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The Northeast Water Polynya as an atmospheric CO_2 sink: A seasonal rectification hypothesis

Patricia L. Yager,[1] Douglas W.R. Wallace,[2] Kenneth M. Johnson,[2]
Walker O. Smith Jr.,[3] Peter J. Minnett,[2] and Jody W. Deming [1]

Abstract. During the multidisciplinary 'NEW92' cruise of the United States Coast Guard Cutter (USCGC) *Polar Sea* to the recurrent Northeast Water (NEW) Polynya (77-81°N, 6-17°W; July-August 1992), total dissolved inorganic carbon and total alkalinity in the water column were measured with high precision to determine the quantitative impact of biological processes on the regional air-sea flux of carbon. Biological processes depleted the total inorganic carbon of summer surface waters by up to 2 mol C m^{-2} or about 3%. On a regional basis this depletion correlated with depth-integrated values of chlorophyll *a*, particulate organic carbon, and the inorganic nitrogen deficit. Replacement of this carbon through exchange with the atmosphere was stalled owing to the low wind speeds during the month of the cruise, although model calculations indicate that the depletion could be replenished by a few weeks of strong winds before ice forms in the autumn. These measurements and observations allowed formulation of a new hypothesis whereby seasonally ice-covered regions like the NEW Polynya promote a unique biologically and physically mediated "rectification" of the typical (ice free, low latitude) seasonal cycle of air-sea CO_2 flux. The resulting carbon sink is consistent with other productivity estimates and represents an export of biologically cycled carbon either to local sediments or offshore. If this scenario is representative of seasonally ice-covered Arctic shelves, then the rectification process could provide a small, negative feedback to excess atmospheric CO_2.

1. Introduction

High-latitude oceans are believed to influence atmospheric CO_2 levels on timescales of hundreds to thousands of years owing to high and variable biological activity and extensive exchange with deep-ocean inorganic carbon [*Knox and McElroy,* 1984; *Sarmiento and Toggweiler,* 1984; *Siegenthaler and Wenk,* 1984]. On a seasonal timescale, biological processes in these regions can cause significant depletions in surface water pCO_2, influencing the local air-sea exchange of carbon [*Codispoti et al.,* 1982, 1986; *Takahashi et al.,* 1993]. Within the Arctic, most biological production occurs over seasonally ice-free continental shelves [*Subba Rao and Platt,* 1984], for which polynyas (ice-free waters within ice-covered regions) are under consideration as model systems [*NEWATER Steering Committee,* 1993].

In the coastal Arctic Ocean, summer is characterized by continuous sunlight and nutrient-bearing waters derived from the ice-covered Arctic basin. Photosynthetic production rates *P* can therefore be high [*Smith et al.,* 1991]. At the same time, summertime respiration rates *R* are believed to be low, in part due to the high incorporation efficiencies of local cold-tolerant microbial communities [*Deming and Yager,* 1992; *Yager and Deming,* 1993; W. Ritzrau and J.W. Deming, unpublished manuscript] and high *P/R* ratios for phytoplankton at low temperature [*Smith and Sakshaug,* 1990]. Continental shelf ecosystems have been considered as either balanced between primary production and respiration or as net heterotrophic (i.e., net sources for atmospheric CO_2 [*Smith and Hollibaugh,* 1993]), in part due to the flux of terrestrial production from rivers but also because wintertime respiratory processes and upwelling of carbon-rich deep waters typically cause supersaturated levels of pCO_2 in surface waters. The potential for high *P/R* ratios in the Arctic distinguishes the region and its carbon cycles from temperate latitudes.

Total dissolved inorganic carbon and total alkalinity were measured in the Northeast Water (NEW) Polynya during the United States Coast Guard Cutter (USCGC) *Polar Sea* cruise (77-81°N, 6-17°W; July-August 1992) in order to determine the quantitative impact of biological processes on the regional air-sea flux of carbon. Detection of a significant impact allowed formulation of an annual carbon cycling hypothesis that would establish the polynya as a net sink for atmospheric CO_2.

2. Methods

Sampling Technique and Analysis

Seawater samples from 10 stations in the NEW Polynya region (Figure 1) were collected for onshore analyses of total dissolved inorganic carbon C_T and total alkalinity A_T. Selected stations corresponded with those where biological processes were being monitored intensively; they were not intended to give complete temporal or spatial coverage. Subsamples for CO_2 parameters were taken, stored, and analyzed according to

[1]School of Oceanography, University of Washington, Seattle.
[2]Ocean and Atmospheric Sciences Division, Department of Applied Sciences, Brookhaven National Laboratory, Upton, New York.
[3]Graduate Program in Ecology, University of Knoxville, Tennessee.

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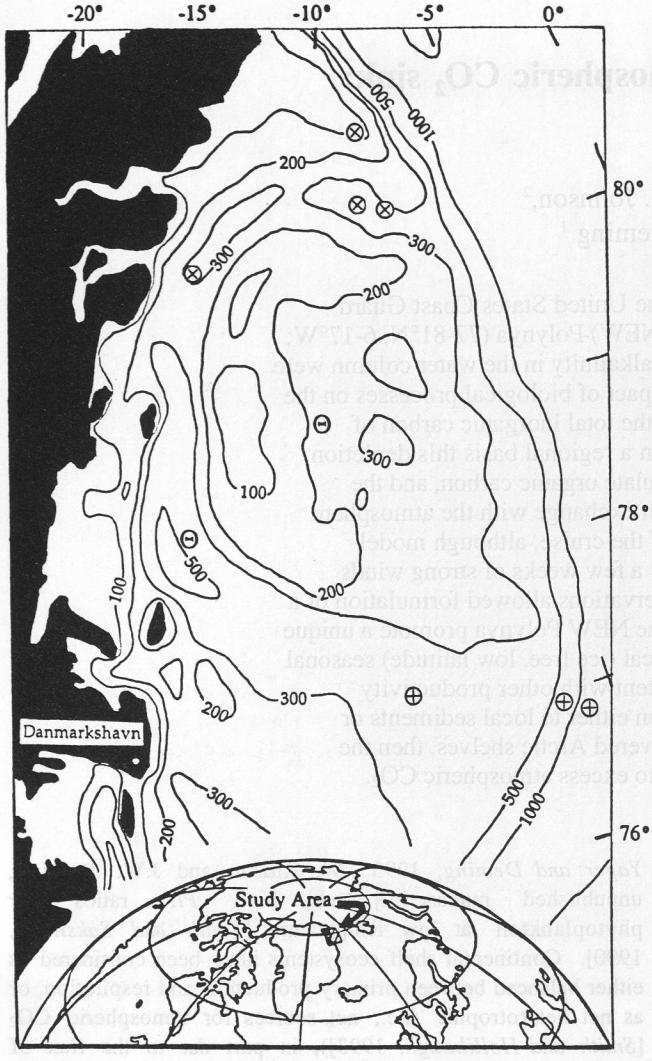

Figure 1. Topographic map of the study site showing sampling locations. Circled crosses indicate polynya (≤ 5/10 ice coverage) and Northern Trough stations; theta symbol, central region; and circled pluses, Southern Trough region. See Table 1 for individual station identification.

standard protocols [*Dickson and Goyet,* 1991] to minimize storage effects. C_T and salinity S were measured in November 1992 by a coulometric titration analyzer fitted with a SeaBird® conductivity sensor [*Johnson et al.,* 1987, 1993]. Measurements (2188.95 ± 1.06 μmol kg^{-1}, number of samples n = 5) of Certified Reference Material [*Dickson,* 1990] compared favorably to the expected value (2188.70 μmol kg^{-1}). A_T was measured in February 1993 using a closed-cell potentiometric titration system [*Bradshaw et al,* 1981; *Brewer et al.,* 1986; *Dyrssen,* 1965]. Precision for C_T and A_T was determined to be ± 1.0 μmol kg^{-1} and 3.6 μeq kg^{-1}, respectively, using 12 pairs of duplicate samples [*Dickson and Goyet,* 1991]. A_T, C_T, and the equilibrium constants of *Goyet and Poisson* [1989] were used with an iterative Newton-Raphson numerical method [*Press et al.,* 1989] to solve for carbonate alkalinity A_C and pCO_2 [*Peng et al.,* 1987]. Precision estimates calculated similarly for A_C and pCO_2 are ± 2.8 μeq kg^{-1} and 6.2 μatm, respectively.

Calculation of Biological Impact on C_T

Using a Lagrangian mass balance approach for C_T (modified from *Broecker and Peng* [1992]) at each sampled depth in the Polar Water (PW) mass (0-70 m) in the polynya, we assumed that all changes in C_T during a water parcel's transit through the polynya region were attributable to dilution D by sea ice melt or rivers, calcium carbonate precipitation or dissolution (+ or - P, respectively, which effectively includes any removal or addition of alkalinity not accounted for by dilution), atmospheric gas exchange due to warming G_w or diffusion G_d, and net biological processes B:

$$C_{T_o} = C_{T_s} - D - P - G_w - G_d - B \quad (1)$$

where subscript o stands for observed values and s for source water values. Mixing between the PW and the deeper Arctic Intermediate Water (AIW) is considered negligible because of the strong density gradient [*Bourke et al.,* 1987; *Schneider and Budéus,* 1994]. We solved for D based on changes in salinity, P based on changes in nitrate-corrected A_C, and G_w based on changes in pCO_2 (using the empirical k = 4.23% °C^{-1} [*Chipman et al.,* 1993]) and K_H (according to the constants of *Goyet and Poisson* [1989]) as a function of temperature T (thereby accounting for the effects of temperature on pCO_2 solubility and all apparent dissociation constants). The remaining difference between source and observed values must be due to G_d and B. Thus for each profile and depth (z),

$$G_d + B_{(z)} = C_{T_s} - \left[C_{T_s}\left(\frac{S_s - S_{o(z)}}{S_s}\right)\right] - \left(\frac{1}{2}\left\{\frac{S_{o(z)}}{S_s}\left[A_c + (NO_3)\right]_s - \left[A_c + (NO_3)\right]_{o(z)}\right\}\right) - \left[K_{H_{o(z)}} pCO_{2_s} exp^{k(T_{o(z)} - T_s)} - K_{H_{o(z)}} pCO_{2_s}\right] - C_{T_{o(z)}} \quad (2)$$

We used C_{T_s} = 2110 μmol kg^{-1}, S_s = 32.276, A_{C_s} = 2178 μeq kg^{-1}, NO_{3_s} = 6 μmol kg^{-1} (or 8 μmol kg^{-1} for four southern stations where East Greenland Current (EGC) influence is greater), pCO_{2_s} = 315 μatm, and T_s = -1.7°C as source water values representing PW at 70 m [*Wallace et al.,* 1994]. Use of these baseline source values required several assumptions. (1) The water column was vertically well mixed in winter. (2) The values at 70 m remained unchanged since winter. (3) Nitrate depletion occurred after meltwater dilution. The first assumption is supported by observations of well-mixed surface waters during the FS *Polarstern* ARKTIS expedition (ARK IX leg 2) in spring of 1993 [*Budéus and Schneider,* 1994]. The second is supported by salinity-scaled C_T - A_T diagrams of the area (see below) and by the observation that the base of the PW (~70 m) was at the maximal extent of the observed 1% light level. This level approximates the compensation depth where biological activity has no net effect on inorganic carbon [*Sverdrup,* 1953]. Moreover, microheterotrophic respiration rates were very low in intermediate waters below the euphotic zone (W. Ritzrau and J.W. Deming, unpublished manuscript) which had a mean depth of 31 ± 12 m in the polynya. Nitrogen depletion (e.g., by ice algae) may have occurred before dilution of surface layers by ice meltwater. In this event the larger removal of nitrate would affect alkalinity and increase the

contribution of precipitation to the total loss of C_T by less than 1% in nearly all cases.

Mean wind speeds in the polynya during the month of the cruise were low (3.9 ± 1.5 m s^{-1} at 16 m above sea level), resulting in low gas transfer velocities [*Erickson,* 1993; *Liss and Merlivat,* 1986] and therefore negligible diffusive gas exchange, regardless of any carbon gradient between the surface ocean and the atmosphere (see below). By setting G_d equal to zero, we solved for $B_{(z)}$, the depth-specific inorganic carbon deficit due to biological processes. Integrating over the entire PW mass gave the biologically mediated C_T deficit B for each station. A Monte Carlo-type error analysis was performed for B. The calculation was repeated 1000 times, using randomly generated values for each parameter from a Gaussian distribution with its own mean and standard deviation [*Press et al.,* 1989]. Mean values in the analysis were either source water values (as above) or average PW values. Standard deviations for each were estimated from measurements on 12 pairs of duplicate samples [*Dickson and Goyet,* 1991].

3. Results and Discussion

Physical and Chemical Processes

Most stations showed a significant reduction of C_T in the surface waters (Figure 2a). Dilution by meltwater was the dominant physical mechanism, responsible for an average of 36% of the total apparent C_T deficit in the polynya (up to 100% at low-productivity stations in the ice-covered central region). Surface (0-70 m) A_T correlated positively with S ($\alpha < 0.01$, data not shown) in this environment where freshwater input produced surface waters with salinities as low as 22.

Calcium carbonate precipitation P accounted for an average of 12% of the total C_T deficit in the polynya. In the surface waters of some stations (notably station 49 in the far northeastern part of the region), however, dissolution of $CaCO_3$ contributed excess carbon up to 61% of the measured difference between observed values and source C_T values. Excess alkalinity due to dissolution can be observed on a plot of salinity-scaled C_T versus A_T (Figure 2b) when D is essentially removed. The extrapolated freshwater alkalinity end-member (y intercept of the S versus A_T plot) was low (57 ± 170 μeq kg^{-1}) compared with the 1400 μeq kg^{-1} end-member observed in the nearby EGC [*Anderson and Dyrssen,* 1981], an excess which has been attributed to alkaline riverine input to the Arctic Ocean. The polynya value can be explained by the local melting of sea ice which contributes up to 112 μeq kg^{-1} in the EGC region [*Tan et al.,* 1983].

Near-surface waters (0-10 m) in the polynya exhibited temperatures as high as 3°C [*Wallace et al.,* 1994], indicating a warming of up to 5°C from initial wintertime conditions (i.e., the freezing point of seawater, approximately -1.8°C). Surface pCO_2 values, however, were never found to be supersaturated (average surface pCO_2 = 218 ± 34; see Table 1). In the most extreme case, warming could have caused only minor oversaturations of pCO_2; source waters from 70 m (pCO_2 ~ 315 μatm), if somehow warmed up to 3°C without any dilution or biological uptake of C_T, would give a maximal pCO_2 of 385 μatm. The average pCO_2 that would be achieved by warming all PW samples to 3°C was 323 ± 62 μatm. Losses of carbon due to warming had a negligible effect on C_T.

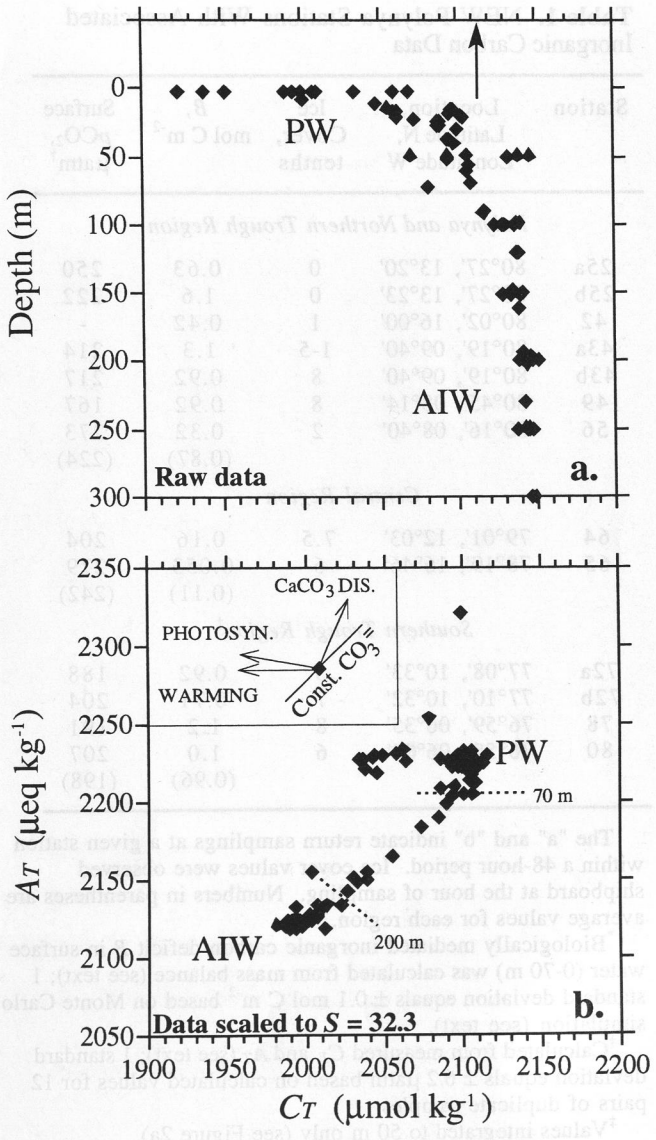

Figure 2. (a) Total dissolved inorganic carbon C_T depth profiles for all stations sampled showing surface depletion. Polar Water (PW) is shallower than 70 m; Arctic Intermediate Water (AIW) is below 70 m. Arrow denotes baseline C_T value for PW. Three data points richer than C_T baseline at 50 m were from the Southern Trough region where the PW layer was shallower. (b) C_T scaled to a salinity of 32.3 and compared to similarly scaled total alkalinity A_T, essentially removing the effects of dilution. PW samples cluster in the top right corner and AIW samples in the bottom left. Sample depth is indicated by dotted lines. Data to the left and above the PW endpoint at C_T ~ 2110 μmol kg^{-1} and A_T ~ 2223 μeq kg^{-1} show the combined influence of photosynthesis, $CaCO_3$ dissolution or precipitation, and warming (inset after *Broecker and Peng* [1989]). The data point with the highest A_T, showing the greatest influence of $CaCO_3$ dissolution, is from the most northeasterly station (49).

Biological depletion

After correcting for the effects of these physical-chemical processes, C_T remained depleted in the surface waters compared to the assumed source water. The range determined for B over the entire region was 0.05 - 1.6 mol C m^{-2} (± 0.1; standard

Table 1. NEW Polynya Stations With Associated Inorganic Carbon Data

Station	Location, Latitude N, Longitude W	Ice Cover, tenths	B, mol C m^{-2} *	Surface pCO_2, µatm†
	Polynya and Northern Trough Region			
25a	80°27', 13°20'	0	0.63	250
25b	80°27', 13°23'	0	1.6	222
42	80°02', 16°00'	1	0.42	-
43a	80°19', 09°40'	1-5	1.3	214
43b	80°19', 09°40'	8	0.92	217
49	80°45', 08°14'	8	0.92	167
56	80°16', 08°40'	2	0.32	273
			(0.87)	(224)
	Central Region			
64	79°01', 12°03'	7.5	0.16	204
65	78°19', 16°46'	6	0.053	279
			(0.11)	(242)
	Southern Trough Region‡			
72a	77°08', 10°33'	5	0.92	188
72b	77°10', 10°32'	7	0.71	204
78	76°59', 06°35'	8	1.2	191
80	76°55', 06°04'	6	1.0	207
			(0.96)	(198)

The "a" and "b" indicate return samplings at a given station within a 48-hour period. Ice cover values were observed shipboard at the hour of sampling. Numbers in parentheses are average values for each region.

*Biologically mediated inorganic carbon deficit B in surface water (0-70 m) was calculated from mass balance (see text); 1 standard deviation equals ± 0.1 mol C m^{-2} based on Monte Carlo simulation (see text).

†Calculated from measured C_T and A_T (see text); 1 standard deviation equals ± 6.2 µatm based on calculated values for 12 pairs of duplicate samples.

‡Values integrated to 50 m only (see Figure 2a).

deviation based on results of Monte Carlo simulation), with low values found in the ice-covered central region and higher values seen in both the open waters of the Northern Trough (also known as the Westwind Trough) and the more ice-covered Southern Trough (or Belgica Trough) region influenced by the EGC (Table 1). Alternative calculations of B assuming predilution depletion of nitrate were lower by less than 1% in nearly all cases. On average, biological processes account for more than half of the depleted inorganic carbon in the polynya and as much as 97% at some stations.

Independent confirmation of biological removal of C_T was provided by comparing B to other biologically relevant parameters on a regional basis. Significant correlations were found between B and integrated chlorophyll a ($\alpha < 0.01$, n = 11; data not shown), integrated particulate organic carbon (POC)($\alpha < 0.05$, n = 10; see Figure 3a), and the dissolved inorganic nitrogen (DIN) deficit (ΔDIN; $\alpha < 0.05$, n = 13, see Figure 3b). Errors on the estimated slopes of each reduced major axis [*Sokal and Rohlf,* 1984] were large, not because of measurement error but probably just because of high variability between stations (see below). This degree of variability agrees with general observations of productivity in the Arctic [*Codispoti et al.,* 1991] and the observed "mosaic" of primary productivity in the polynya [*NEWATER Steering Committee,* 1993], suggesting that the polynya was heterogeneous in both space and time. At each station, however, the biologically mediated C_T deficit B provides a local, time-integrated, unambiguous signature of net organic carbon production.

Despite the high variability between stations and resulting high error estimates on the derived slopes of each reduced major axis (expressed as ± 95% confidence limits below) the regional relationships between B and other biologically important parameters provide some insight to carbon cycling within the polynya. Ratios of B to chlorophyll (114 ± 57 g C g chla^{-1}, based on geometric mean regression of integrated values [*Sokal and Rohlf,* 1984]) were high compared to typical cellular carbon-to-chlorophyll ratios (30, on average for temperate phytoplankton; 25 for vigorously growing phytoplankton, 60 for phytoplankton in nitrate-depleted water [*Antia et al.,* 1963]). Phytoplankton carbon-to-chlorophyll ratios from subsurface chlorophyll maxima averaged about 26 (± 16 g C g chla^{-1}) but increased to values as high as 300 in the near-surface waters (B. Booth, personal communication, 1994). Polar phytoplankton often exhibit carbon-to-chlorophyll ratios higher than temperate phytoplankton. Typical summertime polar algae carbon-to-chlorophyll range from 20 to 200, depending on species composition, irradiance, day length, mixed-layer depth, and temperature [*Sakshaug,* 1989; *Smith and Sakshaug,* 1990]. The B-to-integrated-chlorophyll ratios measured in the polynya may suggest that the late-summer depleted inorganic carbon is in living cells near the surface that have adapated to long day lengths, high light levels, and low temperatures. Alternatively, they may suggest some loss of the chlorophyll relative to depleted inorganic carbon. Mechanisms for the latter include degradation within the POC pool (death of algal cells), particulate carbon export from the euphotic zone (e.g., by sinking), or carbon conversion to other organic pools, such as dissolved organic carbon (DOC) (via UV photolysis or extracellular enzymes [see *Vetter and Deming,* 1995]), nonliving POC, or other biomass.

The overall relationship between B and integrated POC (operationally includes living and nonliving particulate organic carbon) had a slope near unity (1.2 ± 0.63, Figure 3a; geometric mean regression [*Sokal and Rohlf,* 1984]), suggesting POC as the dominant sink for B, although given the error on the slope, we cannot rule out that part of B could also have been exported, converted to DOC, or shunted to higher trophic levels by the time of sampling.

The geometric mean regression of the biologically mediated C_T deficit ($\Delta DIC_B = B$) on the dissolved inorganic nitrogen deficit (ΔDIN) in the upper water column (Figure 3b, $\alpha < 0.05$) gave a ΔDIC_B : ΔDIN slope of 6.2 (± 3.1). *Wallace et al.* [this issue] calculate the C : N ratio in a way that does not presume a preformed NO_3 concentration and come up with a very similar value (7.13 ± 1.53). The ratio also agrees well with the average particulate organic carbon to nitrogen ratio (POC : PON) for the same polynya stations (7.5 ± 3.2), the classical "Redfield" elemental ratio of 6.6 (error bars unknown [*Redfield et al.,* 1963]), and the North Atlantic thermocline ΔC_T : ΔNO_3 ratios (5.5 ± 0.32 [*Takahashi et al.,* 1985]). The observed ΔDIC_B : ΔDIN ratios in the polynya do differ significantly from the higher ratios of 11 - 14 (± 1.7 - 3.1 [*Sambrotto et al.,* 1993]) reported for other high-latitude regions. The latter

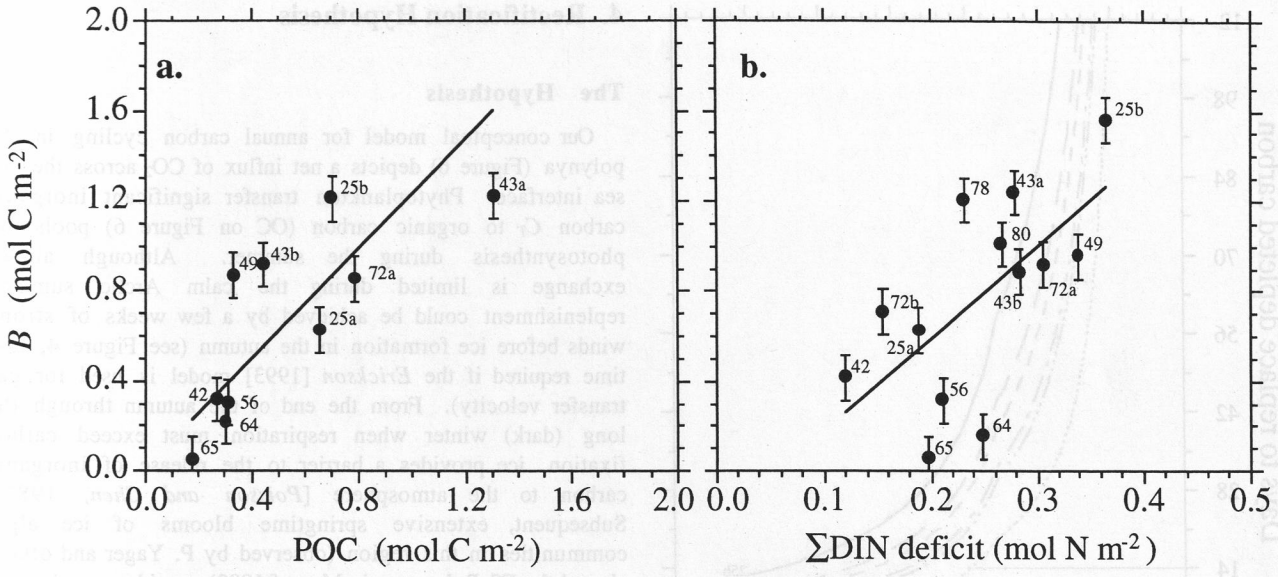

Figure 3. Biologically mediated C_T deficit B (mol C m^{-2}) as a function of (a) integrated particulate organic carbon (POC) (mol C m^{-2}; $r^2 = 0.598$) and (b) salinity-scaled dissolved inorganic nitrogen deficit (ΔDIN) (mol N m^{-2}; $r^2 = 0.434$). Error bars denote 1 standard deviation for B based on Monte Carlo simulation (see text). Solid lines result from geometric mean regression. Numbers adjacent to points indicate stations (see Table 1). Values for B in Figure 3a are sometimes integrated to shallower depths than in Figure 3b to match POC measurements.

ratios have been interpreted to reflect complex nutrient cycling [*Toggweiler,* 1993], perhaps driven by zooplankton grazers [*Banse,* 1994]. The low ΔDIC_B : ΔDIN values at some stations in the polynya resemble that found in protein and bacteria (~4 [*Klapper,* 1977; *Porter,* 1946]) and in healthy phytoplankton cells (~3 for vigorous growth [*Banse,* 1974]) and may have implications for a reduced microbial loop [*Pomeroy and Wiebe,* 1988], consistent with reduced macrograzer populations in the polynya [*NEWATER Steering Committee,* 1993; *Ashjian et al.,* this issue] and for consequent export of high-quality (N rich) food to the benthos [*Ambrose and Renaud,* this issue].

To compare this estimate of biological removal of inorganic carbon to production calculations based on short-term incubations, B must be scaled to a biologically relevant timescale (which may be different for each station). Assuming a constant value of 60 days for production, we estimate an average net production rate for the Northern Trough and polynya region of 14 ± 7.4 mmol C m^{-2} d^{-1} (maximal rate ~26 mmol C m^{-2} d^{-1}). This rate compares well with total primary production observed at the same stations using ^{14}C bicarbonate incubations (average = 21 ± 13 mmol C m^{-2} d^{-1}). Assuming that B approximates export (see discussion below) gives a median e ratio (export : total production) of 0.58, which also compares favorably to directly measured surface f ratios (new : total production) of 0.69 (± 0.16) determined by $^{15}NO_3$ and $^{15}NH_4$ incubations [*Smith,* this issue]. B also compares well with the calculations of particle production estimates based on gradients in suspended particulate matter (31.6 mmol C m^{-2} d^{-1} [*Smith et al.,* this issue]) and particle export based on ^{234}Th budgets (13 mmol C m^{-2} d^{-1} in 1992 Northern Trough and polynya stations [*Cochran et al.,* this issue]). Our range falls below the estimate of export production based on along-trough nitrate gradients in the polynya (41.4 ± 16.1 mmol C m^{-2} d^{-1} [*Wallace et al.,* this issue]). Selection of station-specific time periods over which to scale B (chosen based on forthcoming knowledge of hydrography) should improve the correspondence and resolve questions of production versus export.

Air-Sea Gas Exchange and pCO_2

Surface waters of this region were undersaturated (average pCO_2 = 218 ± 34 μatm, n = 12; see Table 1) relative to the atmosphere (pCO_2 ~ 345 μatm). On the basis of the *Liss and Merlivat* [1986] formulation of the gas transfer velocity, the average wind speed during the cruise, the average polynya air-sea gradient (ΔpCO_2 = 127 μatm), and CO_2 solubility [*Weiss,* 1974], the average late summer air-sea flux was ~1.3 mmol C m^{-2} d^{-1}. This low flux was attributable to the low wind speeds experienced during the summer and validates the assumption of setting G_d equal to zero. Any exchange which may have occurred would have caused an underestimate of B.

In order for biological depletion of inorganic carbon in the NEW Polynya to be replenished locally from the atmosphere, a period of increased wind shear must occur before ice forms in the autumn. For most stations a stormy period of a few weeks would be sufficient to draw enough CO_2 from the atmosphere to replace most of the depleted carbon (Figure 4). The actual number of days depends on which gas transfer velocity formulation is used. A complementary calculation based on buoyancy [*Nelson et al.,* 1989] suggests that these same winds would also mix the upper 70 m. Both of these calculations were based on simplified approximations and require further refinement. Data from a nearby weather station at Danmarkshavn (Figure 5; see Figure 1 for location) suggest that such wind events are not unreasonable, though the observed winds in September 1991 would not have completely removed all of the deficit seen in 1992 at all stations using the conservative *Liss and Merlivat* [1986] formulation of the air-sea gas exchange velocity. *Erickson* [1993] recently showed

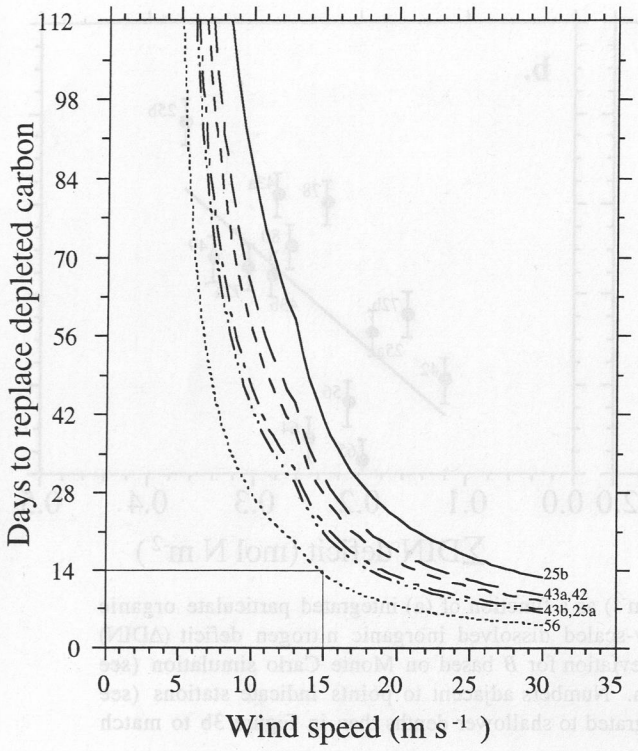

Figure 4. Modeled results of the time required to replenish the biologically mediated C_T deficit B by air-sea gas exchange as a function of wind speed, using the most conservative *Liss and Merlivat* [1986] formulation of the air-sea gas exchange velocity, observed pCO_2 air-sea gradients, calculated biologically mediated carbon deficits, and in situ temperatures to calculate flux. For example, 14 days of winds at 15 m s^{-1} are required to replenish B at station 56. The six stations shown were in the polynya and Northern Trough regions (see Table 1). Using the formulation of *Erickson* [1993] would shorten the required windy period by a factor of about 2 owing to enhanced turbulent mixing by a strong air-sea temperature differential.

that the air-sea gas transfer velocity could be a factor of 2 greater than the *Liss and Merlivat* [1986] formulation at wind velocities in the range of 10-15 m s^{-1} when there is an air-sea temperature gradient such as that commonly seen in the Arctic. Use of this model would allow the Danmarkshavn wind data to replenish the depleted carbon at all stations. Additional wind data are necessary to determine the extent and interannual variability of autumn storm conditions in the polynya region. A partial test of the likelihood of complete replenishment is the degree to which the observed gases at 70 m are in equilibrium with the atmosphere. Late summer oxygen data from deep Polar Water suggest that the late fall mixed layer closely approached equilibrium with the atmosphere (O_2 saturation at 50-100 m = 95-100% [*Wallace et al.*, this issue]). The inorganic carbon data reported here (average pCO_2 at 50-100 m = 318 ± 17), however, do not support as complete an equilibrium. This test assumes that the 70-m water found in the polynya during summer was ventilated in the area during the previous autumn/winter. The validity of this assumption awaits a better understanding of the overall residence time of PW in the polynya region.

4. Rectification Hypothesis

The Hypothesis

Our conceptual model for annual carbon cycling in the polynya (Figure 6) depicts a net influx of CO_2 across the air-sea interface. Phytoplankton transfer significant inorganic carbon C_T to organic carbon (OC on Figure 6) pools by photosynthesis during the summer. Although air-sea exchange is limited during the calm Arctic summer, replenishment could be achieved by a few weeks of strong winds before ice formation in the autumn (see Figure 4; less time required if the *Erickson* [1993] model is used for gas transfer velocity). From the end of the autumn through the long (dark) winter when respiration must exceed carbon fixation, ice provides a barrier to the release of inorganic carbon to the atmosphere [*Poisson and Chen,* 1987]. Subsequent, extensive springtime blooms of ice algal communities in this region (observed by P. Yager and others aboard the FS *Polarstern* in May of 1993) provide a mechanism for initial removal of accumulated respiratory carbon in near-surface layers before the ice melts. In addition, once the ice melts, meltwater creates a thin, near-surface, highly stratified layer which isolates most of the PW from air-sea gas exchange. In this scenario there is no time during the polynya's annual cycle when CO_2 can escape to the atmosphere. We refer to this cancellation of one half of the typical air-sea exchange cycle of an ice-free ocean as "rectification." With this annual cycle of events the polynya becomes a net sink for atmospheric carbon.

The application of this hypothesis to the polynya or any other Arctic region requires better understanding of the local and remote ventilation of the surface water. If there is significant flow of water into the polynya sometime during the

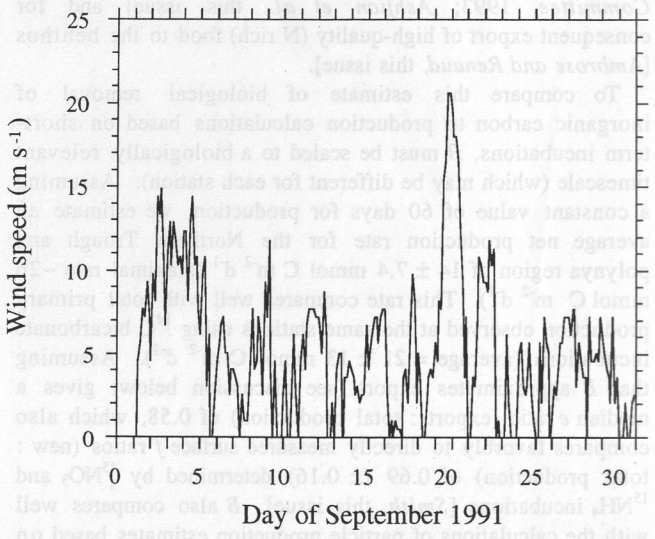

Figure 5. Wind speed data from nearby Danmarkshavn weather station (on the penninsula just south of the Southern Trough; see Figure 1) during September 1991. Measurements were recorded every 3 hours. A week of 10-15 m s^{-1} wind speeds plus several days of up to 20 m s^{-1} wind speeds should replenish most of the depleted inorganic carbon in the surface waters of the polynya.

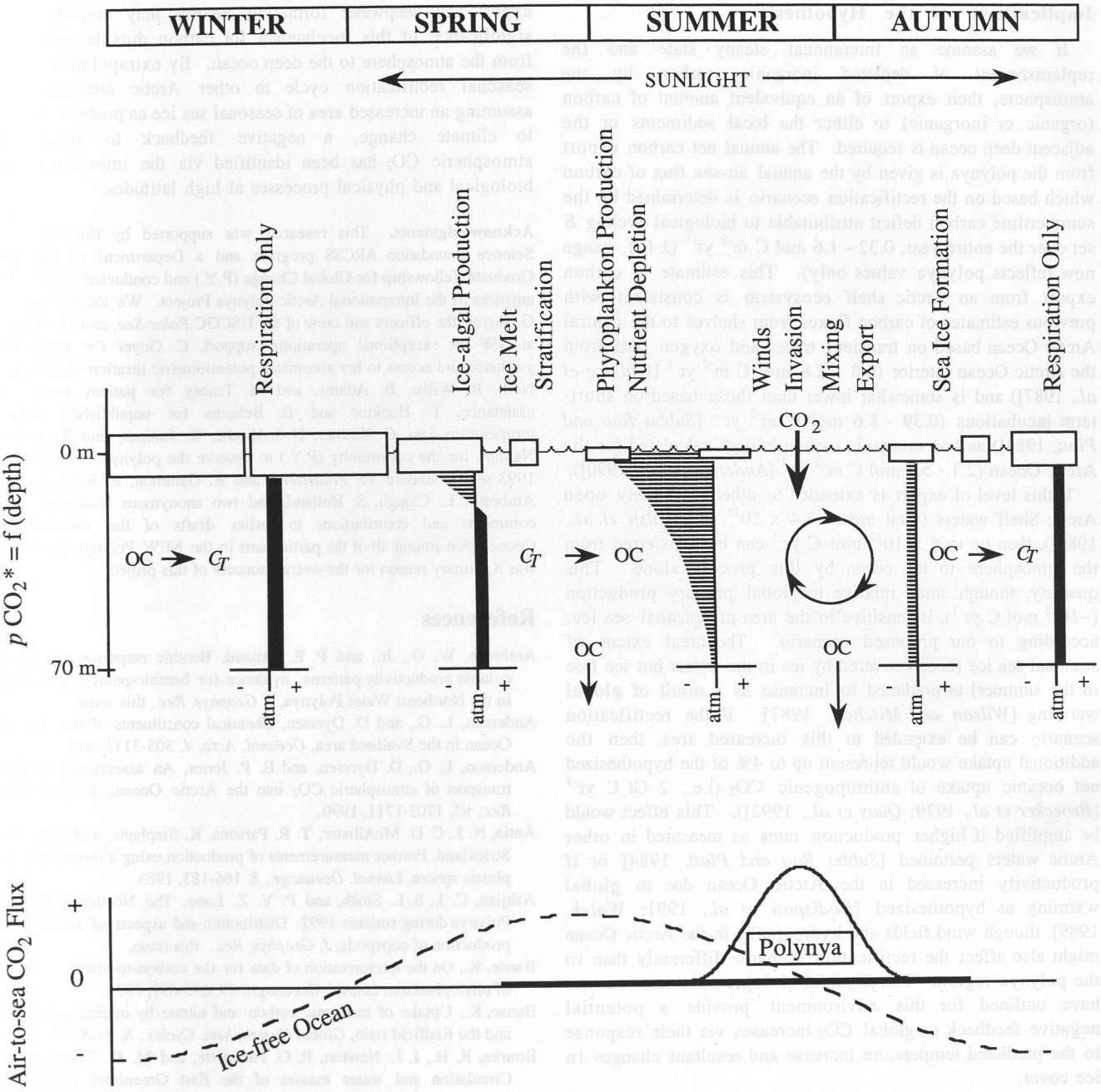

Figure 6. Proposed annual cycle of biological and physical processes affecting CO_2 cycling in regions with seasonal sea ice (see text); top time line indicates vertical profiles of potential pCO_2 (asterix indicates as if at 1 atm), supersaturated (solid) or undersaturated (striped) relative to the atmosphere; bottom time line compares the typical seasonal cycle for air-sea gas exchange in an ice-free ocean (dashed line, schematic only, actual timing may vary) to the proposed "rectification" scenario for polynyas or other seasonally ice-free Arctic shelves (solid line).

annual cycle, then the hypothesized CO_2 replenishment by autumn storms could occur via replacement from nonpolynya waters instead. Source values observed at 70 m should reflect the properties of these waters. Forthcoming understanding of hydrography of this region will ultimately resolve the issue. If significant flow through the polynya region does occur, then the fate and timing of the outflowing, C_T-depleted polynya water will determine the effectiveness of the rectification process. We fully expect that as more data become available for the NEW Polynya and other Arctic regions, the hypothesis will be tested rigorously. Information required for a thorough test of the hypothesis includes seasonal pCO_2 data for the polynya or Arctic shelves in general, more accurate measurements or calculations of air-sea gas exchange [*Erickson,* 1993; *Liss and Merlivat,* 1986]), improved wind data showing the extent of interannual spatial and temporal variability (late summer 1992 appeared to be much less windy than late summer 1993), and a more complete understanding of the hydrography of the region, specifically the extent of flushing of the PW and the degree of mixing in the autumn.

Implications of the Hypothesis

If we assume an interannual steady state and the replenishment of depleted inorganic carbon by the atmosphere, then export of an equivalent amount of carbon (organic or inorganic) to either the local sediments or the adjacent deep ocean is required. The annual net carbon export from the polynya is given by the annual air-sea flux of carbon which based on the rectification scenario is determined by the summertime carbon deficit attributable to biological cycling *B* set over the entire year, 0.32 - 1.6 mol C m^{-2} yr^{-1} (± 0.1, range now reflects polynya values only). This estimate of carbon export from an Arctic shelf ecosystem is consistent with previous estimates of carbon fluxes from shelves to the central Arctic Ocean based on transient tracer and oxygen data from the Arctic Ocean interior (0.8 - 2.8 mol C m^{-2} yr^{-1} [*Wallace et al.,* 1987]) and is somewhat lower than those based on short-term incubations (0.39 - 8.6 mol C m^{-2} yr^{-1} [*Subba Rao and Platt,* 1984]) and an inorganic carbon budget calculated for the Arctic Ocean (2.1 - 5.4 mol C m^{-2} yr^{-1} [*Anderson et al.,* 1990]).

If this level of export is extended to other seasonally open Arctic Shelf waters (total area = 3.4 x 10^{12} m^2 [*Walsh et al.,* 1989]), then up to 6 x 10^{12} mol C yr^{-1} can be transferred from the atmosphere to the ocean by this process alone. This quantity, though small relative to global primary production (~10^{15} mol C yr^{-1}), is sensitive to the area of seasonal sea ice, according to our proposed scenario. The areal extent of seasonal sea ice (ocean covered by ice in the winter but ice free in the summer) is predicted to increase as a result of global warming [*Wilson and Mitchell,* 1987]. If the rectification scenario can be extended to this increased area, then the additional uptake would represent up to 4% of the hypothesized net oceanic uptake of anthropogenic CO_2 (i.e., 2 Gt C yr^{-1} [*Broecker et al.,* 1979; *Quay et al.,* 1992]). This effect would be amplified if higher production rates as measured in other Arctic waters pertained [*Subba Rao and Platt,* 1984] or if productivity increased in the Arctic Ocean due to global warming as hypothesized [*Codispoti et al.,* 1991; *Walsh,* 1989], though wind fields and hydrography in the Arctic Ocean might also affect the rectification scenario differently than in the polynya region. The physical-biological interactions we have outlined for this environment provide a potential negative feedback to global CO_2 increases via their response to the predicted temperature increase and resultant changes in ice cover.

5. Conclusions

During a 1-month summertime study in the NEW Polynya off the northeast coast of Greenland, biological activity was found to have reduced significantly the total dissolved inorganic carbon inventory of the surface waters of most stations. This deficit correlated well on a regional basis with other biological parameters, such as integrated chlorophyll, integrated particulate organic carbon, and the dissolved inorganic nitrogen deficit. It was also consistent with other measurements of productivity in the polynya. Placing this deficit in the context of the annual sequence of events likely to occur in the polynya region allowed us to hypothesize a "rectification" of the typical air-sea CO_2 flux. This rectification would be unique to seasonally ice-covered regions. As a result, up to 2 mol C m^{-2} may be exported annually from the NEW Polynya. The possibility of off-shelf export and deepwater formation nearby may amplify the significance of this mechanism for carbon dioxide removal from the atmosphere to the deep ocean. By extrapolating this seasonal rectification cycle to other Arctic shelves and assuming an increased area of seasonal sea ice as postulated due to climate change, a negative feedback to increased atmospheric CO_2 has been identified via the interaction of biological and physical processes at high latitudes.

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J. W. Deming and P. L. Yager, School of Oceanography, WB-10, University of Washington, Seattle, WA 98195. (Corresponding author's email: yager@u.washington.edu.)

K. M. Johnson, P. J. Minnett, and D. W. R. Wallace, Ocean and Atmospheric Sciences Division, Department of Applied Science, Brookhaven National Laboratory, P.O. Box 5000, Upton, NY 11973.

W. O. Smith Jr., Graduate Program in Ecology, University of Tennessee, Knoxville, TN 37996.

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