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Dissolved inorganic carbon pool dynamics in northern Gerlache Strait, Antarctica

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Abstract. The Research on Antarctic Coastal Ecosystem Rates (RACER) program was designed to study interactions between biological and physical processes in regions west of the Antarctic Peninsula. The field sampling effort was conducted from 1986 to 1992 and consisted of four cruises; three during separate austral spring-summer seasons (RACER I, II and III) and one austral winter cruise (RACER IV). Extensive phytoplankton blooms were documented at several stations in northern Gerlache Strait during the three austral spring-summer seasons. The growth and accumulation of photoautotrophic microorganisms resulted in the net removal of >100 μmol kg^{-1} of salinity normalized dissolved inorganic carbon (DIC). An upper estimate for net ecosystem production of 0.15 mol C m^{-2} d^{-1} was calculated from measured rates of DIC removal at one station (designated station A) that was occupied extensively during all four RACER cruises. Independent measurements of total gross microbial production, based on DNA synthesis rates, ranged from 0.3 to 1.0 mol C m^{-2} d^{-1} at the height of the bloom. The net accumulation of phytoplankton carbon and removal of DIC from the system resulted in an estimated mean air-to-sea flux of 6 mmol C m^{-2} d^{-1}, a negligible fraction of the net removal of carbon by organic matter production. A characteristic feature of each austral spring-summer cruise was the high degree of spatial and temporal heterogeneity in the inorganic carbon system parameters. The exact cause(s) of this variability is not known. As a result of spatial heterogeneity, carbon fluxes were not well constrained, and regional carbon budget closure was problematic.

1. Introduction

The Antarctic marine ecosystem is a complex assemblage of diverse habitats with functionally distinct hydrographical and biogeochemical provinces [*Treguer and Jacques*, 1992]. Together, these open ocean, shelf-slope, and frontal regions may have a considerable impact on the global marine carbon cycle [*Sarmiento and Orr*, 1991]. Nevertheless, a quantitative understanding is lacking because of problems related to large seasonal and interannual variability, especially in the coastal shelf and marginal sea ice zones, and general inaccessibility and limited number of seasonally resolved data sets for any of these key Southern Ocean ecosystems. Independent model estimations of the annual carbon dioxide (CO_2) flux for the Southern Ocean do not even agree on the sign of the net flux [*Tans et al.*, 1990; *Metzl et al.*, 1991; *Takahashi et al.*, 1993, 1997; *Poisson et al.*, 1993; *Robertson and Watson*, 1995]. It is apparent that a more accurate estimation of the air-to-sea flux of CO_2 will require direct measurements of regional fluxes in a variety of the key habitats that compose the Southern Ocean marine ecosystem. Recently completed and ongoing field expeditions conducted under international Joint Global Ocean Flux Study auspices focused on the Ross Sea and the recently established Palmer Long-Term Ecological Research (LTER) program focused on the coastal regions west of the Antarctic Peninsula [*Smith et al.*, 1995] should eventually expand our current understanding of the Southern Ocean carbon cycle.

Open ocean regions at high latitudes (>60°) have elevated nutrient concentrations but relatively low standing stocks of phytoplankton and low rates of primary production. In sharp contrast to these high-nutrient, low-productivity oceanic habitats, coastal regions of Antarctica exposed to the annual advance and retreat of sea ice support seasonal phytoplankton blooms with high rates of primary production [*Smith and Nelson*, 1985; *Holm-Hansen et al.*, 1989]. Coastal and ice-edge regions of Antarctica could potentially represent large, but transient, seasonal sinks for atmospheric CO_2, but these sinks may be offset by equally large sources of CO_2 during the winter as a result of net community respiration and upwelling of CO_2-enriched waters. The potential efflux of CO_2 in the winter can, in theory, be blocked by seasonal ice cover, resulting in a net annual sink of CO_2 to the oceans from the summer phytoplankton blooms [*Yager et al.*, 1995].

The role of the ocean as a reservoir in the global carbon cycle is dependent largely upon the export flux of planktonic primary production from the euphotic zone [*Eppley and Peterson*, 1979; *Williams and von Bodungen*, 1989]. Results from cross-ecosystem analyses (i.e., comparison of two or more different ecosystems) suggest that the export of living and nonliving materials from the euphotic zone is a positive, nonlinear function of total integrated primary production [*Suess*, 1980; *Pace et al.*, 1987; *Martin et al.*, 1987; *Wassmann*, 1990], with values ranging from less than 10% in oligotrophic waters to greater than 50% in productive coastal regions. The intensive austral spring/summer phytoplankton bloom in the Antarctic Peninsula region can result in

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phytoplankton standing stocks in excess of 0.7 g chlorophyll *a* (chl *a*) m^{-2} and sustained production rates of 0.2-0.4 mol C m^{-2} d^{-1} [*Holm-Hansen and Mitchell*, 1991].

Though the presence of seasonal phytoplankton blooms is well documented, we know less about the fate of the accumulated organic matter. Sediment trap-derived particle flux estimates from waters surrounding the Antarctic Peninsula indicate that this region supports both the highest (>0.1 mol C m^{-2} d^{-1} during and immediately following the spring bloom) and the lowest (<0.005 mmol C m^{-2} d^{-1} during austral winter) values reported for the world ocean [*Karl et al.*, 1996]. Furthermore, during the initial stages of the spring-summer phytoplankton bloom, particle export may be decoupled from contemporaneous new production for periods of several weeks or more [*Karl*, 1993]. Spatial and temporal (both seasonal and interannual) variability in Antarctic habitats is dramatically reflected in the results of recent time series sediment trap experiments [*Karl et al.*, 1996], and year round studies have documented the role of sea ice in export processes [*Fischer et al.*, 1988].

The Research on Antarctic Coastal Ecosystem Rates (RACER) program was designed to study living and nonliving carbon pool dynamics in several representative coastal regions of the western portion of the Antarctic Peninsula. An initial 4-month field study (RACER I) conducted in a 25,000-km^2 region of the western Bransfield Strait during the 1986-1987 austral spring-summer documented extensive phytoplankton blooms [*Huntley et al.*, 1991]. These blooms resulted in significant inorganic nutrient depletion and a seasonal removal of dissolved inorganic carbon (DIC) (normalized to 35.00 salinity) in excess of 100 μmol kg^{-1} in selected regions of Gerlache Strait [*Karl et al.*, 1991a]. Subsequent studies (RACER II and III) were confined to a smaller, 4000-km^2 area of Gerlache Strait to study the factors involved in the formation and demise of phytoplankton blooms during the austral spring-summers of 1989-1990 and 1991-1992. A final study (RACER IV) was conducted in the same area as RACER II and III, but during austral winter of 1992. Surface water samples for DIC and alkalinity were collected on RACER II, III, and IV at stations throughout Gerlache Strait, and depth profiles were taken at select stations. As part of the Long-Term Ecological Research (LTER) project, we had the opportunity to obtain underway fugacity of carbon dioxide (fCO_2) measurements during a transect through Gerlache Strait in December 1995. In this paper, we summarize these data and compare the patterns observed for inorganic carbon pool dynamics to other measured carbon fluxes, specifically primary and total microbial carbon production rates and particulate carbon export.

2. Materials and Methods

2.1. Station Location and Sampling Strategy

During each RACER cruise, a grid of stations was sampled rapidly (3-5 days) aboard the R/V *Polar Duke* to obtain a quasi-synoptic physical, chemical, and biological characterization of the study area. These surveys are referred to as fast grids. The RACER I study (1986-1987) area included the western portion of Bransfield Strait and northern Gerlache Strait (Figure 1). The RACER II program (1989) was confined to a smaller sampling area within northern Gerlache Strait and southwestern Bransfield Strait (Table 1 and Figure 1). The RACER III program further reduced the sampling area to include only the northern portion of Gerlache Strait with more stations added to study the complex and dynamic water flow pattern throughout the study area during the austral summer of 1991 (Table 1 and Figure 1). RACER IV was conducted during the 1992 austral winter and repeated the RACER III sampling grid (Table 1 and Figure 1). Selected stations were occupied for longer time periods to record the daily variability and to conduct process-oriented experiments. One such location, Station Andersson (station A), named after the Antarctic researcher Gunnar Andersson (i.e., RACER I station 43), located in northern Gerlache Strait (64°14.00'S and 61°17.00'W) was occupied during all four RACER cruises (Figure 1).

2.2. Dissolved Inorganic Carbon and Alkalinity

Approximately 385 DIC and alkalinity measurements of archived RACER III and RACER IV samples were analyzed during the summer of 1994. RACER II samples were analyzed for DIC during 1990. These samples included surface seawater collected during the fast grids and depth profiles at station A. Samples were collected in 10-L Niskin bottles that were mounted on a 12-place conductivity-temperature-depth (CTD)/rosette system. Samples for DIC and alkalinity were subsampled into 0.3-L borosilicate glass bottles, fixed with 100 μL of a saturated mercuric chloride solution to inhibit bacterial activity and sealed with greased (Apiezon) ground glass stoppers and polyethylene tape [*Karl et al.*, 1991a]. For RACER II-IV, DIC was measured by coulometric determination of extracted CO_2 [*Johnson et al.*, 1987]. In the laboratory, 25 to 30 mL samples were delivered to the coulometer extractor using either a calibrated pipet bulb or gravimetrically using syringes that were weighed before and after sample injection. The coulometer efficiency was determined using known concentrations of high-purity solid sodium carbonate. Analysis of the RACER samples was tracked using a subtropical North Pacific standard seawater sample from the Hawaii Ocean Time-series (HOT) program to determine both accuracy and precision. The DIC content of that surface water sample was evaluated relative to certified reference materials (CRMs) provided by A. Dickson [*Dickson*, 1991; *Winn et al.*, 1998]. Over a 2-month measurement period, the mean DIC of the North Pacific secondary standard was 1967.7 (standard deviation = 1.6) μmol kg^{-1} (n = 23). There was, however, a mean difference of +7.2 μmol kg^{-1} between our coulometric DIC determinations of the North Pacific secondary standard and "blind" independent measurements of the sample material made by HOT program personnel using a single operator multiparameter metabolic analyzer system [*Winn et al.*, 1998]. Consequently, although our measurement precision is acceptable (0.08%), the accuracy of our DIC determinations is less well constrained (~0.3-0.4%). For the large DIC differences observed in the coastal regions of the Antarctic Peninsula (up to 100 μmol kg^{-1} out of a mean concentration of >2200 μmol kg^{-1}) this less than ideal accuracy is probably of minor consequence. Furthermore, the DIC difference measurements (ΔDIC) reported here are independent of absolute measurement accuracy. DIC measurements reported are not normalized unless explicity stated.

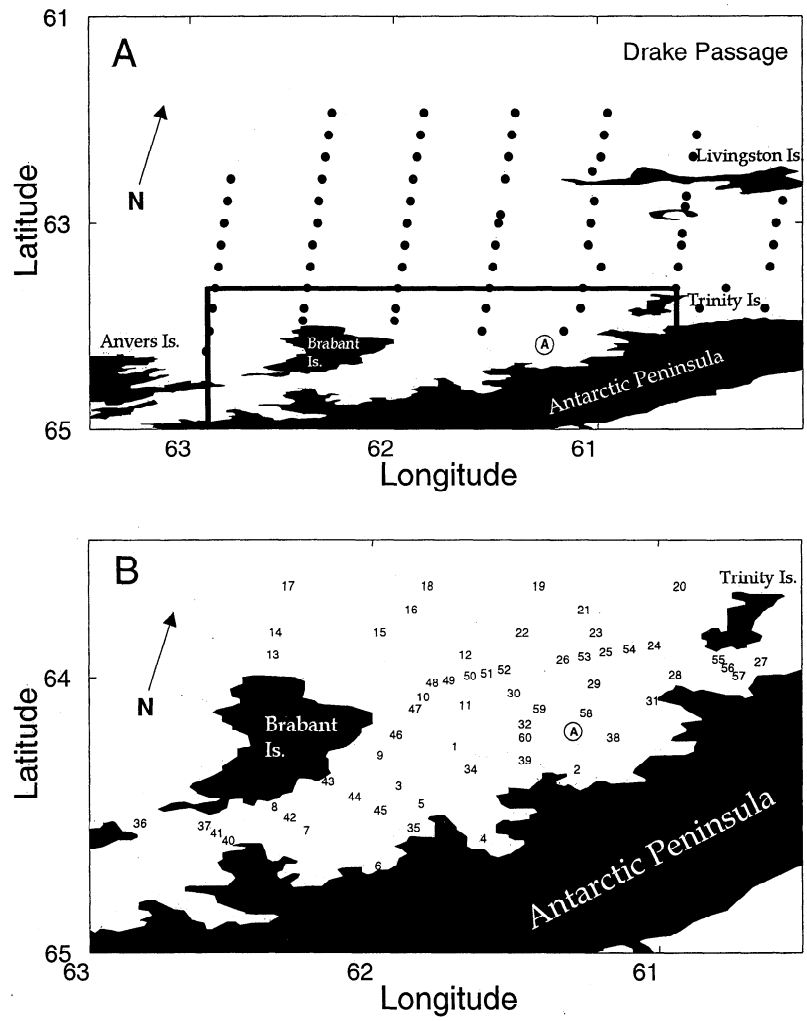

Figure 1. (a) The Research on Antarctic Coastal Ecosystem Rates (RACER) programs I, II, III, and IV study areas in the region west of the Antarctic Peninsula. RACER I station locations are represented with solid circles. Station spacing is approximately 20 km, and the grid was sampled over a period of 5 days (fast grid) four times during the months of December through March 1986 [see *Huntley et al.*, 1991]. Subsequent cruises (RACER II, III, and IV) were restricted to the area of northern Gerlache Strait (small rectangle). Station Andersson (station A, occupied during all four RACER cruises) is represented by the circled letter A in northern Gerlache Strait. (b) Map of Gerlache Strait showing the station numbering and locations for RACER II, III, and IV. This grid of stations was sampled over a period of 3 days (fast grid) four times during the month of November 1989 (RACER II), three times during the month of December 1991 (RACER III), and once during the month of July 1992 (RACER IV). The circled letter A in northern Gerlache Strait represents station A.

Total alkalinity was determined for RACER III and IV by potentiometric titration using hydrochloric acid (HCl). The acid titrant (0.1 *M* HCl in 0.6 *M* NaCl) was calibrated with standard solutions of high-purity sodium carbonate and was compared to a secondary standard from the HOT program [*Winn et al.*, 1994, 1998]. During the 2-month measurement period, the mean alkalinity for the North Pacific Ocean sample was 2302.4 (standard deviation = 1.9) μeq kg^{-1} (n = 20). The mean difference between our analyses and independent "blind" measurements made by HOT program personnel was +10.6 μeq kg^{-1}. Because no CRMs existed at that time for the measurement of alkalinity, we have no way of ascertaining the accuracy of our RACER sample alkalinity.

DIC, alkalinity, salinity, temperature, and nutrient data were used to calculate the fugacity of CO_2 (fCO_2) by applying the apparent thermodynamic dissociation constants for K_1 and K_2 [*Roy et al.*, 1993] using the program of *Lewis and Wallace* [1995]. Values of fCO_2 can differ from measured values by as much as 30 μatm based on the different sets of dissociation constants. Air-sea gas flux estimates were calculated by multiplying the atmosphere (350 μatm) and surface ocean fCO_2 difference by the gas transfer coefficient and solubility of CO_2 in seawater. The gas transfer coefficient was calculated using the equation of *Wanninkhof* [1992]. The solubility of CO_2 in seawater was calculated from *Weiss* [1974]. By convention, a positive value for the air-sea gas flux indicates a net transfer of CO_2 from the atmosphere to the surface ocean.

Table 1. Research on Antarctic Coastal Ecosystem Rates (RACER) Fast Grid Cruise Dates and Approximate Grid Areas

RACER Cruise	Fast A Grid Date	Fast B Grid Date	Fast C Grid Date	Fast D Grid Date	Grid Area
RACER I (1986-1987)	Dec. 15-19	Jan. 19-24	Feb. 20-25	March 12-17	25,000 km^2 includes Drake Passage, Bransfield Strait, Gerlache Strait
RACER II (1989)	Nov. 2-5	Nov. 9-13	Nov. 16-18	Nov. 22-24	4000 km^2 Gerlache Strait
RACER III (1991)	Dec. 15-18	Dec. 21-24	Dec. 26-30	---[a]	4000 km^2 Gerlache Strait
RACER IV (1992)	July 20-25	---	---	---	4000 km^2 Gerlache Strait

[a] Not conducted.

2.3. Underway Measurements of Fugacity of Carbon Dioxide

The fugacity of carbon dioxide was measured in Gerlache Strait during a December 1995 LTER cruise using an underway system for determination of the mixing ratio of CO_2 in a headspace in equilibrium with surface seawater. Seawater was pumped from the bow intake of the R/V *Polar Duke* located approximately 5 m below the sea surface. A stainless steel pump delivered seawater through an insulated fiberglass conduit to a 16-L capacity counterflow rotating disk equilibrator in the shipboard laboratory [*Schink et al.*, 1970]. A Sea-Bird thermosalinograph positioned at the intake measured ambient temperature and conductivity. The high flow rate of this system resulted in less than a 1°C temperature increase (1°C equates to a change of 14.5 µatm in fCO_2) during transit through the interior spaces of the vessel. Ambient marine boundary air, sampled from the bow of the ship, was used as a reference for the estimation of the ΔfCO_2 (i.e., the difference between the fCO_2 of the ocean and the atmosphere; $\Delta fCO_2 = fCO_2$ in the surface ocean $- fCO_2$ in the marine boundary layer). Concentrations of CO_2 and H_2O in the marine boundary air and equilibrator air were measured using a nondispersive infrared analyzer (LI-COR model 6262). The continuous measurement system was periodically calibrated (every 2.5 hours) with compressed gas standards with nominal mixing ratios of 259.28, 303.86 and 373.19 ppm (by volume), which were obtained and certified by the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory against World Meteorological Laboratory standards. The LI-COR 6262 water channel was calibrated with a LI-COR dew point generator. All control commands and data acquisition, including the measurements of equilibrator temperature and pressure, were automated using LabView® for Windows version 3.1. Calculation of $fCO2$ values were made according to the procedures outlined by Dickson and Goyet (1994).

2.4. Primary Carbon Production

The rates of particulate carbon production and particulate carbon export were measured at several stations during each RACER cruise. Only those data from station A are presented herein. Primary production was measured by O. Holm-Hansen (Scripps Institution of Oceanography) using the ^{14}C technique. Water from predetermined depths was drawn into two clear and one opaque 0.25-L borosilicate glass bottles with Teflon® lined screw caps [*Holm-Hansen and Mitchell*, 1991]. The samples were spiked with ^{14}C-bicarbonate (185 kBq per sample) and then returned to depth on a drifting buoy array for 8-24 hours. After recovery of the bottles, samples were filtered through 25-mm-diameter glass fiber filters (Whatman GF/F). The filters were placed into scintillation vials, exposed to concentrated HCl fumes for 6-8 hours and dried. Radiocarbon incorporation was determined by liquid scintillation counting procedures. Incident photosynthetically available radiation (PAR) was measured with a 2-π sensor mounted on a shade-free area of the ship's superstructure. Primary production rates were scaled to the mean light day and to mean monthly irradiance to compensate for day-to-day variations in cloud cover. The RACER I data were originally published by *Holm-Hansen and Mitchell* [1991].

2.5. Total Microbial Production

Total microbial production (bacterial plus algal) was measured using the incorporation of ^3H-adenine into DNA. Samples were collected from rosette-mounted 10-L Niskin bottles, as described in section 2.2. Samples were first screened through a 202-µm Nitex mesh into clean 4-L polycarbonate bottles then transferred into 0.25-L polycarbonate incubation bottles. The samples were spiked with ^3H-adenine (3.7 mBq per sample) and incubated on deck at surface seawater temperatures under simulated in situ light conditions for 12 hours. After incubation, the water samples were extracted and processed for ^3H-ATP and ^3H-DNA, and the rates of DNA synthesis were extrapolated to total microbial production as described previously [*Karl*, 1981; *Karl and Winn*, 1984]. These data, from RACER I only, were originally published by *Karl et al.* [1991b].

2.6. Ancillary Data

Salinity and temperature were measured using a standard conductivity, temperature, and depth (CTD) sensor package. During the first two surveys of RACER I (December and January 1986-1987), a Plessy Model 9040 salinity-temperature-depth (STD) instrument was used. During the second two surveys of RACER I (February and March 1987) and for all stations on RACER II-IV, a Sea-Bird CTD was used. Precruise and postcruise calibrations of the sensors showed a drift in the conductivity cell which equates to a salinity uncertainty of ± 0.02. Comparisons of both

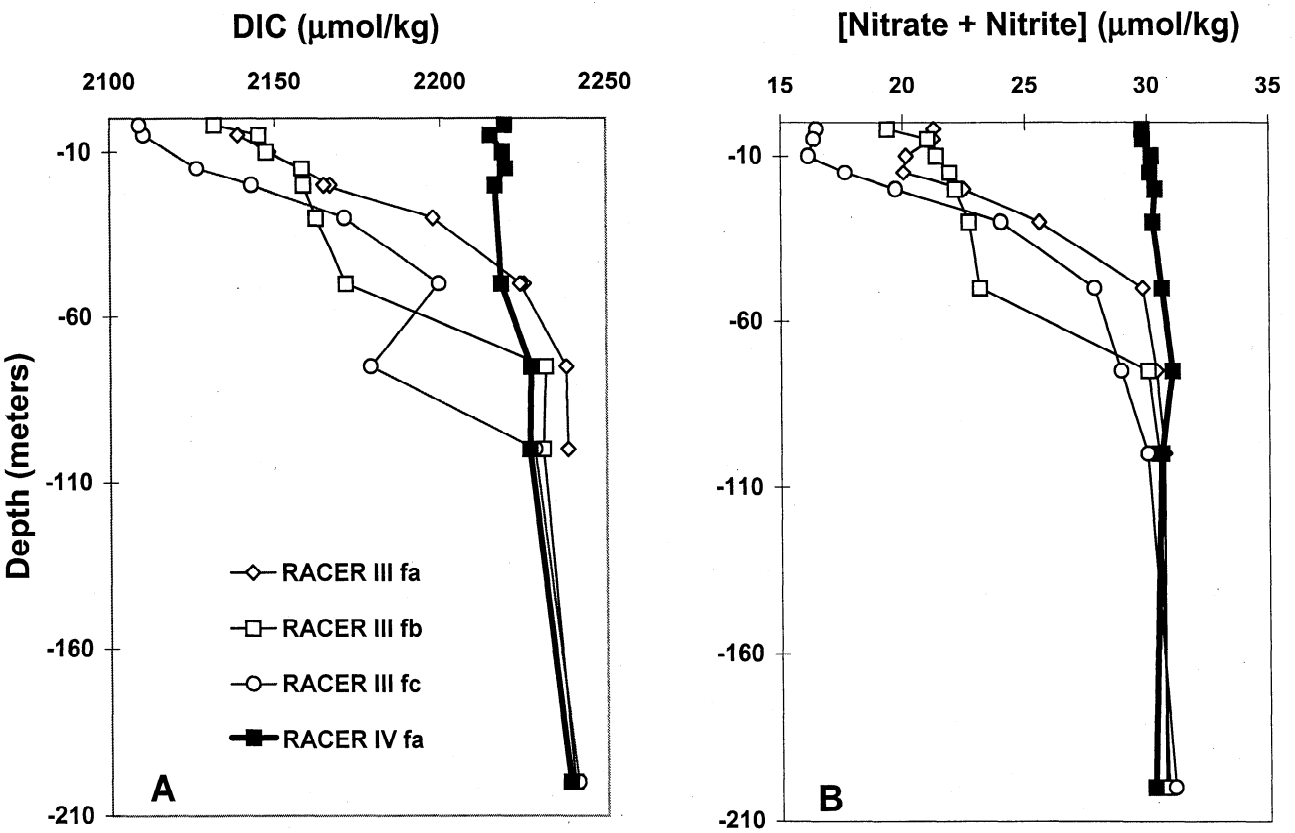

Figure 2. (a) Concentration versus depth profiles for dissolved inorganic carbon (DIC) during the fast grid station A occupations from RACER III and IV. (b) Concentration versus depth profiles for [nitrate+nitrite] during the fast grid station A occupations from RACER III and IV.

instruments at stations where bottle samples were acquired showed a salinity offset of 0.189 which was applied to the STD data set [*Niiler et al.*, 1991]. Nutrients were collected into clean, acid-rinsed, high-density polyethylene sample bottles and either analyzed on board using a Technicon® autoanalyzer (RACER I and II) or Alpkem flow analyzer (RACER III and IV) or stored frozen for subsequent analysis at our shore-based laboratories (Alpkem flow analyzer). Paired samples (fresh versus frozen) showed no measurement bias [*Dore et al.*, 1996].

3. Results and Discussion

3.1. Regional and Temporal Variability in DIC

The depletion of DIC and inorganic nutrients and corresponding increase in chl *a* and oxygen in surface waters of Gerlache Strait are consequences of net biological production of organic matter [*Karl and Hebel*, 1990; *Mitchell and Holm-Hansen*, 1991; *Holm-Hansen et al.*, 1991; *Karl et al.*, 1991b]. Oxygen concentrations up to 150% of air saturation were observed in selected areas of Gerlache Strait (RACER II), suggesting a high rate of net primary production. Seasonal nutrient depletions of approximately 30 µM kg^{-1} of [nitrate+nitrite] were measured during RACER I [*Karl et al.*, 1991a], and similar trends were also evident in subsequent spring-summer seasons in the RACER study area. For example, results at station A from RACER III reveal significant decreases in DIC and [nitrate+nitrite] in surface waters during the development of the phytoplankton bloom (Figure 2). DIC and [nitrate+nitrate] concentrations increase with depth from minimum values of 2109 µmol kg^{-1} and 16.0 µmol kg^{-1} at the surface to 2240 µmol kg^{-1} and 32.0 µmol kg^{-1} at 200 m, respectively. In contrast, the winter data collected during RACER IV show relatively constant concentration versus depth profiles from 0 to 200 m. The molar C:N net uptake ratio of 7.4, calculated from the difference between summer and winter profiles (0-50 m), is close to the expected *Redfield et al.* [1963] ratio of 6.6 but is lower than the C:N ratio of 10.1 calculated during RACER I [*Karl et al.*, 1991a].

For surface waters throughout northern Gerlache Strait during RACER III, comparison of the normalized alkalinity (normalized to a salinity of 35) to normalized DIC (normalized to a salinity of 35) shows depletions of DIC as a result of organic matter production with only negligible implied calcium carbonate formation (Figure 3) (also see *Karl et al.* [1991a] for similar data from RACER I). The relationship between normalized alkalinity and normalized DIC shows a DIC decrease of approximately 100 µmol kg^{-1} compared to a relatively constant alkalinity concentration of 2385 ± 14 µeq kg^{-1} for surface waters throughout northern Gerlache Strait during RACER III (Figure 3). Alkalinity can change in relation to the production and uptake of nitrate [*Brewer and Goldman*, 1976], so net changes are dependent upon the ratio of new versus regenerated production [see *Dugdale and Goering*, 1967]. A plot of salinity versus

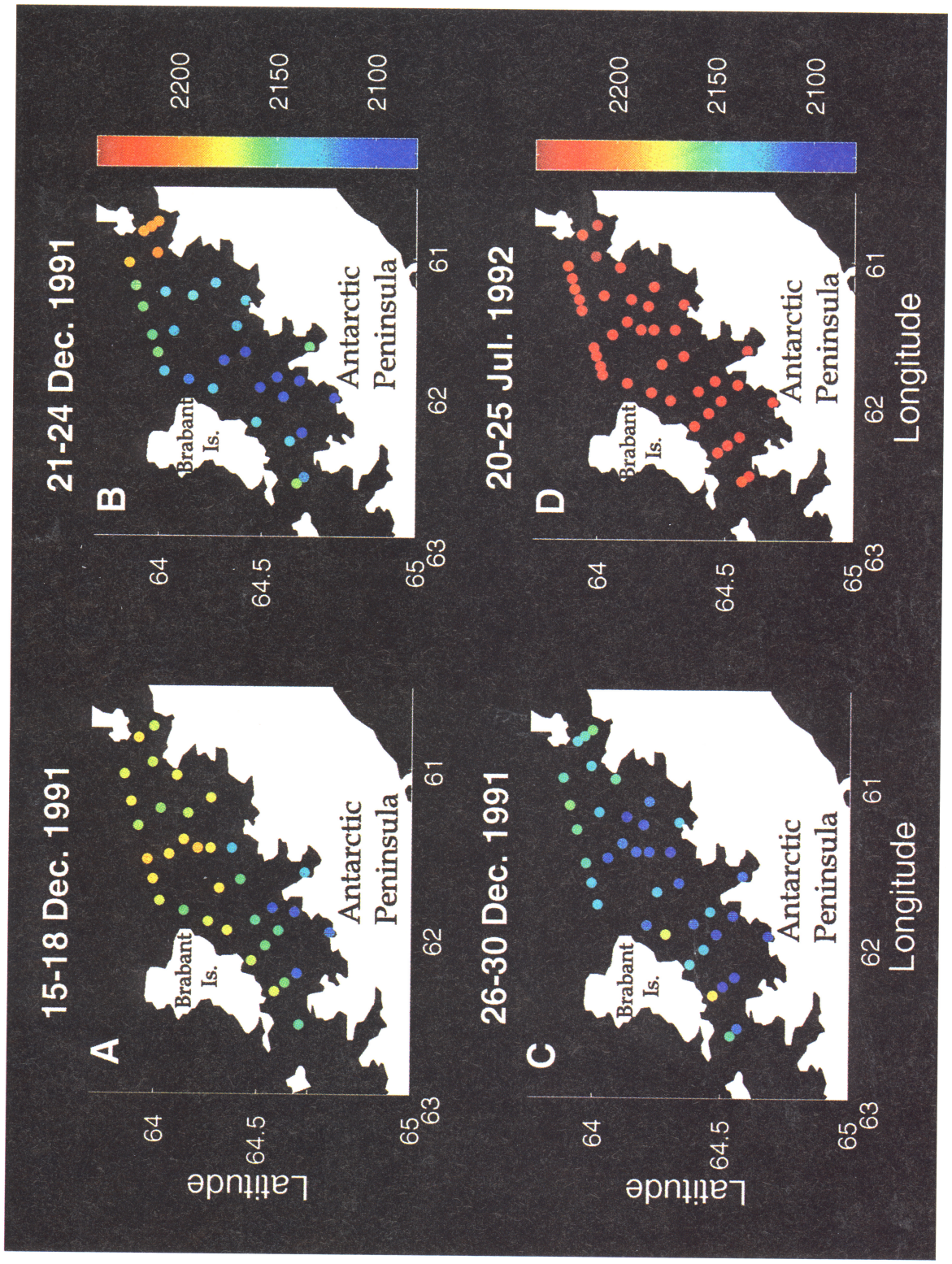

Plate 1. Surface concentrations of DIC during the RACER III and IV fast grid surveys of Gerlache Strait. Concentration is in μmol kg^{-1}. Each station is represented by a colored circle with the color corresponding to a concentration defined by the color bar located to the right. During RACER III, concentrations ranged from 2087.3 to 2199.9 μmol kg^{-1}. During RACER IV, concentrations ranged from 2204.6 to 2236.2 μmol kg^{-1}. (a) RACER III fast grid a. (b) RACER III fast grid b. (c) RACER III fast grid c. (d) RACER IV fast grid a.

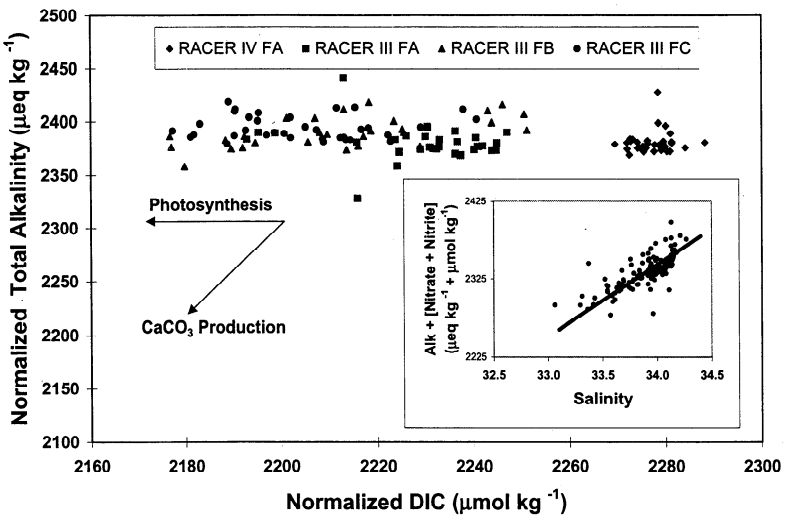

Figure 3. Normalized DIC versus normalized alkalinity for RACER III and IV fast grid surveys. DIC and alkalinity are normalized to a salinity of 35, and concentrations are in µmol kg^{-1} and µeq kg^{-1}, respectively. The theoretical trend curves are presented in the lower left-hand corner of the graph showing how the processes of photosynthesis and calcium carbonate production would affect the parameters analyzed. (Inset) Plot of salinity versus alkalinity + [nitrate + nitrite]. Model II linear regression analysis yields the following equation: alkalinity + [nitrate + nitrite] = 91.918 salinity - 781.9.

alkalinity + [nitrate + nitrite] shows a good correlation between these variables (Figure 3). A model II linear regression analysis revealed the following relationship: alkalinity +[nitrate + nitrite] = 91.918 salinity –781.9.

DIC-depleted surface waters extend throughout Gerlache Strait for the austral summer observations from RACER III (Plate 1a-c). Significant net uptake and dilution of DIC started in the protected bays and fjords during December where freshwater inputs resulting from seasonal ice melt promote density stratification. As the bloom progresses, DIC-depleted waters extend into the strait and are advected northward where they finally join the core of Gerlache Strait just past station A. The substantial regional depletions of DIC and large mesoscale variability that are typically observed during austral summer periods are in sharp contrast to winter conditions where a spatially homogeneous concentration of DIC of approximately 2220 ± 4 µmol kg^{-1} exists throughout the strait (Plate 1d).

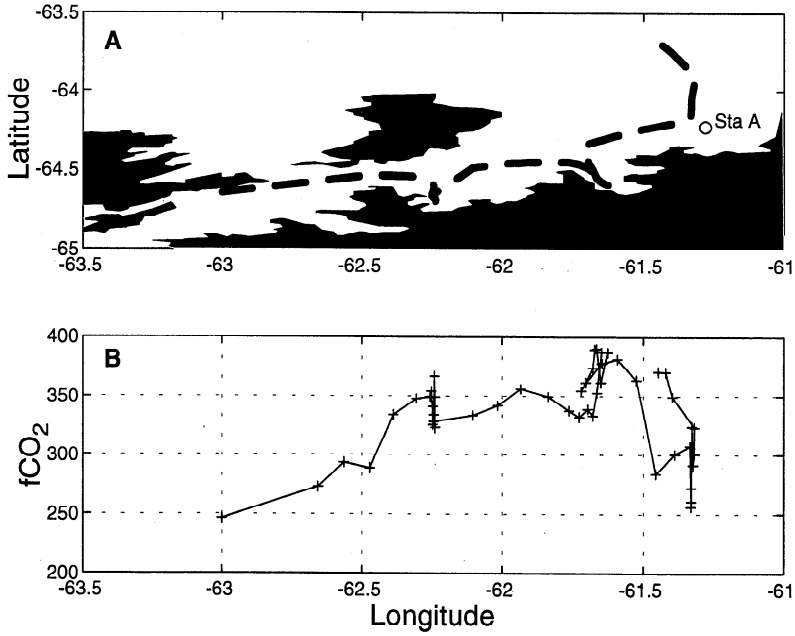

Figure 4. (a) Map of Gerlache Strait showing a transect (dashed line) made by the R/V *Polar Duke* in December 1995. An open circle represents station A. (b) The corresponding longitude of the R/V *Polar Duke*'s transect through Gerlache Strait in December 1995 versus fCO_2 concentrations (in microatmospheres).

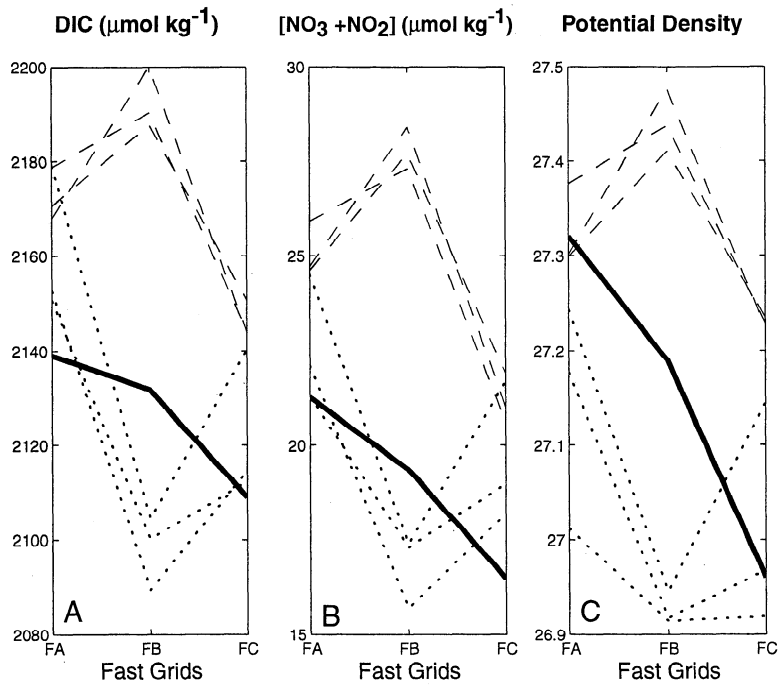

Figure 5. (a) RACER III fast grid surveys a, b, and c versus DIC concentrations (μmol kg^{-1}). The bold solid line in Figures 5a–5c represents station A. Stations located north (stations 24, 28, and 56) of station A are represented by dashed lines in Figures 5a-5c. Stations located south (stations 1, 3, and 34) of station A are represented by a dotted line in Figures 5a-5c. (b) RACER III fast grid surveys a, b, and c versus [nitrate+nitrite] concentrations (μmol kg^{-1}). (c) RACER III fast grid surveys a, b, and c versus potential density.

After the end of RACER, as part of the follow-on Palmer LTER program, we developed the capability for underway fCO_2 measurements in surface ocean waters. In December 1995 we had the opportunity to obtain data from the RACER study area during a transit of opportunity through Gerlache Strait. In contrast to the regional distributions of calculated fCO_2 during RACER II and III, the bays and fjords showed higher fCO_2 concentrations compared to those observed at station A. The relatively low fCO_2 waters encountered near station A could be a result of northward advection of seeded bloom waters from the bays and fjords. The area of maximum gradient in fCO_2 concentration occurred near (~15 km away) station A. High concentrations of fCO_2 (363 μatm) were found in close proximity (<15 km) to low concentrations (256 μatm), suggesting the region is heterogenous (Figure 4).

A characteristic feature of the Gerlache Strait area is the high degree of spatial and temporal variability. Spatial autocorrelation analysis of biological and physical parameters during RACER I documented both a broad coherence in biological community activity in the 20 to 50-km scale [*Bird and Karl*, 1991] and substantial spatial heterogeneity across the study area. Station locations during RACER I were at a minimum distance of 20 km separation, so variability on space scales less then this would not have been detected. Data collected during RACER II, III, and IV also revealed biogeochemical variability on the scale of sampling (~15 km). Some of this variability may be related to the complex physical characteristics of the study area. For example, station A is located on the shelf but is juxtaposed to a relatively deep channel. It is located off the axis of the mean surface current flow, close to the center of a small gyre where the residence time of advected waters is approximately 3 months [*Niiler et al.*, 1990]. Upwelled deep waters may transfer significant amounts of nutrients and inorganic carbon into the upper mixed layer thereby affecting local biogeochemical processes. Ice-edge biological communities and glacial runoff may alter the chemical properties of surface waters.

Evidence of spatiotemporal variability can be seen in the RACER III data set by examining two groups of selected stations located both north and south of station A but all well within Gerlache Strait (Figure 5). Surface waters from stations north of station A show regionally coherent increases in DIC and [nitrate + nitrite] and a corresponding increase in potential density between the first and second fast grids (sampled 6 days apart), with subsequent decreases (Figure 5). These trends are consistent with surface entrainment of recently upwelled water. By comparison, station A displayed a consistent warming and freshening of the upper layer, with temporal decreases in both DIC and [nitrate + nitrite] concentrations. These trends are consistent with phytoplankton bloom progression. Finally, the region south of station A displays initial decreases in DIC and [nitrate + nitrite] with subsequent increases. Variable dynamics of individual stations may be advected horizontally with the surface currents adding to the spatial variability that we observed by underway fCO_2 measurements in 1995 (Figure 4).

Despite these local heterogeneities within Gerlache Strait, surface waters at station A repeatedly displayed characteristic

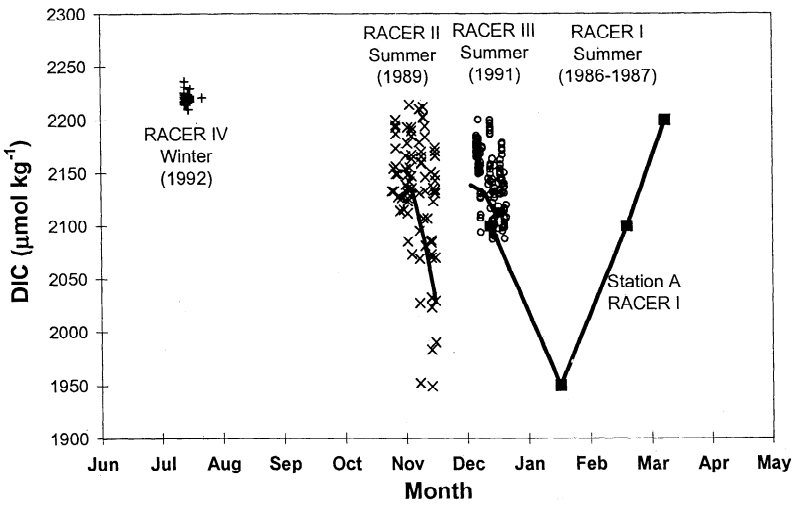

Figure 6. Month versus surface concentrations of DIC (µmol kg^{-1}) for fast grid surveys during RACER II, III, and IV. Concentrations at station A are represented by a solid bold line for RACER cruises I, II, and III. Concentrations at station A during RACER I are represented by solid squares connected by a solid line. RACER IV was conducted during July 1992 and represents winter data. RACER cruises I, II, and III represent austral summer cruises and were conducted during different years. It is important to note that the bloom during RACER II (1989) began in November while the blooms during RACER I and III began more than 1 month later.

temporal decreases in DIC concentrations during the December-January 1986-1987 RACER I field season, November 1989 RACER II field season, and the December 1991 RACER III field season (Figure 6). Once the spring phytoplankton bloom begins, the maximum rate of DIC removal is similar among years (5 µmol kg^{-1} d^{-1}) even though the initiation of the bloom varies considerably (e.g., late October for RACER II to mid December for RACER III). The timing of the bloom may be related to the extent of ice cover in the antecedent winter and timing of sea ice retreat in the spring; 1986-1987 (RACER I) was one of the most extensive ice years on record, and 1989-1990 (RACER II) was a relatively light ice year [*Stammerjohn and Smith* , 1996]. The extent of sea ice coverage during the previous spring (October-December) is a measure of the timing of sea ice retreat. Sea ice extent measured during the previous spring was relatively low for RACER II compared to RACER I and III [*Smith et al.*, 1998]. It is well known that sea ice extent and thickness can both influence plankton populations and, indirectly, the carbon system dynamics [*Gleitz et al.*, 1995; *Hoppema et al.*, 1995]. It has also been suggested that ice dynamics in the region west of the Antarctic Peninsula serves to structure the entire ecosystem from phytoplankton to the apex predators [*Smith et al.*, 1995]. Consequently, we can anticipate the large interannual variations in DIC pool dynamics related to the timing and magnitude of the annual spring-summer phytoplankton bloom.

On the basis of the net removal of DIC at station A during RACER I (December 1986 to March 1987), *Karl et al.* [1991a] estimated an average sustained rate of net community production equivalent to 140 mmol C m^{-2} d^{-1} which agrees well with the maximum net removal rate of DIC estimated from RACER II and III (154 mmol C m^{-2} d^{-1}). As carbon is removed via biological production of organic matter, surface waters become undersaturated with respect to fCO_2 resulting in a concentration gradient from the atmosphere to the ocean. Maximum values for calculated ΔfCO_2 (i.e., the difference between fCO_2 in the atmosphere and fCO_2 at the sea surface) for the winter are -100 µatm and for the summer are 260 µatm. Although the absolute magnitude of the summer gradient is 1.5 times greater than that measured in the winter, the large fCO_2 depletions in the surface waters occur less then 5% of the year, while the higher winter concentrations may be typical of 65-70% of the year. This gradient combined with the piston velocity coefficient for fCO_2 across the air-to-sea interface and the solubility of CO_2 in water drives a flux of carbon from the atmosphere to the ocean during and following bloom events.

It must be recognized that there are many uncertainties such as averaging timescale for wind speed, boundary layer stability, surfactants, and bubbles in current estimates of gas fluxes [*Wanninkhof*, 1992]. Using the *Wanninkhof* [1992] equation (k=0.31u^2(Sc/660)$^{-0.5}$, where Sc is the Schmidt number for CO_2 and u is the wind speed), an average wind speed of 3 m s^{-1} (measured for December 1991 at Palmer Station, Anvers Island), an average ΔfCO_2 at station A (ΔfCO_2= 150 µatm), and calculated CO_2 solubility [*Weiss*, 1974], the estimated air-sea carbon flux was 6 mmol C m^{-2} d^{-1} (i.e., a net transfer to the ocean). This value represents less then 4% of the estimated rate of production measured for this region. *Karl et al.* [1991a] and *Yager et al.* [1995] calculated a carbon flux in the range of 1 to 19 mmol C m^{-2} d^{-1} in the area of Gerlache Strait and the coastal Arctic Ocean, respectively. This represented between 1 and 10% of the net community production rates. *Bates et al.* [1998] calculated an air-to-sea CO_2 flux in the range of 4 to 26 mmol C m^{-2} d^{-1} which represented 2-25% of calculated net community production rates for the Ross Sea. During the winter, portions of Gerlache Strait are covered by annual sea ice and the sea-to-air CO_2 flux is partially blocked.

Table 2. Estimates of Carbon Production and Export Derived from Independent Field Measurements

Parameter	Primary Production,[a] mol C m^{-2} d^{-1}	Microbial Production,[b] mol C m^{-2} d^{-1}	Sediment Traps,[c] mol C m^{-2} d^{-1}	DIC Removal, mol C m^{-2} d^{-1}
Production estimate(s)	0.15-0.16 (Dec.) 0.04-0.07 (Jan.) 0.06-0.09 (Feb.) 0.01 (March)	0.09-0.29 (Dec.) 0.37-1.07 (Jan.) 0.07-0.20 (Feb.) 0.03-0.11 (March)	0.01 (Dec.) 0.03 (Jan.) 0.02 (Feb.) <0.01 (March)	0.15[d]
Production type	net	gross	export	net

[a] Values are based on ^{14}C incubations integrated over depth of euphotic zone. The range of values indicates the estimate derived from daily and mean monthly light levels [*Holm-Hansen et al.*, 1991].

[b] Values are based on measured rates of total microbial DNA synthesis, assuming DNA is 1-3% of total cell carbon [*Karl and Winn*, 1984; *Karl et al.* 1991b].

[c] Traps are at a depth of 100 m [*Karl et al.*, 1991a].

[d] Average rate is based on mean removal rate from RACER I, II, and III.

Mechanisms of gas exchange through partial ice cover and within polynas are poorly known.

Following bloom termination, typically in January [*Mitchell and Holm-Hansen*, 1991], there is a subsequent net increase in DIC of about 5 μmol kg^{-1} d^{-1} until the DIC pool reaches its winter value of 2230 μmol kg^{-1} (Figure 6). Even though station A shows a repetitive pattern each year, not all stations display such predictable DIC pool dynamics. For example, during RACER III, Station 4 (located in Andvord Bay) shows a decrease then a subsequent increase of DIC concentration which is consistent with an upwelling event (Plate 1). However, during RACER II, Station 4 showed a consistent decrease of DIC concentration throughout the study period. The timing and frequency of these events are presently unknown, so regional DIC budgets are poorly constrained. Besides the effects on the DIC pool, these local upwelling events will also affect the regional heat budget and consequently ice dynamics and total ecosystem productivity as well as export production.

3.2. Primary and Total Microbial Production

At station A, euphotic zone depth-integrated rates of net primary production (^{14}C) ranged from 0.04 to 0.16 mol C m^{-2} d^{-1} during the initial phase of the bloom in December 1986 and January 1987. During February and March 1987, rates decreased slightly to 0.01-0.09 mol C m^{-2} d^{-1} (Table 2) [*Holm-Hansen et al.*, 1991]. This range of values was calculated using both daily (observed) and mean (calculated) monthly light levels. Rates of primary production for RACER II fast grids B, C, and D ranged from 0.19 to 0.44 mol C m^{-2} d^{-1} for the mean light day [*Holm-Hansen and Vernet*, 1990]. Estimates of primary production during the RACER III bloom were similar to RACER I for common stations in the study area.

Measured rates of total microbial production based on DNA synthesis and net primary production based on ^{14}C uptake experiments integrated over the depth of the euphotic zone are compared to the net depletions of DIC in the surface water at station A (Table 2). The removal of DIC from the surface water, corrected for air-to-sea exchange, vertical diffusion, mixing, respiration, and horizontal advection, is an estimate of net community biological production and should approximate the local accumulation and vertical and horizontal exports of particulate and dissolved organic carbon. Many of these terms are poorly constrained and direct measurements do not exist for this region. Assuming for the moment that the parcel of water exists in the gyre in the vicinity of station A, an upper estimate of net community production corrected for air-to-sea exchange is 1.56-1.80 g C m^{-2} d^{-1} during the initiation of the spring-summer bloom. As expected, the ranges of total microbial production (bacterial plus phytoplankton) at station A based on rates of DNA synthesis exceeded the measurements of primary production (phytoplankton only), with the greatest difference occurring at the height of the bloom in January (Table 2) [*Karl et al.*, 1991b]. These differences have been attributed to one or more of the following processes: (1) elevated bacterial heterotrophic production, (2) phytoplankton heterotrophic production, (3) gross autotrophic production much greater then net autotrophic production, or (4) error in one or both of the production estimates. The latter possibility seems unlikely because all methods ($[^{14}C]$-HCO_3, $[^3H]$-adenine uptake, and DIC removal) provide similar estimates of production at the beginning stages of the bloom when phytoplankton production dominates [*Karl et al.*, 1991b].

3.3. Export Production

As a result of the spring-summer phytoplankton blooms in Antarctica, large amounts of particulate organic matter (POM) accumulate in the upper 100 m, and a portion of this POM is eventually removed by gravitational settling with enhancements via mesozooplankton grazing or physical aggregation processes. Particle fluxes covaried with high (December-January) and low (March) rates of primary production with an apparent time lag between the production of organic matter in the surface waters and the downward flux at 100 m (Table 2) [*Karl et al.*, 1991b]. However, POM production during the initial phases of the bloom is coupled more to a net increase in POM standing stock than to export from the euphotic zone. During RACER I, the maximum export flux measured using drifting sediment traps at station A was in January (0.03 mol C m^{-2} d^{-1}). This value was only 26% of the estimated total microbial production [*Karl et al.*, 1991a]. Similar export fluxes were also observed during the

RACER II and RACER III experiments. An estimated mean residence time calculated for POM in the upper water column during the summer season was greater than 6 months [*Karl et al.*, 1991b]. The authors concluded that processes other than sinking (i.e., respiration or horizontal transport) might be important processes in controlling the concentration of POM in the upper water column [*Karl et al.*, 1991b].

4. Conclusions

An upper estimate for net ecosystem production of 0.13-0.15 mol C m^{-2} d^{-1} was calculated from measured rates of DIC removal at a station occupied during all RACER cruises covering three separate spring-summer phytoplankton bloom periods. Large interannual variations, especially in the timing of the initiation of the bloom, were observed. Processes such as mixing, horizontal advection, and respiration are not well constrained in Southern Ocean habitats and may contribute to the spatial variability of regional DIC distributions. During upwelling events, nutrients and inorganic carbon are entrained into the mixed layer where they are advected horizontally or, in the case of CO_2, exchanged with the atmosphere. Respiration may be a large local source of CO_2, yet few direct measurements exist for Antarctic waters. Experimentally determined values of net primary and total microbial carbon production agree with estimates based on mesoscale DIC measurements during the initial phases of the phytoplankton bloom but deviate during the height of the bloom. The net production of organic matter associated with the spring-summer bloom results in an estimated mean air-to-sea flux of 6 mmol C m^{-2} d^{-1}. This value represents less then 4% of the estimated rate of production measured for this region.

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