

# Seasonal variability of the carbon-nutrient chemistry in the ocean areas west and north of Iceland

*Taro Takahashi<sup>1)</sup>, Jón Ólafsson<sup>2)</sup>, Wallace S. Broecker<sup>1)</sup>  
John Goddard<sup>1)</sup>, David W. Chipman<sup>1)</sup> and James White<sup>1)</sup>*

<sup>1)</sup> Lamont-Doherty Geological Observatory of Columbia University, Palisades, N. Y. 10964, U. S. A.

<sup>2)</sup> Marine Research Institute, 101 Reykjavik, Iceland.

## ABSTRACT

The results of a seasonal investigation of carbon and nutrient chemistry in the surface waters at two stations located north and south of the Iceland-Greenland Ridge are summarized. These stations were occupied repeatedly at intervals of approximately three months during the period from March 1983 through November 1984 to monitor the seasonal variability of the following quantities: temperature, salinity, partial pressure of CO<sub>2</sub> in surface water and in the atmosphere, carbon-14 in surface water, and the concentrations of dissolved nutrients, oxygen, and CO<sub>2</sub>. The partial pressure of CO<sub>2</sub> in water and the concentrations of nutrients and CO<sub>2</sub> are lowest during the summer, the time when the carbon-14 and oxygen concentrations are greatest. The situation is reversed in winter. The observed summer values are attributable to the increased photosynthetic utilization of carbon and nutrients and reduced vertical mixing rate due to strong summer stratification in the upper water column. The winter values are attributed to the reduced photosynthetic rate due to shortened daylight hours and increased upward mixing of subsurface waters rich in CO<sub>2</sub> and nutrients but low in carbon-14. The CO<sub>2</sub> partial pressure data indicate that the surface water at these stations is an intense sink for atmospheric CO<sub>2</sub> during the summer months, whereas it becomes a weak to neutral sink during the fall, winter and spring months. At the southern station, it even became a weak CO<sub>2</sub> source during March 1984. The CO<sub>2</sub> partial pressure values observed in surface water during the winter and spring are found to be consistent with those estimated on the basis of the subsurface water data. Although the northern high latitude waters are generally considered to be an intense CO<sub>2</sub> sink throughout a year, our observations show this to be erroneous. Thus, in an estimation of the global uptake of atmospheric CO<sub>2</sub> by the oceans, the large seasonal variability in the CO<sub>2</sub> chemistry in the high latitude oceanic areas needs to be taken into consideration.

## INTRODUCTION

The northern North Atlantic is the formation area for the North Atlantic Deep Water mass. In this area, the surface water exchanges heat and chemical substances with the atmosphere, and sinks during the winter to the deep ocean regime. If this water carries with it significant quantities of carbon dioxide dissolved from the atmosphere, it would constitute a major pathway for the removal of industrial carbon dioxide

to the deep interior of the oceans. In addition, since the physical and chemical conditions of high latitude oceans are particularly sensitive to climatic changes, these oceanic areas could play a major role in the climate-oceanic CO<sub>2</sub> feedback processes. In order to evaluate the importance of this pathway, the seasonal variability needs to be observed.

Although numerous physical, chemical and biological investigations of these criti-

cal areas have been conducted, systematic seasonal observations of the carbon and nutrient chemistry are presently lacking. While the summer data indicate that northern high-latitude surface waters are undersaturated with respect to the atmospheric  $\text{CO}_2$  by as much as 50%, and hence the surface waters should take up a large quantity of  $\text{CO}_2$  from the atmosphere, the data for the winter season, when the vertical transport processes are most active, are virtually non-existent. If the situation in summer were significantly different from that in winter, interpretations and models based on the summer data alone would not be valid. For this reason, a cooperative programme was developed between the Lamont-Doherty Geological Observatory (L-DGO) and the Marine Research Institute, Reykjavik (MRI) to study the seasonal variation of the carbon and nutrient chemistry and of carbon-14 isotope concentration in the surface waters in the vicinity of Iceland during 1983–1984. This paper describes the results of the observations made at two stations located north and west of Iceland. These stations have been occupied repeatedly by a research vessel of the Icelandic Marine Research Institute at intervals of about three months starting in March, 1983. The measurements include temperature, salinity, partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ), carbon-14/carbon ratio, and the concentrations of dissolved carbon dioxide, phosphate, nitrate, silica and oxygen in surface water. The data demonstrate that the carbon chemistry of the surface water is strongly influenced by the upwelling of deep water in the winter months and by the biological utilization of carbon in the summer months.

#### STATIONS AND MEASUREMENTS

The two stations, which have been repeatedly occupied in 1983–84, are located in the vicinity of Iceland, one north ( $68^\circ\text{N}$  and

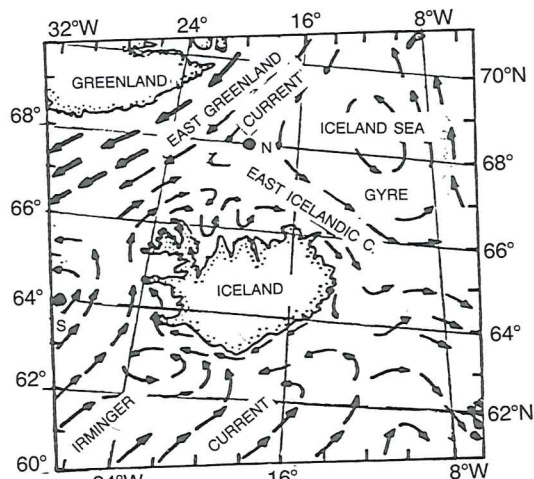


Fig. 1. General circulation of the surface water in the vicinity of Iceland. The two stations occupied for the seasonal study are indicated by N for the northern station ( $68^\circ\text{N}$  and  $19^\circ\text{W}$ ) and by S for the southern station ( $64^\circ\text{N}$  and  $28^\circ\text{W}$ ). The arrows indicate the general direction of flow. After Stefánsson (1961).

$19^\circ\text{W}$ ) and the other south ( $64^\circ\text{N}$  and  $28^\circ\text{W}$ ) of the Iceland-Greenland Ridge as shown in Figure 1. Hereafter, the  $68^\circ\text{N}$  station is referred to as the northern station, and the  $64^\circ\text{N}$  station as the southern station. The northern station (N in Fig. 1) is located in an area where the surface water is under the influence of both the southeastward-flowing East Icelandic Current and the northward-flowing North Atlantic (warmer and more saline) water. On the other hand, the southern station (S in Fig. 1) is located within the Irminger Current, which brings the warmer North Atlantic water from a southwesterly direction.

The measurements of temperature, salinity, nutrients and oxygen were conducted aboard the MRI research vessel by the MRI staff using standard oceanographic methods. Some phosphate values reported in this paper were obtained at the land-based laboratory at L-DGO using poisoned and stored water samples. The internal consistency of the shipboard and land-based analyses has been achieved by close intercalibration of the two sets of analyses.

The water samples (4 litres) for  $p\text{CO}_2$  measurements were equilibrated with marine air using a portable closed-system equilibrator immediately after water sampling. The equilibrated gas sample was isolated from the water, sealed in a Pyrex gas sampling flask, and shipped back to the laboratories at L-DGO for  $\text{CO}_2$  analyses by means of a gas chromatograph (Perkin-Elmer, Model Sigma-10). Air- $\text{CO}_2$  gas mixtures, which have been analyzed by C. D. Keeling of the Scripps Institution of Oceanography, have been used to calibrate the chromatograph. The *in situ* water temperature, the equilibration temperature, the total gas pressure during the equilibration, and the  $\text{CO}_2$  concentration in the initial air sample collected for equilibration are used to obtain the  $p\text{CO}_2$  exerted by the sea water sample. The overall precision of the  $p\text{CO}_2$  measurements is estimated to be about  $\pm 1\%$ . Marine air samples were also collected at the time of water sampling, sealed in Pyrex flasks, and analyzed using the same gas chromatograph to obtain the atmospheric  $\text{CO}_2$  concentration value. In this paper it is reported in the unit of mole fraction of  $\text{CO}_2$  in dry air. The precision of the atmospheric  $\text{CO}_2$  measurements is estimated to be about  $\pm 1$  ppm.

The water samples for the determination of the total  $\text{CO}_2$  concentration dissolved in sea water were collected in Pyrex bottles with ground glass stoppers, poisoned with mercuric chloride for storage, and analyzed at L-DGO using a  $\text{CO}_2$  coulometer (Coulometrics, Model 5010) a few months after collection. The coulometer is calibrated using three different standards (gravimetric  $\text{Na}_2\text{CO}_3$  crystals, gravimetric  $\text{CaCO}_3$  crystals and volumetric  $\text{CO}_2$  gas), all of which yield consistent values within  $\pm 2 \mu\text{M}/\text{kg}$ . The overall precision of the total  $\text{CO}_2$  measurements is estimated to be about  $\pm 4 \mu\text{M}/\text{kg}$ .

$\text{CO}_2$  samples for carbon-14 measurements were extracted from 200-litre sea water samples acidified with hydrochloric acid and

swept with nitrogen gas free of  $\text{CO}_2$ . The  $\text{CO}_2$  gas thus extracted was absorbed in a  $\text{CO}_2$ -free NaOH solution, which was sent back to the laboratories at L-DGO for carbon-14 analyses by means of liquid scintillation counting. In the laboratory, the  $\text{CO}_2$  in the NaOH solution was released by acidification and converted to benzene using a chromium oxide catalyzer. The benzene thus produced was mixed with a scintillation fluor (Butyl/PDB), and counted for carbon-14 activity using a liquid scintillation counter (Beckman Model LS-100C, or LKB Wallac, Model 1217 Rackbeta) for a period of about 67 hours. The carbon-14/carbon ratios reported in this paper are expressed in terms of the difference in the  $^{14}\text{C}/\text{C}$  ratio from the NBS oxalic acid standard. The overall precision of measurements is estimated to be about  $\pm 6\%$  on the  $\Delta^{14}\text{C}$  (‰) scale.

#### OBSERVATIONAL DATA

The data obtained during 1983 and 1984 are summarized in Table 1 and graphically presented in Figures 2 and 3. The mean temperature of surface water observed at these two stations is approximately  $1.3^\circ\text{C}$  at the northern and is approximately  $7.0^\circ\text{C}$  at the southern station. The seasonal peak-to-peak amplitude is about  $5^\circ\text{C}$  at the northern and  $3.5^\circ\text{C}$  at the southern station. The salinity at the southern station is nearly constant throughout the period of our investigation, averaging 35.0. On the other hand, the salinity at the northern station was variable during the summer, being as low as 33.1 in 1983 and 30.7 during the summer of 1984, due most likely to the increased influence of the low salinity East Greenland Current, and local ice melting in July-August 1984. During the rest of the year the salinity at this station was nearly constant at about 34.6. The total alkalinity values, which have been computed from the observed values of the total  $\text{CO}_2$  concentration,  $p\text{CO}_2$ , phos-

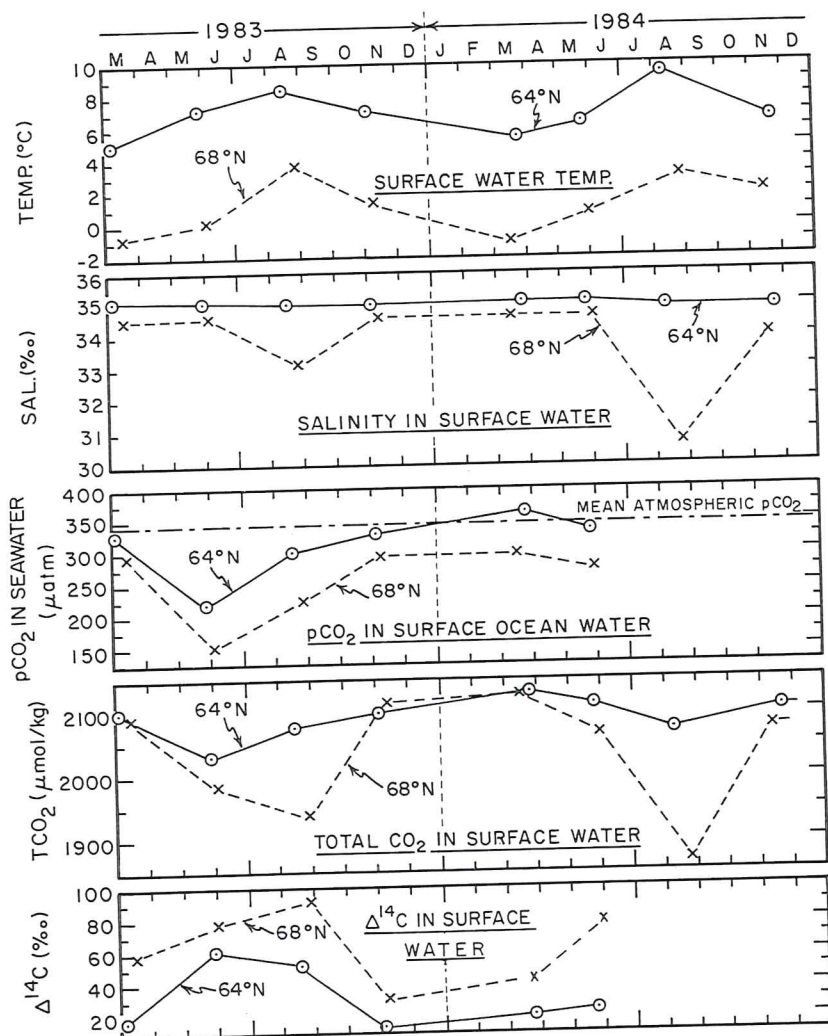


Fig. 2. The temperature, salinity, pCO<sub>2</sub>, total CO<sub>2</sub> concentration and <sup>14</sup>C/C ratio in the surface water observed at the northern (68°N) and southern (64°N) stations during the period from March 1983 through November 1984.

phate, silica, salinity and temperature using the formulation of Takahashi et al. (1982) are also listed in Table 1.

The pCO<sub>2</sub> value in surface sea water is found to be lowest in May-June at both stations, and is highest during the winter months. The lowest summer value is observed at the northern station, and is about 150 μatm, or nearly 200 μatm less than the atmospheric value of 345 μatm observed concurrently. At the southern station, the lowest value observed was about 225 μatm. These observations indicate that the sum-

mer surface water is highly undersaturated with respect to atmospheric CO<sub>2</sub>. Figure 4 shows the distribution of surface water pCO<sub>2</sub> observed in the summer of 1981 during the TTO/NAS Expedition. It is seen that the results of the present investigations are consistent with the 1981 data. From May-June 1983 to the following March the surface water pCO<sub>2</sub> value increase to about 360 μatm at the southern station and to about 300 μatm at the northern station. Although the temperature reached a maximum in August 1983 and had decreased by a

TABLE 1

The results of chemical analyses for the surface water samples (approximately 5 m deep) at the northern and southern stations. The atmospheric CO<sub>2</sub> concentration is expressed in mole fraction of CO<sub>2</sub> in dry air. The total alkalinity, T-ALK, is computed using the total CO<sub>2</sub> concentration, pCO<sub>2</sub>, phosphate and silica with the formulation of Takahashi et al. (1982).

St. No.	Date	Temp. (°C)	Salinity	PO <sub>4</sub>	NO <sub>3</sub>	SiO <sub>4</sub>	O <sub>2</sub>	AOU	TCO <sub>2</sub>	TCO <sub>2</sub> 35		pCO <sub>2</sub> sw (µatm)	Δ <sup>14</sup> C (‰)	T-ALK	
										TCO <sub>2</sub>	TCO <sub>2</sub> 35			(µeq/kg)	(µeq/kg)
<i>Northern station: 68°N, 18°50'W</i>															
83/110	3/15/83	-0.76	34.550	0.83	12.1	6.5	353	5	2091	2118	2118	294	59	2249	2278
83/504	6/3/83	1.11	34.622	0.12	0.3	0.2	427	-86	1982	2004	2004	152	78	2270	2295
83/767	8/27/83	3.79	33.15	0.17	1.2	0.8	311	11	1936	2044	2044	225	93	2143	2263
83/1054	11/10/83	1.42	34.673	0.73	10.8	4.8	338	0	2111	2131	2131	296	37	2285	2307
84/177	3/15/84	-1.02	34.634	0.79	11.5	6.0	355	5	2124	2146	2146	295	42	2284	2308
84/414	5/30/84	0.68	34.685	0.43	5.2	0.1	405	-61	2063	2082	2082	274	99	2239	2259
84/707	8/24/84	3.12	30.687	0.17	0.1	0.6	342	-9	1869	2132	2132	—	—	—	—
84/927	11/13/84	2.10	33.989	0.57	6.4	2.8	325	9	2076	2138	2138	—	—	—	—
<i>Southern station: 64°20'N, 27°55'W</i>															
83/071	3/5/83	4.96	35.076	0.94	14.6	7.8	315	-7	2101	2096	2096	329	18	2282	2277
83/465	5/28/83	7.17	35.108	0.32	5.5	0.4	413	-120	2031	2025	2025	219	61	2303	2296
83/654	8/16/83	8.46	35.018	0.57	8.1	2.6	280	5	2076	2075	2075	301	52	2298	2297
83/1008	11/2/83	7.08	35.020	0.84	12.2	5.5	289	5	2099	2098	2098	329	20	2296	2295
84/247	3/25/84	5.52	35.077	0.94	14.8	7.8	292	13	2130	2125	2125	364	39	2300	2295
84/374	5/25/84	6.37	35.100	0.91	14.2	7.8	351	-53	2116	2116	2116	333	30	2308	2301
84/547	8/9/84	9.47	34.909	0.68	7.8	1.6	286	-7	2070	2075	2075	—	—	—	—
84/940	11/20/84	6.58	34.891	0.84	13.0	6.3	280	17	2107	2114	2114	—	—	—	—

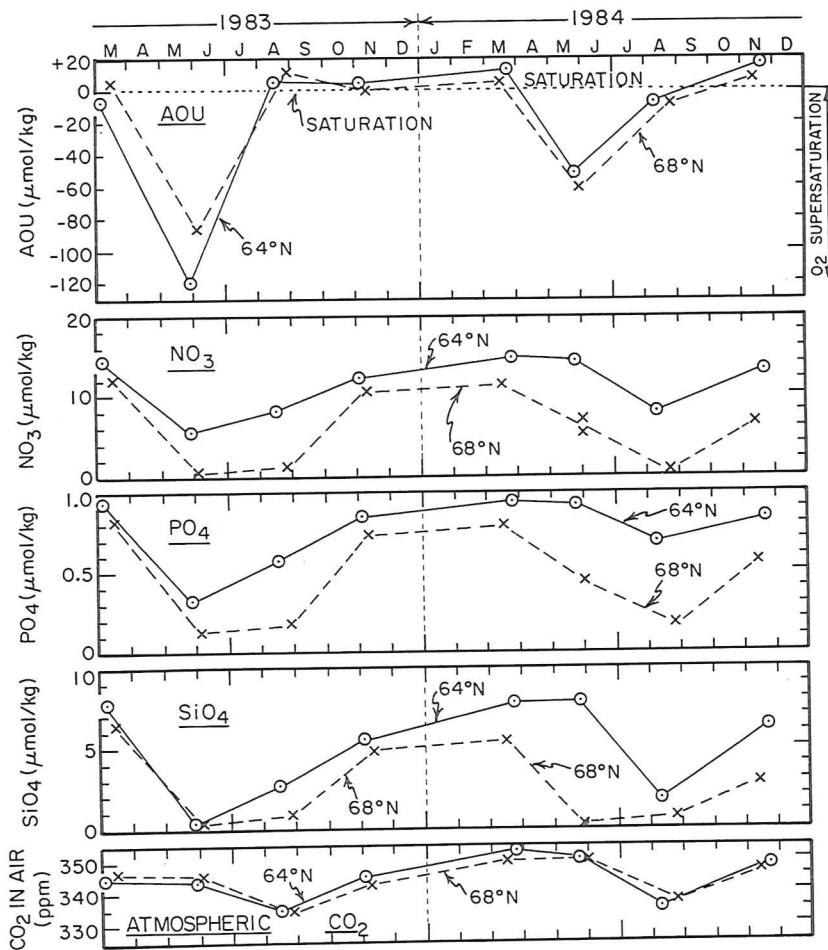


Fig. 3. The surface water concentrations of nitrate, phosphate and silica, AOU and the atmospheric CO<sub>2</sub> concentration observed at the northern and southern stations during the period from March 1983 through November 1984.

few degrees by March 1984, the pCO<sub>2</sub> continued to increase until March 1984. At both stations the March values are similar to those of the subsequent year. Although the winter pCO<sub>2</sub> values in the surface water are considerably higher than the summer values, they remain still lower than the atmospheric values by about 10 μatm at the northern station, and are approximately equal to the atmospheric value at the southern station. Thus, the surface waters are a strong sink for the atmospheric CO<sub>2</sub> in the summer months, and are a weak sink or nearly in equilibrium with the atmosphere during the winter months. Unfortunately, no pCO<sub>2</sub> data were obtained during the

spring through fall months in 1984 due to equipment failure.

The total CO<sub>2</sub> concentration in the surface water at both stations tracks the seasonal trend observed for surface water pCO<sub>2</sub>, being low in the summer months and high in the fall, winter and spring months. The concentrations of nutrients in the surface water are also found to be substantially lower during the summer months, June through September, than the winter and spring values. The concentrations observed at the southern station, located in the open North Atlantic, are consistently greater than those observed at the northern station. The lower nutrient and CO<sub>2</sub> values observed

during the summer months appear to be due to the increased photosynthetic utilization of nutrients and  $\text{CO}_2$  and to the reduced vertical mixing rate resulting from enhanced density stratification of the water column during this period. The winter nutrient values observed in the surface water reach nearly 80% of the values observed at a depth of about 1000 m, and may be attributed to the increased upward mixing of subsurface waters rich in nutrients.

The oxygen concentration data, expressed in terms of AOU (apparent oxygen utilization), show that the water is supersaturated with respect to atmospheric oxygen by as much as 30% in May-June, whereas it is saturated or slightly undersaturated during the rest of the year. The most intense oxygen supersaturation (AOU =  $-120 \mu\text{M/kg}$ ) is seen at the southern station in May-June, 1983. It should be pointed out that the occurrence of maximum oxygen supersaturation, which was presumably produced by intense photosynthesis, coincides with the period of lowest  $\text{pCO}_2$  and nutrient values. The slight oxygen undersaturation observed during the winter-spring months can be attributed to the increased upward mixing of subsurface waters low in oxygen, and to rapid cooling of surface water, in which photosynthesis is virtually absent.

The carbon-14 concentration in the surface water increases with progressing season from about 40‰ to 100‰ in  $\Delta^{14}\text{C}$  at the northern station, and from about 20‰ to 60‰ at the southern station. It is higher at the northern station by about 30‰. The atmospheric carbon-14 concentration during the study period was about 300‰ due to the thermonuclear bomb tests in 1960s (Nydal and Lövseth 1983), while that for the deep Norwegian Sea waters observed at TTO/NAS Station 159 ( $68^\circ44'\text{N}$  and  $10^\circ33'\text{W}$ ) in 1981 was  $-2.8\text{‰}$  at 500 m and  $-28.4\text{‰}$  at 698 m (Östlund, 1983). Thus, the observed lower carbon-14 values in the surface water can be attributed to winter upwelling of subsur-

face waters low in carbon-14, while the higher summer values resulting from the uptake of atmospheric bomb carbon-14 by the surface water, which is more or less isolated from the deep water by strong summer stratification.

The atmospheric  $\text{CO}_2$  concentration observed at the deck level shows that it is highest in March through May at 350–353 ppm, and lowest in August at about 335 ppm with a seasonal peak-to-peak amplitude of about 15–17 ppm. The seasonal phasing and amplitude are consistent with the observations made by Wong et al. (1984) at Sable Island ( $44^\circ\text{N}$ ,  $60^\circ\text{W}$ ) off the coast of Nova Scotia and at Alert ( $82.5^\circ\text{N}$ ,  $62.3^\circ\text{W}$ ), Northwest Territories, Canada. Although their data extend only to mid-1980 and can not be compared directly with our measurements in 1983–84, it appears that our values are somewhat higher than theirs.

A diffusion-advection model study for seasonal variation of the carbon and nutrient chemistry is currently underway in order to evaluate the photosynthetic rate, upwelling rate and  $\text{CO}_2$  uptake rate by the ocean water.

## DISCUSSION

### *Net Air-Sea $\text{CO}_2$ Flux*

The seasonal  $\text{pCO}_2$  data presented in Figure 2 show unequivocally that the surface water located west and north of Iceland is an intense sink for the atmospheric  $\text{CO}_2$  during summer, when the water is warmest. On the other hand, it becomes nearly saturated with atmospheric  $\text{CO}_2$  or is only a weak sink during winter, when the water is coldest. Since the  $\text{pCO}_2$  of water decreases rapidly with falling temperature in an isochemical condition, it has been generally believed that the high latitude oceans become more intense  $\text{CO}_2$  sink during the cold winter months. Our observations prove this to be erroneous. Assuming that the summer

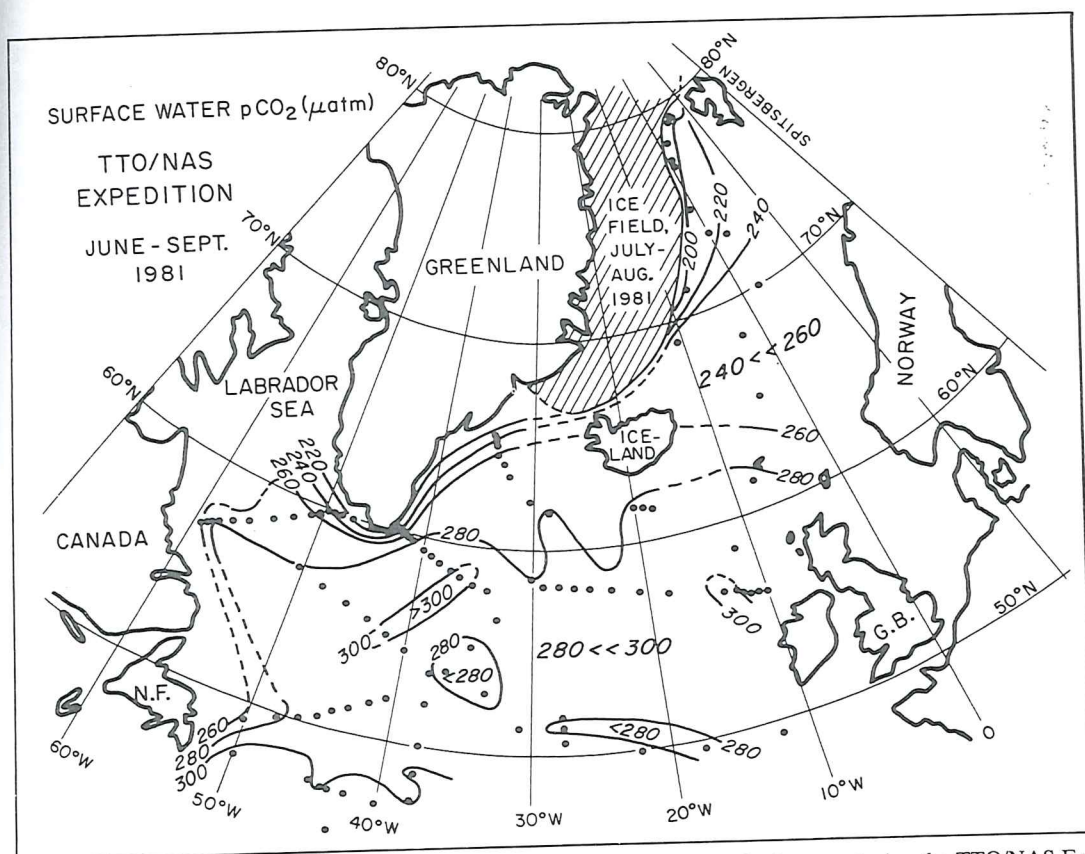


Fig. 4. The surface water  $p\text{CO}_2$  (in  $\mu\text{atm}$ ) observed in the northern high latitude areas during the TTO/NAS Expeditions in June-September 1981. The eastern North Atlantic data were obtained during June-July 1981; the Norwegian-Greenland Sea and the Irminger Sea during July-August 1981; the Labrador Sea and the western North Atlantic during August-September 1981. The mean atmospheric  $p\text{CO}_2$  was about  $330 \mu\text{atm}$  during this period. Thus, the northern high latitude waters were highly undersaturated with respect to atmospheric  $\text{CO}_2$ .

$p\text{CO}_2$  data obtained during the 1981-TTO/NAS Expedition in the Norwegian-Greenland Sea (Fig. 4) represent the mean annual conditions, the net  $\text{CO}_2$  flux from air to sea can be estimated to be about 6 moles  $\text{CO}_2/(\text{m}^2 \cdot \text{yr})$ . For this estimate a mean global  $\text{CO}_2$  gas exchange coefficient of  $0.067 \text{ moles } \text{CO}_2/(\text{m}^2 \cdot \mu\text{atm} \cdot \text{yr})$  is used. This is equivalent to 20 moles  $\text{CO}_2/(\text{m}^2 \cdot \text{yr})$  gas exchange rate estimated by Broecker (1983) on the basis of the steady-state natural carbon-14 distribution in the atmosphere and oceans. In the light of the observations presented in this paper, this estimate must be reduced by at least 50% to about 3 moles

$\text{CO}_2/(\text{m}^2 \cdot \text{yr})$  or less for the mean annual uptake of atmospheric  $\text{CO}_2$  by the surface water of the Norwegian-Greenland Sea. Monthly averaged wind speeds are also lowest in summer and highest in fall and winter, so that the gas exchange rate should be lowest when the  $\text{CO}_2$  sink is strongest. This would further reduce the net  $\text{CO}_2$  uptake rate by the surface ocean water.

#### Seasonal Variation of Surface Water $p\text{CO}_2$

As seen in Figure 2 the seasonal change in surface water temperature is out of phase with that in  $p\text{CO}_2$ . The water is coldest in



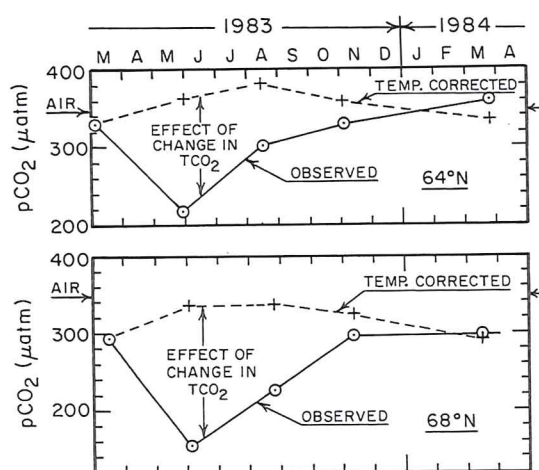


Fig. 5. The effect of temperature change on the surface water  $p\text{CO}_2$  values at the southern ( $64^\circ\text{N}$ ) and northern ( $68^\circ\text{N}$ ) stations. It is assumed that the March 1983 waters at these stations were subjected to the observed seasonal temperature change without change in chemical composition. The isochemical temperature effect of  $4.3\% \text{ pCO}_2/^\circ\text{C}$  was used. These temperature corrected values are indicated by "+". The observed  $p\text{CO}_2$  values (indicated by "o") during the summer and fall months are substantially lower than the temperature corrected March value. This indicates that the total  $\text{CO}_2$  concentration in the surface water was reduced during the summer and fall months, presumably by the photosynthetic utilization.

February-March and warmest in August, whereas the  $p\text{CO}_2$  is lowest in May-June and is highest in March. To show the magnitude of the effect of temperature on the surface  $p\text{CO}_2$ , the seasonal change in  $p\text{CO}_2$  due solely to seasonal temperature changes has been computed using the temperature dependence of  $4.3\%/^\circ\text{C}$  (for an isochemical system), and plotted in Figure 5. It is assumed that the March 1983 water is subjected to temperature change without change in its chemical composition, including the total  $\text{CO}_2$  concentration and alkalinity. Figure 5 shows that the observed summer values are substantially lower than the computed values. This indicates that the observed decrease in  $p\text{CO}_2$  during summer is due mainly to a reduction of the total  $\text{CO}_2$  concentration, which resulted from photosyn-

thetic utilization of  $\text{CO}_2$  in the water. This view is supported by the reduced nutrient concentrations and increased oxygen supersaturation observed in the summer months. Neither the uptake of  $\text{CO}_2$  from the atmosphere nor the upwelling of  $\text{CO}_2$ -rich subsurface waters could compensate for the photosynthetic utilization due to the slowness of the air-sea gas exchange and the enhanced density stratification of water column by summer warming of the upper layers. Northward flow and rapid cooling of the warm and nutrient-deficient North Atlantic waters can account for the low  $p\text{CO}_2$  and low nutrient values observed during the summer, but not the observed oxygen supersaturation. The increase in surface water  $p\text{CO}_2$  observed during the fall through spring months appears to be due mainly to the upward mixing of subsurface waters rich in  $\text{CO}_2$  (and nutrients) and to the reduced photosynthetic rate resulting from decreased daylight hours.

The seasonal variation of the surface water  $p\text{CO}_2$  observed at these stations is further compared with the summer values obtained in the Norwegian and Greenland Seas during the TTO/NAS Expedition, July-August 1981, and in the Labrador Sea in August-September 1981. In Figure 6 the surface water  $p\text{CO}_2$  data are plotted against the surface water temperature. The summer  $p\text{CO}_2$  values in the Norwegian-Greenland Sea waters and in the low-salinity East Greenland Current and Labrador Sea waters correlate with temperature, showing a temperature dependence of about  $4\% \text{ pCO}_2/^\circ\text{C}$ , which is similar to that of  $4.3\% \text{ pCO}_2/^\circ\text{C}$  for sea water in an isochemical system. This similarity may be coincidental if the increase in the total  $\text{CO}_2$  concentration in surface water due to the net  $\text{CO}_2$  uptake via air-sea gas exchange and to vertical mixing of subsurface waters is nearly compensated for by the biological utilization of  $\text{CO}_2$ . Alternatively, this may be causal, if the rate of temperature change is much greater than

that of the change in the total  $\text{CO}_2$  in the surface water, such that the total  $\text{CO}_2$  concentration in surface water remains nearly constant throughout the summer months. The actual situation is probably a combination of these extreme cases.

The 1983 summer values for the northern and southern stations are consistent with the 1981 summer values. On the other hand, the fall, winter and spring values at both stations are considerably greater than the 1981 summer values. The northern station winter values approach the deep water values (at 1000 m) observed at TTO Station 159 ( $68^\circ 44' \text{N}$  and  $10^\circ 34' \text{W}$ ) located in the Iceland Sea, and the southern station winter values are also close to the deep water values (at 1000 m) observed at TTO Station 163 ( $61^\circ 50' \text{N}$  and  $28^\circ 44' \text{W}$ ) located in the Irminger Sea. These observations indicate that the high  $\text{pCO}_2$  values observed during the fall and winter months are due mainly to the upward mixing of subsurface water. Furthermore, Figure 6 demonstrates the magnitude of the seasonal change and its importance in the air-sea  $\text{CO}_2$  exchange in the northern high latitude areas.

Using the alkalinity, total  $\text{CO}_2$ , oxygen and nutrient data obtained during the 1981 TTO Programme, Broecker et al. (1985) computed the initial (or preformed)  $\text{pCO}_2$  values, which would have been exhibited at the time of formation of the subsurface waters in the Denmark Strait area and the Norwegian-Greenland and Labrador Seas. Assuming that these waters were saturated with atmospheric oxygen at the time of formation, they used the AOU values and the Redfield ratios ( $\text{P:N:C}:(-\text{O}_2) = 1:16:106:138$ ) to estimate the biological respiration which occurred in the water column, and obtained the preformed values for total  $\text{CO}_2$ , nitrate and phosphate. The alkalinity was corrected only for nitrate addition, and its change due to growth or dissolution of calcareous tests was assumed to be negligible. These preformed values

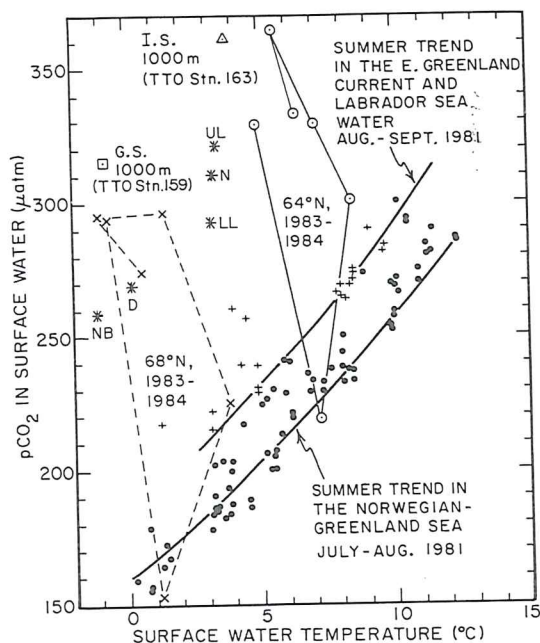


Fig. 6. Relationship between the surface water temperature and the  $\text{pCO}_2$  values (in  $\mu\text{atm}$ ) in the surface waters of the Norwegian-Greenland Sea (filled circles) and the Labrador Sea (+) during the summer of 1981, and at the northern (x) and southern (open circles) stations in 1983 and 1984. The 1981 data were obtained during the TTO/NAS Expeditions. G. S. (an open square) and I. S. (an open triangle) indicate respectively the values at about 1000 m depth observed in the Greenland Sea (TTO/NAS Station 159) and in the Irminger Sea (TTO/NAS Station 163). The fall-winter-spring values observed in 1983-84 are close to the subsurface water values, indicating active vertical mixing of subsurface waters. The initial (or preformed)  $\text{pCO}_2$  values estimated by Broecker et al. (1985) for various subsurface waters are indicated by \*: UL = Upper Labrador Sea water, LL = Lower Labrador Sea water, N = Norwegian Sea water, NB = Norwegian Sea Bottom water, and D = Denmark Strait water.

were then used to compute the initial  $\text{pCO}_2$  for five water types found in the northern high latitude areas. Their assumption of oxygen saturation at the time of water formation appears to be supported by the winter-spring data obtained during the present investigation (Fig. 3). The initial  $\text{pCO}_2$  values thus computed are indicated in Figure 6 with asterisks with letters. The

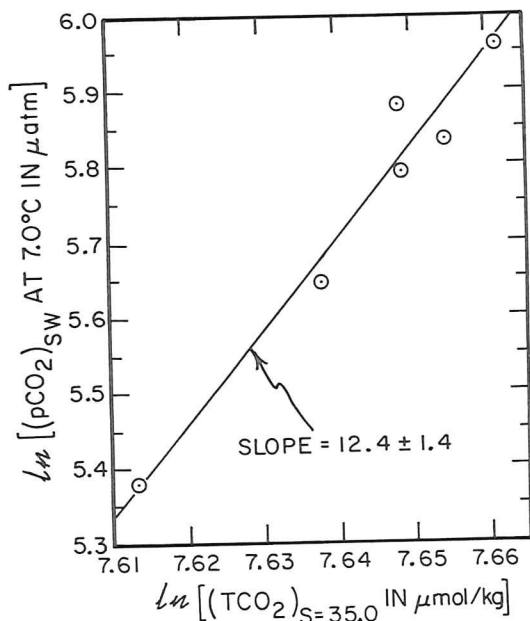


Fig. 7. A plot of the natural logarithm of the  $p\text{CO}_2$  value normalized to  $7.0^\circ\text{C}$  (the annual mean temperature at the southern station) versus that of the total  $\text{CO}_2$  concentration normalized to a salinity of 35.0 (the annual mean salinity at the southern station). The slope indicates the seasonal mean Revelle factor of  $12.4 \pm 1.4$  at the southern station located in the Irminger Sea.

letters UL, LL, N, NB, and D denote respectively the upper Labrador Sea water ( $3.4^\circ\text{C}$  and 34.84 salinity), the lower Labrador Sea water ( $3.2^\circ\text{C}$  and 34.91), Norwegian Sea water ( $3.3^\circ\text{C}$  and 35.02), Norwegian Sea Bottom water ( $-1.1^\circ\text{C}$  and 34.90), and Denmark Strait water ( $0.25^\circ\text{C}$  and 34.88). It is seen in Figure 6 that these initial  $p\text{CO}_2$  values back-calculated from the subsurface water data are in agreement with the surface water values observed during the winter and spring seasons.

#### *Relationship Between $p\text{CO}_2$ and Total $\text{CO}_2$*

At the southern station, the salinity-normalized alkalinity value is nearly constant throughout the year. Therefore, the  $p\text{CO}_2$ - $\text{TCO}_2$  relationship should yield an estimate of the Revelle factor,  $\gamma$ , (or the

buffer factor), which is defined by the following equation for seawater with a constant salinity, alkalinity and temperature:

$$\gamma = (\Delta p\text{CO}_2 / p\text{CO}_2) / (\Delta \text{TCO}_2 / \text{TCO}_2) = (\partial \ln p\text{CO}_2 / \partial \ln \text{TCO}_2)$$

Therefore, the slope of a  $\ln p\text{CO}_2$  vs.  $\ln \text{TCO}_2$  plot gives the value of the Revelle factor. In Figure 7 the natural logarithm of the  $p\text{CO}_2$  values corrected to the annual mean temperature of  $7.0^\circ\text{C}$  is plotted against that of the total  $\text{CO}_2$  concentration normalized to the annual mean salinity of 35.0 at the southern station. It yields a Revelle factor of  $12.4 \pm 1.4$ , which is consistent with 12.0 at  $7^\circ\text{C}$  computed by Takahashi et al. (1980) using the apparent dissociation constants for carbonic acid in sea water determined by Mehrbach et al. (1973). This value represents a seasonally averaged Revelle factor for the northern North Atlantic surface water, which is useful for model computations of the air-sea  $\text{CO}_2$  exchange.

Because of the large seasonal variability in salinity at the northern station, a similar data analysis is considered not valid.

#### *Oxygen Supersaturation and Primary Productivity*

As shown in Figure 3, the surface water was highly supersaturated with respect to atmospheric oxygen during May-June in 1983 and 1984. This oxygen supersaturation was presumably caused by the rate of photosynthetic oxygen production in the mixed layer exceeding the rate of oxygen loss to the atmosphere by gas exchange across the air-sea interface. If these processes are assumed to be in a steady state condition, and if no net oxygen transfer is assumed to have taken place between the mixed layer and the underlying subsurface waters, the oxygen production rate should be equal to the net oxygen evasion rate to the atmosphere. Thus, under these assump-

tions, the photosynthesis rate may be estimated on the basis of the observed AOU value. The oxygen evasion flux,  $F$ , can be evaluated by:

$$F = V_p \cdot \{ (O_2)_{\text{sat}} - (O_2)_{\text{obs}} \} \cdot \rho \\ = V_p \cdot \rho \cdot (-\text{AOU}),$$

where  $V_p$  is the gas exchange piston velocity,  $\rho$  is the density of seawater, and  $(O_2)_{\text{sat}}$  and  $(O_2)_{\text{obs}}$  are respectively the oxygen concentration in seawater in equilibrium with atmospheric oxygen and the observed value. Accordingly, the difference between these oxygen values is equal to the AOU.

The value of  $V_p$  for oxygen has been estimated to be about 3 m/day (Broecker and Peng 1982), and that for  $\rho$  is 1025 kg/m<sup>3</sup>. The AOU values observed at the stations were about  $-55 \pm 5 \mu\text{M}/\text{kg}$  during May-June 1984 (Fig. 3). Therefore we obtain the oxygen evasion flux and hence the photosynthetic oxygen production rate of about  $0.17 \pm 0.02 \text{ moles } O_2/(\text{m}^2 \cdot \text{day})$ . Using the  $O_2/C$  ratio of 138/106 estimated for mean plankton composition by Redfield et al. (1963) or 170/122 ( $\pm 18$ ) estimated by Takahashi et al. (1985) for decomposing biological debris in subsurface waters, this can be converted to the photosynthetic carbon fixation rate of 0.13 moles C/(m<sup>2</sup> · day) (for the  $O_2/C$  of 138/106) or 0.12 moles C/(m<sup>2</sup> · day) (for the  $O_2/C$  of 170/122). The mixed layer depth at these stations ranged from 10 to 15 metres, and the depth for the Secchi disc disappearance (personal communication by T. Thórdardóttir, MRI) ranged from 12 to 14 metres at the time of the oxygen measurements. Assuming that the photosynthesis was distributed uniformly within the upper 10 to 15 metres of the water column, we estimate that the mean primary productivity was approximately 0.007 to 0.01 moles C/(m<sup>3</sup> · day) or 0.08 to 0.1 g C/(m<sup>3</sup> · day). Considering the uncertainties in the estimates for the gas exchange piston velocity, the thickness of

the photic zone as well as the crude assumptions used for deriving the relationship between oxygen supersaturation and primary productivity, this estimate should be uncertain to about  $\pm 50\%$ .

On the other hand, concurrently with the oxygen measurements at these stations, the primary productivity in the mixed layer was measured by T. Thórdardóttir (personal communication) using a carbon-14 incubation method. The observed primary productivity values range between 1.8 and 2.5 mg C/(m<sup>3</sup> · hr). Assuming that these values represent the mean productivity in the study area during the characteristic time for oxygen gas exchange (i.e. one to two weeks), and that the effective daylight hours per day were about 18 hours/day at the time of measurements, the daily primary productivity is estimated to be about 0.05 g C/(m<sup>3</sup> · day). Because of the highly variable nature of primary productivity with time and space, this estimate should be considered as a rough estimate for the mean productivity over the time scale of oxygen gas exchange. Nevertheless, it should be noted that this is broadly consistent with the productivity estimated independently on the basis of the oxygen gas transfer rate and AOU.

#### *Relationship Between Nitrate and Phosphate*

The distribution of nutrients and oxygen in the vicinity of Iceland and the northern Irminger Sea has been extensively investigated by Stefánsson (1968a, 1968b). He observed that while the N/P ratio for the warm ( $T > 6^\circ\text{C}$ ) Atlantic waters is similar to that for the low salinity ( $S < 34.0$ ) Polar waters (i.e. 14.35 vs. 14.10), the phosphate concentration at zero nitrate concentration for the Atlantic waters is about zero and that for the Polar waters is about 0.24  $\mu\text{M}$ -P/kg. The nitrate and phosphate concentrations obtained for surface water at both stations during the present investi-

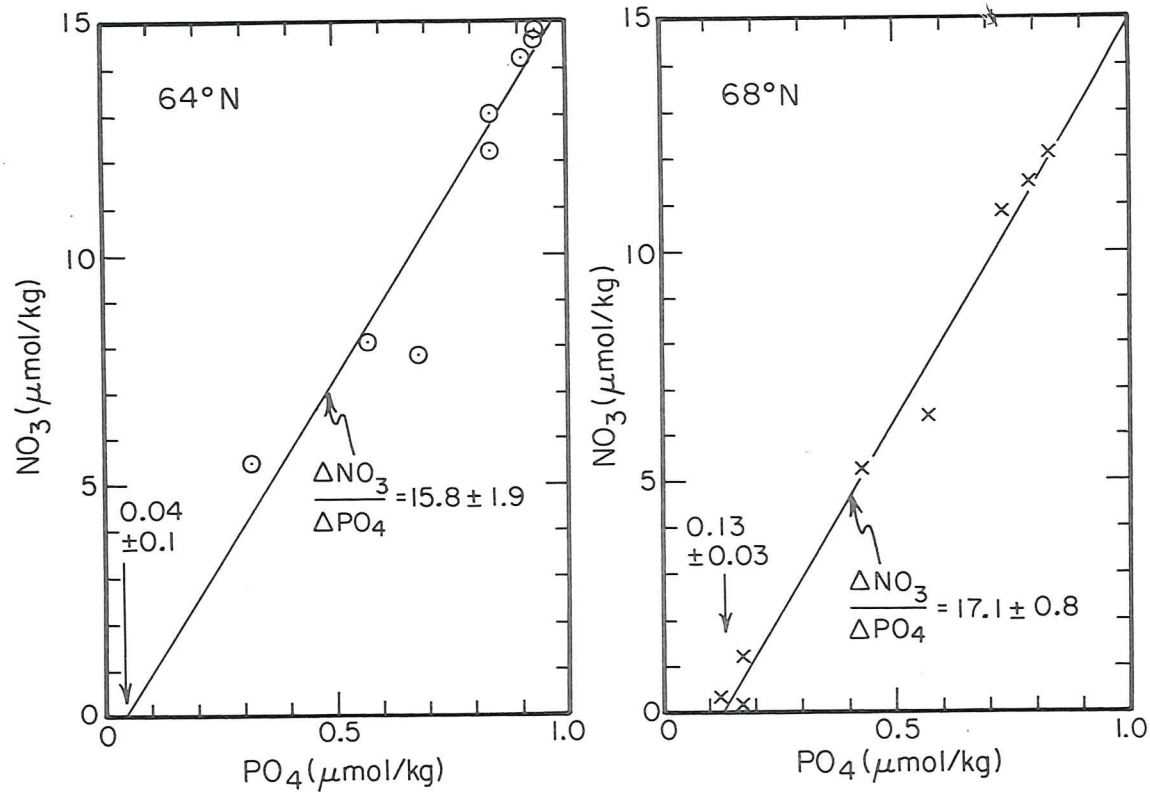


Fig. 8. Plots of the nitrate concentration versus phosphate concentration in surface waters at the southern (left) and northern (right) stations in 1983–84.

gation are shown in Figure 8, and they appear to be linearly related. A linear regression yields an N/P ratio of  $15.8 \pm 1.9$  with an X-axis intercept of  $0.04 \pm 0.1 \mu\text{M-P/kg}$  for the southern station and  $17.1 \pm 0.8$  with an X-axis intercept of  $0.13 \pm 0.03 \mu\text{M-P/kg}$  for the northern station. In view of Stefánsson's observation (1968b), the greater N/P and intercept values observed at the northern station may be attributed to mixing of the low-salinity Polar waters with the Atlantic waters. Although the N/P ratio observed at the southern station, where the salinity was nearly constant throughout the two-year period, is consistent with the mean N/P ratio of 16 in marine plankton (Redfield et al., 1963), the observed N/P ratio can not be taken unequivocally as an expression of the ratio of the photosynthetic

utilization for nitrate and phosphate due to the lack of our knowledge of the mixing proportion of waters having different preformed nutrient concentrations.

#### *Relationship Between Phosphate and Total $\text{CO}_2$*

The relationship between the phosphate and total  $\text{CO}_2$  concentration corrected to the mean annual salinity at the southern station (35.0) is shown in Figure 9-A, and that between phosphate and  $\text{pCO}_2$  normalized to the annual mean temperature at the southern station ( $7.0^\circ\text{C}$ ) is shown in Figure 9-B. It is seen that the northern station data scatter far more than those for the southern station. As noted before, the seasonal variation of the salinity at the southern station is small, whereas that at the northern sta-

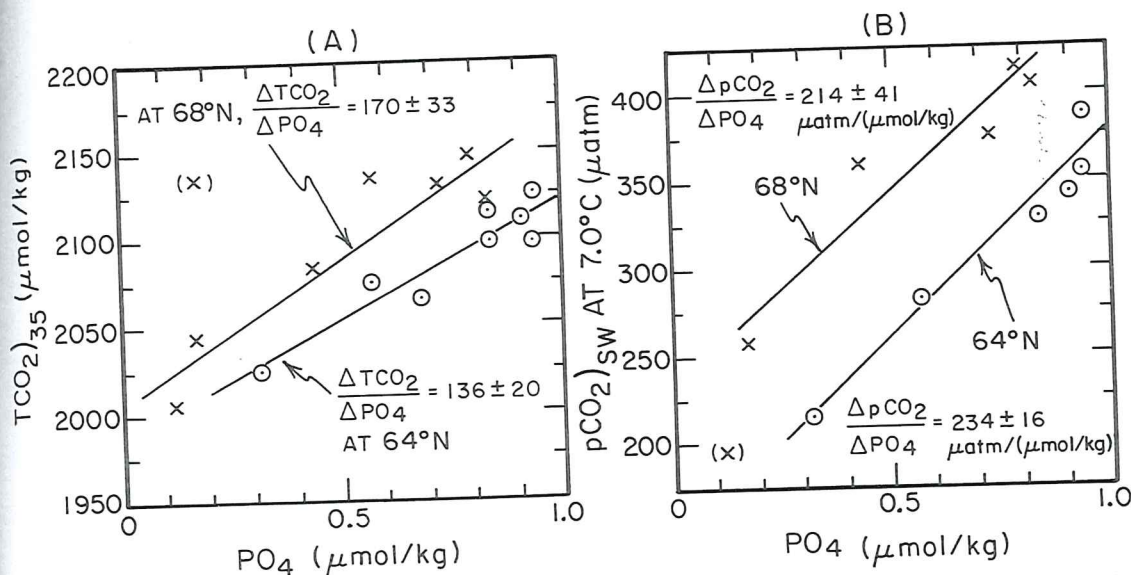


Fig. 9. Relationship between (A) the total CO<sub>2</sub> concentration (normalized to a salinity of 35.0) and phosphate, and (B) the pCO<sub>2</sub> in surface water (normalized to 7.0°C) and phosphate. The northern station data are indicated by "x" and the southern station data by "o". The data points in ( ) were not used for the regression analysis. Greater scatter of the data points for the northern station is due to mixing of various water masses. The pCO<sub>2</sub> and total CO<sub>2</sub> values observed at the northern station are greater than those at the southern station. This suggests that the northern station water is influenced by the low-salinity and high-CO<sub>2</sub> East Greenland Current water.

tion is substantially larger (salinity is as low as 30.7 during August 1984) due mainly to the increased influx of the low-salinity East Greenland Current water and/or melting ice. Thus, the large scatter of the northern station data may be attributed mainly to the effect of mixing among various water masses.

The southern station (64°N) data exhibit a linear relationship, yielding a CO<sub>2</sub>/P ratio of  $136 \pm 20$ . This ratio reflects not only the effect of photosynthetic utilization, but also that of air-sea CO<sub>2</sub> gas exchange, production of calcareous tests and water mixing. Since the surface water pCO<sub>2</sub> is much lower than that of the atmosphere during summer, the summer surface water should have taken up more atmospheric CO<sub>2</sub> than the winter water. Thus, if the observed CO<sub>2</sub> values for the summer water, which has a low phosphate concentration, were corrected for a greater uptake of atmospheric

CO<sub>2</sub>, the slope of the regression line in Figure 9-A should be increased. Therefore, were the uptake of atmospheric CO<sub>2</sub> the only non-biological process to affect the CO<sub>2</sub>/P ratio, the observed ratio should represent the lower limit for the CO<sub>2</sub>/P ratio attributable to biological utilization. In view of the near constancy of the salinity-normalized alkalinity values (with an exception of the March 1983 value) observed at this station, the effect of CO<sub>2</sub> utilization by calcareous shell production appears to be small. However, the effect of mixing of various water types cannot be evaluated on the basis of the present data set.

On the basis of phosphate, total CO<sub>2</sub> concentration and oxygen data obtained along isopycnal horizons in the North Atlantic, Takahashi et al. (1985) observed that the phosphate, CO<sub>2</sub> and O<sub>2</sub> concentrations in the main thermocline waters change with a ratio of 1:93:170. Since the younger

(hence higher oxygen concentration) waters should contain a greater amount of anthropogenic  $\text{CO}_2$ , they interpreted that this value for carbon should represent the lower limit for the decomposition of biological debris in the water column. On the other hand, if nitrogen in the debris is assumed to be in the form of  $\text{NH}_3$ , its oxidation to  $\text{NO}_3^-$  should consume two molecules of  $\text{O}_2$ . Thus, correcting the oxygen consumption for oxidation of  $\text{NH}_3$ , they obtained the upper limit for the P:C: ( $-\text{O}_2$ ) ratio of 1:135:170. The P/C ratio of 1/136 ( $\pm 20$ ) for biological production observed at the southern station during this study tends to support the upper limit for the P/C ratio, 1/135, observed by Takahashi et al. (1985).

#### *CO<sub>2</sub> in the Arctic Waters*

Both the total  $\text{CO}_2$  and  $\text{pCO}_2$  data presented in Figure 9 show that the northern station waters, when normalized to a salinity of 35.0, contain approximately 50  $\mu\text{M}/\text{kg}$  more  $\text{CO}_2$  than the southern station water. The 1981-summer  $\text{pCO}_2$  and temperature data (Fig. 6) also show that the East Greenland Current water and the Labrador Sea water have  $\text{pCO}_2$  values about 15% greater than that of the Norwegian-Greenland Sea surface waters of North Atlantic origin. This may be due to a contribution of colder and higher  $\text{CO}_2$  water of arctic origin. Since the  $\text{pCO}_2$ -temperature relationship observed during the summer of 1981 (Fig. 6) is nearly equal to that for an isochemical sea water, it appears that, although the surface waters were highly undersaturated with respect to atmospheric  $\text{CO}_2$ , they did not take up an appreciable amount of atmospheric  $\text{CO}_2$  via gas exchange as they flowed northward into the Arctic basin through the Norwegian-Greenland Sea. We therefore postulate that during their residence in the Arctic basin, the surface waters take up  $\text{CO}_2$  from the atmosphere over the areas free of ice cover. They might also receive additional  $\text{CO}_2$  by mixing with subsurface waters,

although such mixing should be minimal due to strong density stratification during the summer. The waters thus enriched in  $\text{CO}_2$  flow southward out of the Arctic basin as the East Greenland Current into the Greenland Sea and further into the Labrador Sea. If this were the case, the Arctic Sea, in particular the areas free of ice during summer when photosynthesis is at a maximum, should play an important role in the uptake of atmospheric  $\text{CO}_2$ .

#### SUMMARY AND CONCLUSIONS

The results of a seasonal study of the carbon and nutrient chemistry in surface water conducted at two locations in the areas north and west of Iceland during the period March 1983 through November 1984, lead to the following conclusions:

1) The partial pressure of  $\text{CO}_2$  in surface water and the concentrations of nutrients and total dissolved  $\text{CO}_2$  are lowest during the summer months but are greater in the fall, winter and spring months. On the other hand, the concentrations of dissolved oxygen and carbon-14 in sea water are greatest during the summer months but smaller during the rest of the year.

2) The results of the summer observations can be attributed to accelerated photosynthetic utilization of carbon and nutrients and reduced vertical mixing in the upper water column due to increased density stratification of the water by the summer warming. The winter results are attributable to reduced photosynthetic rates due to shortened daylight hours and to the upward mixing of subsurface waters rich in nutrients and  $\text{CO}_2$  resulting from winter cooling of the surface water. Thus, the carbon and nutrient chemistry in the northern high latitude waters appears to be regulated by the interactions of the photosynthetic utilization of carbon and nutrients and the supply rate of these into the photic zone by upward mixing of subsurface waters. The former is the

dominant process during the summer months, whereas the latter is the major governing process during the winter months.

3) The surface  $p\text{CO}_2$  data indicate that the ocean in this region is an intense sink for the atmospheric  $\text{CO}_2$  in the summer months, whereas it is a weak to neutral sink during the winter months. At the southern station ( $64^\circ\text{C}$ ), the sea even became a weak  $\text{CO}_2$  source during March 1984. This is contrary to the general belief that the northern high latitude areas are intense  $\text{CO}_2$  sinks throughout the year. Seasonal variability in the carbon chemistry of the high latitude water mass formation areas must be taken into consideration for estimating oceanic uptake of the industrial  $\text{CO}_2$ .

4) The initial  $p\text{CO}_2$  values at the time of formation of subsurface waters, which have been computed by Broecker et al. (1985) on the basis of the estimated preformed values for the alkalinity, total  $\text{CO}_2$  and nutrients, are consistent with the values observed during the winter and spring seasons.

5) Based upon the  $p\text{CO}_2$  and total  $\text{CO}_2$  concentration data, the seasonally averaged Revelle (or buffer) factor for  $\text{CO}_2$  has been estimated to be  $12.4 \pm 1.4$  at the southern station located in the Irminger Sea in the North Atlantic.

6) The summer data for the waters of the East Greenland Current and the Labrador Sea show that they have greater total  $\text{CO}_2$  concentrations and higher  $p\text{CO}_2$  values than those of North Atlantic origin. It appears that the North Atlantic water cools rapidly and nearly isochemically as it flows northward into the Norwegian-Greenland Sea and further into the Arctic basin. It appears to acquire additional  $\text{CO}_2$  via air-sea exchange and perhaps by mixing with subsurface waters during its residence in the Arctic basin. The low salinity East Greenland Current water, which flows southward out of the Arctic basin, appears to reflect the results of these processes.

7) These seasonal data serve as the basis for quantitative evaluation of the upward mixing rate, photosynthetic rate and  $\text{CO}_2$  uptake rate by the sea through model studies. A diffusion-advection model study is currently underway.

#### ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support for this project by the EXXON Research and Engineering Company. Without their continued interest and encouragement, this study could not have been carried out. Our participation in the 1981 TTO/NAS study was supported by a grant (OCE-81-10646) from the U.S. National Science Foundation. We have benefited from critical review of the manuscript by Unnsteinn Stefánsson of the Marine Research Institute, Iceland, and W. M. Smethie, Jr. of the Lamont-Doherty Geological Observatory. We thank the staff of the MRI for various assistance during the expeditions, Th. Thórdardóttir of the MRI for primary productivity measurements, and Guy Mathieu and Stewart Sutherland of the L-DGO for conducting analyses of carbon-14, total  $\text{CO}_2$ , and  $p\text{CO}_2$ . This is Lamont-Doherty Geological Observatory Contribution No. 3778.

#### REFERENCES

- Broecker, W. S. 1963. Radioisotopes and large-scale oceanic mixing. In M. N. Hill (Ed.) "The Sea", Vol. 2. Interscience Pub., New York, pp. 88-123.
- and T. H. Peng 1982. "Tracers in the Sea", Lamont-Doherty Geological Observatory, Palisades, N. Y., 690 pp.
- , Takahashi, T. and T. H. Peng 1985. Reconstruction of past atmospheric  $\text{CO}_2$  contents from the chemistry of the contemporary ocean: An evaluation, TRO20, DOE/OR-857, Carbon Dioxide Research Division, U. S. Department of Energy, Washington, D. C., 79 pp.
- Nydal, R. and K. Lövseth 1983. Tracing bomb  $^{14}\text{C}$  in the atmosphere 1962-1980. *J. Geophys. Res.* 88: 3621-3642.



- Mehrbach, C., C. H. Culberson, J. E. Hawley and R. M. Pytkowicz 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.* 18: 897-907.
- Redfield, A. C., B. H. Ketchum and F. A. Richards 1963. The influence of organisms on the composition of sea water. In M. N. Hill (Ed.) "The Sea", Vol. 2. Interscience Publishers, New York, pp. 26-27.
- Stefánsson, U. 1961. "Hafid" (The Ocean.). Almenna bokafelagid, Reykjavik, Iceland, 293 pp.
- 1968a. Dissolved nutrients, oxygen and water masses in the Northern Irminger Sea. *Deep-Sea Res.* 15: 541-575.
- 1968b. Nitrate-phosphate relationships in the Irminger Sea. *J. Cons. int. Explor. Mer* 32: 188-200.
- Takahashi, T., W. S. Broecker, S. R. Werner and A. E. Bainbridge 1980. Carbonate chemistry of the surface waters of the world oceans. In E. Goldberg, Y. Horibe and K. Saruhashi (Eds.) "Isotope Marine Chemistry". Uchida Rokakuho Pub., Tokyo, Japan, pp. 291-326.
- Takahashi, T., D. Chipman, N. Schectman, J. Goddard and R. Wanninkhof 1982. Measurements of the partial pressure of CO<sub>2</sub> in discrete water samples during the North Atlantic Expedition. The Transient Tracers of the Oceans Projects. Technical Report, Lamont-Doherty Geological Observatory, Palisades, N. Y., 268 pp.
- , W. S. Broecker and S. Langer 1985. Redfield ratios based on chemical data from isopycnal surfaces. *J. Geophys. Res.*, 90: 6907-6924.
- Wong, C. S., Y-H. Chan, J. S. Page, R. D. Bellegay and K. G. Pettit 1984. Trends of atmospheric CO<sub>2</sub> over Canadian WMO background stations at Ocean Weather Station P, Sable Island, and Alert, *J. Geophys. Res.* 89: 9527-9539.
- Östlund, H. G. 1983. TTO North Atlantic Study. Tritium and radiocarbon. Tritium Laboratory Data Report No. 83-35, University of Miami, Miami, Fl.