 1967 and a relationship between surface water CO_2 mole fraction and T identified by Kelley [1970] to estimate the 1967 $p\text{CO}_2^{\text{sw}}$. On the basis of data of total inorganic carbon, alkalinity, T, and salinity (S) collected during two recent surveys in the BS, we compute $p\text{CO}_2^{\text{sw}}$ of 2000–2001. In order to be able to account for natural variations of $p\text{CO}_2^{\text{sw}}$ we develop an empirical predictive equation for $p\text{CO}_2^{\text{sw}}$ through multivariable linear regression with the 2000–2001 data of T, S, and apparent oxygen utilization (AOU). This relationship is applied to the 1967 T, S, and AOU data, and the output is compared to the 1967 estimates of $p\text{CO}_2^{\text{sw}}$. The difference is ascribed to net uptake of excess CO_2 . The computations show a $p\text{CO}_2^{\text{sw}}$ increase of $42 \pm 31 \mu\text{atm}$ between 1967 and 2000–2001, which is due to uptake of excess CO_2 . The $p\text{CO}_2$ increase was uniformly distributed in the BS, suggesting that the uptake of the excess carbon from the atmosphere took place outside the BS rather than across the sea-air interface within the BS. Moreover, the computed increase was comparable to the increase in atmospheric $p\text{CO}_2$ ($\sim 47 \mu\text{atm}$), and thus the $p\text{CO}_2$ gradient across the sea-air interface has remained nearly unchanged relative to 1967.

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KEYWORDS: Barents Sea, anthropogenic CO_2 , partial pressure of CO_2 , Atlantic Water

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1. Introduction

[2] Today, approximately 6 Gt C of carbon dioxide (CO_2) is released to the atmosphere each year as a result of combustion of fossil fuel and other human activities. About 50% of this anthropogenic CO_2 remains in the atmosphere, while the rest is absorbed by the ocean and terrestrial biosphere. The exact locations of these sinks are, however, not very well known [Gurney *et al.*, 2002].

[3] As a result of the invasion of the excess anthropogenic carbon, the surface ocean partial pressure of CO_2 ($p\text{CO}_2^{\text{sw}}$) has increased since preindustrial times. For the Atlantic Ocean a long-term change in $p\text{CO}_2^{\text{sw}}$ nearly parallel to the atmospheric $p\text{CO}_2$ rise was observed between 1957 and

1980, based on data of average $p\text{CO}_2^{\text{sw}}$ collected during major Atlantic expeditions (IGY, TTO, GEOSECS), [Millero, 1996, Figure 7.10]. Regional differences in the annual mean rate of increase in $p\text{CO}_2^{\text{sw}}$ may, however, exist within the North Atlantic. In the strongly stratified subtropical gyre $p\text{CO}_2^{\text{sw}}$ increased at a rate ($1.4 \pm 10.7 \mu\text{atm}$) similar to that in atmospheric partial pressure of CO_2 ($p\text{CO}_2^{\text{atm}}$) ($\sim 1.3 \mu\text{atm}$) during the period 1988–1998 [Bates, 2001]. For the subpolar/polar regions, Takahashi *et al.* [1997] noted that the surface waters in this region convectively mix with subsurface waters, in which anthropogenic effects are diluted. For this region they assumed therefore that the rate of increase in $p\text{CO}_2^{\text{sw}}$ is lower than the rate of increase in $p\text{CO}_2^{\text{atm}}$. On the other hand, Anderson and Olsen [2002] have employed a conceptual advective model and calculated the change in the total (natural + anthropogenic) CO_2 flux into seawater for the North Atlantic since preindustrial times. For latitudes north of $\sim 50^\circ\text{N}$, their computation suggest that the increase of $p\text{CO}_2^{\text{sw}}$ driven by the CO_2 increase in the atmosphere is approximately the same (if not slightly higher) as that in $p\text{CO}_2^{\text{atm}}$. Both of the above papers emphasize the importance of vertical mixing and residence time for the rate of increase of $p\text{CO}_2^{\text{sw}}$.

[4] The dilution of anthropogenic CO_2 in high-latitude surface waters has been observed in the northeastern subarctic Pacific [Takahashi *et al.*, 1997]. In the high-latitude

¹Bjerknes Centre for Climate Research, University of Bergen, Bergen, Norway.

²Also at Geophysical Institute, University of Bergen, Bergen, Norway.

³Geophysical Institute, University of Bergen, Bergen, Norway.

⁴Also at Bjerknes Centre for Climate Research, University of Bergen, Bergen, Norway.

⁵Department of Analytical and Marine Chemistry, Göteborg University, Göteborg, Sweden.

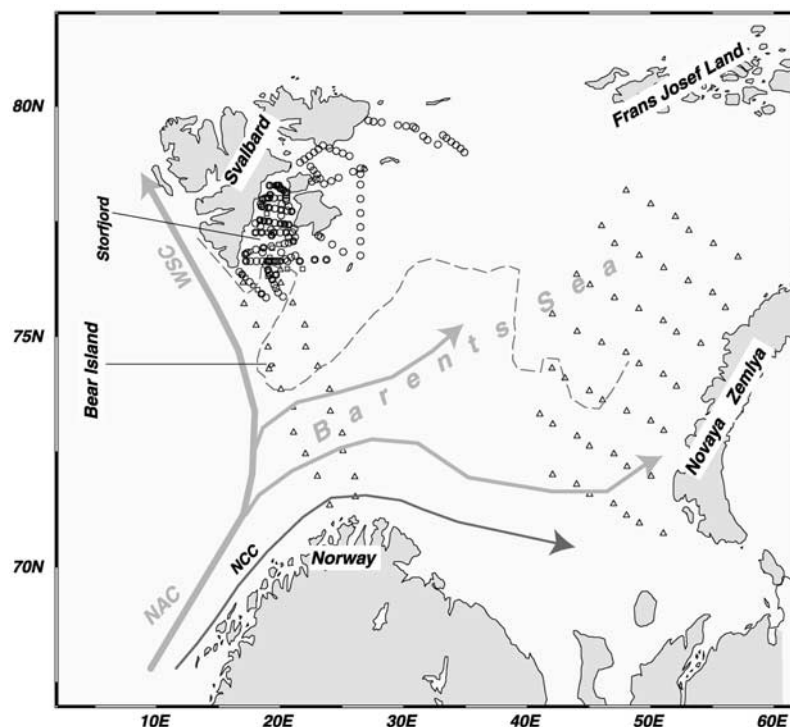


Figure 1. Map of the Barents Sea showing the locations of the stations occupied during the *Håkon Mosby* surveys (2000: circles; 2001: squares) and during the *Eastwind* survey (triangles). The pathway of the Norwegian Atlantic Current (NAC) and Norwegian Coastal Current (NCC) and the approximate mean position of the Polar Front (PF) (dashed line) are also indicated.

North Atlantic, however, observations of long-term trends in $p\text{CO}_2^{\text{sw}}$ have not as yet been presented. In this paper we evaluate the change of $p\text{CO}_2^{\text{sw}}$ between 1967 and 2000–2001 in the Barents Sea (BS), a region fed by water from the Norwegian Atlantic Current.

[5] Atlantic water (Aw) flows along the Norwegian continental shelf and slope as the Norwegian Atlantic Current (NAC) and enters the BS between Norway and Bear Island (Figure 1). As a result, water of Atlantic origin occupy the southern parts of the BS with two tongues that extend further northeast, one in the central parts of the BS and the other along the west coast of Novaya Zemlya. In the northern parts of the BS one finds cold Arctic water (Arw) flowing in the southwest direction. The Polar Front (PF) defines the boundary between these two water masses and divides the BS into two parts of almost equal size (Figure 1). During transit in the BS, heat loss and brine rejection during sea ice formation increase the density of Aw which is then transformed into a subsurface water and continues toward the Arctic Ocean.

[6] Measurements of seawater CO_2 mole fraction ($X\text{CO}_2^{\text{sw}}$), seawater temperature (T), salinity (S), and dissolved oxygen (O_2) were carried out in the BS onboard the USCG icebreaker *Eastwind* in 1967. Kelley [1970] analyzed these data and identified a linear relationship between $X\text{CO}_2^{\text{sw}}$ and T. We first use the relationship of Kelley [1970] and the *Eastwind* temperature data to estimate $X\text{CO}_2^{\text{sw}}$ values for 1967. The results are then converted to $p\text{CO}_2^{\text{sw}}$ values. Next, on the basis of data of total inorganic carbon (C_T), alkalinity (A_T), T, and salinity (S) collected during two recent surveys conducted in the BS

we compute $p\text{CO}_2^{\text{sw}}$ of 2000–2001. By using these two data sets and by applying a procedure which accounts for the natural variability of $p\text{CO}_2^{\text{sw}}$ we evaluate the increase of $p\text{CO}_2^{\text{sw}}$ resulting from net uptake of excess CO_2 between 2000–2001 and 1967. Our methods are detailed in the next section.

2. Data and Methods

2.1. Data and Analytical Methods

[7] The data used in this work originate from three surveys conducted in the BS [*Håkon Mosby*, 2000; *Håkon Mosby*, 2001, and *Eastwind*, 1967]. Figure 1 shows the positions of the stations occupied during these three surveys. Only surface (i.e., depths < 15 m) data from these three cruises are used in this study.

[8] During the *Håkon Mosby* cruises, measurements of C_T , A_T , dissolved oxygen (O_2), T, and S were carried out. Water samples were drawn from CTD bottles and analyzed onboard for chemical parameters. C_T was determined by gas extraction of acidified water samples followed by coulometric titration using a SOMMA system [Johnson *et al.*, 1985, 1987]. Typically the precision was $\pm 4 \mu\text{mol kg}^{-1}$ and the accuracy was set by running Certified Reference Material (CRM) supplied by Andrew Dickson at Scripps Institute of Oceanography, USA. A_T was determined by titrating samples with 0.1 M HCl as described by Haraldson *et al.* [1997]. The precision was determined to $\pm 5 \mu\text{mol kg}^{-1}$ and the accuracy was set in the same way as for C_T . O_2 was determined using the Winkler method with visual detection of the titration end point.

[9] During the *Eastwind* survey, measurements of $X\text{CO}_2^{\text{sw}}$, atmospheric pressure (p), T, S, and O_2 were carried out in the BS. Details on the experimental setup and analysis techniques used to measure $X\text{CO}_2^{\text{sw}}$ are given by Kelley [1970]. However, important to mention here is that seawater was first brought into an equilibrator so that measurement temperatures were up to 0.7°C different from in situ temperatures. Also, the air samples from the equilibrator were dried before passing through the infrared detector. The measurement system was calibrated with reference gases accurate to approximately ± 2 ppm. O_2 was determined using the Winkler method [Kelley, 1970].

[10] We have identified and downloaded profile data of p , T, S, and O_2 acquired during the *Eastwind* cruise which have been made available by the NOAA/National Oceanographic Data Centre (NODC) at the Internet location <http://www.nodc.noaa.gov>. Data of $X\text{CO}_2^{\text{sw}}$ were not available from the NODC database, but these were estimated from temperature data as detailed below.

2.2. Computation Methods

[11] On the basis of the data collected during the *Eastwind* cruise, Kelley [1970] identified a linear relationship between $X\text{CO}_2^{\text{sw}}$ and T according to:

$$X\text{CO}_2^{\text{sw}} = 10T + 191.3 \quad (1)$$

with a standard error of estimates of ± 19.5 ppm.

[12] We use equation (1) and the *Eastwind* T data to estimate $X\text{CO}_2^{\text{sw}}$ of 1967. The result is then converted to seawater $p\text{CO}_2$ ($p\text{CO}_2^{\text{sw}}$) according to:

$$p\text{CO}_2^{\text{sw}} = X\text{CO}_2^{\text{sw}}(p - VP_{\text{H}_2\text{O}}) \quad (2)$$

where p is the total pressure exerted by all gasses present in the air equilibrated with the seawater samples and $VP_{\text{H}_2\text{O}}$ is the water vapor pressure. The latter is included in order to account for the fact that air samples were dried before the detector. p is assumed to be equal to the atmospheric pressure, and $VP_{\text{H}_2\text{O}}$ is calculated from seawater temperature according to the formula given by Cooper *et al.* [1998]. The outcome of equation (2) is a parameter which estimates the 1967 $p\text{CO}_2^{\text{sw}}$ and will be henceforth denoted as $p\text{CO}_2^{\text{sw},67}$.

[13] Seawater $p\text{CO}_2$ of 2000–2001 is computed from data of C_T , A_T , temperature, and salinity acquired during the *Håkon Mosby* cruises, using the constants of Mehrbach *et al.* [1973] refit by Dickson and Millero [1987]. This results in the parameter $p\text{CO}_2^{\text{sw}}(C_T, A_T)$.

[14] Thermal, biological, and water transport processes all influence the oceanic CO_2 system variables and these may have been different in 2000–2001 compared to the situation in 1967. Thus the difference between $p\text{CO}_2^{\text{sw},67}$ and $p\text{CO}_2^{\text{sw}}(C_T, A_T)$ is not a measure of the change of $p\text{CO}_2^{\text{sw}}$ resulting from uptake of excess CO_2 , since it incorporates changes which are due to natural processes. Therefore, in this study we apply a procedure similar to the “multivariate approach” described by Wallace [2001] in order to determine the increase of $p\text{CO}_2^{\text{sw}}$, which is due to uptake of excess CO_2 . The seawater partial pressure of CO_2 in the BS is mainly influenced by the processes of formation and decay of organic matter, sea-air heat exchange, and mixing between

water masses. Moreover, apparent oxygen utilization (AOU) (derived from: saturation O_2 - measured O_2), temperature, and salinity are affected by the above processes. We therefore assume that the natural variability of $p\text{CO}_2^{\text{sw}}$ in the BS can be predicted from a relationship between seawater $p\text{CO}_2$ and these variables. Hence we developed an empirical predictive equation for $p\text{CO}_2^{\text{sw}}(C_T, A_T)$ through a multiparameter linear regression with data of AOU, T, S acquired during the *Håkon Mosby* cruises. The resulting equation is given by:

$$p\text{CO}_2^{\text{sw}}(S, T, \text{AOU}) = 3.545S + 9.242T + 1.015\text{AOU} + 120.211 \quad (3)$$

Equation (3) is henceforth assumed to describe the natural variability of $p\text{CO}_2^{\text{sw}}$ in the BS through its dependency on AOU, T, S.

[15] The uptake of excess carbon is an abiotic perturbation which increases the concentration of CO_2 in seawater (thus $p\text{CO}_2^{\text{sw}}$) without affecting the factors that control the natural variability of $p\text{CO}_2^{\text{sw}}$, here assumed to be AOU, T, S. Hence, when equation (3), which was calibrated by using the 2000–2001 data, is applied to the 1967 AOU, T, and S data to compute $p\text{CO}_2^{\text{sw}}[(S, T, \text{AOU})^{67}]$, then the differences between 2000–2001 and 1967 due to natural processes is taken into account but not the difference due to uptake of excess CO_2 . It then follows, provided that the above assumptions hold, that any systematic offset between $p\text{CO}_2^{\text{sw}}[(S, T, \text{AOU})^{67}]$ and $p\text{CO}_2^{\text{sw},67}$ reflects the change of $p\text{CO}_2^{\text{sw}}$ between 1967 and 2000–2001 resulting from net uptake of excess CO_2 .

3. Results

[16] In Figures 2a–2c, $p\text{CO}_2^{\text{sw},67}$ and $p\text{CO}_2^{\text{sw}}(C_T, A_T)$ are plotted as functions of T, S, and AOU acquired in 1967 and 2000–2001, respectively. The 2000–2001 $p\text{CO}_2$ values are higher than the 1967 values at all temperatures (Figure 2a). We also note that temperature values acquired during the *Eastwind* survey range between 0.5° and 9°C , whereas for the *Håkon Mosby* cruises only a few samples show temperature values higher than 4°C . This difference reflects that the *Håkon Mosby* cruises was conducted north of the core of Aw carried by the NAC (Figure 1). This can also be appreciated from Figure 2b by noting that for the *Eastwind* cruise many more data points fall on salinity > 34.5 than for the *Håkon Mosby* cruises. Another distinctive feature of Figure 2b is that during the *Eastwind* cruise only salinities above 33 were encountered. The low-salinity (< 33) samples in Figure 2b were acquired in 2001 from Storfjord, Svalbard. Other distinctive characteristics of these samples will be discussed in section 4, here we only note that they deviate somewhat from the general trend of increasing $p\text{CO}_2^{\text{sw}}$ with increasing salinity. In Figure 2b, we again note that the 2000–2001 $p\text{CO}_2$ values are higher than the 1967 estimates for nearly all salinity values.

[17] In Figure 2c, the most striking difference is that the *Eastwind* AOU values are confined in a much narrower range (-20 to $5 \mu\text{mol kg}^{-1}$), than the *Håkon Mosby* AOU which ranges from -40 to $40 \mu\text{mol kg}^{-1}$. This indicates that

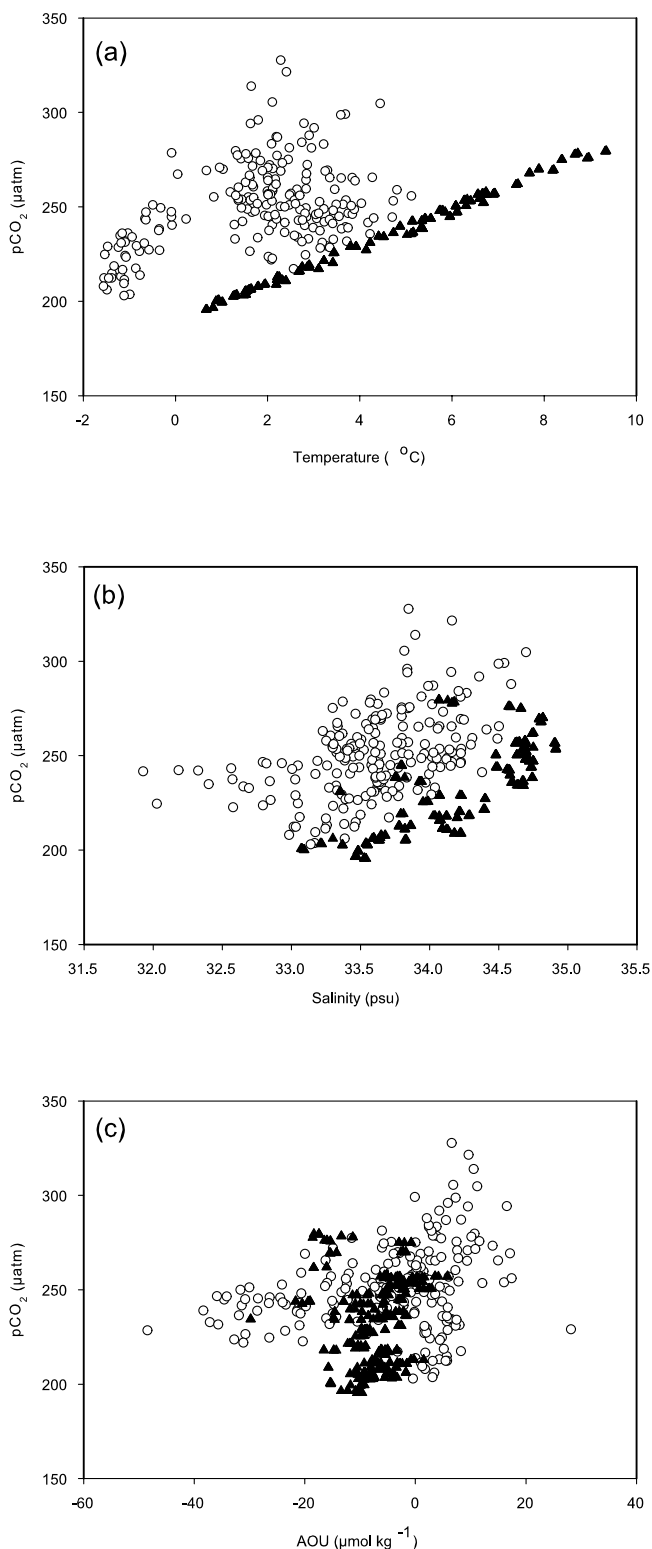


Figure 2. The $p\text{CO}_2^{\text{sw},67}$ (triangles) and $p\text{CO}_2^{\text{sw}}(C_T, A_T)$ (circles) as functions of (a) seawater temperature, (b) salinity, and (c) apparent oxygen utilization. For explanation of the first two parameters, see section 2.2. Please, note that $p\text{CO}_2^{\text{sw},67}$ is plotted against the data measured in 1967, while $p\text{CO}_2^{\text{sw}}(C_T, A_T)$ is plotted against the 2000–2001 data.

although a signature of recent primary production was present in the surface water during all three cruises, both primary production and decay of organic matter were of greater importance during the *Håkon Mosby* cruises. This explains why the 2000–2001 $p\text{CO}_2$ is not a linear function of temperature (Figure 2a).

[18] As a summary of the results depicted in Figures 2a–2c, we realize that all the oceanographic variables assumed to influence the natural variability of $p\text{CO}_2^{\text{sw}}$ (i.e., AOU, T, and S) were different in 2000–2001 compared to the situation in 1967. Thus the correction procedure described in section 2.2 must be applied in order to determine the change of $p\text{CO}_2^{\text{sw}}$ between 1967 and 2000–2001 which is due to net uptake of excess CO_2 .

[19] Before utilizing equation (3) to correct for the natural variability, an evaluation of the quality of the predictions made by this equation is needed. The residuals between the computed $p\text{CO}_2^{\text{sw}}(C_T, A_T)$ values and those predicted from the 2000–2001 data of AOU, T, S by equation (3) are shown in Figures 3a–3c as functions of T, S, and AOU, respectively. As can be seen from these plots, the residuals are centered around zero with relatively large scatter. The zero mean value of the residuals indicates that the predicted values are not biased (i.e., a constant offset is not introduced) by the use of the empirical equation. The relatively large scatter, on the other hand, indicates that the predictive equation inevitably fails to fully capture the natural variability due to some unresolved processes. This highlights the complex nature of the controls of $p\text{CO}_2^{\text{sw}}$ in the areas where these data were acquired. It indicates that probably more fit parameters are required (nutrients for instance) to better predict $p\text{CO}_2^{\text{sw}}$ in this region. As a measure of the uncertainties associated with this limitation of equation (3) we will use the standard deviation of the residuals which is $\pm 16 \mu\text{atm}$.

[20] In Figure 4, $p\text{CO}_2^{\text{sw},67}$ and $p\text{CO}_2^{\text{sw}}[(S, T, AOU)^{67}]$ are plotted as a function of temperature. Both parameters vary linearly with temperature, with almost identical slopes. A clear exception is for temperatures above 7°C at which $p\text{CO}_2^{\text{sw}}[(S, T, AOU)^{67}]$ drops slightly. This feature can also be seen in the original $X\text{CO}_2^{\text{sw}}$ data [see Kelley, 1970, Figure 6]. The fact that the use of equation (3) captures this feature can be taken as a reassuring hint regarding the quality of the reproduction of the 1967 $p\text{CO}_2^{\text{sw}}$. The most striking difference between $p\text{CO}_2^{\text{sw},67}$ and $p\text{CO}_2^{\text{sw}}[(S, T, AOU)^{67}]$ is the nearly constant offset in $p\text{CO}_2^{\text{sw}}[(S, T, AOU)^{67}]$. As argued in section 2.2, this offset is a direct estimate of the increase of $p\text{CO}_2^{\text{sw}}$ between 1967 and 2000–2001 due to net uptake of excess CO_2 . The mean value of this increase as evaluated from the average difference between $p\text{CO}_2^{\text{sw}}[(S, T, AOU)^{67}]$ and $p\text{CO}_2^{\text{sw},67}$ is $42 \pm 31 \mu\text{atm}$. The uncertainty of the estimate is partly (80%) due to uncertainties in $p\text{CO}_2^{\text{sw}}[(S, T, AOU)^{67}]$ and $p\text{CO}_2^{\text{sw},67}$ and partly (20%) due to the temperature difference (max 0.7°C) between sea and equilibrator in 1967. A detailed evaluation of the uncertainties of our results is given in section 5.

4. Discussion

[21] Equation (3) was such an essential tool in our calculations that its spatiotemporal scope deserves a com-

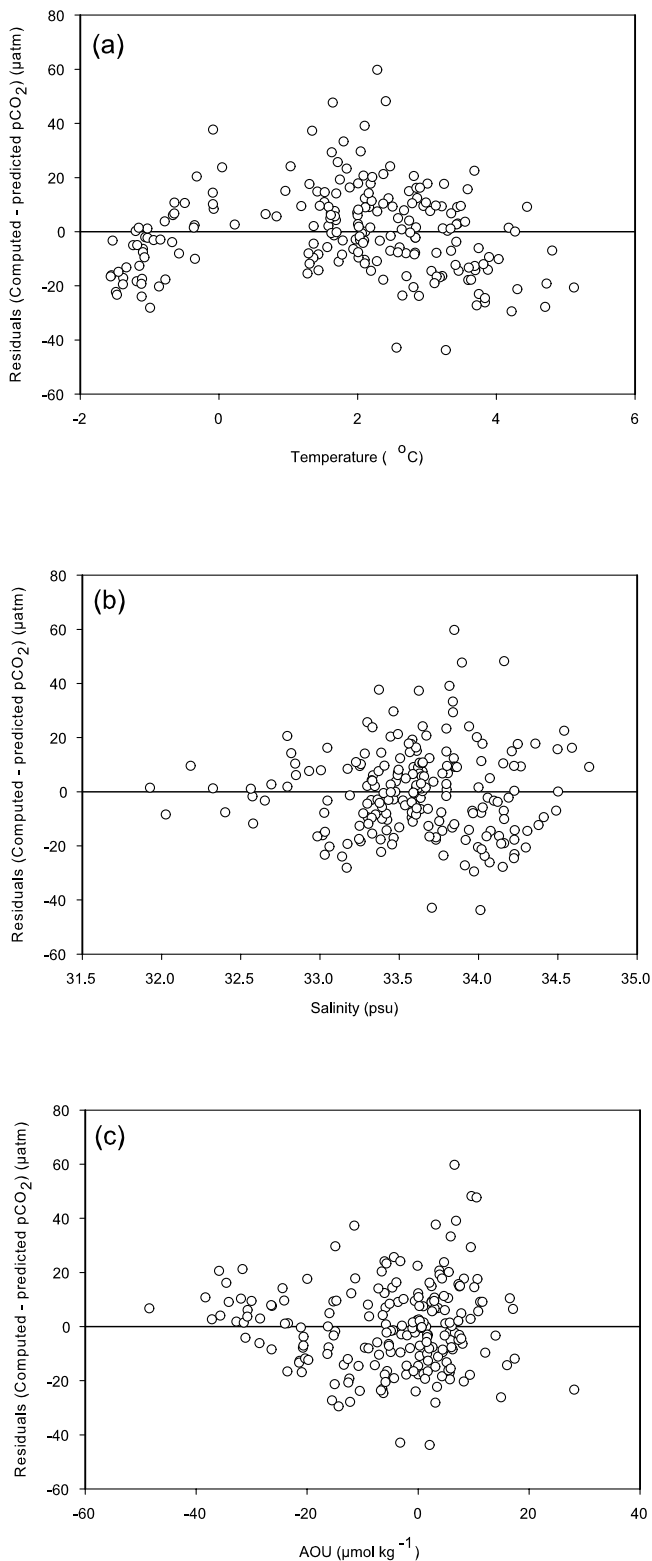


Figure 3. Residuals ($p\text{CO}_2^{\text{sw}}(C_T, A_T) - p\text{CO}_2^{\text{sw}}$ predicted from the 2000–2001 data by equation (3)) as a function of the 2000–2001 seawater (a) temperature, (b) salinity, and (c) apparent oxygen utilization.

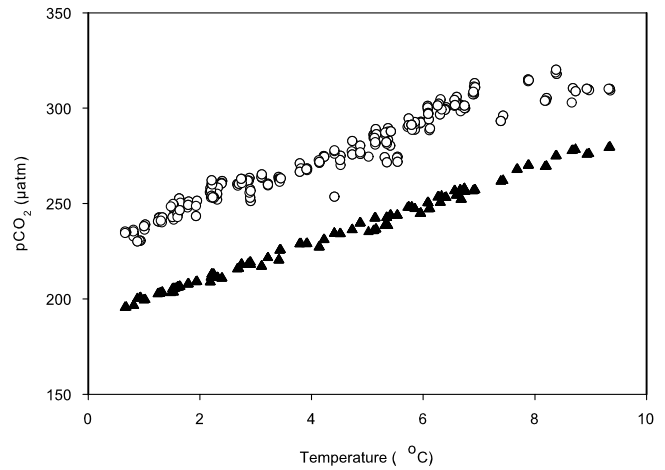


Figure 4. The $p\text{CO}_2^{\text{sw},67}$ (triangles) and $p\text{CO}_2^{\text{sw}}[(S, T, \text{AOU})^{67}]$ (circles) plotted as a function of the 1967 seawater temperature. For explanation of the first two parameters, see section 2.2.

ment. An underlying assumption in our calculations was that (neglecting anthropogenic effects) equation (3) is time and area independent, which is a reasonable assumption as long as $p\text{CO}_2^{\text{sw}}$ is mainly influenced by the processes of formation and decay of organic matter, sea-air exchange, and mixing between water masses. Neither the relationship between solubility of CO_2 and temperature/salinity, nor the way in which mixing between water masses affects seawater salinity is time or area dependent. Therefore potential dependency of equation (3) on area and/or time would most likely be a consequence of spatial, seasonal, and/or inter-annual variations of $\Delta C_T/\Delta \text{AOU}$ (thus $\Delta p\text{CO}_2/\Delta \text{AOU}$). Spatial and water depth variations of this ratio have been reported in the literature [Broecker and Peng, 1982; Thomas, 2002]. However, we believe that this ratio is not significantly variable over the shallow and relatively small BS. Moreover, the most prominent regional differences of most oceanographic variables in the BS are associated with the north-south division of the BS associated with the Polar Front [e.g., Loeng, 1991; Reigstad et al., 2002]. Specifically, seawater temperature, salinity, and $p\text{CO}_2$ decrease from the Aw dominated southern part of the BS toward the Arw dominated northern part, while O_2 changes conversely. As can be seen from Figure 1, the *Eastwind* survey was conducted mainly south of the PF, whereas the *Håkon Mosby* cruises were conducted north of the PF. Therefore, if significant regional differences in the relationship between $p\text{CO}_2$ and S, T, and AOI (described by equation (3)) exist, then the application of equation (3) should be least appropriate for the core of the Aw entering the BS, since equation (3) was based on the *Håkon Mosby* data. However, independent data of $p\text{CO}_2^{\text{sw}}$ which were measured in October 1999 suggest that there are no great regional differences in this relationship and that equation (3) can be extrapolated to the core of Aw. These 1999 $p\text{CO}_2^{\text{sw}}$ data were acquired between 71.5° and 74°N along a section located roughly on 19.5°E , i.e., the area where the core of Aw enter the BS [e.g., Loeng, 1991] (Figure 1). Simultaneous measurements of S, and O_2 were not carried out, and

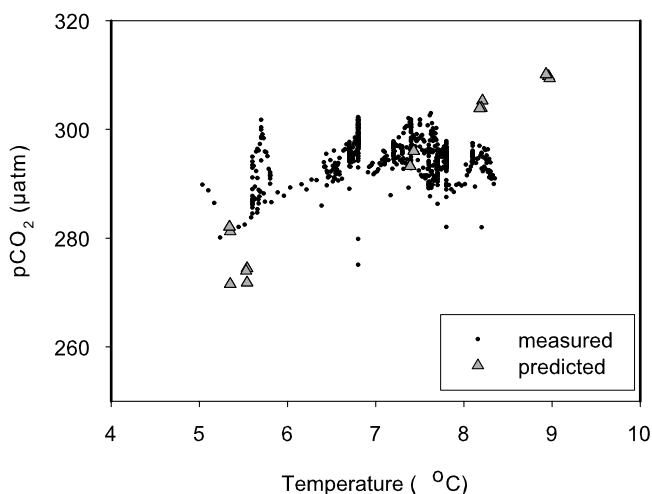


Figure 5. Comparison of seawater $p\text{CO}_2$ measured in 1999 with those predicted from the 1967 data for the area where the core of Atlantic water carried by the Norwegian Atlantic Current enters the Barents Sea, i.e., between 71.5° and 74°N . The 1999 data were measured on 9–10 October along a section located roughly on 19.5°E . The predicted values are estimates of the 1967 seawater $p\text{CO}_2$ plus the net anthropogenic increase as in 2000–2001 and should therefore be comparable to the 1999 values.

thus these $p\text{CO}_2$ data were not utilized for the calibration of equation (3). As depicted in Figure 5, the measured 1999 values are in good agreement with the $p\text{CO}_2^{sw}$ [(S , T , AOU)⁶⁷] values we estimated for the *Eastwind* Aw samples acquired around the same area.

[22] With respect to potential seasonal and interannual variability of the relationship described by equation (3), we emphasize that all data used in this work were acquired during the same season, i.e., August–September. Hence the effect of seasonal changes on our computations should be minimal. Moreover, no accounts on interannual variability of $\Delta C_T/\Delta \text{AOU}$ are known to us, nevertheless, we acknowledge that any interannual variation of this parameter would shift the relationship described by equation (3) and thus affect our results.

[23] The above assumption, that $p\text{CO}_2^{sw}$ is mainly influenced by the processes of formation and decay of organic matter, sea-air heat exchange, and mixing between water masses, intuitively implies that equation (3) will not hold for areas where in situ formation and dissolution of calcium carbonate and/or addition of inorganic carbon by runoff are significant. In the interior parts of the BS none of these processes are of quantitative importance [e.g., *Anderson et al.*, 1988; *Östlund and Hut*, 1984], and thus alkalinity can be approximated from a linear function of salinity. At areas close to the coast, however, runoff may add inorganic carbon to the water column and distort this relationship. During the 2001 survey, the alkalinity values measured in the low-salinity ($S < 33$ psu) samples at stations occupied in Storfjord, Svalbard were consistently higher than what would be predicted from linear function of salinity. We believe this was due to runoff from

Svalbard. The $p\text{CO}_2^{sw}$ values predicted for these low-salinity samples by equation (3) were though not particularly biased, on the contrary they seemed to be of better quality than the rest of the data (Figure 3b). In this study we assumed that coastal water carried by the Norwegian Coastal Current (NCC) behave as these low-salinity samples. Therefore we performed the computations also for samples taken south of the 71.5°N latitude, which can be considered as the northern border of the NCC [e.g., *Loeng*, 1991].

[24] The average CO_2 mole fraction in the atmosphere over the BS ($X\text{CO}_2^{atm}$) during *Eastwind* cruise (August/September 1967) was 313 ppm [*Kelley*, 1970]. The corresponding value in 2000–2001 as calculated from monthly mean values of $X\text{CO}_2^{atm}$ data acquired on Zeppelin Mountain, Spitsbergen (79°N), made available by the NOAA/CMDL Carbon Cycle Greenhouse Gases Group, was 360 ppm. Assuming a total atmospheric pressure of 1 atm, we get an increase of atmospheric $p\text{CO}_2$ of (360–313) 47 μatm between 1967 and 2000–2001. This increase compares well with the estimated increase of $p\text{CO}_2^{sw}$ (42 ± 31 μatm). Hence, although the data used in this study is temporally too limited to resolve the annual mean rate of increase of $p\text{CO}_2^{sw}$ in the BS since 1967, our results suggest that it has been similar to the rate of increase in atmospheric $p\text{CO}_2$.

[25] The fact that the estimated increase of $p\text{CO}_2^{sw}$ is nearly constant throughout the Barents Sea (Figure 4) suggests that the excess CO_2 is advected into the region. If a significant part of the excess CO_2 was taken up (or lost) across the sea-air interface within the Barents Sea, then the difference between $p\text{CO}_2^{sw,67}$ and $p\text{CO}_2^{sw}$ [(S , T , AOU)⁶⁷] (Figure 4) would show a noticeable gradient as one move from the warm Aw sampled at the entrance of the BS toward the colder water sampled in the interior of the sea.

[26] Another way to view the close agreement between the estimated increase of $p\text{CO}_2^{sw}$ and $p\text{CO}_2^{atm}$ is that the $p\text{CO}_2$ gradient across the sea-air interface ($\Delta p\text{CO}_2$) has remained nearly unchanged. Thus the total flux of CO_2 (natural + anthropogenic) has remained essentially unchanged over the last 30 years, provided that other parameters which affect the air-sea CO_2 flux have remained unchanged. Moreover, this would be true also for the Aw supplied by the Norwegian Atlantic Current, since the estimated increase of $p\text{CO}_2^{sw}$ is approximately uniform throughout the BS. As mentioned in the introduction, *Anderson and Olsen* [2002] have employed a conceptual advective model and calculated the change of total CO_2 flux into a water parcel as it flows from low latitude (3.5°N , 16.5°W) to the high latitude (70.5°N , 5.5°W) North Atlantic, by using preindustrial and today's mean values of $p\text{CO}_2^{atm}$ (280 and 370 μatm , respectively). Interestingly, their computations show negligible changes (a slight decrease) in the total flux for latitudes north of $\sim 50^\circ\text{N}$. Although there is a sense of agreement between our computation results and those of the above paper, it must be mentioned, however, that the excess carbon in the BS might have been taken up from the atmosphere within the Nordic Seas and is not necessarily transported from further south in the Atlantic Ocean. In any case, since Aw entering the BS is loaded with anthropogenic carbon, this is one of

the northern high-latitude oceanic regions where anthropogenic carbon is sequestered by formation of subsurface waters.

5. Evaluation of Errors

[27] In section 3, four central parameters, i.e., $p\text{CO}_2^{\text{sw}}(C_T, A_T)$, $p\text{CO}_2^{\text{sw}}[(S, T, \text{AOU})^{67}]$, $p\text{CO}_2^{\text{sw},67}$, and the difference between the latter two, were presented. In the following the sources and magnitudes of the errors associated with these parameters are evaluated.

[28] The random error associated with the computed $p\text{CO}_2^{\text{sw}}(C_T, A_T)$ ($\sigma_{p\text{CO}_2^{\text{sw}}(CT,AT)}$) can be determined by propagating through the imprecision of the parameters required for the calculation, i.e., C_T , A_T , salinity, and temperature. Moreover, measures of the imprecision in C_T and A_T (σ_{C_T} and σ_{A_T}) are their analytical errors, ± 4 and $\pm 5 \mu\text{mol kg}^{-1}$ (section 2.1). The imprecision in both salinity and temperature are significantly lower than σ_{C_T} and σ_{A_T} so they are ignored in the following calculations. We assume that C_T and A_T are independent so that $\sigma_{p\text{CO}_2^{\text{sw}}(CT,AT)}$ can be expressed as [Erdal, 1997]:

$$\sigma_{p\text{CO}_2^{\text{sw}}(CT,AT)} = \sqrt{\left(\frac{\partial p\text{CO}_2}{\partial C_T} \sigma_{C_T}\right)^2 + \left(\frac{\partial p\text{CO}_2}{\partial A_T} \sigma_{A_T}\right)^2} \quad (4)$$

According to Takahashi *et al.* [1993], $\frac{\partial p\text{CO}_2}{\partial C_T} = \frac{p\text{CO}_2}{C_T} RF$ and $\frac{\partial p\text{CO}_2}{\partial A_T} = \frac{p\text{CO}_2}{A_T} K$ where RF and K are constants, the former is known as the Revelle factor. The global values of RF and K are 10, and -9.4 , respectively. Using these global values, the calculated values of $p\text{CO}_2^{\text{sw}}(C_T, A_T)$, the measured values of C_T and A_T , and equation (4), we get a mean value of $\sigma_{p\text{CO}_2^{\text{sw}}(CT,AT)}$ of $\pm 7 \mu\text{atm}$.

[29] We use the standard deviation of the residuals between the computed $p\text{CO}_2^{\text{sw}}(C_T, A_T)$ values and those predicted from the 2000–2001 data of AOU, T, S by equation (3) (Figure 3), to represent the random error associated with $p\text{CO}_2^{\text{sw}}[(S, T, \text{AOU})^{67}]$ ($\sigma_{p\text{CO}_2^{\text{sw}}[(S,T,AOU)^{67}]}$). The value of this standard deviation was $\pm 16 \mu\text{atm}$.

[30] The random error associated with $p\text{CO}_2^{\text{sw},67}$ ($\sigma_{p\text{CO}_2^{\text{sw},67}}$) was calculated from the standard error of $X\text{CO}_2^{\text{sw}}$ reported by Kelley [1970] (± 19.5 ppm). We convert this value into $p\text{CO}_2^{\text{sw}}$ by using the procedure outlined in section 2.2 and get $\sigma_{p\text{CO}_2^{\text{sw},67}}$ to be $\pm 18.9 \mu\text{atm}$. Moreover, during the *Eastwind* cruise the temperature difference between sea and equilibrator was at most 0.7°C [Kelley, 1970]. There is no information on whether the temperature difference was positive or negative, or whether a temperature correction was performed before fitting the 1967 data of $X\text{CO}_2^{\text{sw}}$ to temperature. This represents an additional uncertainty of (at most) $\pm 7.8 \mu\text{atm}$ in $p\text{CO}_2^{\text{sw},67}$. Thus we use a total uncertainty of $26.7 (= 7.8 + 18.9) \mu\text{atm}$ for $p\text{CO}_2^{\text{sw},67}$.

[31] Then, the maximum value of the random error associated with each data point of the difference between $p\text{CO}_2^{\text{sw}}[(S, T, \text{AOU})^{67}]$ and $p\text{CO}_2^{\text{sw},67}$ is given by $[(26.7)^2 + (16)^2]^{0.5}$ or $\pm 31 \mu\text{atm}$. We use this value as the total uncertainty in the computed increase of $p\text{CO}_2^{\text{sw}}$ between 1967 and 2000–2001.

[32] We acknowledge that inconsistency of data measured on different platforms may represent a potential source of

systematic error. We emphasize, however, that consistency of data of oceanic CO_2 system variables used in this work is warranted by use of Certified Reference Material (CRM) in 2000–2001, and the use of reference gases in 1967 [Kelley, 1970]. Moreover, since measurement methods used to determine O_2 , T, and S were established long time ago we do not expect any serious inconsistency in the data of these variables.

6. Conclusions

[33] By comparing 2000–2001 $p\text{CO}_2$ values with estimates of 1967 $p\text{CO}_2$ for Barents Sea surface water, we computed a $p\text{CO}_2$ increase of $42 \pm 31 \mu\text{atm}$ which can be ascribed to net uptake of excess CO_2 between 1967 and 2000–2001. The computed seawater $p\text{CO}_2$ increase was uniformly distributed in the BS, suggesting that the uptake of the excess carbon from the atmosphere took place outside the BS rather than within. Moreover, the computed increase was comparable to the corresponding increase in atmospheric $p\text{CO}_2$ ($\sim 47 \mu\text{atm}$) and thus the $p\text{CO}_2$ gradient across the sea-air interface has remained nearly unchanged.

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- T. Johannessen and A. Olsen, Geophysical Institute, University of Bergen, Allégaten 70, 5007 Bergen, Norway.
- S. Kaltin, Department of Analytical and Marine Chemistry, Göteborg University, Göteborg, Sweden.
- A. Omar, Bjerknes Centre for Climate Research, University of Bergen, Allégaten 55, N-5007 Bergen, Norway. (abdirahman.omar@gfi.uib.no)