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## Nutrient and carbon removal ratios and fluxes in the Ross Sea, Antarctica

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### Abstract

Net community production (NCP) and nutrient deficits (Def(*X*)) were calculated using decreases in dissolved CO<sub>2</sub> and nutrient concentrations due to biological removal in the upper 200 m of the water column during four cruises in the Ross Sea, Antarctica along 76°30'S in 1996 and 1997. A comparison to excess dissolved and particulate organic carbon showed close agreement between surplus total organic carbon (TOC) and NCP during bloom initiation and productivity maximum; however, when TOC values had returned to low wintertime values NCP was still significantly above zero. This seasonal NCP,  $3.9 \pm 1 \text{ mol C m}^{-2}$ , must be equivalent to the particle export to depths greater than 200 m over the whole productive season. We estimate that the annual export was  $55 \pm 22\%$  of the seasonal maximum in NCP. The fraction of the seasonal maximum NCP that is exported through 200 m is significantly higher than that measured by moored sediment traps at a depth of 206 m. The removal of carbon, nitrate and phosphate (based on nutrient disappearance since early spring) and their ratios showed significant differences between regions dominated by diatoms and regions dominated by the haptophyte *Phaeocystis antarctica*. While the  $\Delta\text{C}/\Delta\text{N}$  removal ratio was similar ( $7.8 \pm 0.2$

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for diatoms and  $7.2 \pm 0.1$  for *P. antarctica*), the  $\Delta N/\Delta P$  and  $\Delta C/\Delta P$  removal ratios for diatoms ( $10.1 \pm 0.3$  and  $80.5 \pm 2.3$ ) were significantly smaller than those of *P. antarctica* ( $18.6 \pm 0.4$  and  $134.0 \pm 4.7$ ). The similarity in  $\Delta C/\Delta N$  removal ratios of the two assemblages suggests that preferential uptake of phosphate by diatoms caused the dramatic differences in  $\Delta C/\Delta P$  and  $\Delta N/\Delta P$  removal ratios. In contrast to low  $\Delta C/\Delta P$  and  $\Delta N/\Delta P$  removal ratio in diatom-dominated areas early in the growing season, deficit N/P and C/P ratios in late autumn indicate that the elemental stoichiometry of exported organic matter did not deviate significantly from traditional Redfield ratios. Changes in biologically utilized nutrient and carbon ratios over the course of the growing season indicated either a substantial remineralization of phosphate or a decrease in phosphate removal relative to carbon and total inorganic nitrogen over the bloom period. The species dependence in C/P ratios, and the relative constancy in the C/N ratios, makes N a better proxy of biological utilization of CO<sub>2</sub>. © 2000 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

The large concentrations of macro-nutrients in the Southern Ocean have tempted some to postulate that excess atmospheric CO<sub>2</sub> might be sequestered under conditions favoring complete nutrient utilization (Martin, 1990). Several modeling studies have suggested that an increase in primary production or a decrease in upwelling of CO<sub>2</sub><sup>-</sup> and nutrient-rich waters in the Southern Ocean was primarily responsible for the decrease in atmospheric CO<sub>2</sub> (Sarmiento and Toggwieler, 1984; Knox and McElroy, 1984; Siegenthaler and Wenk, 1984; Peng and Broecker, 1991) observed in ice cores during the last glacial maximum (Delmas et al., 1980; Berner et al., 1980). Other models have predicted that with a decrease in thermohaline circulation due to global warming (Siegenthaler and Sarmiento, 1993; Sarmiento et al., 1996, 1998) there will be a net storage of CO<sub>2</sub> in the deep water as the excess nutrients of the Southern Ocean are utilized over the next 100 years (Sarmiento et al., 1998). In all of the models there is a general assumption that the CO<sub>2</sub> exported will be proportional to a constant carbon/nutrient ratio.

While these estimates of nutrient stoichiometry have been shown to be valid as either an average for a diverse phytoplankton assemblage (Fleming, 1940; Redfield et al., 1963) or as an estimate of ocean-wide remineralization ratios (Takahashi et al., 1985; Anderson and Sarmiento, 1994), they do not account for taxon-specific ratios of exported particulate matter. This is especially significant in view of numerous studies that have observed low N/P and C/P removal ratios throughout the Southern Ocean (Jennings et al., 1984; Karl et al., 1991; Ishii et al., 1998; Bates et al., 1998a, b; Rubin et al., 1998; Takeda, 1998; Arrigo et al., 1999). Some of these studies have identified diatoms as the source of low N/P and C/P removal ratios (Takeda, 1998; Arrigo et al., 1999). In view of these observations of low removal ratios, it is important to establish the export ratio for diatoms as well as other dominant species to model accurately the region's long-term CO<sub>2</sub> removal and sequestration.

Export ratios of diatoms are especially significant in the light of a possible change in species dominance as a result of changes in climate. Specifically, several studies have

noted the overwhelming predominance of diatoms associated with shallower mixed layers in the Southern Ocean (Smith and Nelson, 1985; Arrigo et al., 1998, 1999; Sweeney et al., 2000). This trend, if found to be characteristic of a shoaling mixed layer, would suggest that a shift towards a diatom-dominated assemblage may occur with increased stratification in the Southern Ocean (Arrigo et al., 1999) as a result of predicted global warming (Sarmiento and Le Quere, 1996; Sarmiento et al., 1998). It is also possible that, with an increase in diatom dominance in the Southern Ocean (Arrigo et al., 1999), models such as that described by Sarmiento and Le Quere (1996), and Sarmiento et al. (1998) might over-estimate the impact of primary productivity on export of carbon to the deep ocean using a constant C/P export ratio.

Traditionally, export of particulate matter has been studied using two methods. The first has been the measurement of exported material collected in sediment traps (e.g. Honjo, 1982; Karl et al., 1991). While the direct measurement of the exported particle elemental composition is attractive, errors associated with each of these techniques have yet to be resolved (Gardner et al., 1983; Buesseler et al., 1994). The second method, originally applied by Redfield (1942) and later by Takahashi et al. (1985), Minster and Boulahdid (1987), Boulahdid and Minster (1989) and Anderson and Sarmiento (1994), investigated the proportional changes in nutrients observed along isopycnal surfaces of ocean water due to biological remineralization. Although this method has been useful for basin-wide studies where there are measurable changes in nutrients over the length of an isopycnal, it is not applicable to smaller regions such as the Ross Sea, which has a more heterogeneous mixing regime.

This study employs a variation of the above methods to estimate the export of carbon from the near-surface waters of the Ross Sea. By measuring drawdown in  $\text{TCO}_2$  and nutrients from the upper water column, we calculate biologically utilized carbon or net community production (NCP). The difference between the NCP and the amount of total organic material present in the upper 200 m at the end of the growing season can be interpreted as the amount of particulate organic carbon exported from that depth. It also can be inferred that, in addition to the export of organic carbon, biologically utilized nutrients also are exported as organic matter below 200 m. The nutrient to carbon export ratios are then calculated as the ratio of biologically driven deficits in nutrients and carbon above 200 m.

The 200 m isopleth is important because this is the depth at which sediment traps were placed, as well as the maximum depth to which nutrient drawdown occurs at the end of the seasonal cycle. The 200 m depth is also considered to be the depth of the permanent thermocline for a large portion of the Southern Ocean (Deacon, 1982; Tomczak and Godfrey, 1994), so that export of organic material below this depth may be significant for long-term sequestration of carbon and nutrients — an important consideration in modeling (Sarmiento et al., 1996, 1998).

In addition, observations made during four JGOFS cruises were used to document the seasonal evolution of biologically utilized nutrients and carbon. It was further observed that physical conditions led to spatial separation between two phytoplankton assemblages, which allowed detection of significantly different elemental utilization ratios.

## 2. Materials and methods

### 2.1. Oceanographic cruises

This study summarizes observations made on four oceanographic cruises in the Ross Sea during 1996 and 1997 on the R.V.I. B *Nathaniel B. Palmer* as part of the US Southern Ocean Joint Global Ocean Flux Study (JGOFS/AESOPS, or Antarctic Environment Southern Ocean Process Study; Smith et al., 2000). The first cruise (NBP96-04A) was designed to observe the early spring pre-bloom conditions and document the factors controlling the initiation of the bloom. The second cruise (NBP97-01) was intended to investigate the CO<sub>2</sub> and nutrient dynamics during the austral summer, while the third cruise (NBP97-03), during autumn, was intended to observe the heterotrophic portion of the seasonal cycle where surface-water nutrient and CO<sub>2</sub> return to wintertime values. The fourth cruise (NBP97-08) was conducted during the subsequent austral growing season (late spring) between the periods bracketed by the first and second cruise and was designed to observe the progression of the bloom through the peak in primary productivity and phytoplankton biomass accumulation. A total of 20, 27, 17 and 37 stations were sampled in each cruise, respectively.

This study focused on samples taken from a series of eight stations along 76°30'S, each separated by ca. 60 km across the southwestern Ross Sea (Fig. 1A-D). In the early spring and late spring (NBP96-04A and NBP97-08), extensive concentrations of ice were noted (Smith et al., 2000). However, in the summer (NBP97-01) ice was only observed in the western Ross Sea. Complete ice coverage occurred during the autumn cruise (NBP97-03). Profiles of temperature and salinity were collected at all stations (Gordon et al., 2000) and density ( $\sigma_t$ ) was computed from these data. The depth of all stations sampled in this study ranged from 324 to 700 m. The depth of the mixed layer was defined as the depth that the  $\sigma_t$  changed by 0.02 units from the surface value.

### 2.2. Analytical methods

#### 2.2.1. Nutrients

In general, the methods employed for the bottle salinity, Winkler dissolved oxygen, and nutrient analyses (PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and SiO(OH)<sub>3</sub><sup>-</sup>) were similar to those described in the JGOFS protocols (JGOFS, 1996; <http://usigofs.whoi.edu/protocols.html>). Minor differences in procedure are described in Gordon et al. (2000) and in the files that accompany the archived data (<http://usjgofs.whoi.edu>).

### 2.3. Pigment analysis

For each station, samples for phytoplankton pigments were collected from the euphotic zone at depths corresponding to 100 or 85, 50, 25, 10, 5, and 1% of surface irradiance. Aliquots of seawater (0.5–2.0 l) were filtered through 25 mm GF/F filters. The filters were then frozen in liquid nitrogen and transported to the University of Hawaii at –80°C for subsequent analysis. Pigments were extracted by grinding the filters in 3 ml acetone (+ 50 µl acanthaxanthin internal standard) using a glass-Teflon

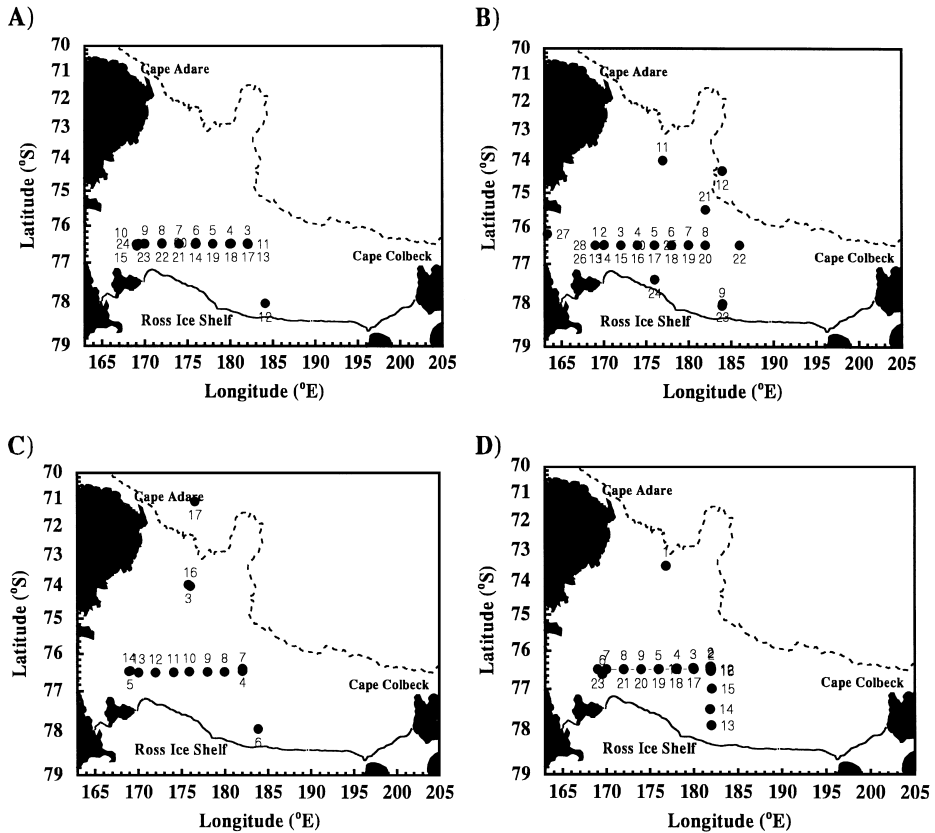


Fig. 1. Station locations. (A) Early spring (NBP96-04A), from October 15, 1996 to November 6, 1998. (B) Mid-summer (NBP97-01), from January 13, 1997 to February 9, 1997. (C) Autumn (NBP97-03), from April 12 to 28, 1997. (D) Late spring (NBP97-08), from November 15, 1997 to December 11, 1997. The fine solid line in the south shows the boundary of the Ross Ice Shelf. The dashed line shows the 1000 m isopleth, which approximates the location of the shelf break.

homogenizer, and concentrations in the extracts were determined by RP-HPLC following the methods described in Andersen et al. (1996). Fucoxanthin, peridinin, 19'-hexanoyloxyfucoxanthin, lutein, and alloxanthin were used as proxies for estimating relative proportions of phytoplankton species such as diatoms, dinoflagellates, *Phaeocystis antarctica*, chlorophytes, and cryptophytes, respectively (Bidigare et al., 1996). Total chlorophyll *a* concentration (monovinyl chlorophyll *a* plus monovinyl chlorophyllide *a*) was used as an index of phytoplankton biomass.

#### 2.4. Organic carbon and nitrogen

Twenty milliliter samples for dissolved organic carbon (DOC) and total organic carbon (TOC) were collected in acid-cleaned, pre-combusted 40 ml vials sealed with

Teflon-lined caps. Sampling for DOC and TOC took place after  $\text{TCO}_2$  and  $\text{pCO}_2$  samples had been collected from the Niskin bottles. Each DOC sample was gravity filtered directly from the Niskin bottle through an in-line, pre-combusted Whatman GF/F filter ( $\sim 0.7 \mu\text{m}$ ) and frozen until analysis, whereas the TOC samples were not filtered. All DOC samples were analyzed on custom-built HTC analyzers designed by the Bermuda Biological Station for Research (BBSR) and Woods Hole Oceanographic Institution (WHOI) groups. The configuration and operating parameters of the two high-temperature combustion (HTC) systems differ slightly, but are described thoroughly in Carlson et al. (1998) and Hansell and Peltzer (1998). The precision of the measurement is  $\pm 1.0 \mu\text{mol l}^{-1}$ . Direct measurement of TOC values were only conducted in the autumn cruise (NBP97-03) when POC and DOC were near “background” levels. All other TOC values reported here are the sum of independently determined DOC and POC concentrations.

Particulate organic carbon (POC) and nitrogen (PON) samples were collected in 2.0 l polypropylene bottles. One liter of sample was then filtered through a pre-combusted ( $450^\circ\text{C}$  for 2 h) Whatman GF/F glass-fiber filter under low vacuum, rinsed with ca. 10 ml of 0.01 N HCl in filtered seawater to remove any inorganic carbonates, placed in combusted glass tubes and capped with combusted aluminum foil, and dried at  $60^\circ\text{C}$ . The samples were then analyzed on a Carlo-Erba Model 252 elemental analyzer. The precision of these measurements was  $\pm 1.0$  and  $\pm 0.4 \mu\text{mol l}^{-1}$  for POC and PON, respectively.

### 2.5. Carbonate system

During the early spring and autumn cruises,  $\text{TCO}_2$  was determined by coulometry using a Single Operator Multiparameter Metabolic Analyzer (SOMMA) system (Johnson et al., 1985, 1987, 1993) with a precision of  $\pm 1.4 \mu\text{mol kg}^{-1}$ . This system was standardized using calibrated volumes of UHP  $\text{CO}_2$  gas at ambient temperature and pressure. During the summer and late spring cruises,  $\text{TCO}_2$  was measured using an LDEO coulometer system (Chipman et al., 1993) with a precision of  $\pm 1.3 \mu\text{mol kg}^{-1}$ , which was also standardized using calibrated volumes of 99.998%  $\text{CO}_2$ . Total  $\text{CO}_2$  values reported in this paper have been corrected using Certified Reference Material (<http://www-mpl.ucsd.edu/people/adickson/> — Batch # 31, # 32, # 33, # 34, # 35; Dickson, 1990), whose  $\text{TCO}_2$  were determined manometrically by C.D. Keeling.

Surface ocean  $\text{pCO}_{2(\text{sw})}$  and atmospheric  $\text{pCO}_{2(\text{atm})}$  were obtained using an infrared analyzer (Licor 6252). Atmospheric samples were dried and pumped directly to the analyzer for measurement. Seawater  $\text{pCO}_2$  was measured using a carrier gas equilibrated continuously with a 30 l shower-type equilibrator (Bates et al., 1998b). The equilibrated gas sample was dried, and the  $\text{CO}_2$  concentration (mole fraction — ppm) determined every 3 min. The underway  $\text{pCO}_2$  measurements were standardized using five  $\text{CO}_2$ -air gas mixtures calibrated against the World Meteorological Organization (WMO) standards (Scripps Institution of Oceanography, unpublished data, 1994). The  $\text{CO}_2$  partial pressures for the atmospheric and equilibrated water samples were computed from the dry gas concentration and ambient barometric pressure

(Atmospheric Instruments Research Inc. Model AB-2A) and corrected for water vapor pressure by assuming saturation at sea surface temperatures. The sea-air  $p\text{CO}_2$  difference,  $\Delta p\text{CO}_2$ , was calculated at each station location throughout the course of the cruise. In addition to  $p\text{CO}_2$  measurements made during the JGOFS/AESOPS cruises, several other cruises in this area during the same year allowed us to estimate seasonal changes of  $\Delta p\text{CO}_2$  for each station. The temporal change in  $\Delta p\text{CO}_2$  for each station was then estimated by fitting the data to a third-order polynomial as a function of time using a least-squares regression from November 11, 1996 to April 28, 1997.

## 2.6. Computational methods

To assess biological utilization of  $\text{CO}_2$  (C), total inorganic nitrogen (N = nitrate + nitrite + ammonium) and phosphate (P) over the bloom period the change in nutrient and  $\text{CO}_2$  concentration ( $\Delta$ ) was calculated using the difference in concentration (per volume units) of chemical species “*i*” between the early spring, which represent winter values ( $X_i(\text{winter})$ ) based on observations by Gordon et al. (2000) and Sweeney et al. (2000), and late spring, summer and autumn value (e.g.  $X_i(\text{summer})$ ):

$$\Delta X_i = X_i(\text{winter}) - X_i(\text{summer}). \quad (1)$$

The  $\text{TCO}_2$  and nutrient values were scaled to a constant salinity to remove the effect of freshwater from ice melt on the  $\Delta X_1/\Delta X_2$  ratio. An area mean salinity of 34.5 was used to scale  $\text{TCO}_2$  and nutrient concentrations. Winter values for  $\text{TCO}_2$  were estimated from the average salinity-scaled deep-water observations during NBP97-01 and NBP97-08 rather than values observed during NBP96-04A as was done for the other nutrients considered because of a possible systematic offset in  $\text{TCO}_2$  measurements made during NBP96-04A (Sweeney et al., 2000).

To obtain estimates of non-volatile nutrient biological drawdown for each station occupied, we computed the integrated nutrient deficits ( $\text{Def}(X_i)$ ) in the upper 200 m as the difference between early spring (winter) and values measured in subsequent cruises (NBP97-08, NBP97-01 and NBP97-03):

$$\text{Def}(X_i) = \int_0^{200} (X_i(\text{winter})) dz - \int_0^{200} (X_i(\text{summer})) dz. \quad (2)$$

Similarly, estimates of surplus organic carbon (e.g.  $\text{Surp}(\text{TOC})$ ), were calculated:

$$\text{Surp}(X_i) = \int_0^{200} (X_i(\text{summer})) dz - \int_0^{200} (X_i(\text{winter})) dz. \quad (3)$$

Although the mixed-layer depth during most of the cruises was less than 100 m, we integrated through 200 m to account for deeper mixing during the early period and late periods when the pycnocline was weaker and deeper. Thus, as long as the pycnocline remains above 200 m, the deficit in nutrients and  $\text{CO}_2$  (Eq. (2)) should not be affected by enrichment from deep water. In the same way, the surplus organic matter (Eq. (3)) should not be affected by deep water depleted in organic matter.

While deficits in nutrients represent the biological utilization of inorganic nutrients, deficits in carbon also must be corrected for the sea–air flux of  $\text{CO}_2$  ( $F_{\text{CO}_2}$ ) integrated from winter ( $t_w$ ) to the specified sampling date later in the season to represent the NCP (per unit area) as illustrated for summer ( $t_s$ ):

$$\text{NCP} = \text{Def}(\text{C}) - \int_{t_w}^{t_s} (F_{\text{CO}_2}) dt. \quad (4)$$

The gas exchange fluxes were estimated based on the  $\text{CO}_2$  gas transfer coefficient across the sea surface and the difference between atmospheric  $\text{pCO}_{2(\text{atm})}$  and surface seawater  $\text{pCO}_{2(\text{sw})}$ . The net sea–air  $\text{CO}_2$  flux was calculated using

$$F_{\text{CO}_2} = ks\Delta\text{pCO}_2, \quad (5)$$

where  $s$  is the solubility coefficient of  $\text{CO}_2$  gas in seawater as a function of temperature and salinity (Weiss, 1974),  $k$  is the gas transfer coefficient, and

$$\Delta\text{pCO}_2 = \text{pCO}_{2(\text{sw})} + \text{pCO}_{2(\text{atm})}. \quad (6)$$

The gas transfer coefficient is taken to be a function of wind speed (Wanninkhof, 1992). Local wind speeds averaged over the last five years have been compiled by National Center for Environmental Prediction–National Center for Atmospheric Research (NCEP–NCAR) (Lamont Climate Group Library — <http://rainbow.ideo.columbia.edu>). These data indicated that during the months of open water (mid–November through late February), monthly mean wind speed,  $u_{\text{av}}$ , rarely exceeds  $3 \text{ m s}^{-1}$ . Appropriate to these low average monthly wind speeds is the gas transfer coefficient of Wanninkhof (1992)

$$k = 0.39u_{\text{av}}^2 (\text{Sc}/660)^{-0.5}, \quad (7)$$

where  $k$  ( $\text{cm h}^{-1}$ ) is the gas transfer coefficient and  $\text{Sc}$  is the Schmidt number, which is a dimensionless function of temperature and salinity. Although this relationship has been found to be consistent with the direct measurements obtained during the recent Gas Ex-98 field study using an eddy-correlation method (Wanninkhof and McGillis, 1999), errors resulting from the non-linear relationship between wind speed and gas transfer velocity can lead to underestimates of average transfer velocities in regions with highly variable wind speeds. Because of highly variable wind speeds in both space and time, the transfer velocity represented by Eq. (5) in the Southern Ocean may be underestimated by as much as 30% (Boutin and Etcheto, 1991).

A time-integrated flux ( $\int(F_{\text{CO}_2}) dt$ ) was calculated using monthly mean wind data and daily mean  $\Delta\text{pCO}_2$  from November 11, when remote-sensed microwave data indicated that the Ross Sea is largely ice free (Jacobs and Comiso, 1989), to the time that the samples were collected. While Jacobs and Comiso (1989) show large inter-annual variability in the time that the Ross Sea became ice free, the fluxes are initially small and will have a small impact on the  $\int(F_{\text{CO}_2}) dt$  and NCP. The magnitude of the sea–air  $\text{CO}_2$  flux ranged from 2 to 10% of the  $\text{CO}_2$  deficit during the summer cruise and as much as 50% in the autumn cruise (Table 1).

Because the effect of precipitation/dissolution of  $\text{CaCO}_3$  was less than 5% of the NCP over the growing season (Sweeney et al., 2000), NCP was considered to be equivalent to the net primary production (primary production minus the community respiration). Thus, NCP must be equal to the TOC retained in the upper 200 m [Surp(TOC)] plus the TOC exported. In this way, the material exported below 200 m ( $\text{Export}_{200}$ ) can be calculated from the following:

$$\text{Export}_{200} = \text{NCP} - \text{Surp(TOC)}. \quad (8)$$

### 3. Results

#### 3.1. Bloom progression

The mixed layer along  $76^\circ 30'S$  in the Ross Sea was deep during the early spring (mean depth 215 m, Table 1) and was characterized by weak vertical gradients in density (Fig. 2A), nutrients, and carbon (Fig. 2C-F). By mid-summer the mixed-layer depth was significantly shallower (mean depth 30 m, Table 1). Salinity-normalized nutrients and  $\text{TCO}_2$  concentrations also dramatically decreased during the mid-summer indicating significant biological utilization of nutrients and  $\text{TCO}_2$ . The summer cruise also showed high concentrations of POC, with a maximum near 80 m

Table 1

Deficit and surplus total, particulate and dissolved carbon and nutrient pools integrated to 200 m based on average background values taken from 200 and 400 m in the early spring cruise. Net community production (NCP) is calculated from the Def(C) and gas exchange predicted over the course of the bloom.  $\text{Export}_{200}$  was calculated as the difference between NCP and Surp(TOC). Mixed-layer depths were determined at the depth of  $\Delta\sigma_t > 0.02$  relative to the surface value. Uncertainties represent the standard deviation in stations occupied

| Surplus/deficit<br>( $\text{mol m}^{-2}$ ) | Early spring<br>(NBP96-04A)<br>10/17/96–11/6/96 | Late spring<br>(NBP97-08)<br>11/15/97–12/11/97 | Summer<br>(NBP97-01)<br>1/13/97–2/9/97 | Autumn<br>(NBP97-03)<br>4/12/97–4/28/97 |
|--|---|--|--|---|
| Def(N)                                     | $0.06 \pm 0.06$                                 | $0.25 \pm 0.18$                                | $1.05 \pm 0.37$                        | $0.46 \pm 0.17$                         |
| Def(P)                                     | $0.00 \pm 0.02$                                 | $0.02 \pm 0.01$                                | $0.06 \pm 0.02$                        | $0.02 \pm 0.01$                         |
| Def(Si)                                    | $0.06 \pm 0.25$                                 | $0.11 \pm 0.23$                                | $0.30 \pm 0.29$                        | $0.49 \pm 0.22$                         |
| Def(C)                                     | $0.2 \pm 3.5$                                   | $1.7 \pm 1.1$                                  | $7.0 \pm 2.2$                          | $2.8 \pm 0.9$                           |
| NCP  | $0.2 \pm 3.6$                                   | $1.6 \pm 1.1$                                  | $7.3 \pm 2.2$                          | $3.9 \pm 0.9$                           |
| Surp(TOC)                                  | $0.1 \pm 0.2$                                   | $1.4 \pm 0.9$                                  | $6.7 \pm 2.4$                          | $0.1 \pm 0.4$                           |
| Surp(POC)                                  | $0.05 \pm 0.2$                                  | $1.2 \pm 0.8$                                  | $5.3 \pm 2.1$                          | $0.2 \pm 0.06$                          |
| Surp(DOC)                                  | $0.05 \pm 0.08$                                 | $0.14 \pm 0.15$                                | $1.2 \pm 0.4$                          | Not measured                            |
| $\text{Export}_{200}$                      |   | $0.2 \pm 0.4$                                  | $0.6 \pm 1.4$                          | $3.8 \pm 0.8$                           |
| Def(N)/Def(P)                              |   | $14.3 \pm 5.7$                                 | $16.7 \pm 2.4$                         | $22.3 \pm 3.2$                          |
| NCP/Def(P)                                 |   | $103.4 \pm 24$                                 | $133.4 \pm 19.5$                       | $193.9 \pm 59.0$                        |
| NCP/Def(N)                                 |   | $7.2 \pm 0.6$                                  | $7.8 \pm 0.7$                          | $9.30 \pm 3.0$                          |
| Mixed-layer depth<br>(range) (m)           | 215<br>(26–650)                                 | 39<br>(16–85)                                  | 30<br>(8–71)                           | 153<br>(26–284)                         |

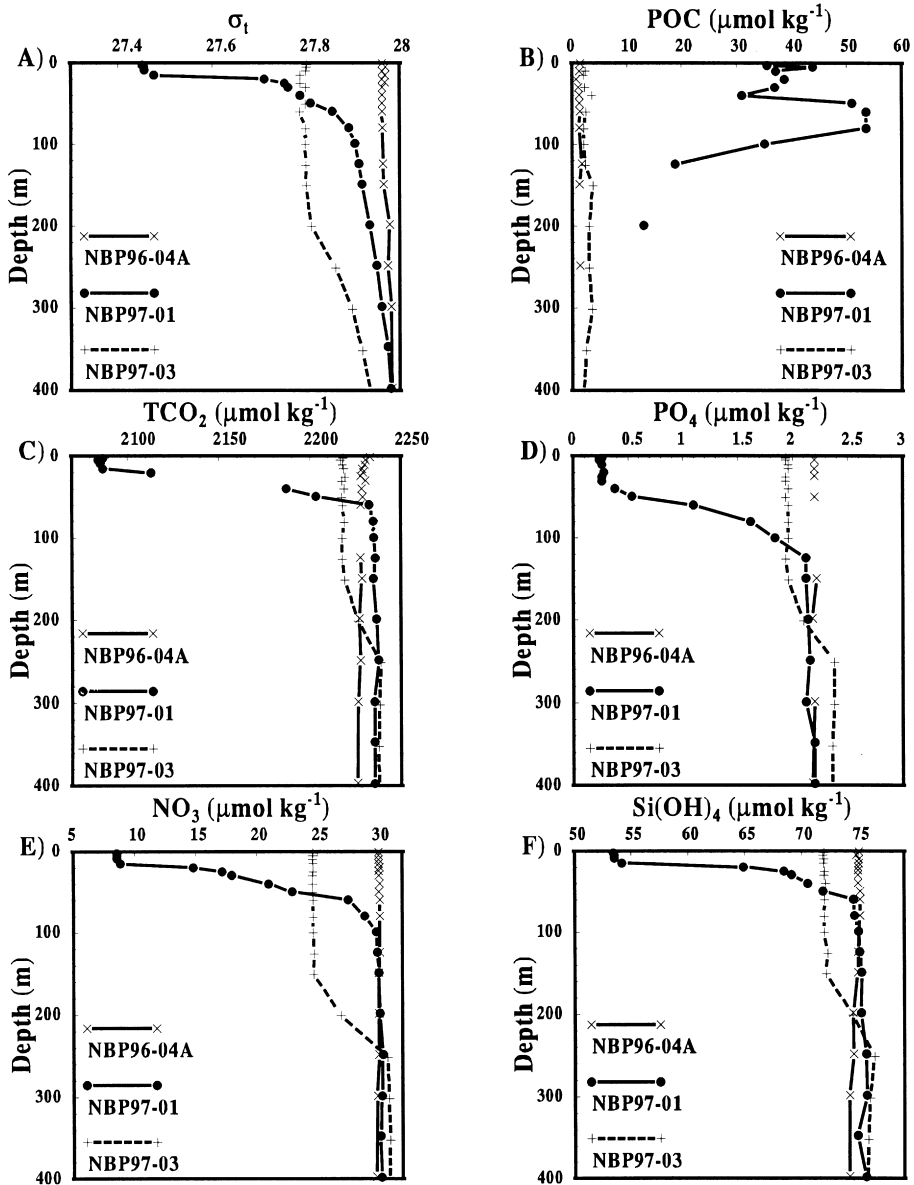


Fig. 2. Vertical profiles of (A)  $\sigma_t$ , (B) POC, (C) salinity-normalized  $\text{TCO}_2$ , (D) salinity-normalized  $\text{PO}_4$ , (E) salinity-normalized  $\text{NO}_3$ , and (F) salinity-normalized  $\text{Si(OH)}_4$  observed during early spring [NBP96-04A, Station 10, October 10, 1996; x], summer [NBP97-01, Station 1, January 13, 1997; •] and autumn [NBP97-03, Station 13, April 13, 1997; +] at  $76^\circ 30'S$  and  $169^\circ 00'E$ . All concentrations normalized to 34.5 (PSS) salinity.

(Fig. 2B). Station 10 occupied during the autumn illustrated that the mixed-layer depth increased (mean depth 153 m, Table 1) from the mid-summer minimum (Fig. 2). Salinity-normalized nutrient and  $\text{TCO}_2$  concentrations also increased in the mixed layer relative to those observed in the mid-summer.

In the early part of the bloom there was a net increase in the  $\text{Surp}(\text{TOC})$ , which peaked during the summer. These data indicate a net increase of  $6.7 \text{ mol TOC m}^{-2}$  from early spring to mid-summer (Table 1). By autumn  $\text{Surp}(\text{TOC})$  values were approximately zero — similar to early spring. The NCP show a peak in the average biological removal of  $7.3 \text{ mol m}^{-2}$  during the summer. Unlike  $\text{Surp}(\text{TOC})$ , NCP calculated for the autumn cruise ( $3.9 \pm 0.9 \text{ mol m}^{-2}$ ) indicated that the inorganic carbon values had not returned to “background” levels. This leads to the conclusion that  $\text{Export}_{200}$  increased substantially from summer through autumn between mid-February and mid-April (Fig. 3C, Table 1). Although the late spring and summer cruises showed some carbon export, it was minor compared with the  $3.8 \text{ mol m}^{-2}$  observed during the autumn cruise.

### 3.2. Removal ratios during late spring

During the late spring occupation of the Ross Sea nutrient and  $\text{CO}_2$  uptake ratios were assessed using net changes in nutrient concentration from early spring to late spring ( $\Delta X_i$ ). Although data from early spring and late spring cruises were from different years, this calculation has been done assuming that the initial conditions, established in the early spring, are the same from year to year. This assumption is justified because of the consistency of deep-water nitrate and phosphate concentrations measured from year to year between 200 and 400 m in the Ross Sea (Gordon et al., 2000; Sweeney et al., 2000). Because average change in the  $\text{TCO}_2$  concentration due to the sea–air  $\text{CO}_2$  flux integrated over this time period ( $\sim 0.25 \mu\text{mol kg}^{-1}$ ) was smaller than the measurement error,  $\Delta C$  was not corrected for gas exchange. The relative dominance of the two primary taxa, diatoms and the haptophyte *Phaeocystis antarctica*, was assessed using two methods. The first was to use the ratio of changes in silicate and nitrate concentrations,  $\Delta\text{Si}/\Delta\text{N}$  (diatoms use large quantities of silicate to form their opal tests, while *P. antarctica* lack an opal test), and the second was using the carotenoid pigments found in each (fucoxanthin (FUCO) in diatoms and 19'-hexanoyloxyfucoxanthin (HEX) in *P. antarctica*). We chose a priori a limit of greater than 1 for the  $\Delta\text{Si}/\Delta\text{N}$  ratio to indicate diatom dominance, and a value of less than 0.5 for the  $\Delta\text{Si}/\Delta\text{N}$  ratio as indicative of dominance by *P. antarctica*. Similarly, if greater than 30% of the total accessory pigment (by weight) was FUCO, the sample was considered to be dominated by diatoms, and if greater than 60% of the total accessory pigment was HEX, the sample was characterized as *P. antarctica* dominated. The relative amount of FUCO to total pigment is smaller in diatoms, whereas in *P. antarctica* the relative amount of HEX to total pigment is larger (see Bellingshausen Sea population estimates in Bidigare et al., 1996) and requires the above selection criteria.

During the late spring the  $\Delta\text{N}/\Delta\text{P}$  and  $\Delta\text{C}/\Delta\text{P}$  ratios associated with high silicate drawdown ( $\Delta\text{Si}/\Delta\text{N} > 1.0$ ) were  $10.1 \pm 0.3$  and  $80.5 \pm 2.3$ , respectively, while those

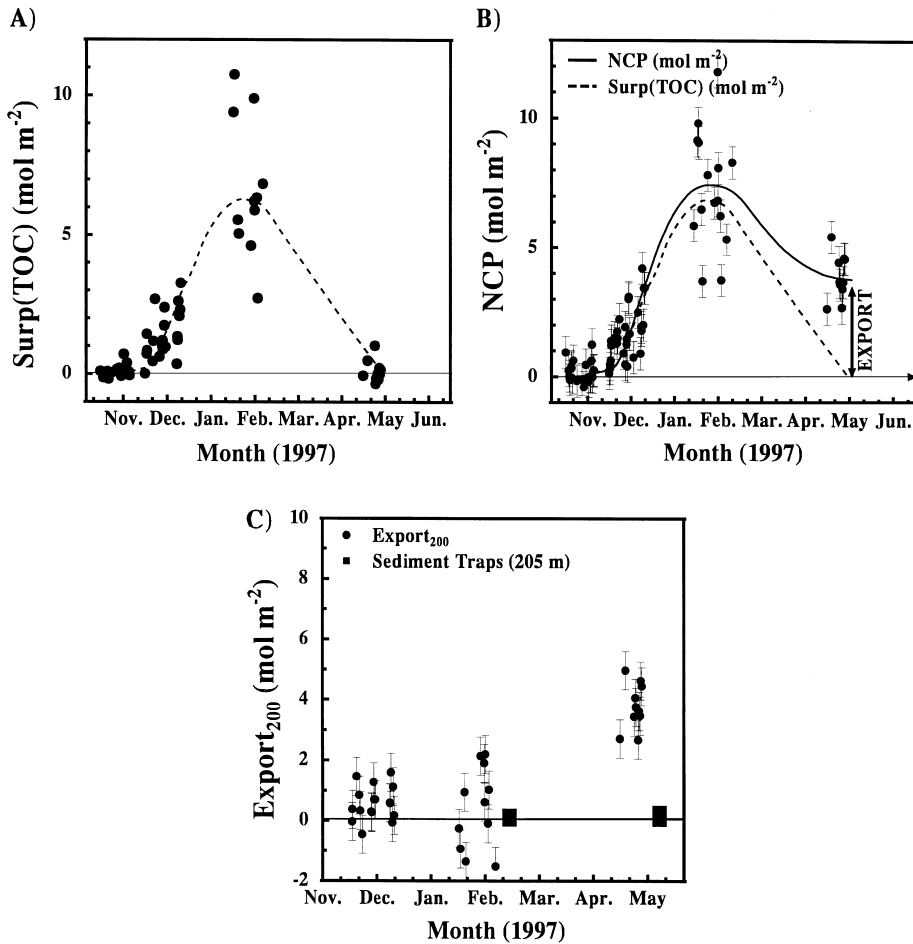


Fig. 3. Temporal change in (A) surplus organic carbon pools Surp(TOC), (B) NCP ( $\text{mol m}^{-2}$ ) and (C) export below 200 m over the course of the bloom along  $76^{\circ}30'S$ . All lines are hand-drawn. The solid line is the temporal change in NCP and short dashed lines are the temporal variations in Surp(TOC). Squares indicate cumulated organic carbon in a sediment trap located at  $76^{\circ}30'S$   $178^{\circ}1'W$  and 206 m.

with low silicate removal ( $\Delta\text{Si}/\Delta\text{N} < 0.5$ ) had removal ratios of  $18.6 \pm 0.4$  and  $134.0 \pm 4.7$ , respectively (Fig. 4A and B). Based on the HPLC criteria, a  $\Delta\text{N}/\Delta\text{P}$  removal ratio of  $10.0 \pm 0.7$  for diatoms and  $19.3 \pm 1.1$  for *P. antarctica* was found (Fig. 4C). Both  $\Delta\text{N}/\Delta\text{P}$  and  $\Delta\text{C}/\Delta\text{P}$  removal ratios measured for diatoms and *P. antarctica* are significantly different from 16 and 106, the canonical values suggested by Redfield et al. (1963). Because no  $\text{TCO}_2$  measurements were made on the same water samples from which the HPLC analysis were drawn, differences in  $\Delta\text{C}/\Delta\text{N}$  and  $\Delta\text{C}/\Delta\text{P}$  removal ratios using pigments were not assessed.

Carbon and nitrogen drawdown relationships within regions dominated by different taxa were then investigated by analyzing both the  $\Delta\text{C}/\Delta\text{N}$  as well as the

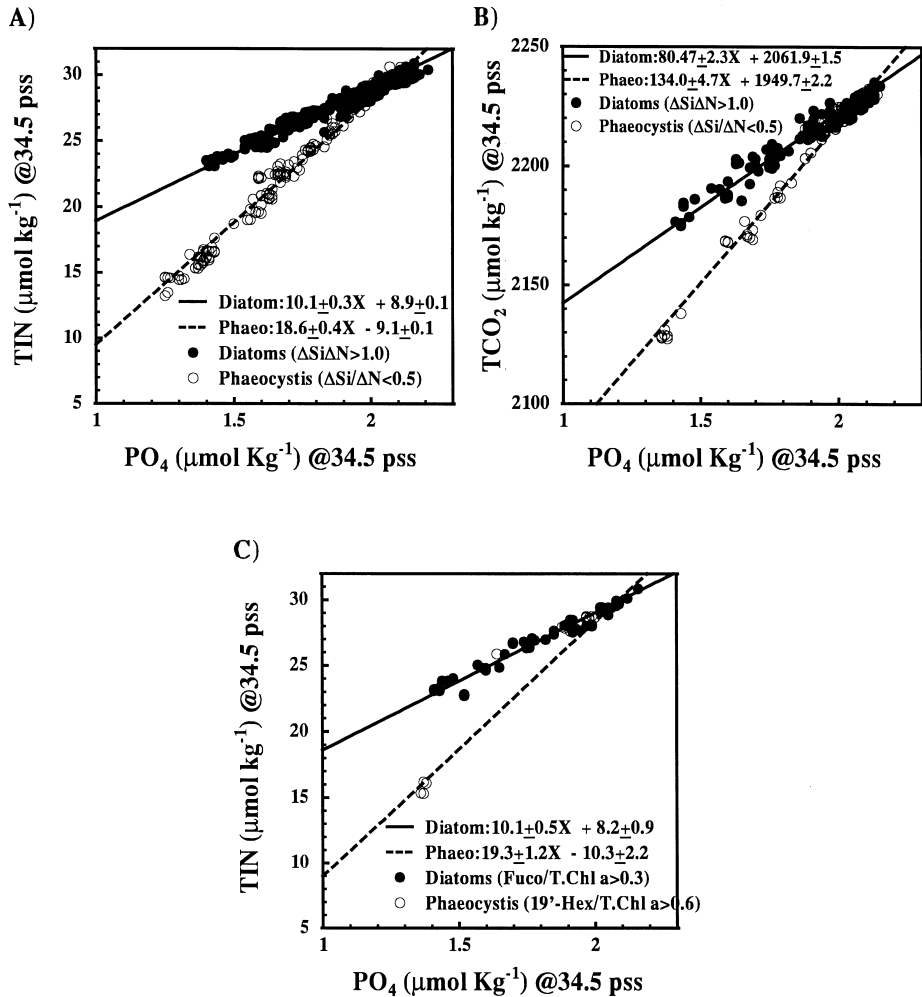


Fig. 4. (A) Relationship between total inorganic nitrogen (TIN) (nitrate + nitrite + ammonium) and phosphate concentrations scaled to a salinity of 34.5 during the late spring cruise (NBP97-08). Solid line represents all points with  $\Delta\text{Si}/\Delta\text{N} > 1.0$  and  $\Delta\text{N} > 0.12 \mu\text{mol kg}^{-1}$  and dashed line represents all points with  $\Delta\text{Si}/\Delta\text{N} < 0.5$  and  $\Delta\text{N} > 0.12 \mu\text{mol kg}^{-1}$ . Each linear regression was forced through an early spring value ( $\text{PO}_4 = 2.14 \mu\text{mol kg}^{-1}$  and  $\text{TIN} = 30.4 \mu\text{mol kg}^{-1}$ ). (B) Relationship between total carbon dioxide and phosphate concentrations. Solid line represents all points with  $\Delta\text{Si}/\Delta\text{N} > 1.0$  and  $\Delta\text{N} > 0.12 \mu\text{mol kg}^{-1}$  and dashed line represents all points with  $\Delta\text{Si}/\Delta\text{N} < 0.5$  and  $\Delta\text{N} > 0.12 \mu\text{mol kg}^{-1}$ . Each linear regression was forced through an early spring value ( $\text{TCO}_2 = 2234 \mu\text{mol kg}^{-1}$  and  $\text{PO}_4 = 2.14 \mu\text{mol kg}^{-1}$ ). (C) Relationship between total inorganic nitrogen and phosphate concentrations. Solid line is a linear regression using all samples with fucoxanthin: total chlorophyll ratio  $> 0.3$  and  $\Delta\text{N} > 0.12 \mu\text{mol kg}^{-1}$ , and dashed line is a linear regression of all points with 19'-hexanoyloxyfucoxanthin: total chlorophyll ratio  $> 0.6$  and  $\Delta\text{N} > 0.12 \mu\text{mol kg}^{-1}$ . Each regression has been forced through an early spring value ( $\text{PO}_4 = 2.14 \mu\text{mol kg}^{-1}$  and  $\text{TIN} = 30.4 \mu\text{mol kg}^{-1}$ ).

$\Delta(\text{POC})/\Delta(\text{PON})$  relationship (Fig. 5A and B). Diatom-dominated assemblages were not significantly different from those dominated by *P. antarctica* as determined by either the  $\text{CO}_2$ /nitrogen reduction or particulate matter appearance. Mean ratios

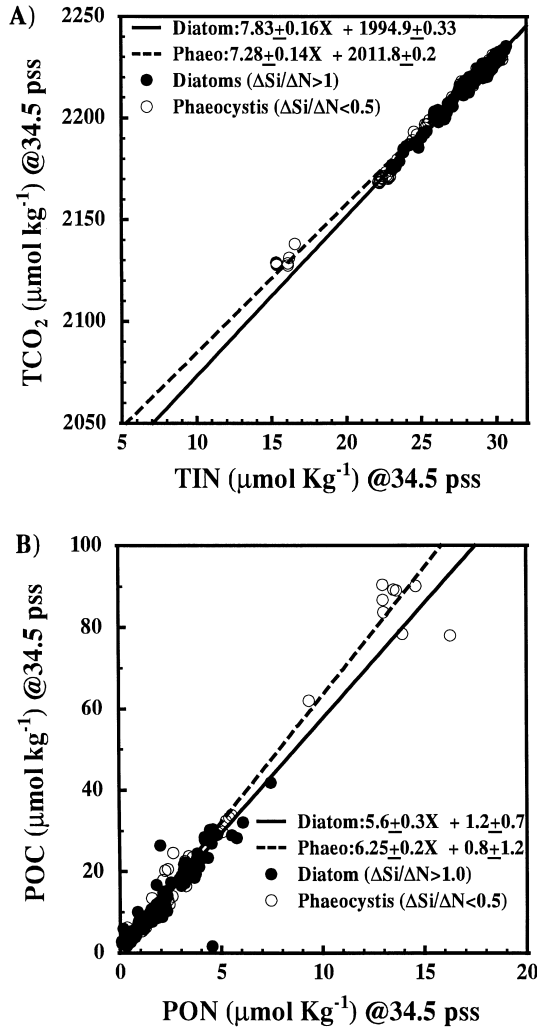


Fig. 5. (A) Relationship between total inorganic nitrogen (TIN) (nitrate + nitrite + ammonium) and total  $\text{CO}_2$  concentrations scaled to a salinity of 34.5 during the late spring cruise (NBP97-08). Solid line represents all points with  $\Delta\text{Si}/\Delta\text{N} > 1.0$  and  $\Delta\text{N} > 0.12 \mu\text{mol kg}^{-1}$ . Dashed line represents all points with  $\Delta\text{Si}/\Delta\text{N} < 0.5$  and  $\Delta\text{N} > 0.12 \mu\text{mol kg}^{-1}$ . Each linear regression was forced through an early spring value ( $\text{TCO}_2 = 2234 \mu\text{mol kg}^{-1}$  and  $\text{TIN} = 30.4 \mu\text{mol kg}^{-1}$ ). (B) Relationship between particulate organic nitrogen (PON) and particulate organic carbon (POC) concentrations during late spring. Solid line represents all points with  $\Delta\text{Si}/\Delta\text{N} > 1.0$  and  $\Delta\text{N} > 0.12 \mu\text{mol kg}^{-1}$ , and dashed line represents all points with  $\Delta\text{Si}/\Delta\text{N} < 0.5$  and  $\Delta\text{N} > 0.12 \mu\text{mol kg}^{-1}$ . Each linear regression was forced through an early spring value ( $\text{POC} = 3.1 \mu\text{mol kg}^{-1}$  and  $\text{PON} = 0.31 \mu\text{mol kg}^{-1}$ ).

determined from nutrient removal for diatoms and *P. antarctica* were  $7.8 \pm 0.2$  and  $7.3 \pm 0.1$ , respectively, whereas ratios calculated from the particulate concentrations were  $5.6 \pm 0.3$  and  $6.25 \pm 0.2$ . These differences will be discussed in subsequent sections.

### 3.3. Seasonal progression of nutrient ratios

In order to show how removal ratios of  $\text{CO}_2$  and nutrients changed from the late spring through autumn, deficit ratios were examined. Def(N)/Def(P) increased through the growing season (Fig. 6, Table 1), suggesting that there is either preferential remineralization or a decrease in the utilization of the phosphate relative to nitrogen as the seasonal cycle progresses. This same trend can be seen in the progression of NCP/Def(P) (Fig. 7, Table 1). The late spring average NCP/Def(P) and Def(N)/Def(P) ratios of  $103 \pm 24$  and  $14 \pm 5$ , respectively, increased to  $193 \pm 58$  and  $22 \pm 3$  by autumn. Although not statistically significant, a small increase in the NCP/Def(N) ratio from a early spring value of  $7.1 \pm 0.5$  to  $9.3 \pm 3.0$  by autumn is observed in Fig. 8. Maximum variability in all ratios was observed in autumn, and probably reflects the propagation of measurement errors relative to the small  $\Delta X_i$  in the upper 200 m.

## 4. Discussion

### 4.1. Seasonal change in NCP and Surp(TOC)

The data collected during the JGOFS/AESOPS cruises are unique for the Southern Ocean because they captured an entire seasonal cycle of changes in the

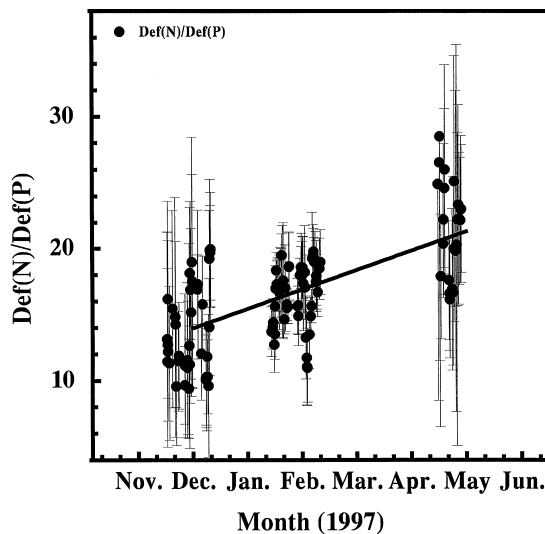


Fig. 6. Temporal change in the Def(N)/Def(P) ratios along  $76^{\circ}30'S$ . Line represents linear least-squares fit.

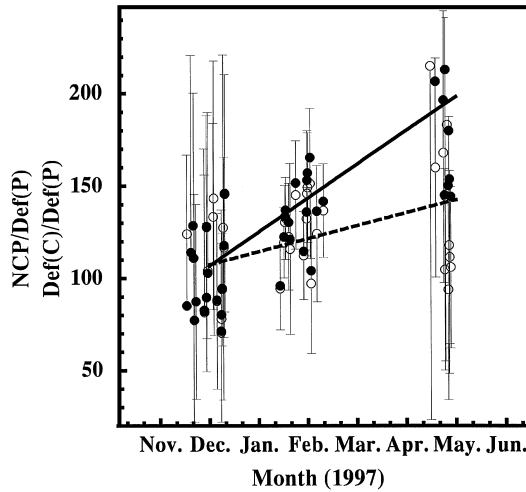


Fig. 7. Temporal change in C/P ratios in the upper 200m along 76°30'S. Solid line and filled circles represent NCP/Def(P), and dashed line and open circles represent Def(C)/Def(P). Lines are linear least-squares fit. The difference between NCP and Def(C) represents the effects of sea-air CO<sub>2</sub> flux.

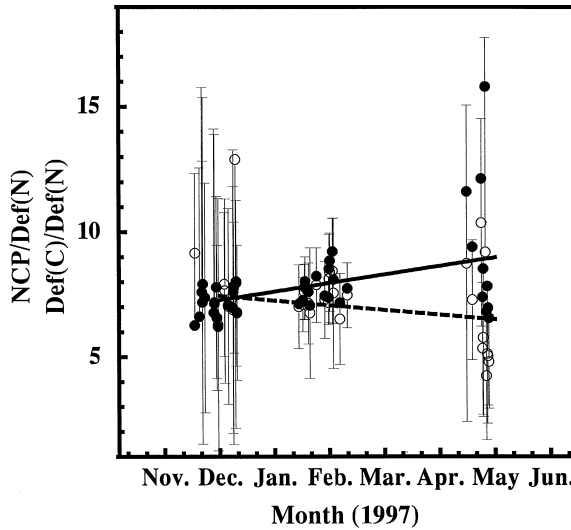


Fig. 8. Temporal change in C/N ratios in the upper 200m along 76°30'S. Solid line and filled circles represent NCP/Def(N), and dashed line and open circles represent Def(C)/Def(N). Lines are linear least-squares fit. The difference between NCP and Def(C) represents the effects of sea-air CO<sub>2</sub> flux.

carbon-nutrient chemistry for the upper water column. It is clear that the concurrent increase in Surp(TOC) and NCP from early spring to mid-summer (Fig. 3A and B) was due to high primary productivity during early and late spring (Smith et al., 2000). By autumn, primary productivity had effectively stopped because of lack of sunlight

and sea-ice accumulation (W. Smith, unpublished) and the TOC had returned to near “background”, indicating that almost all the organic matter produced in the upper 200 m had either been exported or remineralized by autumn.

#### 4.2. Seasonal change in $Export_{200}$ and comparison with sediment traps

Despite the fact that almost no surplus TOC ( $0.1 \pm 0.4 \text{ mol m}^{-2}$ ) remained in the upper 200 m, the NCP ( $3.9 \pm 0.9 \text{ mol m}^{-2}$ ) and Def(C) ( $2.8 \pm 0.9 \text{ mol m}^{-2}$ ) were substantial through the austral autumn, indicating a substantial export flux of particulate organic matter. The fact that TOC values had returned to near background values in the surface 200 m by austral autumn is further supported by transmissometer measurements (Gardner et al., 2000). Although the NCP had peaked during the mid-summer, only a fraction of the organic carbon ( $0.6 \pm 1.4 \text{ mol m}^{-2}$ ) had been exported below 200 m (Table 1) at that time, indicating that most export occurred between mid-summer and autumn. The temporal lag in organic carbon export has also been suggested by both moored and free-floating sediment traps (Dunbar et al., 1998; Asper and Smith, 1999; Collier et al., 2000). Collier et al. (2000) report that the flux of organic matter shortly after the mid-summer cruise represented < 8% of the annual flux. The temporal delay in export relative to euphotic zone productivity and biomass may be due to the slow development of the grazing community which facilitates export by forming fast-sinking aggregates (Wassmann et al., 1996; Dunbar et al., 1998; Asper and Smith, 1999; Sweeney et al., 2000).

It is important to point out that accounting for the lateral transport and vertical mixing along  $76^{\circ}30'S$  would only make our estimates of the regional seasonal export higher. Because the area of the Ross Sea covered by this study is significantly more productive than surrounding areas (Sullivan et al., 1993; Comiso et al., 1993; Smith et al., 1996; Arrigo et al., 1998), lateral transport would entrain waters less depleted in nutrients and  $CO_2$  than the areas surveyed. For this reason, correcting for lateral transport would increase the regional estimated NCP and the resulting estimated regional export. Similarly, correcting for diapycnal mixing across the base of the mixed layer would increase the final estimate of NCP and export for upper 200 m. It is, therefore, hard to account for the dramatic 13-fold difference between our estimate for  $Export_{200}$  ( $3.8 \pm 0.8 \text{ mol m}^{-2}$ ) and the cumulative amount of organic carbon caught in sediment trap positioned at  $76^{\circ}30'S$   $178^{\circ}1'W$  and a depth of 206 m from October 28, 1996 to May 16, 1997 ( $0.29 \text{ mol m}^{-2}$ ) (Collier et al., 2000).

#### 4.3. Possible errors in $Export_{200}$

The 13-fold difference between the seasonal flux estimates of  $Export_{200}$  and the cumulative sediment trap fluxes is significant and requires careful consideration of the source and the magnitude of the possible factors that could contribute to the difference. For the  $Export_{200}$  estimates, possible errors in both NCP and Surp(TOC) must be considered. However, the preceding discussion points out that estimates of NCP represent a minimum due to possible errors associated with lateral and diapycnal mixing. It also has been pointed out earlier that gas exchange could be

underestimated by as much as 30%, which would also contribute to an underestimation of the NCP and, consequently,  $\text{Export}_{200}$ . These observations lead to the consideration of errors in the estimation of  $\text{Surp}(\text{TOC})$ .

#### 4.4. POC measurements using Niskin bottles

In particular, it is likely that measurement of POC using Niskin bottles may contribute to the discrepancy between the  $\text{Export}_{200}$  estimate and the sediment trap flux estimate for the period starting in late November and ending in mid-May. Sediment trap and light scattering sensor data indicate the presence of larger particles and zooplankton during the autumn in the Ross Sea which may not be effectively measured using Niskin bottles (Gardner et al., 2000). While Collier et al. (2000) report that only  $0.29 \text{ mol m}^{-2}$  of organic carbon reached a moored sediment trap at 200 m, they also report that by the following spring this flux had increased to  $0.47 \text{ mol m}^{-2}$ . With nearly complete ice cover and very little solar irradiance in the Ross Sea between austral autumn and early spring, there is no reason to believe that this increase in accumulation was the result of additional autotrophic activity. Instead, this may represent the lag due to the delayed sedimentation of larger particles and zooplankton (i.e. pteropods found by Collier et al., 2000).

Light scattering sensor data also suggest (Gardner et al., 2000) that organic carbon may have resided in the upper 200 m during the autumn as aggregates, which, if captured in a Niskin bottle, could rapidly sink below the spigot level without the turbulent regime of the mixed layer to suspend them. Once these particles sink below the spigot level they cannot be collected in water samples for analysis of POC (Gardner et al., 1993). While this may be a large source of error it is unlikely that more than half the particles will drop to the bottom of the Niskin bottle (W. Gardner, personal communication). It is also possible that these larger aggregates were not captured by the Niskin bottle because of their sparse distribution as suggested by Bishop and Edmond (1976).

An upper limit for the error in  $\text{Surp}(\text{TOC})$  can be estimated if half of the POC captured in the Niskin bottle sank below the spigot prior to sampling and if another 30% of the large particles and zooplankton were not captured by the Niskin bottle due to low statistical probability of their collection. In total,  $\text{Surp}(\text{TOC})$  could be underestimated and, hence,  $\text{Export}_{200}$  overestimated (Eq. (8)) by, at most, a factor of 3.

#### 4.5. Differences in trap fluxes

It is also conceivable that the moored sediment traps may not capture all of the material that is exported from the surface layer. Yu et al. (2000) found using  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  that trapping efficiencies of bottom-tethered sediment traps tend to be lower and more erratic in the mesopelagic zone (depths between 100 and 1200 m) than at greater depths. They explain that the trapping efficiencies were as low as 38–43% at depths of 1110 m due to high percentage of organic carbon and less cohesive particles. While the fluxes measured by Collier et al. (2000) are considered comparable to other

measurements made in the Ross Sea by moored sediment traps (Dunbar et al., 1998), the fraction of new production exported to their traps was substantially lower than that measured by free-floating traps. For example, during a 60-d period during late November to mid-January in 1994 and 1995, Asper and Smith (1999) estimated a flux that was 13% of the nitrate-based primary production at 150 m using floating sediment traps. If particle flux lags production, as observed in this study, it is conceivable that this estimate would dramatically increase after mid-January.

#### 4.6. Mesoscale variability

Despite the possibility that the sediment traps may be missing some of the carbon flux to 200 m, no investigators have ever documented underestimates as large as a factor of 13, implied from this study. Nor have measurements of POC ever been shown to be so aliased by the standing stocks of large aggregates and zooplankton. This difference in estimates of export, however, might be due to the meso-scale variability in productivity. While the  $\text{Export}_{200}$  in the location of the sediment trap ( $3.1 \text{ mol m}^{-2}$ ) was not significantly less than the average along  $76^{\circ}30'S$  based on measurements made in autumn, the NCP at this location during the mid-summer ( $3.7 \text{ mol m}^{-2}$ ) was significantly lower than the average for mid-summer ( $7.3 \pm 2.2 \text{ mol m}^{-2}$ ) among all stations along  $76^{\circ}30'S$ . It is therefore possible that export took place in the more productive areas shortly after the mid-summer cruise leaving behind nutrient-depleted waters which were advected over time to the location of the sediment trap. From this perspective, it can be concluded that NCP and  $\text{Surp}(\text{TOC})$  calculated at the location of the trap overestimated the actual export that took place. Despite this fact, observations of other investigators (R. Dunbar, personal communication) during this time, show that export evaluated using sediment traps at several locations in the Ross Sea did not vary by more than 2-fold. It is, therefore, hard to account for the dramatic difference between the trap data and the exports calculated from nutrient and  $\text{TCO}_2$  deficits at the end of the bloom and this highlights the need to develop more independent and internally consistent methods for evaluating export flux.

#### 4.7. Removal ratios during late spring

The high primary productivity (Smith et al., 2000), the relatively low heterotrophic biomass and production (H. Ducklow, personal communication; Carlson et al., 1998) and the spatial separation of two dominant phytoplankton species allow the use of the change in concentration of nutrients and carbon from winter to late spring ( $\Delta$ ) to estimate the difference in removal ratios between diatoms and *P. antarctica*. The difference in the  $\Delta\text{N}/\Delta\text{P}$  ratios between the regions with high  $\Delta\text{Si}/\Delta\text{N}$  ratios and those with low  $\Delta\text{Si}/\Delta\text{N}$  ratios demonstrates the differences between the removal ratios of diatoms and *P. antarctica* (Figs. 4A). This confirms similar findings by Bates et al. (1998a) and Arrigo et al. (1999). A distinction between diatom and *P. antarctica* uptake ratios is also confirmed by HPLC pigment data as a taxon discriminant (Fig. 4C), as demonstrated by Arrigo et al. (1999). Although confirmation of these

removal ratios using the pigments is useful, there should not necessarily be a direct relationship to the drawdown in nutrients at a particular depth due to gravitational settling of the particles from which pigments are extracted.

Significant differences between  $\Delta C/\Delta P$  removal ratios in the two assemblages also were observed. It is important to note that the  $\Delta C/\Delta P$  ratios in the diatom-dominated areas were smaller than values reported by Arrigo et al. (1999) because the influence of meltwater dilution of nutrients and  $\text{CO}_2$  was accounted for in our study by scaling all concentrations to a salinity of 34.5. This correction is on the order of a few percent, and is largest in the diatom-dominated areas, which tend to be more stratified due to greater meltwater input (Sweeney et al., 2000). The correction is small relative to the observed changes in nutrients (over 50%) through the growing season, whereas it is large relative to the changes in  $\text{TCO}_2$  (only about 5%) over the same period. As a result, biological removal of  $\text{TCO}_2$  is only about 60% of the measured decrease in  $\text{TCO}_2$  (uncorrected for meltwater dilution), and the biological  $\Delta C/\Delta P$  is likewise smaller. The large difference between the  $\Delta C/\Delta P$  uptake ratios in the two communities suggests that there may be species dependence for nutrient and carbon and uptake ratios. The constancy of  $\Delta C/\Delta N$  ratios suggests that most of the variability is due to differences in phosphate uptake. Since most biogeochemical models rely on a single-nutrient productivity dependence, this result implies that N should be the nutrient of choice for this purpose.

#### 4.8. Carbon–nitrogen ratios in water and particles

Although the difference in  $\Delta C/\Delta N$  ratios between taxa is small, a significant difference appears to exist between the mean  $\Delta C/\Delta N$  ratio in seawater ( $7.8 \pm 0.2$  for  $\Delta \text{Si}/\Delta \text{N} > 1$  and  $7.3 \pm 0.1$  for  $\Delta \text{Si}/\Delta \text{N} < 0.5$ , Fig. 5A) and the mean  $\Delta \text{POC}/\Delta \text{PON}$  ratio ( $5.6 \pm 0.3$  for  $\Delta \text{Si}/\Delta \text{N} > 1$  and  $6.25 \pm 0.2$  for  $\Delta \text{Si}/\Delta \text{N} < 0.5$ , Fig. 5B) during late spring. Assuming that little material was lost from the upper 200 m or advected from the study area from the onset of the bloom to the time the measurements were taken in the late spring, this difference may be accounted for if the  $\Delta \text{DOC}/\Delta \text{DON}$  ratio is much higher than 7.5. Because the surplus DOC produced in the Ross Sea was rarely found to be greater than 19% of the  $\text{TCO}_2$  deficit (Carlson et al., 2000; Sweeney et al., 2000),  $\Delta \text{DOC}/\Delta \text{DON}$  ratios must be greater than 16 in order to balance the carbon budget. While Karl et al. (1991) estimate a mean DOC/DON ratio of 11 or higher in the Bransfield Strait based on similar calculations, these estimates are much higher than those of Carlson et al. (2000) who measured a  $\Delta \text{DOC}/\Delta \text{DON}$  ratio of  $6.4 \pm 5.2$  in the surface waters of the Ross Sea. This discrepancy between the calculated and measured  $\Delta \text{DOC}/\Delta \text{DON}$  ratios clearly indicates that further investigation will need to be done to properly balance and interpret the carbon budget.

This imbalance in the carbon and nitrogen budget also was observed by Arrigo et al. (1999), who reported that the  $\Delta C/\Delta \text{NO}_3$  (9.23) and  $\Delta \text{POC}/\Delta \text{PON}$  (6.37) ratios in diatom-dominated were significantly different. They concluded that “indirect evidence suggests that the use of other N sources by diatoms is the likely explanation for the difference between the  $[\Delta C/\Delta \text{NO}_3]$  and  $[\Delta \text{POC}/\Delta \text{PON}]$ ”. They specifically suggested  $\text{NH}_4^+$  as the source. While this is a possibility, the data in our study do not support

this conclusion. Measurements of  $\text{NH}_4^+$  indicate a net increase in concentrations in the upper 200 m of the Ross Sea throughout the growing season (Gordon et al., 2000). Therefore, by including  $\text{NH}_4^+$  in  $\Delta\text{N}$ , the  $\Delta\text{C}/\Delta\text{N}$  ratio will increase and the difference between the  $\Delta\text{C}/\Delta\text{N}$  ratio and the  $\Delta\text{POC}/\Delta\text{PON}$  ratio will actually increase — not decrease — compared to situations where only  $\text{NO}_3$  is included in  $\Delta\text{N}$  (Arrigo et al., 1999). Although normalizing the  $\text{TCO}_2$  to a constant salinity could account for some of the differences between the  $\Delta\text{C}/\Delta\text{NO}_3$  and  $\Delta\text{POC}/\Delta\text{PON}$  ratio observed by Arrigo et al. (1999) in diatom-dominated regions, it is unlikely to be sufficient to properly balance the carbon and nitrogen budget. It is also important to point out that although the Arrigo et al. (1999) measurements were made a month later in the previous year there is little reason to believe that exported particulate matter with high C/N could help account for the imbalance. Even if 50% of the NCP was exported in diatom-dominated areas at the time that Arrigo et al. (1999) made measurements, the exported particulate matter would need to have  $\Delta\text{POC}/\Delta\text{PON}$  ratios of at least 12 — a C/N ratio that is exceedingly high for newly exported material.

The small difference between  $\Delta\text{C}/\Delta\text{N}$  removal ratios for the diatom and *P. antarctica*, and the large differences in  $\Delta\text{N}/\Delta\text{P}$  and  $\Delta\text{C}/\Delta\text{P}$  ratios illustrate that diatoms preferentially remove phosphate with respect to *P. antarctica*. These results, however, do not indicate what happens to the phosphate in its organic form, and we can only speculate on the fate of the excess phosphate removed by diatoms. Copin-Montegut and Copin-Montegut (1978, 1983) suggest that smaller POC/POP and PON/POP ratios occur in areas where dissolved phosphate is in excess ( $> 1.5 \mu\text{mol l}^{-1}$ ). Phosphate is stored possibly as polyphosphate and mobilized for cellular requirements when needed (Hooper, 1967 and references therein); furthermore, polyphosphate abundance is correlated with the phosphate concentration in the growth medium (Walsh and Hunter, 1992). It is possible that the large vacuoles in diatoms serve as sites for polyphosphate storage. To understand more clearly where the phosphate is stored (e.g. as polyphosphate molecules), further studies are necessary.

#### 4.9. Export ratios and the role of diatoms

Given that diatoms remove soluble reactive phosphate from seawater at lower C/P and N/P ratios than *P. antarctica* during the late spring, it is important to understand how much of it is exported to the deep ocean. Because diatoms are often associated with export production (Eppley and Peterson, 1979; Michaels and Silver, 1988; Dugdale et al., 1995; Dugdale and Wilkerson, 1998), their C/P and N/P ratios of exported organic matter are particularly important. Some of the particulate organic matter will be remineralized to  $\text{PO}_4^{3-}$  and  $\text{TCO}_2$ , while another fraction will enter the dissolved organic pool. The final fraction will be exported to the deep ocean. Both the removal ratios during the late spring presented in this study and those presented by Arrigo et al. (1999) (even after being corrected for fresh-water dilution) show that the  $\text{TCO}_2/\text{PO}_4^{3-}$  removal ratio for diatoms is well below the traditional  $\text{TCO}_2/\text{PO}_4^{3-}$  ratio observed by Redfield et al. (1963); however, there are no data indicating that the exported particulate matter has a C/P ratio equivalent to the removal ratio. Without knowing the organic carbon to organic nitrogen or phosphate ratio of the exported

POM, the consequences for carbon export of phytoplankton assemblage dominated by diatoms versus one dominated by *P. antarctica* remain uncertain. This is an important question since many comparative studies of the Antarctic and the North Atlantic have demonstrated that diatoms are a far more efficient means to transport carbon to the depth than *P. antarctica*, as diatoms are often the preferred food for zooplankton and are packaged into rapidly sinking fecal pellets (Honjo et al., 1984; Passow and Wassmann, 1994; Riebesell et al., 1995; Smith and Dunbar, 1998; Dunbar et al., 1998).

While it is clear that diatoms and *P. antarctica* initially have different  $\Delta N/\Delta P$  and  $\Delta C/\Delta P$  ratios, later in the season it becomes difficult to discriminate between diatom-dominated and *P. antarctica*-dominated regimes. Because diatom frustules are opal, their dissolution is largely controlled by the solubility of silica in seawater, while the remineralization of organic matter is largely a function of heterotrophic processes (Azam and Hodson, 1977). As such, carbon and silica cycles become de-coupled in polar waters, resulting in the preferential remineralization of carbon and the export of silica (Nelson et al., 1996). This de-coupling makes the use of dissolved  $\Delta Si/\Delta N$  ratios as a taxonomic indicator in autumn problematic. Similarly, the export of all surplus TOC by autumn reduces the phytoplankton pigment levels, and hence HPLC analyses are of limited use for identifying taxa during the autumn. Finally, lateral mixing and species succession (Sweeney et al., 2000) over the 150-d bloom period make it difficult to delineate the particular taxa responsible for the nutrient deficits.

In order to identify the specific export ratios of diatoms, it is necessary to look in areas of the ocean where the bloom is more completely dominated by diatoms. In the Ross Gyre, Rubin et al. (1998) showed a  $Def(Si)/Def(C)$  ratio of 0.66 in the seasonal thermocline, which suggests a predominance of diatoms. The  $\Delta NO_3^-/\Delta P$  and  $\Delta C/\Delta P$  ratios measured in the upper 60 m of water during the decline of the bloom (February/March) was 13.0 and 91.0, respectively, also indicating preferential phosphate incorporation by diatoms. Below 150 m Rubin et al. (1998) reported a  $\Delta NO_3^-/\Delta P$  ratio of 14.0, which is smaller than the mean global deep water. Because this ratio results from deep-water remineralization of particulate matter, it suggests that the low  $\Delta NO_3^-/\Delta P$  ratio found in the diatom bloom is exported and has a discernible effect on the deep-water chemistry. Unfortunately, because no data were collected over the course of the growing season in the Ross Gyre, we can only speculate that the  $\Delta C/\Delta P$  and  $\Delta NO_3^-/\Delta P$  ratios that Rubin et al. (1998) observed late in the growing season were higher than the removal ratios observed in the late spring during our study due either to preferential remineralization of phosphate or to a progressive increase in  $\Delta N/\Delta P$  and  $\Delta C/\Delta P$  removal ratios throughout the growing season. Preferential remineralization of phosphate also has been observed by Anita et al. (1963) using large-volume enclosures. While Anita et al. (1963) demonstrated the preferential release of phosphate relative to both carbon and nitrogen, they observed only a small increase in the  $\Delta C/\Delta N$  ratio. The increase in the  $\Delta C/\Delta N$  ratio they found was similar in magnitude to the changes that we observed. Minster and Boulahdid (1987) found  $\Delta N/\Delta P$  ratios to change over a range of isopycnals, which suggests that P was being remineralized more rapidly at shallower depths than N. It is therefore likely that the  $NCP/Def(P)$  (Fig. 7) and  $Def(N)/Def(P)$  (Fig. 6) ratios in the Ross Sea increased from

late spring to autumn due to a combination of additional removal of C, P and N by *P. antarctica* at high C/P and N/P ratios together with the preferential release of phosphate during heterotrophic degradation of diatoms and *P. antarctica* organic matter.

## 5. Conclusions

This study in the Ross Sea, Antarctica, examined the seasonal progression of the deficits observed in seawater for CO<sub>2</sub> and nutrients that result from phytoplankton growth, and the “surplus” of organic carbon produced over a complete bloom period during 1996 and 1997. Because Surp(TOC) had returned to near pre-bloom values by autumn, we were able to use the net community production at that time to estimate export below 200 m to be  $3.8 \pm 0.8 \text{ mol C m}^{-2}$  over the course of the growing season. This annual export was  $55 \pm 22\%$  of the maximum deficit in salinity-scaled TCO<sub>2</sub> observed during the mid-summer occupation of 76°30'S. It was also significantly higher than the  $0.29 \text{ mol C m}^{-2}$  estimated from bottom-moored sediment traps at 206 m during the same time period. Errors due to inability of the sediment traps to capture the sinking particle flux, errors in the POC measurements using Niskin bottles and errors associated with meso-scale variability were suggested as reasons for the discrepancy between estimates of organic carbon export made from sediment traps data and the carbon budget of the upper 200 m.

The elemental removal ratios ( $\Delta\text{C}/\Delta\text{N}$ ,  $\Delta\text{N}/\Delta\text{P}$  and  $\Delta\text{C}/\Delta\text{P}$ ) calculated from water chemistry data during the late spring showed significant differences between the diatoms and *P. antarctica*. The difference in  $\Delta\text{C}/\Delta\text{N}$  removal ratios was small ( $7.8 \pm 0.2$  for diatoms and  $7.2 \pm 0.1$  for *P. antarctica*), whereas the  $\Delta\text{N}/\Delta\text{P}$  and  $\Delta\text{C}/\Delta\text{P}$  removal ratios for diatoms ( $10.1 \pm 0.3$  and  $80.5 \pm 2.3$ ) were found to be significantly smaller than for *P. antarctica* ( $18.6 \pm 0.4$  and  $134.0 \pm 4.7$ ). The small difference in  $\Delta\text{C}/\Delta\text{N}$  removal ratios indicated that variable uptake of phosphate caused the dramatic differences in  $\Delta\text{C}/\Delta\text{P}$  and  $\Delta\text{N}/\Delta\text{P}$  removal ratios. Without any particulate and dissolved organic phosphate measurements, we can only speculate that the increased phosphate removal is for luxury storage as polyphosphate molecules in diatoms. If luxury storage of phosphate is a general phenomenon in nutrient-rich waters, then diatom removal ratios are likely to change when phosphate becomes limiting in the Southern Ocean.

Although initial  $\Delta\text{N}/\Delta\text{P}$  and  $\Delta\text{C}/\Delta\text{P}$  removal ratios in diatom-dominated regions were significantly below those predicted by Redfield et al. (1963), the effect on N/P and C/P ratios of biogenic material exported below 200 m appears to be small by the end of the growing season. This conclusion is supported by the increase in the Def(N)/Def(P) and NCP/Def(P) ratios through the growing season. The most likely explanations for the increase in Def(N)/Def(P) and NCP/Def(P) ratios with time are that phosphate is preferentially remineralized or that the uptake of phosphate relative to carbon and nitrogen decreased over the bloom period. Although there was some increase in NCP/Def(N) over the course of the bloom, it was not statistically significant. Despite the preferential remineralization of phosphate or increase in  $\Delta\text{N}/\Delta\text{P}$  and

$\Delta C/\Delta P$  removal ratios with the time seen in this study, export N/P and C/P ratios determined in other studies of diatom-dominated regions (e.g. Rubin et al., 1998) were below those predicted by Takahashi et al. (1985), Boulahtid and Minster (1989) and Anderson et al. (1994). Because of the variability in removal and export C/P ratios, biogeochemical models that use C/P ratios rather than C/N ratios to predict carbon export may introduce considerable uncertainty into their predictions.

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