Cadmium in the North Atlantic: Implication for global cadmium-phosphorus relationship

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Abstract

Dissolved cadmium (Cd) distribution was determined in the tropical-subtropical North Atlantic along GEOTRACES GA03 Section (US GEOTRACES 2010 and 2011 cruises). A pronounced mid-depth Cd maximum extends from the productive tropical eastern North Atlantic where subsurface waters in the upper thermocline are depleted in dissolved oxygen. At this Cd maximum, Cd depletion relative to phosphate (PO₄) is observed in the Cd vs. PO₄ plot, but the relative Cd depletion is not present in the plot of Cd:PO₄ ratio vs depth. The apparent relative Cd depletion at the Cd maximum appears to reflect a depth-dependent variation of Cd:PO₄ ratio commonly observed in the world ocean. Such depth dependent variation of Cd:PO₄ ratio may result from the regeneration of Cd from Cd-poor particulate organic carbon (POC) in the upper ocean and from Cd-rich POC in the deep ocean. The vertical Cd regeneration may lead to the observed difference in deep water Cd:PO₄ ratio between the North Atlantic and North Pacific, if Cd to phosphorus ratio in the POC flux to the deep ocean is higher in the Pacific than in the Atlantic.

Introduction

Cadmium (Cd) occurs in oceanic waters at picomolar to nanomolar concentrations and has a oceanic distribution similar to phosphate (PO₄) (Boyle et al., 1976; Bruland, 1980). The similarity between Cd and PO₄ in their oceanographic distribution and the correlation of the Cd:Ca ratio of foraminiferal shells with that of seawater lead to the suggestion that the Cd:Ca ratio recorded in foraminifera tests may be used as a proxy for past ocean PO₄ (Boyle, 1981). This idea has been the basis to infer paleo deep ocean circulation from the Cd:Ca ratio of benthic foraminifera (Boyle, 1988) and the paleo PO₄ utilization in the surface water of the Southern Ocean from Cd:Ca ratio of planktonic foraminifera (Elderfield and Rickaby, 2000). A mechanistic understanding of the relationship between Cd and PO₄ distribution in the present-day ocean is necessary if we are to appropriately interpret paleo foraminifera Cd:Ca data.

A compilation of global data sets shows that the plot of Cd vs PO₄ has a ‘kink’ at 1.3 μM PO₄ (Boyle, 1988; de Baar et al., 1994; Loscher et al., 1997; Cullen, 2006), and that the Cd:PO₄ ratio increases with depth in the upper thermocline, reaches a maximum at or above the individual dissolved maxima of Cd and PO₄ and remain constant below this depth with a higher deep water value in the North Pacific (~350 pM/μM) than in the North Atlantic (~200 pM/μM) (Loscher et al., 1997; Elderfield and Rickaby, 2000). The mechanism responsible for such Cd-PO₄ relationships is not well understood. While the coincidence of Cd and PO₄ maxima observed in the global ocean argues against the suggestion that Cd has a deeper regeneration cycle relative to PO₄ (Boyle, 1988), the different deep water Cd:PO₄ ratio between the North Atlantic and the North Pacific cannot be explained solely by the the intrusion of Antarctic

Intermediate Water (AAIW) and Antarctic Bottom Water (AABW) (Frew, 1995; Yeats, 1998; Frew and Hunter, 1992), or by the preferential Cd extraction relative to PO₄ from surface waters (Boyle, 1981, Saager and de Baar, 1993; Elderfield and Rickaby, 2000) during Zn or Fe limitation (Sunda and Huntsman, 2000; Cullen and Sherrell, 2005; Cullen, 2006; Lane et al., 2009). The measured Cd and PO₄ in the subsurface water are composed of preformed and regenerated components. While the AAIW and AABW supply much of the preformed component, in-situ degradation of particles sinking from the euphotic zone is responsible mainly for the regenerated component observed in the deep ocean. Because the AAIW and AABW ventilate to both the Atlantic and the Pacific, the different Cd:PO₄ ratio between the North Atlantic and North Pacific is likely to result mainly from the different ratios of Cd and PO₄ regenerated from sinking particles between the two oceans.

In this paper, we present the distribution of Cd and PO₄ across a large gradient of surface productivity and subsurface dissolved oxygen in tropical-subtropical North Atlantic along GEOTRACES GA03 section during US GEOTRACES North Atlantic 2010 and 2011 cruises. The measured Cd profiles are compared with those simulated using a simple model that considers the effect of preformed Cd, particle scavenging and Cd regeneration, to test the hypothesis that the increase of Cd:PO₄ ratio with depth in the oceanic thermocline is mainly due to Cd regeneration from two groups of particulate organic carbon (POC) sinking from the surface ocean: the Cd-poor non-ballast POC and the Cd-rich ballast-associated POC, and that the higher Cd:PO₄ ratio in the North Pacific than in the North Atlantic is due to higher Cd:P ratio of the ballast-POC in the North Pacific than in the North Atlantic.

Sampling and Analysis

Seawater samples were collected along GEOTRACES GA03 section during the US North Atlantic GEOTRACES 2010 and 2011 cruises (November-December 2010 and 2011). During the 2010 cruise, the transect begins at a station near the strait of Gibraltar (38.3 °N, 9.7 °W) and extends southward to a station (17.4 °N, 24.5 °W) at the oxygen minimum zone of tropical eastern North Atlantic off northwest Africa. During the 2011 cruise, the transect begins at a station (39.7 °N, 69.8 °W) in the continental slope of the western North Atlantic and extends eastward across the oligotrophic Atlantic basin to the station at 17.4 °N, 24.5 °W that was also occupied in the 2010 cruise (Figure 1a). During the 2010 cruise, eight vertical profiles of 24 samples were sampled from entire water column. During the 2011 cruise, thirteen vertical profiles of 24 to 36 samples were sampled from the entire water column. Water samples were collected with 12 L Teflon coated Go-FLO bottles mounted on US GEOTRACES carousel attached to plastic coated cable. Seawater samples were passed through 0.2 µm pore Acropak cartridge filter within 12 hours after the sample collection. The sample filtrates were acidified to pH 1.7-2.0 using 2.8 ml Q-HCl (~9 N, sub-boiling distilled in Savillex all Teflon still, Cd blank is less than 10 pmol Cd per liter of HCl) per liter of seawater within 12 hours of sample filtration. The acidified samples were stored in 1-L narrow mouth low-density polyethylene bottles at room temperature for more than six months before analysis. Dissolved cadmium (Cd) concentrations were measured in 2-ml replicates with Mg(OH)₂ co-precipitation isotope dilution (Wu and Boyle, 1997) using a multiple collector high resolution ICPMS (Finnigan Neptune) at the University of Miami. The detection limit (3 σ) of the method was ~5 pM Cd with an average precision of 2 % at 50 pM Cd. All sample handling and analyses were carried out using trace

metal clean procedures. PO₄ was analyzed with spectrophotometry (Strickland and Parsons, 1972).

Results and Discussion

The distribution of dissolved Cd and PO₄ is shown in Figure 1b and 1c and the data are listed in Table 1. Dissolved Cd and PO₄ show similar patterns of surface depletion and subsurface enrichment reflecting biological uptake of Cd and P in the surface and their regeneration from sinking POC at subsurface depths. There is a pronounced Cd maximum extending from the eastern boundary (Figure 1b). The Cd maximum coincides with PO₄ and AOU maximum at the thermocline depths (100-800 m) at stations USGT10-09 - USGT10-12 (Figure 1c and 1d). These stations lie in the oxygen minimum zone (OMZ) (Figure 1e) resulting from excess consumption of dissolved oxygen by microbial degradation of sinking POC due to stagnant water circulation and an enhanced surface productivity induced by upwelling (Stramma et al., 2008). The coincidence of Cd, PO₄ and AOU maxima and dissolved O₂ minimum reflects the concurrent Cd and PO₄ regeneration and dissolved oxygen consumption in the OMZ.

When Cd is plotted against PO₄ (Figure 2), the Cd concentration at depths above 400 m in the OMZ (station USGT10-09 - USGT10-12 and USGT11-20 - USGT11-24) falls below the Cd-PO₄ linear lines as defined by the data points determined at stations outside the OMZ (USGT10-01 - USGT10-07 and USGT11-01 - USGT11-18), suggesting a severe depletion of Cd relative to PO₄ in the OMZ. As vertical particle export is high in the OMZ, one may wonder if Cd removal via scavenging by sinking particles can account for the observed apparent relative Cd depletion. If particle scavenging is the major cause of the relative Cd depletion, a lower

Cd:PO₄ ratio in the OMZ than outside the OMZ would be expected because of the excessive Cd removal relative to PO₄ by particle scavenging at the subsurface depths. However, when Cd:PO₄ ratio is plotted vs depth (Figure 3), such lower Cd:PO₄ ratio is not observed in the OMZ (station USGT10-09 - USGT10-12). In contrast, the Cd:PO₄ ratio in this region is similar to those outside the OMZ at similar depths (Figure 3), suggesting that the apparent relative Cd depletion in the OMZ may reflect a common depth dependent variation of Cd:PO₄ ratio, rather than a preferential Cd removal by particle scavenging.

As shown in Figure 3, Cd:PO₄ ratio at stations in the OMZ increases with depth. Such depth dependent variation of Cd:PO₄ ratio is also observed at stations outside the OMZ and is similar to those reported in other oceanic regions (de Baar et al., 1994; Elderfield and Rickaby, 2000). It is likely that the apparent relative Cd depletion in the OMZ (Figure 2) is the commonly observed depth-dependent variation of Cd:PO₄ ratio showing as an artefact of Cd depletion in the Cd-PO₄ plot. The Cd concentration at upper thermocline depths of the OMZ falls below that predicted from the linear Cd-PO₄ trend observed for stations outside the OMZ because of the low Cd:PO₄ ratios commonly observed at shallow depths combining with the high Cd and PO₄ concentrations resulting from the enhanced regeneration of Cd and PO₄ in the OMZ. As the data points at the upper thermocline depths of the OMZ have high Cd and PO₄ concentration and low Cd:PO₄ ratio, they tend to fall below those observed in the deep oceanic waters that have similar Cd and PO₄ concentrations but higher Cd:PO₄ ratios. As shown in Figure 2, data points at the upper thermocline depths of the OMZ that show apparent relative Cd depletion tend to fall between two linear lines with slopes of 100 pM/μM and 200 pM/μM respectively. These slopes represent the Cd:PO₄ ratios observed at 100-500 m depth at stations outside the OMZ, suggesting similar Cd:PO₄ ratio between the stations in the OMZ and the stations outside the

OMZ. Thus, the apparent Cd depletion at the Cd maximum in the OMZ is likely to reflect a vertical regeneration feature showing as an artefact of Cd depletion in the Cd-PO₄ plot. Such depth dependent variation of Cd:PO₄ ratio may also be responsible for the “kink” observed in the global Cd-PO₄ plots (Boyle, 1988, de Baar et al., 1994) as the transition from low Cd:PO₄ ratio in the upper water column to high Cd:PO₄ ratio in the deep ocean would produce this ‘kink’.

The depth-dependent variation of Cd:PO₄ ratio is likely to result from the difference in the Cd:P ratio in the POC sinking from the euphotic zone. As the majority of the POC is hydrated detritus that originates in plankton cell material and microbes, the light specific gravity of the POC make them difficult to sink unless they are aggregated and ballasted by heavier particles. If the two major groups of POC sinking from the surface ocean (Armstrong et al., 2002) have different Cd to phosphorus (P) ratios: the non-ballast POC containing a lower Cd:P ratio and the ballast-associated POC containing a higher Cd:P ratio, the regeneration of Cd and P from these POCs would fractionate Cd relative to PO₄, increase Cd:PO₄ ratio with depth, and result in the coincident Cd and PO₄ maxima observed in the global ocean (de Baar et al., 1994). This mechanism can be illustrated by simulating vertical profiles of Cd and Cd:PO₄ ratio determined in the North Atlantic (station USGT11-10 at 31.8 °N 64.2 °W) and the North Pacific (at 30 °N 145 °W near SAFe station), using a “pipe” model applied along isopycnal surfaces.

In this model, subsurface waters of the ocean are considered to derive from the advection of source water from high latitude surface ocean along isopycnal surfaces. During the water transit at depths, the variation of Cd and PO₄ concentration in the source water is determined by the difference between the regeneration of Cd and PO₄ from POC remineralization and their removal by particle scavenging, according to the relationships:

$$\frac{d[PO4]}{dt} = F_P - k_P \times [PO4]$$

$$\frac{d[Cd]}{dt} = F_{Cd} - k_{Cd} \times [Cd]$$

where F_P and F_{Cd} represent the regeneration flux for P and Cd respectively, and k_P and k_{Cd} represent the scavenging rate constant for P and Cd respectively. The analytical solution for these equations are:

$$[PO4] = [PO4]^0 \times e^{-k_P t} + \frac{F_P}{k_P} (1 - e^{-k_P t}) \quad (1)$$

$$[Cd] = [Cd]^0 \times e^{-k_{Cd} t} + \frac{F_{Cd}}{k_{Cd}} (1 - e^{-k_{Cd} t}) \quad (2)$$

where $[PO4]^0$ and $[Cd]^0$ represent PO4 and Cd concentration in the source water and t is the water ventilation time.

The Cd and P regeneration fluxes F_{Cd} and F_P are assumed to result from the remineralization of two major groups of POC: the “excess” POC mainly composed of soft tissue organic matter (F_P^{excess} and F_{Cd}^{excess}) and the “protected” POC mainly composed of organic matter that is associated with and protected by ballast minerals ($F_P^{protected}$ and $F_{Cd}^{protected}$) (Armstrong et al., 2002), according to the relationships:

$$F_P = F_P^{excess} + F_P^{protected} \quad (3)$$

$$F_{Cd} = F_{Cd}^{excess} + F_{Cd}^{protected} \quad (4)$$

Both F_P^{excess} and $F_P^{protected}$ are assumed to decrease exponentially with depth following a power-law curve (Martin et al., 1987), according to the relationships:

$$F_P^{excess} = F_{100}^{excess} \times \left(\frac{Depth}{100} \right)^{-b1} \quad (5)$$

$$F_P^{protected} = F_{100}^{protected} \times \left(\frac{Depth}{100}\right)^{-b2} \quad (6)$$

Both F_{Cd}^{excess} and $F_{Cd}^{protected}$ are calculated from F_P^{excess} and $F_P^{protected}$ and the Cd:P ratios in the POC fluxes: $[Cd/P]^{excess}$ and $[Cd/P]^{protected}$ according to the relationships:

$$F_{Cd}^{excess} = F_P^{excess} \times [Cd / P]^{excess} \quad (7)$$

$$F_{Cd}^{protected} = F_P^{protected} \times [Cd / P]^{protected} \quad (8)$$

The values of $[PO4]^0$, $[Cd]^0$, t , k_p and k_{Cd} that are used in this simulation are listed in Tables 2 and their vertical distributions are shown in Figure 4. The preformed PO4, $[PO4]^0$, is estimated based on the relationship: $[PO4] = [PO4]^0 - \frac{AOU}{138}$. The estimated $[PO4]^0$ increases with depth and has a lower value in the Atlantic ($\sim 0.9 \mu M$) than in the Pacific ($\sim 1.1 \mu M$) at 5000 m.

The preformed Cd, $[Cd]^0$, is estimated using the relationship: $[Cd]^0 = [PO4]^0 \times \frac{[Cd]^0}{[PO4]^0}$. For the western North Atlantic at $31.8^\circ N$ $64.2^\circ W$, the $[Cd]^0:[PO4]^0$ ratio increases linearly with depth from 100 pM/ μM at 100 m to 300 pM/ μM at 750 m, decrease to 220 pM/ μM at 2000 m and then increase to 300 pM/ μM at 5000 m. The $[Cd]^0:[PO4]^0$ values at 700, 2000 and 5000 m represent the typical ratios measured in the Antarctic Intermediate Water, North Atlantic Deep Water and Antarctic Bottom Water respectively (de baar et al., 1994; Elderfield and Rickaby, 2000). For the North Pacific at $30^\circ N$ $145^\circ W$, the $[Cd]^0:[PO4]^0$ ratio increases linearly with depth from 100 pM/ μM at 100 m to 300 pM/ μM at 750 m, and then remains constant at 300 pM/ μM at depths below 750 m. The $[Cd]^0:[PO4]^0$ value of 300 pM/ μM at depths below 750 m represents the ratio in the source water from the Southern Ocean (de Baar et al., 1994; Elderfield and Rickaby, 2000).

The mean water ventilation time t in Table 2 is estimated using a combination of ^3H - ^3He age, CFC age, and ^{14}C mean age (Stuiver et al., 1983; Jenkins, 1998; Smethie et al., 2000; Fine et al., 2002; Khatiwala et al., 2012) tuned to obtain the same F_P^{excess} and $F_P^{protected}$ in the North Atlantic as in the North Pacific. The mean water residence time estimated in this way is 280 yr for the North Atlantic at 5000 m and 820 yr for the North Pacific at 5000 m which are consistent with those estimated by Stuiver et al. (1983). Phosphate scavenging rate constant k_p is assumed

to be equal to cadmium scavenging rate constant k_{Cd} . Both k_p and k_{Cd} are assumed to vary in proportion to the sum of F_p^{excess} and $F_p^{protected}$, to achieve a scavenging residence time of ~50 ky at 5000 m, which falls within the reported oceanic residence time of 20-100 kyr for P and ~50 ky for Cd (Boyle et al., 1976; Paytan and McLaughlin, 2007).

In the model simulation, we first estimate the values of F_{100}^{excess} , $F_{100}^{protected}$, b_1 and b_2 by matching the simulated [PO4] to the measured [PO4], and then use these values to calculate $[Cd/P]^{excess}$ and $[Cd/P]^{protected}$ by matching the simulated [Cd] to the measured [Cd]. Based on the values of $[PO4]^0$, $[Cd]^0$, t , k_p and k_{Cd} in Tables 2, we obtain F_{100}^{excess} of 0.4 $\mu M/yr$, $F_{100}^{protected}$ of 0.046 $\mu M/yr$, b_1 of 3.5, b_2 of 0.84, $[Cd/P]^{excess}$ of 30 pM/ μM for both the North Atlantic and the North Pacific, $[Cd/P]^{protected}$ of 210 pM/ μM for the North Atlantic, and $[Cd/P]^{protected}$ of 340 pM/ μM for the North Pacific. The vertical distribution of F_p^{excess} , $F_p^{protected}$, measured and modeled [PO4], [Cd] and Cd:PO4 ratio are shown in Figure 4. The Cd vs PO4 plot is shown in Figure 5.

The above results indicate that the non-ballast POC export that is higher at the surface but attenuates faster with depth ($F_p^{excess} = 0.4 \times (\frac{Depth}{100})^{-3.5}$) has a low $[Cd/P]^{excess}$ (30 pM/ μM), and that the ballast-associated POC export that is a lower at the surface and attenuates more slowly with depth ($F_p^{protected} = 0.046 \times (\frac{Depth}{100})^{-0.84}$) has a $[Cd/P]^{protected}$ ratio that is higher in the North Pacific (340 pM/ μM) than the North Atlantic (210 pM/ μM). The $[Cd/P]^{excess}$ value is lower than $[Cd/P]^{protected}$ because a $[Cd/P]^{excess}$ ratio lower than or equal to $[Cd/P]^{protected}$ would result in a Cd:PO4 maximum in the upper water column. The $[Cd/P]^{protected}$ value is higher in the North Pacific than the North Atlantic because a higher $[Cd/P]^{protected}$ in the North Atlantic than North Pacific would result in a higher Cd:PO4 ratio in the deep North Atlantic than the deep North Pacific.

The lower $[Cd/P]^{excess}$ (30 pM/ μM) than $[Cd/P]^{protected}$ (210-340 pM/ μM) is consistent with the observation that a larger percentage of P than Cd is released from plankton samples to

the seawater suspension during the two hours it took to get the samples into the ship's laboratory for processing (Collier and Edmond, 1984), suggesting that more P than Cd would be released into the shallow water column as the POC sinks. The lower $[\text{Cd}/\text{P}]^{\text{excess}}$ (30 pM/ μM) than $[\text{Cd}/\text{P}]^{\text{protected}}$ (210-340 pM/ μM) is also consistent with results of laboratory culture experiments (Lane et al., 2009). Lane et al. (2009) showed that *Phaeocystis P. Pouchetti* solitary cells that have sinking rates of less than 1 m/day (Becquevort and Smith, 2001; Peperzak et al., 2003) has a low intracellular Cd/P ratio of 13-23 pM/ μM .

The lower $[\text{Cd}/\text{P}]^{\text{protected}}$ in the North Atlantic than in the North Pacific may be expected in light of contrasting distribution of biogenic opal and biogenic CaCO_3 between the two oceans. Although CaCO_3 and opal are not significant carriers of Cd, these minerals can act as ballast for POC sinking to the oceanic interior. While the entire Atlantic Ocean is depleted with regard to biogenic Si export flux and enriched in coccolithophore CaCO_3 , the dominant ballast mineral responsible for carbon export is diatom opal in the North Pacific (Honjo et al., 2008). Thus, if Cd:P ratio in the POC associated with opal ballast is higher than the ratio in the POC associated with CaCO_3 ballast, the deep water Cd:PO4 ratio would be higher in the North Pacific than in the North Atlantic. This hypothesis is consistent with higher intracellular Cd/P ratio for diatom *T. oceanica* (540-1100 pM/ μM) than for coccolithophore *E. huxleyi* (320-610 pM/ μM) determined in laboratory culture experiments (Lane et al., 2009, Finkel et al., 2007; Ho et al., 2003).

Bruland and Franks (1983) and Sherrell and Boyle (1992) reported that in the North Atlantic the seawater dissolved Cd to PO4 ratio is similar to the Cd:PO4 ratio of suspended particles at each depth throughout the water column. The compositions of sinking (>51 μm) and suspended (>1-51 μm) particulate matters were also determined along the GEOTRACES GA03 section. Data are available at BCO-DMO website: (<http://osprey.bco-dmo.org/dataset.cfm?id=>

14219&flag=viewa and <http://osprey.bco-dmo.org/dataset.cfm?id=14220&flag=viewa>). The slope of particulate Cd vs particulate P plot reflects the ratio of Cd to P net exchange among sinking ($>51 \mu\text{m}$) and suspended ($>1-51 \mu\text{m}$) particulate and dissolved phases, and this slope in entire water column at offshore stations (USGT11-12, 14, 18, 20, 22) is $130 \pm 6.6 \mu\text{mol/mol}$ (1σ) and $48.3 \pm 11.8 \mu\text{mol/mol}$ (1σ) for sinking and suspended particles respectively. These values are in good agreement with Cd/P regeneration ratios used in the model. Relatively low standard deviation of the above slopes ($6.6/130=5\%$ and $11.8/48.3=24\%$) indicates high correlation between particulate Cd and P and supports our hypothesis that particles are the major cause of strong Cd-P correlation in dissolved phase. Nonetheless there are two reasons that may make particulate ratios differ from the ratios inferred from the model. First, the change of Cd and P concentration of sinking and suspended particles reflects the net changes in the combined effect of remineralization, aggregation/dis-aggregation and scavenging processes, whereas the Cd/P regeneration ratios used in our model reflect only the Cd/P ratios in the remineralization flux. Second, the categorization of particles in our model is not based upon particle size. In other words, the protected vs. excess characteristics of particles may not result in their size characteristics. Despite the similarity between determined particulate Cd/P ratios and the regeneration ratios used in our model, particulate Cd/P ratios cannot be linked directly to the dissolved Cd/P ratios. Further studies are needed to determine Cd/P ratio in “protected” and “excess” particles.

Our hypothesis that the Cd:PO₄ ratio in the deep nutrient regeneration flux is lower in the North Atlantic than in the North Pacific is consistent with the scenario where high eolian Fe deposition to the North Atlantic (Duce et al., 1986) relieves Fe limitation of marine phytoplankton and decreases their intracellular Cd/P ratio (Cullen et al., 2003; Lane et al., 2009).

A lower $[\text{Cd}/\text{P}]^{\text{protected}}$ in the North Atlantic than the North Pacific is required to balance the Cd and PO₄ supply to the North Atlantic via Subantarctic Mode Water (SAMW, Williams et al., 2006). The SAMW tends to have a lower Cd:PO₄ ratio than AAIW and AABW, because Cd:PO₄ ratio in oceanic surface water increases with latitude (Elderfield and Rickaby, 2000) and the SAMW originates from lower latitude than the AAIW and AABW (Hanawa and Talley, 2001; Drijfhout et al., 2005). As Cd:PO₄ ratio in the deep North Pacific is high (~350 pM/μM as compared to ~200 pM/μM for the deep North Atlantic, Löscher et al., 1997; Elderfield and Rickaby, 2000), a high $[\text{Cd}/\text{P}]^{\text{protected}}$ in the North Pacific is needed to balance the upward flux of Cd and PO₄ from the subsurface ocean in this region. If $[\text{Cd}/\text{P}]^{\text{protected}}$ is lower than the Cd:PO₄ ratio in the upward Cd and PO₄ flux, the removal of Cd and PO₄ by biological growth would result in a high Cd:PO₄ ratio in the dissolved Cd and PO₄ pool remaining in the surface water. The surface return flow that carries this Cd and PO₄ pool of high Cd:PO₄ ratio to the North Atlantic would lead to a high Cd:PO₄ ratio in the subsurface waters of the North Atlantic, but such high Cd:PO₄ ratio has not been reported in the present-day North Atlantic. If the POC export to the upper ocean has a lower Cd:PO₄ ratio than the POC export to the deeper ocean, the return flow from the North Pacific to the Atlantic in near surface currents will carry this low Cd:PO₄ ratio to the Atlantic resulting in a lower Cd:PO₄ ratio in the deep North Atlantic.

If global Cd vs P relationship is controlled mainly by algal species composition in the euphotic zone (diatoms, coccolithophore and the algal species producing non-ballast POC), rather than Rayleigh type preferential Cd uptake (Elderfield and Rickaby, 2000) or enhanced Cd uptake during Zn or Fe limitation (Sunda and Huntsman, 2000; Cullen et al., 2003; Lane et al., 2009), one would expect an influence of dissolved Cd:PO₄ ratio in the Southern Ocean surface water by the northward transition of the dominant form of carbon export from biogenic opal-

associated ballast POC export at the high latitude, to biogenic CaCO_3 -associated ballast POC export and non- ballast associated POC export at the lower latitudes (Honjo et al., 2008), by an enhanced opal-associated export production resulting from the relaxation of Fe-limitation during last glacial maximum (LGM) (Martin, 1990), and by a switch in species composition and reduced diatom export production south of the APF during the LGM (Mortlock et al., 1991). An integration of such influences into models of Cd:PO₄ ratio in the Southern Ocean surface water that considers the Cd and PO₄ supply via upward mixing would be necessary to properly use Cd:P ratio recorded in planktonic foraminifera to infer paleo-PO₄ utilization in the Southern Ocean. Future studies are needed to further examine these hypothesis.

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Figure captions

Fig. 1a

Dissolved O₂ distribution at 400 m depth from the WOCE dataset with sampling station location shown as black and red filled circles for US GEOTRACES 2010 and 2011 cruises respectively. The term “USGT10-” for the 2010 cruise and “USGT11-” for the 2011 cruise are omitted from the station number label because of space limitation in the plot. Station USGT01-24 is label in white as it is at the same location as USGT10-12.

Fig. 1b

Dissolved Cd distribution in the tropical-subtropical North Atlantic along GEOTRACES GA03 section during US GEOTRACES 2010 and 2011 cruises showing a subsurface Cd maximum extending from the OMZ at the eastern boundary.

Fig. 1c

Phosphate distribution in the tropical-subtropical North Atlantic along GEOTRACES GA03 section during US GEOTRACES 2010 and 2011 cruises showing a subsurface maximum in the OMZ at the eastern boundary coinciding with the Cd maximum.

Fig. 1d

AOU distribution in the tropical-subtropical North Atlantic along GEOTRACES GA03 section during US GEOTRACES 2010 and 2011 cruises showing a subsurface AOU maximum in the OMZ at the eastern boundary coinciding with the Cd and PO₄ maxima.

Fig. 1e

Dissolved O₂ distribution in the tropical-subtropical North Atlantic along GEOTRACES GA03 section during US GEOTRACES 2010 and 2011 cruises showing a subsurface dissolved O₂ minimum in the OMZ at the eastern boundary coinciding with the Cd and PO₄ maxima and AOU maximum.

Fig. 2

Cd vs PO₄ plot showing linear relationship between Cd and PO₄ outside the OMZ as represented by the black solid lines, and the apparent Cd depletion relative to PO₄ in the upper thermocline waters of the OMZ as shown by data points below the black solid lines. The two red dash lines that have the slope of 100 pM/μM and 200 pM/μM represent the range of Cd:PO₄ ratio for waters in the upper thermocline.

Fig. 3

Cd:PO₄ ratio distribution in the tropical-subtropical North Atlantic along GEOTRACES GA03 section during US GEOTRACES 2010 and 2011 cruises showing increasing Cd:PO₄ ratio with depth. A Cd depletion relative to PO₄ is not observed at the OMZ.

Fig. 4a

Comparison of preformed PO₄, measured PO₄ and model PO₄ in the North Atlantic (31.7521°N, 64.1720°W, Stn USGT 11-10) and the North Pacific (32.8 °N, 145°W, Bruland, 1980). The data in this plot are listed in Table 2.

Fig. 4b

Comparison of preformed Cd, measured Cd and model Cd in the North Atlantic (31.7521°N, 64.1720°W, Stn USGT 11-10) and the North Pacific (32.8 °N, 145°W, Bruland, 1980). The data in this plot are listed in Table 2.

Fig. 4c

Ventilation time in the North Atlantic and the North Pacific that are used in the model simulation. The data in this plot are listed in Table 2.

Fig. 4d

The scavenging residence time of PO₄ ($1/k_p$) and Cd ($1/k_{Cd}$) used in the model simulation. The data for this plot are listed in Table 2.

Fig. 4e

POC export flux used in the model simulation. The “excess” POC that is mainly composed of soft tissue organic matter follows the relationship: $F_p^{excess} = 0.4 \times \left(\frac{Depth}{100}\right)^{-3.5}$. The “protected” POC that is mainly composed of organic matter and is associated with and protected by ballast minerals follows the relationship: $F_p^{protected} = 0.046 \times \left(\frac{Depth}{100}\right)^{-0.84}$. The data in this plot are listed in Table 2.

Fig. 4f

Comparison of measured Cd:PO₄ ratio with modeled Cd:PO₄ ratio for the North Atlantic (31.75°N, 64.17°W, Stn USGT 11-10) and the North Pacific (32.80°N, 144.90°W, Bruland, 1980). The model simulation uses a $[Cd/P]^{excess}$ of 30 pM/μM for both the Atlantic and Pacific and a $[Cd/P]^{protected}$ of 210 pM/μM for the Atlantic and 340 pM/μM for the Pacific. The data in this plot are listed in Table 2. The Cd-PO₄ plot based on these data is shown in Figure 5.

Fig. 5

Cd-PO₄ plot for the North Atlantic (31.75°N, 64.17°W, Stn USGT 11-10) and the North Pacific (32.80°N, 144.90°W, Bruland, 1980) showing a “kink” at ~1.3 μM PO₄. The model simulation uses a $[Cd/P]^{excess}$ of 30 pM/μM for both the Atlantic and Pacific and a $[Cd/P]^{protected}$ of 210 pM/μM for the Atlantic and 340 pM/μM for the Pacific. The data in this plot are listed in Table 2.

Table 1. Summary of water column Cd data

Station ID	Depth (m)	Cd (pM)	PO4 (μM)
USGT10-01 (38.32°N,9.66°W)	24	8	0.01
	35	12	0.07
	40	12	0.06
	68	5	0.11
	136	41	0.39
	199	72	0.51
	300	114	0.64
	401	155	0.79
	506	176	0.85
	642	121	0.66
	777	136	0.69
	876	149	0.76
	900	150	0.74
	990	148	0.74
	1150	152	0.75
	1293	202	0.93
	1480	188	0.93
	1701	246	1.13
	1901	260	1.21
	2101	289	1.27
	2301	284	1.32

USGT10-03 (35.20°N,16.00°W)	2501	301	1.36
	2601	315	1.38
	2701	332	1.40
	35	2	0.00
	51	2	0.01
	77	2	0.02
	100	18	0.23
	136	32	0.30
	191	54	0.40
	301	115	0.61
	401	133	0.68
	490	176	0.86
	611	223	0.99
	777	233	1.08
	876	243	1.08
	994	232	1.06
	1051	229	1.07
	1201	247	1.11
	1351	247	1.14
	1501	251	1.14
	1701	270	1.18
	1901	284	1.22
	2101	292	1.26
	2300	297	1.30
	2501	309	1.34

USGT10-05 (31.00°N,22.00°W)	2601	335	1.36
	2681	347	1.38
	31	2	0.00
	52	2	0.00
	81	3	0.00
	101	2	0.01
	136	15	0.15
	187	24	0.20
	251	46	0.35
	351	76	0.48
	553	165	0.81
	802	294	1.29
	963	298	1.32
	1202	298	1.26
	1501	275	1.24
	1800	279	1.23
	2100	302	1.28
	2401	318	1.32
	2701	336	1.37
	3001	352	1.42
	3301	366	1.46
	3600	379	1.49
	3899		1.50
	4199	381	1.51
	4549	403	1.51

	4899	404	1.51
USGT10-07	35	2	0.09
(24.00°N,22.00°W)	46	2	0.06
	71	2	0.10
	152	94	0.96
	202	127	0.94
	353	193	0.98
	400	205	0.97
	454	309	1.35
	504	306	1.26
	757	458	1.87
	1010	446	1.77
	1212	387	1.57
	1516	355	1.51
	1771	342	1.47
	2024	351	1.46
	2277	386	1.46
	2534	361	1.45
	2789		1.47
	3043	357	1.48
	3299	368	1.48
	3554	396	1.50
	3892	398	1.50
	4231	397	1.52
	4580		1.51

USGT10-09	28	2	0.04
(17.35°N,18.25°W)	49	5	0.69
	89	151	1.52
	109	170	1.51
	135	241	1.57
	185	275	1.64
	221	329	1.68
	285	381	1.78
	361	468	1.93
	665	553	2.17
	797	569	2.22
	965	565	2.15
	1095	510	1.98
	1200	485	1.91
	1236	436	1.85
	1385	427	1.73
	1538	387	1.63
	1787	378	1.54
	1883	361	1.52
	2088	370	1.49
	2294	360	1.47
	2585	370	1.48
	2900	367	1.52
	2999	389	1.54
USGT10-10	32	1	0.04

(17.35°N,20.82°W)	51	7	1.15
	85	148	1.53
	101	197	1.56
	141	226	1.53
	188	228	1.62
	237	242	1.65
	293	274	1.77
	424	279	1.97
	503	489	2.08
	607	538	2.31
	806	519	2.28
	973	597	2.14
	1110	531	1.99
	1261	483	1.86
	1514	397	1.66
	1770	416	1.55
	2022	406	1.47
	2277	380	1.46
			1.47
	2735	372	1.46
	3042	381	1.51
	3371	399	1.53
USGT10-11	30	2	0.05
(17.35°N,22.78°W)	62	0	0.26
	85	41	0.85

	136	137	1.07
	180	180	1.17
	200	197	1.20
	250	259	1.36
	301	332	1.53
	351	384	1.61
	450	449	1.81
	600	511	2.04
	801		2.12
	964	503	2.04
	1098	492	1.92
	1248	423	1.78
	1499	376	1.63
	1748	349	1.52
	1998	345	1.47
	2248	350	1.44
	2499	348	1.43
	2748	345	1.43
	2998	354	1.44
	3198	361	1.45
	3298	371	1.46
USGT10-12	38	4	0.02
(17.35°N,24.50°W)	48	0	0.07
	72	2	0.22
	90	10	0.43

	135	32	0.57
	185	116	1.00
	235	191	1.29
	286	286	1.51
	351	345	1.68
	451	351	1.85
	601	402	2.05
	801	506	2.17
	964	537	2.07
	1099	507	1.90
	1257	458	1.75
	1499	415	1.62
	1749	372	1.52
	1999	366	1.48
	2248	340	1.45
	2499	348	1.45
	2749	355	1.45
	2998	360	1.44
	3198	364	1.46
	3498	379	1.47
USGT11-01	30	42	0.07
(39.70°N,69.80°W)	59	45	0.16
	91	126	0.68
	111	173	0.90
	135	197	1.01

	186	305	1.39
	236	298	1.35
	286	366	1.52
	326	363	1.56
	421	329	1.47
	476	333	1.40
	526	316	1.34
	600	297	
	666	288	1.36
	826	264	1.14
	966	279	1.15
	1076	289	1.18
	1201	268	1.14
	1351	273	1.11
	1501	276	1.11
	1652	268	1.12
	1800	273	1.12
	2001	268	1.13
	2050	272	1.14
USGT11-02	35.3	20	0.04
(39.35°N,69.54°W)	46.6	51	0.22
	69.7	119	0.61
	101.7	179	0.90
	136.8	226	1.10
	186.4	294	1.35

	237.6	321	1.49
	286.5	376	1.58
	326.7	362	1.56
	422	306	1.38
	476.4	304	1.31
	526.3	280	1.28
	600.6	289	1.23
	665.9	273	1.22
	826.1	264	1.19
	965.4	268	1.17
	1200.6	273	1.17
	1350.5	258	1.17
	1501	256	1.17
	1650.4	266	1.18
	1800.3	272	1.19
	2000.8	267	1.19
	2199.7	275	1.20
	2461.1	262	1.17
USGT11-03	28	2	0.02
(38.69°N,69.09°W)	61	4	0.01
	83	5	0.01
	112	34	0.23
	137	31	0.27
	187	15	0.13
	237	27	0.17

	288	28	0.19
	418	139	0.74
	537	365	1.59
	663	329	1.48
	802	292	1.33
	966	265	1.20
	1078	272	1.18
	1201	278	1.17
	1353	275	1.19
	1500	264	1.17
	1801	271	1.17
	2100	266	1.18
	2400	275	1.19
	2700	285	1.23
	2899	274	1.16
	3124	274	1.17
	3274	276	1.18
USGT11-06	41	4	0.01
(37.57°N,68.45°W)	66	2	0.00
	90	11	0.00
	112	0	0.00
	142	23	0.12
	166	63	0.34
	237	105	0.59
	286	136	0.73

352	195	1.05
422	309	1.32
487	325	1.45
602	355	1.53
666	295	1.41
750	298	1.33
851	279	1.26
966	277	1.22
1085	256	1.20
1201	254	1.19
1302	266	1.19
1401	267	1.18
1501	250	1.18
1600	253	1.18
1699	262	1.18
1799	253	1.18
1951	263	1.15
2100	268	1.17
2400	259	1.22
2699	267	1.22
2999	293	1.25
3299	291	1.23
3598	293	1.25
3798	309	1.28
3997	319	1.29

	4197	322	1.32
	4432	336	1.37
	4532	343	1.38
USGT11-08	32	2	0.00
(35.42°N,66.53°W)	65	0	0.00
	112	5	0.09
	137	8	0.07
	185	20	0.19
	236	13	0.14
	288	16	0.13
	423	23	0.17
	552	80	0.45
	804	309	1.34
	1003	312	1.36
	1203	273	1.24
	1500	286	1.17
	1800	286	1.18
	2101	288	1.19
	2399	293	1.21
	2699	292	1.23
	2999	291	1.23
	3299	316	1.24
	3598	313	1.26
	3898	325	1.28
	4247	332	1.32

USGT11-10 (31.75°N,64.17°W)	4572	355	1.36
	4896	381	1.44
	40	5	0.03
	67	5	0.02
	85	2	0.02
	97	11	0.08
	136	9	0.00
	187	11	0.04
	238	28	0.11
	289	24	0.15
	348	29	0.14
	424	32	0.19
	505	58	0.33
	581	121	0.54
	671	221	1.04
	809	360	1.46
	885	371	1.53
	1087	332	1.41
	1213	290	1.31
	1366	289	1.23
	1518	277	1.20
	1670	260	1.19
	1780	259	1.19
	1821	254	1.19
	1975	262	1.19

	2100	267	1.21
	2330	274	1.21
	2533	273	1.21
	2738	284	1.21
	3043	288	1.22
	3351	290	1.23
	3657	300	1.26
	3966	313	1.29
	4273	334	1.33
	4427	342	1.32
	4520	340	1.34
	4564	325	1.34
	4613	328	1.34
USGT11-12	41	7	0.00
(29.70°N,56.82°W)	66	0	0.00
	100	2	0.00
	137	4	0.04
	188	9	0.16
	238	18	0.17
	288	25	0.19
	351	30	0.26
	421	69	0.33
	504	124	0.56
	667	187	1.00
	753	288	1.31

	874	345	1.48
	999	333	1.44
	1099	317	1.36
	1199	290	1.32
	1349	286	1.25
	1499	254	1.22
	1648	258	1.19
	1799	268	1.22
	1948	269	1.23
	2098	277	1.26
	2249	277	1.28
	2398	291	1.28
	2548	294	1.29
	2698	294	1.32
	2997	289	1.32
	3295	293	1.31
	3597	301	1.31
	3896	315	1.36
	4294	357	1.41
	4694	370	1.48
	5093	385	1.50
	5393	391	1.55
	5454	401	1.56
	5607	431	1.56
USGT11-14	41	7	0.00

(27.58°N,49.63°W)	70	3	0.00
	101	7	0.00
	116	4	0.00
	136	9	0.00
	185	20	0.10
	235	31	0.20
	286	33	0.24
	351	58	0.32
	430	80	0.47
	551	147	0.75
	651	236	1.07
	774	354	1.40
	965	376	1.55
	1199	346	1.38
	1448	295	1.27
	1799	292	1.27
	2098	299	1.29
	2398	324	1.32
	2697	318	1.34
	2997	347	1.34
	3398	359	1.40
	3797	366	1.42
	4221	380	1.43
USGT11-16	41	0	0.00
(26.14°N,44.83°W)	56	0	0.00

92	5	0.00
108	0	0.00
136	5	0.00
186	8	0.14
235	16	0.23
285	35	0.27
338	53	0.34
421	89	0.57
512	147	0.75
602	198	1.04
799	378	1.58
965	354	
1199	276	
1500	275	1.29
1650	290	1.29
1798	283	1.26
1949	291	1.29
2099	286	1.30
2248	309	1.31
2399	314	1.33
2698	326	1.36
2999	306	1.38
3252	306	1.37
3275	328	1.38
3330	322	1.39

	3342	267	1.39
	3420	322	1.39
	3587	329	1.40
USGT11-18	40	5	0.01
(24.15°N,40.22°W)	67	3	0.00
	76	8	0.00
	111	5	0.00
	137	8	0.01
	186	21	0.10
	236	21	0.21
	286	51	0.32
	352	73	0.47
	421	137	0.68
	511	196	0.89
	601	253	1.10
	776	286	1.38
	966	401	1.61
	1151	375	1.53
	1325	338	1.41
	1501	332	1.36
	1800	314	1.34
	2098	323	1.37
	2550	345	1.41
	3000	362	1.43
	3399	377	1.45

USGT11-20 (22.33°N,35.87°W)	3799	375	1.47
	4297	391	1.49
	41	-2	0.00
	66	0	0.00
	76	-1	0.00
	106	2	0.05
	137	23	0.18
	187	13	0.31
	236	41	0.53
	301	82	0.61
	376	141	0.86
	441	168	0.95
	501	209	1.06
	601	287	1.37
	700	350	1.48
	810	397	1.69
	926	409	1.79
	1061	388	1.73
	1199	357	1.61
	1349	314	1.48
	1500	303	1.45
	1626	297	1.41
	1750	306	1.41
	1897	298	1.37
	2099	299	1.37

	2298	296	1.38
	2497	304	1.39
	2698	313	1.40
	3096	340	1.42
	3496	358	1.44
	3896	360	1.46
	4295	362	1.47
	4696	362	1.49
	4892	368	1.48
	5096	370	1.49
	5243	374	1.48
	5384	363	1.49
	5792	367	1.48
USGT11-22	51	2	0.00
(19.43°N,29.38°W)	81	0	0.00
	95	1	0.02
	125	12	0.38
	186	119	0.86
	236	154	0.93
	286	191	1.00
	391	266	1.20
	552	403	1.65
	665	433	1.80
	901	508	2.02
	1200	416	1.75

	1498	365	1.49
	1798	336	1.41
	2098	328	1.40
	2397	327	1.40
	2697	342	1.41
	2997	355	1.43
	3296	412	1.45
	3595	401	1.47
	3895	388	1.48
	4194	392	1.49
	4595	400	1.49
	4979	396	1.50
USGT11-24	40	10	0.00
(17.40°N,24.50°W)	51	4	0.00
	71	4	0.13
	91	11	0.47
	136	76	0.75
	187	149	1.04
	237	251	1.47
	288	316	1.60
	354	383	1.68
	454	443	1.87
	605	487	1.98
	808	532	2.11
	973	514	2.03

1109	474	1.93
1269	438	1.72
1515	394	1.65
1768	347	1.47
2022	334	1.43
2276	350	1.42
2531	340	1.41
3040	337	1.40
3245	364	1.41
3346	354	1.42
3572	380	1.45

Table Parameters used in the model along with the model results compared with measured data at the

2. North Atlantic and the North Pacific

				[Cd] ⁰ /[P] ⁰				Model	Model	Cd:PO4
	Depth (m)	t (yr)	[P] ⁰ (μM)	(pM/μ M)	[Cd] ⁰ (pM)	1/k _p (yr)	1/k _{Cd} (yr)	[PO4] (μM)	[Cd] (pM)	(pM/μ M)
Model	100	0.2	0.01	1.0	1	224	224	0.08	4	55
N Atlantic	150	0.3	0.03	1.2	3	772	772	0.07	6	92
	200	0.5	0.05	1.3	6	1638	1638	0.08	9	121
	250	0.8	0.06	1.5	9	2667	2667	0.09	13	142
	300	1	0.08	1.6	13	3727	3727	0.11	17	159
	350	4	0.10	1.8	17	4751	4751	0.18	31	172
	400	8	0.12	1.9	22	5721	5721	0.25	47	184
	450	10	0.13	2.1	28	6634	6634	0.28	55	196
	500	12	0.15	2.2	33	7500	7500	0.31	64	206
	600	17	0.25	2.5	63	9117	9117	0.43	99	230
	750	80	0.40	3.0	120	11347	11347	1.10	262	238
	950	125	0.60	2.9	172	14098	14098	1.48	353	239
	1150	125	0.60	2.7	165	16694	16694	1.34	318	237
	1400	125	0.60	2.6	155	19798	19798	1.23	285	233
	1700	130	0.61	2.4	147	23378	23378	1.17	262	225
	2000	150	0.63	2.2	138	26841	26841	1.18	254	215
	2500	180	0.65	2.3	152	32418	32418	1.20	267	222
	3000	200	0.68	2.5	167	37808	37808	1.20	277	230

3500	245	0.70	2.6	182	43049	43049	1.26	300	237
4000	265	0.77	2.7	210	48169	48169	1.31	324	247
4500	280	0.83	2.9	239	53185	53185	1.35	348	257
5000	280	0.90	3.0	270	58112	58112	1.38	370	269

Measur
ed

Measure Measure
d ed Cd:PO4

	Depth (m)	[PO4] (μ M)	[Cd] (pM)	(pM/ μ M)
Measured	85	0.02	2	88
N Atlantic	97	0.08	11	150
Stn USGT11-10	289	0.15	24	160
31.75°N	424	0.19	32	176
64.17°W	505	0.33	58	177
	581	0.54	121	227
	671	1.04	221	213
	809	1.46	360	247
	885	1.53	371	243
	1087	1.41	332	235
	1213	1.31	290	221
	1366	1.23	289	235
	1518	1.20	277	232
	1670	1.19	260	218

1780	1.19	259	218
1821	1.19	254	214
1975	1.19	262	220
2100	1.21	267	221
2330	1.21	274	226
2533	1.21	273	226
2738	1.21	284	235
3043	1.22	288	236
3351	1.23	290	236
3657	1.26	300	238
3966	1.29	313	243
4273	1.33	334	251
4427	1.32	342	259
4520	1.34	340	253
4564	1.34	325	243
4613	1.34	328	244

Model										d
	Depth (m)	t (yr)	[P] ⁰ (μM)	[Cd] ⁰ /[P] ⁰		1/k _p (yr)	1/k _{Cd} (yr)	[PO ₄] (μM)	[Cd] (pM)	Cd:PO ₄ (pM/μM)
				(pM/μM)	(pM)					
Model	100	0.2	0.01	1.0	1	224	224	0.08	5	67
N Pacific	150	0.3	0.07	1.2	8	772	772	0.11	12	113
	200	10	0.13	1.3	17	1638	1638	0.74	115	155

250	20	0.19	1.5	28	2667	2667	0.94	182	194
300	38	0.26	1.6	41	3727	3727	1.27	285	225
350	58	0.32	1.8	56	4751	4751	1.53	379	248
400	80	0.38	1.9	73	5721	5721	1.76	467	265
450	105	0.44	2.1	91	6634	6634	2.00	557	278
500	130	0.50	2.2	112	7500	7500	2.21	637	288
600	195	0.57	2.5	144	9117	9117	2.67	815	305
750	280	0.67	3.0	200	11347	11347	3.09	994	322
950	360	0.80	3.0	240	14098	14098	3.30	1074	325
1150	392	0.81	3.0	244	16694	16694	3.12	1019	327
1400	440	0.83	3.0	250	19798	19798	3.01	987	327
1700	480	0.86	3.0	257	23378	23378	2.87	940	327
2000	530	0.88	3.0	263	26841	26841	2.82	921	327
2500	620	0.91	3.0	274	32418	32418	2.79	912	327
3000	680	0.95	3.0	286	37808	37808	2.72	886	326
3500	730	0.99	3.0	297	43049	43049	2.65	863	325
4000	780	1.03	3.0	308	48169	48169	2.62	849	324
4500	810	1.06	3.0	319	53185	53185	2.56	828	324
5000	820	1.10	3.0	330	58112	58112	2.49	802	323

Measur ed			
Measure		Measur	Cd:PO4
Depth	d	ed	
(m)	[PO4] (μM)	[Cd] (pM)	(pM/μ M)

Measured	0	0.06	2	33
N Pacific	75	0.18	5	25
32.80 °N	185	0.81	170	210
144.90°W	375	1.56	490	314
(Bruland, 1979)	595	2.87	830	289
	780	3.27	970	297
	985	3.33	1040	312
	1505	2.95	1000	339
	2025	2.80	910	325
	2575	2.77	910	329
	3055	2.71	840	310
	3533	2.61	830	318
	4000	2.54	870	343
	4635	2.48	770	310
	4875	2.43	810	333

Figure 1a

Figure 1b

Figure 1c

Figure 1d

Figure 1e

Figure 2

Figure 3

Figure 4a

Figure 4b

Figure 4c

Figure 4d

Figure 4e

Figure 4f

Figure 5