

## Annual carbon fluxes in the upper Greenland Sea based on measurements and a box-model approach

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### ABSTRACT

Measurements of nitrate and the carbonate system parameters performed mainly from 1993 to 1997 have been used to estimate the evolution of the concentration fields over the year in the surface and underlying waters of the central Greenland Sea. This, together with synoptic surface wind data from the NCEP/NCAR reanalysis project, is used to evaluate the vertical mixing, the biological production and decay, as well as the air–sea exchange of CO<sub>2</sub> in the region. In the winter season, the vertical mixing dominates the change of the nitrate concentration in the surface water. The mixing factor estimated for this season is used to compute the addition of chemical constituents to the surface water from below. The residual nitrate concentration change, after the mixing contribution has been subtracted, is attributed to biological production or decay. The computations are performed with a 1-day resolution and initially the advective contribution is neglected, as the horizontal gradients in the central Greenland Sea gyre are small. Following this approach, the air–sea flux of CO<sub>2</sub> is directed into the sea all year around, with an annual uptake of  $53 \pm 4 \text{ g C m}^{-2} \text{ yr}^{-1}$  for the years 93 to 97. The carbon flux as driven by biology shows a strong primary production peak around Julian day 140 followed by a decrease which turns into decay of organic matter at about day 200. Summarizing the biological activity in the surface water over the year gives a new production of  $34 \text{ g C m}^{-2} \text{ yr}^{-1}$ . The vertical flux of dissolved inorganic carbon into the surface water from below amounts to  $11 \text{ g C m}^{-2} \text{ yr}^{-1}$ . The build up of carbon in the surface water,  $30 \text{ g C m}^{-2} \text{ yr}^{-1}$ , is explained by that the temperature of the outflowing water is approximately 2°C colder than the inflowing water, giving a higher dissolved inorganic carbon concentration as a result of the increase in the solubility of carbon dioxide with lower temperatures. The uncertainties in the above stated numbers are  $\pm 20\%$ .

### 1. Introduction

The Greenland Sea is a region of deep water formation and as such transports chemical constituents from the surface to the deep ocean. This deep water formation has been mentioned as a significant sink of anthropogenic carbon dioxide,

i.e., carbon dioxide produced by human activities like deforestation and fossil fuel burning. The role of the oceans in taking up anthropogenic carbon dioxide and the processes that control the air–sea exchange of carbon dioxide has been given much attention (Volk and Hoffert, 1985; Siegenthaler and Sarmiento, 1993; Stocker et al., 1994). The deep convection areas, where water in contact with the atmosphere gains a density high enough to sink and form deep water, tends to bring carbon

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dioxide away from contact with the atmosphere. This newly formed deep water will thus carry the anthropogenic  $\text{CO}_2$  to the deep oceans.

The Greenland Sea deep water (GSDW) is a relatively young water mass as deduced from its content of anthropogenic tracers such as tritium, helium, argon, krypton, and CFCs (Rhein, 1991; Schlosser et al., 1991; Bönsch and Schlosser, 1995; Bönsch et al., 1997). In order to explain the measured chloro-fluoro-carbon (CFC) data in the Greenland Sea, Anderson et al. (1999) applied a ventilation model giving an annual renewal by deep water formation of around 1% below 1500 m, corresponding to a mean ventilation of  $0.17 \pm 0.05$  Sv. This ventilation gave a sequestering of anthropogenic carbon dioxide, which in 1995 equaled  $2.4 \pm 0.7 \times 10^{12} \text{ g C yr}^{-1}$ .

Carbon is also transported from the surface to the abyss by the biological pump, i.e., biologically produced particles, both living plankton and dead organic matter. The new production in the Greenland Sea has been reported to  $57 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Noji et al., 1996). Of this new production,  $1.7 \text{ g C m}^{-2} \text{ yr}^{-1}$  is found as total organic carbon in sediment traps at both around 1000 and 2000 m depth (Noji et al., 1996). An additional flux of carbon is attributed to vertical migration of zooplankton to deep waters (down to 2000 m) during the winter season, which can add a net flux of  $3.5 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Noji et al., 1996). Furthermore, dissolved organic carbon can be transported from the surface layer in the fall by vertical mixing with DOC-poor underlying waters (Carlson et al., 1994).

The different surface water processes are essential for both the physically and biologically mediated vertical carbon flux. These processes are seasonal, with cold winters of low biological activity and relatively warm summers with high biological activity. In this work we investigate the seasonal evolution of nitrate and dissolved inorganic carbon in the surface water during the mid 1990s and apply a box model to elucidate the carbon fluxes by air-sea exchange, biological activity and vertical mixing to and from this surface water.

## 2. Analytical methods

Nitrate was determined using a standard spectrophotometric technique (Grasshoff, 1983). The

precision and accuracy of the nitrate determination should be significantly higher than the variability within the data set of each cruise.

All total dissolved inorganic carbon ( $C_T$ ) determinations were performed by gas extraction from acidified samples followed by coulometric titration (Johnson et al., 1985; 1987). The precision was better than  $\pm 1 \mu\text{mol kg}^{-1}$ , determined as the standard deviation of replicate analyses on samples. The accuracy was set by running a certified reference material supplied by A. Dickson (Scripps Institution of Oceanography, USA) at each change of cell solution. The precision when analysing the reference water was the same as for samples, and the ratio of the certified concentration to the measured was used to correct the seawater samples. The absolute correction was less than  $20 \mu\text{mol kg}^{-1}$  and as the sample concentration and that of the reference water deviated less than  $200 \mu\text{mol kg}^{-1}$ , this one point calibration should be sufficient for the accuracy to be within double the precision.

Total alkalinity ( $A_T$ ) was determined by titrating the samples with 0.1 M HCl and measuring the change in pH with a potentiometric method (Haraldsson et al., 1997). The estimate of precision for  $A_T$  followed the same procedures as for  $C_T$ , and was better than  $\pm 2 \mu\text{mol kg}^{-1}$  during all cruises. Also the accuracy for  $A_T$  was determined by analysing the Dickson reference material for all cruises after 1995, when it was certified for  $A_T$ . As the precision when running the reference material was the same as when analysing samples, the accuracy should be within double that of the precision.

## 3. Data

The data used in this evaluation was collected during the European Subpolar Program (ESOP) and complemented by a few nitrate data available from ICES data centre (Table 1). All data used were collected in the central Greenland Sea (73 to 78°N and 15°W to 5°E, Fig. 1). The mean profiles in the upper 200 m of nitrate, normalized  $C_T$  and normalized  $A_T$  for the different cruises are presented in Fig. 2.

For the evaluation of the seasonal variability of the total dissolved inorganic carbon concentration and total alkalinity, data were collected in the

Table 1. *Cruise information*

| Expedition             | Time<br>(Julian day) | NO <sub>3</sub> <sup>-</sup> | C <sub>T</sub> |
|------------------------|----------------------|------------------------------|----------------|
| Hakon Mosby, 1994      | 50                   | y                            | y              |
| Hakon Mosby, 1995      | 55                   | n                            | y              |
| Hakon Mosby, 1997      | 70                   | y                            | y              |
| Hakon Mosby, 1994      | 70                   | y                            | y              |
| Johan Hjort, 1997      | 105                  | n                            | y              |
| Johan Hjort, 1993      | 125                  | y                            | n              |
| Johan Hjort, 1995      | 135                  | y                            | y              |
| Johan Hjort, 1994      | 150                  | y                            | y              |
| James Clark Ross, 1996 | 180                  | y                            | y              |
| Johan Hjort, 1993      | 220                  | y                            | y              |
| Johan Hjort, 1998      | 225                  | n                            | y              |
| BS, 1972               | 235                  | y                            | n              |
| Johan Hjort, 1995      | 315                  | y                            | y              |
| Hakon Mosby, 1996      | 315                  | y                            | y              |

Julian days during which the data used in this work were collected, with the notation y (yes) and n (no) indicating whether nitrate and/or total dissolved inorganic carbon (C<sub>T</sub>) were determined.

time period 1993 to 1997. Using only these recent data for the carbonate system has two advantages, one being that the analytical technique has developed significantly during the last 10 years (introduction of the coulometric technique and the availability of reference material, Dickson and Goyet, 1994) and the second that a short time period minimizes the problem with the time-dependent anthropogenic contribution. Total alkalinity is not affected by this anthropogenic contribution. The concentration of  $A_T$  normalized to a salinity of 35 is fairly constant over the year,  $2293 \pm 12 \mu\text{mol kg}^{-1}$  ( $n = 219$ ) in the surface water (Fig. 2c). The normalized  $C_T$  concentration on the other hand shows a seasonal trend in the top 30 m (Fig. 3a). From the fit to the normalized  $C_T$  and the constant normalized  $A_T$  together with a fit to the observed salinity, the  $C_T$  and  $A_T$  concentration functions were computed. These in turn were used together with salinity and temperature to calculate the fugacity of carbon dioxide ( $f\text{CO}_2$ , Fig. 3b) using the carbonate system speciation program of Lewis and Wallace (1998).

In order to evaluate the air–sea flux of  $\text{CO}_2$ , the difference in  $f\text{CO}_2$  between the atmosphere and the surface mixed layer, as well as the wind speed was needed. The atmospheric  $f\text{CO}_2$  was taken in 1992 from weather station “Mike” in the Norwegian Sea (Conway et al., 1994), while the

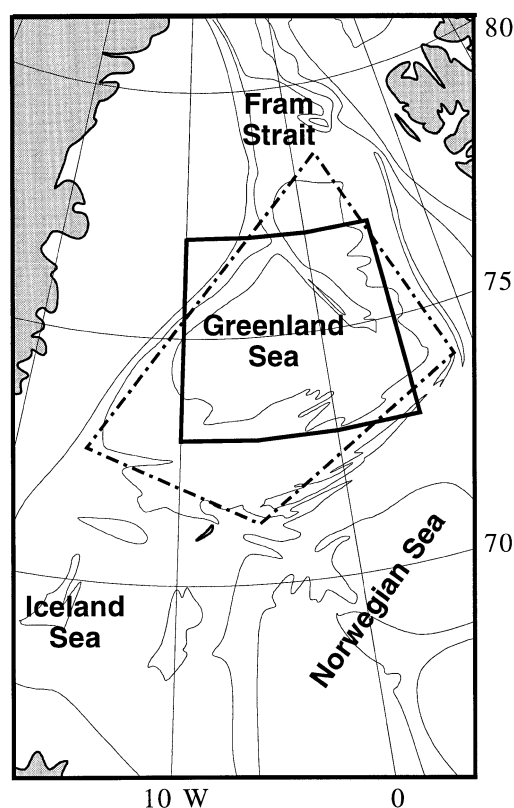


Fig. 1. Map of the Greenland Sea. The data have been collected in the area within the solid line. The area used for the computation of the total fluxes is within the dotted line.

wind speed for years 1993 to 1997 (Fig. 3c) was taken from the synoptic surface wind data within the NCEP/NCAR reanalysis project (Kalnay et al., 1996).

#### 4. The model computations

For the evaluation of the fluxes we apply a simple box model (schematically illustrated in Fig. 4). The model follows the concentration changes in the surface water over a year with time steps of one day. In the initial state we assume that the horizontal in- and out-flux are balanced. To avoid the problem with varying depth of the surface mixed layer we compute the deficit in the top 150 m, relative to the mean concentration in the subsurface water (150 to 300 m). This is done

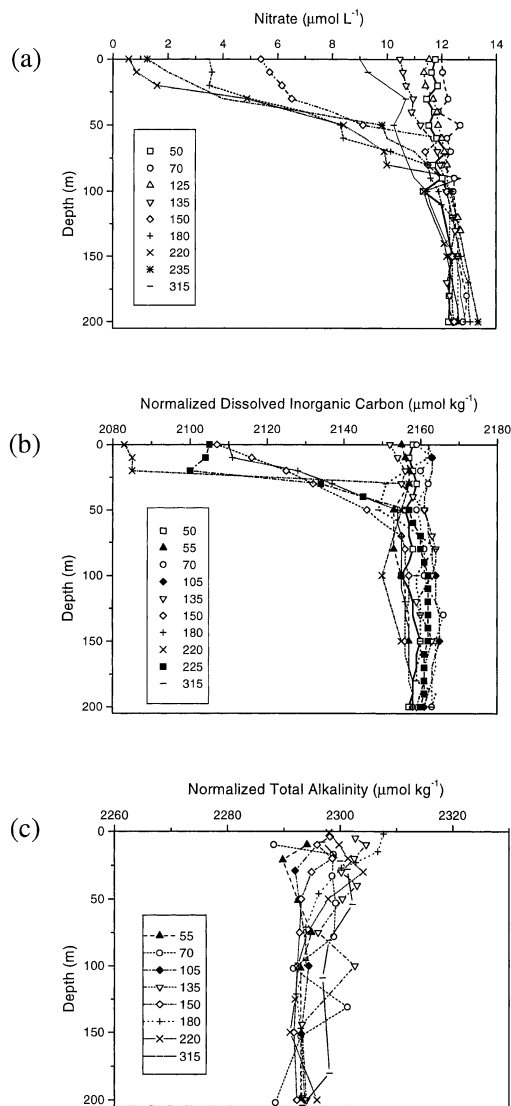


Fig. 2. Mean depth profiles of (a) nitrate, (b) total dissolved inorganic carbon (normalized to a salinity of 35) and (c) total alkalinity (normalized to a salinity of 35) for each cruise in the upper 200 m of the central Greenland Sea. The numbers indicate the average Julian day of observations.

by subtracting the concentration ( $\text{mol m}^{-3}$ ) at every 10 m interval between the surface and 150 m (Fig. 2) from the mean subsurface water concentration ( $\text{mol m}^{-3}$ ), multiplying them by 10 and add them all together. The deficits are plotted versus Julian day and annual functions are manu-

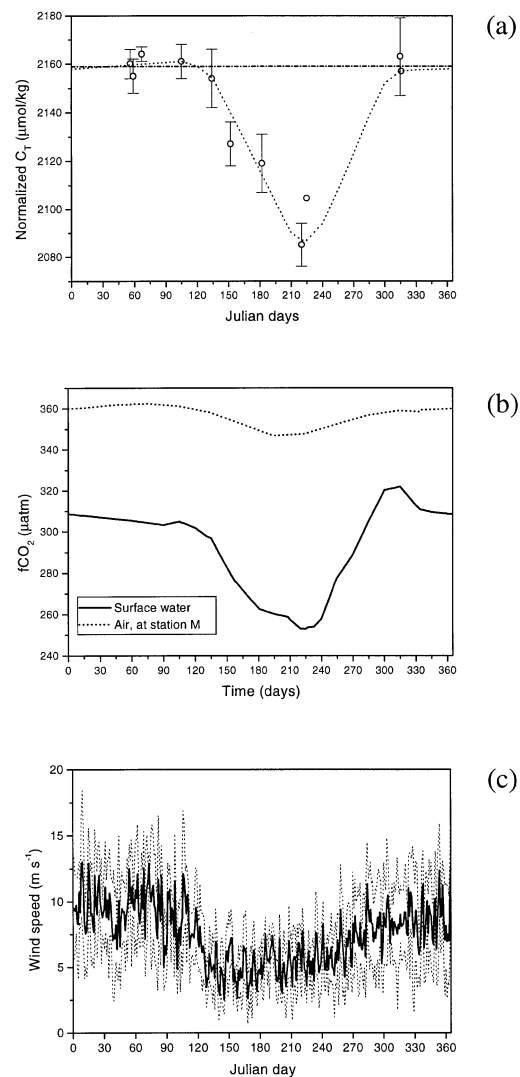


Fig. 3. The average properties in the top 30 m of (a) total dissolved inorganic carbon, normalized to a salinity of 35 ( $NC_T$ ), (b)  $f\text{CO}_2$  computed from  $NC_T$ , total alkalinity, salinity, temperature and phosphate concentrations, together with the atmospheric record from weather ship "Mike", and (c) the synoptic 24-h surface wind (mean, solid line,  $\pm$  standard deviations, dotted lines, for the years 1993 to 1997).

ally fitted to the deficits of nitrate and  $C_T$  (Fig. 5). These functions are used in the further evaluation.

The model describes the volumetric enhancement of nitrate in the surface water (SW) during winter time, and is based on a mixed layer model

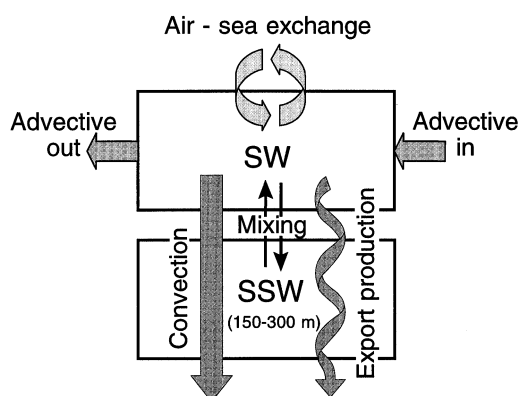


Fig. 4. Schematic illustration of the processes considered in the model used for the evaluation, where SW equals the surface water (0–150 m depth) and SSW equals the subsurface water (150–300 m depth).

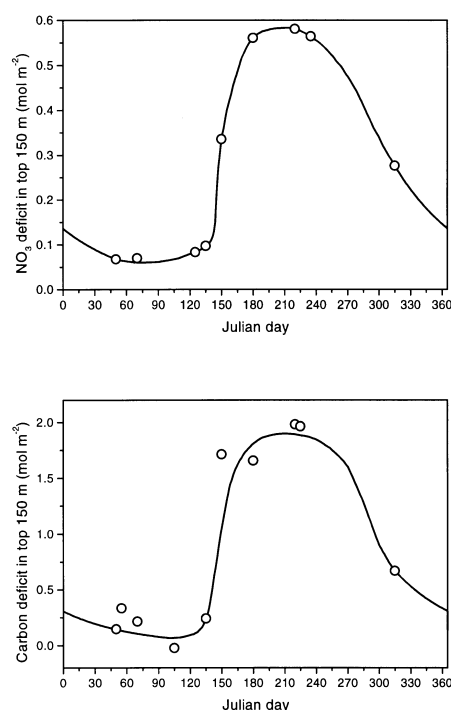


Fig. 5. The deficit of (a) nitrate and (b)  $C_T$  in the top 150 m (relative to the mean concentration in the depth range 150–300 m). The points represent the data from the different cruises, except for the one at Julian day 315, which is computed from two cruises as mainly surface water data are available from the Hákon Mosby, 1996 cruise. Lines have manually been fitted to the data points.

developed for idealised annual plankton cycles (Evans and Parslow, 1985). If the thickness of the surface water (SW) is  $H$  (m), the evolution of  $H$  is expressed by

$$\frac{dH}{dt} = m_v, \quad (1)$$

where  $t$  (d) is time, and  $m_v$  ( $\text{m d}^{-1}$ ) is the rate of change of  $H$ . During winter  $H$  increases and  $m_v > 0$ . The average concentration of nitrate in the SW,  $N_{\text{SW}}$  ( $\text{mmol m}^{-3}$ ), can then be expressed by the equation

$$\frac{dN_{\text{SW}}}{dt} = \frac{m_v}{H} (\overline{N_{\text{SSW}}} - N_{\text{SW}}), \quad (2)$$

where  $\overline{N_{\text{SSW}}}$  ( $\text{mmol m}^{-3}$ ) is the mean subsurface water (SSW) nitrate concentration over the depth interval 150 to 300 m.

The nitrogen deficit  $D_N$  ( $\text{mmol m}^{-2}$ ) is defined as the difference between the mean subsurface concentration and the surface water concentrations of nitrate, according to

$$D_N = \int_{z=0}^{150} (\overline{N_{\text{SSW}}} - N_{\text{SW}}) dz. \quad (3)$$

Since the subsurface concentration of nitrate is relatively constant during winter, we have that

$$\frac{d\overline{N_{\text{SSW}}}}{dt} \approx 0. \quad (4)$$

Eq. (2) can hence be put in the form

$$\frac{dD_N}{dt} \approx -\frac{m_v}{H} D_N. \quad (5)$$

If one considers the deficit of nitrogen over the uppermost 150 m of the water column, eq. (5) can be expressed as:

$$\frac{dD_N}{dt} \approx -\frac{m'_v}{150} D_N, \quad (6)$$

where  $m'_v$  ( $\text{m d}^{-1}$ ) is a modified (or scaled) rate of change of  $H$  given by

$$m'_v = m_v \frac{150}{H}, \quad (7)$$

$m'_v$  can be determined directly from eq. (6)

$$m'_v \approx -\frac{150}{d^{\text{end}} - d^{\text{start}}} (\ln D_N^{\text{end}} - \ln D_N^{\text{start}}), \quad (8)$$

where  $d^{\text{start}}$  and  $d^{\text{end}}$  are the starting and ending

day of integration with nitrogen deficits  $D_N^{\text{start}}$  and  $D_N^{\text{end}}$ , respectively.

We have used the time period from Julian day 315 to Julian day 50 to determine  $m'_v$  ( $d^{\text{end}} - d^{\text{start}} = 100$  days). This time period has been chosen since biological activity should be at minimum at this time of the year (Sverdrup, 1953), so changes in the surface water concentration of nitrate is mainly governed by deepening of the surface layer. Furthermore, it is the period from the latest measurements in the fall to the earliest in the winter. It is found that a daily increase in  $H$  corresponding to  $m'_v = 2.1 \text{ m d}^{-1}$  is needed to decrease the deficit as shown in Fig. 5 from  $0.276 \text{ mol m}^{-2}$  at day 315, to  $0.067 \text{ mol m}^{-2}$  at day 50.

Following this we apply the obtained value of  $m'_v$  to both the nitrate and  $C_T$  functions when the density stratification is less than 0.1 sigma units, that is from day 328 to day 158, as evaluated from the  $T$ - $S$  properties in the top 200 m (covering the interface between the surface and the subsurface waters). When the density gradient is larger, a constant background mixing is assumed.

The background mixing velocity  $m'_v$  during the stratification period is not easily determined. However, for a tracer concentration  $C$  ( $\text{mol m}^{-3}$ ),  $m'_v$  can be expressed as (Smolarkiewicz, 1983)

$$m'_v = \frac{K_v}{C} \frac{\partial C}{\partial z}, \quad (9)$$

where  $K_v$  ( $\text{m}^2 \text{ s}^{-1}$ ) is the vertical mixing coefficient, and  $\partial C / \partial z$  denotes the change of  $C$  over a vertical distance  $z$  (m). From Fig. 2a, we have that for the uppermost 150 m of the water column,  $\partial \text{NO}_3 / \partial z$  can be approximated as  $10/150 \text{ } \mu\text{mol l}^{-1} \text{ m}^{-1}$ , and that a typical (mean) value of nitrate is  $6 \text{ } \mu\text{mol l}^{-1}$ . Therefore, for  $K_v$  equal to  $1 \cdot 10^{-4} \text{ m}^2 \text{ s}^{-1}$  (Drange, 1994), we get that  $m'_v$  is  $0.1 \text{ m d}^{-1}$ . This value is similar to the value used by Fasham et al. (1990) for zero-dimensional ecosystem modelling in the North Atlantic. Based on the uncertainties involved in determining  $m'_v$ , we consider  $m'_v$  to be bracketed by  $0.05 \text{ m d}^{-1}$  and  $0.2 \text{ m d}^{-1}$ , with the value  $0.1 \text{ m d}^{-1}$  as our base case.

The time period with density difference less than 0.1 unit is longer than the time period used to evaluate the vertical mixing, biological activity occurs towards the end of this period. In the spring the nitrate and  $C_T$  concentrations decrease before the density gradient develops, which is

likely the result of a combination of local primary production and occasional mixing events (see Eilertsen (1993) and Townsend et al. (1992) for a discussion of phytoplankton spring blooms in the absence of stratification).

The daily flux of nitrate and  $C_T$  to the surface water by vertical mixing is computed using the above value of  $m'_v$  for the different time periods and the deficit functions of Fig. 5. The change in the fitted nitrate deficit, from one day to the next, that is not caused by vertical mixing, is attributed to biological processes, assuming that no other process affects this concentration. This computation can not be performed using the  $C_T$  function, as also air-sea flux effects it. The daily change in nitrate deficit is converted to carbon equivalents by using a  $C/N$  ratio of 7.5 as measured in organic matter collected in the Greenland Sea (Rey, unpublished data). The corresponding change in carbon units does thus represent the net effect of biological production and decay in the surface water.

The daily flux of carbon caused by vertical mixing and biological activity is shown in Fig. 6. As seen a significant flux of carbon from below occurs in the spring before stratification builds up. This vertical flux of carbon is a function of the mixing rate and the difference in carbon concentration between the surface and subsurface water. The relatively high flux in the spring is a result of the fact that the increase in  $C_T$  deficit starts around day 140 (Fig. 5b), while the stratification, hampering the vertical mixing, does not start until day 158, see above. For the same reason the flux increases in the fall (around day 330) when the stratification breaks down. The discontinuity in the vertical flux in Fig. 6 is a result of the simplified mixing formulation applied, see above.

The flux due to biological activity in Fig. 6 shows a strong negative peak associated with the spring bloom around day 140 and the production continues to be larger than the decay to around day 200, after which the flux gets positive when the decay of organic matter is larger than the productivity. Adding the fluxes over the year results in a flux of  $11 \text{ g C m}^{-2} \text{ yr}^{-1}$  from below and an export production of  $34 \text{ g C m}^{-2} \text{ yr}^{-1}$ . The annual export production is computed from the nitrate consumed in the surface water. As the only source of nitrate in our computation is the vertical

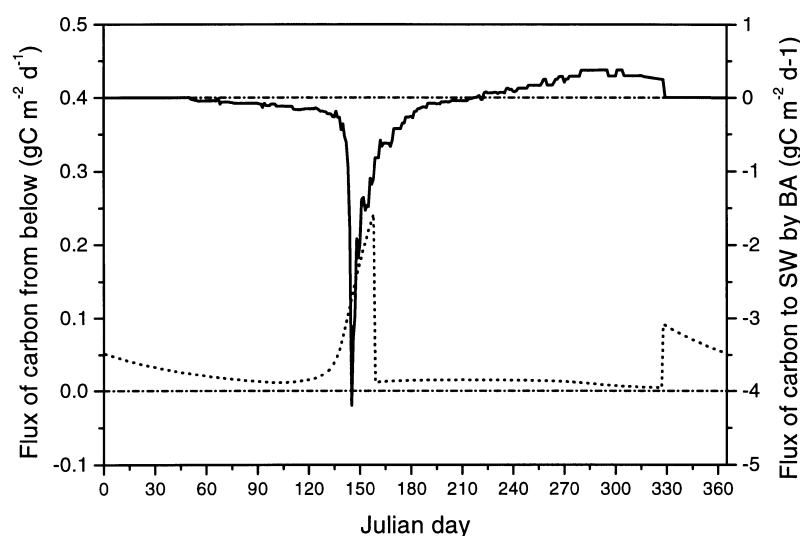


Fig. 6. The computed daily flux of carbon into the surface water (SW), caused by mixing from below (dotted line) and by biological activity (BA) (solid line). Note the order of magnitude difference in the two scales.

mixing, the annual export production is proportional to the flux of nitrate from below.

If the computed fluxes are assumed to be constant in the open deep Greenland Sea, we can compute the total flux by subtracting the ice covered part of the deep Greenland Sea area of  $0.36 \times 10^{12} \text{ m}^2$  (dotted line in Fig. 1). In Fig. 7, the relative ice cover over this region is shown for the years 1993 to 1997 (Kalany et al., 1996), the period during which the carbon system was studied. When the daily variability of the ice cover for the years 1993 to 1997 are used together with the daily carbon fluxes (Fig. 6), the computed total fluxes equal  $3.3 \pm 0.3 \times 10^{12} \text{ g C yr}^{-1}$  from below and  $10.4 \pm 1.6 \times 10^{12} \text{ g C yr}^{-1}$  as export production. The stated uncertainty is a result of the variability in the ice cover over the period 1993 to 1997.

## 5. Air–sea exchange

The flux of  $\text{CO}_2$  over the air–sea interface,  $F$ , is a function of the difference in fugacity and wind speed, plus some parameters related to the properties of the  $\text{CO}_2$  gas, according to:

$$F = 0.31u^2 K_0 \sqrt{\frac{660}{Sc}} \Delta f \text{CO}_2, \quad (10)$$

where  $K_0$  is the solubility of  $\text{CO}_2$ ,  $u$  is the 10 m wind speed (synoptic NCAR/NCEP surface wind data),  $Sc$  is the Schmidt number and  $\Delta f \text{CO}_2$  is the difference in fugacity between the atmosphere and that of the very surface water (Wanninkhof, 1992). In our computation we have used the mean value in the top 30 m of the water column (see Section 3) and the  $\Delta f \text{CO}_2$  is always positive and largest during the productive summer (Fig. 3b). However, during the winter the wind is stronger (Fig. 3c), resulting in a variable flux over the year but with no clear trend (Fig. 8). The short time variability is mainly caused by the variable wind field.

The daily fluxes presented in Fig. 8 are the averages  $\pm$  the standard deviations caused by the wind for the years 1993 to 1997. The atmospheric  $f \text{CO}_2$  record used for the different years is the annual record of 1992 at weather station “Mike” (Conway et al., 1994) plus  $1.6 \mu\text{atm}$  per year in order to compensate for the build up of atmospheric  $\text{CO}_2$  by anthropogenic emissions. The small error in the atmospheric record by this approach is negligible in relation to the  $\Delta f \text{CO}_2$ , which is in the range 50 to  $100 \mu\text{atm}$ .

The summarized air–sea flux over the years 1993 to 1997 adds up to  $52.9 \pm 3.5 \text{ g C m}^{-2} \text{ yr}^{-1}$ , which represents the averaged flux in the open

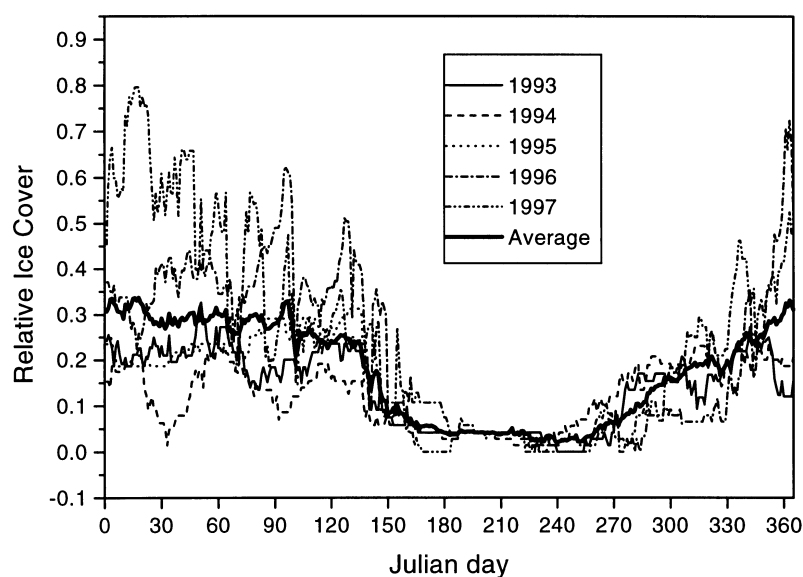


Fig. 7. The relative ice cover of the deep Greenland Sea for the years 1993 to 1997. The full line represents the annual average ice cover for this time period.

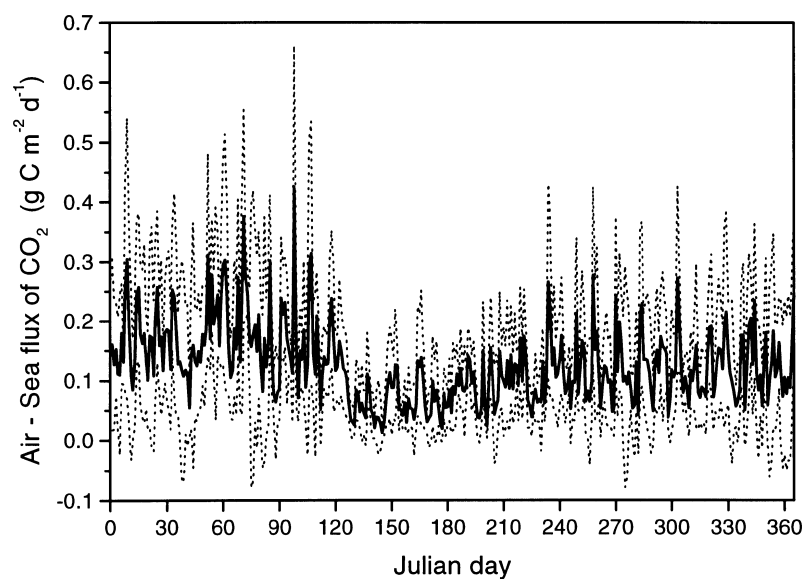


Fig. 8. The daily flux of  $\text{CO}_2$  from the atmosphere to the sea, as computed from the surface wind for the years 1993 to 1997 and the difference in fugacity over the air–sea interface. The atmospheric  $f\text{CO}_2$  record is corrected to correspond to the year of the surface wind used.

ocean. This value agrees well with that estimate by Hood et al. (1999) of  $55 \text{ g C m}^{-2} \text{ yr}^{-1}$ , based on a combination of buoy data and sea surface temperature relationships. Both estimates are

based on the Wanninkhof (1992) formulation for gas exchange using synoptic wind.

Sea ice has to be considered when the total flux of carbon dioxide into the Greenland Sea is com-

puted as a large fraction of the region is covered by ice. A combination of the daily air–sea carbon dioxide flux (Fig. 8) and the daily open water area of the deep Greenland Sea (Fig. 7) for each of the years 1993 to 1997, results in an average annual flux of  $15.4 \pm 1.4 \times 10^{12}$  g C. The error in this estimate is a combination of the variability in wind speed and sea ice cover during the period.

## 6. Uncertainties

The above calculations are based on several assumptions that give rise to uncertainties. The first and probably most critical is how much the measured data vary between the years and how well the fitted line of the annual deficit of nitrate and  $C_T$  represents an “average year”? This question can only be addressed by looking at how well the measured data follow a general trend in Fig. 5. As is obvious, the nitrate data fall close to the fit, while the  $C_T$  data show more scatter. The latter might be a result of both interannual variability and variability within the observed concentrations of one data set. The latter variability (illustrated in Fig. 3a) is another general error, which results in an uncertainty in the deficit estimates of approximately 10%. Hence, we conclude that the approach of combining the different years is acceptable as the largest error is caused by the uncertainty in the deficit estimates for each time period.

The nitrate deficit in the spring, before primary production occurs, is relatively constant (Fig. 5a). The computation of the entrainment of subsurface water into the surface water is directly related to this deficit as well as the starting deficit in the fall. The latter is based on one data set (Julian day 315) and will thus give a corresponding uncertainty in the vertical flux. As the annual export production is proportional to the vertical flux of nitrate (see Section 4), the uncertainty will also be reflected in this estimate. On the other hand a corresponding change of the vertical flux of  $C_T$  will result, and hence the relation of export production to vertical flux of  $C_T$  will not be significantly affected. For example, if the mixing during the summer season,  $m'_v = 0.1 \text{ m d}^{-1}$ , is set to the bracketing values  $0.05 \text{ m d}^{-1}$  ( $2 \text{ m d}^{-1}$ ), the modelled biological production changes from 34 to  $32 \text{ g C m}^{-2} \text{ yr}^{-1}$  ( $39 \text{ g C m}^{-2} \text{ yr}^{-1}$ ), while the

mixing of  $C_T$  up into the surface water changes from 11 to  $10 \text{ g C m}^{-2} \text{ yr}^{-1}$  ( $13 \text{ g C m}^{-2} \text{ yr}^{-1}$ ).

In the estimate of biological activity we have neglected atmospheric deposition of nitrogen, as well as all other species of nitrogen except nitrate in the water column. The first will underestimate the annual primary production, while the second will have a minor impact in the annual budget. However, if we had full control over all the nitrogen species, the shape of the deficit curve might have been slightly different, changing the flux distribution of carbon caused by biological activity.

The use of the measured  $C/N$  ratio of 7.5 is in the range of reported values between 7 and 8.5 for decay of organic matter (Jones et al., 1984; Takahashi et al., 1993; Anderson and Sarmiento, 1994; Wallace et al., 1995). Hence, the variability of the computed export production is about  $\pm 10\%$  if this span of  $C/N$  ratios is considered. The above uncertainties for the export production and vertical mixing of  $C_T$  would add up to a total uncertainty of about 20%.

The computed air–sea flux of carbon dioxide is based on the formulation of Wanninkhof (1992) which includes some uncertainties. These uncertainties have been much debated (Liss and Merlivat, 1986; Watson et al., 1991; Wanninkhof, 1992; Keeling, 1993), and we do not go into any detailed discussion on this topic. We only stress that the computed values most likely include an uncertainty of at most a factor 2.

## 7. Summary and conclusions

The different computed fluxes are summarized in Table 2, where the horizontal flux is given to balance the budget. The largest absolute carbon flux to the surface water in the Greenland Sea is a result of the spring bloom around Julian day 140 (Fig. 9). The rest of the year the daily flux is fairly low, but is mainly into the surface water adding up to a total of  $30 \text{ g C m}^{-2}$  for the whole year.

The fluxes of carbon to the surface water of the Greenland Sea by different processes considered in our computations result in this build up of carbon in the surface water which is significantly larger than the uncertainties of the model computations. This build up must correspond to the net

Table 2. A summary of the annual computed mean carbon fluxes to the surface water (SW) of the Greenland Sea (GS) during the years 1993 to 1997

| Process                        | Fluxes to the SW of the GS          |                               |
|--------------------------------|-------------------------------------|-------------------------------|
|                                | $\text{g C m}^{-2} \text{ yr}^{-1}$ | $10^{12} \text{ g C yr}^{-1}$ |
| air-sea flux                   | $52.9 \pm 3.5^{(a)}$                | $15.4 \pm 1.4^{(a)}$          |
| export production              | $-34^{(b)}$                         | $-10.4 \pm 1.6^{(a)}$         |
| vertical mixing of $C_T$       | $11.3^{(b)}$                        | $3.3 \pm 0.3^{(a)}$           |
| summary                        | $30 \pm 8$                          | $8 \pm 2^{(a)}$               |
| horizontal flux <sup>(c)</sup> | $-30 \pm 8$                         | $-8 \pm 2^{(a)}$              |
| total                          | 0                                   | 0                             |

<sup>(a)</sup> The noted errors are only due to the variability in wind field and sea ice extent during the time period.

<sup>(b)</sup> Error is estimated to be in the order 20%, see text.

<sup>(c)</sup> Computed to balance the budget.

horizontal flux, in order to balance the budget for the surface water. A horizontal net flux corresponding to  $30 \text{ g C m}^{-2} \text{ yr}^{-1}$  gives that the top 150 m of the outflowing water has a concentration of  $C_T$  that is  $20 \mu\text{mol kg}^{-1}$  higher than that of the inflowing water. This increase of  $C_T$  is likely a result of that the outflowing water is colder than the inflowing and thus has a higher solubility of  $\text{CO}_2$ . Surface water in contact with the atmosphere at these latitudes will increase the concentration of dissolved inorganic carbon by close to

$10 \mu\text{mol kg}^{-1}$  for each degree the water get colder, if it keeps the same relative  $\text{CO}_2$  saturation. Hence, a temperature decrease of the surface water during its stay in the Greenland Sea of about  $2^\circ\text{C}$  will explain the computed carbon build up. Such a temperature change is about what has been observed during all seasons between the surface waters in the Norwegian Atlantic Current and those north east of Iceland (Gathman, 1986).

From the above it is concluded that our assumption that the horizontal in- and out-flux are balanced, does not hold for  $C_T$ . However, it is more likely that this is the case for nitrate, as nitrate does not have an atmospheric source or sink (at least marginal in this area). Furthermore, it is only for nitrate that the assumption is critical, as the computation of biological activity relies on no other sources or sinks than vertical mixing. The computations based on the  $C_T$  measurements are not affected by the imbalance in the horizontal fluxes.

The annual export production as estimated by this method is proportional to the addition of nitrate to the photic zone through vertical mixing. This vertical mixing also adds  $C_T$  to the surface water. The difference between the export production and addition of  $C_T$  from below,  $23 \text{ g C m}^{-2} \text{ yr}^{-1}$ , is close to 50% of the air-sea exchange. Hence, the annual flux of carbon dioxide

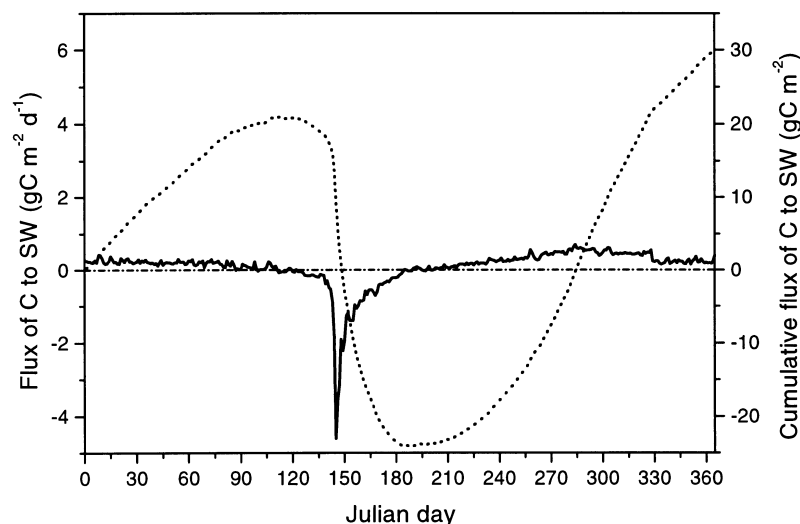


Fig. 9. A summary of the fluxes to the surface water (SW) over the year, both on a daily basis (solid line) and cumulative (dotted line).

from the atmosphere into the surface water of the Greenland Sea is equally driven by heat exchange, lowering the surface water temperature and thus also increasing the solubility of carbon dioxide, and the biological primary production, lowering the surface water  $f\text{CO}_2$ . However, the primary production causes a larger decrease in the surface water  $f\text{CO}_2$  than the heat loss does, but the corresponding difference in the gas exchange is reduced due to the relatively low wind speeds during the summer season.

The different fluxes (Table 2) are between 1.4 and 6.4 times larger than the sequestering of anthropogenic  $\text{CO}_2$  deeper than 1500 m (Andreson et al., 1999). This sequestering is a result of the ventilation to these depths with water having an anthropogenic concentration of  $36 \mu\text{mol kg}^{-1}$  and does not consider where the

anthropogenic  $\text{CO}_2$  was taken up by the surface ocean. In fact most of the anthropogenic  $\text{CO}_2$  is taken up by the surface water outside the Greenland Sea. Hence, it is not possible to discuss the anthropogenic flux in relation with the ones evaluated in this work in any other way than to compare the numbers.

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