

Interannual variability of $f\text{CO}_2$ in the Greenland and Norwegian Seas

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ABSTRACT

The $f\text{CO}_2$ in the Greenland and Norwegian Seas surface water varied significantly during the period from 1995 to 1997. Comparison of $f\text{CO}_2$ data from winter 1995 with data from winter 1997 showed that sea surface $f\text{CO}_2$ decreased between these winters by 20 to 30 μatm in the central Greenland Sea, and the potential CO_2 uptake during the winters of 1995 and 1997 was $3.9 \cdot 10^{-3} \text{ Gt C month}^{-1}$ and $5.9 \cdot 10^{-3} \text{ Gt C month}^{-1}$ (based on Wanninkhof's relationship for the gas transfer coefficient), respectively. This difference in CO_2 fluxes can be attributed to lower sea surface temperatures and more extensive sea ice cover in 1997, and these observations were related to increased convection in the Greenland Sea during winter 1997. Larger amplitudes in the seasonal variations of CO_2 flux were also seen during the other seasons in the period 1996–97, compared to 1995. Over the years of investigation in the Greenland Sea, the carbon flux showed an increasing trend of $9 \cdot 10^{-4} \text{ Gt C yr}^{-1}$ into the ocean, which may be related to the anthropogenic input of carbon to the atmosphere. The Greenland and Norwegian Seas appear to be sinks for atmospheric CO_2 and together absorb approximately $0.12 \pm 0.015 \text{ Gt C yr}^{-1}$.

1. Introduction

The anthropogenic release of carbon from fossil-fuel burning and tropical deforestation between 1980 to 1989 was approximately $7.0 \pm 1.1 \text{ Gt C yr}^{-1}$, (Siegenthaler and Sarmiento, 1993), and this CO_2 has been distributed between the atmospheric, oceanic and terrestrial reservoirs. Considerable effort has been put into determining the annual oceanic CO_2 uptake, and model results give an estimate of 2 Gt C yr^{-1} (Siegenthaler and Sarmiento, 1993), which corresponds to an annual increase in total inorganic carbon, C_T , in surface water of $1\text{--}2 \mu\text{mol kg}^{-1}$.

Essential for the carbon uptake in the ocean is

the transport of carbon from the surface water to depth. In this respect, the Nordic Seas, are of particular importance, because this area is highly dynamic, in terms of surface mixed layer variations, wind stress and water circulation. In the Greenland Sea, low sea surface temperatures and sea ice formation increase the water density, and the resulting winter convection periodically produces deep water. In this convection process, CO_2 is drawn down to greater depths, thereby isolating the carbon from further contact with the atmosphere, and this removing of carbon from the sea surface may also induce further CO_2 uptake from the atmosphere.

The deep water flux is variable, and for the period 1980–94 a relatively low rate of deep water formation was observed (Bönisch et al., 1997), corresponding to the low North Atlantic Oscillation Index in this period (Dickson et al.

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1996). However, during 1996 and 1997, the rate of deep-water formation appeared to increase again, an observation supported by a recent SF₆ tracer release experiment in the Greenland Sea (A. Watson, personal communication). In this paper, we present carbon partial pressure data from these waters during these two periods of time, providing valuable insight about the relationship between the carbon cycle and deep water formation.

The CO₂ transfer between the atmosphere and the ocean is driven by the difference in the partial pressure of CO₂ between the two reservoirs, $\Delta p\text{CO}_2 = p\text{CO}_2(\text{SW}) - p\text{CO}_2(\text{air})$, and $p\text{CO}_2$ is defined as

$$p\text{CO}_2(\text{g}) = \frac{[\text{CO}_2^*(\text{aq})]}{K}, \quad (1)$$

(DOE, 1994), where $p\text{CO}_2$ expresses the CO₂ pressure in the gas phase just above sea surface, $\text{CO}_2^*(\text{aq})$ expresses the sum of CO₂ and carbonic acid, H₂CO₃ in surface water, and K denotes the temperature- and salinity-dependent solubility of CO₂ in seawater, known as Henry's law constant (Weiss, 1974). The oceanic $p\text{CO}_2$ is much more variable both spatially and temporally than the atmosphere. Correcting $p\text{CO}_2$ for the non-ideal nature of the CO₂ gas gives the fugacity

$$f(\text{CO}_2) = x(\text{CO}_2)p \times \exp\left(\int_0^p \frac{(V(\text{CO}_2) - RT/p') dp'}{RT}\right), \quad (2)$$

(DOE, 1994), where $x(\text{CO}_2)$ is the mole fraction of CO₂ in gas phase. Under the conditions encountered in the oceans, $f\text{CO}_2$ differs from $p\text{CO}_2$ by less than 0.5%. If the difference in fugacity between the air and sea surface, $\Delta f\text{CO}_2$, is negative, the ocean represents a sink of CO₂. The flux of CO₂ between the two reservoirs is related to $\Delta f\text{CO}_2$, and this flux per unit area can be represented as

$$F_{\text{CO}_2} = V_p K \Delta f\text{CO}_2 = E \Delta f\text{CO}_2 \quad (3)$$

(Tans et al., 1990), where V_p is the piston velocity and E is the gas transfer coefficient. For a grid box of area A , the total flux is given by

$$F_{\text{CO}_2} = A E \Delta f\text{CO}_2 \quad (4)$$

(Takahashi et al., 1997). The piston velocity depends on both wind speed and temperature, but as a simplification, the temperature dependence in V_p and K nearly counteract each other, and the gas transfer coefficient is generally assumed to be

mostly dependent upon the wind speed. A lot of effort has been put into identifying the relationship between wind speed, v , and the gas transfer coefficient, and two of the most common relationships are: $E[\text{CO}_2 \text{ mol m}^{-2} \text{ yr}^{-1} \mu\text{atm}^{-1}] = 0.0083 (v - 3.39)$, for $3.6 \leq v \leq 13 \text{ m s}^{-1}$ (Liss and Merlivat, 1986), and $E = 0.00113 v^2$ (Wanninkhof, 1992). The two relationships use different approaches to time averaging the wind speed. Liss and Merlivat (L&M) use wind speeds averaged over a few days, while Wanninkhof's equation (W) is based on long-term average wind speeds. The first relationship appears to give fluxes that are half the size of the latter. In our case, we used 2–3 month wind speed averages and so, have chosen to use the gas transfer relationship from Wanninkhof (1992). Because wind speeds are highly variable in the Nordic Seas, particularly during the winter season, and the relationship between wind speed and gas transfer rate is non-linear, the fluxes calculated here are minimum estimates.

2. Methods

The cruises from 1995 to 1997 (in addition to one from 1993) are listed in Table 1 and shown in Fig. 1. This study was primarily focused on the Greenland Sea, with a total area of $0.81 \cdot 10^6 \text{ km}^2$ (Simonsen and Haugan, 1996), and our coverage of the Norwegian Sea ($1.39 \cdot 10^6 \text{ km}^2$) was less comprehensive.

To fully describe the inorganic CO₂ system during these cruises, we determined *total dissolved inorganic carbon*, C_T ; *total alkalinity*, A_T ; and $f\text{CO}_2$; (DOE, 1994; Dickson, 1981) in addition to hydrographic data and nitrate. Our sampling techniques follow the WOCE manual (WOCE, 1994), and for a closer description of the equipment, sampling and analyses during 1995 see Miller et al. (in press).

Discrete samples were collected for C_T , A_T , nitrate, and salinity, while an uncontaminated continuous seawater stream, drawn from 4–5 m depth, supplied the $f\text{CO}_2$ analyser. For C_T and A_T measurements, seawater was collected in 250 ml glass bottles, the former samples were poisoned with 0.02%, by volume, of a saturated HgCl₂ solution, and the samples were stored cold and in the dark for a few hours up to a few days before analysis at room temperature (20°C). Samples for nitrate were collected in plastic vials,

Table 1. *Cruises from 1993 to 1997*

Cruise id.	Vessel	Month	Year	Area	$f\text{CO}_2$	C_T/A_T	Mixed layer depth
Sum93	Johan Hjort	July–Aug.	1993	GS, NS	×	yes	10 m
Win95	Håkon Mosby	Feb.–March	1995	GS, NS	yes	yes	100 m
Spr95	Johan Hjort	May	1995	GS, NS	yes	yes	20 m
Sum95	Håkon Mosby	July–Aug.	1995	NS	yes	×	×
Fall95	Johan Hjort	Nov.	1995	GS, NS	yes	yes	20 m
Sum96	James C. Ross	July–Aug.	1996	GS, NS	yes	yes	10 m
Fall96	Håkon Mosby	Nov.–Dec.	1996	GS	yes	yes	20 m
Win97	Håkon Mosby	Feb.–March	1997	GS, NS	yes	yes	100 m
Spr97	Johan Hjort	May	1997	GS, NS	yes	×	20 m

Fugacity of CO_2 , $f\text{CO}_2$ is measured both in the surface water and atmosphere; C_T is the total dissolved inorganic carbon; and A_T is the total alkalinity in seawater. GS denotes the Greenland Sea, and NS is the Norwegian Sea. × means not measured.

stored at 4°C without preservatives and analysed within 24 hours for the Sum96 and Spr97 cruises. For the two cruises in between (Fall96 and Win97), nitrate samples were collected and frozen, still without preservatives, and analysed respectively 5 and 2 months after the cruises.

Total alkalinity, A_T , was determined on the cruises from 1996 to 1997 using a rapid, open, potentiometric titration (Haraldsson et al., 1997). The precision, obtained from replicate analysis of the samples, was 1.5–2.5 $\mu\text{mol kg}^{-1}$. Certified reference material (CRM) supplied by A. Dickson at Scripps Institution of Oceanography, USA, was used to determine the accuracy, which for A_T was 1–2 $\mu\text{mol kg}^{-1}$. *Total carbon*, C_T , was determined using gas extraction from acidified seawater samples, followed by coulometric titration with photometric detection (Johnson et al., 1985, 1987). The precision was 1.5–2.5 $\mu\text{mol kg}^{-1}$, and the accuracy, based on CRM measurements, was 2.5 $\mu\text{mol kg}^{-1}$. Analyses of *nitrate* were performed using standard methods with autoanalysers and photometric detection (Grasshoff et al., 1983), and the precision was 0.1 $\mu\text{mol kg}^{-1}$ for nitrate. Underway $f\text{CO}_2$ measurements (measured while the vessel is moving) were based on infra-red analysis of CO_2 in a gas sample equilibrated with seawater (Cooper et al., 1998). The CO_2 gas was not dried prior to detection, which gave us the advantage of measuring fugacity directly. Therefore, all $f\text{CO}_2$ values shown in figures and tables are at 100% humidity. The $f\text{CO}_2$ instrument was kept calibrated against three secondary standards (CO_2 in synthetic air). These dry stand-

ards were corrected to 100% humidity, and the data were corrected for temperature differences (0.3–3°C) between the incoming seawater and the water in the equilibration cylinder (Takahashi et al., 1993). NOAA/CMDL of Boulder, USA, provided us with WMO certified gas standards, and the values of secondary standards were derived from intercalibration with the NOAA primary standards. The $f\text{CO}_2$ measurements had a precision of 1–2 μatm . Intercalibration tests have been carried out at sea and in laboratories, and the measurements were within 1–2 μatm between different systems. The largest differences between results from different groups were not due to the analytical technique used, but mainly due to different methods of calculating $f\text{CO}_2$.

In addition to direct $f\text{CO}_2$ measurements, we have calculated $f\text{CO}_2$ from total C_T and A_T data, using the carbon species calculation program developed by Lewis and Wallace (1998), with the following settings, as recommended by the authors: CO_2 constants from Roy et al. (1993), total pH scale, and dissociation constant for KSO_4^- from Dickson (1990). The salinity, C_T , and A_T data used were from the mixed layer (see Table 1) at discrete stations. A comparison between the measured and calculated $f\text{CO}_2$ in the surface ocean is shown in Fig. 2.

3. Results

Our data can be divided into two time periods; the first covers the whole year of 1995

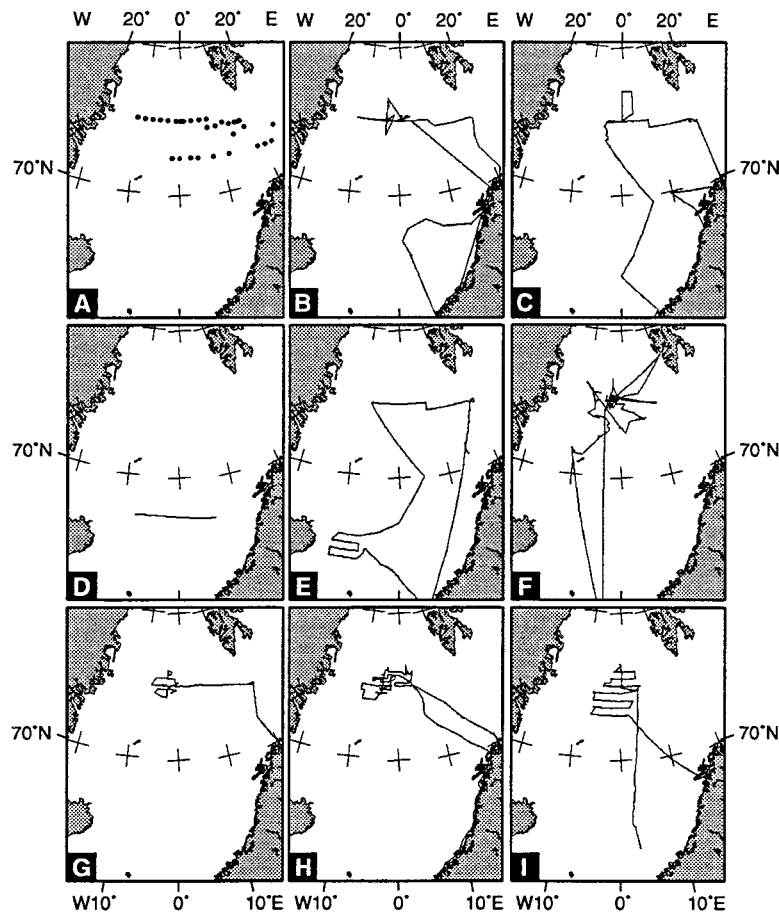


Fig. 1. The Nordic Seas surrounded by Greenland in the upper left corner and Norway in the lower right corner. Cruise tracks from A; summer 1993, B; winter 1995, C; spring 1995, D; summer 1995, E; fall 1995, F; summer 1996, G; fall 1996, H; winter 1997, and I; spring 1997 are shown.

(Johannessen et al., 1996), and the second is the annual cycle starting in summer 1996 and ending in spring 1997 (Table 1). For the 1995 summer season, our data set covered only the Norwegian Sea, NS, and for representative summer $f\text{CO}_2$ in the Greenland Sea, GS, we used surface mixed layer C_T and A_T data from summer 1993 to calculate $f\text{CO}_2$. This approximation rested on the observation that there were no significant interannual variations in the GS during the years 1993 to 1995 (Miller et al., in press).

In general, during the winter season, sea surface $f\text{CO}_2$ values were relatively high, close to the atmospheric values, and during the spring, $f\text{CO}_2$

was quite patchy until it stabilised at low values during summer. In the fall, a return to winter situation was observed, caused by the general breakdown of the thermocline and mixing with deeper water just below the seasonal thermocline.

During our investigation, we were in the field for short, representative periods of the year, and our observations are brief snap-shots of the $f\text{CO}_2$ in the sea surface and the atmosphere. The fluxes introduced in the following paragraphs were calculated from eq. (4) and Wanninkhof's relationship for gas transfer coefficient (1992). Also, we have estimated uncertainties in these fluxes, based on standard deviations in the wind speed and the

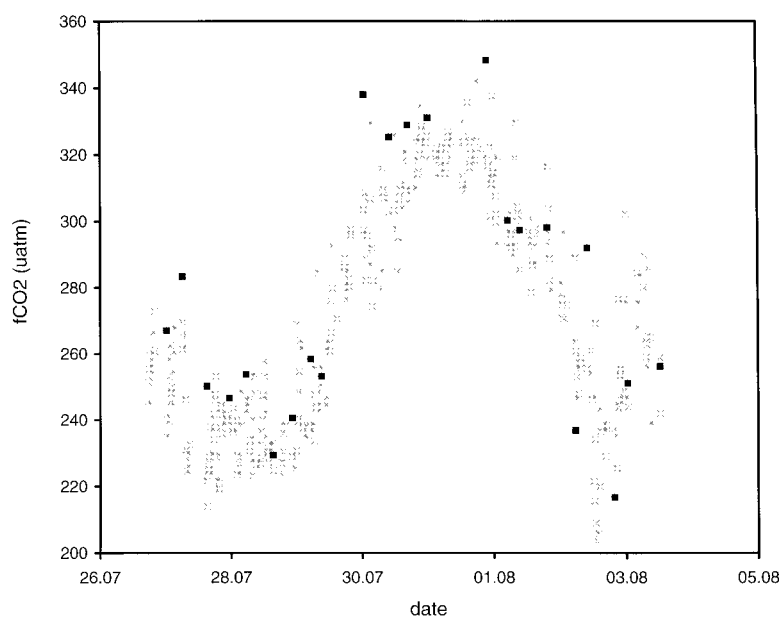


Fig. 2. An example of the fit between measured sea surface $f\text{CO}_2$ values, X, and calculated $f\text{CO}_2$ values based on measured A_T and C_T (Sum96 cruise).

natural variability observed in the $f\text{CO}_2$ measurements, and these are shown in Table 2.

3.1. Winter 1995 to fall 1995

Fig. 3 shows sea surface temperature, SST, in the GS during winter 1995, with relatively cold water in the central GS surrounded by warmer water to the south and east. In particular, the warm North Atlantic Current is clearly seen to the east, and the colder Polar Surface Water (PSW) is seen to the west. Between the areas dominated by PSW and North Atlantic Surface Water (NASW), we find the Arctic Surface Water (ASW), which is a mixing product of the two (Aagaard et al., 1985). Fig. 4 shows the seasonal variability in air and sea $f\text{CO}_2$ and in SST along 75°N in 1995. Even within the same season $f\text{CO}_2$ is considerably variable, particularly in spring. Throughout 1995, the partial pressure of CO_2 in the sea surface was lower than in the air. During the winter, an underpressure of about $30 \mu\text{atm}$ was measured in the ocean surface, and summer $f\text{CO}_2$ values were as low as $210 \mu\text{atm}$ to the west in the GS. Note that this latter value was based on calculated ocean surface $f\text{CO}_2$ from summer

1993. In general, $f\text{CO}_2$ during spring was similar to the winter values in the eastern part of the GS, but the values differed in the western part, where $f\text{CO}_2$ was very patchy. This indicates that biological production and the following drawdown of CO_2 had started in the west. This statement is further confirmed by the nutrient data (F. Rey, personal communication).

Fig. 5 shows the seasonal variability in $f\text{CO}_2$ in the NS. The seasonal change was occasionally larger than in the GS. During winter in the NS, the sea surface $f\text{CO}_2$ values were close to atmospheric $f\text{CO}_2$ values, and during the spring bloom, we measured a drop in surface $f\text{CO}_2$ of about $35 \mu\text{atm}$. The seasonal change in temperature was less than that observed in the GS.

The estimated seasonal air-sea CO_2 fluxes in the central GS and NS for 1995, are shown in Table 2. For the central GS, the calculations are based on data from $74.5\text{--}75.5^\circ\text{N}$, $5^\circ\text{W}\text{--}3^\circ\text{E}$, and for the NS, data from $64.5\text{--}70.5^\circ\text{N}$, $7^\circ\text{W}\text{--}5^\circ\text{E}$ was used. Mean monthly wind speeds were based on pressure field data (Eide et al., 1985; Falck, 1993), and these wind speeds were further averaged over the time periods of the $f\text{CO}_2$ data. Fluxes of CO_2 varied from $0.40 \text{ mol } \text{CO}_2 \text{ m}^{-2} \text{ month}^{-1}$ during

Table 2. Calculated air–sea CO₂ fluxes in the Greenland Sea (GS) and in the Norwegian Sea (NS)

Greenland Sea				
Year/ season	Wind speed (m s ⁻¹)	Mean $\Delta f\text{CO}_2$ (μatm)	Flux mol CO ₂ (m ⁻² month ⁻¹)	Flux (Gt C month ⁻¹)
1995 winter	10.8	–36	–0.40	–0.0039 ± 0.0010
1995 spring	8.2	–57	–0.36	–0.0035 ± 0.0014
1993 summer	7.2	–109	–0.53	–0.0051 ± 0.0017
1995 fall	11.2	–50	–0.59	–0.0057 ± 0.0011
1996 summer	7.2	–82	–0.40	–0.0039 ± 0.0013
1996 fall	11.2	–79	–0.92	–0.0090 ± 0.0019
1997 winter	10.8	–55	–0.61	–0.0059 ± 0.0019
1997 spring	8.2	–70	–0.44	–0.0043 ± 0.0011
Norwegian Sea				
1995 winter	10.8	–8	–0.091	–0.0015 ± 0.0011
1995 spring	8.2	–52	–0.32	–0.0054 ± 0.0024
1995 summer	7.2	–63	–0.30	–0.0051 ± 0.0014
1995 fall	11.2	–23	–0.27	–0.0045 ± 0.0014
1996 summer	7.2	–60	–0.29	–0.0049 ± 0.0015
1997 winter	10.8	–12	–0.13	–0.0022 ± 0.0020
1997 spring	8.2	–51	–0.32	–0.0053 ± 0.0020

Fluxes in mol CO₂ m⁻² month⁻¹ are based on data from 74.5–75.5°N, 5°W–3°E, and 64.5–70.5°N, 7°W–5°E, and fluxes in Gt C month⁻¹ are based on the total areas of the GS (0.81 · 10⁶ km²) and NS (1.39 · 10⁶ km²). The gas transfer relationship from Wanninkhof (1992) was used. Negative signs denote fluxes into the ocean. The uncertainties in the fluxes are estimated based on standard deviations in the wind speed and the natural variability observed in the $f\text{CO}_2$ measurements.

winter to 0.53 mol CO₂ m⁻² month⁻¹ during summer. As can be seen in Table 2, the calculated CO₂ flux is more sensitive to changes in wind speed than to changes in $\Delta f\text{CO}_2$, which is in line with what we expected, due to the quadric of wind speed in Wanninkhof's (1992) equation.

3.2. Summer 1996 to spring 1997

During winter 1997 (Fig. 6), parts of the Nordic Seas were distinctively colder than in winter 1995. In Fig. 7, a strong seasonal change from summer 1996 to spring 1997 in sea surface $f\text{CO}_2$ and SST was observed in the central GS, and there was also a large variability within each season. In addition, there was a year-round underpressure of CO₂ in the sea surface of approximately –50 μatm during winter, and as low as –140 μatm during the summer season. Seasonal variations appeared to be large in the ASW, and decreased towards the east in the NASW. There were also large seasonal variations in SST, with differences up to 10°C between winter and summer in the eastern part of the GS. According to Skirrow (1975) and Takahashi et al.

(1993), this change in temperature from winter to summer corresponds to a potential increase in surface $f\text{CO}_2$ of about 130 μatm . No such increase was seen between these two seasons, but rather a decrease in sea surface $f\text{CO}_2$ of 90 μatm , which might reflect a strong biological activity in this area during summer and an extensive drawdown of $f\text{CO}_2$ in the sea surface.

For the NS (Fig. 5) the observed change between surface $f\text{CO}_2$ in winter 1997 and summer 1996 was approximately –60 μatm . Correspondingly, the SST change was about 6°C, and the potential of biologically induced drawdown of CO₂ was approximately 140 μatm . Table 2 shows the calculated air–sea CO₂ flux for the different seasons in the GS and the NS for the period 1996–97.

3.3. Comparison

When we compare the two periods, 1995 and 1996–97, in the GS, an obvious difference is evident in the winter seasons. During winter 1997, the sea surface $f\text{CO}_2$ in the GS was 20–30 μatm

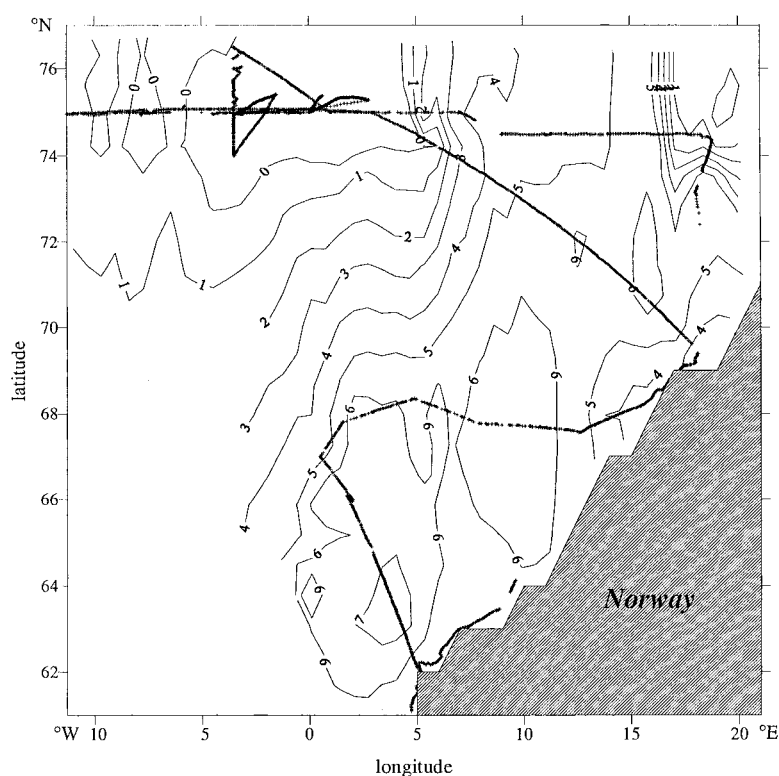


Fig. 3. Sea surface temperatures from winter 1995 in the Greenland and Norwegian Seas.

lower than in winter 1995. The majority of this difference can be explained by the lower SST and surface salinity in winter 1997; ΔT is as large as 1.5°C , and $\Delta S = 0.1$. Thus, wintertime $f\text{CO}_2$ values appear to be largely dependent upon water characteristics, in agreement with the assumption that biological activity is insignificant in these waters at this time of year. Another important factor is the variable ice cover in the GS. During winter 1995, most of the basin was covered by open water, while two years later, the ice cover was more extensive and fluctuated. The ice cover might serve as a shield against air–sea gas exchange, and may be an additional explanation for the low $f\text{CO}_2$ in the sea surface during winter 1997.

The two summer seasons in the GS were also significantly different from each other. While nitrate was almost completely consumed in summer 1993, nitrate values were as high as $5 \mu\text{mol kg}^{-1}$ in the 1996 summer season in the central GS. Similar values were also measured in the same area at that time by Rey (1996). The ice cover was extensive

during summer 1996, and a thin fresh water layer covered almost the whole area, both indications of distinctively different oceanic conditions from our first period of sampling.

While the central GS appeared to be a sink for CO_2 throughout the year, the NS had winter seawater $f\text{CO}_2$ values relatively close to those of the atmosphere in both 1995 and 1996–97, and for short periods of time, this ocean might have been a source for CO_2 . However, the NS was primarily a sink for atmospheric CO_2 , on the order of $0.049 \text{ Gt C yr}^{-1}$, for the whole period of study. The GS and NS, together, were estimated to be a sink of $0.12 \text{ Gt C yr}^{-1}$, based on data from 1996–1997.

4. Discussion

The Nordic Seas are assumed to be an important sink for CO_2 throughout the year, due to cooling of surface water along the northward

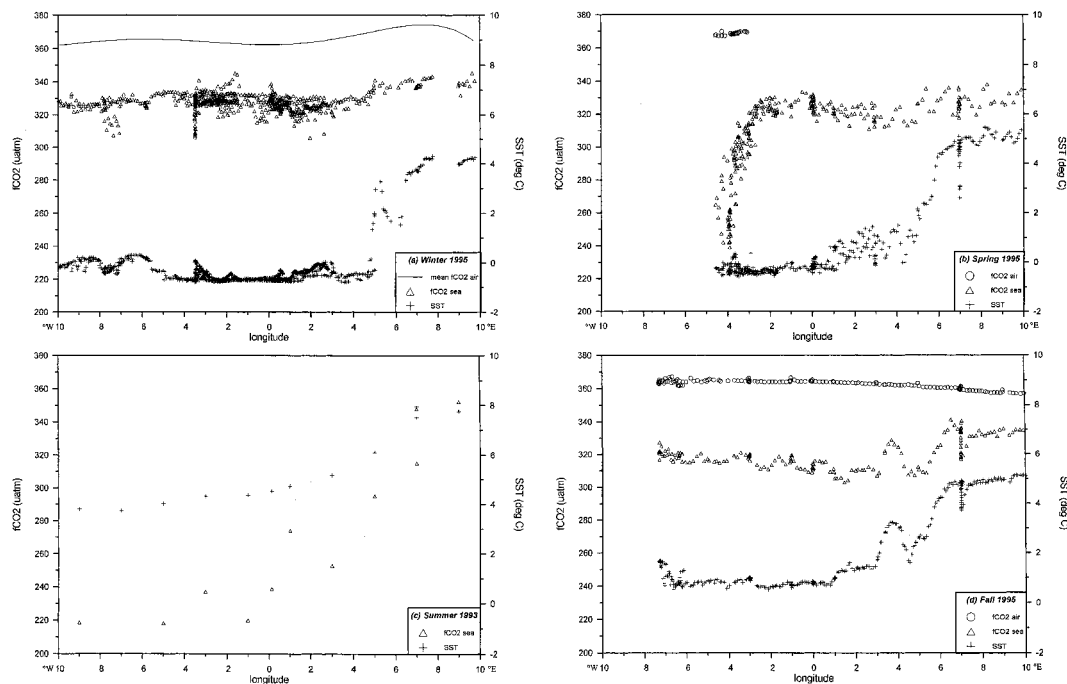


Fig. 4. Seasonal air $f\text{CO}_2$, sea surface $f\text{CO}_2$ and surface temperatures (SST) along 75°N in the Greenland Sea during 1995 (summer data from 1993). (a) Winter, (b) spring, (c) summer, and (d) fall. The solid line indicates the mean $f\text{CO}_2$ in air. The sea surface $f\text{CO}_2$ in summer 1993 was calculated from C_T and A_T .

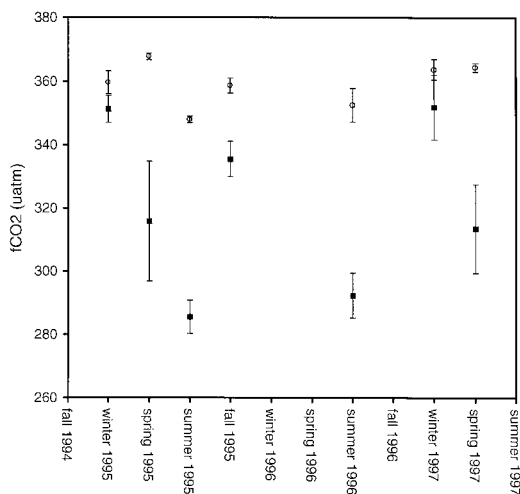


Fig. 5. Fugacity of CO_2 in surface water, $\blacksquare$, and the atmosphere, $\circ$, in the Norwegian Sea ($64.5\text{--}70.5^\circ\text{N}$, $7^\circ\text{W}\text{--}5^\circ\text{E}$) from 1995 to 1997. The symbols indicate the mean value of all data during a cruise in the actual area and season. The error bars indicate the temporal variability (1σ) in the measurements.

passage of the North Atlantic Current and the convection of the ASW in the GS, and the data presented in this paper validate this assumption. The area of the Nordic Seas is rather small compared to the area of the world ocean, and for this reason, the sink seems not to be of crucial importance on a global scale. However, the deep convection is very sensitive to small changes in heat exchange or fresh water release into the GS, and if the rate of deep water formation decreases dramatically, this will influence global oceanic circulation. Deep water formation in this area has fluctuated significantly between glacial and interglacial periods, and has apparently stopped altogether at times (Labeyrie et al., 1992). Under present conditions (1996–97), deep water formation in the GS, seems to carry $0.074 \pm 0.011 \text{ Gt C yr}^{-1}$ into the deep ocean.

Large seasonal variations are apparent in the calculated air–sea fluxes in the GS shown in Table 2. In addition, interannual variations are seen when comparing winter flux data from different years, and the same tendency is seen during

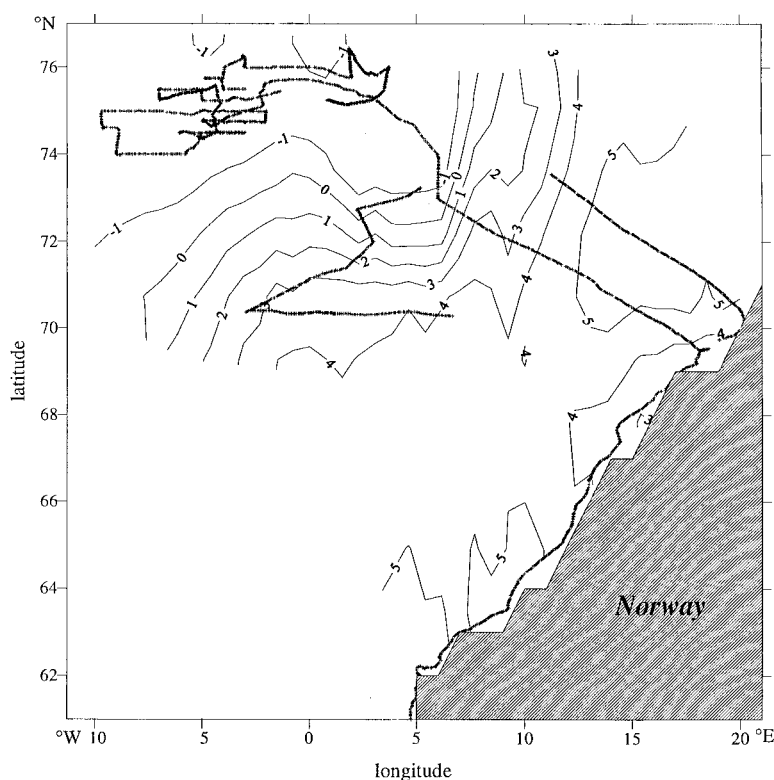


Fig. 6. Sea surface temperatures from winter 1997 in the Greenland and Norwegian Seas.

the spring and fall seasons. This interannual variability is consistent with the observations of colder surface waters and intensified deep water formation in the GS during recent years, and the GS seems to be less stable during these latter years than in our first period of study. Beside this increasing amplitude of the seasonal air–sea fluxes, the flux showed an increasing trend in the uptake of CO_2 of about $9 \cdot 10^{-4} \text{ Gt C yr}^{-1}$. It is not clear if this trend is significant, though it might indicate that the air–sea exchange in the GS has increased on the order of an expected increase in $f\text{CO}_2$ due to anthropogenic input of carbon (Oudot et al., 1995). The $f\text{CO}_2$ time series presented here are not particularly long, but it is worth pointing out that our observation of an increase in the potential CO_2 uptake seems to correlate with the change in the North Atlantic Oscillation (NAO) Index, which, after being positive for a 10-year period, changed to a strongly negative value for the one winter 1996 (the NAO winter index from

December to March). A correlation between changes in the NAO index and rates of deep water formation in the GS have been shown (Dickson et al., 1996). For the NS, there is no significant increase in the seasonal amplitudes of the air–sea CO_2 exchange through recent years, as observed in the GS. On the other hand, we see an increasing trend in the flux of CO_2 , corresponding to the probable anthropogenic signal observed in the GS, but the trend in NS seems to be weaker than in the GS.

The areas over which we have averaged our $f\text{CO}_2$ data to be used in the flux calculations, are quite large, though they represent only 2–3% of the total area of these oceans; in the GS, we have averaged data over an area of $2.56 \cdot 10^{10} \text{ m}^2$ ($74.5\text{--}75.5^\circ\text{N}$, $5^\circ\text{W}\text{--}3^\circ\text{E}$), and for the NS, the area used was $3.38 \cdot 10^{10} \text{ m}^2$ ($64.5\text{--}70.5^\circ\text{N}$, $7^\circ\text{W}\text{--}5^\circ\text{E}$). The natural variability in the $f\text{CO}_2$ data from these large areas was often high during periods of sampling, particularly during spring and summer seasons

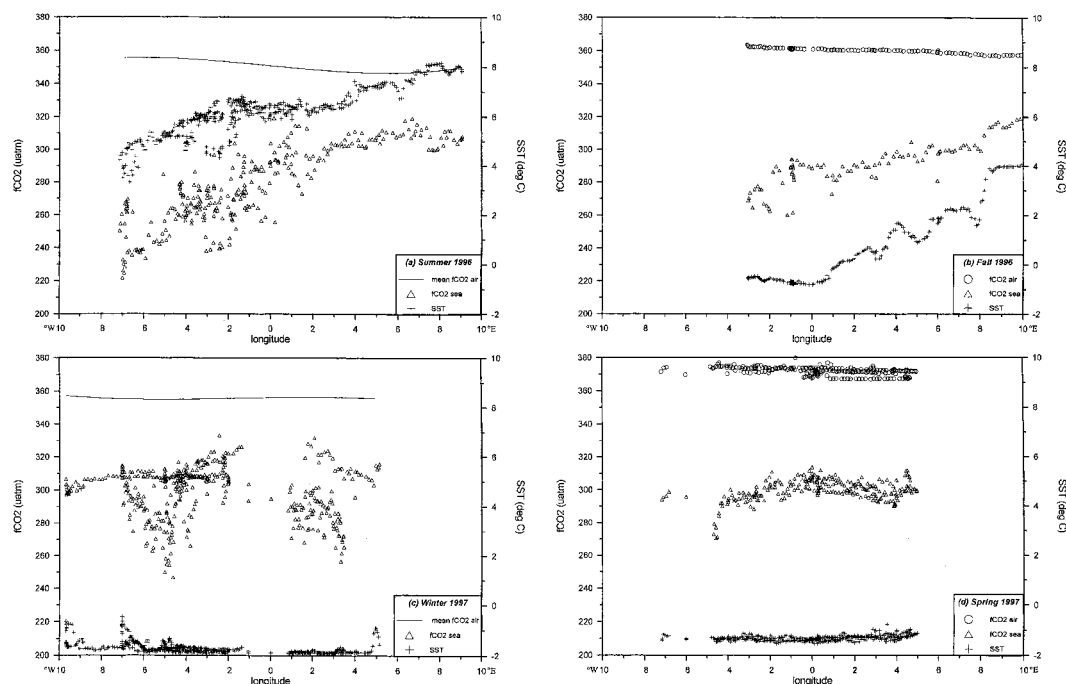


Fig. 7. Seasonal air $f\text{CO}_2$, sea surface $f\text{CO}_2$ and surface temperatures (SST) along 75°N in the Greenland Sea, during 1996–97. (a) Summer 1996, (b) fall 1996, (c) winter 1997, and (d) spring 1997. The solid line indicates the mean $f\text{CO}_2$ in air.

($\pm 15 \mu\text{atm}$), and as a consequence, we get large uncertainties in our estimated CO_2 fluxes (Table 2). In addition, uncertainties in the flux calculation are also influenced by the deviation of the wind speeds ($1\sigma = \pm 1 \text{ m s}^{-1}$) and the uncertainties in the relationships for the gas transfer coefficient.

Table 3 shows the temperature and nitrate

changes between seasons, and the associated effects on $f\text{CO}_2$, in the GS. From winter to summer 1995, we observed a drop in $f\text{CO}_2$ of $87 \mu\text{atm}$, while the calculated drop based on the temperature increase and nitrate consumption, assuming a Redfield ratio of 16:106 for nitrate to carbon, was $41 \mu\text{atm}$. This implies that

Table 3. Changes in sea surface $f\text{CO}_2$, $\delta f\text{CO}_2$, between seasons in the central Greenland Sea

Greenland Sea				
Season (year)	δT ($^\circ\text{C}$)	δNO_3 ($\mu\text{mol kg}^{-1}$)	$\delta f\text{CO}_2$ calculated (μatm)	$\delta f\text{CO}_2$ observed (μatm)
Winter–summer (1995)	5.1	–10.8	–41	–87
Summer–fall (1995)	–3.6	9.0	42	74
Fall–winter (1995)	–1.5	1.9	–1	13
Winter–summer (1996/97)	7.7	–9.3	9	–30
Summer–fall (1996)	–6.4	5.8	–25	12
Fall–winter (1996/97)	–1.4	3.5	17	19

Calculated $\delta f\text{CO}_2$ is based on the influence of biological activity and temperature change, assuming: $\Delta T = +1^\circ\text{C} \Rightarrow \Delta f = +13 \mu\text{atm}$ (Skirrow, 1975); $\Delta C_T = +1 \mu\text{mol kg}^{-1} \Rightarrow \Delta f = 1.5 \mu\text{atm}$ (Watson et al., 1993); and $N:C = 16:106$ (Redfield, 1963).

$30 \mu\text{mol C kg}^{-1}$ of carbon was removed from the surface water by some mechanism other than biological consumption, reducing $f\text{CO}_2$ by an additional $46 \mu\text{atm}$ compared to the $41 \mu\text{atm}$ calculated. In the central GS, surface water is advected into the region from the surrounding oceans. Some of the advected water from the East Greenland Current (EGC, average characteristics; $T = -1^\circ\text{C}$, $S = 33.7$ psu, according to Hopkins, 1991) is transported under sea ice, and if we assume that the water is not supersaturated with respect to carbon, due to mixing with water masses below, and since ice cover will effectively reduce or prevent air–sea gas exchange, we might also assume that the advected water contained less carbon than if the EGC had been ice-free. The mixing of water masses might therefore result in a lower $f\text{CO}_2$ value, compared to the expected value based on changes in temperature and biological activity. The same analysis of the winter and summer seasons in 1996–97 gave a difference in the observed central GS surface $f\text{CO}_2$ of $-30 \mu\text{atm}$, while the calculated $f\text{CO}_2$ values based on the temperature increase and nitrate consumption gave a difference of $+9 \mu\text{atm}$, which indicates a slightly smaller difference between the observed and calculated $f\text{CO}_2$ than in 1995. The water masses PSW and NASW mix in the GS, and since the mixing ratio may change from year to year, the CO_2 content in the resulting water mass may also vary over time. During 1996–97, the GS was covered by sea ice both in summer and winter, and therefore, we would have expected an even larger discrepancy between the observed and calculated $f\text{CO}_2$. However, the increased vertical mixing, which occurred in the convective area (A. Watson, personal communication), counteracted the effect of the sea ice cover.

5. Conclusions

The dynamics of the Greenland and Norwegian Seas vary both on seasonal to interannual time-scales, and after about a decade of restricted deep water formation (Bönisch et al., 1997), convection to deeper levels in the water column was observed in this area during 1996–97 (A. Watson, personal communication). Due to the colder temperatures,

more intense sea ice formation and stronger convection in the Greenland Sea during winter 1997, larger air–sea CO_2 fluxes were observed, compared to previous winters.

The surface waters of the Greenland Sea were undersaturated with respect to CO_2 in the air throughout the year and were therefore a sink for CO_2 the year around. The Norwegian Sea was also a CO_2 sink for most of the year, but during the winter season, $\Delta f\text{CO}_2$ was small. The annual sink in these two seas during 1996–97 was estimated to be $0.12 \pm 0.015 \text{ Gt C yr}^{-1}$.

A comparison between the winter periods in the Greenland Sea in 1995 and 1997 showed a $20\text{--}30 \mu\text{atm}$ lower sea surface $f\text{CO}_2$ during winter 1997. The CO_2 uptake during the winters of 1995 and 1997 was $3.9 \cdot 10^{-3} \text{ Gt C month}^{-1}$ and $5.9 \cdot 10^{-3} \text{ Gt C month}^{-1}$, respectively (mean winter wind speed = 10.8 m s^{-1}). The lower sea surface $f\text{CO}_2$ in 1997 could be explained by the extended ice cover and colder surface temperatures in the Greenland Sea Gyre in 1996–97, compared to 1995. During the last year (1996–97), the Greenland Sea probably “fed” the deep water with approximately $0.074 \pm 0.011 \text{ Gt C yr}^{-1}$.

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REFERENCES

- Aagaard, K., Swift, J. H. and Carmack, E. C. 1985. Thermohaline circulation in the Arctic Mediterranean Seas. *J. Geophys. Res.* **90**, 4833–4846.
- Bönisch, G., Blindheim, J., Bullister, J. L., Schlosser, P. and Wallace, W. R. 1997. Long-term trends of temperature, salinity, density, and transient tracers in the central Greenland Sea. *J. Geophys. Res.* **102**, 18,553–18,571.
- Cooper, D. J., Watson, A. J. and Ling, R. D. 1998. Variations of P_{CO_2} along a North Atlantic shipping route (UK to the Caribbean): a year of automated observations. *Mar. Chem.* **60**, 147–164.
- Dickson, A. G. 1981. An exact definition of total alkalinity, and a procedure for the estimation of alkalinity and total carbon from titration data. *Deep-Sea Res.* **28A**, 609–623.
- Dickson, A. G. 1990. Standard potential of the reaction: $AgCl(s) + 1/2H_2(g) = Ag(s) + HCl(aq)$, and the standard acidity constant of the ion HSO_4^- in synthetic sea water from 273.15 to 318.15 K. *J. Chem. Thermodyn.* **22**, 113–127.
- Dickson, R., Lazier, J., Meincke, J., Rhines, P. and Swift, J. 1996. Long-term coordinated changes in the convective activity of the North Atlantic. *Prog. Oceanog.* **38**, 241–295.
- DOE 1994. *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water* (eds. A. G. Dickson and C. Goyet), vers. 2.
- Eide, L. I., Reistad, M. and Guddal, J. 1985. *Database av beregnede vind og bølgeparametre for Nordsjøen, Norskehavet og Barentshavet, hver 6. time for årene 1955–81*. Prosjekt “Hindcast-database”. Norwegian Meteorological Institute, Norway, 1–38.
- Falck, E. 1993. *Oksygenflukser gjennom overflaten og biologisk netto produksjon i De nordiske hav*. Master thesis, Geophysical Institute, University of Bergen, Norway, 1–80.
- Grasshoff, K., Ehrhardt, M. and Kremling, K. 1983. *Methods of seawater analysis*. Verlag Chemie, Germany.
- Haraldsson, C., Anderson, L. G., Hasselöv, M., Hulth, S. and Olsson, K. 1997. Rapid, high-precision potentiometric titration of alkalinity in the ocean and sediment pore waters. *Deep-Sea Res. I* **44**, 2031–2044.
- Hopkins, T. S. 1991. The GIN Sea — a synthesis of its physical oceanography and literature review 1972–1985. *Earth-Science Reviews* **30**, 175–318.
- Johannessen, T., Skjelvan, I., Miller, L. A., Stoll, M. H. C., Jansen, E. and Anderson, L. G. 1996. Air/sea fluxes of carbon in the Nordic Seas with emphasis on the Greenland Sea. In: *European subpolar ocean programme: sea ice-ocean interactions* (eds. Wadhams, P., Wilkinson, J. P. and Wells, S. C. S.), 2, Scott Polar Research Institute, Cambridge, 491–503.
- Johnson, K. M., King, A. E. and Sieburth, J. M. 1985. Coulometric TCO_2 analyses for marine studies: an introduction. *Mar. Chem.* **16**, 61–82.
- Johnson, K. M., Sieburth, J. M., Williams, P. J. and Brandstrom, L. 1987. Coulometric total carbon dioxide analysis for marine studies: automation and calibration. *Mar. Chem.* **21**, 117–133.
- Labeyrie, L. D., Duplessy, J.-C., Duprat, J., Juillet-Leclerc, A., Moyes, J., Michel, E., Kallel, N. and Shackleton, N. J. 1992. Changes in the vertical structure of the North Atlantic Ocean between glacial and modern times. *Quaternary Science Reviews* **11**, 401–413.
- Lewis, E. R. and Wallace, D. W. R. 1998. *Program developed for CO_2 system calculations*. ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Dep. of Energy, Oak Ridge, Tennessee.
- Liss, P. S. and Merlivat, L. 1986. Air-sea gas exchange rates: introduction and synthesis. In: *The rôle of air-sea exchange in geochemical cycling* (ed. Buat-Menard, P.). NATO ASI Series C: Mathematical and Physical Sciences **185**, D. Reidel Publishing Company, 113–127.
- Miller, L. A., Johannessen, T., Noji, T. T., Rey, F. and Skjelvan, I. 1999. Seasonal dissolved inorganic carbon variations in the Greenland Sea and implications for atmospheric CO_2 exchange. *Deep-Sea Res. II*, in press.
- Oudot, C., Terner, J. F. and Lecomte, J. 1995. Measurements of atmospheric and oceanic CO_2 in the tropical Atlantic: 10 years after the 1982–1984 FOCAL cruises. *Tellus* **47B**, 70–85.
- Redfield, A. C., Ketchum, B. H. and Richards, F. A. 1963. The influence of organisms on the composition of seawater. In: *The sea* (ed. Hill, M. N.). John Wiley, New York, 26–77.
- Rey, F. 1996. *Cruise report from cruise JH 1996210*. Institute of marine research, Bergen, Norway.
- Roy, R. N., Roy, L. N., Vogel, K. M., Porter-Moore, C., Pearson, T., Good, C. E., Millero, F. J. and Campbell, D. M. 1993. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45 deg C. *Mar. Chem.* **44**, 249–267.
- Siegenthaler, U. and Sarmiento, J. L. 1993. Atmospheric carbon dioxide and the ocean. *Nature* **365**, 119–125.
- Simonsen, K. and Haugan, P. M. 1996. Heat budgets of the Arctic Mediterranean and sea surface heat flux parametrizations for the Nordic Seas. *J. Geophys. Res.* **101**, 6553–6576.
- Skirrow, G. 1975. The dissolved gases — carbon dioxide. In: *Chemical oceanography* (eds. Riley, J. P. and Skirrow, G.), 2. Academic Press, London, 1–192.
- Takahashi, T., Olafsson, J., Goddard, J. G., Chipman, D. W. and Sutherland, S. C. 1993. Seasonal variations of CO_2 and nutrients in the high-latitude surface oceans: a comparative study. *Global Biogeochem. Cycles* **7**, 843–878.

- Takahashi, T., Feely, R. A., Weiss, R. F., Wanninkhof, R. H., Chipman, D. W., Sutherland, S. C. and Takahashi, T. T. 1997. Global air-sea flux of CO_2 . An estimate based on measurements of sea-air $p\text{CO}_2$ difference. *Proceedings from National Academy of Science, USA* **94**, 8292–8299.
- Tans, P. P., Fung, I. Y. and Takahashi, T. 1990. Observational constraints on the global atmospheric CO_2 budget. *Science* **247**, 1431–1438.
- Wanninkhof, R. 1992. Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* **97**, 7373–7382.
- Watson, A. J., Robertson, J. E. and Ling, R. D. 1993. Air-sea exchange of CO_2 and its relation to primary production. In: *Interactions of C, N, P and S biogeochemical cycles and global change* (eds. Wollast, R., Mackenzie, F. T. and Chou, L.). Springer-Verlag, Berlin, 249–257.
- Weiss, R. F. 1974. Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Mar. Chem.* **2**, 203–215.
- WOCE. 1994. WOCE Operations Manual, vol. 3, Section 3.1, Part 3.1.2. Revision 2. WHP Office Report 90-1, WOCE Report No. 67/91.