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Distribution, Partitioning and Fluxes of Dissolved and Particulate Organic Carbon, Nitrogen and Phosphorus in the Eastern North Pacific and Southern Oceans

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**Distribution, Partitioning and Fluxes of Dissolved and Particulate Organic Carbon,
Nitrogen and Phosphorus in the Eastern North Pacific and Southern Oceans**

A Thesis

Presented to

The Faculty of the School of Marine Science

Virginia Institute of Marine Science

The College of William and Mary in Virginia

In Partial Fulfillment

Of the Requirements for the Degree of

Master of Science

by

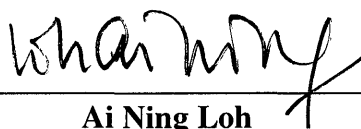
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1998

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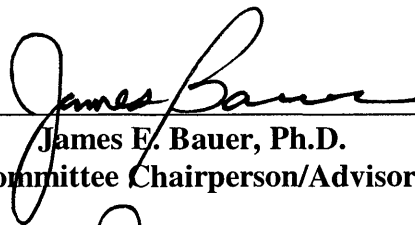
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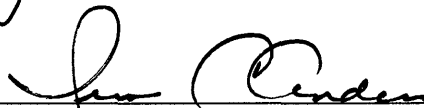


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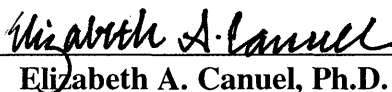
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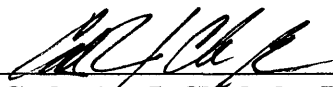
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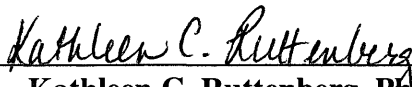
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DEDICATION

This thesis is dedicated to my parents, Loh Sun Yow and Choong Kwai Ho, for their constant love and support, and for believing in my ability to succeed.

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Abstract

The distributions of organic carbon in seawater, as dissolved and particulate organic matter (DOM and POM, respectively) have historically received much greater attention than the organic forms of nitrogen and phosphorus. This study presents the first concurrent vertical measurements of dissolved and suspended particulate organic carbon (DOC and POC), nitrogen (DON and PON) and phosphorus (DOP and POP), as well as suspended particulate inorganic phosphorus (PIP), in the open ocean water column. Water column samples were collected along a three-station transect from the continental slope to the abyssal plain in the eastern North Pacific and from a single station in the Southern Ocean. Elemental distributions in DOM and POM were established for both regions. Surface sedimentary organic matter (SOM) was measured at each location, while sinking POM was measured at the main station in the eastern North Pacific. In addition to elemental compositions, C:N, C:P and N:P ratios were also calculated to provide a first-order estimate of the stoichiometry and potential lability of C, N and P in the various organic pools.

Concentrations of DOC, DON and DOP across all study sites ranged from 35-72 μM C, 1.5-5.2 μM N and 0.073-0.229 μM P, respectively. Suspended POC, PON and POP concentrations were generally about 1-2 orders of magnitude less than the respective DOM pools. Surface sedimentary organic C, N and P ranged from 2.75-16.1 mg C gdw^{-1} , 0.51-1.83 mg N gdw^{-1} and 0.094-0.100 mg P gdw^{-1} , respectively. Sinking POC fluxes measured over a 110-day period with moored sediment traps in the eastern North Pacific ranged from 6.3-21.9 mg C $\text{m}^{-2} \text{d}^{-1}$; sinking PON and POP fluxes ranged from 0.71-2.37 mg N $\text{m}^{-2} \text{d}^{-1}$ and 0.022-0.097 mg P $\text{m}^{-2} \text{d}^{-1}$, respectively. PIP was found to comprise 10-80% of total particulate P in suspended and sinking POM and SOM.

Ratios of C:N, C:P and N:P for DOM and POM were similar and displayed similar trends with depth. The C:P and N:P ratios for both DOM and POM pools were found to be much higher than average Redfield ratios and increased with depth, suggesting selective remineralization of P relative to C and N. Ratios of C:N, C:P and N:P in SOM and sinking POM were higher than Redfield, also suggesting preferential remineralization of both N and P relative to C in these pools.

A one-dimensional vertical eddy diffusive model was used to evaluate the contributions of dissolved and suspended particulate organic C, N and P fluxes from the upper mixed layer to the abyssal oceans. Vertical DOM fluxes were found to be an important component of the total organic matter fluxes, comprising of 25-65% of the total organic matter fluxes.

**DISTRIBUTION, PARTITIONING AND FLUXES OF DISSOLVED AND
PARTICULATE ORGANIC CARBON, NITROGEN AND PHOSPHORUS IN THE
EASTERN NORTH PACIFIC AND SOUTHERN OCEANS**

Introduction and Background

The remineralization of organic matter, coupled with ocean circulation, controls the concentrations of oxygen, nutrients and CO₂ in the oceanic water column (Ittekkot, 1996). Therefore, an understanding of the distributions and fluxes of organic matter in the open ocean is critical for evaluating its role not only in the nitrogen and phosphorus cycles, but ultimately the global carbon cycle. Previous studies of seawater organic matter have focused primarily on organic carbon (C, see Appendix I for Abbreviation Key) (Benner *et al.*, 1992; Ducklow *et al.*, 1995; Druffel *et al.*, 1996, Bauer *et al.*, 1998b). The inclusion of organic forms of the major nutrient elements, especially nitrogen (N) and phosphorus (P), in the study of organic matter is important for elucidating its composition, as well as evaluating the potential biological availability of these nutrients (Jackson and Williams, 1985; Smith *et al.*, 1986; Karl *et al.*, 1993).

Dissolved nitrogen and phosphorus are essential nutrients for the growth of marine primary and secondary producers. In natural waters, these nutrient elements occur in both organic and inorganic forms, the sum of these yielding the total dissolved nitrogen and phosphorus contents, respectively. Historically, dissolved inorganic nitrogen (DIN), in the forms of nitrate (NO₃⁻), nitrite (NO₂⁻) and ammonium (NH₄⁺), was thought to be the major biochemically available form of N (Butler, 1979). More recent studies suggest that at least certain components of the dissolved organic nitrogen (DON) pool are also available as sources of N for microheterotrophic and photoautotrophic

utilization (Butler *et al.*, 1979; Jackson and Williams, 1985; Smith *et al.*, 1986; Bronk *et al.*, 1994). Similarly, in addition to dissolved inorganic phosphorus (DIP), primarily as orthophosphate (HPO_4^{2-}), dissolved organic phosphorus (DOP) may be utilized by marine photoautotrophs as well as by microheterotrophs (Jackson and Williams, 1985; Smith *et al.*, 1986; Orrett and Karl, 1987; Björkman and Karl, 1994). In addition, recent findings of rapid turnover rates of dissolved organic matter (DOM, collectively as dissolved organic C, DOC; DON and DOP) in surface ocean waters suggest that at least a portion of the DOM is turned over on short (hours to weeks) timescales (Kirchman *et al.*, 1991; Carlson *et al.*, 1994; Ducklow *et al.*, 1995; Cherrier *et al.*, 1996).

Previous studies have found that DON and DOP can comprise up to about 50% of the total dissolved N and P pools in the euphotic zone of the open ocean while inorganic forms predominate (>~90%) in deeper waters (Williams *et al.*, 1980; Jackson and Williams, 1985; Smith *et al.*, 1986; Karl *et al.*, 1993). Distributions of total dissolved and total particulate N and P have also been examined previously (Strickland and Austin, 1960; Butler *et al.*, 1979; Williams *et al.*, 1980; Boynton *et al.*, 1995). These studies found that the organic N and P pools are a significant component (~40%) of the total combined dissolved plus particulate pools, especially in surface waters. However, to date there are no published studies on the distributions of organic C, N and P among their co-occurring dissolved and particulate forms.

The understanding of the sources and molecular-level characteristics of DOC, DON and DOP is limited. Williams and Druffel (1988) surmised that the world's surface ocean DOC consists of ~15% total (free and combined) amino acids and carbohydrates, 1-2% of lipids and 20-50% of humic substances; in deeper waters, DOC consists of ~7-8%

of amino acids, carbohydrates and lipids combined and >10% of humic substances. Recent studies have found the high molecular weight (>~1kD) portion of ultrafiltered DOM to consist mainly (~50%) of polysaccharides and oligosaccharides with a small proportion of amino acids (Benner *et al.*, 1992; Vernonclark *et al.*, 1995; McCarthy *et al.*, 1996; Aluwihare *et al.*, 1997). Highly reactive polysaccharides such as carbohydrates were also found to comprise similar proportions of DOM throughout the different ocean basins (McCarthy *et al.*, 1996). Total dissolved amino acid distributions found in this same study were similar to those from unfractionated seawater, suggesting no preferential remineralization of high molecular weight DON. Aluwihare *et al.* (1997) also suggest these high molecular weight oligosaccharides were phytoplankton-derived, and that similar compositions between surface and deep water DOM indicate a significant contribution of algal-derived organic matter to total DOM concentrations over long timescales (~4000-6000 years, the turnover time for DOC, Bauer *et al.*, 1992; Druffel *et al.*, 1992).

For open ocean surface waters, previous work suggests that to obtain a Redfield (Redfield *et al.*, 1963) ratio of 16:1 for dissolved N:P, the dissolved organic fractions of the N and P pools must be included in calculating the ratio (Jackson and Williams, 1985; Takahashi *et al.*, 1985; Smith *et al.*, 1986; Karl *et al.*, 1993). These studies found that in surface waters, measured dissolved N:P ratios were always less than the Redfield ratio of 16:1, suggesting that a fraction of these dissolved nutrient elements are being “missed”. A recent study of Georges Bank DOM by Hopkinson *et al.* (1997) found that the C:N, C:P and N:P ratios of dissolved organic matter increased with depth, indicating preferential decomposition of DON and DOP. The depth-dependent increase in C:N ratios of DOM

has also been found in other studies of shallower surface ocean waters (Sambrotto and Langdon, 1993; Sambrotto *et al.*, 1993; Amon and Benner, 1994).

Although the fluxes of inorganic N and P in the marine environment have been widely studied, little is known about the fluxes of the corresponding organic N and P pools. Using a one-dimensional vertical eddy diffusion model, Carlson *et al.* (1994) found DOC export to the deep ocean to be equal to or greater than the measured sinking particulate organic C (POC) flux in the northwestern Sargasso Sea. This supports the concept that DOC is an important component of the oceanic carbon cycle, as well as a major component of organic C fluxes, and that DOC fluxes must be included in oceanic organic carbon budgets (Carlson *et al.*, 1994; Bates *et al.*, 1995; Ducklow *et al.*, 1995; Michaels *et al.*, 1995). Smith *et al.* (1986) used a similar one-dimensional Fickian model to calculate the downward fluxes of DON and DOP relative to the upward fluxes of DIN and DIP, although their model results were not compared to the total N and P fluxes in all its co-occurring forms. Therefore, by analogy, DON and DOP vertical fluxes may also be predicted to contribute significantly to the total organic N and P flux from the mixed layer to deeper waters.

This study provides the first simultaneous collection of data on open ocean DOC, DON and DOP and suspended POC, particulate organic N (PON, assumes all particulate N is organically bound; see Materials and Methods for discussion of this assumption) and particulate organic P (POP) distributions measured concurrently. Depth profiles of these chemical constituents are presented here for two different ocean regions: a three-station transect in the eastern North Pacific Ocean and a single station in the Southern Ocean. Distributions of C, N and P in selected sinking particulate organic matter (POM,

collectively as POC, PON and POP) samples, as well as in surface sedimentary organic matter (SOM, collectively as sedimentary organic C, N and P; SOC, SON and SOP) samples at these sites are also included. Elemental ratio profiles of DOM and suspended POM, as well as for selected sinking POM and surface SOM are also presented. In this study, a one-dimensional flux model similar to that of Carlson *et al.* (1994) is used to estimate the downward vertical eddy diffusive input of organic C, N and P (both dissolved and suspended particulate) from the mixed layer to the deep ocean. These fluxes are then compared to the deep sinking particulate organic fluxes of these elements.

Research Objectives

The goals and objectives of this study were based on the following three hypotheses.

1. The partitioning of C, N and P between dissolved and particulate organic matter varies as a function of water depth and oceanic regime. DOM concentrations are major fractions of the total organic matter pool relative to POM. The percentage of total organic matter comprised of DOM increase with depth and differ between the two study sites due to such factors as mixed layer productivity, organic matter remineralization, and the physical structure of the water column (including the thermocline and deep water masses).
2. C:N:P ratios in dissolved and particulate organic matter vary as a function of size class and water depth. The C:N:P ratios of POM are closer to average Redfield ratios compared to DOM ratios, although ratios for both increase with depth. This is due to preferential remineralization of N and P in DOM and POM, as well as to differences in the respective degradation processes of the different size classes of organic matter.
3. In the open ocean, dissolved organic nitrogen and phosphorus comprise a significant fraction of the total N and P downward vertical fluxes from the mixed layer. The eddy diffusive fluxes of dissolved organic nitrogen and phosphorus are an important component of total N and P fluxes from the mixed layer to the deep ocean, similar to previous findings for DOC. This results from the expected surface-to-deep ocean gradients in dissolved organic N and P.

Materials and Methods

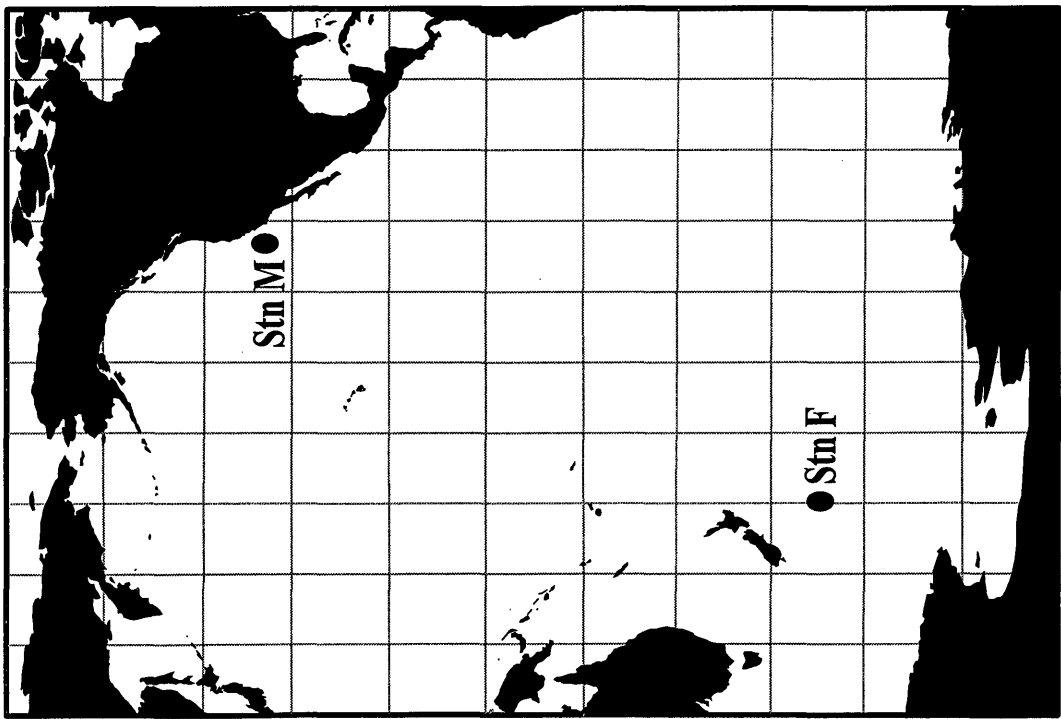
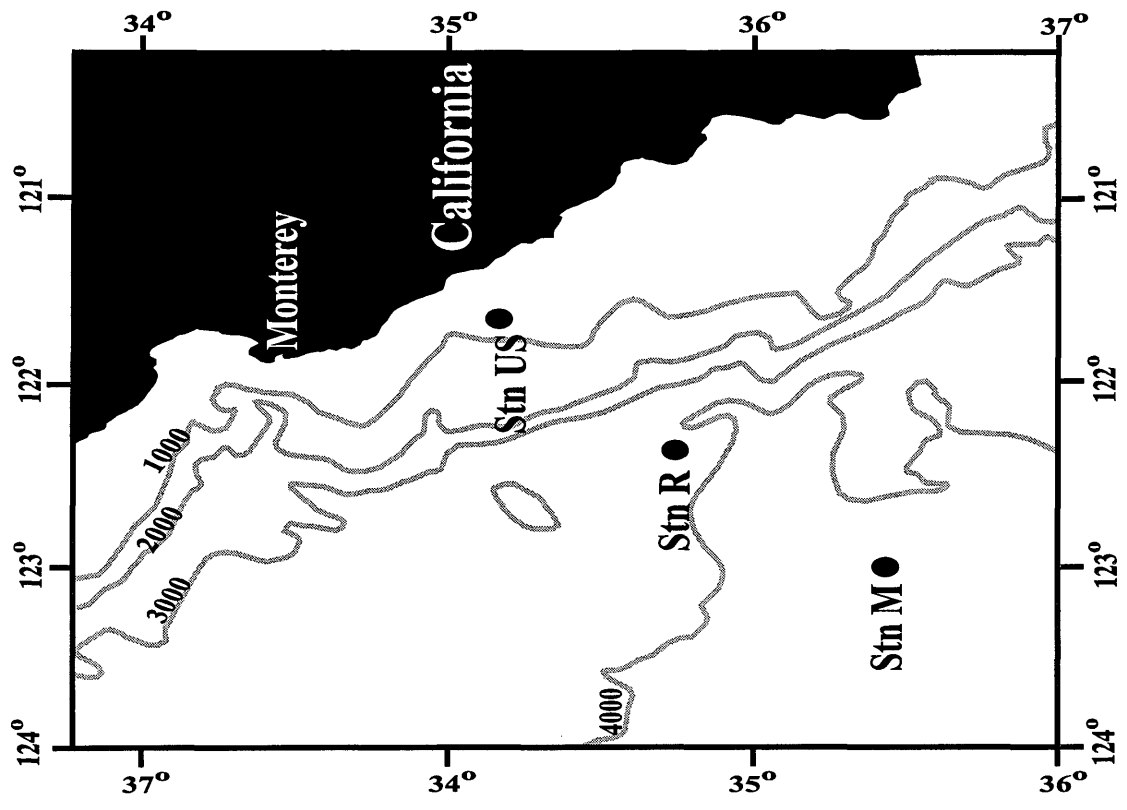
Study Sites

Water column samples were collected during one cruise to the eastern North Pacific Ocean and one cruise to the Southern Ocean (Figure 1). The main study station in the eastern North Pacific (*Station M*, 34° 50' N, 123° W, depth ~4100 m) is located about 220 km west of Point Conception, California. Station M is a time series station that has been occupied approximately every four months since 1989. It experiences a strong thermocline in the summer (June-August) that weakens during the winter months (December-February), with the vertical water column structure consisting mainly of a surface mixed layer that is separated from Pacific Deep Water by the permanent thermocline (Pickard and Emery, 1990). The major deep water mass structure of this station is not known (Pickard and Emery, 1990). Surface waters are dominated by the southward flowing California Current, with coastal upwelling of nutrient-rich deep water in spring and summer, which fuels a seasonal primary productivity maxima by late spring (Mann and Lazier, 1991; SIO, 1995; SIO, 1996), with a secondary bloom in early fall. Primary productivity in this area ranges from 0.7-1.2 g C m⁻² d⁻¹ (CalCOFI, 1995; Bauer *et al.*, 1998b). This seasonal primary productivity causes vertical “pulses” of sinking particulate organic matter from the upper mixed layer to the seafloor, with maximum fluxes during late spring and early fall (Smith *et al.*, 1994; Druffel *et al.*, 1996, Druffel *et al.*, 1998). Dissolved and suspended particulate organic C, N and P samples were collected during one cruise aboard the *R/V New Horizon* of Scripps Institution of

Oceanography, which took place from June 1 to 14, 1995 (cruise Pulse-26). Two additional stations along a transect from the deep-sea station to the upper continental slope were also occupied during this particular cruise. Station R (35° 27' N, 122° 21' W, depth ~3720 m) was on the continental rise and Station US (35° 40' N, 121° 27' W, depth ~500 m) was on the upper continental slope. Two additional cruises to Station M were also conducted in May 29 to June 7, 1996 (Pulse 30) and October 7 to 16, 1996 (Pulse 31). Results from these cruises are presented in Appendix II.

Station F is located in the Southern Ocean at 54° 00' S, 176° 40' W and has a water depth of ~5200 m. Samples were collected during a single cruise from December 11, 1995 to January 4, 1996 aboard the *R/V Melville* of the Scripps Institution of Oceanography. This area was last visited by the GEOSECS expedition in 1974 (Station 292: Broecker *et al.*, 1982). Station F is located in the region between the Antarctic Convergence to the north and the Antarctic Divergence to the south (Mann and Lazier, 1991) and does not experience the annual formation of sea ice. The surface current in this region is dominated by the westward flowing Antarctic Circumpolar Current. The vertical structure of this site is characterized by a) a weak thermocline, even in the summer (Broecker *et al.*, 1982), b) intrusion of Pacific Deep Water from ~1000-2500 m, c) intrusion of North Atlantic Deep Water from ~2500-4500 m, and d) intrusion of Antarctic Bottom Water at depths >4500 m (Reid, 1986). Primary productivity in this region has been estimated previously at ~0.2-2.8 g C m⁻² d⁻¹ (Bathmann, 1996)

Figure 1. Locations of study sites. a) Pacific and Southern Oceans and the relative positions of Stn M and Stn F. b) Eastern North Pacific, off the coast of California, with transect of Stns M, R and US.



Sample Collection

Water column samples were collected for dissolved and suspended particulate organic carbon, nitrogen and phosphorus, as well as for suspended particulate inorganic phosphorus, inorganic nutrients (N and P), salinity and alkalinity analyses. Dissolved oxygen (DO) measurements were conducted aboard the ship as soon as samples were collected. Expendable bathythermograph (XBT) temperature profiles covering a depth range of 0-1800 m were collected on the eastern North Pacific transect, while conductivity, temperature and density (CTD) profiles covering the entire water column were obtained for the Southern Ocean site.

Water samples were collected using pre-cleaned (MeOH, 10% HCl and distilled water) 12-L and 30-L Go-Flo bottles (Figure 2). The contents of the bottles were gravity-filtered immediately after collection through pre-combusted (525°C, 4 hours), 0.7 µm nominal pore size Whatman GF/F glass fiber filters into pre-cleaned glass bottles. DOC samples were collected in 1 L amber glass bottles, that had been combusted at 525°C for 4 hours, and sealed with acid-cleaned, Teflon-lined caps. DON/DIN and DOP/DIP samples were collected in 500 mL amber glass bottles, that had been soaked overnight with 10% HCl, rinsed thoroughly with 18 MΩ Nanopure water and combusted at 525°C for 4 hours, and then sealed with Teflon-lined caps. All samples were frozen immediately at -20°C until analysis.

Suspended particulate organic C, N and P samples (suspended POC, PON and POP, respectively) as well as samples for suspended particulate inorganic P (PIP) were collected using *in situ* particle (“Yentsch”) pumps (Figure 3), as described in Laird *et al.* (1967) and Druffel and Williams (1990). Seawater was pumped for varying amounts of

Figure 2. Flow diagram for the collection and analysis of dissolved constituents.

12- or 30-L

Go-flo



Cleaned w/MeOH,
dilute HCl, dist. H₂O

0.7 μm GF/F
filtration

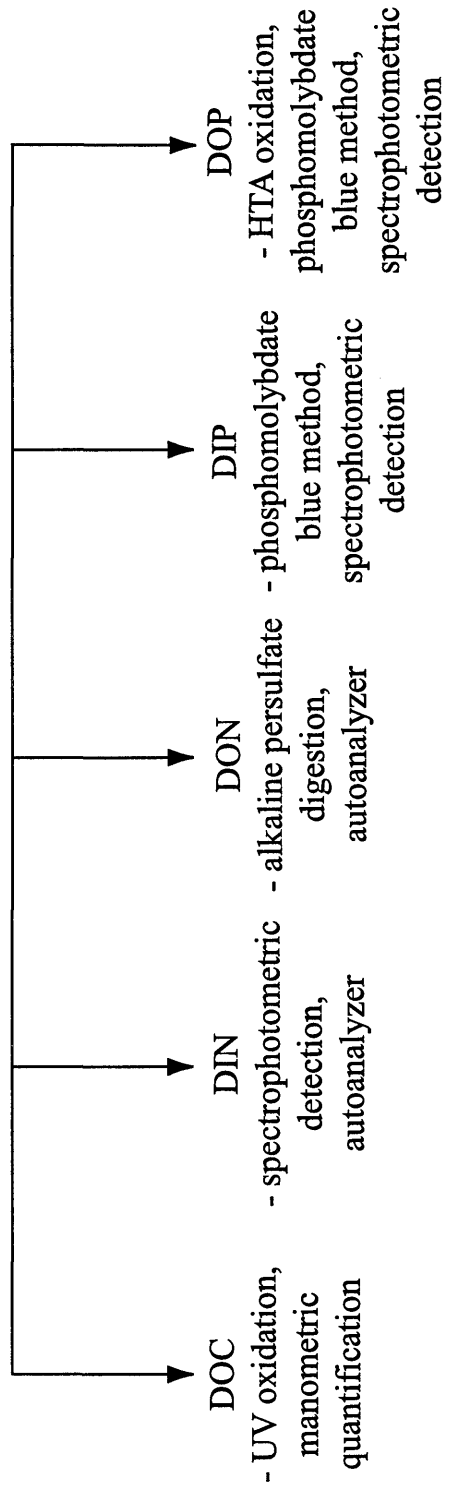
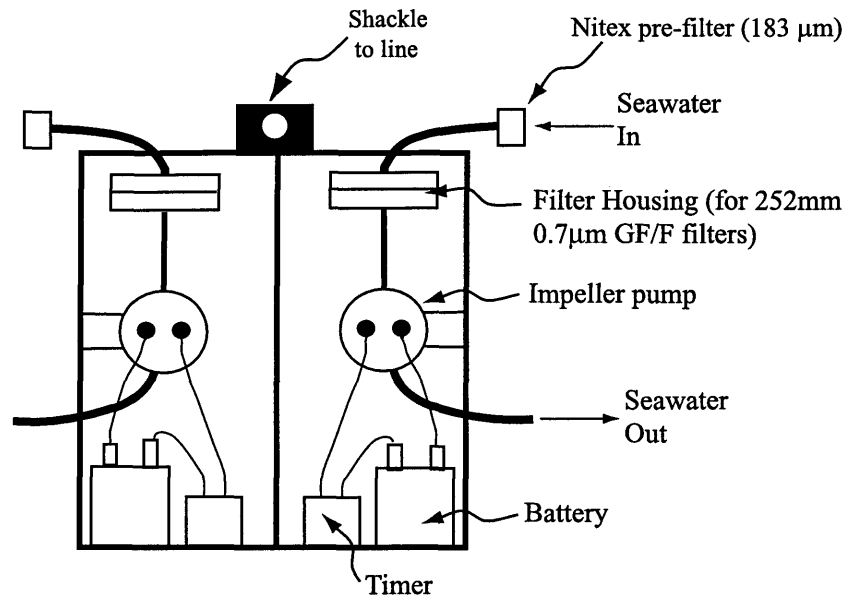
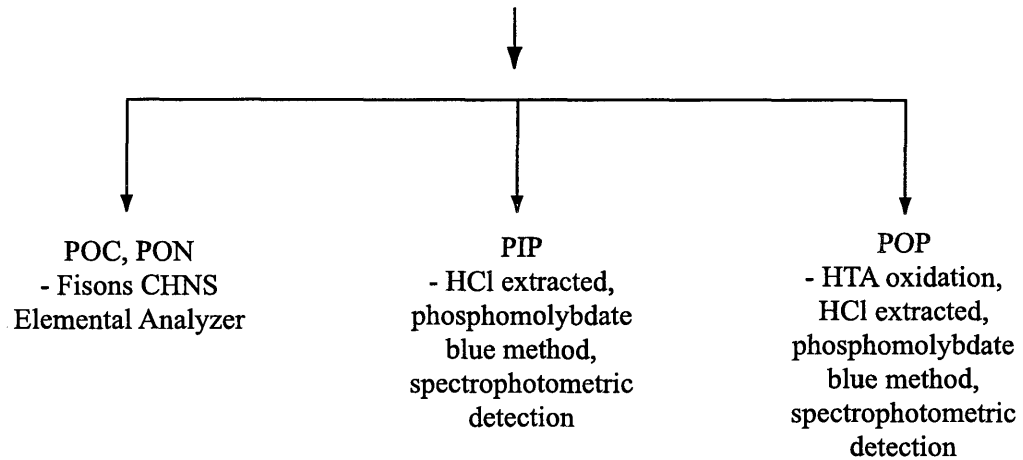


Figure 3. Schematic of the pump used for *in situ* collection of suspended POM and the methods used for the analysis of the particulate constituents in the present study.



Yentsch Pump



time through pre-combusted 0.7 μm GF/F filters. Several samples were collected on pre-combusted quartz-fiber filters (Whatman QM-A, 0.8 μm pore size). Samples collected on QM-A filters were only analyzed for PIP and POP. Pumping times ranged from 2-4 hours for shallow and mesopelagic depths (25-900 m), and from 6-8 hours for greater depths (900-5100 m). Volumes of seawater pumped at each deployment ranged from several hundred to several thousand liters, depending upon pumping times and particle load. Upon recovery of the pumps, the filters were removed from the PVC filter housings, folded and placed in pre-combusted glass jars, and frozen at -20°C until analysis. Volumes pumped for each sample are listed in Table 3 and Table 6 (for eastern North Pacific and Southern Ocean, respectively).

Sinking particulate organic C, N and P samples (sinking POC, PON and POP, respectively), as well as sinking particulate inorganic P (sinking PIP) samples, were collected at Station M in the eastern North Pacific (but not at Station F in the Southern Ocean) as part of an ongoing study of particle fluxes at this station (Baldwin *et al.*, 1998; Druffel *et al.*, 1998). Sinking particles were collected using moored sediment traps at 650, 600 and 50 meters above bottom (mab). Details of trap design and deployment are as described in Smith *et al.* (1994) and Druffel *et al.* (1996). The traps consist of funnel cones (Teflon-coated fiberglass, 120 cm high, 57 cm diameter) with an effective mouth opening of 0.25 m^2 (Bruland *et al.*, 1981). Each trap was equipped with an assembly of sequencing collection cups at the bottom of the cone. Cups were filled with pre-filtered water obtained from the deployment depth and poisoned with a filtered HgCl_2 solution (final concentration = 3.0 mM). Samples were collected every 10 days at each depth for a total of 4 months. Particles collected in each cup were then concentrated by gentle

vacuum filtration of the ~700 mL trapped liquid onto pre-combusted QM-A filters (45 mm diameter, 0.8 μm pore size) and frozen in pre-combusted aluminum foil at -20°C .

Surface sediments from Station US and Station F were collected using a 1.8-meter long gravity corer (2 inch diameter core liner). Cores were sectioned immediately upon recovery into 1-4 cm thick layers and frozen in pre-combusted glass jars at -20°C . For Station US, the surface sample collected consisted of the top 1 cm of the core while for Station F, the surface sample consisted of a homogenized sample of the top 3 cm.

Sample Analysis

A major challenge in measuring DON and DOP concentrations in seawater is the difficulty in achieving precision and accuracy with the methods available. As these components cannot be measured directly, the concentrations of DON and DOP are calculated as the difference between the total dissolved N and P pools (TDN and TDP) and the dissolved inorganic N and P pools (DIN and DIP), such that:

$$[\text{DON}] = [\text{TDN}] - [\text{DIN}] \quad (\text{Eq. 1})$$

$$[\text{DOP}] = [\text{TDP}] - [\text{DIP}] \quad (\text{Eq. 2})$$

The total dissolved nitrogen and phosphorus in seawater are oxidized and then hydrolyzed to their inorganic forms for analysis, usually by spectrophotometric techniques. In order to obtain good precision and accuracy in measuring DON and DOP concentrations, the methods used for oxidizing the DON and DOP to their predominant inorganic forms (nitrate and orthophosphate) must be efficient enough so that all dissolved organic species of nitrogen and phosphorus are quantitatively oxidized. Because of these methodological concerns and the difficulties involved with the oxidation

of N- and P-containing compounds, especially recalcitrant species (Walsh, 1989; Ridal and Moore, 1990), few studies have examined the distributions of the dissolved organic pools of these nutrient elements.

As a check on the efficiencies of the N and P oxidation methods, random natural samples, spiked with known concentrations of inorganic and organic N and P, were analyzed as periodic checks on total N and P recoveries. Also, known concentrations of 8-9 model DON and DOP compounds each, were oxidized using those same methods used for sample analyses to test the recoveries of the oxidation methods (Appendix II).

DOC concentrations were quantified by UV oxidation of the seawater samples as a routine part of the measurement of natural abundance ^{14}C in DOC (Bauer *et al.*, 1998b). Samples were placed in optical-grade quartz tubes, acidified to pH 2-3 with 85% H_3PO_4 , sparged free of inorganic carbon for 45 minutes with ultra-high purity nitrogen and saturated with ultra-high purity oxygen. Sample were then irradiated for 120 minutes with a 2400 W, medium pressure mercury arc UV lamp equipped with a reflector assembly (Canrad-Hanovia Co., Newark, NJ.). Following the oxidation step, the CO_2 produced was purged from the quartz tube using ultra-high purity nitrogen and transferred to a vacuum extraction line. A KIO_3^- trap was used to remove the Cl_2 gas and the CO_2 was cryogenically purified and quantified using an absolute pressure gauge (MKS Corp.) (Williams and Druffel, 1987; Druffel *et al.*, 1992; Bauer *et al.*, 1998b). Analytical error of this method averaged $\pm 1 \mu\text{M C}$.

DON samples were analyzed using the wet alkaline persulfate oxidation method as described in Koroleff (1983), followed by nitrate analysis by a Skalar nutrient autoanalyzer. Duplicate 10 mL aliquots of samples were sealed in 20 mL pre-combusted

(525°C, 4 hours) glass ampoules containing 1 mL of the 5% alkaline persulfate oxidizing reagent, and then boiled under pressure in an autoclave for 1 hour. All nitrogen species in the sample were oxidized to nitrate, which was subsequently quantified on the Skalar nutrient autoanalyzer. The dissolved inorganic N species (NO_3^- , NO_2^- and NH_4^+) in unoxidized aliquots of the samples were also analyzed by autoanalyzer. Concentrations of DON were obtained by taking the difference between the TDN concentrations in the oxidized aliquot and the total inorganic N species concentrations (DIN) in the unoxidized aliquot (Eq. 1). Average standard deviation of replicate samples using this method was $\pm 0.25 \mu\text{M N}$.

DOP was oxidized using a high-temperature ashing (HTA) oxidation method as described in Solorzano and Sharp (1980), followed by spectrophotometric quantification of the total orthophosphate produced. Duplicate aliquots of 10 mL of each sample were dried with 0.2 mL additions of 0.17 M MgSO_4 solution in pre-cleaned (10% HCl soaked overnight, rinsed with Nanopure water and baked at 525°C for 4 hours) scintillation vials. The samples were then ashed at 500°C for 2 hours, followed by heating with 3.0 mL of 0.75 M HCl for 20 minutes at 80°C. The hydrolysis was completed by adding 7.0 mL of Nanopure water to the samples and heating it for another 10 minutes at the same temperature. The total orthophosphate concentration was then quantified using a Spectronic Model 401 single-beam UV/VIS spectrophotometer and a 10-cm pathlength cell, with the phosphomolybdate blue method as described by Koroleff (1983). The DIP concentrations in unoxidized aliquots of the samples were also analyzed spectrophotometrically using the same method. DOP concentrations were obtained by taking the difference between the TDP concentrations in the oxidized aliquot and the DIP

concentrations in the unoxidized aliquot (Eq. 2). Average standard deviation of replicate samples using this method was $\pm 0.01 \mu\text{M P}$.

Suspended and sinking POC and PON, as well as SOC and SON were measured using a Fisons EA-1108 Elemental Analyzer. Samples were prepared according to the method as described in UNESCO (1994). For suspended POC and PON samples, duplicate subcores of 14.57 mm diameter were taken from each of the 147 mm GF/F filters and fumed with concentrated HCl in a desiccator to remove carbonates prior to analysis. For sinking POC and PON samples, the mass of the material collected on the QM-A filters was weighed and subsequently scraped off the filter. 50-300 mg of this material was prepared and analyzed as above. SOC and SON were analyzed in a similar manner. All particulate N in this study is assumed to be organically bound, although sorption of NH_4^+ onto clay particles in certain sediments has been found to occur (Ruttenberg and Goñi, 1997), which may lead to slight overestimate of SON. However, in the water column, NH_4^+ concentrations are expected to be minimal, and ionic strength considerations result in competition with NH_4^+ for available sorption sites on suspended and sinking particles. Therefore, the validity of the assumption that all particulate N is organic in nature is more likely to hold in the water column. Average standard deviation of replicate samples using this method were approximately $\pm 1 \mu\text{g C L}^{-1}$ and $\pm 0.1 \mu\text{g N L}^{-1}$.

Suspended and sinking POP, as well as SOP samples were oxidized using a high-temperature ashing oxidation method as described by Aspila *et al.* (1976), and then analyzed spectrophotometrically for orthophosphate using the phosphomolybdate blue method. Duplicate subcores of 14.57 mm diameter from the 147 mm GF/F filters were

taken as for suspended POC and PON analysis. Phosphorus on the filters was extracted using 30 mL of 1 M HCl prior to and after high-temperature ashing the particles at 550°C for 1.5 hours, and then analyzed as for orthophosphate. The orthophosphate content of the HCl extract before dry ashing gives the PIP (and sedimentary inorganic P, SIP) content while the orthophosphate content of the HCl extract after dry ashing gives the total particulate P and total sedimentary P (TPP and TSP, respectively) content. POP and SOP content is then determined by the difference of these two pools. However, this PIP pool could also include potentially labile organically-bound P due to the strong acid used for its analysis. In their evaluation of the hydrolysis of DOP compounds in acid, Monaghan and Ruttenberg (submitted) found that there is negligible hydrolysis of DOP compounds in 0.1M HCl acid. Average standard deviation of replicate samples using this method was approximately $\pm 0.01 \mu\text{g P L}^{-1}$ for both PIP (and SIP) and POP (and SOP).

Results

Distributions of DOM, Suspended POM and SOM

Eastern North Pacific Ocean

The XBT temperature profiles for Stations M, R and US are shown in Figure 4. Surface temperature decreased from offshore to onshore and the temperature range over the entire water column also decreased (Table 1). The water column at Station M is characterized by a strong seasonal thermocline at ~70 m and a permanent thermocline at ~200-800 m. Water column stratification intensifies going offshore from Station US to Station M, as a result of the decreasing influence of upwelling. The oxygen minimum occurs at 722 m, 681 m and 483 m for Stations M, R and US, respectively. Discrete temperature data from reversing thermometers, salinity and oxygen data are given in Table 1.

Concentrations of DOC at Stations M, R and US (Figure 5a, Table 2) ranged from a nearly constant background value of ~37 $\mu\text{M C}$ below the mixed layer, to surface maxima of 56-72 $\mu\text{M C}$, with surface DOC concentrations decreasing going onshore.

Concentrations of DON at all three stations (Figure 5b, Table 2) ranged from 1.5-4.5 $\mu\text{M N}$, while DOP concentrations (Figure 5c, Table 2) ranged from 0.073-0.229 $\mu\text{M P}$.

Concentrations DON and DOP showed similar depth and on-shore, off-shore gradients as for DOC, although these gradients were less pronounced for DON and DOP profiles. At

Figure 4. XBT temperature profiles (0 - 1800 m) for a) Stn M, b) Stn R, and c) Stn US in the eastern North Pacific transect.

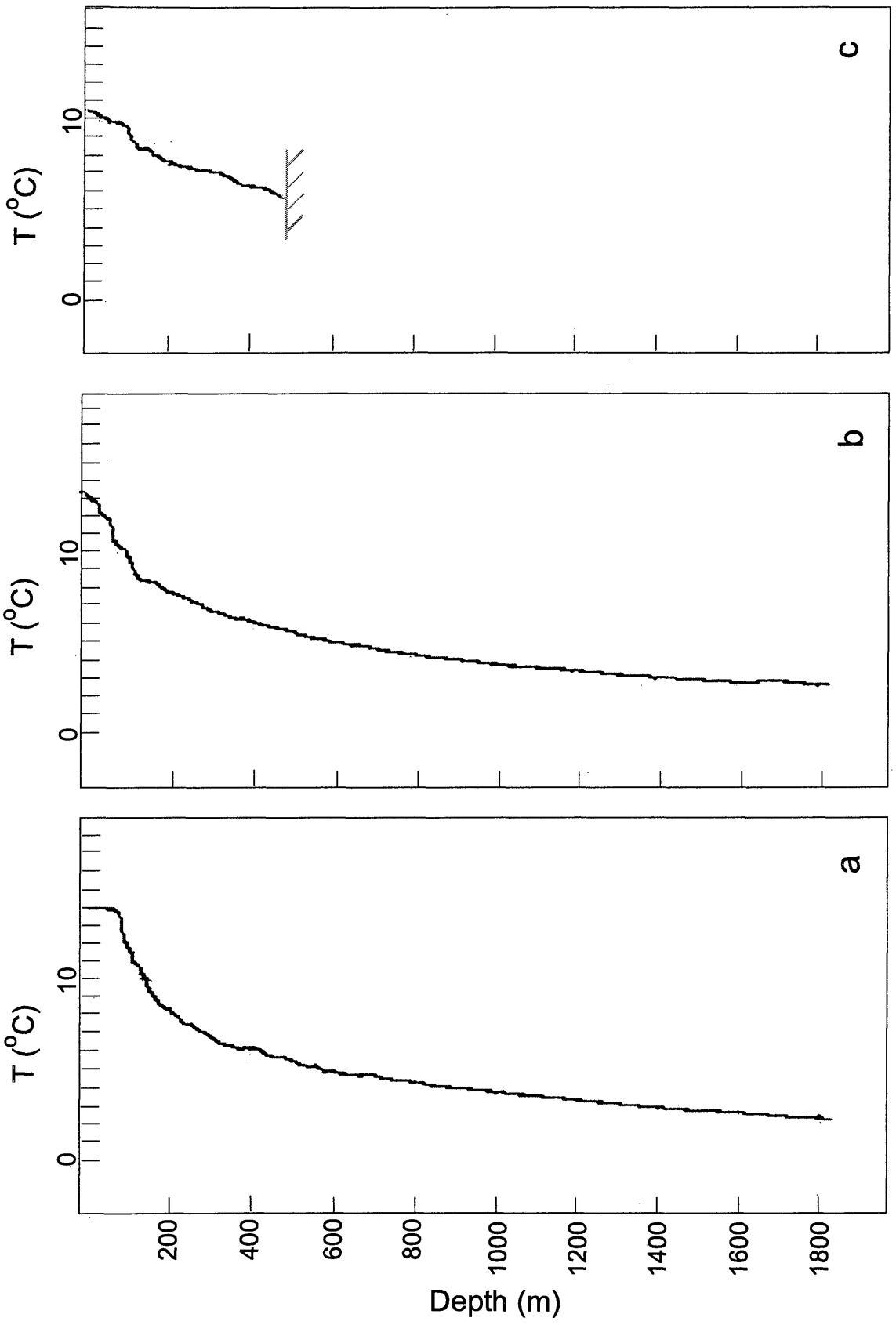
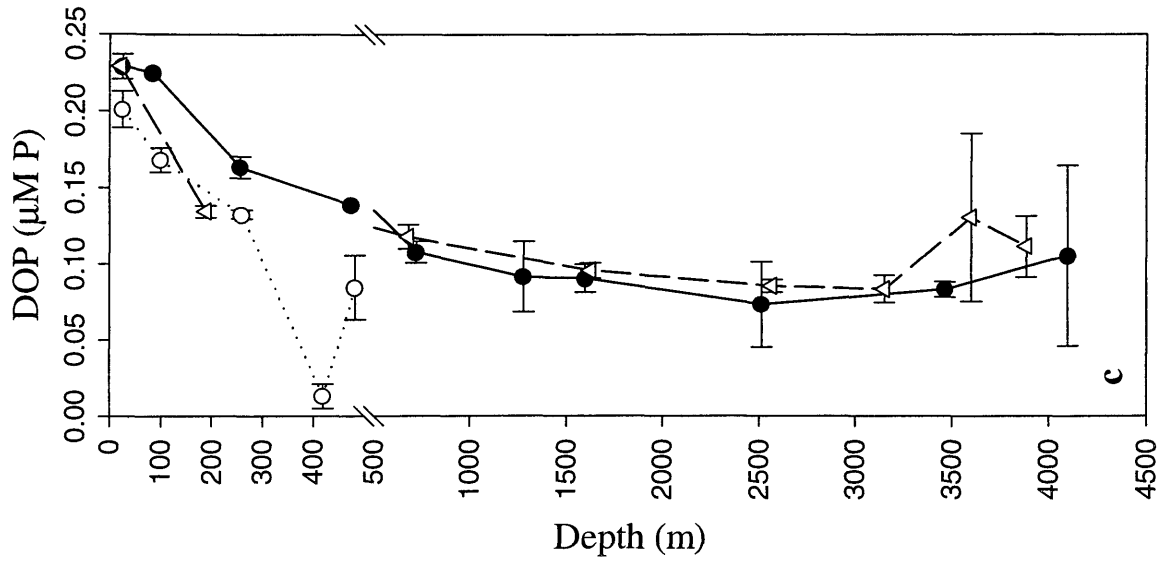
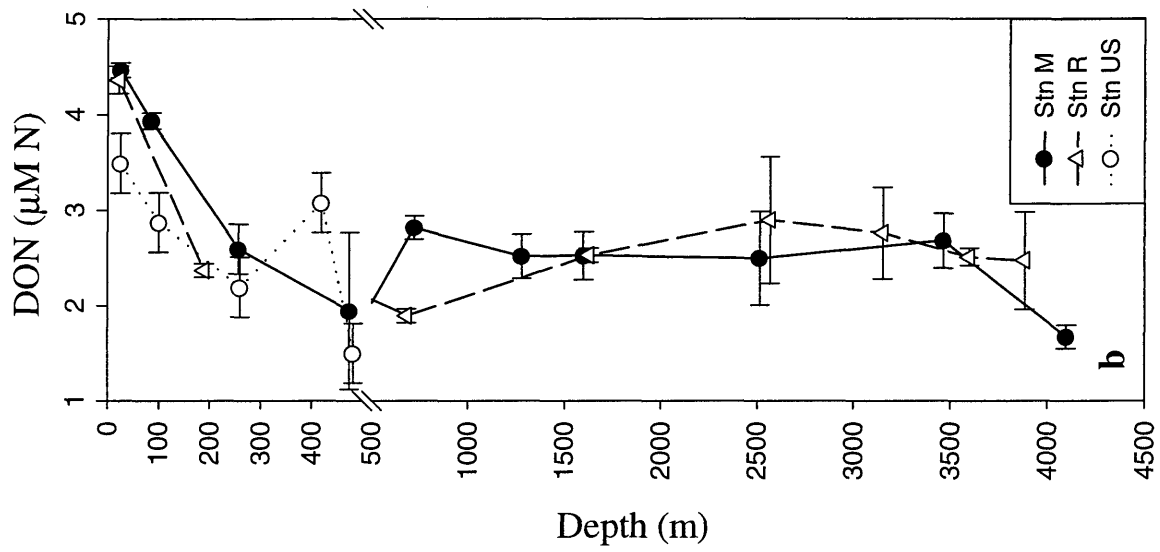
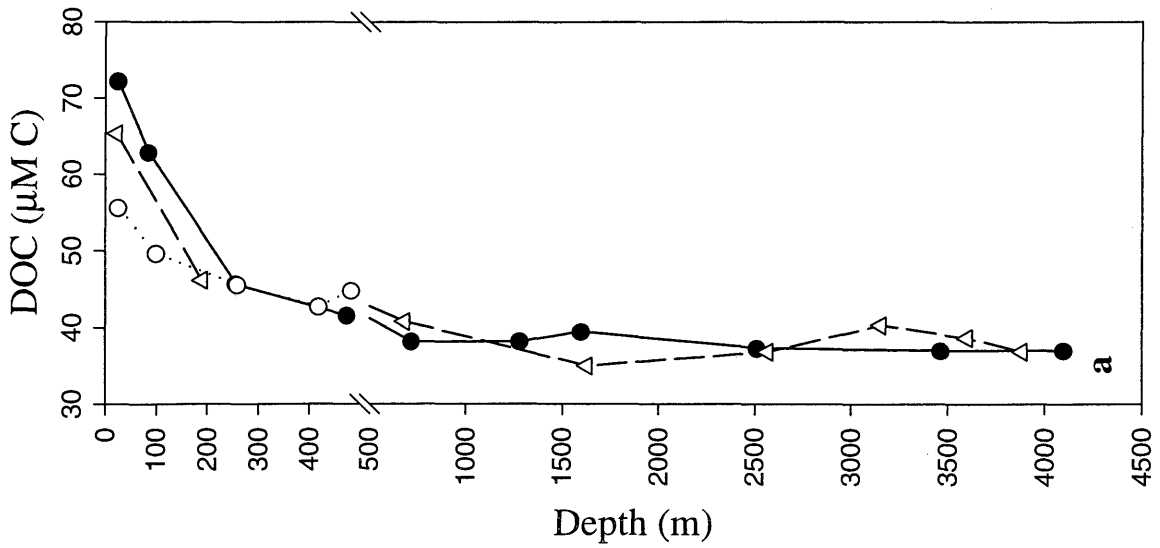


TABLE 1. Hydrographic data for Eastern North Pacific

Depth (m)	Temperature (°C)	Salinity	Oxygen (mL L ⁻¹)
<i>Station M</i>			
25	13.9	32.814	6.16
85	13.6	33.098	5.70
256	7.49	33.992	2.64
475	5.95	34.161	0.70
722	4.94	34.326	0.13
1282	3.26	34.497	0.77
1600	-	34.556	0.90
2515	1.77	34.652	3.30
2515	-	-	-
3466	1.52	34.677	3.12
4097	1.50	34.690	3.01
<i>Station R</i>			
22	12.9	33.187	6.46
189	8.08	33.992	2.70
681	4.76	34.336	0.30
1628	2.63	34.571	1.26
2568	1.77	34.657	2.68
3152	1.63	34.663	3.01
3601	1.60	34.666	3.11
3884	1.57	34.686	3.34
<i>Station US</i>			
25	10.5	33.442	4.93
100	10.2	33.824	3.14
259	7.47	34.126	1.62
419	6.04	34.188	0.73
483	5.82	34.213	0.70

Figure 5. Water column profiles of a) DOC, b) DON, and c) DOP concentrations for the Eastern North Pacific transect. Symbols used in all figures are: Stn M - filled circles; Stn R - open circles and Stn US - open triangles. Note break in depth axes at 500m. Error bars plotted for DON and DOP were ± 1 SD of duplicate measurements. Analytical error for DOC was $\pm 1 \mu\text{M C}$.



Stn US, there was a sudden increase in near-bottom DOP concentrations. This was observed for DOC concentration although not for DON concentrations.

Concentrations of DIN and DIP (Figure 6, Table 2) showed strong surface depletions ($0.60 \mu\text{M N}$ and $0.262 \mu\text{M P}$, respectively), increasing to maximum concentrations ($42 \mu\text{M N}$ and $3.18 \mu\text{M P}$, respectively) at the depth of O_2 minimum, decreasing to constant background concentrations throughout the rest of the water column. Surface concentrations of DIN and DIP increased going onshore from 0.60 - $16 \mu\text{M N}$ and 0.262 - $1.38 \mu\text{M P}$, respectively.

Suspended POC, PON and POP concentrations at the three eastern North Pacific stations ranged from 1.03 - $69.2 \mu\text{g C L}^{-1}$, 0.17 - $12.8 \mu\text{g N L}^{-1}$ and 0.016 - $1.16 \mu\text{g P L}^{-1}$, respectively, decreasing by ~ 100 -fold with depth (Figure 7a-c, Table 3). Suspended POM, however, did not show the same horizontal gradient as DOM for surface concentrations along the transect. Suspended PIP profiles (Figure 7d, Table 3) for the eastern North Pacific transect were similar to the suspended POP profiles (range: 0.012 - $0.584 \mu\text{g P L}^{-1}$) and comprised $\sim 50\%$ of the total suspended particulate P. There was also no apparent horizontal gradient with respect to surface concentrations of suspended PIP along this transect.

Surface (0-1 cm) concentrations of SOC, SON and SOP (Table 3) for Station US were $16.1 \text{ mg C gdw}^{-1}$ (gdw = g dry weight), $1.83 \text{ mg N gdw}^{-1}$ and $0.100 \text{ mg P gdw}^{-1}$, respectively. The surface concentration of SIP for this station was $0.761 \text{ mg P gdw}^{-1}$, which comprised of $\sim 88\%$ of the total sedimentary P. Surface SOC concentrations for Stns M and R listed in Table 3 were taken from a concurrent study by Druffel *et al.*

Figure 6. Depth profiles of a) DIN, and b) DIP concentrations for the eastern North Pacific transect. Error bars plotted for DIN and DIP were ± 1 SD of duplicate measurements.

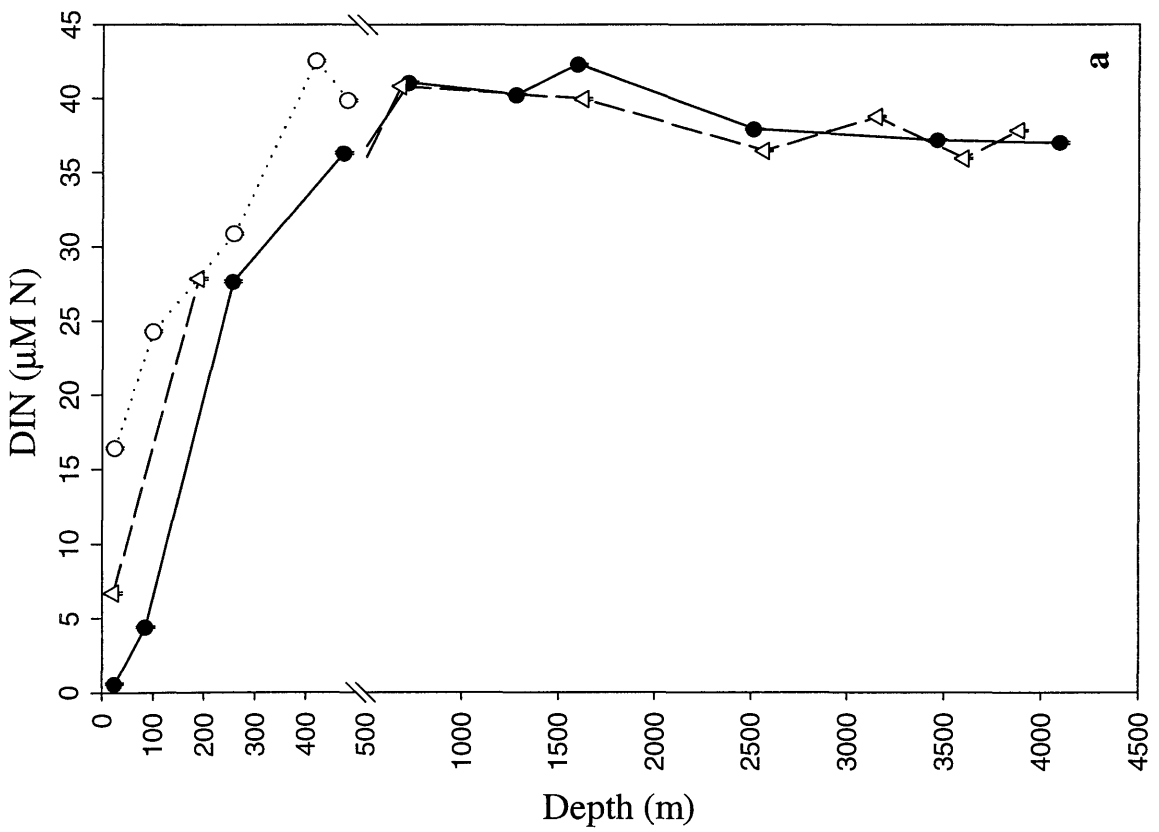
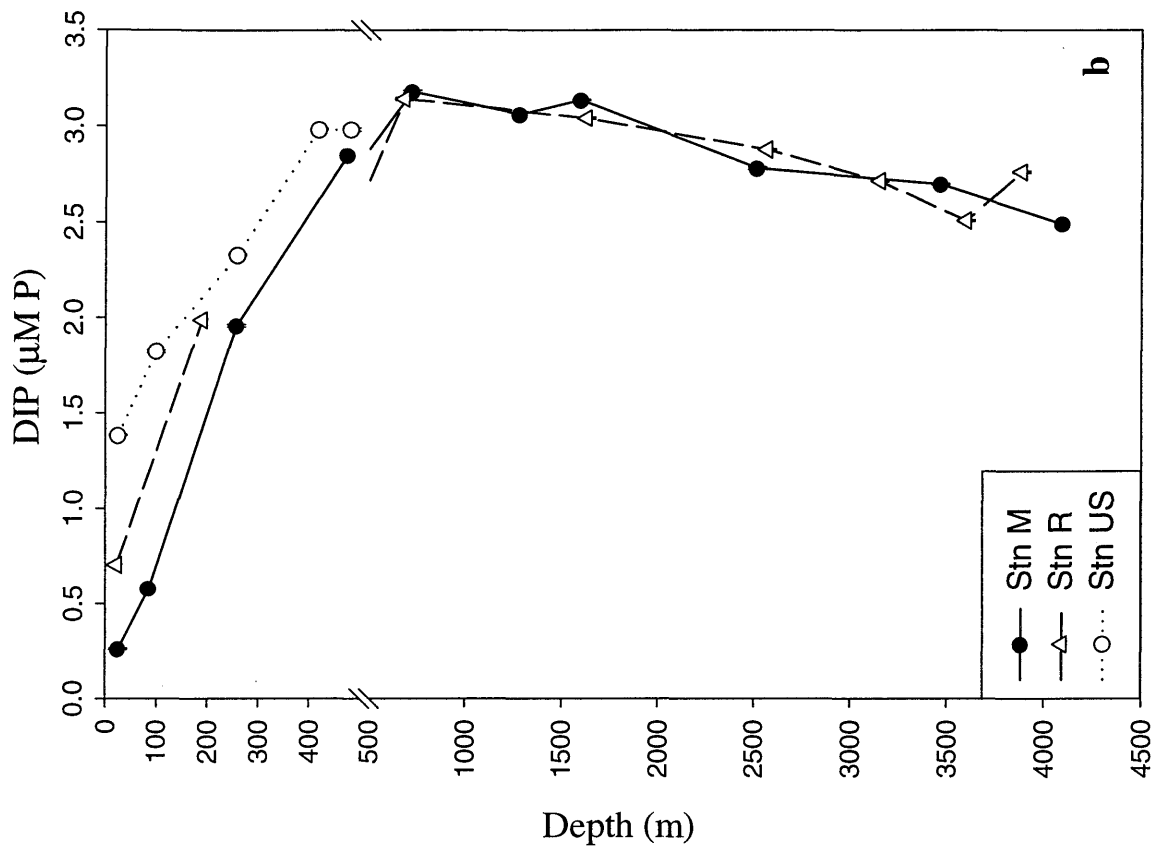


TABLE 2. Concentrations and Elemental Ratios of Dissolved Constituents for Eastern North Pacific

Depth (m)	Concentrations (µM N) ± 1 SD				Elemental Ratios								
	DOC	DON	DOP	DIP	DOC:DON	DOC:DOP	DON:DOP	DIN:DIP	TDN:TDP				
<i>Station M</i>													
25	72	4.5	0.08	0.229	0.008	0.60	0.262	0.003	16	316	20	2.3	10
85	63	3.9	0.08	0.225	0.000	4.4	0.578	0.000	16	280	18	7.6	10
256	46	2.6	0.26	0.163	0.007	28	1.95	0.007	18	280	16	14	14
475	42	1.9	0.83	0.138	0.000	36	2.84	0.000	21	301	14	13	13
722	38	2.8	0.12	0.107	0.007	41	3.18	0.007	14	355	26	13	13
1282	38	2.5	0.23	0.091	0.023	40	3.06	0.000	15	420	28	13	14
1600	40	2.5	0.25	0.090	0.009	42	3.13	0.004	16	437	28	14	14
2515	37	2.5	0.49	0.073	0.028	38	2.78	0.007	15	511	34	14	14
3466	37	2.7	0.29	0.083	0.005	37	2.69	0.004	14	445	32	14	14
4097	37	1.7	0.12	0.105	0.059	37	2.48	0.000	22	352	16	15	15
<i>Station R</i>													
22	65	4.4	0.14	0.229	0.000	6.7	0.704	0.000	15	285	19	9.5	12
189	46	2.4	0.07	0.134	0.004	28	1.98	0.000	19	346	18	14	14
681	41	1.9	0.07	0.117	0.008	41	3.14	0.007	22	348	16	13	13
1628	35	2.5	0.07	0.095	0.005	40	3.04	0.004	14	367	27	13	14
2568	37	2.9	0.66	0.085	0.004	36	2.87	0.004	13	434	34	13	13
3152	40	2.8	0.48	0.083	0.009	39	2.71	0.004	15	486	33	14	15
3601	39	2.5	0.09	0.130	0.055	36	2.50	0.003	15	297	19	14	15
3884	37	2.5	0.51	0.111	0.020	38	2.76	0.004	15	330	22	14	14
<i>Station US</i>													
25	56	3.5	0.31	0.201	0.012	16	1.38	0.003	16	277	17	12	13
100	50	2.9	0.31	0.168	0.008	24	1.82	0.007	17	296	17	13	14
259	46	2.2	0.31	0.132	0.003	31	2.33	0.003	21	345	17	13	13
419	43	3.1	0.31	0.013	0.008	43	2.98	0.004	14	3243	233	14	15
483	45	1.5	0.31	0.084	0.021	40	2.98	0.007	30	537	18	13	14

Figure 7. Depth profiles of suspended a) POC, b) PON, c) POP, and d) PIP for the eastern North Pacific transect. Average standard deviation of replicate samples for suspended POC and PON were $\pm 1.147 \mu\text{g C L}^{-1}$ and $\pm 0.142 \mu\text{g N L}^{-1}$, respectively. Suspended POP and PIP had average standard deviation for replicate samples of $\pm 0.022 \mu\text{g P L}^{-1}$.

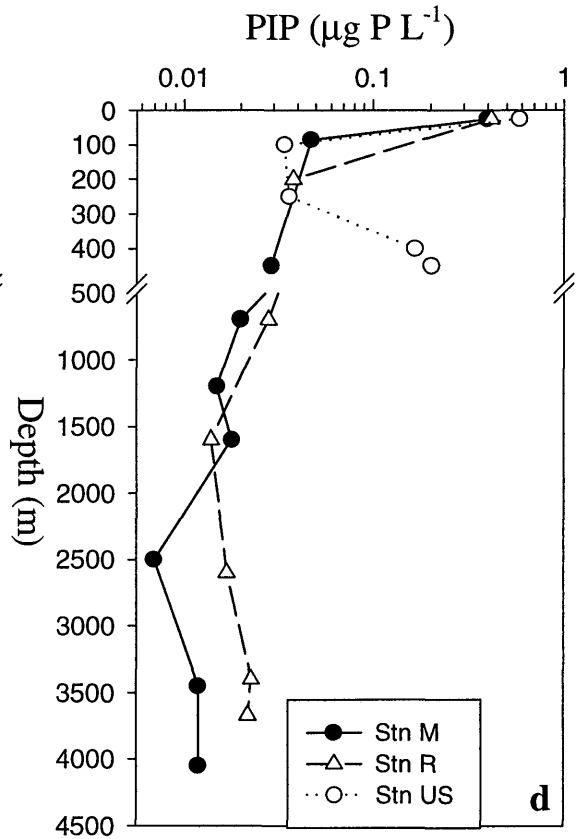
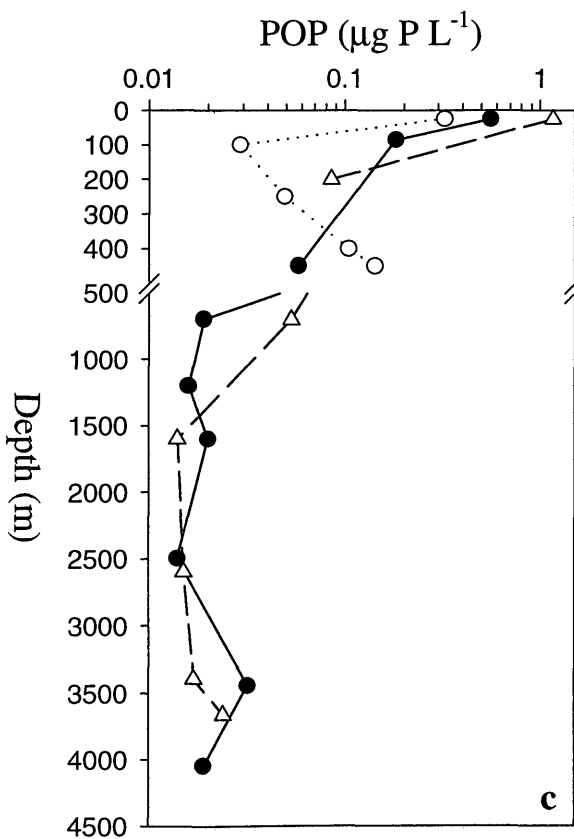
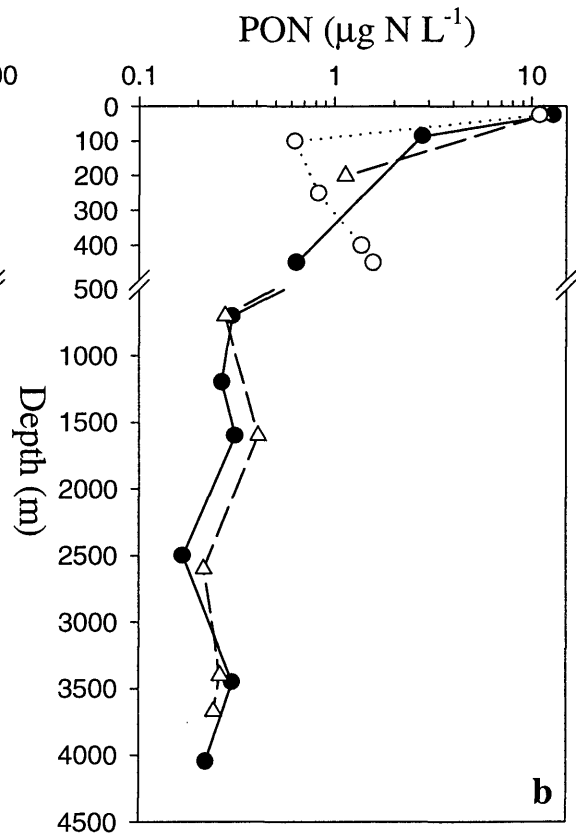
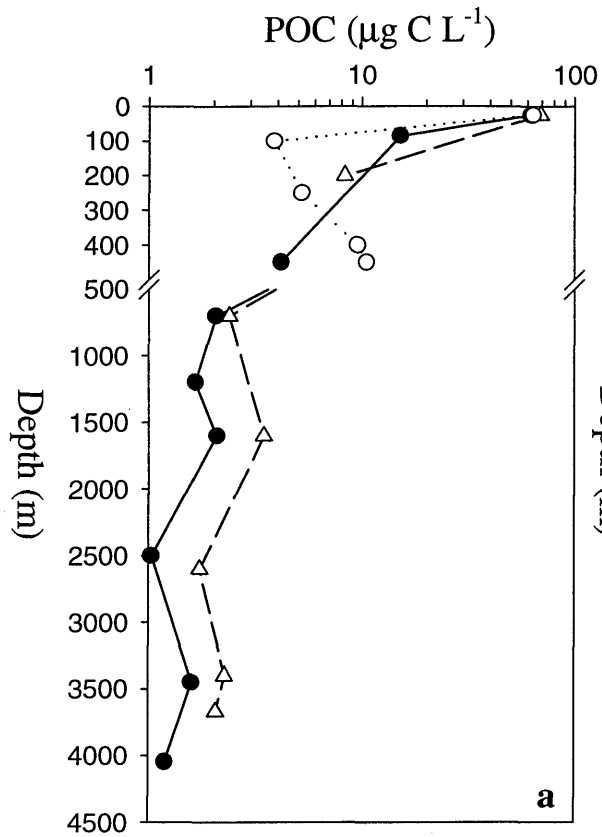


TABLE 3. Concentrations and Elemental Ratios of Suspended Particulate Matter for Eastern North Pacific

Depth (m)	Volume Pumped (L)	POC ($\mu\text{g C L}^{-1}$) ± 1 SD	PON ($\mu\text{g N L}^{-1}$) ± 1 SD	POP ($\mu\text{g P L}^{-1}$) ± 1 SD	PIP ($\mu\text{g P L}^{-1}$) ± 1 SD	Elemental Ratios						
						POC:PON	POC:POP	PON:POP	POC:POP			
<i>Station M</i>												
25	131.9	62.8	2.05	12.8	6.89	0.556	0.266	0.395	0.125	5.71	292	51.1
85	574.2	15.2	9.98	2.79	1.51	0.182	0.382	0.047	0.000	6.36	216	33.9
450	1208.3	4.16	0.25	0.64	0.03	0.058	0.016	0.029	0.000	7.55	184	24.4
700	1657.9	2.06	0.10	0.30	0.02	0.019	0.005	0.020	0.002	7.99	276	34.6
1200	2878.6	1.66	0.08	0.27	0.03	0.016	0.002	0.015	0.002	7.24	265	36.6
1600	1474.2	2.08	0.01	0.31	0.04	0.020	0.062	0.018	0.022	7.78	268	34.4
2500	1804.7	1.03	0.16	0.17	0.03	0.014	0.007	0.007	0.002	7.15	193	27.1
3450	771.3	1.59	0.04	0.30	0.04	0.032	0.003	0.012	0.003	6.15	130	21.2
4050	1100.7	1.19	0.03	0.22	0.01	0.019	0.016	0.012	0.002	6.29	165	26.3
*Sediment (in mg gdw ⁻¹)		14										
<i>Station R</i>												
25	153.4	69.2	1.64	11.4	0.31	1.16	0.071	0.415	0.019	7.08	154	21.8
200	1284.0	8.29	0.91	1.14	0.20	0.085	0.009	0.038	0.005	8.50	251	29.5
700	1066.0	2.38	5.21	0.28	0.17	0.053	0.210	0.028	0.140	10.0	117	11.6
1600	1416.7	3.46	0.03	0.41	0.00	0.014	0.007	0.014	0.002	9.88	630	63.8
2600	2655.0	1.73	0.00	0.22	0.00	0.015	0.004	0.017	0.004	9.36	299	32.0
3400	1421.1	2.27	0.58	0.26	0.01	0.017	0.022	0.023	0.016	10.1	341	33.8
3670	1780.4	2.06	0.16	0.24	0.00	0.024	0.003	0.022	0.000	9.89	226	22.8
*Sediment (in mg gdw ⁻¹)		30										
<i>Station US</i>												
25	195.2	63.7	49.9	10.9	7.05	0.325	4.00	0.584	3.83	6.80	506	74.4
100	1745.4	3.86	0.24	0.63	0.02	0.029	0.015	0.034	0.014	7.20	349	48.5
250	889.9	5.21	0.00	0.83	0.04	0.049	0.007	0.036	0.003	7.35	278	37.8
400	499.5	9.58	0.92	1.38	0.14	0.105	0.072	0.167	0.032	8.09	237	29.3
450	459.2	10.5	0.55	1.58	0.09	0.143	0.043	0.203	0.041	7.75	190	24.5
Sediment (in mg gdw ⁻¹)		16.1										
		0.87										
		1.83										
		0.06										
		0.048										
		0.761										
		0.013										

*From Druffel *et al.* (1998, see text)

(1998), as no samples from these stations were available for this study. Stn M surface sediment (0-0.25 cm) from Druffel *et al.* (1998) were from a box core during a cruise in June 1991 while Stn R surface sediments (0-1 cm) were from a gravity core during the same cruise as this study.

Southern Ocean

The temperature profile for Station F as measured by CTD is shown in Figure 8. Assuming that the permanent thermocline is present at depths greater than 300 m (from Figure 8, the observed permanent thermocline was between ~300-1300 m), a relatively weak seasonal thermocline was observed at the time this station was occupied during this study. The oxygen minimum at this station occurred at ~1500 m. Discrete temperature data from reversing thermometers, salinity and oxygen data are presented in Table 4.

Concentrations of DOC at Station F (Figure 9a, Table 5) ranged from a surface maximum of 53 $\mu\text{M C}$ to an average of ~40 $\mu\text{M C}$ at depths greater than 1000 m. DON and DOP concentrations (Figure 9b and c, Table 5) had proportional surface to deep water gradients, with concentration ranges of 2.5-4.4 $\mu\text{M N}$ and 0.074-0.225 $\mu\text{M P}$, respectively, although DON gradients were less pronounced than those of DOC or DOP.

Concentrations of DIN and DIP (Figure 10, Table 5) did not show strong surface depletions at Station F, although surface minima of 15 $\mu\text{M N}$ and 1.07 $\mu\text{M P}$, respectively, were observed. Below the mixed layer, these concentrations increased to maxima of 34 $\mu\text{M N}$ and 2.32 $\mu\text{M P}$, respectively, also at the depth of O_2 minimum, and decreased to relatively constant background values throughout the rest of the water column.

Figure 8. Temperature profile of Stn F (Southern Ocean) as measured by CTD.

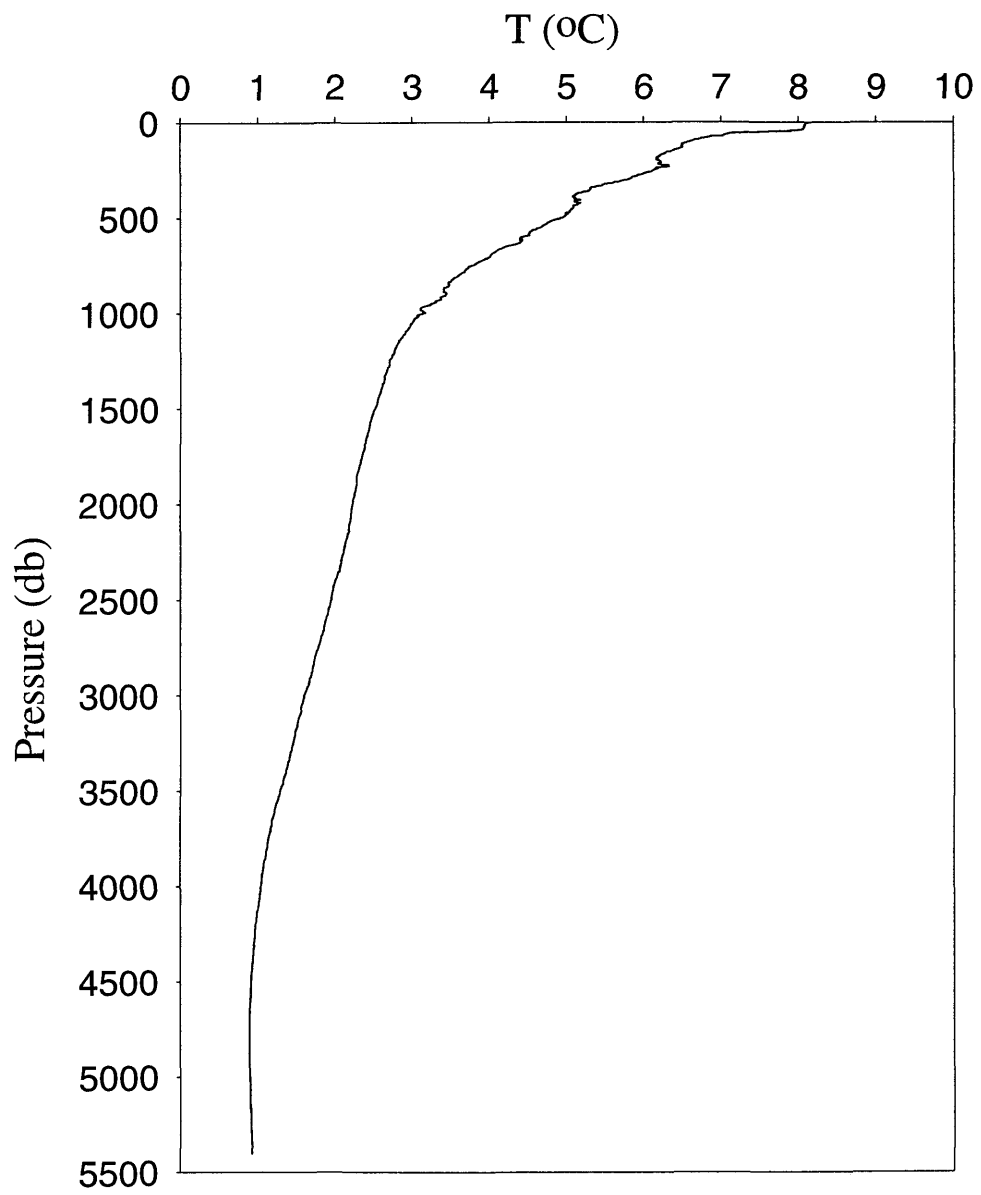


TABLE 4. Hydrographic data for Southern Ocean

Depth (m)	Temperature (°C)	Salinity	Oxygen (mL L ⁻¹)
<i>Station F</i>			
3	-	34.284	6.400
10	-	34.281	6.496
20	7.837	34.290	6.377
94	7.169	34.366	6.142
142	6.366	34.265	6.455
245	6.578	34.330	6.117
434	5.050	34.380	5.386
565	4.427	34.281	6.759
772	3.668	34.469	4.505
974	3.206	34.406	4.383
1289	2.606	34.517	3.881
1490	2.469	34.592	3.160
1700	-	34.664	3.825
1900	-	34.693	3.944
2221	2.082	-	4.190
2533	1.869	-	4.203
2876	1.591	-	4.280
3493	1.355	34.736	4.386
3392	1.250	-	4.434
3600	-	34.715	4.503
4295	0.937	34.700	4.379
4905	0.903	34.712	4.518
5336	0.914	-	4.477
5408	0.938	34.524	4.007

Figure 9. Concentration profiles of a) DOC, b) DON, and c) DOP for Stn F. Error bars plotted for DON and DOP were ± 1 SD of duplicate measurements. Analytical error for DOC was $\pm 1 \mu\text{M C}$.

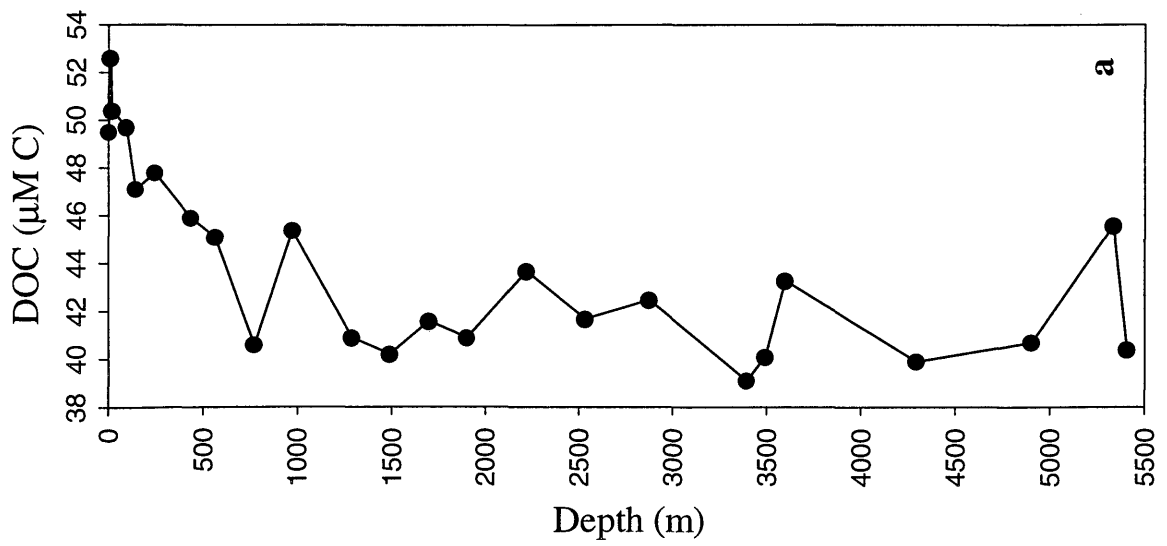
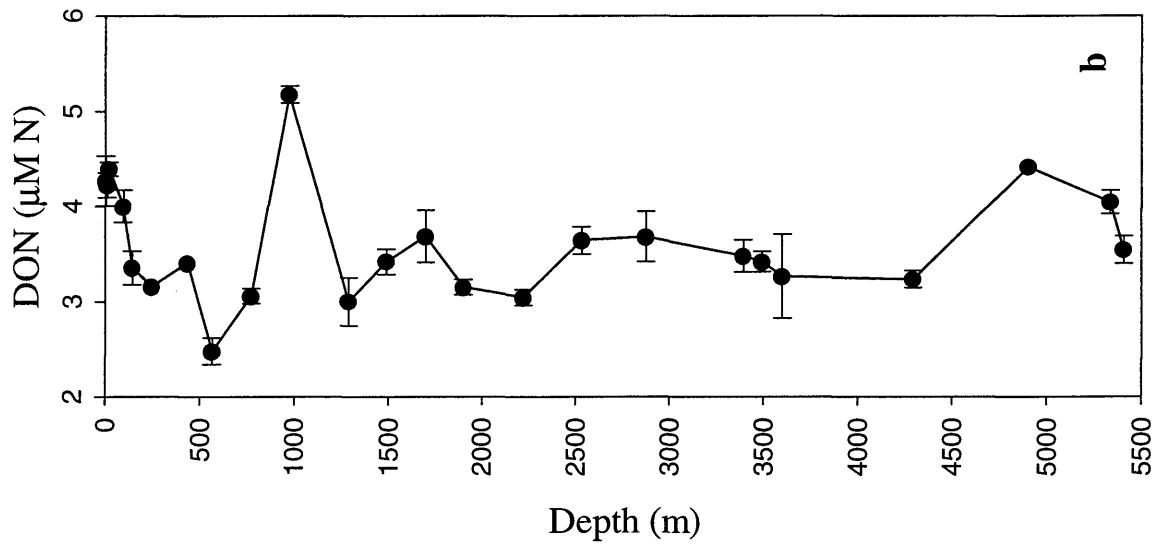
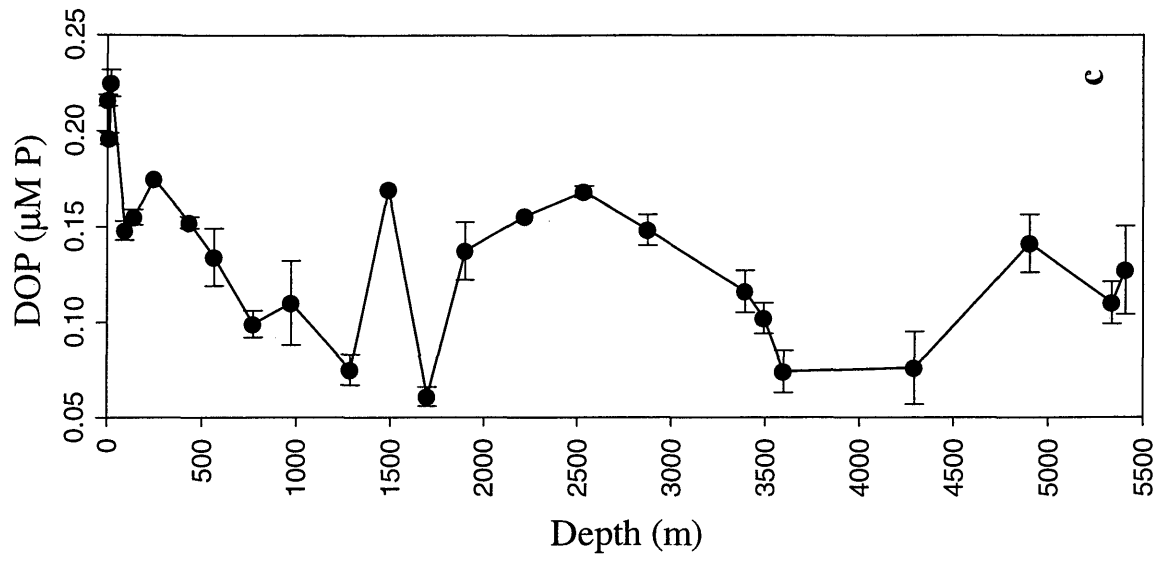
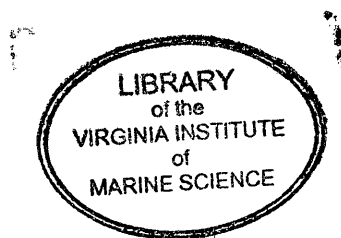


Figure 10. Concentration profiles of a) DIN, and b) DIP for Stn F. Error bars plotted for DIN and DIP were ± 1 SD of duplicate measurements.



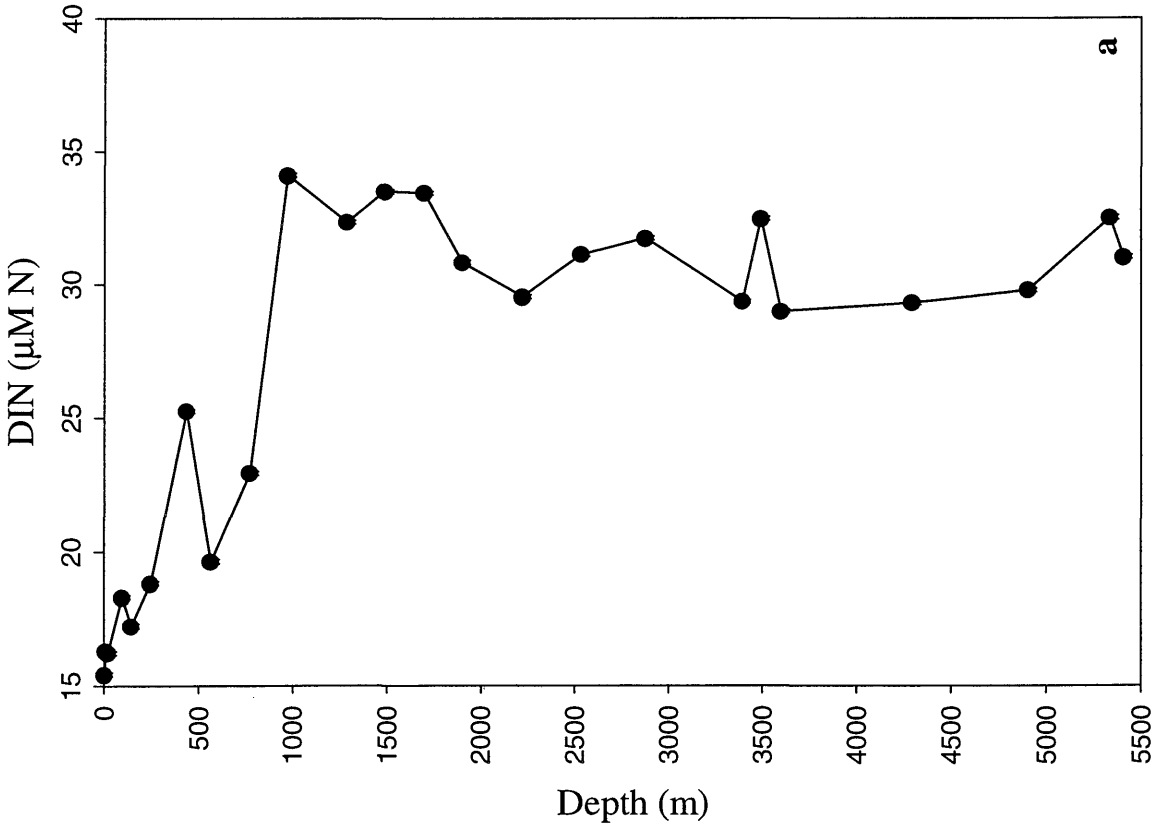
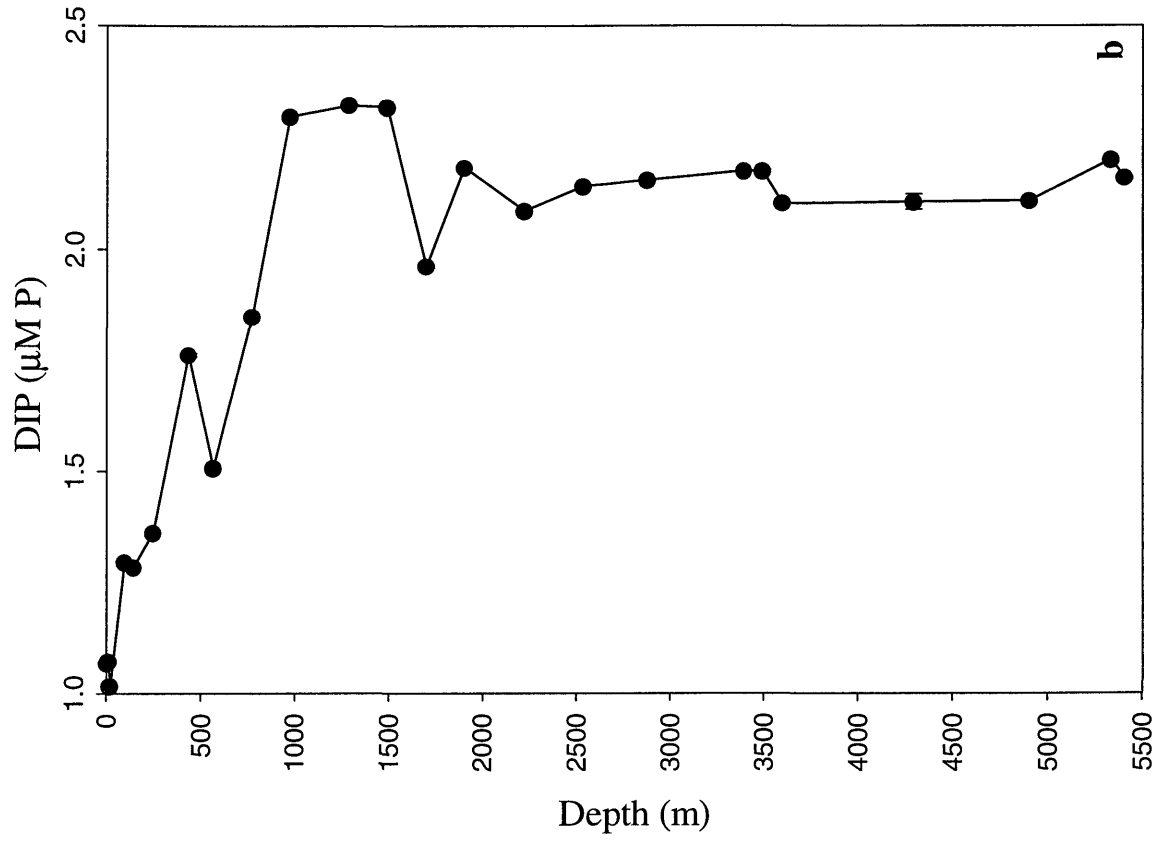


TABLE 5. Concentrations and Elemental Ratios of Dissolved Constituents for Southern Ocean

Depth (m)	DOC			DON			DOP			DIP			Elemental Ratios										
	($\mu\text{M C}$)	± 1 SD	($\mu\text{M N}$)	($\mu\text{M N}$)	± 1 SD	($\mu\text{M P}$)	($\mu\text{M P}$)	± 1 SD	($\mu\text{M N}$)	($\mu\text{M N}$)	($\mu\text{M P}$)	($\mu\text{M P}$)	± 1 SD	DOC:DON	DOC:DOP	DOC:DIP	DON:DOP	DON:DIP	TDN:DIP	TDN:TDP			
<i>Station F</i>																							
3	50	4.3	0.26	0.216	0.003	15	1.07	0.003	12	229	20	14	15	12	229	20	14	15	12	229	20	14	15
10	53	4.2	0.13	0.196	0.003	16	1.07	0.003	12	269	22	15	16	12	269	22	15	16	12	269	22	15	16
20	50	4.4	0.07	0.225	0.007	16	1.02	0.000	11	224	20	16	17	11	224	20	16	17	11	224	20	16	17
94	50	4.0	0.17	0.148	0.005	18	1.30	0.003	12	335	27	14	15	12	335	27	14	15	12	335	27	14	15
142	47	3.4	0.18	0.155	0.004	17	1.28	0.000	14	304	22	13	14	14	304	22	13	14	14	304	22	13	14
245	48	3.2	1.4	0.175	0.000	19	1.36	0.000	15	274	18	14	14	15	274	18	14	14	14	274	18	14	14
434	46	3.4	1.7	0.152	0.003	25	1.76	0.003	13	301	22	14	15	13	301	22	14	15	13	301	22	14	15
565	45	2.5	0.14	0.134	0.015	20	1.51	0.000	18	336	18	13	13	18	336	18	13	13	18	336	18	13	13
772	41	3.1	0.08	0.099	0.007	23	1.85	0.000	13	410	31	12	13	13	410	31	12	13	13	410	31	12	13
974	45	5.2	0.09	0.110	0.022	34	2.30	0.000	9	414	47	15	16	9	414	47	15	16	9	414	47	15	16
1289	41	3.0	0.25	0.075	0.008	32	2.32	0.003	14	545	40	14	15	14	545	40	14	15	14	545	40	14	15
1490	40	3.4	0.13	0.169	0.000	34	2.32	0.000	12	238	20	14	15	12	238	20	14	15	12	238	20	14	15
1700	42	3.7	0.27	0.061	0.005	33	1.96	0.003	11	682	60	17	18	11	682	60	17	18	11	682	60	17	18
1900	41	3.2	0.08	0.137	0.015	31	2.18	0.000	13	299	23	14	15	13	299	23	14	15	13	299	23	14	15
2221	44	3.0	0.08	0.155	0.000	30	2.08	0.000	14	282	20	14	15	14	282	20	14	15	14	282	20	14	15
2533	42	3.6	0.14	0.168	0.003	31	2.14	0.003	11	249	22	15	15	11	249	22	15	15	11	249	22	15	15
2876	43	3.7	0.26	0.148	0.008	32	2.15	0.003	12	288	25	15	15	12	288	25	15	15	12	288	25	15	15
3493	39	3.5	0.17	0.116	0.011	29	2.17	0.000	11	337	30	14	14	11	337	30	14	14	11	337	30	14	14
3392	40	3.4	0.11	0.102	0.008	33	2.17	0.003	12	392	33	15	16	12	392	33	15	16	12	392	33	15	16
3600	43	3.3	0.44	0.074	0.011	29	2.10	0.000	13	585	44	14	15	13	585	44	14	15	13	585	44	14	15
4295	40	3.2	0.09	0.076	0.019	29	2.11	0.017	12	528	43	14	15	12	528	43	14	15	12	528	43	14	15
4905	41	4.4	1.6	0.141	0.015	30	2.11	0.000	9	288	31	14	15	9	288	31	14	15	9	288	31	14	15
5336	46	4.0	0.12	0.110	0.011	33	2.20	0.000	11	416	37	15	16	11	416	37	15	16	11	416	37	15	16
5408	40	3.5	0.14	0.127	0.023	31	2.16	0.003	11	318	28	14	15	11	318	28	14	15	11	318	28	14	15

Suspended POC and PON concentrations at Station F ranged from 0.58-41.7 $\mu\text{g C L}^{-1}$ and 0.06-6.87 $\mu\text{g N L}^{-1}$, respectively, again decreasing by ~ 100 -fold with depth (Figure 11a,b; Table 6). Suspended POP and PIP concentrations (Figure 11c,d; Table 6) also decreased with depth, ranging from 0.008-0.418 $\mu\text{g P L}^{-1}$ and 0.003-0.856 $\mu\text{g P L}^{-1}$, respectively over the entire water column. However, suspended POP concentrations increased at near-bottom depths while suspended PIP concentrations increases at about 3000 m. Suspended PIP comprised between ~ 10 and 50% of the total suspended particulate P.

Surface (0-3 cm) concentrations of SOC, SON and SOP (Table 6) were 2.75 mg C gdw^{-1} , 0.51 mg N gdw^{-1} and 0.094 mg P gdw^{-1} , respectively. The concentration of surface SIP was 0.546 mg P gdw^{-1} , comprising $\sim 86\%$ of total sedimentary P at Station F.

Elemental Ratios of DOM, Suspended POM and SOM

Eastern North Pacific Ocean

Elemental molar ratios of DOC:DON:DOP in DOM (Figure 12, Table 2) were nearly always greater than Redfield (C:N:P = 106:16:1) at the eastern North Pacific stations, with DOC:DON, DOC:DOP and DON:DOP ranging from 13-30, 277-537 and 14-34, respectively. For all stations, DOC:DON ratios increased with depth over the upper 500 m, while DOC:DOP ratios increased with depth over the entire water column. However, DON:DOP ratios for all stations approached Redfield in the upper 500 m, increasing with depth below 500 m. Conversely, ratios for DIN:DIP were always lower than Redfield, especially in surface waters, but N:P ratios more closely approximated Redfield when DON and DOP were included (Figure 13, Table 2). The effect of adding

Figure 11. Concentration profiles of suspended a) POC, b) PON, c) POP, and d) PIP for Stn F. Average standard deviation of replicate samples for suspended POC and PON were $\pm 0.121 \mu\text{g C L}^{-1}$ and $\pm 0.25 \mu\text{g N L}^{-1}$, respectively. Suspended POP and PIP had average standard deviation for replicate samples of $\pm 0.008 \mu\text{g P L}^{-1}$.

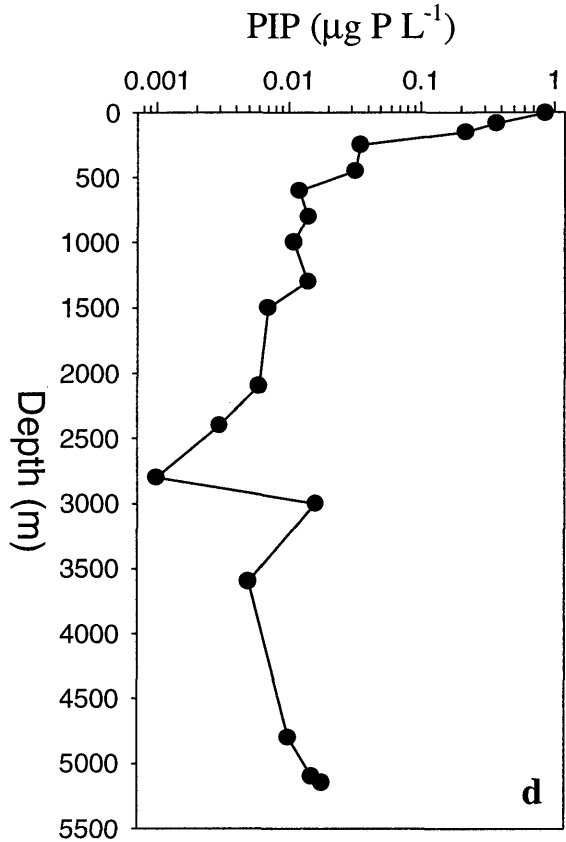
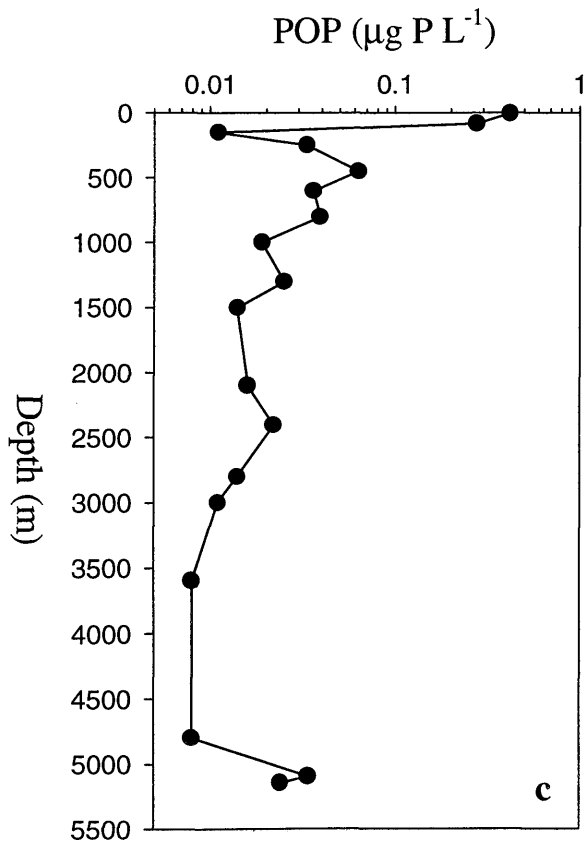
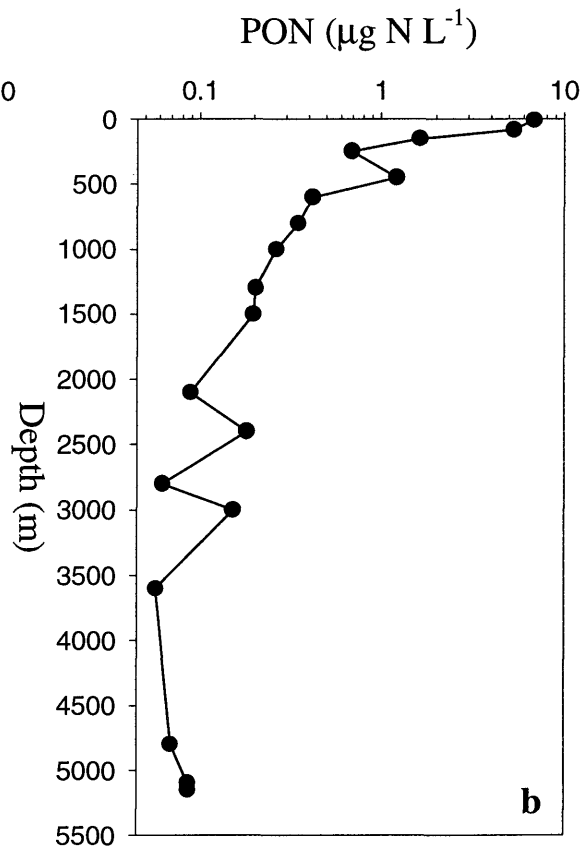
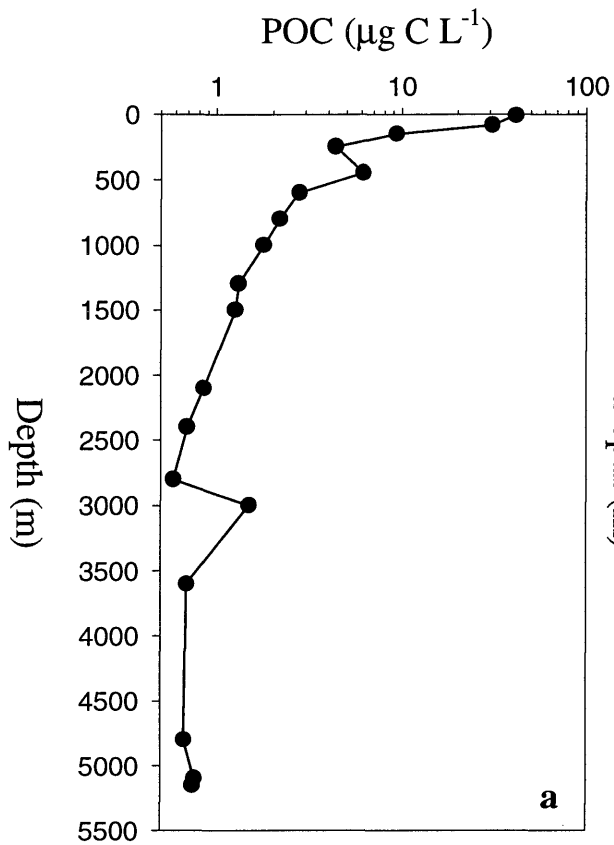


TABLE 6. Concentrations and Elemental Ratios of Suspended Particulate Matter for Southern Ocean

Depth (m)	Volume Pumped (L)	Concentrations ($\mu\text{g L}^{-1}$) ± 1 SD				Elemental Ratios						
		POC	PON	POP	PIP	POC:PON	POC:POP	PON:POP				
<i>Station F</i>												
6	498.3	41.7	2.98	6.87	0.51	0.418	0.262	0.856	0.249	7.09	258	36.4
85	356.5	30.8	3.18	5.30	1.23	0.277	0.217	0.367	0.061	6.78	288	42.5
150	612.2	9.30	0.18	1.64	0.02	0.011	0.031	0.217	0.030	6.63	2238	338
250	785.0	4.37	0.50	0.69	0.09	0.033	0.008	0.035	0.008	7.37	337	45.7
450	1072.5	6.14	0.25	1.22	0.07	0.063	0.014	0.032	0.009	5.89	251	42.5
600	1262.5	2.77	0.23	0.42	0.05	0.036	0.002	0.012	0.000	7.70	196	25.5
800	1395.6	2.19	0.00	0.35	0.01	0.039	0.005	0.014	0.004	7.29	144	19.8
1000	1356.6	1.79	0.00	0.26	0.01	0.019	0.005	0.011	0.005	7.89	238	30.2
1300	1823.1	1.31	0.17	0.20	0.01	0.025	0.018	0.014	0.012	7.50	134	17.8
1500	2085.6	1.26	0.08	0.20	0.02	0.014	0.005	0.007	0.003	7.44	238	32.0
2100	1421.3	0.85	0.05	0.09	0.01	0.016	0.004	0.006	0.000	11.1	136	12.3
2400	1310.3	0.69		0.18		0.022	0.000	0.003	0.000	4.44	81.5	18.3
2800	1444.0	0.58	0.03	0.06	0.00	0.014	0.002	0.001	0.002	11.0	105	9.51
3000	1300.9	1.49	0.06	0.15	0.04	0.011	0.004	0.016	0.000	11.4	336	29.5
3600	2392.3	0.69	0.02	0.06	0.01	0.008	0.002	0.005	0.000	14.2	226	15.9
4800	2135.4	0.67	0.03	0.07	0.01	0.008	0.003	0.010	0.001	11.4	217	19.1
5100	1055.0	0.76	0.19	0.09	0.01	0.034	0.011	0.015	0.000	10.3	58.5	5.66
5150	1129.3	0.75	0.03	0.09	0.00	0.024	0.012	0.018	0.005	10.1	79.7	7.86
Sediment (in mg gdw ⁻¹)		2.75	0.17	0.51	0.00	0.094	0.036	0.546	0.011	6.29	75.6	12.0

Figure 12. Depth profiles of DOM elemental ratios for the eastern North Pacific transect for a) DOC:DON, b) DOC:DOP, and c) DON:DOP. The average Redfield ratios of C:N (6.6), C:P (106) and N:P (16) were plotted as dashed vertical lines for comparison. DOC:DOP and DON:DOP ratios for 400 m at Stn US were not plotted. The values were 3243 and 233.2 respectively.

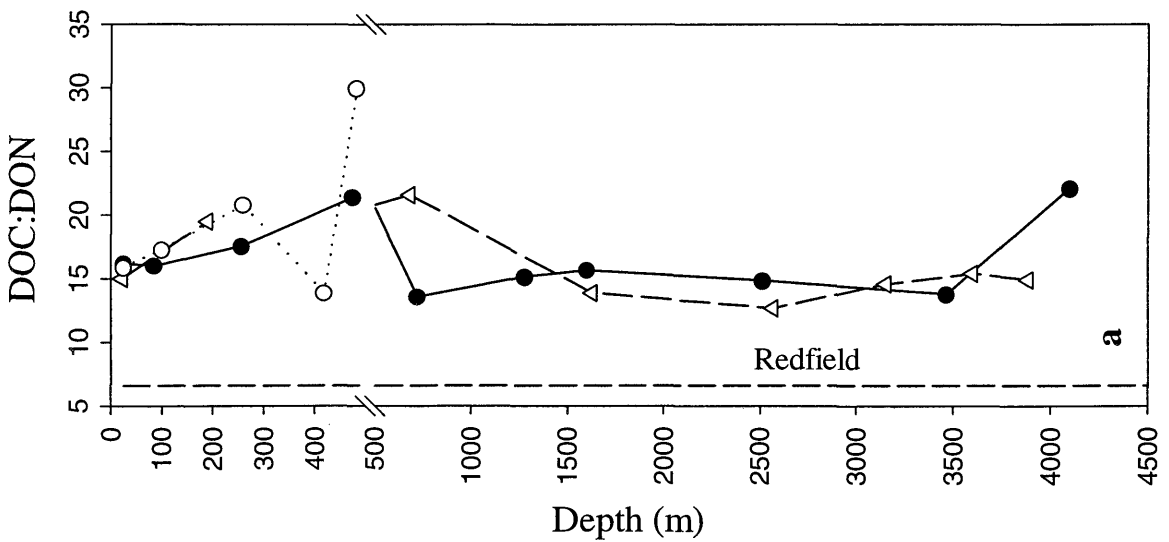
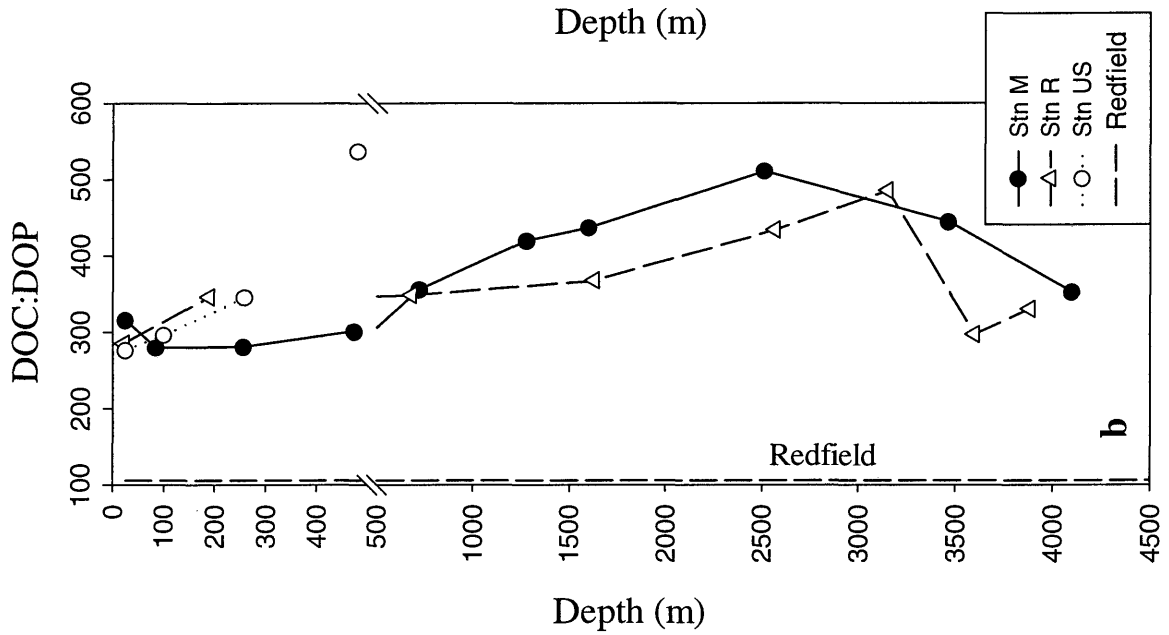
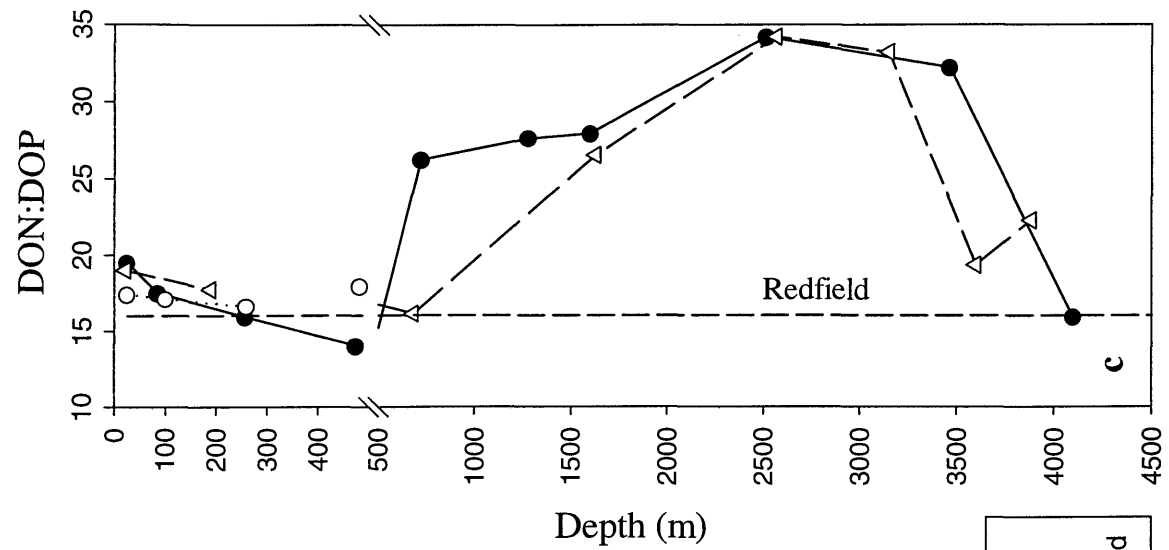
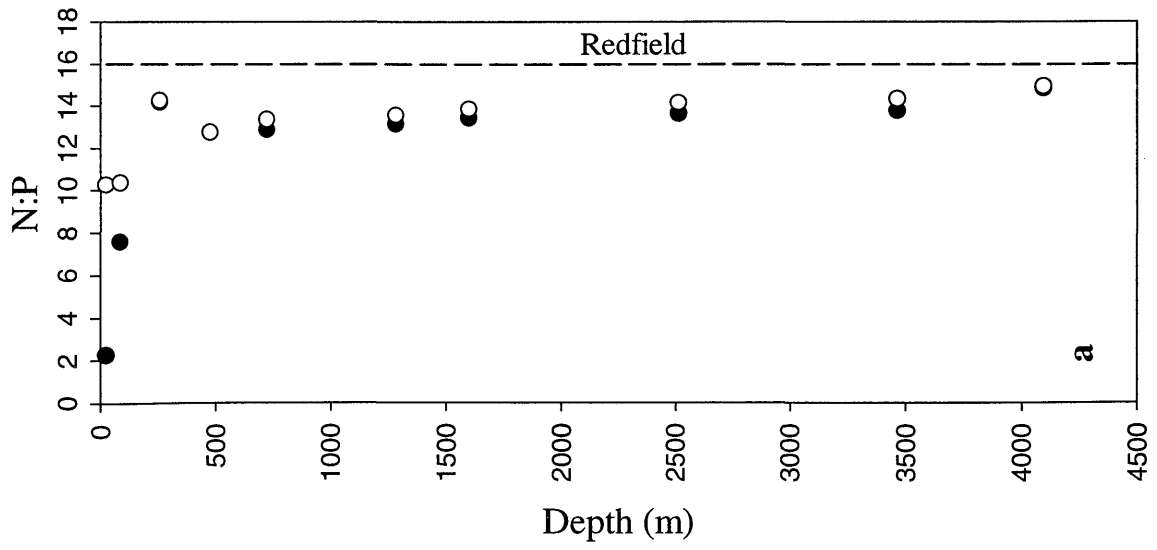
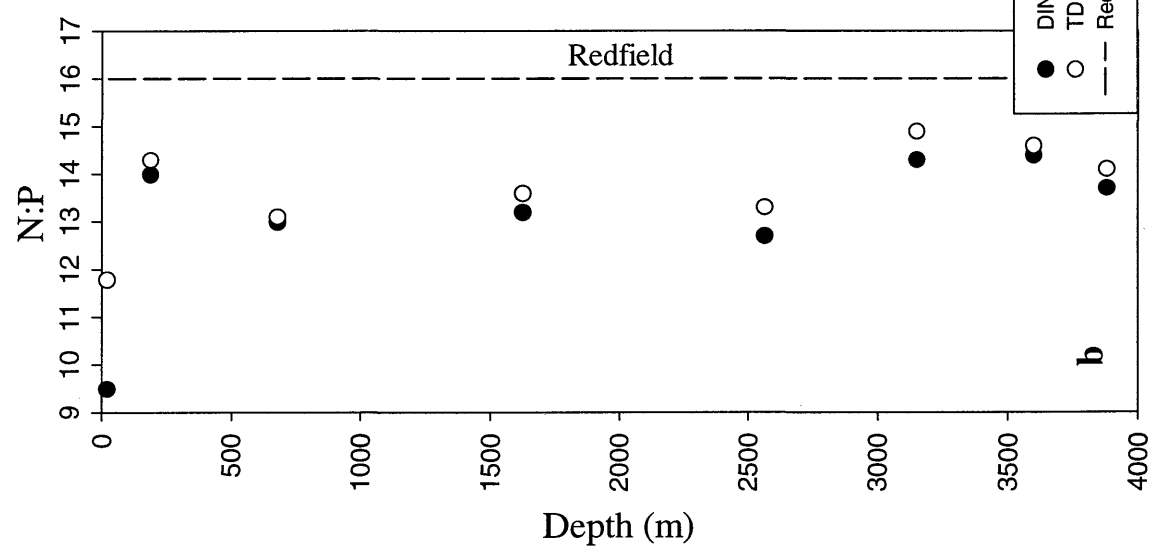
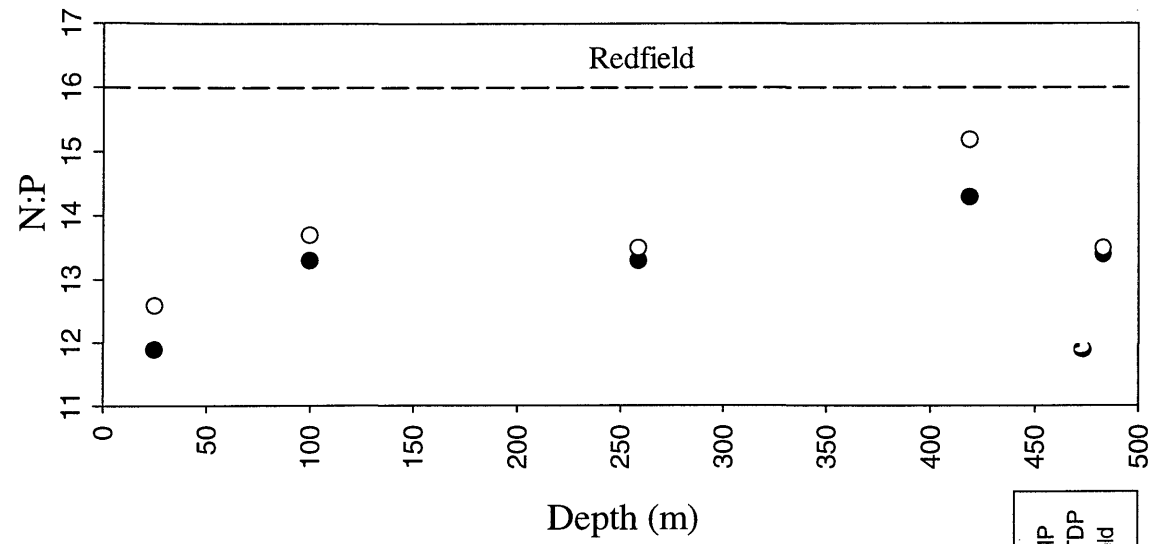


Figure 13. Depth profiles of dissolved N:P ratios for a) Stn M, b) Stn R, and c) Stn US in the eastern North Pacific. Symbols used are: DIN:DIP ratios - filled circles and TDN:TDP ratios - open circles.



● DIN:DIP
 ○ TDN:TDP
 --- Redfield

DON and DOP to dissolved N:P ratios was most pronounced in DIN and DIP-depleted surface waters in the eastern North Pacific.

Elemental ratios for suspended POM (Figure 14, Table 3), were also generally higher than Redfield, although suspended POC:PON ratios in surface waters had overall ratios lower than deeper waters. These ratios ranged from 5.71-10.2, 117-630 and 11.6-74.4 for suspended POC:PON, POC:POP and PON:POP, respectively. Elemental ratios for the surface SOM sample were also all higher than Redfield, with SOC:SON, SOC:SOP and SON:SOP of 10.2, 417 and 40.7, respectively (Table 3).

Southern Ocean

As was found in the eastern North Pacific, elemental ratios of DOM at Station F (Figure 15a-c, Table 5) were all greater than Redfield with DOC:DON, DOC:DOP and DON:DOP ranging from 9-18, 229-682 and 12-47, respectively. DOC:DON ratios increased with depth over the upper 500 m, while DOC:DOP and DON:DOP ratios increased with depth over the upper 1500 m. Ratios of DON:DOP in the upper 500 m showed similar near-Redfield ratios as for the eastern North Pacific transect. DIN:DIP ratios were lower than Redfield, especially in surface waters, but like the eastern North Pacific, dissolved N:P ratios also more closely approximated Redfield when DON and DOP were included (Figure 15d, Table 5).

Elemental ratios for suspended POM (Figure 16, Table 6), were generally higher than Redfield in Southern Ocean samples, ranging from 4.44-14.2, 58.5-336 and 5.66-45.7 for suspended POC:PON, POC:POP and PON:POP, respectively. For the SOM sample, elemental ratios observed were all lower than Redfield, unlike all of the other organic

Figure 14. Depth profiles of suspended POM elemental ratios for the eastern North Pacific transect; a) POC:PON, b) POC:POP, and c) PON:POP.

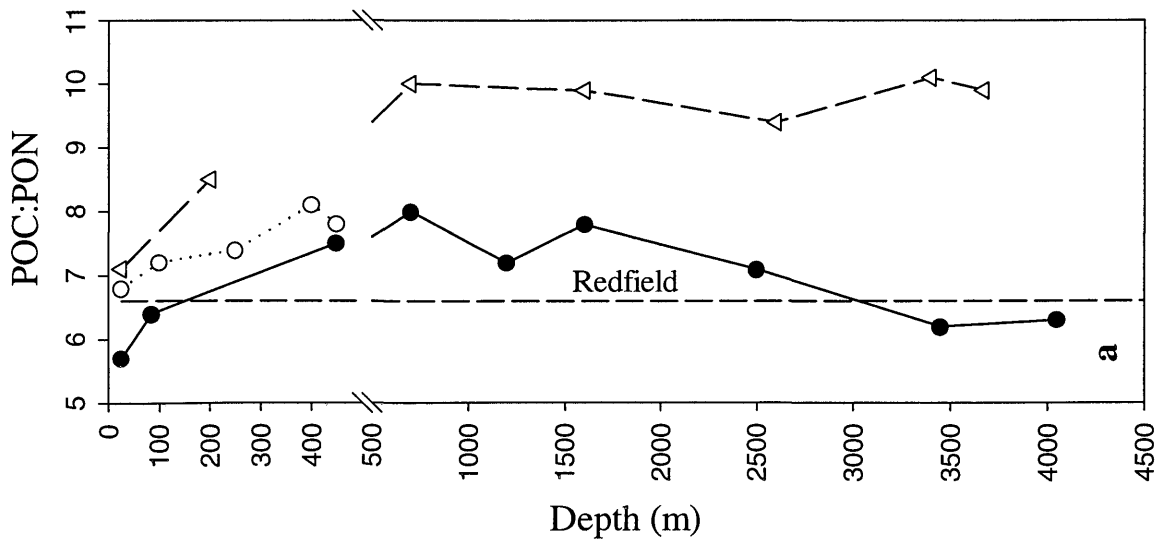
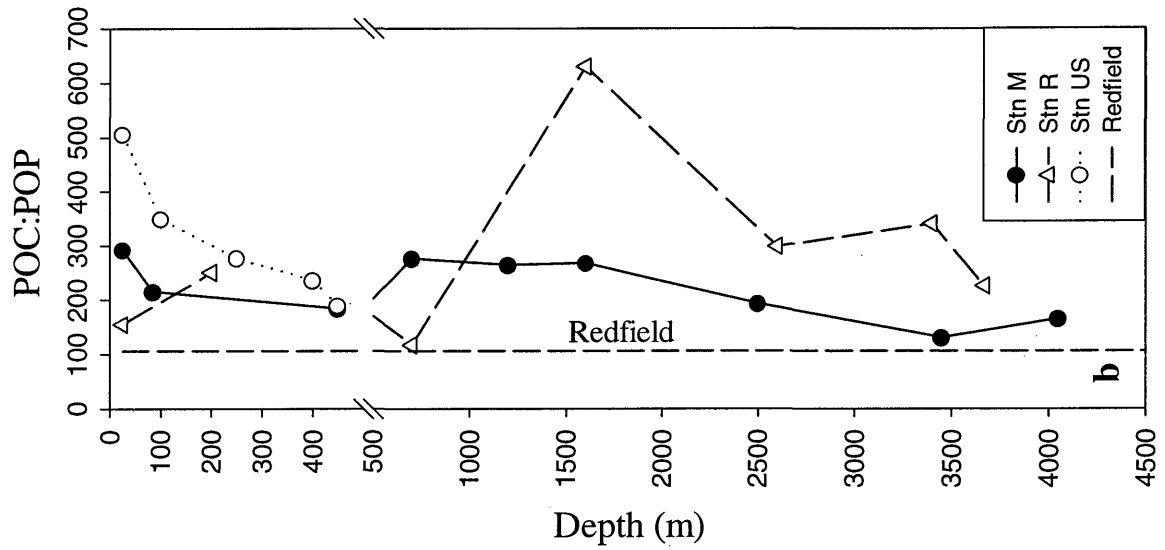
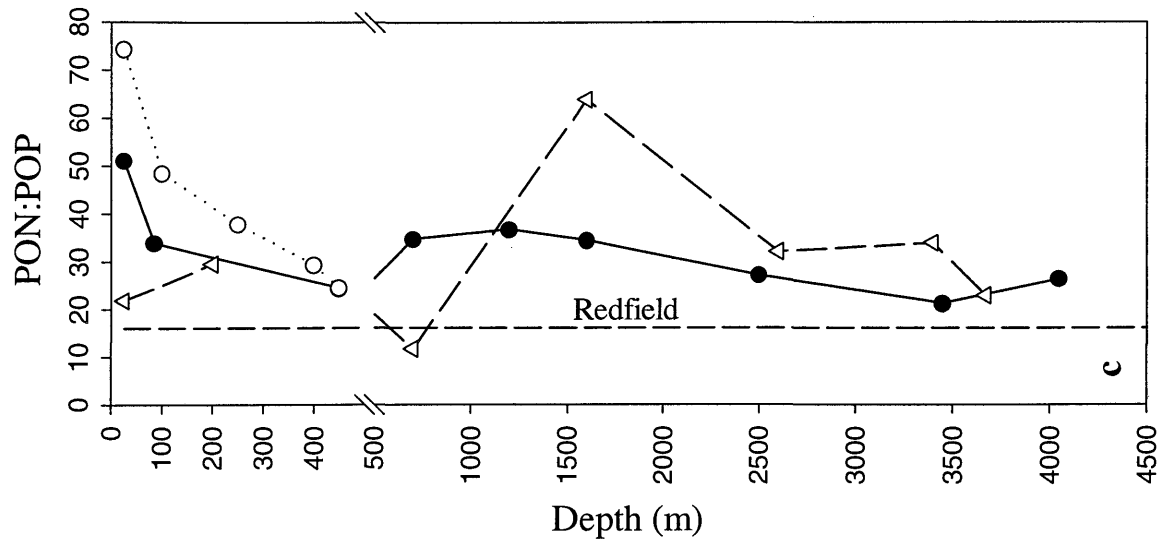


Figure 15. Profiles of a) DOC:DON, b) DOC:DOP, c) DON: DOP, and d) dissolved N:P for Stn F. Symbols used for Fig. 15d are: DIN:DIP ratios - filled circles and TDN:TDP ratios - open circles.

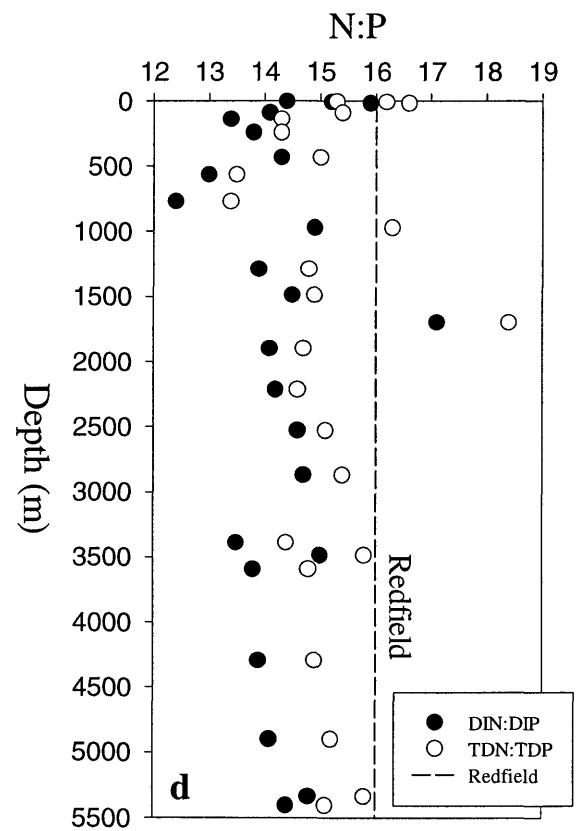
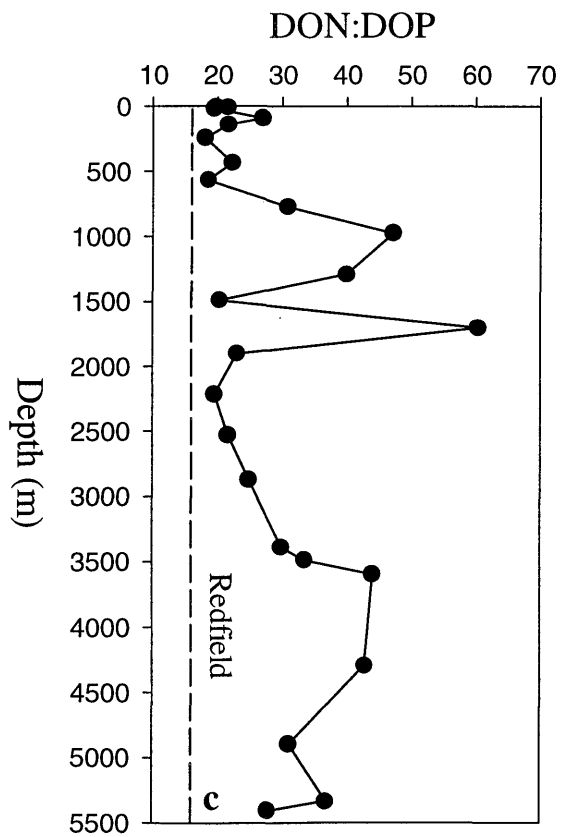
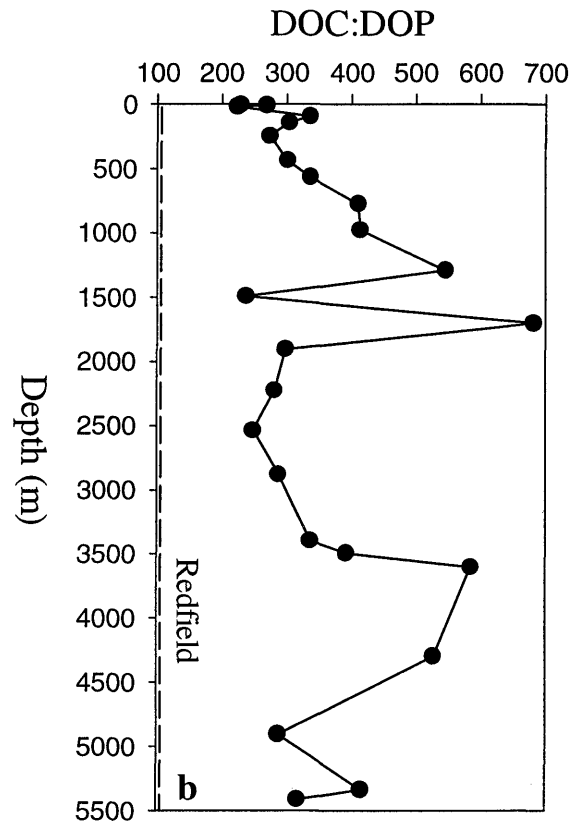
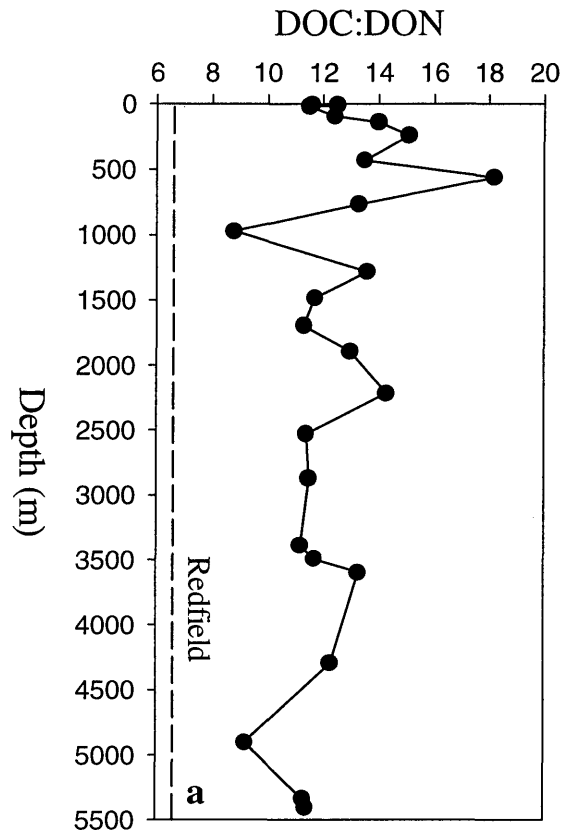
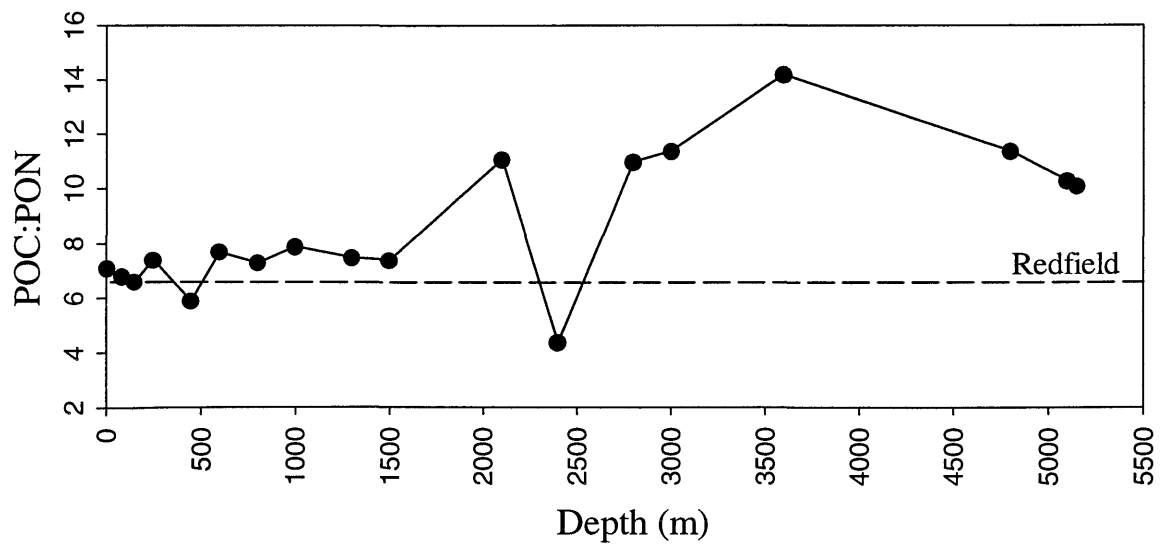
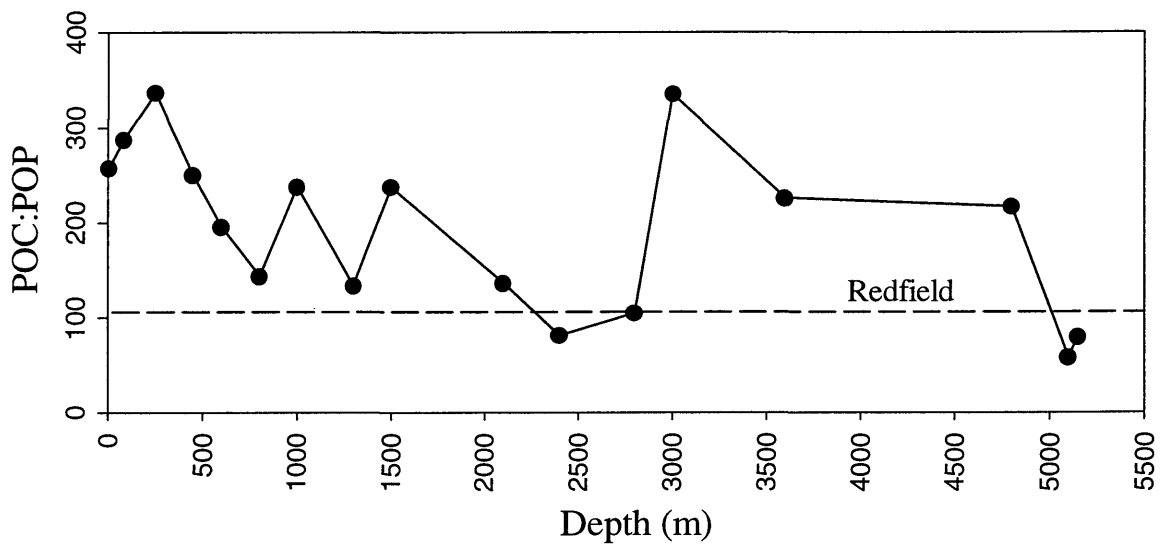
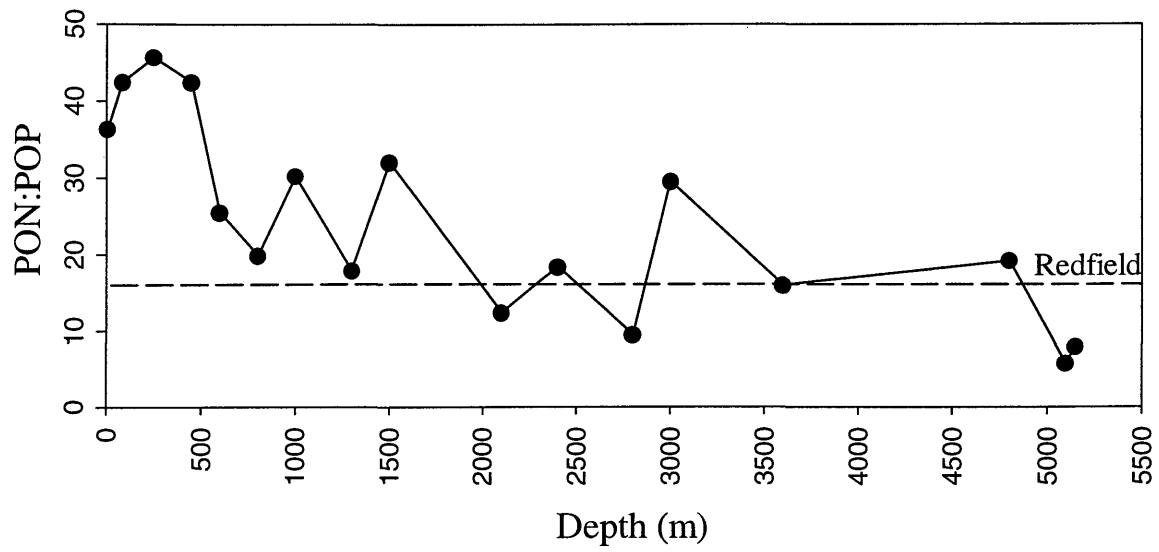


Figure 16. Depth profiles of suspended POM elemental ratios for Stn F; a) POC:PON, b) POC:POP, and c) PON:POP. POC:POP and PON:POP ratios for 150 m were not plotted. The values were 2238 and 338 respectively.



matter pools in this study. These ratios were 6.29, 75.6 and 12.0 for SOC:SON, SOC:SOP and SON:SOP, respectively, at Station F (Table 6).

Sinking POM Fluxes and Flux Ratios

The sinking mass fluxes (Figure 17a) at Station M for 650 mab sediment traps ranged from 114.4-392.0 mg m⁻² d⁻¹ over the 110-day sampling period. Of these total mass fluxes, ~5-7% was sinking POC, ~0.5-0.8% PON, ~0.02-0.06% POP and ~0.02-0.07% PIP (Table 7). These fractions amounted to particle fluxes to 650 mab of 6.3-21.9 mg C m⁻² d⁻¹ in POC, 0.73-2.37 mg N m⁻² d⁻¹ in PON and 0.022-0.097 mg P m⁻² d⁻¹ in POP, while PIP fluxes ranged from 0.063-0.189 mg P m⁻² d⁻¹ (Figure 17b-c, Table 7). The sinking mass flux increased over the course of the 110 day period, with the sinking POC and sinking PON fluxes corresponding closely to this trend. The sinking POP fluxes did not, however, follow this same pattern; increasing to a peak of 0.09 mg P m⁻² d⁻¹ from February 16-March 28, 1995, decreasing sharply for the next 10 days and steadily increasing to ~0.08 mg P m⁻² d⁻¹ over the remainder of the sampling period. Sinking PIP and sinking TPP fluxes, however, did increase over the course of the sampling period. In general, sinking PIP fluxes were greater than sinking POP fluxes, with the exception of February 26-March 18, 1995 and accounted for an average of ~60% of the total sinking P flux.

Flux ratios for sinking POM at Station M were all much greater than Redfield over the 110-day period. Ratios for sinking POC:PON, POC:POP and PON:POP ranged from 10-11.4, 205-1099 and 20.6-100, respectively (Figure 18, Table 7). These ratios did not

follow the sinking mass fluxes, indicating that the quality (and ratios) of sinking organic matter is not controlled by fluxes of the sinking mass.

Figure 17. Fluxes of a) sinking mass, b) POC, c) PON, and d) P to 650 mab for Stn M collected from February 16 to June 06, 1995. Symbols used for Fig. 17d are: POP - filled circles, PIP - open circles and TPP - closed triangles.

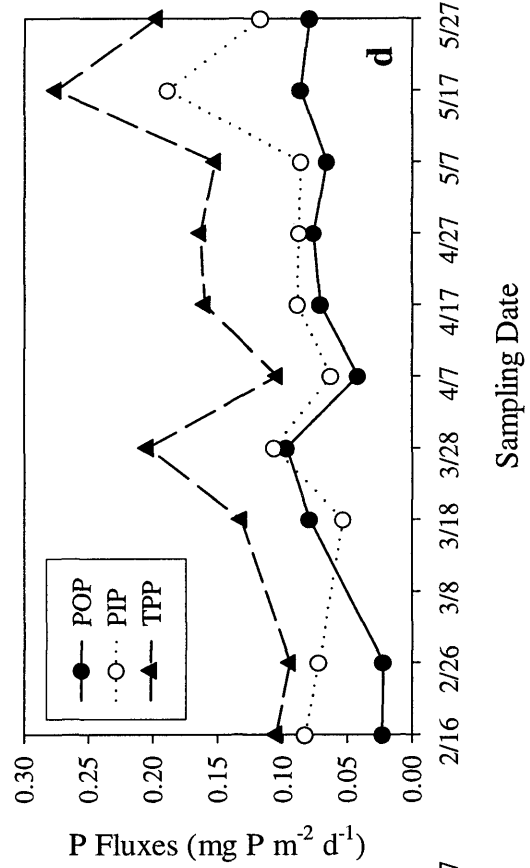
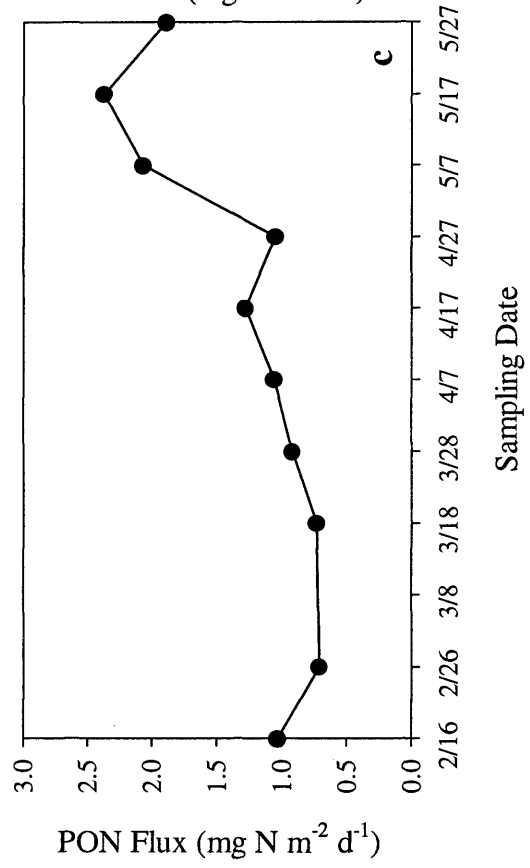
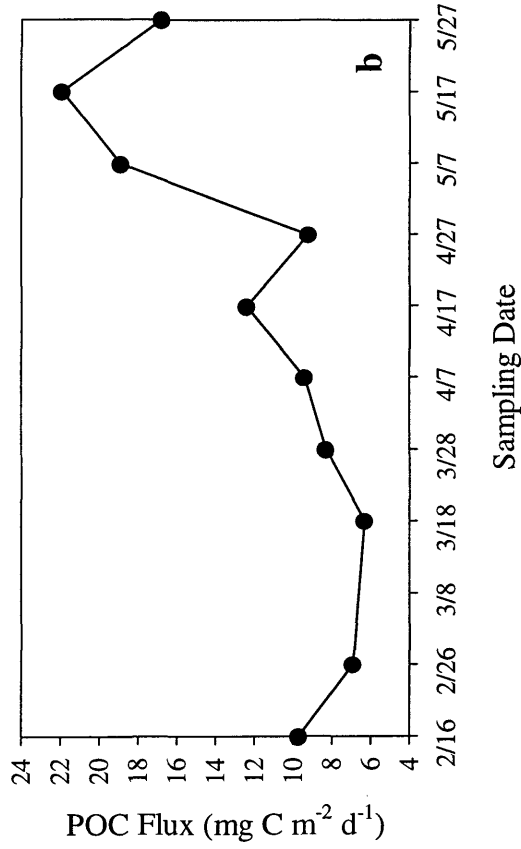
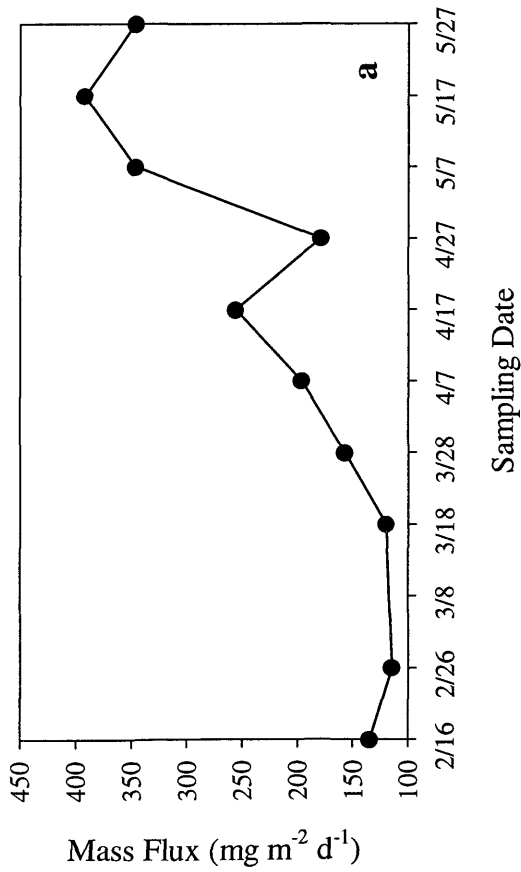


Figure 18. Flux ratios of sinking a) POC:PON, b) POC:POP, and c) PON:POP to 650 mab for Stn M collected from February 16 to June 06, 1995.

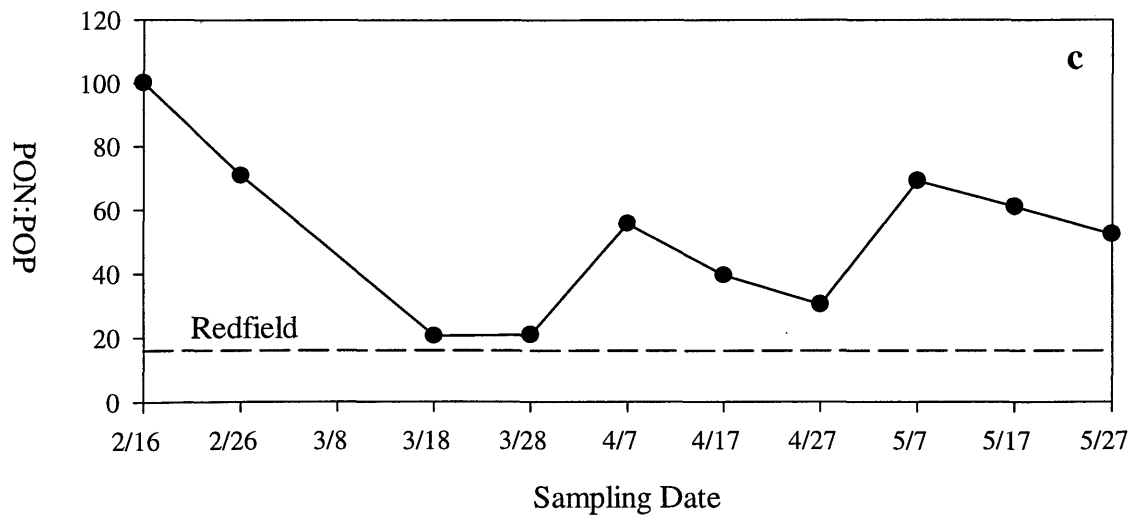
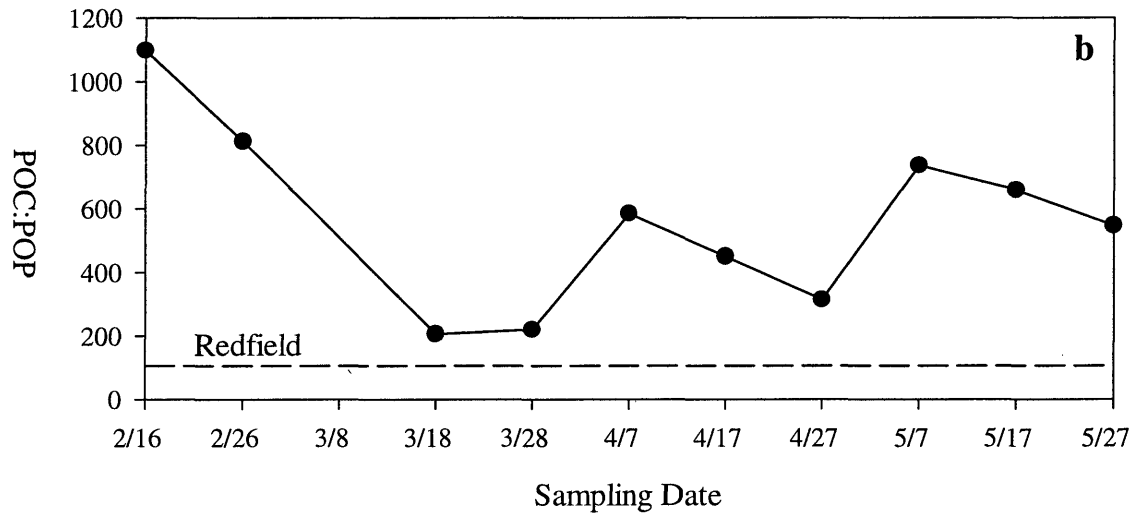
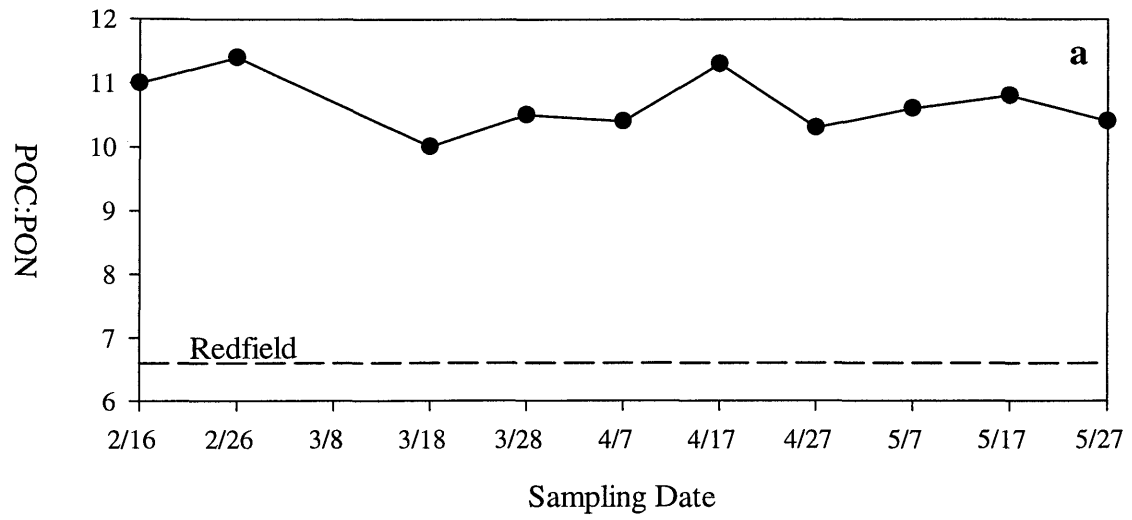


TABLE 7. Sinking Particulate Matter Fluxes and Flux Ratios for Station M at 650 mab

Sample dates	Mass				Fluxes ($\text{mg m}^{-2} \text{d}^{-1}$)				% Total				Flux Ratios			
	POC	PON	POP	TPP	POC	PON	POP	TPP	POC	PON	POP	PIP	TPP	POC:PON	POC:POP	PON:POP
2/16	134.4	9.7	1.03	0.105	0.023	0.082	0.105	7.22	0.768	0.017	0.061	0.078	11.0	1099	100	
2/26	114.4	6.9	0.71	0.094	0.022	0.072	0.094	6.05	0.617	0.019	0.063	0.082	11.4	812	71.0	
3/18	120.0	6.3	0.73	0.132	0.079	0.053	0.132	5.23	0.611	0.066	0.044	0.110	10.0	205	20.6	
3/28	157.2	8.3	0.92	0.204	0.097	0.107	0.204	5.25	0.585	0.062	0.068	0.129	10.5	220	21.0	
4/7	196.4	9.4	1.06	0.104	0.042	0.063	0.104	4.80	0.538	0.021	0.032	0.053	10.4	585	56.1	
4/17	256.0	12.4	1.28	0.160	0.071	0.089	0.160	4.83	0.499	0.028	0.035	0.062	11.3	450	39.9	
4/27	178.8	9.2	1.05	0.163	0.076	0.087	0.163	5.17	0.586	0.043	0.049	0.091	10.3	314	30.5	
5/7	346.4	18.9	2.07	0.152	0.066	0.086	0.152	5.44	0.598	0.019	0.025	0.044	10.6	737	69.4	
5/17	392.0	21.9	2.37	0.275	0.086	0.189	0.275	5.59	0.605	0.022	0.048	0.070	10.8	658	61.1	
5/27	346.0	16.8	1.89	0.197	0.079	0.117	0.197	4.85	0.545	0.023	0.034	0.057	10.4	546	52.6	
Mean	224.2	12.0	1.31	0.159	0.064	0.094	0.159	5.44	0.595	0.032	0.046	0.078	10.7	563	52.2	

Fluxes ($\text{mmol m}^{-2} \text{d}^{-1}$) 0.997 0.0936 0.00207 0.00305 0.00511

From Smith *et al.* (1994)

Mass = $95.3 \text{ mg m}^{-2} \text{d}^{-1}$

POC = $6.55 \text{ mg C m}^{-2} \text{d}^{-1}$ = $0.55 \text{ mmol m}^{-2} \text{d}^{-1}$

PON = $0.77 \text{ mg N m}^{-2} \text{d}^{-1}$ = $0.055 \text{ mmol m}^{-2} \text{d}^{-1}$

POP¹ = $0.0012 \text{ mmol m}^{-2} \text{d}^{-1}$

PIP¹ = $0.0017 \text{ mmol m}^{-2} \text{d}^{-1}$

TPP¹ = $0.0029 \text{ mmol m}^{-2} \text{d}^{-1}$

¹estimated (see text)

Discussion

Distributions of DOM, Suspended POM and SOM

Profiles of DOC, DON and DOP from this study at both sites were qualitatively similar to DOC, DON and DOP profiles previously reported for various parts of the world's oceans (Holm-Hansen *et al.*, 1966; Williams *et al.*, 1980; Ridal and Moore, 1992; Hopkinson *et al.*, 1997). Although the concentration range for DOC for the eastern North Pacific (35-72 $\mu\text{M C}$) was similar to those found by Holm-Hansen *et al.* (1966; 40-80 $\mu\text{M C}$) for Santa Catalina Basin, Williams *et al.* (1980; 40-60 $\mu\text{M C}$) for the central North Pacific gyre, and Hopkinson *et al.* (1997; 50-80 $\mu\text{M C}$) for Georges Bank, surface DOC concentrations were higher than those observed by Williams *et al.* (1980) and deep water concentrations were lower than those reported by Hopkinson *et al.* (1997). The DOC concentrations at the Southern Ocean site were lower than those observed by Hopkinson *et al.* (1997) but fell within the range observed by Williams *et al.* (1980). Deep water DOC concentrations for both sites were the same as those observed by Hansell and Carlson (submitted) for deep global ocean waters (42 $\mu\text{M C}$ for the Southern Ocean and 39 $\mu\text{M C}$ for the North Pacific).

Concentrations of DON (1.5-5.2 $\mu\text{M N}$) for both sites were lower than those reported by Holm-Hansen *et al.* (1966; 3-8 $\mu\text{M N}$) and Williams *et al.* (1980; 4-6 $\mu\text{M N}$) but were similar to those observed by Smith *et al.* (1986; 1.5-4 $\mu\text{M N}$) for the North Pacific Gyre, and Hopkinson *et al.* (1997; 2-5 $\mu\text{M N}$). Concentrations of DOP (0.073-

0.229 $\mu\text{M P}$) for both sites were lower than those determined by Holm-Hansen *et al.* (1966; 0.1-0.4 $\mu\text{M P}$) and Williams *et al.* (1980; 0.1-0.3 $\mu\text{M P}$), but were higher than those reported by Hopkinson *et al.* (1997; 0.02-0.017 $\mu\text{M P}$). Concentrations of DOP from this study, however, were similar to those observed by Smith *et al.* (1986; 0.05-0.2 $\mu\text{M P}$) and Ridal and Moore (1992; 0-0.25 $\mu\text{M P}$, for the northeast subarctic Pacific).

Concentrations of suspended POC and PON for the eastern North Pacific fell within the same range ($\sim 3\text{-}24 \mu\text{g C L}^{-1}$ and $\sim 0.2\text{-}5 \mu\text{g N L}^{-1}$, respectively) as those reported by Williams *et al.* (1980), although suspended POC and PON concentrations for the Southern Ocean were lower. Surface suspended POC and PON concentrations for both sites, however, were 2-3 times higher than those observed by Williams *et al.* (1980).

Comparing the two study sites, surface DOC concentrations at the eastern North Pacific sites were higher than at the Southern Ocean site, although deep ocean concentrations were slightly higher in the Southern Ocean than in the eastern North Pacific (compare Figures 5a and 9a). In their survey of the world's deep oceans, Hansell and Carlson (submitted), found similar deep ocean DOC concentration gradients. They found that deep ocean DOC concentrations were highest in the North Atlantic Ocean where extensive deep water formation occurs, and lowest in the North Pacific, at the terminus of the global ocean conveyor. Concentrations of DON (Figures 5b and 9b) also showed a decrease from Station F to the eastern North Pacific, although surface concentrations were about the same. Northward flowing deep water (i.e. from the Southern Ocean to the North Pacific) along the global conveyor belt that is getting older and has organic matter that is being degraded over time could explain the deep ocean DOC and DON concentration gradients between the two sites. This is consistent with the

relative ages of the DOC pool between these two sites measured concurrently during this study (Druffel and Bauer, 1998). DOC and DON are cumulatively remineralized as they are transported through the deep world ocean, causing both DOC and DON concentrations to decrease with time (and space) and inorganic nutrients to accumulate along the course of the mean deep water flow. Microbial decomposition of DOC and DON in excess of “locally produced” DOM could further explain this phenomenon (Hansell and Carlson, submitted). Concentrations of DOP, however, were similar at both sites (Figures 5c and 9c), showing no difference in concentrations for either surface or deep waters with the exception of those at Stn US. The increase in near-bottom DOP concentration could possibly be attributed to sediment porewater inputs at this site.

Concentrations of DIN and DIP showed an opposite gradient to DOM, with surface DIN and DIP concentrations in the Southern Ocean being higher than those found in the eastern North Pacific, while deep ocean concentrations were lower in the Southern Ocean than in the eastern North Pacific (Figures 6 and 10). This difference in the nutrient concentrations between the two sites is also most likely explained by the relative position of the two sites along the path of deep ocean water transport. The differences in surface nutrient concentrations, however, are better explained by upward advection of deep ocean nutrients. Higher nutrient concentrations in the surface waters at the Southern Ocean site can be explained by greater advective input of deep ocean nutrients at this site relative to the eastern North Pacific site due to a weaker seasonal thermocline at Station F compared to at Station M.

Along the eastern North Pacific transect, the decrease in surface DOC concentrations going onshore, from Station M to Station US (Figure 5a), reflects the

upwelling of DOC-poor deeper waters (Bauer *et al.*, 1998b). Similar distributions were also seen for DON and DOP surface concentrations (Figures 5a and 5b), although preferential utilization of DON and DOP (based on elemental ratios of surface DOM that were higher than Redfield - see below) by surface microheterotrophic communities may cause this onshore-offshore gradient to be less pronounced. The increase in surface concentrations of DIN and DIP (Figures 6a and 6b) going onshore is also likely explained by the upwelling of nutrient-rich deep water.

Suspended POC, PON and POP concentrations were similar for the eastern North Pacific and Southern Oceans (Figures 7 and 11), both in surface and deep waters, suggesting that the concentrations of suspended POM may be controlled by different factors than for DOM. Biological alteration and disaggregation of sinking POM to suspended POM, and dissolution of suspended POM to DOM have been found to be important in the transformation of particulate to dissolved organic phases (McCave, 1975; Wakeham and Canuel, 1988; Druffel *et al.*, 1998). It has also been postulated that DOC may sorb onto suspended POC (Druffel *et al.*, 1998).

Surface water concentrations of suspended PIP were higher in the Southern Ocean than in the eastern North Pacific (Figures 7d and 11d), although deep ocean concentrations were similar. It should be noted that the apparent high suspended PIP concentrations, especially in surface ocean samples, could in part be an experimental artifact resulting from hydrolysis of labile organic P compounds during acid extraction of the inorganic particulate P phase (Ruttenberg, 1992; Ruttenberg and Goñi, 1997). Concentrations of suspended POC, PON, POP and PIP (Figure 7) along the eastern North Pacific transect did not show any onshore-offshore surface gradients, suggesting

that upwelling is not important in the control of suspended particulate matter distributions for surface waters at these stations. Using $\Delta^{14}\text{C}$ and biomarkers such as pyropheophorbide-*a* of suspended POC, other studies in the eastern North Pacific have suggested that resuspended POC may be laterally transported along the slope over a near-bottom depth range (Bianchi *et al.*, 1998; Druffel *et al.*, 1998; Sherrell *et al.*, 1998), thus contributing to the near-bottom peak in suspended POM concentrations at Stn US.

Surface SOC, SON and SOP concentrations in the eastern North Pacific were much higher than in the Southern Ocean (Tables 3 and 6). Since primary production at both sites were of similar magnitude, a possible explanation for this is that lateral transport of resuspended SOM along the continental slope at the eastern North Pacific site could be a contributing factor to the higher SOM concentrations (Druffel *et al.*, 1998). Reimers *et al.* (1992) sampled more intensively (5 stations) along the same transect as the eastern North Pacific transect from this study and found that surface SOC concentrations increased from their off-shore to their on-shore stations, indicating possible lateral transport of SOC from the slope to the abyssal oceans. Surface SIP concentrations (Tables 3 and 6) were also higher in the eastern North Pacific, but this is not surprising as the eastern North Pacific site lies closer to continental influences than the Southern Ocean site and thus may experience greater inputs of inorganic P from continental weathering and deposition by rivers.

Elemental Ratios of DOM, Suspended POM and SOM

In this study, elemental ratios observed for DOM were generally much greater than Redfield. This is consistent with ratios observed by Hopkinson *et al.* (1997), who reports DOM ratios ranging from 11-15 for DOC:DON, 400-800 for DOC:DOP, and 24-55 for DON:DOP. Similar ratios were also observed by Williams *et al.* (1980) for DON:DOP. It was also observed that TDN:TDP (i.e., DIN+DON and DIP+DOP) ratios approached Redfield than inorganic ratios alone, as been previously reported by Jackson and Williams (1985) for the Pacific Ocean, and Karl *et al.* (1993) at the US-JGOFS time-series station near Hawaii. This implies that in order to balance N and P budgets for the open ocean water column, surface concentrations of inorganic N and P must be “supplemented” by other pools (i.e. DON and DOP pools).

Elemental ratios for DOM (Figures 12 and 15) fell within similar ranges for the two sites studied here. DOM ratios in the eastern North Pacific and Southern Oceans in nearly all cases exceeded Redfield, indicating that as a general rule, DOP is preferentially remineralized relative to DOC and DON. The increase in DOC:DON ratios with depth over the upper 500 m at both sites indicate that there is preferential remineralization of DON relative to DOC with depth in the upper 500 m of the water column. Increases in DOC:DOP ratios at both sites also indicate that DOP is preferentially remineralized with depth relative to DOC. Although there was a small increase in DON:DOP ratios with depth at the Southern Ocean site, there was almost a two-fold increase in DON:DOP ratios with depth at the eastern North Pacific, suggesting that DOP may be preferentially remineralized with depth. This gradient was more apparent at the eastern North Pacific site than in the Southern Ocean, probably due to greater vertical advective mixing at the

Southern Ocean site. Elemental ratios for DOM along the eastern North Pacific transect did not show any on- or offshore pattern (Figure 12).

Elemental ratios in suspended POM (Figures 14 and 16) for both the eastern North Pacific and Southern Ocean also exceeded Redfield, but generally by less than DOM ratios. Ratios of POC:PON, POC:POP and PON:POP showed a high level of variability throughout the water column at both sites and fell within the same ranges as DOM ratios. Suspended POC:PON ratios for deep waters were lower in the eastern North Pacific compared to the Southern Ocean although there were no differences in surface ratios. Suspended POC:POP and PON:POP ratios in the eastern North Pacific were similar to those observed in the Southern Ocean. For the eastern North Pacific transect, there was a decrease in surface POC:PON ratios going offshore, suggesting that surface suspended POM at Station M is relatively N-rich.

Surface SOM between the two sites (Station M and F) had very different elemental ratios (Table 3 and 6). For the eastern North Pacific, ratios were all higher than Redfield while SOC:SOP and SON:SOP ratios for the Southern Ocean were all lower than Redfield (although the SOC:SON ratio approach Redfield at the Southern Ocean site). This suggests that most of the POM produced in the mixed layer at the eastern North Pacific site has undergone some sort of degradation, with the preferential loss of N and P, before reaching the seabed, with the O₂ minimum zone contributing to the enhancement of microbial processes. Martin *et al.* (1987) found that ~50% of organic C is regenerated in the upper 300 m at their VERTEX sites. The low SOC:SOP and SON:SOP ratios observed in the Southern Ocean is not uncommon in organic carbon-poor (< 0.5% organic C) marine sediments from the world's oceans (Froelich *et al.*, 1982; summary) and

Amazon River plume sediments (Ruttenberg and Goñi, 1997). Low SOC:SOP and SON:SOP ratio could be due to the presence of refractory organic P compounds at this site (Froelich *et al.*, 1982; Ruttenberg and Goñi, 1997).

Sinking POM Fluxes and Flux Ratios

Sinking POC fluxes (Table 7) at Station M during this study were the same as sinking POC fluxes reported by Knauer *et al.* (1979; $1.0 \text{ mmol C m}^{-2} \text{ d}^{-1}$) for their 1050 m open ocean sediment trap in the eastern North Pacific gyre, while sinking PON and TPP fluxes were respectively 3 and 5 times greater than those observed by Knauer *et al.* (1979; $0.034 \text{ mmol N m}^{-2} \text{ d}^{-1}$ and $0.0011 \text{ mmol P m}^{-2} \text{ d}^{-1}$, respectively). However, sinking POC and PON fluxes from this study were only twice as high as those estimated using the normalized power function by Martin *et al.* (1987) for their open ocean composite (OOC) for sinking POC and PON. The sinking POC and PON fluxes measured in this study were comparable to those observed in previous years' studies at this station, for a similar time period (Smith *et al.*, 1994). When compared to the long-term average sinking POC and PON fluxes for this station ($0.55 \text{ mmol C m}^{-2} \text{ d}^{-1}$ and $0.055 \text{ mmol N m}^{-2} \text{ d}^{-1}$, respectively, Smith *et al.*, 1994), fluxes observed during this study were about twice as high.

The differences in fluxes of sinking particulate matter for Station M observed during this study compared to the long-term average fluxes from Smith *et al.* (1994) are a result of the spring-summer pulses of organic matter at this station (Smith *et al.*, 1994; Druffel *et al.*, 1996). Since the time period for this study in the eastern North Pacific was coincident with a high flux period, it is reasonable that the fluxes measured in this study

were higher than the long term average fluxes estimated by Smith *et al.* (1994). Also, sinking POM fluxes at this station are likely controlled in part by the lateral transport of organic matter from relatively high productivity, nearshore up-welling areas, and continental shelf and upper slope sediments (Bianchi *et al.*, 1998; Druffel *et al.*, 1998; Sherrell *et al.*, 1998). This also explains the relatively high fluxes measured in this study compared to Martin *et al.*'s (1987) open ocean composite estimates. In deriving their composite of sinking POM flux for the open ocean, Martin *et al.* (1987) used only sediment trap data from sites that were farthest away from any potential input of organic matter by lateral transport.

Sinking POC:PON flux ratios from this study were the same as those estimated from the open ocean composite by Martin *et al.* (1987) and those observed by Smith *et al.* (1994) for this station. These ratios, however were about 3 times lower than those measured by Knauer *et al.* (1979). Sinking POC:POP flux ratios were ~1.5 times lower than those observed by Knauer *et al.* (1979), while sinking PON:POP flux ratios were ~1.5 times greater. Elemental ratios of the sinking POM fluxes did not follow C, N, and P mass fluxes over the sampling period (Figure 18, Table 7), although all ratios were much higher than Redfield, suggesting preferential remineralization of N and P in these sinking particles. Flux ratios for sinking POM greater than Redfield (C:N:P = 910:31:1) were also observed by Knauer *et al.* (1979) for their 1050 m open ocean sediment trap in the eastern North Pacific gyre.

Fluxes and Flux Ratios of DOM, Suspended POM and Sinking POM: A Comparison

In order to evaluate the contributions of DOM and suspended POM to overall organic C, N and P fluxes at the two main study sites, a simple one-dimensional vertical eddy diffusion model was used to estimate fluxes of DOM and suspended POM from the upper mixed layer (above the permanent thermocline) to the deep ocean using Fick's First Law:

$$F = - K_z \frac{dC}{dz} \quad (\text{Eq. 3})$$

where F is flux (in $\text{mmol m}^{-2} \text{d}^{-1}$), K_z is the vertical eddy diffusion coefficient (in $\text{m}^2 \text{d}^{-1}$) and dC/dz (dC in μM and dz in m) the concentration gradient from the surface to the base of the permanent thermocline. Eq. 3 can be rewritten as:

$$F = - K_z \frac{C_{\max} - C_{\min}}{z_{\max} - z_{\min}} \quad (\text{Eq. 4})$$

The concentration gradient (dC/dz) for each parameter was calculated by taking the difference between the maximum surface concentration (C_{\max}) and the concentration (C_{\min}) at the base of the main thermocline, divided by the corresponding depth interval ($z_{\max} - z_{\min}$). Vertical eddy diffusion coefficients (K_z) were taken from Li *et al.* (1984) for the North Pacific ($1.8 \text{ cm}^2 \text{ s}^{-1}$) and the South Pacific ($2.8 \text{ cm}^2 \text{ s}^{-1}$). These values were based on averaged tritium profiles for each oceanic region. Based on Eq. 4, fluxes of DOM and suspended POM were calculated for Station M in the eastern North Pacific and Station F in the Southern Ocean and are listed in Tables 8 and 9.

These flux estimates are considered to be representative of long-term (i.e. seasonal to annual) average values based on two basic assumptions. a) Surface to deep concentration gradients of DOM and suspended POM are relatively constant throughout

TABLE 8. DOM Fluxes and Flux Ratios for Eastern North Pacific and Southern Oceans

Site	C_{\max} (μM)	C_{\min} (μM)	Z_{\max} (m)	Z_{\min} (m)	ΔC	Δz	Flux ($\text{mmol m}^{-2} \text{d}^{-1}$)
<u>DOC</u>							
ENPac	72	38	25	722	34	-697	0.76
SOce	50	41	3	1289	9	-1286	0.17
<u>DON</u>							
ENPac	4.5	2.8	25	722	1.3	-697	0.030
SOce	4.3	3.0	3	1289	1.3	-1286	0.024
<u>DOP</u>							
ENPac	0.229	0.107	25	722	0.12	-697	0.0027
SOce	0.216	0.075	3	1289	0.14	-1286	0.0026

<u>Flux ratios</u>		
	<u>ENPac</u>	<u>SOce</u>
<u>DOC:DON</u>	25	7.1
<u>DOC:DOP</u>	283	64
<u>DON:DOP</u>	11	9.1

Diffusive coefficient, K_z (Li et al., 1984)

$$\text{NPac} = 1.8 \text{ cm}^2 \text{ s}^{-1} = 15.6 \text{ m}^2 \text{ d}^{-1}$$

$$\text{SPac} = 2.8 \text{ cm}^2 \text{ s}^{-1} = 24.2 \text{ m}^2 \text{ d}^{-1}$$

TABLE 9. Suspended POM Fluxes and Flux Ratios for Eastern North Pacific and Southern Oceans

Site	C_{\max} ($\mu\text{g L}^{-1}$)	C_{\min} ($\mu\text{g L}^{-1}$)	z_{\max} (m)	z_{\min} (m)	ΔC	Δz	Flux ($\text{mg m}^{-2} \text{d}^{-1}$)	Flux ($\text{mmol m}^{-2} \text{d}^{-1}$)
<u>POC</u>								
ENPac	62.8	2.06	25	700	60.8	-675	1.40	0.117
SOce	41.7	1.31	6	1300	40.4	-1294	0.76	0.063
<u>PON</u>								
ENPac	12.8	0.30	25	700	12.5	-675	0.290	0.0207
SOce	6.87	0.20	6	1300	6.66	-1294	0.125	0.0089
<u>POP</u>								
ENPac	0.556	0.019	25	700	0.536	-675	0.0124	0.00040
SOce	0.418	0.025	6	1300	0.393	-1294	0.0073	0.00024
<u>PIP</u>								
ENPac	0.395	0.020	25	700	0.375	-675	0.0087	0.00028
SOce	0.856	0.014	6	1300	0.842	-1294	0.0157	0.00051
<u>TPP</u>								
ENPac	0.95	0.039	25	700	0.91	-675	0.0211	0.00068
SOce	1.27	0.039	6	1300	1.23	-1294	0.0231	0.00074

<u>Flux ratios</u>		
	<u>ENPac</u>	<u>SOce</u>
<u>POC:PON</u>	5.7	7.1
<u>POC:POP</u>	293	266
<u>PON:POP</u>	52	38

Diffusive coefficient, K_z (Li et al., 1984)

$$\text{NPac} = 1.8 \text{ cm}^2 \text{ s}^{-1} = 15.6 \text{ m}^2 \text{ d}^{-1}$$

$$\text{SPac} = 2.8 \text{ cm}^2 \text{ s}^{-1} = 24.2 \text{ m}^2 \text{ d}^{-1}$$

the year. Seasonal to annual concentration gradients of DOM at Stn M ranged only over a factor of 1.6 (24-38 $\mu\text{M C}$; Bauer *et al.*, 1998a) while concentration gradients of suspended POM ranged over a factor of 2.1 (36-74 $\mu\text{g C L}^{-1}$; Druffel *et al.*, 1996). b) By definition (see above), the surface to deep ocean DOM and suspended POM concentration gradients imply that these two pools are potentially available for eddy diffusive transport to the deep ocean.

At the eastern North Pacific site, calculated DOM fluxes were usually greater than the long-term (over two years) average sinking POM fluxes from Smith *et al.* (1994) (Table 10). Downward diffusive DOC and suspended POC fluxes accounted for 53% and 8%, respectively, of the total organic C flux to the deep ocean compared to the 39% contributed by average long-term sinking POC flux. However, downward diffusive DON and suspended PON fluxes were calculated to be 28% and 20%, respectively, of the total organic N flux, compared to 52% contributed by average sinking PON flux. Using the ratios of the long-term average sinking POC and PON fluxes to those obtained from this study, long-term average fluxes for sinking P were estimated to be: POP (0.0012 $\text{mmol P m}^{-2} \text{d}^{-1}$), PIP (0.0017 $\text{mmol P m}^{-2} \text{d}^{-1}$) and TPP (0.0029 $\text{mmol P m}^{-2} \text{d}^{-1}$). Using these estimates, DOP and suspended POP fluxes were found to contribute 65% and 9% to the total organic P flux. Even when these DOM and suspended POM fluxes were compared to the sinking POM fluxes for Station M measured during the high-flux study period, the fractions contributed by DOM and suspended POM fluxes to the total organic matter flux were not significantly changed. This indicates the importance of DOM fluxes from the upper mixed layer to the deep ocean at this site, regardless of whether they are evaluated against high- or low-flux periods of sinking POM.

TABLE 10. Summary of Dissolved, Suspended and Sinking Organic Matter Fluxes

Site	Flux ($\text{mmol m}^{-2} \text{d}^{-1}$)			Total
	Dissolved ¹	Suspended Particulate ¹	Sinking Particulate ^{2,3}	
<u>OC</u>				
² ENPac	0.76	0.117	0.55	1.4
³ SOce	0.17	0.063	0.46	0.69
<u>ON</u>				
ENPac	0.030	0.0207	0.055	0.11
SOce	0.024	0.0089	0.047	0.080
<u>OP</u>				
⁴ ENPac	0.0027	0.00040	0.0012	0.0043
SOce	0.0026	0.00024	-	0.0029
<u>IP</u>				
⁴ ENPac	-	0.00028	0.0017	0.0020
SOce	-	0.00051	-	0.00051
<u>TP</u>				
⁴ ENPac	0.0027	0.00068	0.0029	0.0063
SOce	0.0026	0.00074	-	0.0034

¹This study

²Long-term average for sinking POM fluxes from Smith *et al.* (1994)

³Sinking POM fluxes estimated from Martin *et al.* (1987) OOC

⁴estimated (see text)

In the Southern Ocean, DOC, DON, suspended POC, PON and POP diffusive fluxes to the deep ocean were 1.5-2.5 times lower than in the eastern North Pacific (Table 10). DOP fluxes, however were the same for both sites (Table 10), although suspended PIP fluxes in the Southern Ocean were ~1.7 times greater than those in the eastern North Pacific. As there are no published sediment trap data for the region of the Southern Ocean site, data from this study were compared with estimates of sinking POC and PON fluxes from Martin *et al.*'s (1987) open ocean composite. When compared with the estimated sinking POC flux from the open ocean composite, DOC and suspended POC fluxes in the Southern Ocean accounted for 25% and 9%, respectively, of the total organic C flux from the upper mixed layer to the deep ocean (Table 10). Fractions of DON and suspended PON fluxes were similar, contributing 30% and 11%, respectively, to the total organic N flux. As Martin *et al.* (1987) did not measure sinking P fluxes, DOP flux for the Southern Ocean were compared only with the suspended particulate P (POP and PIP) fluxes. Suspended PIP fluxes were twice as high as suspended POP fluxes (Table 10) in the Southern Ocean, although each consist of only 15% and 7%, respectively, of the total P fluxes for this site (not including any sinking P fluxes since no data were available). Vertical DOP fluxes at this site account for 76% of the total P fluxes, indicating that P fluxes in the Southern Ocean were dominated by DOP fluxes.

For Station M, while calculated C:N flux ratios for DOM and sinking POM were found to be higher than Redfield, the C:N flux ratios for suspended POM were lower than Redfield. This may be due to suspended POM being enriched in N in surface samples. All C:P flux ratios for the three organic matter pools were higher than Redfield, as were N:P flux ratios for suspended and sinking POM. Flux ratios of N:P for DOM, however,

were lower than Redfield in the eastern North Pacific. For the Southern Ocean, all flux ratios of DOM and suspended POM were higher than Redfield, with the exception of N:P flux ratio for DOM, which was not. These differences in flux ratios among the different pools of organic matter suggest that each of the pools that is being removed to the deep ocean has different chemical characteristics. Complex processes such as disaggregation (and/or aggregation), dissolution, sorption and selective remineralization could control the partitioning of organic C, N and P among the three different pools (sinking, suspended and dissolved) in the open ocean water column.

In summary, concentrations of DOM and suspended POM in the open ocean found in this study displayed unique C, N and P distributions, and were likely influenced by very different factors. While dissolved constituents were more likely to be influenced by the physical regime of the study site (e.g. upwelling in the eastern North Pacific or vertical advective inputs in the Southern Ocean), suspended particulate matter distributions and concentrations were more likely to be controlled by biological and chemical alteration of particulate matter in the ocean (Druffel *et al.*, 1998). This can be seen from the lack of surface-depletion in dissolved inorganic nutrients at Station F and the differences in surface DOC concentrations between Station F and Station M. The similar distributions and concentration ranges observed for suspended POM between the two sites also support this hypothesis.

Elemental ratios determined in this study reveal that DOP and suspended POP are preferentially remineralized at both sites. A slight increase in DOC:DOP and DON:DOP ratios for both study sites suggest that DOP also is being preferentially degraded with depth for the eastern North Pacific and Southern Oceans. Elemental ratios of DOM and

suspended POM observed for both sites were not significantly different from each other, suggesting that ocean regime does not necessarily control the qualitative characteristics of organic matter composition. Inclusion of DON and DOP concentrations in estimates of total dissolved N and P concentrations is important, as N and P concentrations will be underestimated if these organic nutrient pools are excluded, especially in surface waters.

Although organic C and N fluxes (for both dissolved and suspended particulate pools) were higher in the eastern North Pacific Ocean than in the Southern Ocean, organic P fluxes were similar for both sites. Suspended PIP fluxes in the Southern Ocean, however, were higher than in the eastern North Pacific. The contributions of DOM to the overall total organic C, N and P fluxes to the deep ocean cannot be ignored as they form a significant fraction of the overall organic matter flux. The contributions of DOM fluxes to the total organic flux are equally important even during high-flux periods of sinking POM, as demonstrated at Station M.

Summary and Conclusions

Surface and deep ocean concentrations of DOM and inorganic nutrients between the Southern Ocean and the eastern North Pacific displayed distinct differences although concentrations of suspended POM were similar at both sites. At both sites, DOM and suspended POM generally had elemental ratios that were much higher than Redfield, indicating that there was preferential remineralization of N and P relative to C in these pools. Although there were no distinct trends of C:N ratios in DOM and suspended POM with depth, an increase in C:P and N:P ratios were observed for DOM with depth for both sites, indicating preferential remineralization of DOP with depth.

Estimated eddy diffusive fluxes of DOM indicate the importance of this pool to the total organic matter flux from the upper mixed layer to the deep ocean at both sites, with DOM fluxes accounting for up to ~65%. Suspended POM fluxes accounted for up to ~20% of the total organic matter (as C, N and P) fluxes to the deep ocean.

These findings have potentially significant implications for C, N and P fluxes estimated in the deep open ocean, as these fluxes have traditionally been determined by sediment trap data. From the present findings, not only are dissolved and suspended particulate organic matter fluxes an important portion of the downward organic matter flux but that fluxes measured by sediment traps exclusively could significantly underestimate the flux of organic matter from the surface to the deep ocean.

Appendix I

Abbreviation Key

DOM	- dissolved organic matter, refers collectively to DOC, DON and DOP
POM	- particulate organic matter, refers collectively to POC, PON and POP
SOM	- sedimentary organic matter, refers collectively to SOC, SON and SOP
DOC, DON, DOP	- dissolved organic carbon, nitrogen, phosphorus
POC, PON, POP	- particulate organic carbon, nitrogen, phosphorus
SOC, SON, SOP	- sedimentary organic carbon, nitrogen, phosphorus
DIN, DIP	- dissolved inorganic nitrogen, phosphorus
PIP, SIP	- particulate and sedimentary inorganic phosphorus
TDN, TDP	- total dissolved nitrogen, phosphorus
TPP, TSP	- total particulate and sedimentary phosphorus

Appendix II

Two other cruises were conducted to Station M in the eastern North Pacific. However, only DOM samples were collected during these cruises. Pulse 30 was conducted from May 29 to June 7, 1996 and Pulse 31 were from October 7 to 16, 1996. Profiles of DOC, DON and DOP from Pulse 30 (filled circles) and 31 (open circles) are presented in Figure 19. Profiles of DIN and DIP from Pulse 30 (filled circles) and 31 (open circles) are presented in Figure 20. Elemental ratio profiles for DOM from Pulse 30 (filled circles) and 31 (open circles) are presented in Figure 21. DON:DOP ratios were higher for Pulse 31 than they were for Pulse 30. This shows preferential remineralization of DOP relative to DON over the course of 3 months. The Pulse 26 DON:DOP ratios do not show the same depth gradient as for Pulse 30, indicating that there are inter-annual differences in the quality of DOM at Stn M, as well as possible seasonal differences. Ratios of DIN:DIP and TDN:TDP are presented in Figure 22. All data from Pulse 30 and 31 are listed in Table 11.

Figure 19. Concentration profiles of a) DOC, b) DON, and c) DOP for Stn M.

Symbols used for all profiles were: Pulse 30 - filled circles; Pulse 31 - open circles. Error bars plotted for DON and DOP were ± 1 SD of duplicate measurements. Analytical error for DOC was $\pm 1 \mu\text{M C}$.

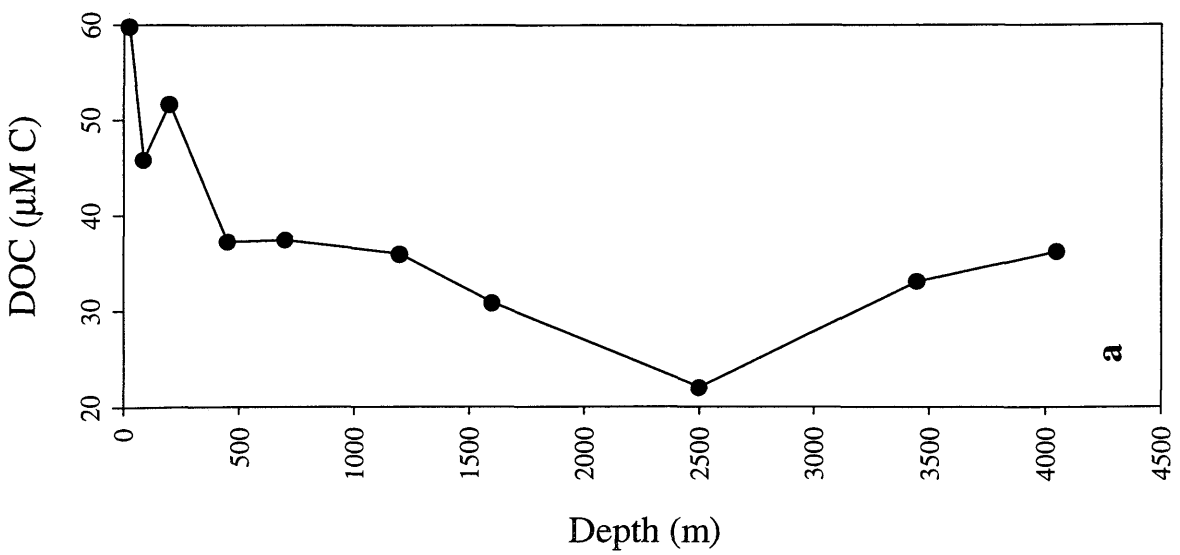
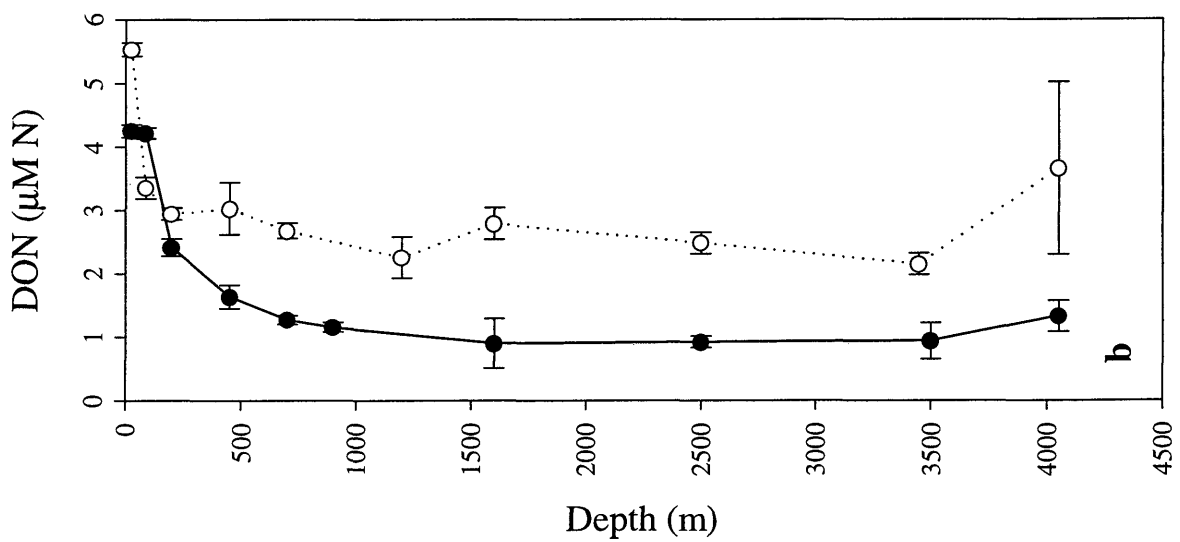
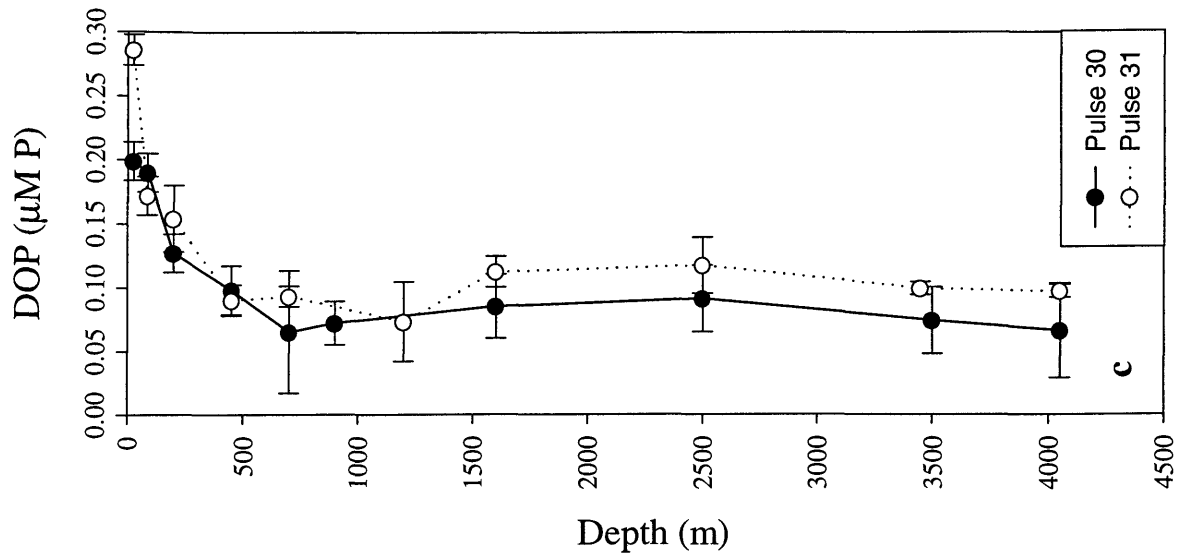


Figure 20. Depth profiles of a) DIN, and b) DIP concentrations for Stn M. Error bars plotted for DIN and DIP were ± 1 SD of duplicate measurements.

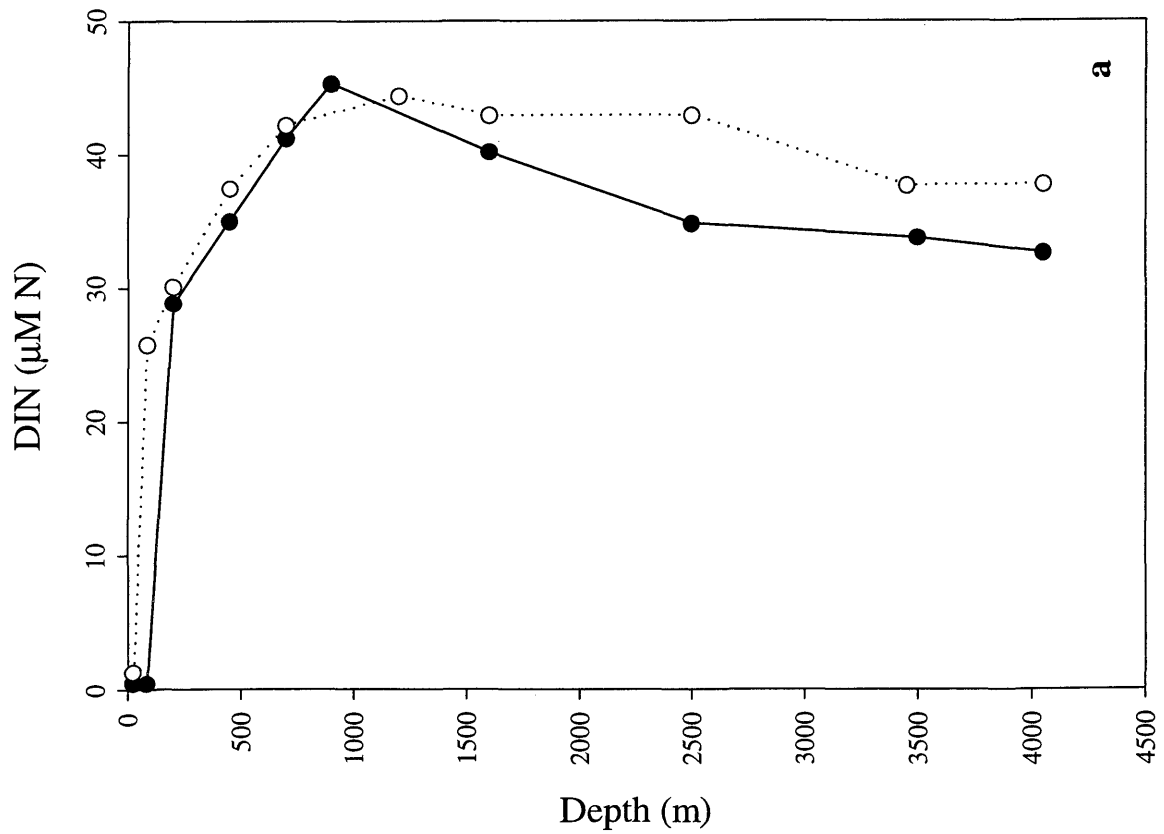
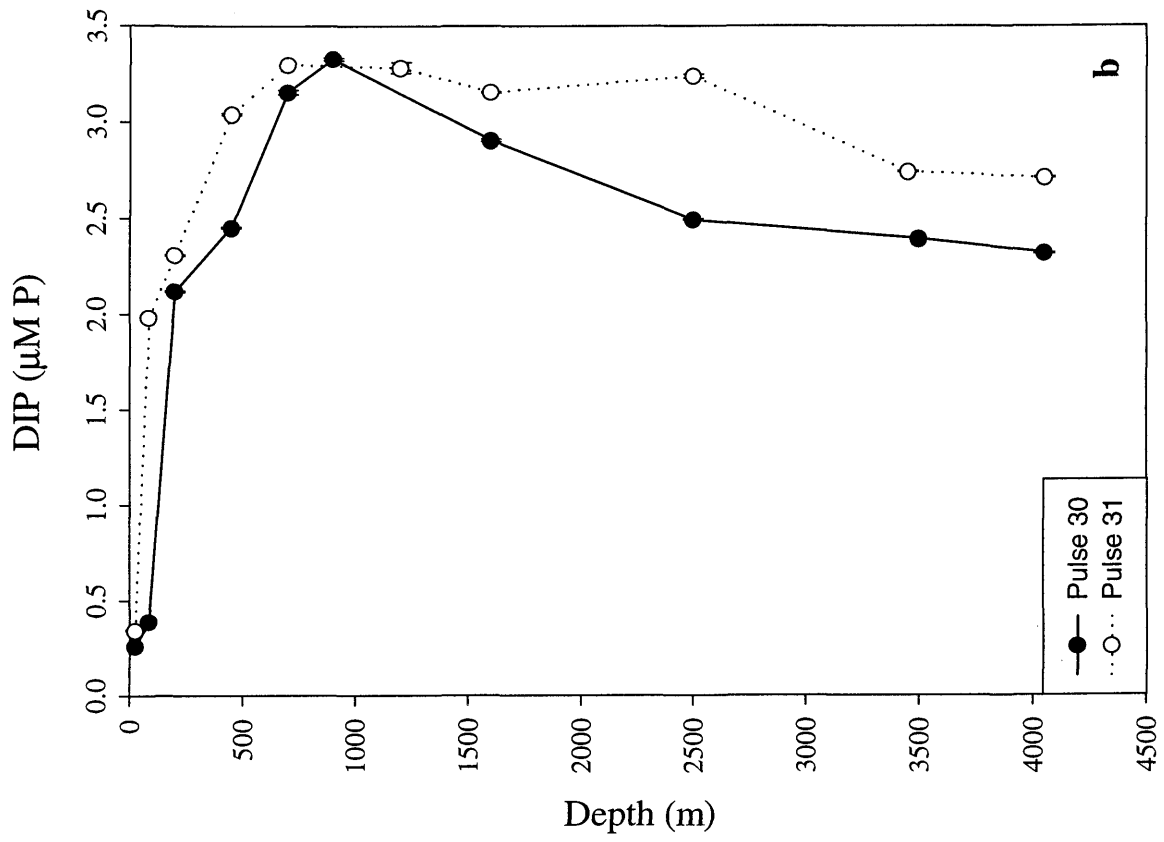


Figure 21. Depth profiles of DOM elemental ratios for Stn M for a) DOC:DON, b) DOC:DOP, and c) DON:DOP. Average Redfield ratios of C:N (6.6), C:P (106) and N:P (16) were plotted as dashed vertical lines for comparison.

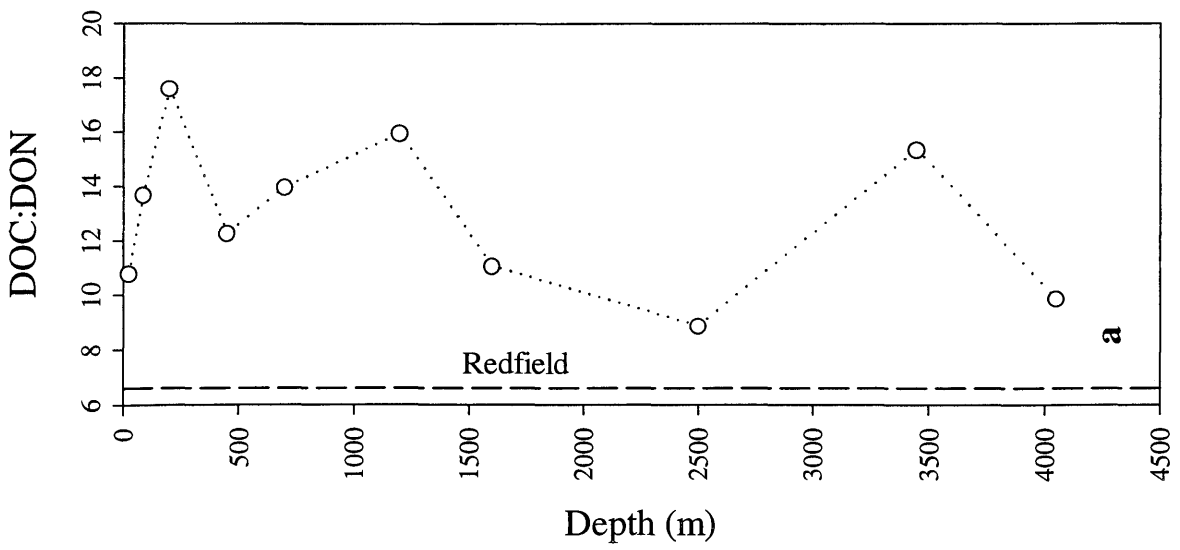
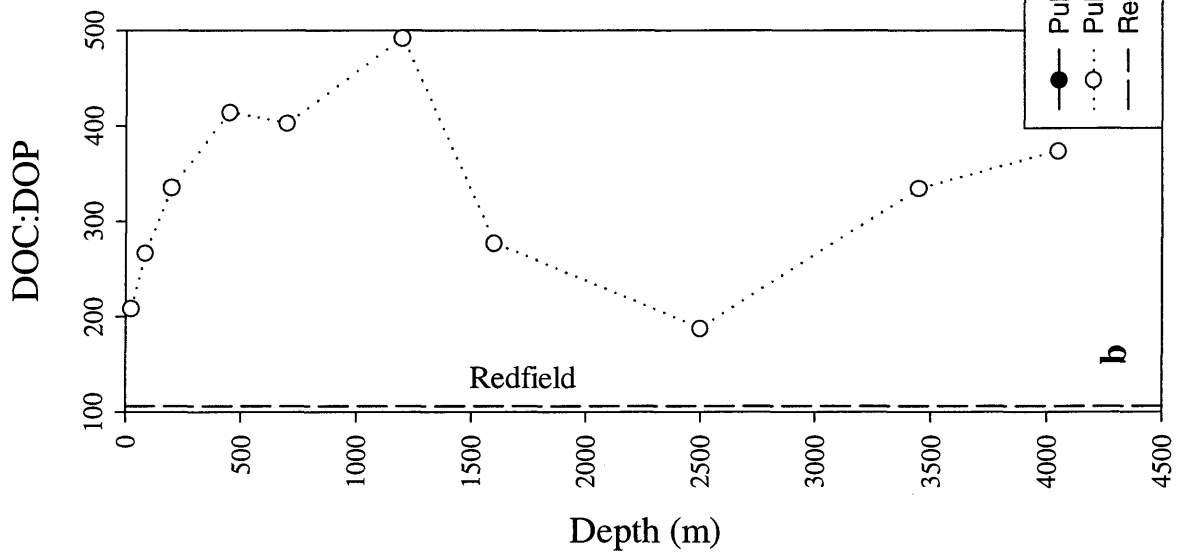
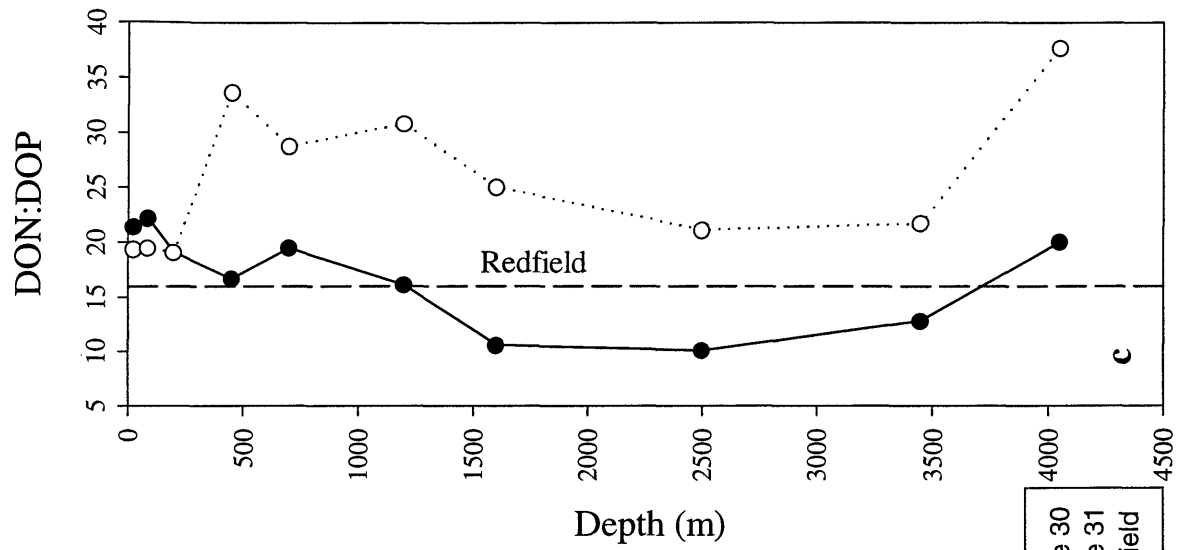


Figure 22. Depth profiles of dissolved N:P ratios for a) Pulse 30 and b) Pulse 31 for Stn M. Symbols used were: DIN:DIP ratios - filled circles and TDN:TDP ratios - open circles.

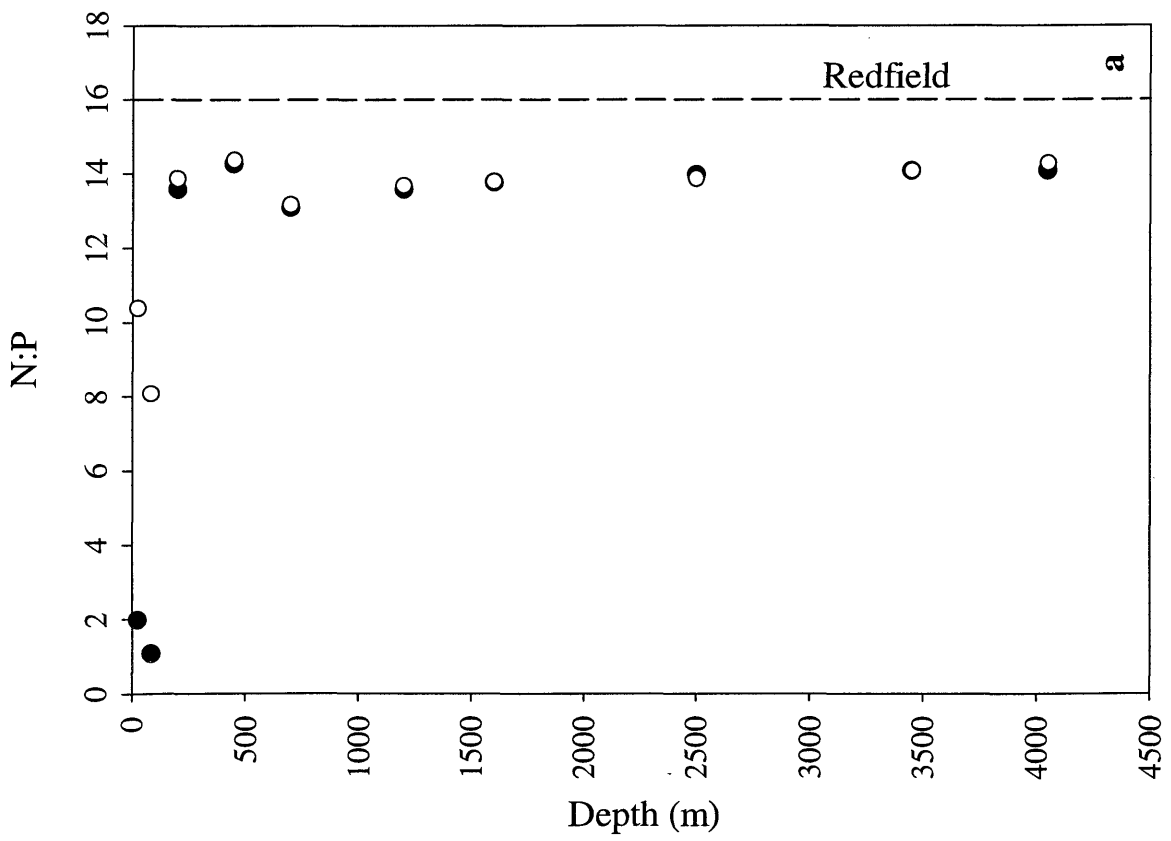
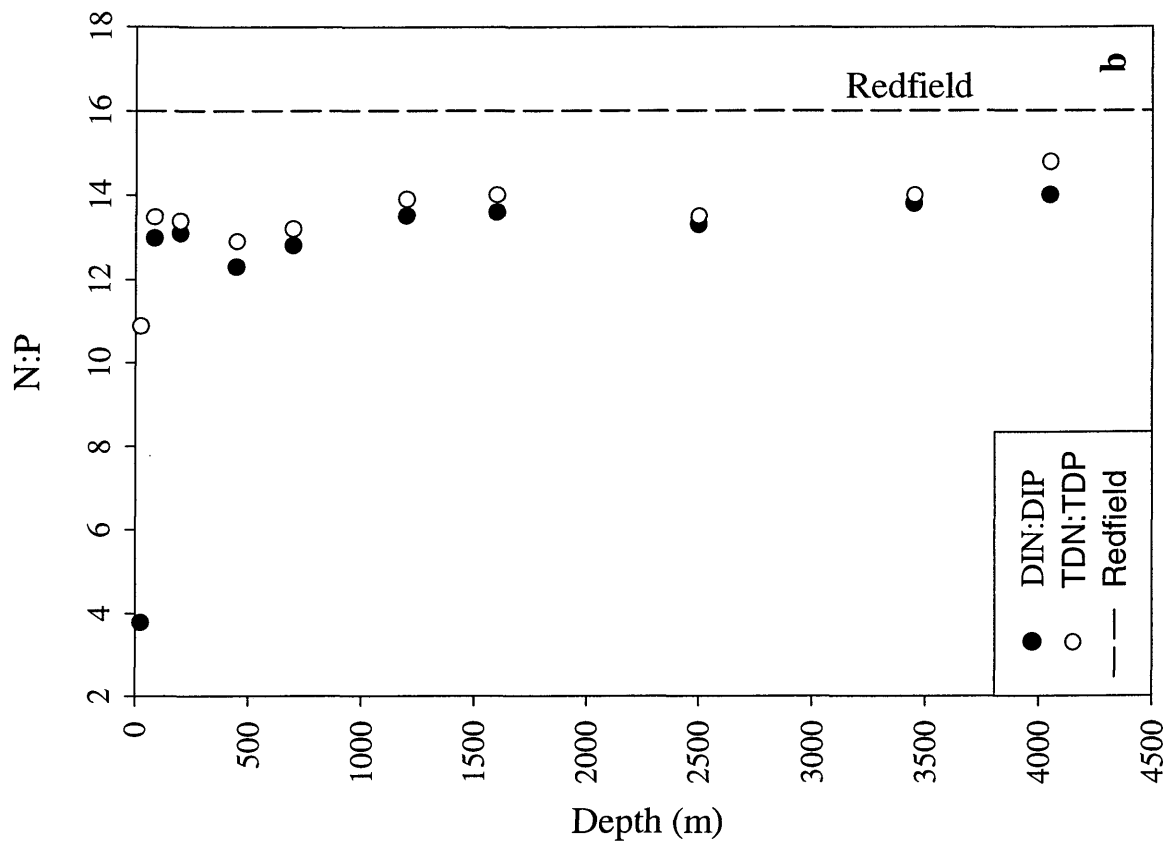


TABLE 11. Concentrations and Elemental Ratios of Dissolved Constituents for Pulse 30 and Pulse 31

Depth (m)	Pulse 30				Pulse 31				Elemental Ratios				
	DOC ($\mu\text{M C}$)	DON ($\mu\text{M C}$)	DOP ($\mu\text{M C}$)	DIP ($\mu\text{M C}$)	DOC:DON	DON:DOP	DOC:DOP	DIN:DIP	DOC:DON	DON:DOP	DOC:DOP	DIN:DIP	TDN:TDP
<i>Pulse 30</i>													
25	4.3	0.10	0.199	0.015	0.51	0.257	0.000			21	2.0	10	10
85	4.2	0.08	0.190	0.015	0.44	0.387	0.000			22	1.1	8.1	8.1
200	2.4	0.14	0.127	0.015	29	2.12	0.003			19	14	14	14
450	1.6	0.18	0.098	0.019	35	2.45	0.003			17	14	14	14
700	1.3	0.07	0.065	0.048	41	3.16	0.011			19	13	13	13
900	1.2	0.07	0.072	0.017	45	3.33	0.007			16	14	14	14
1600	0.9	0.39	0.085	0.025	40	2.90	0.007			11	14	14	14
2500	0.9	0.09	0.091	0.026	35	2.49	0.003			10	14	14	14
3500	0.9	0.28	0.074	0.026	34	2.39	0.000			13	14	14	14
4050	1.3	0.25	0.066	0.037	33	2.32	0.003			20	14	14	14
<i>Pulse 31</i>													
25	60	5.5	0.11	0.286	0.012	1.3	0.343	0.003	11	209	3.8	11	11
85	46	3.4	0.17	0.150	0.035	26	1.99	0.003	14	305	13	14	14
200	52	2.9	0.09	0.190	0.011	30	2.32	0.000	18	272	13	13	13
450	37	3.0	0.41	0.117	0.012	37	3.00	0.004	12	318	13	13	13
700	37	2.7	0.12	0.158	0.030	42	3.26	0.011	14	238	13	13	13
1200	36	2.3	0.32	0.058	0.017	44	3.26	0.007	16	621	14	14	14
1600	31	2.8	0.25	0.112	0.012	43	3.15	0.004	11	277	14	14	14
2500	22	2.5	0.17	0.117	0.022	43	3.24	0.011	9	188	13	14	14
3450	33	2.1	0.17	0.099	0.005	38	2.74	0.004	15	334	14	14	14
4050	36	3.7	1.36	0.097	0.005	38	2.71	0.004	10	374	14	15	15

Appendix III

Nine model compounds for DON and DOP were used to determine the efficiency of the DON and DOP oxidation method chosen for this study. Known concentrations of these compounds were prepared in a clean, full-strength (35 ppt) saline matrix and oxidized using the wet alkaline persulfate oxidation (for DON) and the high-temperature ashing (for DOP) methods. Percent recoveries were calculated based on the amount of N and P recovered. The DON and DOP compounds used and the respective percent recoveries are presented in Figures 23 and 24.

All DON compounds were recovered in excess of 90% with the exception of adenosine triphosphate (ATP). All DOP compounds were also recovered in excess of 90% with the exception of phosphonoacetic acid and D-glucose-6-phosphate, which had recoveries of 70% and 84%, respectively. These two compounds were visibly hygroscopic, thus affecting the ability to weigh them accurately, which could lead to an underestimation of the percent recoveries of these two compounds. Although recoveries for phosphonoacetic acid and D-glucose-6-phosphate were below 90%, similar studies using the same oxidation method found recoveries of greater than 90% (Monaghan and Ruttenberg, submitted; and all references therein).

Different volumes of a pure culture of the diatom *Chaetoceros calcitrans* were filtered and the filters analyzed for PIP and TPP content using the ashing method as described in Aspila *et al.* (1976) as an optimization of this method. Concentrations of PIP, TPP and POP were plotted against the volume of the diatom culture filtered and a

regression of each plot was taken (Figure 25). Regressions from PIP and TPP gave r-square values of 0.944 and 0.925, respectively, indicating that inorganic and organic P is conservatively extracted over a concentration range. The presence of PIP in a pure diatom culture could be due to chemical bonding of orthophosphate with the high-surface area of amorphous silica. However, this apparent PIP content could be due to the hydrolysis of labile POP from a relatively fresh diatom culture. Therefore, this difference method could actually overestimate PIP concentrations and underestimate POP concentrations, especially in high productivity surface waters.

Figure 23. Percent recovery of DON compounds using the wet alkaline persulfate oxidation method. Error bars were ± 1 SD.

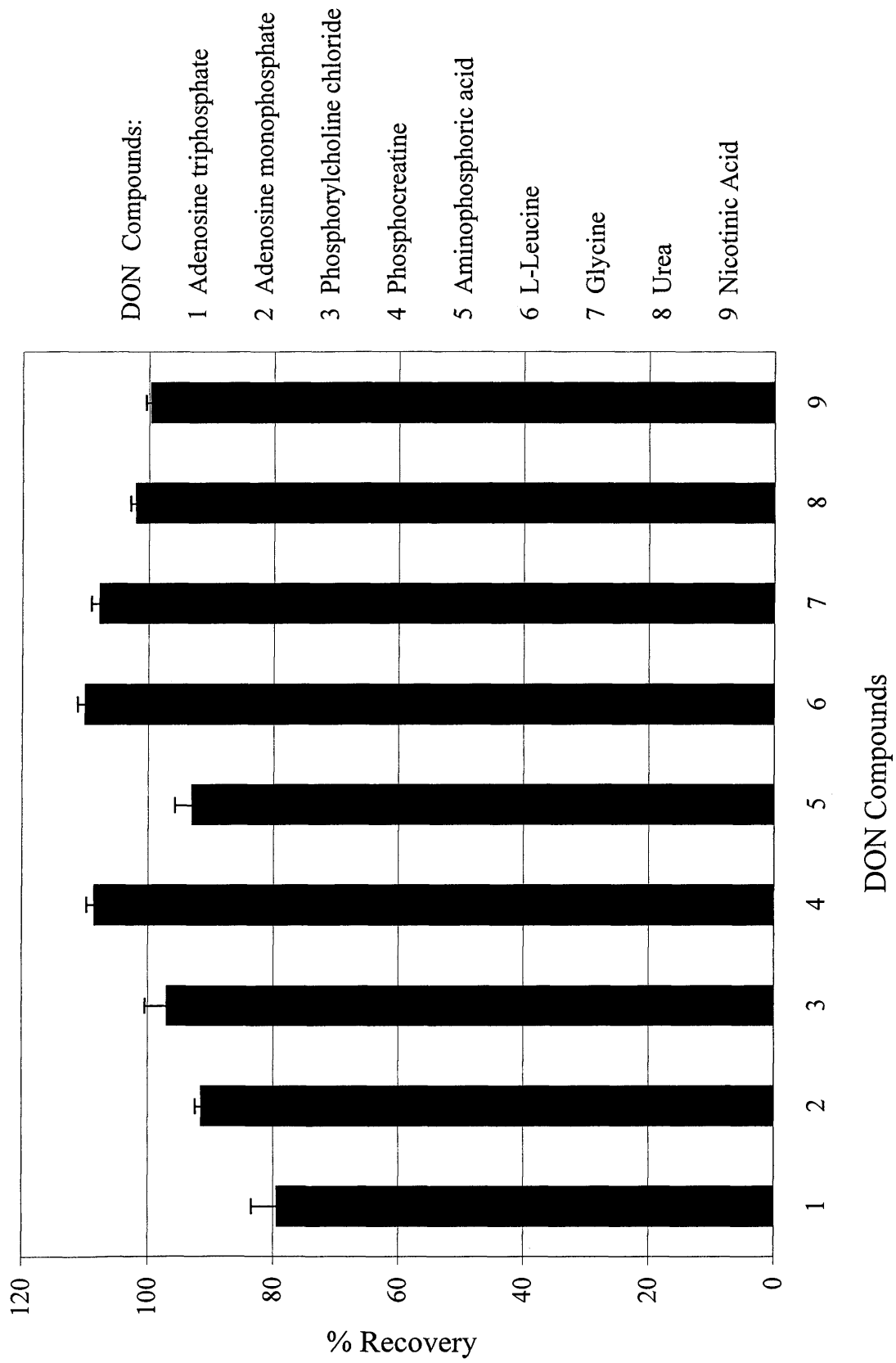


Figure 24. Percent recovery of DOP compounds using the high-temperature ashing oxidation method. Error bars were ± 1 SD.

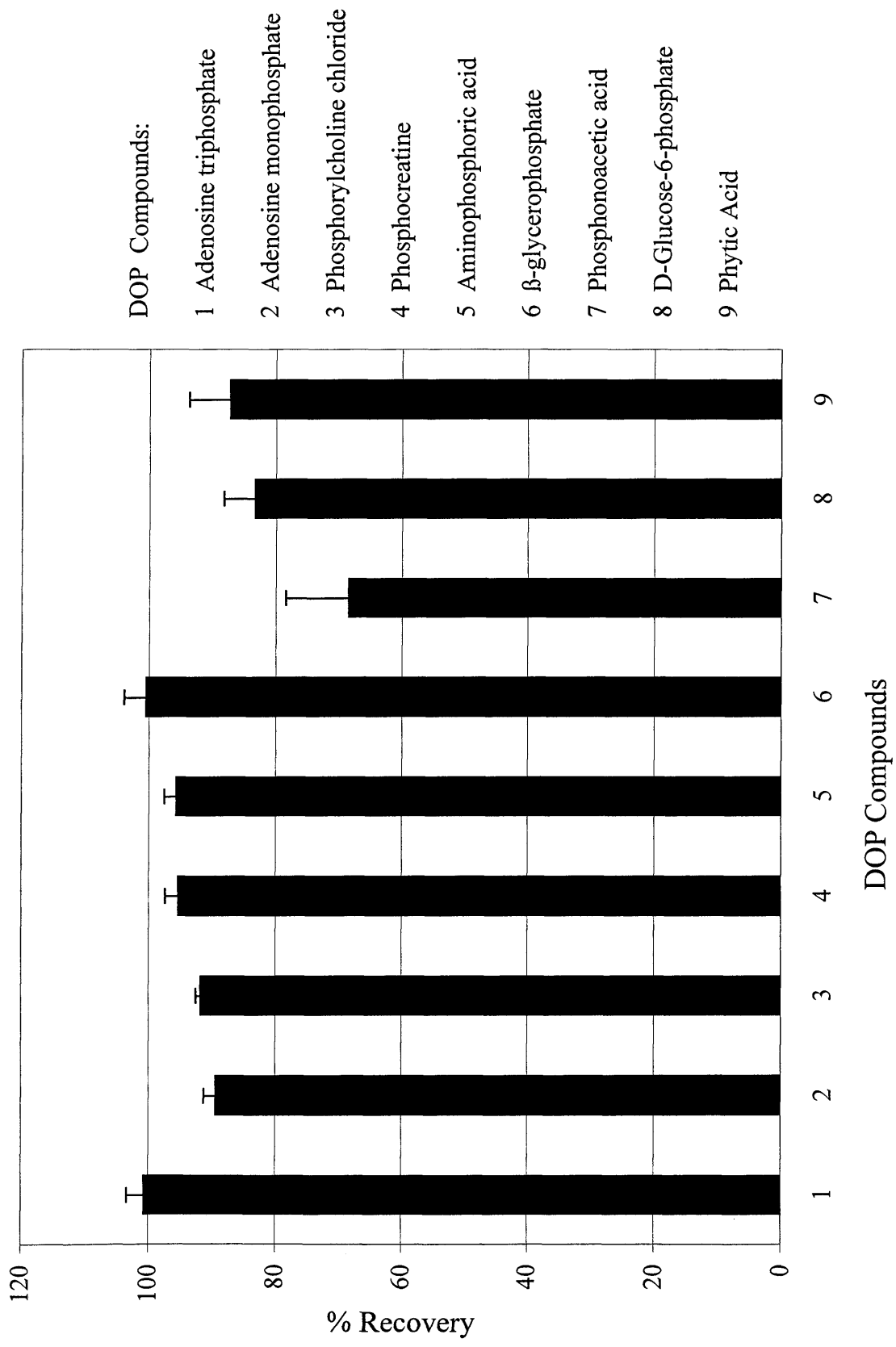
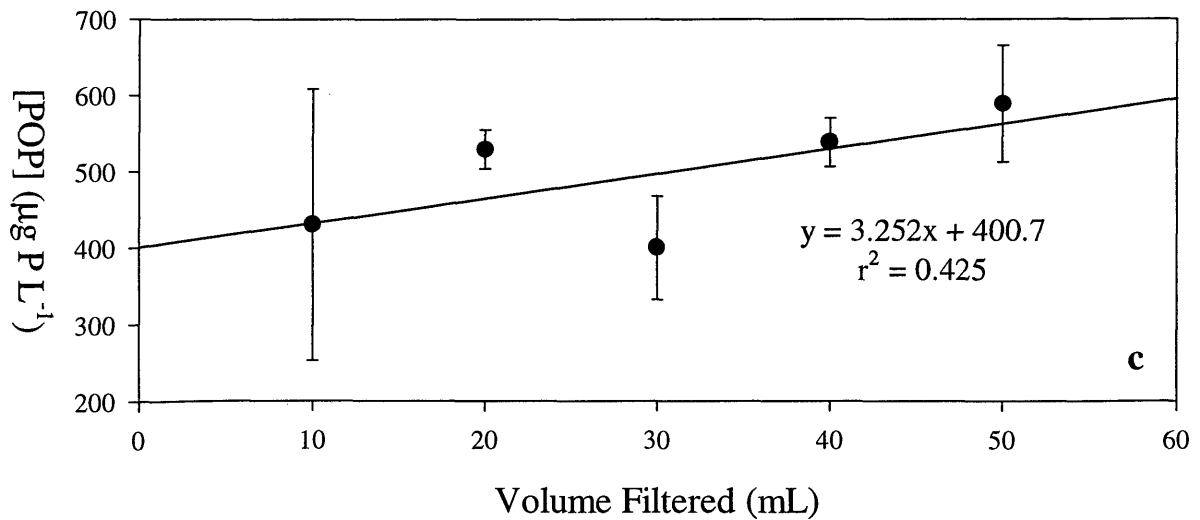
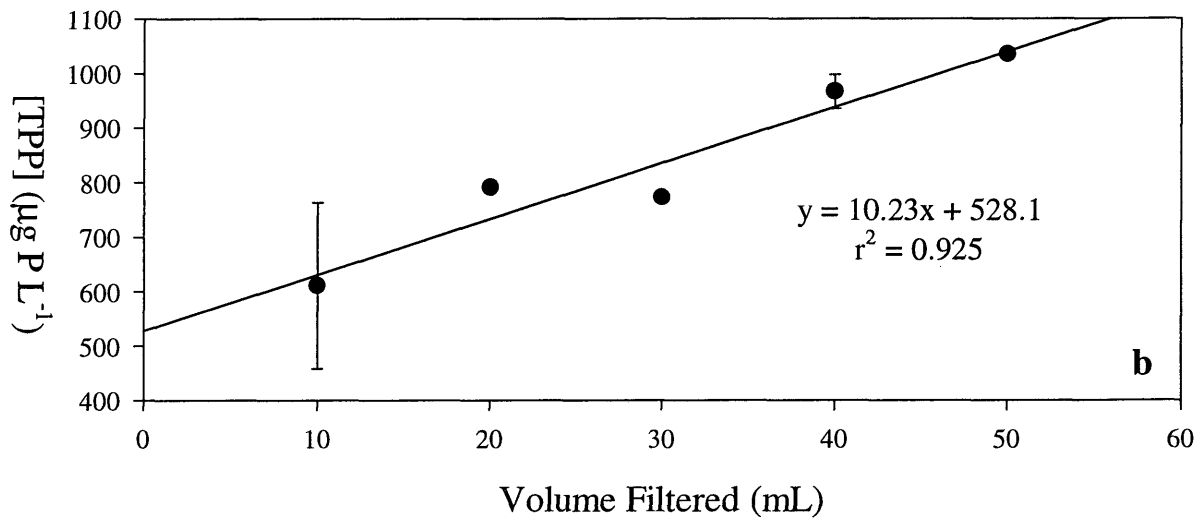
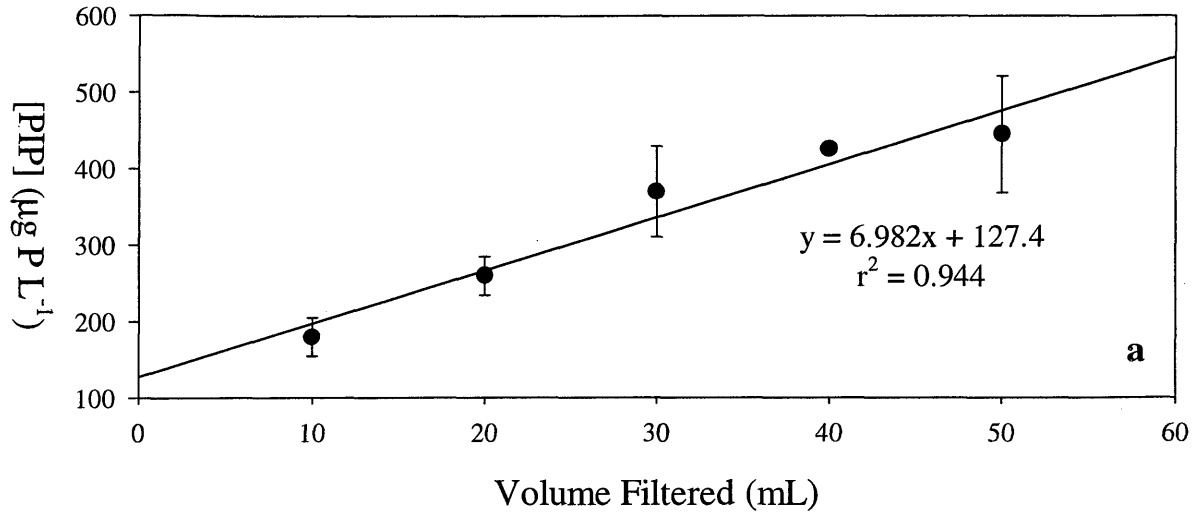


Figure 25. Plots and regressions of a) PIP, b) TPP, and c) POP concentrations with volume filtered for a pure diatom culture, *Chaetoceros calcitrans*, as recovered by the high-temperature ashing oxidation method described in Aspila *et al.* (1976). Error bars are ± 1 SD.



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