NON-REDFIELD PRODUCTION AND EXPORT OF MARINE ORGANIC MATTER: A RECURRENT PART OF THE ANNUAL CYCLE IN THE ROSS SEA, ANTARCTICA

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Data collected from the Ross Sea, Antarctica, during a 20-day cruise between December 19, 1996, and January 8, 1997, have shown that drawdown ratios of N/P and C/P in waters dominated by diatoms and *Phaeocystis antarctica* differ significantly from each other and from the canonical Redfield ratios of 16:1 and 106/1. By expanding this initial data set to include information from 10 additional cruises between 1990 and 1998, we show that the non-Redfield N/P and C/P drawdown ratios measured during 1996-97 are a consistent feature of Ross Sea nutrient dynamics. Ratios of N/P drawdown for waters dominated by *P. antarctica* ranged from 17.5 to 19.7 mean = 18.5), consistently exceeding the Redfield ratio of 16 and with no apparent seasonal trend. Similarly, the C/P drawdown ratio for *P. antarctica*-dominated waters ranged from 133 to 162, 25-53% greater than the Redfield ratio of 106. In contrast, waters dominated by diatoms exhibited lower ratios than Redfield for N/P (range = 10.1 to 15.2, mean = 12.5) and C/P (range = 73 to 101, mean = 87) drawdown. Again, there was no apparent seasonal trend to either the N/P or the C/P drawdown data for diatoms. Data from particulate matter suspended in the upper water column in November/December 1998 confirms the non-Redfield uptake of nutrient elements into different algal communities, with particulate organic matter in *P. antarctica*-dominated waters carrying up to 3.5 times as much N and C per mole of P relative to diatom-dominated waters. Results from sediment traps deployed in the Ross Sea show that the organic C/total P ratio for samples dominated by input from *P. antarctica* (212) was ~30% greater than that of the diatom-dominated samples (162). Taken together, these results suggest that the large difference between the C/P drawdown ratios for diatom- and *P. antarctica*-dominated waters is also expressed as a difference in particulate C/P ratio that is subsequently exported to the deep water column and seabed. We provide evidence that non-Redfield nutrient uptake by different phytoplankton communities impacts the nutrient/C ratio of particulate matter undergoing export to the deep sea, reinforcing suggestions that the biological pump of C in the ocean may be altered by climate change over decadal timescales.

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INTRODUCTION

Marine phytoplankton are an important component of the global carbon cycle. Their utilization of inorganic C, N, Si, P, and trace elements such as Fe, Mn, and Zn represents the primary mechanism by which major biogeochemical cycles in the ocean are coupled. Drawdown of CO_2 in surface waters during photosynthesis, and its eventual export to depth as organic C, maintains an air/sea CO_2 gradient that supports the influx of atmospheric CO_2 into the ocean. The efficiency of this biological C pump is determined in part by nutrient availability, which determines phytoplankton cell size, the rate of new production, and the nature of trophic interactions.

Another important factor controlling nutrient utilization in surface waters and the elemental composition of exported particulate material is the Redfield ratio [*Redfield* 1934, 1958]. The Redfield ratio describes the stoichiometric relationship between phytoplankton cellular C and the major inorganic nutrients that are required by phytoplankton for growth. Measurements of the Redfield ratio in most of the ocean show that it is relatively stable and uniform, averaging 106:16:1 for C/N/P on a molar basis [*Copin-Montegut and Copin-Montegut* 1983; *Tyrrell and Law* 1997]. Understanding the Redfield ratio is important because it is used in a wide variety of studies to predict utilization of one element based on the measured drawdown of another. For example, the Redfield ratio is used in contemporary studies to model nutrient uptake by phytoplankton [e.g., *Hoppema et al.* 2002] and CO_2 uptake by the ocean [e.g., *Sarmiento et al.* 1998] as well as in paleoclimate studies to assess the nutrient dynamics required to explain glacial-interglacial changes in atmospheric pCO_2 [*Sigman and Boyle* 2000; *Stephens and Keeling* 2000].

Recently, a number of studies have suggested that the Redfield ratio in the marine environment is not as universally applicable a constant as was once thought, varying both in space and time [*Rubin et al.* 1998; *Daly et al.* 1999; *Pahlow and Riebesell* 2000; *Bury et al*. 2001]. For example, C and N uptake by phytoplankton in the North Atlantic are decoupled, indicating that Redfield ratios may be inappropriate for converting nitrate-estimated new production to carbon export values [*Bury et al*. 2001]. Furthermore, a study of the glacial-interglacial CO_2 cycle suggests that the concept of a stable Redfield ratio may have to be abandoned [*Archer et al*. 2000]. Finally, a number of studies in the Ross Sea, Antarctica, have shown that the drawdown of C, N, and P deviates substantially from Redfield ratios, exhibiting marked phytoplankton taxonomic variation [*Bates et al.* 1998; *Arrigo et al*. 1999, 2000; *Sweeney et al*. 2000a; *Smith and Asper* 2001].

Taxonomic variability in C, N, and P drawdown ratios can have important biogeochemical implications. *Arrigo et al*. [2000] showed that in the Ross Sea, removal of CO_2 from surface waters was 100% greater per mole of PO_4 removed when the phytoplankton community was dominated by *P. antarctica* than when it was dominated by diatoms. Furthermore, these results implied that the ultimate limiting macronutrient for diatom biomass accumulation was PO_4 while for *P. antarctica* it was NO_3. During 1996-97 in the Ross Sea, *Phaeocystis* versus diatom dominance appears to be correlated with deeper, less turbulent (*Phaeocystis*) and shallower, more turbulent (diatoms) surface mixed layers [*Arrigo et al*. 1999, 2000; *Goffart et al*. 2000]. Should phytoplankton communities shift from *P. antarctica* to diatom dominance in response to enhanced upper ocean stratification [*Sarmiento et al*. 1998], then these data indicate that the CO_2 drawdown estimated from the C/P ratio would be reduced in these areas by about 50%. In addition, large-scale biogeochemical models assume that CO_2 is drawn down by phytoplankton in constant proportion to the removal of PO_4 until PO_4 is exhausted [*Sarmiento and Le Quere* 1996, *Sarmiento et al*. 1998]. Thus, the relationship between changes in phytoplankton community structure and CO_2 drawdown represents a feedback mechanism not currently included in models of global climate.

Our initial observations of taxon-specific variability in C:N and C/P drawdown ratios for the Ross Sea [*Arrigo et al*. 1999] were based on a nutrient data set collected during a 20-day period between December 19, 1996, and January 8, 1997. These results are of lesser importance if 1) 1996/97 was a unusual year and the taxon-related differentiation in nutrient drawdown ratios is either non-existent or less pronounced during more representative years, 2) the effects of either remineralization or nutrient limitation, later in the austral summer but prior to most export events, act to reverse spring nutrient drawdown trends such that by autumn the net seasonal nutrient drawdown ratios approximate Redfield values, 3) the non-Redfield signal is not exported to the deep water column and/or seabed in sinking particulate material.

In this paper we use nutrient data from 11 cruises spanning 8 annual bloom cycles in the Ross Sea to determine the extent to which the N/P and C/P drawdown signatures reported for waters dominated by diatoms versus *P. antarctica* in the spring persist through the summer and autumn, and are repeated each year. We also report C/N/P ratios in particulate organic matter sampled in diatom versus *P. antarctica* waters. Finally,

we present data from a Ross Sea sediment trap experiment that reveals a significant difference in C/P ratios in the export flux to the deep Ross Sea water column in areas dominated by diatom versus *P. antarctica* productivity.

METHODS

To address these questions, we analyzed salinity-normalized nutrient and ΣCO_2 data collected from the upper water column (0-150 m) by CTD hydrocast during 11 separate cruises to the Ross Sea between 1990 and 1998 (Table 1). Cruises include the multi-year efforts of the Ross Sea Flux Experiment during 1990-1992 [*DeMaster et al.* 1992; *Nelson et al.* 1996], ROAVERRS during 1996-1998 [Research on Ocean-Atmosphere Variability and Ecosystem Response in the Ross Sea; *Arrigo et al.* 1999, 2000], the Ross Sea Experiment during 1994-1996 [*Smith and Gordon* 1997; *Smith et al*. 1999] and the JGOFS AESOPS program during 1996-1998 [Joint Global Ocean Flux Study Antarctic Environment Southern Ocean Process Study; *Smith et al.* 2000; *Sweeney et al.* 2000a,b]. We restricted our compilation to the Ross Sea continental shelf south of 73°30' (Figure 1). The exact study area within the Ross Sea was different between investigations, with some cruises obtaining hydrocasts primarily within the southwestern and south central Ross Sea and others focusing mainly on one, or at most a few, transects (e.g., 75°S and 76°30'S). Samples were excluded if they did not include all of the following analyses: $Si(OH)_4$, PO_4, NO_3, and NO_2. Altogether, data from 675 stations (>720 hydrocasts) were used, resulting in 8,325 discrete water samples with complete nutrient, T, and S data sets collected from above 150 m. This is the largest compilation available to date for a nutrient drawdown analysis in Antarctic coastal waters. Digital copies of the raw and processed 1990-1998 data set are available upon request from the senior author (dunbar@stanford.edu).

Hydrocast samples were sorted for diatom versus *Phaeocystis* dominance in three ways: i) pigment analysis, ii) microscopic cell counts, and iii) differential uptake of dissolved $Si(OH)_4$ and total inorganic nitrogen ($\Delta Si/\Delta TIN$).

Pigment Analyses

Suspended particles were collected by filtration of water samples through Whatman GF/F glass-fiber filters for analysis of phytoplankton pigments. Filters were immediately frozen in liquid nitrogen and stored at -80°C until they could be processed. High Performance Liquid Chromatography (HPLC) analysis of pigment composition, including chlorophylls and carotenoids, was performed using a modification of the ammonium acetate ion pairing method as described in *DiTullio and Geesey* [2002].

Phytoplankton Species Composition

For stations where HPLC pigments were available, the dominant phytoplankton taxa were determined from HPLC analysis of phytoplankton pigment composition. Two marker pigments were used for distinguishing the major taxa: fucoxanthin (FUCO) for diatoms and 19'-hexanoyloxyfucoxanthin (HEX) for *Phaeocystis antarctica* Karsten [*DiTullio et al.* this volume]. The contribution of each of the three taxa to the Chl *a* signal was determined using the approach of *Everitt et al*. [1990] as described in *Arrigo et al*. [2000].

Cell Counts

For microscopic determination of phytoplankton taxonomic composition, algae were fixed in 2% gluteraldehyde (final concentration) for several minutes and then concentrated by filtration under low pressure through a 0.2 µm Poretics filter. Filters were mounted on glass slides using Type FF non-fluorescing immersion oil and stored frozen. Cells were counted at both 400x and 1000x using epi-fluorescence microscopy.

Nutrient Analyses

Inorganic macronutrient concentrations were determined on board ship using a Technicon AutoAnalyzer II system according to the JGOFS protocols described in *Knap et al*. [1996]. Detection limits were 0.05 µmol l^{-1} for NO_3, 0.005 µmol l^{-1} for NO_2, 0.005 µmol l^{-1} for NH_4, µmol l^{-1} for PO_4 and 0.1 µmol l^{-1} for $Si(OH)_4$. Total inorganic N (TIN) was calculated as the sum of NO_3 + NO_2 + NH_4. Nutrient concentrations were converted to units of µmol kg^{-1}.

Total Dissolved Inorganic Carbon (ΣCO_2)

We use total dissolved inorganic carbon (ΣCO_2) data measured during the 6 most recent cruises used in this study. Water samples were collected from rosette bottles following JGOFS gas sampling protocols [*Knap et al*. 1996]. During ROAVERRS cruise NBP 96-6, ΣCO_2 was measured using an integrating thermal conductivity detector to measure the amount of CO_2 in a helium carrier gas stream after stripping of 5 ml seawater samples within a bubbler system upon acidification. Analysis of replicate aliquots was typically completed within several hours. During all AESOPS cruises and

ROAVERRS cruises NBP 97-9 and NBP 98-7, ΣCO_2 was measured by coulometer detection following gas stripping as described by *Johnson et al.* [1987] and *Millero et al.* [2000] for the SOMMA system, and *Chipman et al.* [1993] and *Takahashi et al.* [2000] for the LDEO system. Standardization and calibration for ΣCO_2 analysis on all cruises was performed via a combination of i) injections of calibrated volumes of pure CO_2 delivered from stainless steel gas loops and ii) frequent analysis of seawater standards supplied by Dr. A. Dickson [Scripps Institution of Oceanography; http://www-mpl.ucsd.edu/people/adickson/CO2_QC/index.html]. Based on replicate analyses, our precision (1 standard deviation) during NBP 96-6, when analyses used a thermal conductivity detector rather than a coulometer, was 11 μmol kg^{-1} or about 0.5% of an average surface water value of 2242 μmol kg^{-1}. In comparison, ΣCO_2 drawdown in the upper water column during NBP 96-6 ranged from 20 to 200 μmol kg^{-1}, or 1 to 9%. Precisions based on multiple replicate analyses of the Dickson certified reference materials during all other cruises were greater, ranging between 0.9 and 2.0 μmol kg^{-1}.

ΣCO_2 in the upper water column may be influenced by any of the following processes: net community production (NCP) of organic matter, net community precipitation of calcium carbonate, and air-sea gas exchange. Our target in this paper is biological uptake of ΣCO_2 relative to dissolved nutrients so the relative importance of non-NCP processes must be evaluated. *Sweeney* [2000a, b] found that during AESOPS, the effect of calcium carbonate precipitation/dissolution was <5% of NCP. In addition, the magnitude of air-sea CO_2 exchange was only 2 to 10% of the net summertime deficit in ΣCO_2. Given that these effects are relatively small, and that their precise estimation is difficult because of key unquantified variables, in this present paper we make no corrections to account for changes in surface water ΣCO_2 as a result of possible air-sea CO_2 gas exchange or carbonate precipitation/dissolution.

Particulate Organic Matter and Sediment Trap Samples

During ROAVERRS cruise NBP 98-7, water samples were collected using a CTD rosette. Two to 12 liters of seawater were filtered through precombusted Whatman GFC filters, air-dried, and returned to Stanford University for analysis of suspended particulate C, N, and P. Sinking particulate matter was collected during the ROAVERRS program (1996-1998) using 15-cup time-series Oregon State University multi-tracer sediment traps and McClane Lab sediment traps [*Dunbar et al.* 1998] located 50 m above the seabed at several Ross Sea locations (Figure 1). Trap samples were preserved during both mooring deployment and transit to the laboratory using a Na borate-buffered 5% formalin solution. Trap samples were split using a Folsom plankton splitter. Replicate splits were centrifuged, decanted, rinsed with deionized water, and dried. Particulate C and N in filter and sediment trap samples were analyzed using a Carlo Erba NA1500 elemental analyzer/Conflo II device and a Finnigan Delta Plus mass spectrometer. Elemental compositions were measured using the mass 44 beam intensity on the Delta Plus, calibrated against the mass 44 beam intensity of at least 5 standards that were analyzed throughout the course of each run. Relative reproducibility based on standards averaged 0.11% for N and 0.65% for C. Total particulate phosphorous was measured using ignition and acid extraction followed by spectrophotometric analysis of dissolved phosphate [*Karl et al.* 1991]. Total phosphorous in sediment trap samples was corrected for loss of phosphorous to the supernatant. Relative reproducibility based on standards was 0.78% for total particulate phosphorous.

Data Treatment

All nutrient and ΣCO_2 data were either acquired in, or converted to, units of μmol kg^{-1} and were normalized to 34.5 psu, the long-term average salinity of the Ross Sea upper water column, to remove the effects of dilution from melting sea ice or precipitation, and brine injection associated with sea ice formation. Samples were grouped according to the dominant phytoplankton taxa (either diatoms or *P. antarctica*) by either microscopic cell counts, pigment composition, or differential removal of $Si(OH)_4$ with respect to total inorganic nitrogen ($\Delta Si/\Delta TIN$). Using analyses from NBP 96-6 and NBP 97-9, where all 3 taxonomic determination methods were employed and could be compared (Figures 2 and 3), the following $\Delta Si/\Delta TIN$ criteria were selected for use with all cruise data sets: $\Delta Si/\Delta TIN < 0.90$ indicates *Phaeocystis* dominance and $\Delta Si/\Delta TIN > 2.15$ indicates diatom dominance. Samples with $\Delta Si/\Delta TIN$ values between 0.90 and 2.15 were not considered to be dominated by either taxon. Drawdown of $Si(OH)_4$ and TIN was calculated as the difference from presumed winter values as described by *Sweeney et al*. [2000a] but using the following Ross Sea deep water values as an estimate of winter water concentrations: $Si(OH)_4$ = 81.5 μmol kg^{-1}, TIN = 32 μmol kg^{-1}. All regressions slopes and standard deviations were determined using a model II reduced major axis regression, wherein the x variable is first regressed upon y, then y upon x, and the reported slope is the geometric mean of the two intermediate slopes. The reduced major axis regression method is

suitable for use where variables cannot be assigned independent and dependent attributes.

RESULTS AND DISCUSSION

The data required to investigate spatial, temporal and taxonomic differences in N/P and C/P drawdown ratios are available from 11 separate cruises to the southwestern Ross Sea between 1990 and 1998 (Table 1). In total, 8325 discrete samples satisfying our data requirements were collected from Ross Sea waters shallower than 150 m during the 1990's. Sample abundance ranges from a low of 447 samples collected during the NBP 97-3 cruise to a high of 1205 collected during NBP 98-7. Although water samples appropriate for this analysis have been collected throughout the southwestern Ross Sea region, sample density is greatest along the latitudes of 75°S and 76°30'S (Figure 1). If all field seasons are combined, monthly coverage is virtually complete between early November and the end of February, encompassing the peak of both the *P. antarctica* and diatom blooms (Table 1). Unfortunately, no nutrient data currently exist for the period between early March and mid-April, a critical time when surface waters of the Ross Sea are recharged with CO_2 and particulate organic carbon (POC) levels return to their background levels as a result of autumn particle flux events [*Langone et al.* this volume].

Modes of Taxonomic Discrimination

During the more recent cruises, HPLC pigment data were collected in conjunction with water samples, facilitating the determination of phytoplankton taxonomic composition using marker pigments appropriate to either *P. antarctica* or diatoms [*Arrigo et al*. 2000]. Earlier cruises did not have this capability, however, and phytoplankton taxonomic composition could only be determined by the degree of Si drawdown. The rationale for this approach is that waters dominated by diatoms will have a relatively high Si/N drawdown ratio ($\Delta Si/\Delta TIN$), due to the high Si requirement of diatoms, while those dominated by *P. antarctica* will exhibit a lower ratio. One obvious concern is that estimates of phytoplankton taxonomic abundance may differ between the two approaches, thereby introducing error into estimates of elemental drawdown ratios by *P. antarctica* and by diatoms.

To investigate this possibility, samples were collected during the ROAVERRS NBP 96-6 and NBP 97-9 cruises that enabled the determination of phytoplankton taxonomic abundance using three different approaches (direct cell counts, marker pigments, and $\Delta Si/\Delta TIN$ drawdown ratio; see Figures 2 and 3 for comparisons made during NBP 97-9). Because *P. antarctica* cells are small relative to diatoms, we considered surface waters to be "dominated" only if >99% of the cells counted by microscopy or >95% of the biomass assessed by pigment analysis were *P. antarctica.* Our "dominance" thresholds were somewhat lower for diatoms, >90% diatoms by cell counts and >70% diatoms for pigment analysis. $\Delta Si/\Delta TIN$ drawdown ratio cutoffs were then set at <0.90 as indicating *P. antarctica* dominance and at >2.15 as indicating diatom dominance. Although the exact values of these cutoffs are somewhat arbitrary, we note that using these values yields sufficient numbers of diatom- versus *P. antarctica*-dominated water samples during each cruise for statistical analysis and that furthermore, small changes in the cutoff values (e.g., up to 1.0, or down to 2.0) do not significantly change the calculated nutrient drawdown ratios. Discrimination into waters dominated by diatoms versus *P. antarctica* was not possible for cruises NBP 96-4A (10/17 – 11/6/96) or NBP 97-3 (4/12 – 4/30/1997) as the ranges in nutrient concentrations were greatly reduced at these times, with most samples close to winter values.

The use of pigment ratios to quantify the contribution of different phytoplankton groups requires particular care to avoid misrepresenting dominance [e.g., *Prezelin et al*. 2000]. We developed specific algorithms for *Phaeocystis*, diatoms and other minor components of the phytoplankton, with coefficients for these algorithms calculated for each cruise. Past studies have used much simpler means to distinguish between *Phaeocystis* and diatoms, such as the relative amounts of HEX and FUCO, respectively [e.g., *Goffart et al*. 2000, *Smith and Asper* 2001]. We have found that it is critical to account for the FUCO content of *Phaeocystis* before estimating diatom biomass from FUCO. For example, *Smith and Asper* [2001] defined diatom-dominated samples as those with more FUCO than HEX. Based on the algorithms and the range of coefficients determined for the ROAVERRS cruises, this definition could represent values wherein diatoms in fact accounted for as little as 38% of the total phytoplankton biomass. As shown by *Arrigo et al.* [1999, 2000], the definition of dominance needs to be more conservative (>70%) in order to distinguish taxon-specific drawdown ratios from those of a mixed population. The loose definition of "diatom-dominated" by *Smith and Asper* [2001] could explain why they estimate much higher drawdown ratios of N/P (compared to *Arrigo et al*. 1999, 2000 and *Sweeney et al.* 2000a) and report no significant relationships between mixing depth and taxonomic dominance [as reported by *Arrigo et al*. 1999, 2000, and *Goffart et al.* 2000].

In the case of both N/P and the C/P drawdown ratios during NBP 96-6 and NBP 97-9, there was no significant difference between results of the three approaches for distinguishing samples dominated by *P. antarctica* from those dominated by diatoms. During NBP 97-9, N/P drawdown ratios for *P. antarctica*–dominated waters calculated using direct cell counts, marker pigments, and the ΔSi/ΔTIN drawdown ratio as a taxonomic discriminator were within 5% of each other, being 17.7 (Figure 2a), 18.6 (Figure 2b), and 18.3 (Figure 2c), respectively. Similarly, the N/P drawdown ratios for diatom-dominated waters using these three approaches were calculated to be 11.5 (cell counts, Figure 3a), 11.7 (pigments, Figure 3b), and 10.3 (ΔSi/ΔTIN drawdown, Figure 3c), respectively, resulting in a maximum difference between estimates of 12%.

Similar results were obtained by the same comparisons made during NBP 96-6, albeit with a smaller data set (494 water samples versus 808 for NBP 97-9). Consequently, we are confident that elemental drawdown ratios calculated for early cruises (1990 – 1996) using ΔSi/ΔTIN as a determinant of phytoplankton taxonomic composition are comparable to similar estimates made during more recent cruises [e.g., *Arrigo et al*. 2000] using phytoplankton marker pigments and cell counts. However, for consistency we use the ΔSi/ΔTIN drawdown criteria to assess taxon dominance for all 11 cruises. Figures 4 and 5 show trajectories for N/P and C/P uptake ratios for the aggregated sample set from all 11 cruises. In each figure, the top panel shows all samples, the middle panel shows water samples dominated by *P. antarctica* (ΔSi/ΔTIN < 0.9), and the lower panel shows water samples dominated by diatoms (ΔSi/ΔTIN > 2.15).

N/P Drawdown Ratios

N/P drawdown ratios calculated for each of the 11 cruises to the Ross Sea (including both diatom- and *P. antarctica*-dominated waters as well as from waters with mixed phytoplankton assemblages) exhibited modest interannual variability of approximately ±15%, averaging 16.4 (range = 14.0-18.9), near the Redfield ratio of 16 (Table 2). Six of the 11 cruises exhibited aggregate N/P drawdown ratios that were within 10% of Redfield. It is not surprising, therefore, that the potential for phytoplankton taxonomic differences in the N/P drawdown ratio had not been considered previously. However, as can be seen below, these differences can be substantial.

Ratios of N/P drawdown for waters dominated by *P. antarctica* exhibited a relatively small amount of interannual variability (~13%), ranging from 17.5 to 19.7 and averaging 18.6 for the entire data set (9 cruises where taxon-specific dominance could be determined; Table 2, Figures 4 and 6a). The N/P drawdown ratio for each of these cruises exceeded the canonical Redfield ratio of 16. These high values support the initial findings of *Arrigo et al*. [1999, 2000] who, using the data from a 20-day observing period during NPB 96-6, concluded that *P. antarctica* waters had an N/P drawdown ratio significantly higher than Redfield. This aggregate data set clearly demonstrates that higher than Redfield N/P drawdown ratios are a consistent feature of the southwestern Ross Sea, and not merely a spurious event.

Because the 11 cruises covered most of the *P. antarctica* growth season between early November and the end of February, it is possible to investigate seasonal changes in the N/P drawdown ratio (Figure 6a). The earliest cruise in our data set (NBP 96-4A) took place between October 17 and November 6, 1996, before any blooms had begun [*Smith et al*. 2000]. Consequently, there was very little nutrient drawdown and the phytoplankton populations had not yet segregated into diatom and *P. antarctica* dominated regions. Not surprisingly, the low nutrient demand and lack of taxonomic dominance during this time period resulted in an N/P drawdown ratio that was 16.6, very close to Redfield (Figure 6a). However, between the middle of November and the middle of December of 1994, 1997, and 1998, the N/P drawdown ratios were dramatically higher in what were clearly *P. antarctica*-dominated waters: 18.3, 19.1, and 19.1, respectively. During the early summer, N/P drawdown ratios remained high, with values of 17.6, 18.7, and 18.3, during 1995/96, 1996/97, and 1997/98, respectively. Ratios were similarly high during the two cruises that spanned January/February (RSFE90: 18.3, and NBP 97-1: 19.7). Even as late as February (RSFE92), the N/P drawdown ratio in waters where *P. antarctica* dominated had dropped only slightly, to 17.5.

Sea ice began to re-form in the southwestern Ross Sea in late February, and by the time of the NBP 97-3 cruise in April 1997, nutrient concentrations had nearly increased to pre-bloom values. Nutrient recharging of surface waters at this time was due to both remineralization of particulate organic matter and some degree of vertical mixing between the sea surface and nutrient-rich deep waters, driven by increased winds and decreased surface stability as newly formed sea ice produced high salinity brines [*Arrigo et al.* 1998; *Langone et al.* this volume]. The relatively small nutrient depletion observed during NBP 97-3 precluded the assessment of water samples as being either diatom or *P. antarctica* dominated using the ΔSi/ΔTIN method. However, we note that the overall N/P drawdown signature observed during NBP 97-3 of 18.9 is similar to the

value of 18.4 reported for all samples collected 2 to 3 months early during cruise NBP 97-1. This high N/P ratio observed during the one autumn cruise in our data set probably reflects the maintenance of a residual and cumulative N/P drawdown signal associated with the relative dominance of *P. antarctica* in the Ross Sea through most of the 1996/1997 algal bloom period.

N/P drawdown ratios for diatom-dominated waters in the Ross Sea exhibited more interannual variability (±20%) than did those where *P. antarctica* were most abundant. Mean values for specific cruises ranged from 10.1 to 15.2, averaging 12.6 for the entire data set. In contrast to the N/P drawdown ratio for *P. antarctica*, which consistently exceeded the Redfield N/P ratio of 16, the diatom N/P drawdown ratio was always lower than the Redfield ratio for each of the 9 cruises where taxon-specific dominance could be determined. Whereas the mean N/P drawdown ratio for *P. antarctica* for the entire data set was 16% above Redfield, the mean diatom N/P drawdown ratio was 21% below Redfield. Consequently, the N/P drawdown ratio for *P. antarctica*-dominated waters nearly 50% higher than for diatoms.

The offset from Redfield in N/P drawdown ratio for diatoms is opposite that for *P. antarctica* (Figure 6a). The early NBP 96-4A cruise showed no evidence of non-Redfield N/P drawdown ratios, although as noted earlier, it was impossible to distinguish between diatom and *P. antarctica* dominated samples. N/P drawdown ratios measured between the middle of November and the middle of December had dropped, however, ranging from 10.8 to 15.2. N/P values were low for the three cruises that sampled the Ross Sea between mid-December and mid-January, with N/P drawdown ratios of 12.9, 10.1, and 10.3 during 1995/96, 1996/97, and 1997/98, respectively (Table 2, Figure 6a). By mid January-early February, there is some indication that the N/P drawdown ratio may have increased toward Redfield, with values of 13.3 and 14.3 being measured during RSFE90 and NBP 97-1, respectively. A similar N/P drawdown ratio of 13.6 was observed during a February cruise (RSFE92). This is the latest time period for which a diatom N/P ratio can be assigned, as substantial remineralization and mixing had already taken place by the April cruise.

It may be tempting to infer seasonally controlled variability in N/P drawdown ratio with a significant taxonomic component from the data shown in Figure 6a. The N/P drawdown ratio for *P. antarctica*-dominated waters appears to increase from a near-Redfield pre-bloom value to an elevated value during the spring and summer bloom. Similarly, the N/P drawdown ratio for diatoms starts out near Redfield, drops dramatically during the peak of the spring and summer bloom only to increase to near or above Redfield by autumn. These apparent patterns are largely driven by the near-Redfield N/P drawdown ratios measured in the very early spring and the above-Redfield N/P ratio observed during the April, 1997 cruise. In the case of the early spring cruise, independent N/P drawdown ratios could not be determined for either *P. antarctica* or for diatoms. It is possible, and even likely, given the distinctly different N/P ratios that have been measured whenever taxonomic discrimination was possible, that the near-Redfield N/P drawdown ratio measured in early spring was simply a consequence of sampling a mixed *P. antarctica*-diatom population, with both taxa removing N and P in their own unique ratios. In this case, the net N/P drawdown ratio from a mixed *P. antarctica*-diatom community would be expected to be closer to Redfield.

In the case of the autumn cruise, a combination of horizontal mixing, remineralization of particulates, and vertical mixing of deep waters (with their characteristic Redfield N/P ratio of NO_3/PO_4 = 32 μM/2.2 μM = 14.5) into the surface ocean had expunged any distinct taxonomic signals. However, the bulk N/P drawdown ratio still remnant at this time appears to reflect the cumulative impact of a bloom season dominated that year by *P. antarctica*. If both the spring and autumn cruises are eliminated from the N/P time series, the apparent seasonal variation associated with either diatoms or *P. antarctica* largely disappears. There are no data to suggest that either phytoplankton taxa start the growth season or end it with N/P drawdown ratios that are near Redfield. The available evidence suggests then, that the N/P drawdown ratios for diatoms and *P. antarctica* are distinctly different, and remain that way throughout the season. We note however, that relative nutrient concentrations in near-surface waters of the Ross Sea will evolve differently in any given year, driven by the relative abundance of diatom versus *P. antarctica* productivity and particle export, and their cumulative effects from spring through autumn. This year-to-year variability is also present in Figure 6, and confounds the analysis of seasonal variability. A more rigorous assessment of seasonally controlled variability in taxon-specific N/P uptake ratios may require continuous summer-into-autumn water sampling over a single annual cycle.

C/P Drawdown Ratios

ΣCO_2 data showing significant variability were collected on the most recent 6 of the 11 cruises used in this analysis, allowing assessment of temporal and taxonomic variability in the C/P drawdown ratio (Table 2, Figures 5 and 6b). Despite this more limited data set, there were a total of 2286 samples upon which to per-

form this analysis, all of which were collected in conjunction with either the ROAVERRS or the AESOPS programs. The C/P drawdown ratio for the aggregate data set averaged 120, 13% higher than the Redfield C/P ratio of 106. Values ranged from a minimum of 98 for the NBP 97-9 ROAVERRS cruise to a maximum of 144 for the NBP 98-7 ROAVERRS cruise. There were no significant differences between ratios calculated from data collected during the ROAVERRS (3 cruises, mean C/P = 120) and AESOPS (3 cruises, mean C/P = 120) programs.

The inability to determine the phytoplankton taxonomic composition of the samples (as discussed above) during the autumn Ross Sea cruise (NBP 97-3) resulted in a somewhat reduced data set on which to investigate taxonomic differences in C/P drawdown. Nevertheless, the remaining data show that the differences in the C/P drawdown ratios for diatoms and *P. antarctica* were even more extreme than was the case for the N/P ratio (Table 2). For all five cruises from which taxonomic data were available, the C/P drawdown ratio in *Phaeocystis*-dominated waters was 25-53% greater than the Redfield ratio of 106, ranging from 133 to 162, and averaging 141, for the 342 samples in the aggregate data set. In contrast, the C/P drawdown ratio for diatom-dominated waters ranged from 73 to 101 with a mean value of 83, 22% below the Redfield ratio of 106. For this calculation, we only use data from 4 cruises spanning 2 years (NBP 96-6, NBP 97-1, NBP 97-8, and NBP 97-9). We determined a C/P uptake slope for diatom-dominated waters during NBP 98-7 of 109, but this ratio was also associated with the lowest r^2 value (0.50) for any of the model II regressions used in this study. We have no ready explanation for this low correlation coefficient. However, because the levels of nutrient and CO_2 drawdown observed during NBP 98-7 were also low, which increases uncertainty in our computed slopes, we discount this result in our summaries, although we report it in Table 2.

Similar to the N/P drawdown ratio, the C/P ratio for diatom-dominated waters exhibited greater interannual variability (±17%) than did waters dominated by *P. antarctica* (±10%). Until more data become available, the cause for increased variability in diatom-dominated waters will be difficult to determine. One possibility worth exploring is that the greater variability in diatom N/P and C/P uptake ratios reflects species-level differences among the *Fragilariopsis* and *Nitzschia* species observed dominating these waters.

The data from the cruises from which taxonomic C/P drawdown data are available represent only three distinct time periods (Figure 6b): mid-November to mid-December (2 cruises), mid-December to early January (2 cruises), and mid-January to early February (1 cruise). This lack of resolution, combined with interannual variability, makes interpretation of possible seasonal trends in the C/P drawdown ratio tenuous, at best. What is most clear, however, is that there is no obvious seasonal signal in the C/P drawdown ratio in waters dominated by *P. antarctica*. The C/P uptake for ratio for *P. antarctica* starts out high in November, and remains significantly higher than the Redfield ratio of 106 throughout the duration of the bloom period, which is over by February [*Arrigo et al.* 2000]. Even during January, when the *P. antarctica* bloom is typically in a state of decline, the C/P drawdown ratio remains 53% above the Redfield C/P ratio.

A seasonal cycle of C/P drawdown for diatom-dominated waters is more difficult to interpret. With the exception of a single cruise (NBP 97-1), all of the C/P drawdown values fall between 73 and 88, well below the Redfield ratio of 106. However, data from the NBP97-1 cruise, which provide the latest point in the time series, indicate that the C/P drawdown ratio by diatoms was 101, much closer to Redfield than values from earlier cruises. The dramatic increase in the C/P drawdown ratio between December-January and January-February (Figure 6b) suggests perhaps that the diatom C/P drawdown ratio increases in early summer from well below Redfield to near-Redfield by February. This dramatic shift toward Redfield is difficult to explain and inconsistent with the temporal patterns exhibited by all other nutrient drawdown data.

However, the high C/P drawdown ratio for diatoms determined from data collected during NBP 97-1 cannot simply be dismissed as an outlier; it has a very high r^2 (0.96) despite a relatively small sample size (77). Furthermore, the NBP 97-1 cruise sampled the Ross Sea from mid-January to early February, when diatoms in many regions of the Ross Sea are at their peak abundance. It might reasonably be assumed then that these data are more representative of diatom populations than the data from the earlier cruises. There is a potential problem with this interpretation, however. The NBP 97-1 cruise followed closely after NBP 96-6, which had sampled virtually the same waters during the preceding month (plus other regions). The NBP 97-1 cruise focused its sampling entirely along 76° 30', which had been overwhelmingly dominated by *P. antarctica* during NBP 96-6. It is likely that the diatom-dominated waters sampled during NBP 97-1 were previously dominated by *P. antarctica* (whose populations had declined dramatically between the two cruises) and that a residual *P. antarctica* C/P drawdown signal remained, resulting in a C/P drawdown ratio (101) that was intermediate between that of the multiple-cruise average ratios for diatoms (83) and *P. antarctica* (141). This hypothesis is supported by the N/P drawdown ratio for

diatom-dominated waters during NBP 97-1 (14.3) which was the highest value measured during any of the ROAVERRS or AESOPS cruises and was similarly intermediate between the overall N/P drawdown ratio of diatoms (12.6) and *P. antarctica* (18.6). Taking into account our suggestion that the C/P drawdown ratio for diatoms determined from the NBP 97-1 cruise is not truly representative of diatom drawdown characteristics, the apparent seasonal variability in the ratio disappears.

It should be noted that the N/P and C/P drawdown ratios presented here for the NBP 96-6 cruise are slightly different from those reported by *Arrigo et al*. [1999]. This difference is the result of both the different method used to assign algal dominance as well as the salinity normalization procedure that was performed in the present study. The effect of salinity normalization is to increase disparity in the N/P and C/P ratios between diatom and *P. antarctica* dominated waters. This is because salinity normalization had a greater impact on diatom samples, which tended to dominate in stratified regions with substantial sea ice melt, and therefore, reduced salinity. Salinity normalization further reduced the diatom nutrient drawdown ratios relative to both Redfield and to *P. antarctica*, especially in the case of the C/P ratio because of the relatively low signal-to-noise ratio for ΣCO_2 drawdown (ΣCO_2 drawdown is always a small fraction of ΣCO_2 availability and hence is more sensitive to salinity normalization). This normalization procedure only served to strengthen the contention presented by *Arrigo et al*. [1999] that the nutrient drawdown ratios by diatoms and *P. antarctica* are dramatically different.

C/N Drawdown Ratios

The average C/N (ΣCO_2/TIN) drawdown ratio for the aggregate data set (2286 samples from 6 cruises) is 7.23±0.03, slightly higher than the Redfield ratio of 6.6. Within individual cruises or for the entire aggregate data set, there is no significant taxon-specific difference in C/N uptake ratios in diatom-dominated versus *P. antarctica*-dominated waters, similar to our observations during NBP 96-6 [*Arrigo et al.* 1999]. For all data from 6 cruises, we report C/N uptake ratios of 7.6±0.1 for *P. antarctica*-dominated waters, and 7.5±0.1 for diatom-dominated waters.

Effects of non-Redfield N/P and C/P drawdown on Particulate Chemistry and Export Ratios

The implications of the taxon-specific non-Redfield nutrient uptake ratios have been discussed previously with respect to their implementation in climate models [*Arrigo et al*. 1999, 2000] and to their likely impact on CO_2 drawdown should stratification increase in response to predicted changes in global climate [*Arrigo et al.* 1999, 2000]. Another important consideration is whether the non-Redfield nutrient drawdown ratios exhibited by *P. antarctica* and diatoms result in a signal that is exported to depth. There are two steps in assessing this link; first, establishing that non-Redfield uptake signatures are expressed within particulate organic matter suspended within the upper water column; and second, whether any observed non-Redfield signatures are then exported to the deeper water column.

First we examine nutrient ratios within particulate organic matter collected from the upper 150 meters of the water column. Although abundant data sets are available from the AESOPS and ROAVERRS programs that document C/N ratios in near-surface particulate matter, measurements of particulate phosphorous are rare. Here we use a small data set (n = 77) derived from ROAVERRS cruise NBP 98-7 wherein 2 to 11 liters of seawater were filtered and the resulting particulate material analyzed for total P, N, and organic C, as well as total chlorophyll and algal pigments. Figure 7 shows the variability in particulate phase N/P and C/P as a function of the ratio of FUCO to (FUCO + HEX), taken as a rough indicator of relative taxon dominance [*Ditullio and Smith* 1996]. Many N/P and C/P ratios in the sample set are higher than Redfield, some significantly so, as expected given the greater lability of phosphorous relative to both nitrogen and carbon during algal cell senescence and particle breakdown and degradation. Nevertheless, significant trends are apparent in both N/P and C/P ratios as a function of algal dominance. The lowest ratios of FUCO/(FUCO + HEX) imply dominance by *P. antarctica* [*Ditullio and Smith* 1996; *Smith and Asper* 2001]. For these samples, particulate N/P ratios range from 9 to 120 (Figure 8a) and particulate C/P ratios range from 70 to 870. Higher pigment ratios are associated with diatoms; these samples have N/P ratios ranging from 5 to 23 and C/P ratios ranging from 38 to 155. If we use conservative cutoff values for the FUCO/HEX ratio of <0.1 to indicate *P. antarctica* dominance and >1.5 to indicate diatom dominance [c.f. *Ditullio and Smith* 1996 and *Smith and Asper* 2001, but in light of our comments regarding the use of pigment ratios to establish dominance above] we get the following average N/P and C/P ratios for suspended particulate matter during NBP 98-7: *P. antarctica* (n = 22) N/P = 38, C/P = 259; diatoms (n = 20) N/P = 11, C/P = 73. The small size of our sample set precludes extrapolation to other years and other areas of the Ross Sea (and also prevents us from constructing a strawman P budget), however it appears that during NBP 98-7, the taxon-specific non-Redfield ratios observed via nutrient draw-

down are also seen in the suspended particulate matter, with *P. antarctica*-associated particles carrying up to 3.5 times as much N and C per mole of P than diatom-associated particles.

Next we examine evidence for export of this non-Redfield drawdown signal to depth. Table 3 shows N/P, C/P, and Si_{bio}/C ratios for the net annual sediment flux to 50 meters above the seabed at 3 locations within the Ross Sea during 1998. The two westernmost sites (Figure 1), Chinstrap and Adelie, are influenced by the western Ross Sea ice edge during much of the summer; these are areas of recurrent diatom blooms [*Smith and Nelson* 1985; *Nelson and Smith* 1986; *DeMaster et al.* 1992]. Site Gentoo is located in the central Ross Sea where a large portion of the primary production is due to non-biosiliceous algae such as *P. antarctica* [*DiTullio and Smith*, 1995; *Leventer and Dunbar* 1996; *Nelson et al.*1996]. During the 1998 sediment trap experiment, the lower ratio of biogenic Si to organic C confirms the lesser importance of diatomaceous sedimentation at Gentoo (Table 3). N/P ratios from the trapped sediment at the two diatom sites (Adelie and Chinsrap) are 18 to 12% lower than at the *P. antarctica* site (Gentoo). C/P ratios at the diatom sites are 27 to 23% lower than at the *P. antarctica* site. Again, although the data set is limited in terms of numbers of moorings, traps samples provide an integrated view of export that is currently not attainable by other methods. Near-bottom sediment traps in the Ross Sea collect material from a footprint region in the upper water column that is on the order of many 10's of km across [*Jaeger et al.* 1996] and that settled through the water column throughout the year. Our analyses of nutrient element ratios in trapped sediment samples are consistent with the export of the non-Redfield signal observed in surface waters, e.g. that organic C export fluxes per mole of P are higher in areas of *P. antarctica* dominance relative to diatoms.

SUMMARY

We have shown that taxon-specific non-Redfield nutrient drawdown ratios are a common and recurrent feature of the Ross Sea ecosystem where diatom- and *P. antarctica*-dominated communities are often segregated in time and space during the summer algal bloom. During each of 7 different spring-summer-fall bloom cycles, monitored during 11 cruises, *P. antarctica* blooms removed N at a higher ratio to P relative to diatom blooms, with the aggregate ratio averaging 18.6±0.09 and 12.6±0.04, respectively. Similarly, during a series of multi-year cruises, *P. antarctica* blooms removed C at a higher ratio to P relative to diatom blooms, with the aggregate ratio averaging 141±2 and 83±1, respectively. Furthermore, we see no evidence that this non-Redfield behavior is seasonally-dependent and it appears that these taxonomically distinct blooms each remove C, N, and P at their own non-Redfield ratios that are roughly the same both early (November) and late (February) during the annual bloom cycle.

We have also shown that during November-December 1998, non-Redfield nutrient drawdown ratios are strongly recorded in the standing stock of suspended particulate matter in the upper water column with organic matter in *P. antarctica*-dominated waters carrying up to 3.5 times as much N and C per mole of P relative to diatom-dominated waters. In addition, results from sediment traps deployed in the deep Ross Sea water column during 1998 show that the organic C/P ratio for samples dominated by input from *P. antarctica* (212) was ~30% greater than that of the diatom-dominated samples (162) whereas the N/P ratio was ~15% greater (27.4 versus 23.3, respectively). Of course, definitive conclusions cannot be drawn from a single set of water column suspended particulate matter data and 3 sediment trap moorings. Nevertheless, these data sets are consistent with our much larger nutrient uptake analysis and support the likelihood that taxonomic-controlled differences in nutrient drawdown ratios do translate into differences in elemental composition of exported particulate material. This likelihood and its potential impact on biogeochemical modeling in the Southern Ocean underscores the need for more analyses of production and export that include careful measurements of particulate and dissolved organic phosphorous so that an accurate P budget can be constructed.

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FIGURE CAPTIONS

Figure 1. Distribution of the 675 hydrographic stations in the Ross Sea used in this analysis (diamonds). Also shown are the locations of sediment trap moorings (circles) deployed during 1996-1998 (Adelie: 76° 42.4'S, 169° 1.34'E; Chinstrap: 76° 20.5'S, 165° 1.78E; Gentoo: 76° 20.3'S, 172° 56.19'E) discussed in the text.

Figure 2. Comparison of the relationship between PO_4 and TIN for waters dominated by *P. antarctica* during NBP 97-9 determined using three different methods for assessing phytoplankton taxonomic dominance. The methods include a) direct microscopic cell counts (in this case only samples with >99% *P. antarctica* cells were used to indicate dominance), b) phytoplankton accessory pigment differences (in this case only samples comprised of >95% *P. antarctica* as determined by our algorithm were used to indicate dominance), and c) the $\Delta Si/\Delta TIN$ nutrient drawdown ratio (a relative drawdown ratio of < 0.90 was used to indicate *P. antarctica* dominance). All samples were taken from the upper 150 m and normalized to a salinity of 34.5 psu.

Figure 3. Comparison of the relationship between PO_4 and TIN for waters dominated by diatoms during NBP 97-9 determined using three different methods for assessing phytoplankton taxonomic dominance. The methods include a) direct microscopic cell counts (in this case only samples with >90% diatom cells were used to indicate dominance), b) phytoplankton accessory pigment differences (in this case only samples comprised of >70% diatoms were used to indicate dominance), and c) the $\Delta Si/\Delta TIN$ nutrient drawdown ratio (a relative drawdown ratio of > 2.15 was used to indicate diatom dominance). All samples were taken from the upper 150 m and normalized to a salinity of 34.5 psu.

Figure 4. Comparison of the relationship between TIN and PO_4 for all 11 cruises for a) all water samples, b) waters dominated by *P. antarctica* (as determined by $\Delta Si/\Delta TIN < 0.9$), and c) waters dominated by diatoms (as determined by $\Delta Si/\Delta TIN > 2.15$).

Figure 5. Comparison of the relationship between ΣCO_2 and PO_4 for the 6 most recent cruises for a) all water samples, b) waters dominated by *P. antarctica* (as determined by $\Delta Si/\Delta TIN < 0.9$), and c) waters dominated by diatoms (as determined by $\Delta Si/\Delta TIN > 2.15$).

Figure 6. Time series of a) N/P and b) C/P drawdown ratios for waters dominated by *P. antarctica* (open boxes) and diatoms (gradient-filled boxes). The solid black boxes are for cruises for which no discrimination between diatom- and P. antarctica dominance was possible. The length of each box denotes the length of the cruise for which the ratio was calculated.

Figure 7. Particulate total N to total P molar ratios (a) and particulate organic C to total P molar ratios for 77 suspended particulate samples collected from the upper water column during NBP 98-7. Relative algal dominance is roughly indicated along the abscissa by the ratio of fucoxanthin (FUCO) to (FUCO + 19'-hexanoyloxyfucoxanthin (HEX)), following *Ditullio and Smith* [1996]. High ratios indicate relative dominance by diatoms. Low ratios indicate relative dominance by *P. antarctica*.

Table 1. Ross Sea data sets used for nutrient and C drawdown analysis.

Cruise	Dates	Vessel	Samples	Stations[a]
RSFE90	12 Jan 90 – 5 Feb 90	*Polar Duke*	927	100
RSFE92	5 Feb 92 – 29 Feb 92	*Polar Duke*	626	51
NBP94-6	12 Nov 94 – 5 Dec 94	*N.B. Palmer*	969	118
NBP95-8	19 Dec 95 – 15 Jan 96	*N.B. Palmer*	748	60
NBP96-4A	17 Oct 96 – 6 Nov 96	*N.B. Palmer*	533	21
NBP96-6	19 Dec 96 – 8 Jan 96	*N.B. Palmer*	494	78
NBP97-1	13 Jan 97 – 9 Feb 97	*N.B. Palmer*	803	24
NBP97-3	12 Apr 97 – 30 Apr 97	*N.B. Palmer*	447	14
NBP97-8	15 Nov 97 – 12 Dec 97	*N.B. Palmer*	765	36
NBP97-9	21 Dec 97 – 8 Jan 98	*N.B. Palmer*	808	79
NBP98-7	11 Nov 98 – 12 Dec 98	*N.B. Palmer*	1205	94
All 11 cruises			8325	675

[a]Some stations included multiple hydrocasts.

Table 2. Nutrient removal ratios for waters shallower than 150 m collected during 11 Ross Sea Cruises between 1990 and 1998.

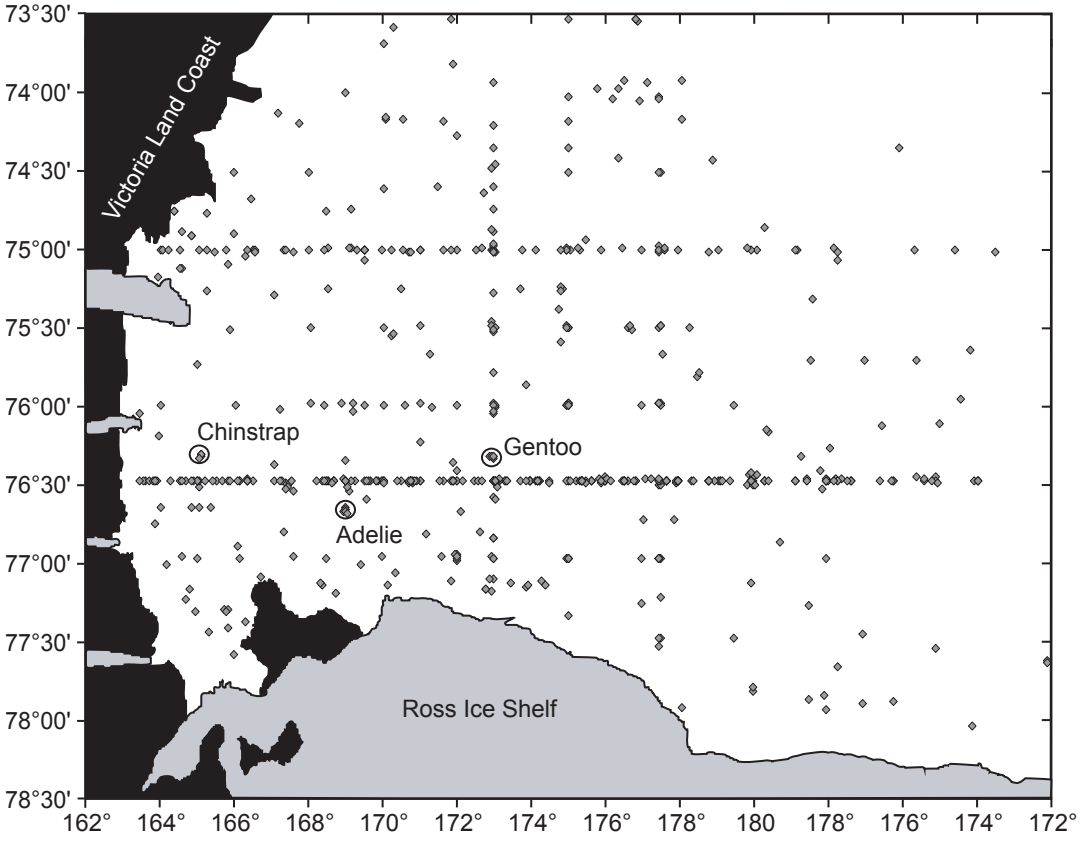
Cruise	Dates	Julian Day	N/P	$N/P_{P.\ ant.}$	N/P_{Diatom}	C/P	$C/P_{P.\ ant}$	C/P_{Diatom}
RSFE90	1/12 - 2/5/90	377	14.9±0.1	18.3±0.4	13.3±0.1			
RSFE92	2/5 - 2/29/92	401	15.1±0.1	17.5±0.1	13.6±0.2			
NBP94-6	11/12 - 12/5/94	316	17.7±0.2	18.3±0.2	15.2±0.2			
NBP95-8	12/19 - 1/15/96	354	14.6±0.1	17.6±0.5	12.9±0.1			
NBP96-4A	10/17 - 11/6/96	291	16.6±0.3					
NBP96-6	12/19 - 1/8/97	354	16.1±0.3	18.7±0.5	10.1±0.2	117±4	150±10	(88±5)
NBP97-1	1/13 - 2/9/97	378	18.4±0.1	19.7±0.3	14.3±0.1	142±2	162±7	101±2
NBP97-3	4/12 - 4/30/97	467	18.9±0.4			108±4		
NBP97-8	11/15 - 12/12/97	319	15.7±0.2	19.1±0.3	10.8±0.2	109±2	137±3	87±3
NBP97-9	12/21 - 1/8/98	355	14.0±0.1	18.3±0.3	10.3±0.1	98±2	133±3	73±2
NBP98-7	11/11 - 12/12/98	315	18.5±0.2	19.1±0.3	11.6±0.2	144±2	154±5	(109±4)*
All Cruises (by sample)			15.8±0.04	18.6±0.09	12.6±0.04	120±1	141±2	83±1
All Cruises (by cruise)			16.4±1.7	18.5±0.7	12.5±1.8	120±19	147±12	87±11

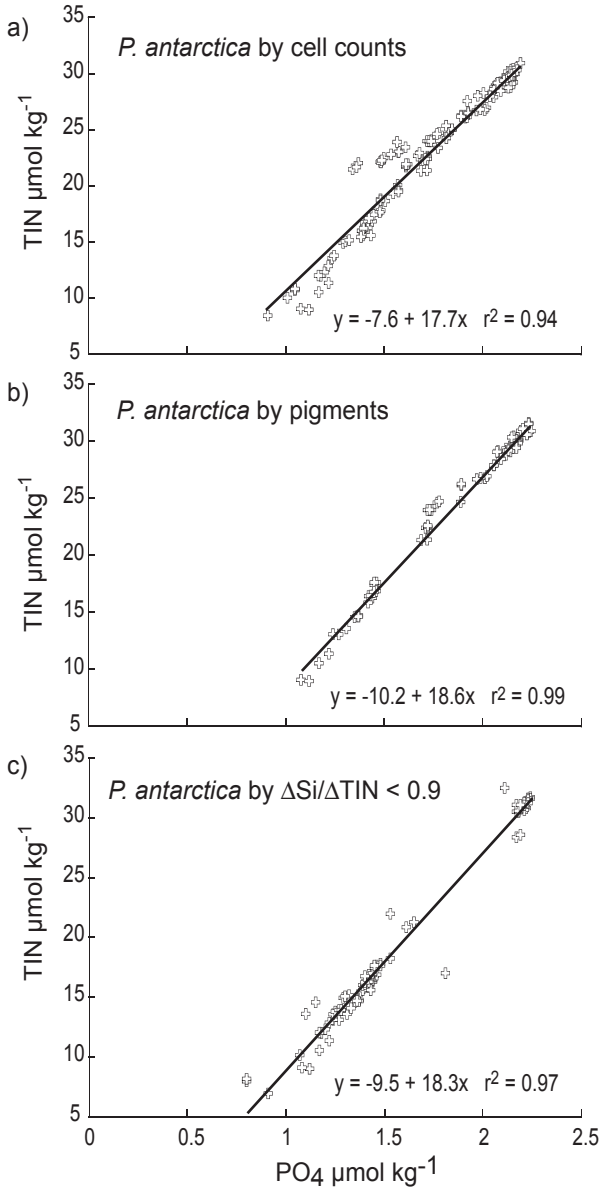
Julian day column indicates the julian day for the starting date of each cruise (with dates from January through April added to 365 for use with Figure 6). N/P and C/P ratios, calculated using a model II reduced major axis regression, are given for all samples for each cruise as well as for samples collected from waters dominated by *P. antarctica* versus diatoms. Dominance during uptake was assessed by $\Delta Si/\Delta TIN < 0.9$ for *P. antarctica* and $\Delta Si/\Delta TIN > 2.15$ for diatoms. Discrimination of water samples according to diatom versus *P. antarctica* dominance was not possible for the early spring NBP96-4A and autumn NBP97-3 cruises due to the small range in observed nutrient concentrations. The summary ratios for all 11 cruises are based on analysis of all 8,325 samples (by sample) as well as the mean of each of the cruise-specific ratios (by cruise). ± values are either one standard deviation of the slope of the model II regression, or in the case of the mean slopes determined from the values for each cruise [All Cruises (by cruise)], one standard deviation of that mean. Model II regression coefficients are above 0.8 (and are mostly above 0.9) for all slopes except those indicated in parentheses.

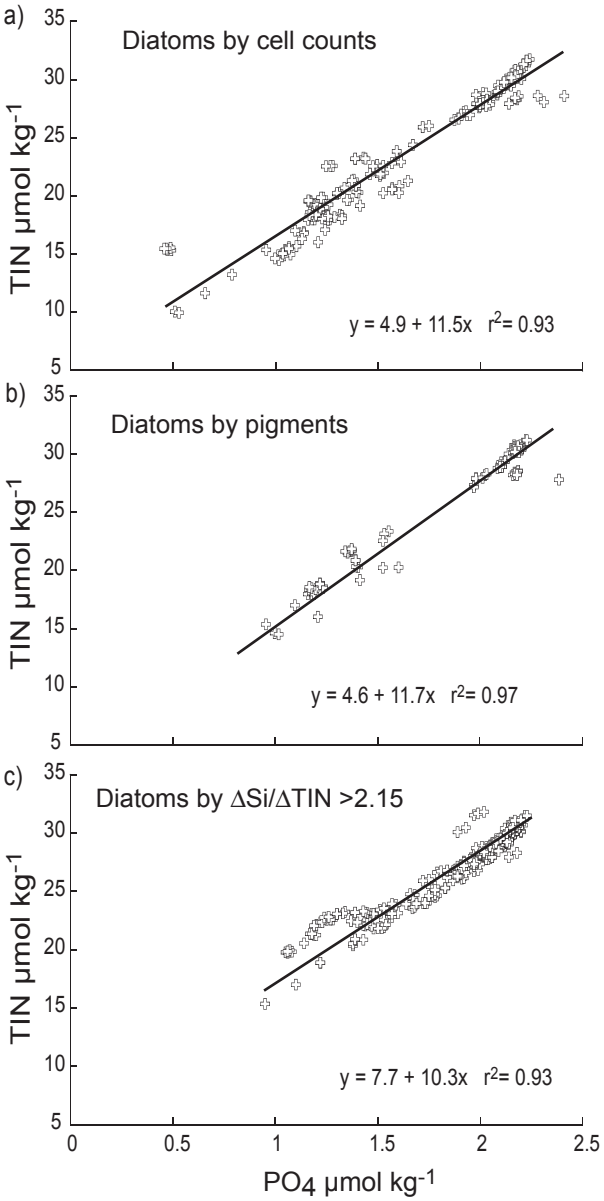
*Because of the combination of a low correlation coefficient (0.71) and low amount of ΣCO_2 drawdown during cruise NBP98-7, this value was not used in calculating the "by cruise" mean and standard deviation of C/P_{diatom} drawdown ratio.

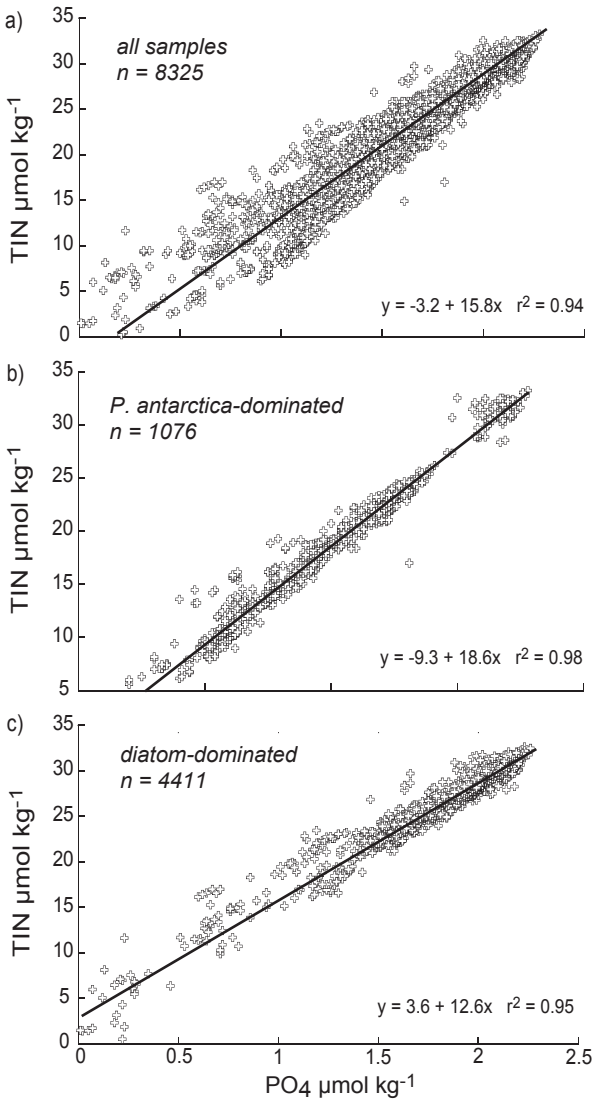
Table 3. Molar ratios of biogenic Si/organic C, total N/total P, and organic C/total P in annual sediment flux to sediment traps deployed 50 meters above the seabed in the Ross Sea between December/January 1997 and December 1998. Mooring sites Chinstrap and Adelie are in areas normally characterized by diatomaceous productivity whereas site Gentoo is in the central Ross Sea polynya, an area of recurrent *P. antarctica* blooms.

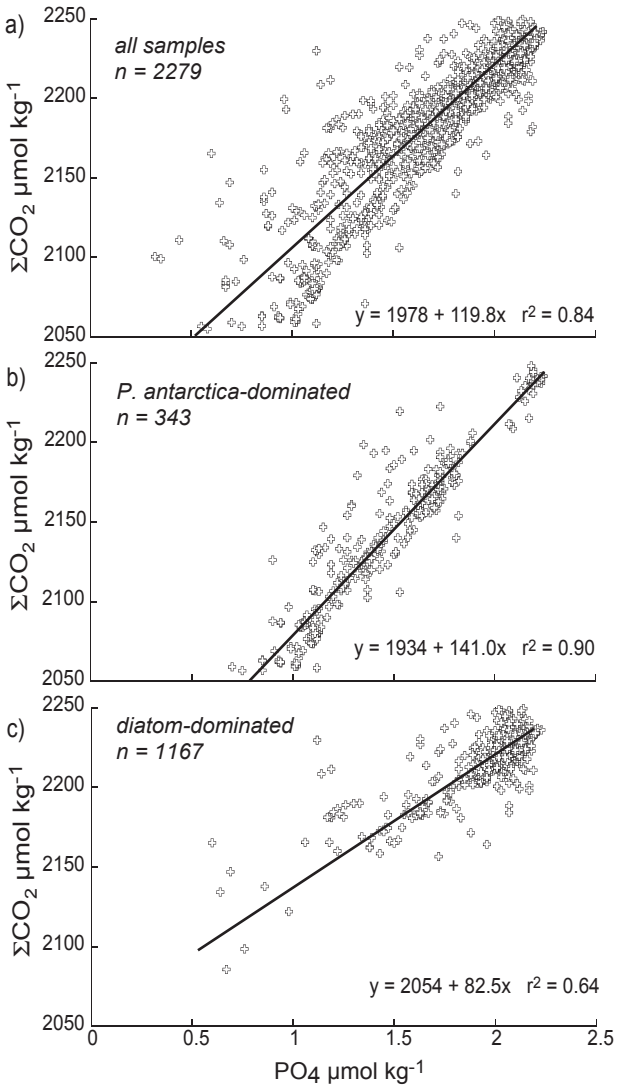
Mooring	Trap depth (m)	Si_{bio}/C	N/P	C/P
Chinstrap	763	1.53	24.3	166
Adelie	772	1.48	22.4	158
Gentoo	570	1.25	27.4	216

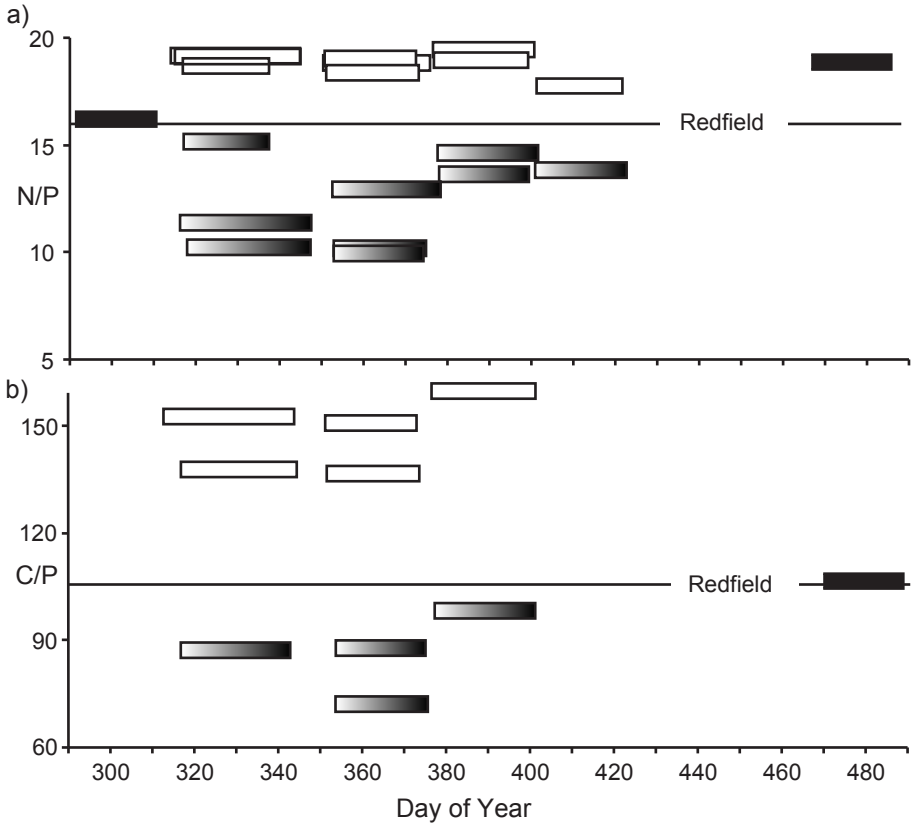

73°30'
74°00'
74°30'
75°00'
75°30'
76°00'
76°30'
77°00'
77°30'
78°00'
78°30'
162°
164°
166°
168°
170°
172°
174°
176°
178°
180
178°
176°
174°
172°
Victoria Land Coast
Chinstrap
Gentoo
Adelie
Ross Ice Shelf

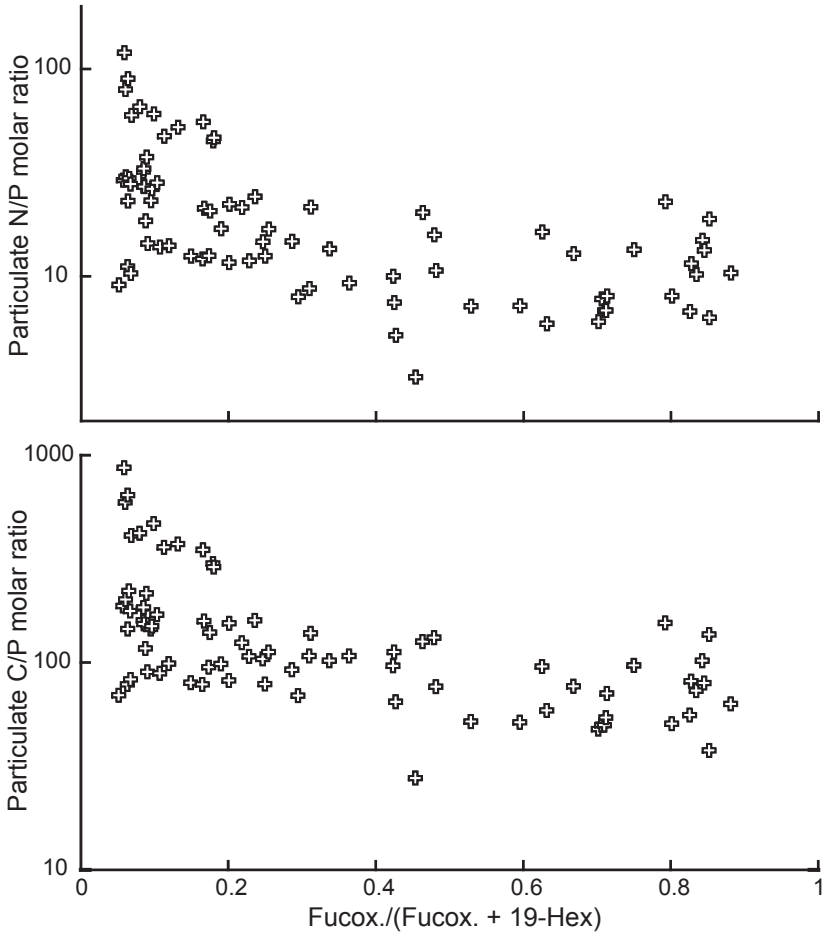

a)
P. antarctica by cell counts
TIN µmol kg^{-1}
y = -7.6 + 17.7x r^2 = 0.94
b)
P. antarctica by pigments
TIN µmol kg^{-1}
y = -10.2 + 18.6x r^2 = 0.99
c)
P. antarctica by ΔSi/ΔTIN < 0.9
TIN µmol kg^{-1}
y = -9.5 + 18.3x r^2 = 0.97
PO$_4$ µmol kg^{-1}


a)
Diatoms by cell counts
y = 4.9 + 11.5x r2= 0.93
b)
Diatoms by pigments
y = 4.6 + 11.7x r2= 0.97
c)
Diatoms by ΔSi/ΔTIN >2.15
y = 7.7 + 10.3x r2= 0.93
TIN µmol kg-1
PO4 µmol kg-1
5
10
15
20
25
30
35
0
0.5
1
1.5
2
2.5


a)
all samples
n = 8325
y = -3.2 + 15.8x r2 = 0.94
b)
P. antarctica-dominated
n = 1076
y = -9.3 + 18.6x r2 = 0.98
c)
diatom-dominated
n = 4411
y = 3.6 + 12.6x r2 = 0.95
TIN µmol kg-1
PO4 µmol kg-1
0
5
10
15
20
25
30
35
0.5
1
1.5
2
2.5


a)
all samples
n = 2279
y = 1978 + 119.8x r² = 0.84
b)
P. antarctica-dominated
n = 343
y = 1934 + 141.0x r² = 0.90
c)
diatom-dominated
n = 1167
y = 2054 + 82.5x r² = 0.64
ΣCO2 µmol kg-1
2250
2200
2150
2100
2050
0
0.5
1
1.5
2
2.5
PO4 µmol kg-1


a)
20
15
N/P
10
5
Redfield
b)
150
120
C/P
90
60
Redfield
300
320
340
360
380
400
420
440
460
480
Day of Year


Particulate N/P molar ratio
100
10
Particulate C/P molar ratio
1000
100
10
0
0.2
0.4
0.6
0.8
1
Fucox./(Fucox. + 19-Hex)