

# CO<sub>2</sub> air-sea exchange in the Nordic Seas. An attempt to make an estimate based on data

CO<sub>2</sub>  
Air-sea exchange  
Nordic Seas  
Gas exchange

CO<sub>2</sub>  
Échange air-mer  
Mers nordiques  
Échange de gaz

Lena LUNDBERG

Department of Oceanography, University of Gothenburg, Box 4038, S-400 40 Gothenburg, Sweden.

Present address: Geophysical Institute, University of Bergen, Allégaten 70, N-5007 Bergen, Norway.

Received 26/04/93, in revised form 17/01/94, accepted 24/01/94.

## ABSTRACT

The net air-sea exchange of CO<sub>2</sub> in the ocean area enclosed by the Fram Strait in the north and by the Greenland-Scotland ridge in the south is estimated on the basis of oceanic pCO<sub>2</sub> data from three different expeditions. The data comprise observed pCO<sub>2</sub> as well as pCO<sub>2</sub> calculated from data on dissolved inorganic carbon (C<sub>T</sub>), total alkalinity (TA) and pH. Data on atmospheric content of CO<sub>2</sub> are available from two of the expeditions and are supplemented with monthly mean values from ocean station "M" (66°N, 2°E). Wind speed drawn from a data set with a spatial resolution of 75 km and a temporal resolution of six hours are used in the calculation. The pCO<sub>2</sub> data are interpolated to the same spatial resolution as that of the wind speed data, before calculating the net flux.

The objective of this work is to supplement earlier estimates of the net CO<sub>2</sub> flux between atmosphere and ocean in the Nordic Seas, and to find a plausible shape of the seasonal variation of the net CO<sub>2</sub> air-sea exchange. The calculations, performed with the parameterization of the gas exchange coefficient according to Liss and Merlivat (1986), give a net uptake by the Nordic Seas of atmospheric CO<sub>2</sub> amounting to approximately 2.4 moles C m<sup>-2</sup> year<sup>-1</sup>. This is equivalent to 0.05 Gtonnes C year<sup>-1</sup>, if the ice-free area is assumed to be 1.7\*10<sup>12</sup> m<sup>2</sup>. The estimate is in the lower range of the earlier estimates.

Sensitivity tests of the calculated fluxes are performed as to the influence on the results by the choice of parameterization of the gas exchange coefficient, errors of observation in the pCO<sub>2</sub> data, choice of time scale of wind speed data and choice of interpolation method.

The sensitivity tests indicate that the largest variations of the individual net fluxes arise from the uncertainty of the parameterization of the gas transfer and in the case of pCO<sub>2</sub> calculated from C<sub>T</sub>, TA and pH, also from errors of observation. The results from three different equations of gas transfer (Liss and Merlivat, 1986; Tans *et al.*, 1990; Wanninkhof, 1992) are compared. The parameterizations by Tans *et al.* and by Wanninkhof result in an increase of the estimated net fluxes of approximately 75 % compared to the net fluxes obtained by using the equations by Liss and Merlivat. Regarding the situation examined here, this uncertainty corresponds to an error of observation in oceanic pCO<sub>2</sub> of 3-11 %. The choice of time scale of the wind speed data and the choice of interpolation method do not seem to be of the same significance as far as the uncertainty of the result is concerned. Another uncertainty of the estimated yearly net flux arises from the fact that the pCO<sub>2</sub> data are very sparse in time, but the magnitude of this uncertainty is difficult to estimate.

*Oceanologica Acta*, 1994. 17, 2, 159-175.

## RÉSUMÉ

Échange de CO<sub>2</sub> atmosphère-océan dans les mers nordiques. Une tentative d'estimation expérimentale

Une estimation de l'échange net atmosphère-océan de CO<sub>2</sub> dans la zone délimitée au nord par le détroit de Fram, et au sud par la chaîne sous-marine reliant l'Écosse au Groenland, est effectuée sur la base de données provenant de trois expéditions. Les mesures du pCO<sub>2</sub> océanique proviennent d'observations directes, ainsi que de résultats calculés à partir des mesures du carbone inorganique dissous (C<sub>i</sub>), de l'alcalinité totale (TA) et du pH. Le pCO<sub>2</sub> atmosphérique provient d'observations effectuées lors de deux des trois expéditions, complétées par des valeurs moyennes mensuelles de la station "M" (66°N, 2°E). Des données sur la vitesse du vent, avec une résolution spatiale de 75 km et une résolution temporelle de six heures, sont utilisées pour calculer le flux net, et une interpolation des données du pCO<sub>2</sub> est effectuée afin d'obtenir la même résolution spatiale.

Le but de ce travail est de compléter les estimations précédentes du flux net atmosphère-océan de CO<sub>2</sub> dans les mers nordiques, et de déduire une forme plausible pour les variations saisonnières de l'échange net de CO<sub>2</sub>. Les résultats, obtenus selon la paramétrisation d'échange gazeux de Liss et Merlivat (1986), indiquent une absorption marine nette de CO<sub>2</sub> d'environ 2.4 moles C m<sup>-2</sup> par année. Ceci correspond à 0.05 Gtonnes C par année, si la surface libre de glace est estimée à 1.7\*10<sup>12</sup> m<sup>2</sup> ; ce résultat est relativement inférieur aux précédents.

De l'évaluation des influences dues aux erreurs de mesure, ou au choix de la paramétrisation du coefficient d'échange gazeux, de la résolution temporelle de la vitesse du vent, et de la méthode d'interpolation, il résulte que le choix de la paramétrisation et les incertitudes du pCO<sub>2</sub>, calculés à partir des mesures de C<sub>i</sub>, TA et pH, affectent de manière importante les estimations du flux. Une comparaison des résultats, obtenus selon trois équations d'échange gazeux différentes (Liss et Merlivat, 1986; Tans *et al.*, 1990 ; Wanninkhof, 1992), indique que les paramétrisations de Tans *et al.* et de Wanninkhof augmentent les estimations du flux net d'environ 75 %, par rapport à celle obtenue avec la paramétrisation de Liss et Merlivat. Pour les cas considérés lors de cette étude, cela correspond à une erreur de mesure du pCO<sub>2</sub> océanique de 3-11 %.

Par contre, la résolution temporelle de la vitesse du vent et la méthode d'interpolation ne les influencent que peu. Le fait que les données de pCO<sub>2</sub> soient mal réparties dans le temps contribue également à l'incertitude du flux annuel. Cependant, il est difficile d'en estimer la contribution.

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## INTRODUCTION

The Nordic Seas form a rather small ocean area in the North Atlantic, enclosed by the Fram Strait at approximately 80°N and by the Greenland-Scotland ridge slightly north of 60°N. Although comparatively small, this area has attracted a lot of interest with respect to, among other things, the air-sea heat exchange (*e. g.* McCartney and Talley, 1984), the deep water formation (*e. g.* Aagaard *et al.*, 1985), the exchange of water with the North Atlantic (*e. g.* Hansen, 1985) and also as a possible sink to atmospheric carbon dioxide, CO<sub>2</sub> (*e. g.* Takahashi *et al.*, 1985; Peng *et al.*, 1987) the latter being the question addressed here.

One of the first assessments of the net oceanic uptake of atmospheric CO<sub>2</sub> in the North Atlantic Ocean was done by Roos and Gravenhorst (1984). On the basis of oceanic pCO<sub>2</sub> data covering the time period 1903-1973, they estimated the net oceanic uptake to amount to 0.31-0.34 Gtonnes C year<sup>-1</sup> in the area between 50° and 80°N (0.17-0.20

Gtonnes C year<sup>-1</sup> between 60°N and 80°N). Tans *et al.* (1990) estimated the net oceanic CO<sub>2</sub> uptake north of 50°N to be somewhat less; 0.12-0.23 Gtonnes C year<sup>-1</sup>. Tans *et al.* also based their assessment on observational pCO<sub>2</sub> data but used a parameterization of the gas transfer velocity which was slightly different from that used by Roos and Gravenhorst.

In order to set the figures in a global perspective it can be mentioned that calculations based on oceanic carbon models give a global net uptake of atmospheric CO<sub>2</sub> of about 2 ± 0.8 Gtonnes C year<sup>-1</sup> by the oceans. (Houghton *et al.*, 1990). Tans *et al.* (1990) estimated the global oceanic CO<sub>2</sub> uptake to amount to approximately 1.6 Gtonnes C year<sup>-1</sup>, based on oceanic pCO<sub>2</sub> data. However, model simulations of the distribution of sources and sinks corresponding to the observed atmospheric pCO<sub>2</sub> distribution led Tans *et al.* to conclude that the global oceanic uptake is even smaller (0.3-0.8 Gtonnes C year<sup>-1</sup>) and that there exists a hitherto unrecognized terrestrial sink to atmosphe-

ric CO<sub>2</sub> on the northern hemisphere. Sarmiento and Sundquist (1992) revised these carbon budgets, arguing that the pre-industrial ocean was a net source to atmospheric CO<sub>2</sub> due to the net supply of carbon to the ocean by rivers and rain. They estimated the present oceanic uptake of atmospheric CO<sub>2</sub> as amounting to 1.09 Gtonnes C year<sup>-1</sup> (as net air-sea exchange, based on a revision of the budget by Tans *et al.*) or to 1.69 Gtonnes C year<sup>-1</sup> (based on an ocean carbon model). The difference, 0.60 Gtonnes C year<sup>-1</sup>, corresponds to the estimate of net outgassing of the pre-industrial ocean.

Returning to the contemporary air-sea exchange of CO<sub>2</sub> in the Nordic Seas, the different estimates agree on the fact that there is a yearly net uptake of atmospheric CO<sub>2</sub>. Regarding the seasonal variation of the uptake, Takahashi *et al.* (1985) concluded, on the basis of repeated measurements of surface water pCO<sub>2</sub> taken north of Iceland and data from the Transient Tracers in the Oceans-North Atlantic Study (TTONAS) 1981, that the yearly net flux of CO<sub>2</sub> from the atmosphere to the ocean, in the area of the Nordic Seas varies from approximately zero in winter time to 6 moles C m<sup>-2</sup> year<sup>-1</sup> in summer time.

Here sea-surface pCO<sub>2</sub> data from three different expeditions are combined. A plausible shape of the seasonal cycle of the CO<sub>2</sub> air-sea exchange is introduced and used to estimate the yearly net flux of CO<sub>2</sub> between the Nordic Seas and the atmosphere. A few sensitivity tests of the calculated fluxes are performed in order to obtain an indication of the uncertainty of the estimate. The results from three different parameterizations of the gas exchange coefficient are compared, the influence of errors of observation in pCO<sub>2</sub> is tested as well as the variation arising from whether the wind speed data are averaged in time or not, before calculating the net flux. Since all the pCO<sub>2</sub> data are spatially interpolated and since the choice of interpolation method may influence the result, the results from two different interpolation methods are compared. From two of the three expeditions there are surface water pCO<sub>2</sub> data from samples taken at hydrographic stations as well as from samples taken frequently when the ship was under way, which makes it possible to compare the results calculated from spatially scarce data with those based on spatially much denser data sets. However, since there are only three data sets available to represent the entire year, the estimated yearly net flux is impaired by an uncertainty, which is difficult to estimate, arising from the fact that it is known neither how the surface water pCO<sub>2</sub> varies between the different seasons, during which the data were collected, nor how well the data represent these seasons.

## MATERIALS AND METHODS

The data used in the calculation of the net air-sea exchange in the Nordic Seas are:

- Data from the TTONAS expedition, 25 July to 8 August 1981 (direct observations of pCO<sub>2</sub>, comprising more than 600 data, and data on C<sub>t</sub> and TA from sixteen hydrographic stations);

- Data from the R/V *Hudson* expedition, 26 February to 3 April 1982 (direct observations of pCO<sub>2</sub>, comprising more than one thousand data, and data on C<sub>t</sub> and TA from thirty hydrographic stations);

- Data from the R/V *Haakon Mosby* expedition, 14 August to 8 September 1991 (data on pCO<sub>2</sub>, C<sub>t</sub>, TA and pH from 28 hydrographic stations);

- Monthly mean values of atmospheric content of CO<sub>2</sub> from ocean station "M" (66°N, 2°E);

- Wind speed and atmospheric pressure data given every six hours in a grid covering the area of the Nordic Seas, with a grid size of 75 km × 75 km;

- Monthly mean values of the sea ice extension.

### Data on oceanic pCO<sub>2</sub>

The pCO<sub>2</sub> data from the TTONAS expedition (Transient Tracers in the Oceans-North Atlantic Study), which took place in summer 1981, comprise direct (ship track) observations of atmospheric pCO<sub>2</sub> as well as of oceanic pCO<sub>2</sub> (Weiss *et al.*, 1992), and data on TA, pCO<sub>2</sub> and C<sub>t</sub> from water sampled at hydrographic stations (Brewer *et al.*, 1986 *a*). Direct analyses of pCO<sub>2</sub> were carried out using ship-board gas chromatography. Water, from a nominal depth of 3 m, and air for direct pCO<sub>2</sub> observations were sampled approximately twice an hour, which corresponds to a spatial resolution of the data of approximately 10 km when the ship is under way. The method is further described by Weiss *et al.* (1992). The C<sub>t</sub> and TA data obtained at hydrographic stations are discussed by Brewer *et al.* (1986 *b*). Even though there are direct observations of pCO<sub>2</sub> obtained at hydrographic stations, only the data on TA and C<sub>t</sub> are used here. This is done in order to have the same type of data that are available from the R/V *Hudson* expedition, *i.e.* directly observed ship track pCO<sub>2</sub> data on the one hand, and pCO<sub>2</sub> calculated from observations of C<sub>t</sub> and TA at hydrographic station on the other hand. Only the data from the Nordic Seas are used here, even though data from outside this region are available from the TTONAS 1981 expedition.

The ship track pCO<sub>2</sub> data from the R/V *Hudson* expedition, which took place in winter 1982, are from Weiss *et al.* (1992) and obtained in the same way as the TTONAS 1981 ship track pCO<sub>2</sub> data. The C<sub>t</sub> and TA data from the R/V *Hudson* expedition (E.P. Jones, Bedford Institute of Oceanography, personal communication) are further discussed by Chen *et al.* (1990). Some of the *Hudson* data are from ice covered areas and these are excluded from the calculations discussed here. In a few cases it is difficult to distinguish whether or not the data are from ice-covered areas and the data are excluded if the surface water temperature is less than - 1.7°C. The TA, pCO<sub>2</sub> and C<sub>t</sub> data from the R/V *Hudson* expedition, as well as from the TTONAS expedition, are used only when salinity, temperature and silicate and phosphate concentrations were measured simultaneously.

The R/V *Haakon Mosby* expedition to the Nordic Seas took place between 14 August to 8 September 1991.

During the cruise, water samples for measurements of different components of the ocean carbon system, were taken at several hydrographic stations in the Nordic Seas area. Samples were collected with Niskin bottles mounted on a Neil Brown CTD. Shipboard analyses with respect to  $p\text{CO}_2$ , pH and dissolved inorganic phosphate were performed soon after sampling. Water samples for analyses of dissolved inorganic carbon and total alkalinity were stored in glass bottles and analysed after the cruise.

The  $p\text{CO}_2$  in sea water (unpublished data, S. Molander, Botanical Institute, University of Gothenburg, personal communication) was determined by infrared gas analysis (IRGA) of air equilibrated with the water sample, using an ADC 225 Mk 3 gas analyzer (ADC, Hoddesdon, UK). The instrument was run in the absolute measurement mode. The water samples were filled in Pyrex bottles and placed in a water-bath during equilibration with the air, which was circulated in a loop and bubbled through the sea water sample. The temperature of the samples was measured directly before and after the equilibration using a calibrated thermometer with a resolution of  $0.1^\circ\text{C}$ . The average temperature increase during the measurements was  $1.4^\circ\text{C}$ . A standard gas of  $\text{CO}_2$  in  $\text{O}_2$  was used to calibrate the instrument before and after each station. The standard gas was calibrated after the expedition, using gas mixtures ( $\text{CO}_2$  in air) calibrated at the Institute of Meteorology, University of Stockholm. The uncertainty concerning the observed  $p\text{CO}_2$  stems from various sources of errors originating both in the measurement process itself and in the subsequent calculations to evaluate the observed  $p\text{CO}_2$  at in situ sea water temperature. Data with an uncertainty larger than 5 % are omitted. The resulting average overall uncertainty is 3.5 %, ranging from 2.3 to 4.9 % (6.6 to 21.8 ppmv).

Potential of hydrogen (pH) was measured with a Orion Ross 8103 combination electrode, combined with a Pt-100 sensor for measuring the temperature of the sample. The electrode voltage and the temperature signal were registered using a HP 3478A multimeter with a resolution of 0.1 mV. The system was built at the Department of Oceanography, University of Gothenburg, following the ideas outlined in Almgren *et al.* (1975). Hansson buffer (also called Tris buffer), as described by Almgren *et al.* (1975), was used to calibrate the pH-meter prior to each set of measurements (*i. e.* before each station). Each pH observation was performed in two-four replicates. The mean absolute difference in pH<sub>20</sub> (observed pH converted to  $20^\circ\text{C}$ ) of replicate samples from 151 observations is 0.0063 pH units. 95 % of the observations have an absolute difference between the replicate measurements of less than 0.03 pH units. The pH data used here are the mean values of the replicate samples of the respective observation. The data are not used if the standard deviation of the individual mean value exceeds 0.006 pH units.

Phosphate concentration was determined manually according to the modified molybdenum method with ascorbic acid as reductant. The method is given by Murphy and Riley (1962) and modified by Koroleff (1965). The absorbance was measured with a Hitachi U-1000 spectrophotometer, using a 5 cm cell. The precision of the method ranges from  $\pm 1\%$  for concentrations exceeding  $1\ \mu\text{mole}$

$\text{P l}^{-1}$  to  $\pm 30\%$  for concentrations below  $0.2\ \mu\text{moles P l}^{-1}$  (Koroleff, 1965). At a few stations water samples were preserved and stored for later on-shore analyses of nutrient content, using an autoanalyzer (unpublished data, T. Johannessen, Centre for Studies of Environment and Resources, University of Bergen, personal communication). Silicate concentrations from these samples have been used in the  $p\text{CO}_2$  calculations when available. Phosphate concentrations obtained with the autoanalyzer differed somewhat (often less than  $0.1\ \mu\text{moles P l}^{-1}$ ) but sometimes substantially (occasionally almost  $0.9\ \mu\text{moles P l}^{-1}$ ), from the results obtained by shipboard, manual analyses. Since the phosphate concentration so far has been used only in the calculations of  $p\text{CO}_2$ , the cause of the difference has not been investigated further.

The water samples for analyses of  $C_t$  were stored in serum bottles with EPDM rubber stoppers. The samples were poisoned with  $\text{HgCl}_2$  and stored in the dark during the cruise and under dark and cold conditions after the cruise until analyses were performed, in duplicates, using a  $\text{CO}_2$  coulometer (Coulometrics, Model 5011). The analyses were completed within six weeks of the cruise. The equipment was checked subsequently to the analyses by measurements on standard water, supplied by the Department of Analytical and Marine Chemistry, University of Gothenburg and prepared by Dr. Andrew G. Dickson, Scripps Institution of Oceanography, La Jolla. The standard water had a salinity of 33.363 psu and a dissolved inorganic carbon content of  $1978.78\ \mu\text{moles C kg}^{-1}$ . Control measurements gave  $C_t = 1973\ \mu\text{moles C kg}^{-1}$  ( $n = 9$ , 2 S.D. =  $3.6\ \mu\text{moles C kg}$  or 0.18 %). The observed  $C_t$  concentrations have therefore been multiplied by the factor 1.0029 (=  $1978.78/1973$ ).

The quality of the  $C_t$  data suffer from the fact that the blanks of the coulometric measurements were high and variable. Blanks were mostly between 2-3  $\mu\text{g C/5 min.}$  and did not exceed 4.51  $\mu\text{g C/5 min.}$  The maximum error arising from the variability of the blanks is estimated to be 1.8  $\mu\text{g C}$ , which is equal to the maximum absolute difference between two subsequent blanks. Since the amount of  $C_t$  in the samples was around 280  $\mu\text{g C}$ , the error arising from the variability of the blanks is estimated to be  $1.8/280 = 0.64\%$ . The total uncertainty of the reported  $C_t$  data is estimated to be  $0.18 + 0.64\% \approx 0.8\%$ , where the figure 0.18 % is the 2 S.D. of the mean value of the control measurements on standard water.

The water samples for total alkalinity measurements were stored in Pyrex bottles with no preservative added. The bottles were kept in the dark during the cruise and under dark and cold conditions after the cruise. Analyses were completed within eleven weeks of the cruise. A semi-automatic potentiometric titration method on weighted samples was employed. Titration was performed with 0.1 M HCl. The titration curves were evaluated with Gran functions. The method is further described by Anderson and Wedborg (1985).

A comparison between observed and calculated carbon data, which can be carried out since more than two of the four variables  $C_t$ , TA, pH and  $p\text{CO}_2$  were measured in

some water samples, indicate that the TA data are systematically too low by approximately 1 %. The cause of the low alkalinity data is not known, but all the TA data from the R/V *Mosby* expedition are multiplied by the factor 1.01. To visualize the uncertainty of the  $C_t$ , TA and  $p\text{CO}_2$  data, the calculated variables are plotted versus the respective observed variables in Figure 1 a-1 c. Note that the observed TA data in the plots are multiplied by 1.01. The scatter of the data around the line  $y = x$  in Figures 1 a-1 c is within the uncertainty of the observations (with the exception of a few  $p\text{CO}_2$  data), if the uncertainties of the observed variables are estimated to be  $C_t$ :  $\pm 0.8$  %,  $p\text{CO}_2$ : 2.3 - 4.9 %, pH:  $\pm 0.03$  units and TA:  $\pm 0.8$  %.

Pressure, temperature and conductivity data were recorded during the CTD casts with frequent discrete salinity samples to calibrate the sensor. Pressure, temperature and conductivity for use in the subsequent calculations of  $p\text{CO}_2$  were registered manually from the CTD deck unit on each occasion when water was sampled with a Niskin bottle. Salinity data from salinometer analyses were used when available. Positions noted are positions when the CTD underwater unit reached its deepest sampling depth, normally 50 m above the bottom.

The observed data, as well as detailed descriptions of the analytical methods employed, will also be given in a separate report.

Figure 1 a

Total dissolved inorganic carbon ( $C_t$ ), calculated from observed, corrected total alkalinity ( $\text{TA} \times 1.01$ ) and observed partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) or from observed  $\text{TA} \times 1.01$  and observed pH, as a function of observed  $C_t$ . The data were obtained during the R/V Haakon Mosby expedition, which took place from 14 August to 8 September 1991.

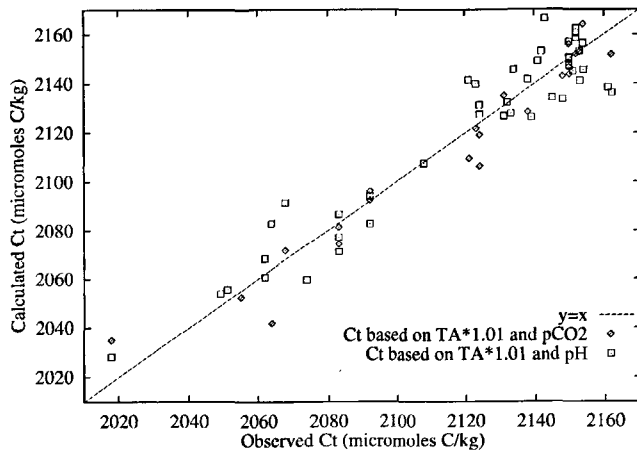


Figure 1 b

Total alkalinity (TA), calculated from observed  $C_t$  and observed  $p\text{CO}_2$  or from observed  $C_t$  and observed pH, as a function of observed and corrected total alkalinity ( $\text{TA} \times 1.01$ ). The data were obtained during the R/V Haakon Mosby expedition in 1991.

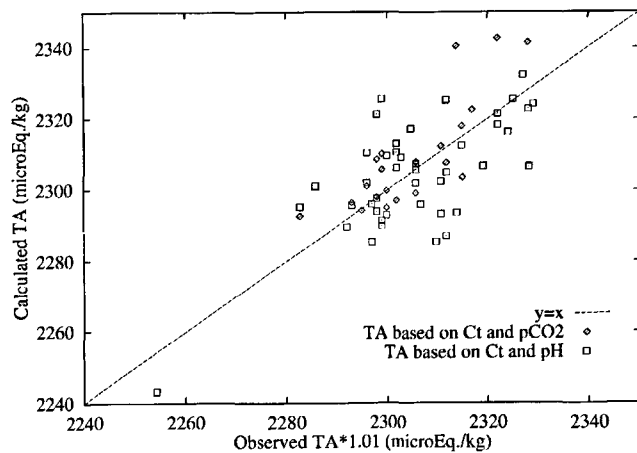
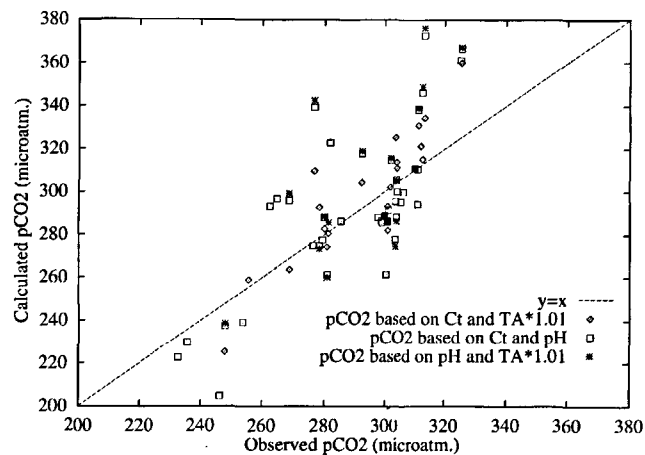


Figure 1 c

Partial pressure of carbon dioxide in sea water ( $p\text{CO}_2$ ), calculated from observed  $C_t$  and observed  $\text{TA} \times 1.01$ , from observed  $C_t$  and observed pH, or from observed  $\text{TA} \times 1.01$  and observed pH, as a function of observed  $p\text{CO}_2$ . The data were obtained during the R/V Haakon Mosby expedition in 1991.



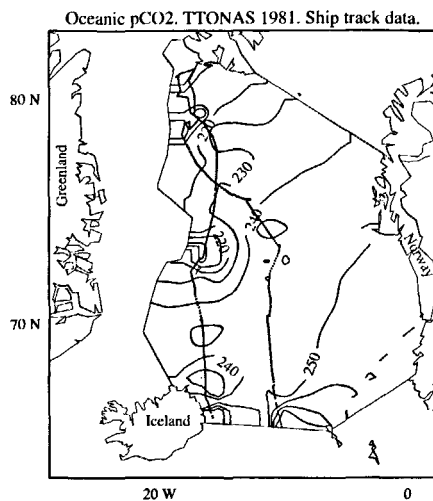


Figure 2 a

Interpolated surface water  $p\text{CO}_2$  ( $\mu\text{atm.}$ ) in the Nordic Seas in summer 1981. The interpolation is based on 656 direct observations of surface water  $p\text{CO}_2$ , obtained during the TTONAS expedition, from 25 July to 8 August 1981 (Weiss et al., 1992). The positions of the  $p\text{CO}_2$  observations are indicated by dots, which appear as an irregular line in the figure. The data are bilinearly interpolated into a rectangular grid, which consists of  $24 \times 28$  cells and which covers the entire area. Land, ice covered areas and the Barents Sea are excluded from the interpolation.

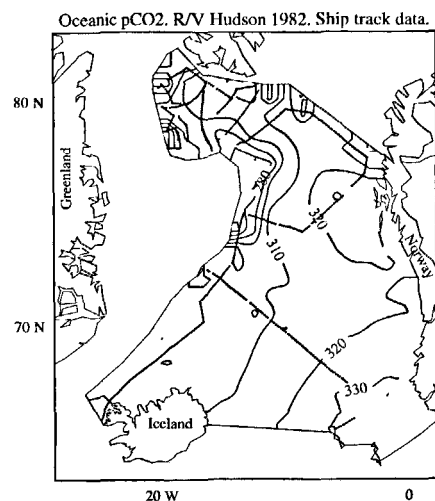


Figure 2 c

Interpolated surface water  $p\text{CO}_2$  ( $\mu\text{atm.}$ ) in the Nordic Seas in late winter 1982. The interpolation is based on 1139 direct observations of surface water  $p\text{CO}_2$ , obtained during the R/V Hudson expedition, from 26 February to 3 April 1982 (Weiss et al., 1992). The positions of the  $p\text{CO}_2$  observations are indicated by dots, which appear as a broken, irregular line in the figure. The data are interpolated in the same manner as the data in Figures 2 a and 2 b.

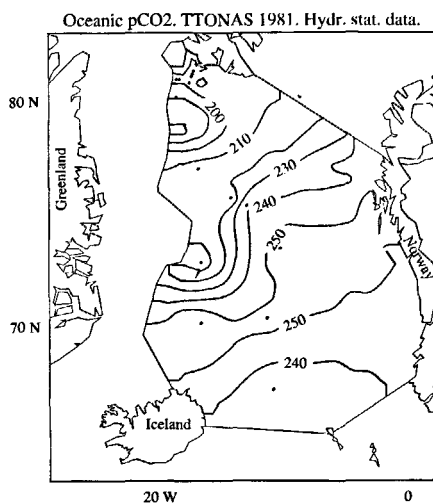


Figure 2 b

Interpolated surface water  $p\text{CO}_2$  ( $\mu\text{atm.}$ ) based on calculated surface water  $p\text{CO}_2$ , in summer 1981. The  $p\text{CO}_2$  data are calculated from observations of  $C_t$  and TA. The  $C_t$  and TA data are from sixteen hydrographic stations (indicated by dots in the figure), carried out during the TTONAS expedition in 1981 (Brewer et al., 1986 a). The data are interpolated in the same manner as the data shown in Figure 2 a, which illustrates the same situation, but based on 656 observations.

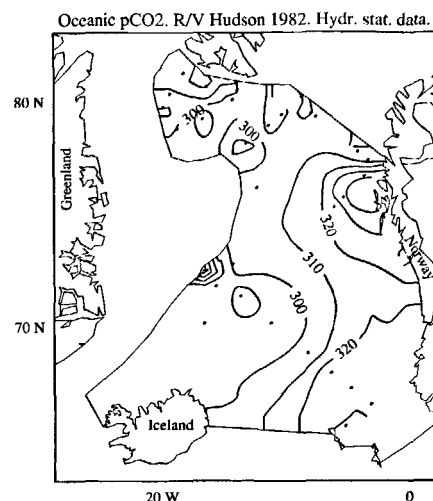


Figure 2 d

Interpolated surface water  $p\text{CO}_2$  ( $\mu\text{atm.}$ ) based on calculated surface water  $p\text{CO}_2$ , in late winter 1982. The  $p\text{CO}_2$  data are calculated from observations of  $C_t$  and TA. The  $C_t$  and TA data are from thirty hydrographic stations (indicated by dots in the figure), carried out during the R/V Hudson expedition in 1982 (E.P. Jones, personal communication). The  $C_t$  data are multiplied by 0.989 before they are used in the calculation of  $p\text{CO}_2$ . The  $p\text{CO}_2$  data are interpolated in the same manner as the data shown in Figures 2 a and 2 c (cf. Fig. 2 c, which illustrates the same situation, but which is based on 1139 observations).

The calculations of  $p\text{CO}_2$  from  $C_t$ , TA and pH are performed using the stability constants for the ocean carbon dioxide system from Unesco (1987), the stability constants of phosphate and silicate from Johansson and Wedborg (1982) and the stability constant of water from Millero (1979). The expression for the solubility of carbon dioxide in sea water is from Weiss (1974). In what follows, the  $p\text{CO}_2$  values, calculated on the basis of  $C_t$ , TA (and pH) data obtained at hydrographic stations, will be referred to

as hydrographic station  $p\text{CO}_2$  (or  $p\text{CO}_2$ -hydr.stat.) data, without any further reference to the underlying calculation. The  $p\text{CO}_2$  obtained by direct measurements on water sampled when the ship was under way will be referred to as ship track  $p\text{CO}_2$  (or  $p\text{CO}_2$ -shiptrack) data. Regarding the R/V *Mosby* data, a mean value of the individual  $p\text{CO}_2$  values is used for the depths where the carbon system is overdetermined. Figures 2 a-2 e show the isolines of the spatially interpolated  $p\text{CO}_2$  for each respective data set.

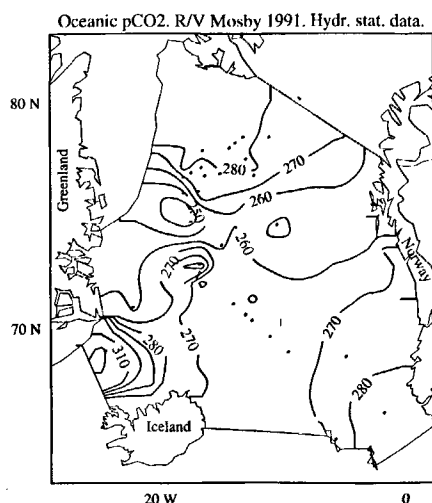


Figure 2 e

Interpolated surface water pCO<sub>2</sub> (µatm.), based on a combination of directly observed and calculated surface water pCO<sub>2</sub>, obtained during the R/V Haakon Mosby expedition, from 14 August to 8 September 1991. The calculation of pCO<sub>2</sub> is done on the basis of observations of C<sub>T</sub>, pH and TA. The TA data are corrected by a factor of 1.01 before the data are used to calculate pCO<sub>2</sub>. The data are from 28 hydrographic stations and interpolated in the same manner as the data shown in Figures 2 a and 2 d. The positions of the hydrographic stations are indicated by dots in the figure.

### Data on atmospheric pCO<sub>2</sub>

The data on atmospheric pCO<sub>2</sub> used in the calculations are:

1) Direct (ship track) observations (approximately two samples per hour) from the TTONAS 1981 expedition and from the R/V Hudson expedition (Weiss *et al.*, 1992), measured with shipboard gas chromatography.

2) Monthly mean values of the atmospheric concentration of carbon dioxide, sampled at ocean station "M" at 66° N 2° E, and reported in Trends 1991 (Conway *et al.*, 1991).

In order to compare the net air-sea CO<sub>2</sub> fluxes calculated from the ship track data with the fluxes calculated from the hydrographic station data, the ship track atmospheric pCO<sub>2</sub> data are only used together with the oceanic pCO<sub>2</sub>-shiptrack data. The hydrographic station data are combined with the monthly mean values on atmospheric pCO<sub>2</sub> from station "M". Since none of the three expeditions cover exactly a calendar month, a weighted mean (weighted by number of cruise days in each month) for each expedition is calculated. Regarding the year 1991, no atmospheric pCO<sub>2</sub> data are yet available from ocean station "M". An estimate is therefore used based on an extrapolation in time from 1990 (the last year for which data on atmospheric pCO<sub>2</sub> at station "M" are reported). The mean atmospheric CO<sub>2</sub> concentrations are listed in Table 1.

### Data on wind speed and atmospheric pressure

The wind-speed data and atmospheric pressure data are obtained from a data base developed at the Norwegian Meteorological Institute. The data base gives the wind velocity components and the total atmospheric surface pressure in a grid net covering the northern North Atlantic,

Table 1

Mean atmospheric content of CO<sub>2</sub> during the respective expeditions. The atmospheric concentration of CO<sub>2</sub> is given as volume parts in dry air (ppmv) and as partial pressure (µatm.). The data are from the TTONAS expedition in 1981 and the R/V Hudson expedition in 1982 (ship track data, Weiss *et al.*, 1992) as well as from Ocean Station "M" (Conway *et al.*, 1991). The ship track data are spatially averaged over the ice-free area of the Nordic Seas.

Cruise period	Ship track data (ppmv)	Ship track data (µatm)	Station "M" data (ppmv)	Station "M" data (µatm)
TTONAS, 25/7-8/8/1981	332	327	335	330
R/V Hudson, 26/2-3/4/1982	348	341	346	339
R/V Mosby, 14/8-8/9/1991	-	-	347	341

the Nordic Seas, Barents Sea and parts of the Arctic. Here only the part covering the Nordic Seas is used. The grid size is 75 km \* 75 km and the projection is polar stereographic with correct scale at 60°N. Data are given every six hours. The atmospheric pressure data are based on objective analyses of routine weather maps and observations. The wind is the geostrophic wind at 10 m height above sea level, calculated from the atmospheric surface pressure field and modified with a two-layer model of the friction boundary layer under the assumption of a neutral stratification.

A more detailed description of the data base is given by Eide *et al.* (1985) in Norwegian.

### Data on sea ice

The extension of sea ice during the three different expeditions is drawn from monthly mean sea ice charts compiled by the Norwegian Meteorological Institute.

### Compatibility of the different oceanic pCO<sub>2</sub> data sets and inferred correction terms

Before combining the pCO<sub>2</sub> data, which originate from different expeditions, a check on the compatibility of the data from the different expeditions has to be made. The consistency of pCO<sub>2</sub>-shiptrack data and pCO<sub>2</sub>-hydrographic station data has to be checked in order to make the comparison between sparse and dense data sets informative.

The compatibility of the different data sets is checked by comparing the deep-water carbon data, assuming the deep water to be homogeneous in time and space. It should,

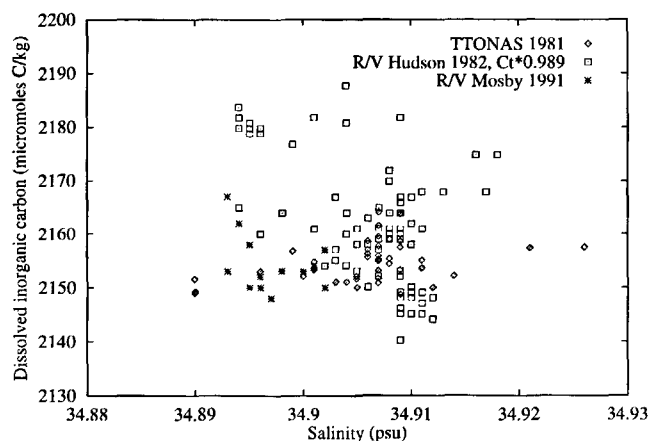


Figure 3 a

Total dissolved inorganic carbon ( $C_t$ ) in deep water as a function of salinity. The data were obtained during the TTONAS, the R/V Hudson and the R/V Mosby expeditions. Note that the R/V Hudson  $C_t$  data in the figure are multiplied by a factor of 0.989, since the original data appear to be systematically too high. The data in the figure are from water samples taken at depths greater than 2 000 m.

however, be borne in mind that such an assumption is likely to be too simplistic, e. g. due to different ages of different water masses and due to the anthropogenic perturbation of atmospheric  $\text{CO}_2$ . The consistency of ship track and hydrographic station  $\text{pCO}_2$  data is checked by comparing the relation between  $\text{pCO}_2$  and surface water temperature of the respective data sets.

The deep-water  $C_t$  data vary from approximately 2 150 to 2 210  $\mu\text{mol kg}^{-1}$ . The deep-water TA data vary from around 2 270 to 2 325  $\mu\text{Eq. kg}^{-1}$ . It is likely that part of the variation can be explained in terms of true temporal and spatial variability. However, systematic differences can probably not be excluded, since Hudson  $C_t$  data tend to be higher and Mosby TA data tend to be lower than the other data. The interpretation that the R/V Hudson  $C_t$  data are too high is supported by the fact that the  $\text{pCO}_2$ -hydrographic station data from the R/V Hudson expedition are higher than the corresponding  $\text{pCO}_2$ -ship track data. It is found that if all the R/V Hudson  $C_t$  data are multiplied by the factor of 0.989, the agreement between the two R/V Hudson  $\text{pCO}_2$  data sets, as well as the agreement between the deep water  $C_t$  data from the different expeditions, improve.

Regarding the R/V Mosby data, the comparisons between observed and calculated carbon species, mentioned above, support the impression from the comparison with the other TA data, namely that the R/V Mosby TA data are systematically too low. If the R/V Mosby TA data are multiplied by a factor of 1.01, the agreement with the other TA deep water data and, as discussed above, the internal consistency of the R/V Mosby carbon data improve.

Thus, on the basis of these comparisons, the R/V Hudson  $C_t$  data are corrected *ad hoc* with a factor of 0.989 and the R/V Mosby TA data are corrected *ad hoc* with a factor of 1.01. No correction is introduced for TTONAS data. Figure 3 a shows the  $C_t$  data from depths greater than 2 000 m, as a function of salinity for the three data sets (R/V Hudson

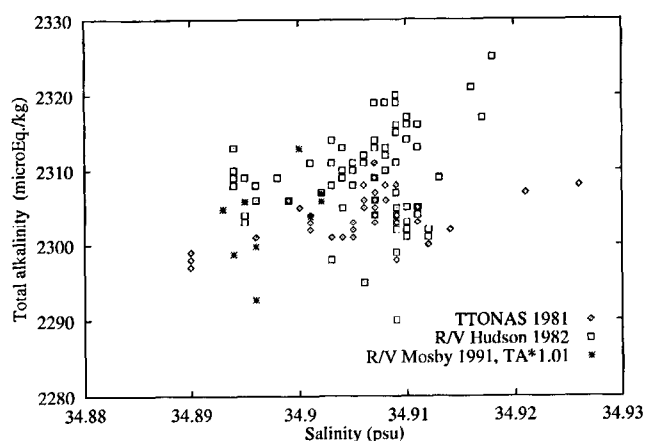


Figure 3 b

Total alkalinity (TA) in deep water (here: depth greater than 2 000 m) as a function of salinity. The data were obtained during the TTONAS, the R/V Hudson and the R/V Mosby expeditions. Note that the R/V Mosby TA data in the figure are multiplied by a factor of 1.01, since the original data appear to be systematically too low.

$C_t$  data are *ad hoc* corrected). Figure 3 b shows the corresponding TA data (R/V Mosby TA data, are *ad hoc* corrected). The surface water  $\text{pCO}_2$  data (ship track data and hydrographic station data) from the TTONAS and the R/V Hudson expeditions are plotted versus surface water temperature in Figure 4 a. Note that the R/V Hudson  $C_t$  are multiplied by a factor of 0.989 before calculating  $\text{pCO}_2$ . Note also that one, apparently outlying, calculated  $\text{pCO}_2$  datum is excluded from the calculation of the  $\text{CO}_2$  air-sea exchange. The hydrographic station  $\text{pCO}_2$  data, based on original TTONAS data and on corrected R/V Hudson and R/V Mosby data, are plotted as a function of surface water temperature in Figure 4 b.

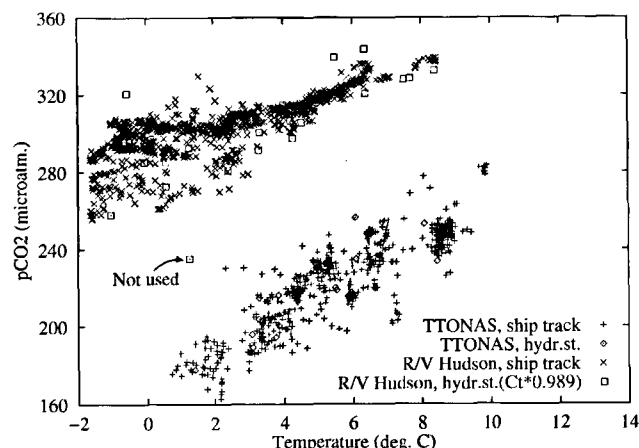


Figure 4 a

Comparison between the directly observed (ship track) and calculated (hydrographic station)  $\text{pCO}_2$  data from the R/V Hudson expedition and from the TTONAS expedition. The calculated  $\text{pCO}_2$  data from the R/V Hudson expedition are based on corrected  $C_t$  ( $C_t * 0.989$ ).



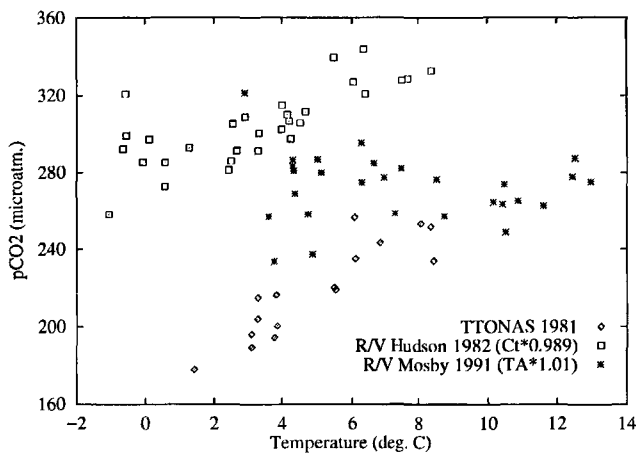


Figure 4 b

Hydrographic station surface water  $p\text{CO}_2$  data used in the calculations, as a function of surface water temperature. Note that the R/V Hudson and R/V Mosby calculated  $p\text{CO}_2$  data are based on corrected  $C_i$  and corrected TA respectively.

### Spatial interpolation of data

In order to calculate areal means of the net flux and to utilize the fact that wind speed data are given with a high spatial resolution for the entire region, the irregularly spaced data (*i. e.* surface water temperature, oceanic  $p\text{CO}_2$  and atmospheric  $p\text{CO}_2$ ) are spatially interpolated. The interpolation is carried out using the interactive computer program Unimap, which is based on Uniras subroutines.

The irregular data are interpolated into the 75 \* 75 km grid and to the same positions as those given for the wind and pressure data. Land, ice-covered areas and areas outside the Nordic Seas are excluded from the interpolation. If the minimum and/or maximum values of the original data set are exceeded by the interpolation, this interpolation method, or choice of options, is not used. Since the length scale of the grid cells changes with latitude and longitude, a correction for this is used when spatial mean values, based on interpolated data, are calculated.

The interpolation of irregularly distributed  $p\text{CO}_2$  involves a certain degree of arbitrariness, *e. g.* due to choice of interpolation method and choice of options. In principle, there are two interpolation methods in Unimap which are applicable to the available data, a bilinear method, which exists in two versions, and a bicubic method which demands regularly distributed data. The interpolation can thus either be done by a bilinear interpolation directly into the 75 \* 75 km grid or by a bilinear interpolation into a grid with an arbitrary spatial resolution, followed by a bicubic interpolation into the 75 \* 75 km grid. The two Unimap bilinear methods have several options, but it transpires that the above-mentioned constraint on the extreme values of the interpolated data limits the number of applicable options. It also transpires that if the constraint is fulfilled the variation arising from using different interpolation methods (and options) is smaller than if the constraint is not fulfilled.

Two different interpolation methods are employed and compared:

1) A bilinear interpolation into the 75 \* 75 km grid, which gives the interpolated data in 24 \* 28 grid cells. The interpolation is done using the Unimap bilinear method denoted "Fault".

2) A bilinear interpolation into a grid with a spatial resolution that depends on the spatial density of the original data set. In this approach the number of grid cells varies from 10 \* 11 to 60 \* 70. The interpolation is done using one of the two Unimap bilinear methods denoted "Fault" and "Bilinear". The bilinear interpolation is followed by a bicubic interpolation into the 75 \* 75 km grid.

### Gas exchange parameterization

The net flux of an unreactive, soluble or slightly soluble gas through the sea surface is generally described by an equation of the following form:

$$Q_i = k_{wi} \times \alpha_i \times (p_{i \text{ sea}} - p_{i \text{ atm}}) \quad (1)$$

where  $Q_i$  is the net flux of the gas  $i$ ,  $k_{wi}$  is the transfer velocity of the gas  $i$ ,  $\alpha_i$  is the solubility of the gas  $i$ ,  $p_{wi \text{ sea}}$  and  $p_{i \text{ atm}}$  are the partial pressures of the gas  $i$  in the mixed surface layer in the sea and in the well mixed air above the sea surface, respectively.

For a discussion of the hypothesis underlying this parameterization, *see e. g.* Liss and Slater (1974), Liss and Merlivat (1986) and Wanninkhof (1992).

A frequently employed parameterization of  $k_w$  is suggested by Liss and Merlivat (1986) and based on assessments of  $k_w$  from laboratory and lacustrine experiments. The parameterization is also supported by results from ocean experiments at high wind speed (Watson *et al.*, 1991). Liss and Merlivat (1986) suggest the following parameterization of  $k_w$ :

$$k_w = 0.17 \times W \times \left( \frac{600}{Sc} \right)^{2/3} \quad W \leq 3.6 \quad (2a)$$

$$k_w = (2.85 \times W - 9.65) \times \left( \frac{600}{Sc} \right)^{1/2} \quad 3.6 < W \leq 13 \quad (2b)$$

$$k_w = (5.9 \times W - 49.3) \times \left( \frac{600}{Sc} \right)^{1/2} \quad W > 13 \quad (2c)$$

where the equations (2 a)-(2 c) give  $k_w$  in  $\text{cm h}^{-1}$ .  $W$  is the wind speed in  $\text{m s}^{-1}$  at 10 m height.  $Sc$  is the Schmidt number ( $Sc = \nu/D$ ,  $\nu$  is the kinematic viscosity of water and  $D$  is the diffusivity of the gas in water). 600 is the Schmidt number of  $\text{CO}_2$  in water at a temperature of 20°C.

As pointed out by Etcheto and Merlivat (1988) the temperature dependence of  $(600/Sc)^r \alpha$  is much smaller than the temperature dependence of  $(600/Sc)^r$  and  $\alpha$  one by one. The small temperature dependence of  $(600/Sc)^r \alpha$  is sometimes taken advantage of when parameterizing the  $\text{CO}_2$  gas exchange, by using equations which are functions of wind speed (and type of gas) only. Tans *et al.* (1990) employ the following parameterization of the gas exchange coefficient,  $E$ :

$$E = 0 \quad W < 3 \quad (3 a)$$

$$E = 0.016 * (W - 3) \quad W > 3 \quad (3 b)$$

where E is given in moles CO<sub>2</sub> m<sup>-2</sup> year<sup>-1</sup> μatm<sup>-1</sup> and W is the wind speed at 10 m height.

The equations (2 a-c) and (3 a-b) give numerical values of k<sub>w</sub> (or E) which differ by a factor of approximately two for the same wind speed. According to Murphy *et al.* (1991) and Wanninkhof (1992) part of the difference of the numerical values of k<sub>w</sub> may be due to the fact that the wind speeds, which underlie the different parameterizations, are averaged over different time intervals. Equations (2 a-c) parameterize k<sub>w</sub> as a function of wind speeds averaged over one-two days while equations (3 a-b) are adapted to long-time averaged wind speeds. Wanninkhof (1992) suggests a quadratic dependence of k<sub>w</sub> on wind speed, with different proportionality factors for long-time averaged wind speeds (W<sub>av</sub>) and for steady wind speeds [W (*i. e.* from spot measurements, scatterometers, *etc.*)]:

$$k_w = 0.39 \times W_{av}^2 \times \left( \frac{600}{Sc_{seawtr}} \right)^{1/2} \quad (4 a)$$

$$k_w = 0.31 \times W^2 \times \left( \frac{660}{Sc_{seawtr}} \right)^{1/2} \quad (4 b)$$

where W is the wind speed in m s<sup>-1</sup> and 660 is the Schmidt number of CO<sub>2</sub> in seawater at a temperature of 20°C. The equations (4 a-b) give k<sub>w</sub> in cm h<sup>-1</sup>.

The parameterizations of the transfer velocity or of the gas exchange coefficient given above do not take into consideration any possible enhancement of the flux due to chemical reactions of CO<sub>2</sub> in sea water. Wanninkhof (1992) discusses this and concludes that chemical reactions of CO<sub>2</sub> in sea water might enhance the flux considerably for wind speeds below 4 m s<sup>-1</sup>. This is not taken into account here, since wind speeds in the area of the Nordic Seas generally exceed 4 m s<sup>-1</sup>.

### Calculation of the net CO<sub>2</sub> air-sea flux

The net CO<sub>2</sub> flux is calculated for each data set separately. The oceanic pCO<sub>2</sub>-shiptrack data are combined with the corresponding atmospheric pCO<sub>2</sub>-shiptrack data, while the hydrographic station pCO<sub>2</sub> data are combined with data on atmospheric pCO<sub>2</sub> from station "M". The latter is done in order to make the calculation based on *TTONAS* and *R/V Hudson* hydrographic station data similar to the calculation based on the *R/V Mosby* data set, which lacks simultaneous observations of atmospheric pCO<sub>2</sub>.

The atmospheric pCO<sub>2</sub> from station "M" as well as all the pCO<sub>2</sub>-shiptrack data are given as volume parts (ppmv) in dry air. The data are converted to absolute pressure (μatm), before calculating the net CO<sub>2</sub> fluxes, according to:

$$pCO_{2atm} = vCO_{2atm} * (P_{atm} - e_{ws}) \quad (5)$$

where pCO<sub>2atm</sub> is the atmospheric partial pressure of CO<sub>2</sub>, vCO<sub>2atm</sub> is the partial volume of CO<sub>2</sub> in dry air, P<sub>atm</sub> is the

atmospheric total pressure, and e<sub>ws</sub> is the water vapour saturation pressure.

The water vapour pressure is calculated assuming that the air is saturated with water vapour at the temperature of the sea surface. The pCO<sub>2</sub>-shiptrack data are converted prior to the interpolation and using data on surface water temperature and atmospheric pressure reported with the pCO<sub>2</sub> data. The station "M" pCO<sub>2</sub> data are converted using the spatially interpolated surface water temperature from the hydrographic station pCO<sub>2</sub> data sets and total atmospheric pressure data from the DNMI data base.

The gas exchange coefficient is calculated according to the parameterization of k<sub>w</sub> given by Liss and Merlivat (1986), *i. e.*:

$$E = 0.17 \times W \times \left( \frac{600}{Sc} \right)^{2/3} \times \alpha \quad W \leq 3.6 \quad (6 a)$$

$$E = (2.85 \times W - 9.65) \times \left( \frac{600}{Sc} \right)^{1/2} \times \alpha \quad 3.6 < W \leq 13 \quad (6 b)$$

$$E = (5.9 \times W - 49.3) \times \left( \frac{600}{Sc} \right)^{1/2} \times \alpha \quad W > 13 \quad (6 c)$$

where W is the wind speed, Sc is the Schmidt number and α is the solubility of CO<sub>2</sub>. The Hindcast wind speed data given every six hours are used. The temperature dependency of the factor (600/Sc)<sup>f</sup> \* α is calculated based on the spatially-interpolated temperature data from each respective pCO<sub>2</sub> data set. This implies that any temporal variation of surface water temperature during the expeditions is not accounted for. However, this is probably of little importance to the result, since the factor (600/Sc)<sup>f</sup> \* α does not vary much with temperature. The following parameterization is found to reproduce reasonably well the temperature dependence of (600/Sc)<sup>f</sup> \* α.

$$\left( \frac{600}{Sc} \right)^{2/3} \times \alpha = 29.7 + 0.14 \times T + 0.002 \times T^2 \quad W \leq 3. \quad (7 a)$$

$$\left( \frac{600}{Sc} \right)^{1/2} \times \alpha = 36.1 - 0.22 \times T + 0.0037 \times T^2 \quad W > 3.6 \quad (7 b)$$

where T is the seawater temperature in °C. Data on the temperature dependence of the Schmidt number, Sc, is from Jähne *et al.* (1987). The solubility of CO<sub>2</sub>, α, is calculated according to the algorithm given by Weiss (1974) for a salinity of 35 psu. The variation of the surface water salinity is not taken into account in the calculations.

The variation of (600/Sc)<sup>f</sup> \* α with salinity is estimated to be only of the order of 0.2 % psu<sup>-1</sup>, based on a comparison between the parameterization of Sc for CO<sub>2</sub> at a salinity of 35 psu, given by Wanninkhof (1992), and data on Sc for CO<sub>2</sub> in fresh water from Jähne *et al.* (1987). The surface water salinity varies with a few psu, with the exception of the East Greenland Current, where the salinity is significantly lower than in the rest of the Nordic Seas. The East Greenland Current accounts for only a small part of the total area of the Nordic Seas, and the use of a constant salinity in the calculation of (600/Sc)<sup>f</sup> \* α does probably not imply any large errors.

The gas exchange coefficients, *E*, calculated for every six hours, are averaged over the time period during which the respective expedition took place. The pCO<sub>2</sub> data are interpolated into the 75 km \* 75 km grid using the Unimap bilinear method denoted "Fault". The net CO<sub>2</sub> air-sea exchange is calculated in Hindcast grid coordinates using the

time-averaged gas exchange coefficients and the spatially-interpolated pCO<sub>2</sub> data. The spatially averaged fluxes are listed in Table 2.

Net fluxes calculated on the basis of *TTONAS* and *R/V Hudson* ship-track data and on *R/V Mosby* hydrographic station data are shown in Figures 5 a-5 c.

Table 2

Spatially-averaged CO<sub>2</sub>-fluxes in mmoles C m<sup>-2</sup> day<sup>-1</sup>. A positive flux implies a flux out of the sea. The fluxes are calculated with the parameterization of the gas-exchange coefficient by Liss and Merlivat (1986) and with wind speed given every six hours.  $\sigma$  denotes the root mean square deviation of the spatially-averaged CO<sub>2</sub>-flux. The ice-free area of the Nordic Seas varies between 1.5-2 \* 10<sup>12</sup> m<sup>-2</sup>, depending on the season.

Cruise period	Ship track pCO <sub>2</sub> data	Hydrographic station pCO <sub>2</sub> data
WINTER ( <i>R/V Hudson</i> , 26/2-3/4/1982)	-5.17 $\sigma = 2.23$	- 5.36 $\sigma = 2.50$
SUMMER ( <i>TTONAS</i> , 25/7-8/8/1981)	- 8.06 $\sigma = 2.27$	- 9.13 $\sigma = 3.05$
AUTUMN ( <i>R/V Mosby</i> , 14/8-8/9/1991)	No such data for <i>Mosby</i> 1991	- 10.97 $\sigma = 2.66$

CO<sub>2</sub> air-sea net exchange. Winter 1982. Ship track data.

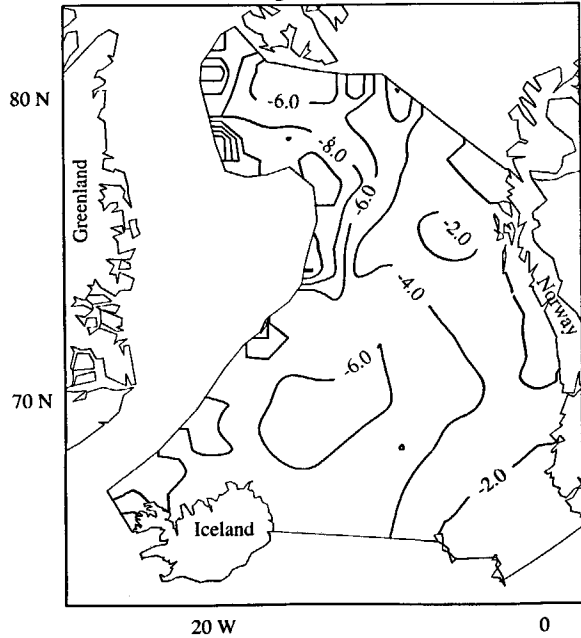


Figure 5 b

As in Figure 5 a, but in winter 1982 and based on ship track pCO<sub>2</sub> data from the *R/V Hudson* expedition.

CO<sub>2</sub> air-sea net exchange. Summer 1981. Ship track data.

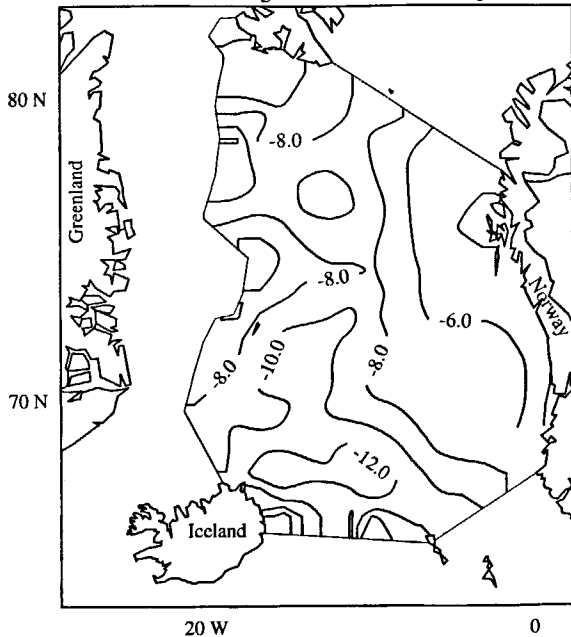


Figure 5 a

The calculated net CO<sub>2</sub> flux (mmoles C m<sup>-2</sup> day<sup>-1</sup>) through the sea surface in summer 1981. The calculation is based on bilinearly interpolated ship track pCO<sub>2</sub> data from the *TTONAS* expedition. The gas exchange coefficient is calculated according to the parameterization by Liss and Merlivat (1986), using wind speed given every six hours. The flux is positive when directed out of the sea.

CO<sub>2</sub> air-sea net exchange. Autumn 1991. Hydr. stat. data.

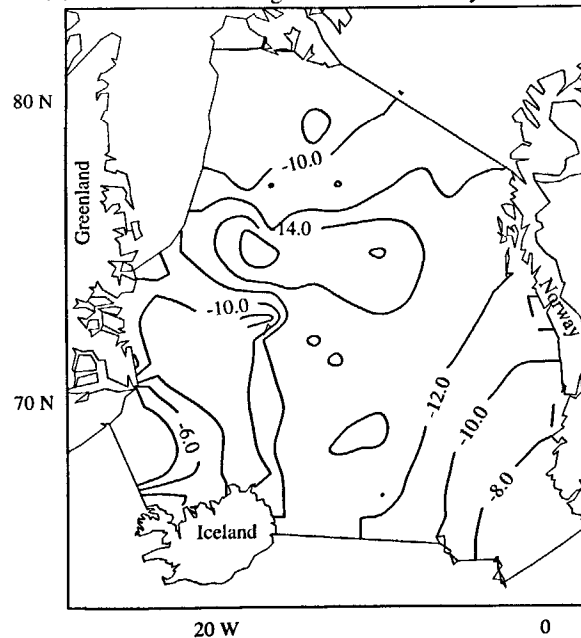


Figure 5 c

As in Figure 5 a, but in autumn 1991 and based on hydrographic station pCO<sub>2</sub> data from the *R/V Mosby* expedition.

### Sensitivity tests of the calculated net fluxes

In order to obtain an indication of the uncertainty of the calculated fluxes, a few tests are performed. Since the yearly net CO<sub>2</sub> flux is estimated on the basis of spatially-averaged net fluxes, the comparison between the results from the different tests is also performed using spatially-averaged results. The results are given as percentage increase (or decrease) of the averaged net flux calculated as described in the paragraph above, *i. e.*:

$$\varepsilon (\%) = \left( \frac{Q_{CO_2, \text{pert.}} - Q_{CO_2, \text{orig.}}}{Q_{CO_2, \text{orig.}}} \right) \times 100 \quad (8)$$

where  $Q_{CO_2, \text{orig.}}$  is the averaged net flux, listed in Table 2, and  $Q_{CO_2, \text{pert.}}$  is the spatially averaged result of the test. The results from the sensitivity tests are summarized in Table 3. The following tests are done:

1) A simple test of the maximum influence of errors of observation in oceanic pCO<sub>2</sub> is performed by adding the errors, estimated on the basis of the uncertainties reported with each data set respectively, to the (non-interpolated) pCO<sub>2</sub> data and then performing the flux calculations, as outlined in the previous paragraph.

The uncertainty of ship track pCO<sub>2</sub> data is estimated on the basis of the reported standard deviation of the observational method employed, which is 0.04 % (Weiss *et al.*, 1992). The error of observation is assumed to amount to two standard deviations and a contribution from the uncertainty of the surface water temperature data, the latter is assumed to be ± 0.005°C (corresponding to approximately

0.02 % in pCO<sub>2</sub>). This gives 0.1 % in both oceanic pCO<sub>2</sub> and atmospheric pCO<sub>2</sub>, which is approximated to 0.2 % in oceanic pCO<sub>2</sub>. The uncertainty of the *TTONAS* hydrographic station pCO<sub>2</sub> data is estimated on the basis of the reported uncertainty of the TA data, which is 0.4 % (Brewer *et al.*, 1986 *b*) and the assumption that the uncertainty in the C<sub>t</sub> data is approximately the same. The R/V *Hudson* C<sub>t</sub> and TA data are measured with a standard deviation of 8.1 μmoles Ckg<sup>-1</sup> and 5.6 μEqkg<sup>-1</sup> respectively (Chen *et al.*, 1990) and the error of observation is assumed to amount to two standard deviations. The uncertainty of the calculated pCO<sub>2</sub> data from R/V *Mosby* is estimated assuming the uncertainty to be 0.8 % in C<sub>v</sub>, 0.8 % in TA and ± 0.03 pH units in pH (compare Fig. 1 *a-1 c*). The directly observed pCO<sub>2</sub> data from the R/V *Mosby* expedition have an average uncertainty of 3.5 %, ranging from 2.3 to 4.9 %.

The uncertainty of the atmospheric pCO<sub>2</sub> data from ocean station "M" is assumed to be smaller than the uncertainty of the calculated oceanic pCO<sub>2</sub> and is neglected in the test of the hydrographic station data. With the above-mentioned errors of observation, the mean values of the uncertainty of the respective pCO<sub>2</sub> data are: The pCO<sub>2</sub>-shiptrack: ± 0.2 %, the *TTONAS* pCO<sub>2</sub>-hydrographic station data: ± 9 %, the R/V *Hudson* pCO<sub>2</sub>-hydrographic station data: ± 18 %, the R/V *Mosby* pCO<sub>2</sub>-hydrographic station data: ± 12 %.

2) The influence of using different parameterizations of  $k_w$  is tested. The test is carried out on the basis of the same data and following the same procedure as that described in the previous paragraph, but using parameterizations by Tans *et al.* (1990), equations (3 *a-b*), and by Wanninkhof (1992), equation (4 *b*). The results from these two parameterizations are similar and therefore only the results obtained by using equation (4 *b*) are listed in Table 3.

Table 3

The magnitude of different contributions to the uncertainty of the CO<sub>2</sub> flux estimate. The contributions are expressed as relative changes of the spatially-averaged CO<sub>2</sub> net fluxes in Table 2. The parameterization of the gas exchange given by Tans *et al.* (1990) give similar results as the parameterization of  $k_w$  by Wanninkhof (1992) in the second column. The last column "scarcity of data" is the difference between the averaged flux based on hydrographic station data and the averaged flux based on ship-track data, relative to the flux based on ship track pCO<sub>2</sub> data. The figure in parenthesis in the same column is the mean value of the absolute differences, in each grid point, between these two estimates. The mean value is expressed as percent of the flux calculated on the basis of ship track pCO<sub>2</sub> data.

RELATIVE VARIATION OF THE NET CO <sub>2</sub> FLUX DUE TO						
Data set	Observational error in ΔpCO <sub>2</sub> or in pCO <sub>2, sea</sub>	$k_w$ according to Wanninkhof (1992)	Wind speed averaged over cruise period	Wind speed at each station Flux interpol.	Bilinear -bicubic interpolation	Scarcity of data
<i>TTONAS</i> 1981 Ship track data	± 0.6 %	71.3 %	- 8.7 %	23.9 %	0 %	-
<i>TTONAS</i> 1981 Hydrographic station data	± 22.2 %	71.5 %	- 8.4 %	33.5 %	- 1.4 %	13.3 % (17.6 %)
R/V <i>Hudson</i> 1982 Ship track data	± 2.1 %	75.6 %	- 10.1 %	3.3 %	- 7.4 %	-
R/V <i>Hudson</i> 1982 Hydrographic station data	± 174.2 %	75.2 %	- 10.3 %	14.0 %	4.1 %	3.7 % (29.8 %)
R/V <i>Mosby</i> 1991 Hydrographic station data	± 48.2 %	74.6 %	- 10.4 %	- 10.5 %	0.2 %	-

3) The influence of the time scale of the wind speed observation is tested in two different ways. The first test is performed by using the time average of the wind speed instead of the wind speed given every six hours. The wind speed is averaged, in each grid cell and over the time period of each respective expedition, before calculating the net flux following the same procedure as outlined in the previous paragraph.

The second test is performed by calculating the net flux at each position where pCO<sub>2</sub> is observed, without interpolating the pCO<sub>2</sub> data first. The wind speed data (and total atmospheric pressure data) are taken from the grid cell and time closest to the position and time of the observed pCO<sub>2</sub>. Regarding the hydrographic station data, the wind and pressure data given at 1 200 h is used. The calculations are performed using the parameterization of the transfer velocity given by Liss and Merlivat (1986). The flux is interpolated, using the Unimap 'Fault' method, before calculating the spatial mean value.

4) The uncertainty which arises from the interpolation is difficult to assess, but two tests are performed to obtain an indication of the contribution from this uncertainty. The first involves flux calculations on the basis of pCO<sub>2</sub> and surface water temperature data which are interpolated using a combination of the Unimap bilinear and bicubic interpolation methods. The data are first bilinearly interpolated into a grid of varying number of grid cells, where the number of cells depends on the number of observations. The number of grid cells varies from 10 \* 11 (hydrographic station data) to 60 \* 70 (R/V *Hudson* ship track data). The bilinear interpolation is then followed by a bicubic interpolation into the 75 \* 75 km grid (which comprises 24 \* 28 grid cells).

The second test is done by comparing the results based on interpolated ship track data with the results based on interpolated hydrographic station data. In addition to compare the spatially averaged net fluxes according to equation (8), the spatial mean value of the absolute difference between the two results in each grid cell is calculated. The mean absolute difference is expressed as percentage of the averaged net flux calculated on the basis of interpolated ship track data. The results from the last test are listed in the column denoted "Scarcity of data" in Table 3. Note that this test can only be done on the *TTONAS* and R/V *Hudson* data.

### Estimation of the yearly net CO<sub>2</sub> flux

The yearly net CO<sub>2</sub> flux is estimated on the basis of the spatially-averaged net fluxes obtained from the calculations based on *TTONAS*, R/V *Hudson* and R/V *Mosby* data. Regarding the *TTONAS* and R/V *Hudson* data, only results obtained using ship-track data are used, since these are more accurate and comprise a larger number of observations than the hydrographic station data. The spatially averaged net fluxes are assumed to be representative for the time period during which the respective expedition took place.

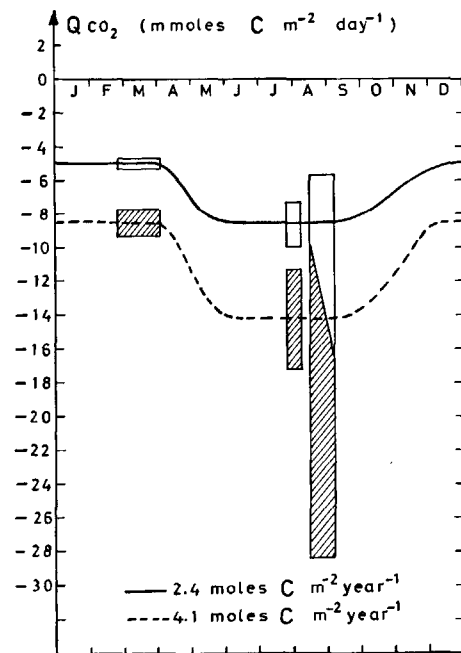


Figure 6

Seasonal variation of the spatially-averaged net CO<sub>2</sub> flux through the sea surface in the Nordic Seas, based on data from the *TTONAS*, R/V *Hudson* and R/V *Mosby* expeditions. The empty boxes represent net fluxes calculated using the parameterization of the gas exchange given by Liss and Merlivat (1986). The dashed boxes represent the net fluxes calculated using the parameterization of the gas exchange given by Wanninkhof (1992). Note that the two boxes showing the estimated net flux during August and September overlap. The fluxes in March and July are based on ship-track pCO<sub>2</sub> data, while the flux in August/September is based on hydrographic station pCO<sub>2</sub> data. The breadth of the boxes corresponds to the time period during which the data were obtained. The height of the boxes corresponds to the estimated uncertainty of the calculated flux. The large uncertainty of the August/September net flux is due to an average uncertainty of oceanic pCO<sub>2</sub> of approximately ± 12%. The curves show a hypothesis on the seasonal variation of the net flux, assuming that the seasonal variation of the air-sea exchange of CO<sub>2</sub> is similar to the seasonal variation of the oxygen air-sea exchange.

The spatially averaged CO<sub>2</sub> fluxes are plotted as boxes in Figure 6. The breadth of each box represents the time period of each respective expedition. The height of the boxes represents the estimated uncertainty of the fluxes, except for the variation that follows from using a different gas exchange coefficient. The latter is taken into account by plotting two fluxes (boxes) for each expedition. Note that the two boxes showing the estimated net flux during August and September (based on R/V *Mosby* data) overlap. The results obtained by using the gas exchange parameterization given by Liss and Merlivat (1986) are shown as empty boxes. The dashed boxes represent the results obtained by using the parameterization given by Wanninkhof (1992). The fluxes obtained by using the parameterization by Tans *et al.* (1990) give similar results as the parameterization by Wanninkhof, and are not plotted.

Results from an investigation of the spatially-averaged O<sub>2</sub> air-sea net exchange in the Nordic Seas (Falck, 1993), indicate a pronounced increase of the net oxygen flux from the ocean to the atmosphere from March to May and a similarly pronounced decrease from August to November. The

curves in Figure 6, which illustrate a possible shape of the seasonal variation of the net CO<sub>2</sub> air-sea exchange, are based on the hypothesis that the net CO<sub>2</sub> flux varies in a similar way as the net oxygen flux (but with reversed sign).

## RESULTS

### Oceanic pCO<sub>2</sub>

The available data, which represent a late winter, a summer and an early autumn situation, all show surface waters that are undersaturated with respect to pCO<sub>2</sub>, though the undersaturation is most pronounced during summer and least during winter. If the data are representative, it is possible that the Nordic Seas are undersaturated with respect to pCO<sub>2</sub> throughout the entire year.

Regarding the spatial distribution of the observed oceanic pCO<sub>2</sub>, the bilinearly interpolated data from the three expeditions are shown in Figures 2 a-2 e.

The detailed structure of the interpolated data is somewhat uncertain, as can be seen by comparing the plots based on ship-track data (Fig. 2 a and 2 c) and the plots based on hydrographic station data (Fig. 2 b and 2 d). The plots based on ship track data and the plots based on hydrographic station data exhibit similar overall horizontal distributions of surface water pCO<sub>2</sub>, but the interpolated hydrographic station data do not resolve all the details that are present in the horizontal mappings based on ship track data. The surface water temperature data, corresponding to the interpolated pCO<sub>2</sub> data, are also interpolated (but not shown here). Compared to other mappings of surface water temperature (e. g. Dietrich, 1969; Koltermann and Lüthje, 1989), the temperature plots indicate that the interpolation reproduces a distribution which on the whole looks realistic, but that some details are missing or uncertain, especially when the interpolation is based on few points. Pronounced temperature gradients as well as the temperature distribution close to the ice border and off Spitsbergen do not seem to be well reproduced in the interpolated data.

However, even if the detailed structure is questionable, it can be noted that the lowest pCO<sub>2</sub> values are encountered in the northern part of the Nordic Seas in both summer and winter. The region of inflowing North Atlantic Water (the southeastern part) seems to have relatively high values of surface water pCO<sub>2</sub>, except during the R/V *Mosby* expedition.

### CO<sub>2</sub> fluxes

As expected from the available pCO<sub>2</sub> data, the net flux is directed from the atmosphere to the sea during all the seasons represented by the data. The net uptake of atmospheric CO<sub>2</sub> increases with more than 50 % from the late-winter situation to the summer situation, while the average wind speed is approximately 30 % lower during summer than during late winter. The early autumn net uptake is larger than the summer uptake which depends on higher wind

speeds and not on decreased  $\Delta p\text{CO}_2$  ( $= p\text{CO}_{2,\text{sea}} - p\text{CO}_{2,\text{atm}}$ ). The magnitude of the net fluxes depends strongly on which of the parameterizations of the gas exchange coefficient is used. The fluxes calculated according to the equation by Wanninkhof (1992) are 70-75 % higher than those calculated according to the equation by Liss and Merlivat (1986). If the equations by Tans *et al.* (1990) are used, the estimated fluxes increase by 70-90 % compared to the fluxes calculated on the basis of the equation by Liss and Merlivat. The simple test of the maximum uncertainty arising from errors of observation indicates that this uncertainty is smaller than the uncertainty of the parameterization of the gas exchange, except for situations where  $|\Delta p\text{CO}_2|$  is small and/or pCO<sub>2</sub> is calculated from observations of C<sub>t</sub> and TA, as is the case of the R/V *Hudson* hydrographic station data and the R/V *Mosby* data. The employment of averaged wind speed or six hours wind speed does not seem to be crucial to the results. The net flux decreases with around 10 % if the time averaged wind speed is used instead of the wind speed given every six hours. If the net flux is calculated on the basis of non-interpolated pCO<sub>2</sub> data and wind speed from the grid cell closest to the position of the pCO<sub>2</sub> observation, the result changes noticeably in a few situations, but not in all, cf. Table 3. The choice of interpolation method does not imply any large variation of spatially-averaged results.

The difference between calculations based on ship-track data and on hydrographic station data is no greater than 4 % (R/V *Hudson*) and 17 % (*TTONAS*) of the net flux, if the spatially-averaged results are compared. Note, however, that the errors of observation in the hydrographic station pCO<sub>2</sub> data are larger than the errors of observation in the ship track pCO<sub>2</sub> data.

If the results based on ship-track data and on hydrographic station data are compared grid cell by grid cell, the mean absolute difference amounts to 30 % (R/V *Hudson*) and 18 % (*TTONAS*) of the net flux.

The yearly net flux, calculated as the integral of the solid curve in Figure 6 (based on the equation by Liss and Merlivat, 1986) give a yearly net uptake of atmospheric CO<sub>2</sub> of 2.4 moles C m<sup>-2</sup> (0.05 Gtonnes C, assuming the ice-free area of the Nordic Seas to be  $1.7 \cdot 10^{12}$  m<sup>2</sup>). The net flux, based on calculations according to the equation by Wanninkhof (the integral of the broken curve in Fig. 6) give a yearly net uptake of approximately 4.1 moles C m<sup>-2</sup> (approximately 0.08 Gtonnes C).

## DISCUSSION

The uncertainty of the gas exchange parameterization appears to be the major obstacle to an accurate assessment of the net CO<sub>2</sub> air-sea exchange. Even when the calculations are based on the large pCO<sub>2</sub> ship-track data sets, which are reported to have a high accuracy, from the *TTONAS* and the R/V *Hudson* expeditions, and combined with wind speed data with high spatial and temporal resolution, the uncertainty of the parameterization of the gas exchange gives results which vary with a factor of almost two.

The spatial interpolation of the pCO<sub>2</sub> data is another step in the calculations which may introduce errors. Judging from the interpolated surface water temperature, which can be compared with other observations, it appears that the interpolation does not correctly reproduce the detailed structure of the spatial distribution of the interpolated variables. This is probably partly due to the fact that the original data themselves do not resolve this spatial structure. Even the ship track data sets leave parts of the Nordic Seas without pCO<sub>2</sub> observations. To improve the estimate with respect to the spatial distribution, it seems necessary to have further observations. If only spatially-averaged results are considered, it appears from the comparison between the ship-track data and the hydrographic station data that the spatial density of the data is not crucial to the result. However, it is difficult to draw any general conclusions about this, since this is likely to depend on the variability of the surface water pCO<sub>2</sub> during the expedition and on whether or not the few points are representative for the situation. In this connection, it is also worth noting that performing the calculation on the basis of non-interpolated pCO<sub>2</sub> data and wind speed from the grid cell closest to the position of the pCO<sub>2</sub> observation may have a relatively large influence on the result, as in the case of the *TTONAS* data.

Regarding the estimate of the yearly net flux, there is also an uncertainty due to the fact that there are only three data sets available. The magnitude of this uncertainty is difficult to estimate. Are the calculated fluxes representative for the respective time of the year, for which they are calculated? The fact that the oceanic pCO<sub>2</sub> is lower in summer time than in winter time can be expected from the biological activity, but when does the drop in surface water pCO<sub>2</sub>, associated with the onset of the spring bloom, occur? Is this a sudden or slow process? When does the surface water pCO<sub>2</sub> start to increase again? Is the increase a slower process than the drop associated with the onset of the spring bloom? These questions are difficult to answer without further measurements. The curves in Figure 6 are based on the simple hypothesis that the seasonal variation of the CO<sub>2</sub> air-sea exchange is similar to the seasonal variation of the spatially averaged oxygen net flux (Falck, 1993), but with reversed sign, and constrained by the results based on the available data. However, observations of surface water pCO<sub>2</sub>, carried out in the vicinity of Iceland (Takahashi *et al.*, 1993), indicate that the drop in pCO<sub>2</sub>, associated with the onset of the spring bloom, is a sudden process that takes place during a couple of weeks. But it is likely that the onset of the spring bloom occurs at later times of the year further north. Averaged over the area of the Nordic Seas the decrease of surface water pCO<sub>2</sub>, and the associated increase of the net flux, will probably take longer time than at one specific place and thus change in a manner similar to the net O<sub>2</sub> air-sea exchange. Regarding the increase in pCO<sub>2</sub> during autumn, the observations from off Iceland indicate that surface water pCO<sub>2</sub> changes more slowly during autumn than during spring. This also appears to be true as to the spatially-averaged oxygen net flux, but the difference between the development during spring and during autumn is less pronounced. The curves in Figure 6 are therefore only slightly steeper during spring than during autumn.

It should also be noted that there are some sources to systematic errors in the calculated net fluxes, which have been neglected in the calculations. One is the effect of the surface thermal skin (Robertson and Watson, 1992); another is the possible importance of the coupling of heat and matter fluxes (Phillips, 1991). The surface skin temperature effect has simply been neglected since the correction is likely to be smaller than most of the other uncertainties associated with the calculated fluxes. Regarding the effect of coupling of heat and matter fluxes, it has not been possible to investigate its influence on the calculated net CO<sub>2</sub> fluxes due to the fact that atmospheric temperature data have not been available in this work. Since there is a yearly net heat flux from the Nordic Seas to the atmosphere, such a coupling might be of importance to the yearly net CO<sub>2</sub> uptake by the Nordic Seas. According to the equations of coupled heat and matter transfer given by Phillips (1991), a heat flux from the sea to the atmosphere will enhance a simultaneous CO<sub>2</sub> outgassing and decrease a simultaneous oceanic CO<sub>2</sub> uptake.

#### SUMMARY AND CONCLUSION

Data on oceanic pCO<sub>2</sub> from three different expeditions form the basis of an estimate of the yearly net CO<sub>2</sub> air-sea exchange in the Nordic Seas. The following questions are addressed:

- What is the yearly net CO<sub>2</sub> air-sea exchange in the Nordic Seas and what can be inferred about its seasonal variation from the available data?
- How do the choice of gas exchange coefficient, errors of observation, the treatment of the wind speed data and the choice of interpolation method influence the estimate?
- How large is the difference between the flux based on ship-track data and the flux based on hydrographic station data (*i.e.* between dense and scarce data sets)?

The data indicate that the spatially-averaged net flux of CO<sub>2</sub> is directed from the atmosphere to the sea during the entire year but the data are too sparse to provide unambiguously the seasonal variation of the net flux. A hypothetical curve is introduced to describe the seasonal variation of the CO<sub>2</sub> air-sea exchange. The yearly net flux is found to amount to 2.4 - 4.1 moles C m<sup>-2</sup> (0.05-0.08 Gtonnes C year<sup>-1</sup>), directed from the atmosphere to the sea. The range of the estimate stems from the employment of different parameterizations of the gas exchange coefficient. The contribution from errors of observation in pCO<sub>2</sub> to the overall uncertainty of the estimate appears to be larger than the uncertainty of the gas exchange parameterization only (but not always) when pCO<sub>2</sub> is calculated from observations of C<sub>p</sub>, TA and pH.

The difference between the spatially-averaged net flux calculated on the basis of ship track data and on hydrographic station data is not very large (at most 13 % of the net flux). If the respective fluxes are compared grid cell by grid cell, the mean value of the absolute difference is found to amount to 18-30 % of the net flux.

The choice of interpolation method and the employment of averaged wind speed data, instead of wind speed given every six hours, do not seem to influence the final result to the same extent as the uncertainty of the gas exchange parameterization, or the uncertainty due to errors of observation (in the case when  $p\text{CO}_2$  calculated from observations of  $C_t$ , TA and pH).

A further uncertainty, difficult to estimate, arises from the fact that it cannot be concluded how well the seasonal variation is represented by the three data sets used here.

### Acknowledgements

The data from the R/V *Hudson* expedition were kindly made available by Dr. E.P. Jones, Department of Fisheries and Oceans, Bedford Institute of Oceanography,

Canada. I wish to express my gratitude to Magnar Reistad, Norwegian Meteorological Institute, who made the wind and atmospheric pressure data available and helped with the data transfer. I am grateful to the crew of R/V *Haakon Mosby* for all the help during the expedition and to Ph. D. Truls Johannessen, Centre for Studies of Environment and Resources, University of Bergen, who made his phosphate and silicate data from the R/V *Mosby* expedition available to me. I wish to express my sincere thanks to Ph. D. Sverker Molander, Botanical Institute, University of Gothenburg, for allowing me to use his  $p\text{CO}_2$  data and for always being ready for new discussions. I am indebted to Professor Gösta Walin for helpful discussions and valuable comments on the work. Thanks are also due to Birger Biskopshavn for preparing the manually-drawn figures. This work was supported by the Nordic Council for Physical Oceanography (Nordisk Kollegium för Fysisk Oceanografi).

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