@AGU PUBLICATIONS

Global Biogeochemical Cycles

10.1002/2016GB005556

Kev Points:

- correlations in the near-surface and deep waters of the Eastern Tropical Pacific
- The Cd:PO₄³⁻ regenerated:preformed deep Eastern Tropical Pacific but
- Differences between shallow and deep regenerated:preformed Cd:PO₄³⁻ ratios may be explained by Cd speciation or plankton Cd requirements

Supporting Information:

Correspondence to:

J. Wu,

Citation:

Roshan, S., Wu, J., & DeVries, T. (2017). Controls on the cadmium-phosphate relationship in the tropical South Pacific. Global Biogeochemical Cycles, 31. 1516-1527. https://doi.org/10.1002/ 2016GB005556

Received 18 OCT 2016

RESEARCH ARTICLE

- Dissolved Cd and PO_4^{3-} show different
- ratio is ~1.8(plus/minus 0.06):1 in the ~1.1(plus/minus 0.6):1 above 250 m

Data Set S1

• Supporting Information S1

jwu@rsmas.miami.edu

Accepted 25 SEP 2017 Accepted article online 3 OCT 2017 Published online 20 OCT 2017

©2017. American Geophysical Union. All Rights Reserved.

Controls on the Cadmium-Phosphate Relationship in the Tropical South Pacific

Saeed Roshan^{1,2} (D), Jingfeng Wu^{1,3} (D), and Timothy DeVries^{2,4} (D)

¹Rosenstiel School of Marine and Atmospheric Science, University of Miami, Coral Gables, FL, USA, ²Department of Geography, University of California, Santa Barbara, CA, USA, ³College of Life Science and Oceanography, Shenzhen University, Shenzhen, China, ⁴Earth Research Institute, University of California, Santa Barbara, CA, USA

G

Abstract The relationship between dissolved cadmium (Cd) and phosphate (PO_4^{-3}) can elucidate a biological role for Cd in the ocean and help to evaluate the usefulness of Cd as a tracer of past ocean circulation and nutrient distributions. Here we determine and analyze this relationship in the poorly studied region of the tropical South Pacific. The dissolved Cd distribution is generally similar to PO_4^{3-} , but a plot of Cd versus PO_4^{3-} shows a clear concavity resulting from distinct Cd: PO_4^{3-} ratios in waters local to our transect and in waters formed distally in higher latitudes. To determine the factors affecting the subsurface $Cd:PO_4^{3-}$ ratio along our transect, we used an ocean circulation model and a multilinear regression model to determine the preformed and regenerated components of dissolved Cd and PO_4^{3-} . We found that both the preformed and regenerated Cd:PO₄³⁻ ratios are low in the shallow, locally formed water masses along the transect and significantly higher in the deeper and older water masses. Overall, the regenerated: preformed $Cd:PO_4^{3-}$ ratio in the deep waters (>1,000 m) along our transect is ~1.8:1, reflecting the basin-wide average Cd:PO₄³⁻ "fractionation factor" during biological uptake. However, we find a lower fractionation factor in local waters of 1.1 (± 0.6). We suggest that this locally lower biological fractionation factor is due to either the chemical speciation of Cd or to a lower efficiency of Cd assimilation by the picoplankton and nanoplankton species found in our study region.

1. Introduction

Among dissolved trace metals in the ocean, the distribution of dissolved cadmium (Cd) displays the highest degree of resemblance to the macronutrients phosphate (PO_4^{3-}) and nitrate (NO_3^{-}). The similarity between Cd and PO₄³⁻ has been discussed in many studies (e.g., Boyle et al., 1976; Bruland, 1980) and suggests a possible role for Cd in oceanic nutrient cycles and primary productivity. Indeed, Cd has been observed as a cofactor in carbonic anhydrase (Lane & Morel, 2000), although it has also been hypothesized that its assimilation by plankton species is accidental (Horner et al., 2013). Whichever mechanism leads the oceanic dissolved Cd distribution to be nutrient type (Morel, 2013), it is well established that the dissolved $Cd-PO_4^{3-}$ relationship in the ocean is an outcome of the decomposition of marine biogenic particulate matter, which is responsible for a large fraction of the dissolved Cd and PO_4^{3-} residing in the subsurface ocean (Elderfield & Rickaby, 2000; Quay et al., 2015; Roshan & Wu, 2015; Wu & Roshan, 2015). However, it remains unclear what processes govern the Cd:PO₄³⁻ uptake and regeneration ratio in biogenic particles. Understanding the controls on this ratio may shed light on the biological role of Cd and the proximity of a system to any possible limitation by this trace metal. Knowing the biological role of Cd might also help to evaluate its usefulness as a tracer of past ocean circulation (Boyle, 1988; Roshan & Wu, 2015).

Numerous studies have examined variations between Cd and PO_4^{3-} concentrations to provide clues about the biogeochemical processes controlling the dissolved Cd distribution in the ocean (Quay et al., 2015). One of the most widely discussed variations is the higher Cd:PO₄³⁻ ratio in the deep Pacific than in the deep Atlantic (Boyle et al., 1976; Bruland, 1980; de Baar et al., 1994; Wu & Roshan, 2015). Another well-discussed feature of the global Cd-PO₄³⁻ relationship is a deviation toward lower dissolved Cd in the Cd-PO₄³⁻ plot, which is considered either a "kink," a stepwise increase in slope for the data points with higher concentrations of Cd and PO₄³⁻ (de Baar et al., 1994), or "concavity" (Elderfield & Rickaby, 2000). These spatial variations have been used to determine the effect of nutrient availability on Cd uptake by phytoplankton and to elucidate the role of Cd in phytoplankton growth. An analysis of global Cd data showed that the $Cd:PQ_4^{3-}$ uptake ratio increases with ambient PO₄³⁻ concentration (Elderfield & Rickaby, 2000) but is nearly a constant proportion



Figure 1. The GEOTRACES GP16 transect occupied during the U.S. GEOTRAES 2013 cruise in the equatorial South Pacific (red line) and the stations determined for the total dissolved Cd and PO_4^{3-} concentration in this study (black triangles).

(referred to as the "fractionation factor") of the ambient $Cd:PO_4^{3-}$ concentration ratio. More recent studies have shown that the $Cd:PO_4^{3-}$ fractionation factor can vary due to variations of other nutrient trace metals such as iron (Fe), zinc (Zn), and manganese (Mn) (Baars et al., 2014), indicating that these trace metals might have interactive roles during algal growth (Twining & Baines, 2013). In particular, a strong influence of Fe availability has been inferred from many field studies, which all indicate that the Cd uptake is enhanced under low Fe conditions (Baars et al., 2014; Cullen et al., 2003; Cullen & Sherrell, 2005; Quay et al., 2015). Enhanced Cd uptake under low Fe conditions is also supported by experiments conducted on lab-cultured algae (Lane et al., 2009; Sunda & Huntsman, 2000).

In this study, we determine the dissolved Cd distribution and its correlation with PQ_4^{3-} in the open ocean tropical South Pacific along the western segment of the GEOTRACES GP16 transect. Only a few studies of dissolved Cd have been conducted in the South Pacific and the Pacific sectors of the Southern Ocean (Ellwood, 2004; Ellwood, 2008; Fitzwater et al., 2000; Frew & Hunter, 1992). The surface waters of the transect are depleted in nutrient trace metals such as Fe and Zn (Resing et al., 2015; Roshan et al., 2016), making it an ideal location to study the effect of nutrient trace metal availability on Cd-PO₄³⁻ fractionation factor in the tropical South Pacific is not significantly higher than 1. By contrast, the basin-wide fractionation factor inferred from deep waters along our transect is closer to 2. We discuss two possible reasons for this discrepancy. First, that there may be a low abundance of bioavailable "free Cd" (Cd²⁺) due to the low total Cd concentrations in the region. Or second, that the plankton community in the region, which is dominated by picoplankton and nanoplankton, has a lower Cd assimilation efficiency than plankton in other high-productivity regions of the Pacific Ocean.

2. Sampling, Analysis, and Modeling

Seawater samples were collected on board the R/V *Thompson* along cruise track GP16 in the tropical South Pacific from Manta, Ecuador to Papeete, French Polynesia in October–November 2013. This cruise track was undertaken by the U.S. GEOTRACES program and is also known as Eastern Pacific Zonal Transect. In this study, we determined dissolved cadmium along the western section of GP16 (Figure 1) with the easternmost and westernmost stations located at 15°S, 109°W and 10.5°S, 152°W, respectively.

The sampling procedure was the same as described by Cutter and Bruland (2012). In brief, a carousel-shaped sampler equipped with twenty-four 12 L Teflon-coated GO-FLO bottles and a rosette package was used to sample seawater for the contamination-prone trace elements and their isotopes. The sampler was moved through the water column and craned to and from the sea by means of a winch, an A-frame, and a polyester-jacketed cable. The seawater-filled GO-FLO bottles were carried to a clean van upon recovery of the sampler. The seawater samples were filtered through Pall Acropak capsule filter with pore size 0.2 μ m. After discarding a certain amount of filtrate (~0.5 L), the filtered seawater samples were collected in precleaned 0.5-L LDPE bottles. Within 2 months after transportation of the bottled seawaters to a land-based

Table 1

Cd Concentrations Determined in SAFe Seawater Samples in Comparison With Consensus Values

Reference seawater	This work		Consensus (as of May 2013)
S (pmol/kg)	5 ± 5	n = 25	1.1 ± 0.3
D2 (pmol/kg)	995 ± 28	n = 32	986 ± 23

lab, samples were acidified by double-distilled trace metal-rated nitric acid (HNO_3) to pH~1.8. The acidified samples were stored at room temperature for more than 2 months prior to analysis.

Determination of total dissolved Cd in the acidified samples was carried out through $Mg(OH)_2$ coprecipitation method coupled with an isotope dilution technique (Wu & Roshan, 2015). A spike solution containing ¹¹⁰Cd was added to the seawater before the coprecipitation step in order to quantify the recovery of the preconcentra-

tion step. The ¹¹⁰Cd/¹¹⁴Cd ratio was determined by means of a multicollector inductively coupled plasma mass spectrometer (Neptune by Thermo/Finnigan) at the University of Miami. This method is a modified version of the method developed by Wu and Boyle (1997) and has an average accuracy within 20 pM for 1,000 pM Cd in seawater. In order to validate the quality of the method, SAFe standard seawaters were determined through the same procedure (Table 1). The standard deviation among replicates of surface water samples was ~5 pM. A number of samples were subsampled and acidified on board the ship using trace metal-rated hydrochloric acid (HCl). The concentrations determined in the shipboard-acidified subsamples were in excellent agreement with those in the lab-acidified samples. Hydrography and nutrient data were produced on board the ship by the Ocean Data Facility group using standard methods (Gordon et al., 1993). The data presented in this study are appended to the online version of the paper as supporting information. More information on the hydrography of this transect can be found in Bowman et al. (2016).

For the modeling part, we use a global ocean circulation inverse model with $2^{\circ} \times 2^{\circ}$ horizontal resolution and 24 depth levels (DeVries, 2014). The model circulation has been constrained through an inverse approach using observational data sets of potential temperature, salinity, natural Δ^{14} C, CFC-11, sea surface height anomaly, sea surface heat, and freshwater fluxes. The resulting circulation is available in an offline transport matrix model, which allows computationally efficient tracer simulations. The model details have been described elsewhere (DeVries, 2014; DeVries & Primeau, 2011). The climatological $1^{\circ} \times 1^{\circ}$ World Ocean Atlas 2013 version 2 (https://www.nodc.noaa.gov/OC5/woa13/) was also used as the global data set of nutrients. Satellite-derived surface concentration of Chlorophyll *a* (Chl *a*) was downloaded from http://www.science.oregonstate.edu/ocean.productivity/ for the period of 1997–2009. Throughout the entire paper, we applied 1.027 kg/L as the density of seawater to convert liter to kilogram (or *vice versa*) for concentration unit adjustment.







Figure 3. The distribution of phosphate (PO_4^{3-}) along the western section of the GP16 transect as determined in the same samples as in Figure 2.

3. Results and Discussion

The distribution of dissolved Cd along the transect shows a nutrient-type pattern, as expected (Figure 2). Dissolved Cd concentration is very low in the surface (~10 pM on average) and increases sharply with depth to a maximum of ~900 pM at 1,000–1,500 m. Below this maximum, dissolved cadmium gradually decreases with depth to ~800 pM (deep stations to <800 pM). Comparing the dissolved Cd vertical profiles determined in this study with profiles from the North Atlantic (Wu & Roshan, 2015), South Atlantic (Xie et al., 2015), and North Pacific (Bruland, 1980) reveals the nutrient-like accumulation of dissolved Cd along the conveyor belt circulation, with a consistent increase in dissolved Cd from the North Atlantic (~300 pM) to the North Pacific (~900 pM). The patterns of all profiles are similarly nutrient type (i.e., increase with depth due to uptake in the surface and regeneration in the subsurface) except in the South Atlantic (Figure 2b). Nonetheless, the South Atlantic profile is similar to that of PO_4^{3-} , and the nonnutrient feature below 3,000 m is due to the influx of high- PO_4^{3-} Southern Ocean waters (Baars et al., 2014; Xie et al., 2015).

3.1. Relationship Between Cd and PO₄³⁻

The distribution of dissolved PO_4^{3-} as determined in the same samples (Figure 3) is similar to that of dissolved Cd. However, after plotting the dissolved Cd concentration against PO_4^{3-} , we do not observe a correlation as tight as that observed in the North Atlantic (Wu & Roshan, 2015) and the North Pacific (Bruland, 1980), and the plot is concave rather than linear (Figure 4a). The concavity toward lower dissolved Cd is similar to that observed by Elderfield and Rickaby (2000) for a global data set. The Cd-PO₄³⁻ plot can be approximated by two groups of data points (separated at $[PO_4^{3-}] = \sim 2.15 \,\mu$ M) following two distinct regression lines (Figure 4a). Data points with $[PO_4^{3-}] < 2.15 \,\mu$ M display a much lower slope (211 pmol/µmol) compared to the rest of the data points (slope = 440 pmol/µmol). In order to better reveal average trends, we binned the data onto our circulation model grid and zonally averaged along the transect (Figure 4b). Points shallower than 250 m fall along a shallower trend line with slope = 88 pmol/µmol, while points deeper than 250 m exhibit a steeper trend line with slope = 420 pmol/µmol. Thus, the local waters which impact the near surface are characterized by a fourfold lower Cd: PO_4^{3-} slope than deeper waters which were formed more distally.

The variability of the dissolved $Cd:PO_4^{3-}$ concentration ratio with depth is similar to the generic pattern observed in previous studies (de Baar et al., 1994; Elderfield & Rickaby, 2000; Wu & Roshan, 2015), which

CAGU Global Biogeochemical Cycles



Figure 4. (a) Cd versus PO_4^{3-} for all samples along our transect. The two regression lines were derived for data points above and below 2.15 μ M PO_4^{3-} . (b) Cd versus PO_4^{3-} after binning the observations onto our model grid and averaging horizontally. Two regression lines were derived for data above and below 250 m depth. (c) Vertical profiles of the Cd: PO_4^{3-} concentration ratio along our transect.

increases from very low values at the surface to high values in the deep ocean (Figure 4c). The Cd:PO₄³⁻ concentration ratio average at depths >2,000 m (314 ± 25 pmol:µmol; Figure 4c) is in good agreement with those of the Southern Ocean and North Pacific (~330 pmol:µmol; Baars et al., 2014; Bruland, 1980) and is lower than the North Atlantic ratio (~220 pmol: µmol; Wu & Roshan, 2015). The increase with depth in the Cd:PO₄³⁻ concentration ratio is thought to be due to a high Cd:PO₄³⁻ uptake ratio (compared to the dissolved Cd:PO₄³⁻ concentration ratio) in the surface ocean, which pumps more dissolved Cd than PO₄³⁻ to the subsurface waters via subsequent regeneration, and can be modulated by mixing to some extent (Bruland, 1980; de Baar et al., 1994; Quay et al., 2015; Xie et al., 2015). As mentioned above, the degree of this excess uptake of Cd relative to PO₄³⁻ (relative to the Cd:PO₄³⁻ ratio in surface waters) is referred to as the biological fractionation factor (Elderfield & Rickaby, 2000; Quay et al., 2015).

This biological fractionation, which can eventually lead to a substantial concavity in the Cd versus PQ_4^{3-} plots, has been attributed to Fe limitation in previous studies in the Southern Ocean (Baars et al., 2014; Cullen et al., 2003; Cullen & Sherrell, 2005; Ellwood, 2004; Ellwood, 2008) and can also be modulated by the availability of Zn and Mn (Baars et al., 2014; Sunda & Huntsman, 2000). In addition, this biological fractionation can also be impacted by the chemical speciation of Cd and by phytoplankton type (Baars et al., 2014; Ellwood, 2004; Finkel et al., 2007; Quigg et al., 2011).

3.2. Preformed and Regenerated Cd and PO₄³⁻ Along the Transect

In order to better understand the factors governing the observed $Cd:PO_4^{3-}$ ratios in our study region, we calculated the preformed and regenerated components of Cd and PO_4^{3-} along our transect. The preformed (conservative) component is the concentration that is mixed downward into the interior from the surface ocean, while the regenerated (nonconservative) component is added to or subtracted from the preformed concentration due to reactions in the subsurface. In the case of Cd and PO_4^{3-} , the primary nonconservative process in the subsurface is regeneration due to decomposition of sinking biogenic particles. Recent studies also show that dissolved Cd can be removed by precipitation of CdS within particle-associated anoxic micro-environments (Conway & John, 2015; Janssen et al., 2014). However, analysis of particles collected during the GEOTRACES GP16 study shows that CdS precipitation is probably not occurring in our study region (Ohnemus et al., 2017). Thus, the only nonconservative process affecting Cd along our transect is regeneration, similar to PO_4^{3-} .

To calculate preformed Cd and PO_4^{3-} concentrations, we used our ocean circulation model to propagate surface concentrations to the interior and defined the regenerated concentration as the difference between the observed concentration and the preformed concentration. This procedure avoids known issues with

Global Biogeochemical Cycles



Figure 5. MLR-predicted dissolved Cd versus observed Cd for the upper 50 m of our compiled global data set. The red solid line is the regression line, whose equation and R^2 are written on the plot. The solid yellow lines indicate the 95% confidence interval of the MLR prediction.

methods that use Apparent Oxygen Utilization (AOU) and a constant stoichiometry to calculate regenerated concentrations (e.g., Anderson & Sarmiento, 1994; Roshan & Wu, 2015). These approaches require that AOU itself has no preformed components (i.e., AOU = 0 in the surface ocean) and that the oxygen to nutrient stoichiometry ratio is not variable within the ocean. However, neither of these requirements is met in reality (DeVries & Deutsch, 2014; Ito et al., 2004).

The limiting factor with our model approach to calculating preformed and regenerated nutrients is that it requires global maps of surface concentrations. Such surface maps are currently available for the macronutrients in the World Ocean Atlas climatology (https://www.nodc.noaa. gov/OC5/woa13/; Garcia et al., 2014a, 2014b), but we do not have global maps of surface Cd concentrations due to the difficulty in sampling and analysis of Cd. We therefore analyzed a compilation of high-quality observations of surface dissolved Cd for a relationship between Cd and macronutrients which we could extrapolate globally. Our compilation builds on that of Quay et al. (2015) to a large extent and also includes a large number of observations from the GEOTRACES Intermediate Data Product 2014 (Mawji et al., 2015). The compiled data set was binned to the WOA2013 grid, and the upper 50 m was isolated for the surface relationship analysis. We then performed a multilinear

regression (MLR) to predict surface Cd concentrations from surface macronutrient concentrations. In addition to PO_4^{3-} , we also used SiO_4^{4-} and NO_3^{-} in our MLR, because the relation between these two in the upper



Figure 6. (a) Colors show the global distribution of surface dissolved Cd derived from the MLR relationship shown in Figure 5. Circles are observed surface (< 50 m depth) Cd concentration from our global data compilation. (b) The standard deviation of the MLR-predicted surface dissolved Cd concentration.



Figure 7. Distributions of (a) regenerated and (b) preformed components of dissolved Cd along our transect. Waters inside the dashed contours contain less than 100 μ mol/kg dissolved oxygen.

ocean is governed to some extent by iron availability, which can also be a factor in the relative uptake of Cd versus PO_4^{3-} by phytoplankton (Baars et al., 2014; Cullen et al., 2003; Cullen & Sherrell, 2005; Ellwood, 2008; Franck et al., 2000; Hutchins & Bruland, 1998). We found that these three macronutrients can be used to predict surface Cd concentrations with $R^2 = 0.78$ and RMSE = 0.085 nmol/kg, according to the equation Cd (nmol/kg) = $-0.201(\pm 0.00794) + 0.0835(\pm 0.0352) \cdot PO_4^{3-}$ (µmol/kg) + $0.00444(\pm 0.00231) \cdot NO_3^{-}$ (µmol/kg) + $0.00351(\pm 0.00339) \cdot SiO_4^{4-}$ (µmol/kg) (Figure 5). The MLR equation above was then used to produce a global surface dissolved Cd map from the surface PO_4^{3-} , SiO_4^{4-} , and NO_3^{-} climatology (Garcia et al., 2014a; Figure 6a). Uncertainties in the MLR coefficients were propagated to uncertainty in the surface dissolved Cd concentration, assuming independence of errors in the MLR coefficients, using a Monte Carlo approach (Figure 6b).

Preformed Cd and PO_4^{3-} was calculated using the procedure described by DeVries and Deutsch (2014). Briefly, we solve the following equation at steady state

$$\frac{\mathrm{d}C_{\mathrm{pref}}}{\mathrm{d}t} = \mathbf{A}C_{\mathrm{pref}} \tag{1}$$

where C_{pref} is the preformed concentration and **A** is the transport matrix for our circulation model, subject to the boundary condition $C_{\text{pref}} = C_{\text{observed}}$ in the surface layer of the model. This equation was solved for both dissolved Cd and PO_4^{3-} using the MLR-derived surface Cd concentrations for observed Cd (Figure 6a), and World Ocean Atlas surface PO_4^{3-} climatology for observed PO_4^{3-} (Garcia et al., 2014a), after interpolation to our model grid. The regenerated components were calculated along the transect for both species by subtracting the preformed components from the total concentrations observed in this study.

The distribution of regenerated Cd along the transect shows an accumulation of regenerated Cd (>0.6 nmol/kg) at ~1,000–2,000 m, consistent with a source from regeneration of sinking particles (Figure 7a). Below 2,000 m, regenerated Cd concentrations generally decrease deeper into the water



Figure 8. (a) Surface potential density anomaly (σ_0 , color map and dashed contours) and the water mass formation regions analyzed in this study. (b) Modeled fraction of water along our transect originating from each region shown in Figure 8a, determined using dye tracers in our ocean circulation model. The legend of Figure 8b shows the average preformed Cd:PO₄³⁻ ratio in each of the water mass formation regions of Figure 8a and the overall preformed Cd:PO₄³⁻ along the transect using the global surface Cd and PO₄³⁻ fields.

column, due to attenuation of the sinking particle flux. Preformed Cd increases with depth throughout the water column, reaching the highest values (~0.3 nmol/kg) below 3,000 m along the transect (Figure 7b), consistent with the poleward increase in both density and Cd concentration in the Southern Ocean (Figure 6a). The depth range of the highest regenerated Cd concentrations (500-2,000 m) is not colocated with the minimum in oxygen concentrations and indicates that the highest rates of Cd regeneration may be occurring in Sub-Antarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) water masses, which dominate the depths between 500 and 2,000 m (Talley et al., 2011). This is supported by the distribution of water masses in the model, where we defined water masses based on surface potential density anomaly (σ_0) to obtain regions (Figure 8a) generally superimposable on the known formation regions of major water masses (Talley et al., 2011). In this water mass decomposition, the depth range ~300–1,300 m is dominated by Sub-Tropical Mode Water ($25 < \sigma_0 < 26.2$ kg/m³), SAMW $(26.2 < \sigma_0 < 26.6 \text{ kg/m}^3)$, and AAIW $(26.6 < \sigma_0 < 27.2 \text{ kg/m}^3)$ (Figure 8b). Below 1,300 m, Antarctic Bottom Water (AABW; 27.2 kg/m³ $< \sigma_0$) becomes increasingly important as the dominant water mass along the transect (Figure 8b). The regeneration signal along our transect therefore originates mainly from the productive high-latitude regions, with a minimal contribution from the decomposition of particles produced in the oligotrophic surface waters of our transect.

Examining the ratios of preformed and regenerated Cd:PO₄³⁻, we see that both increase with depth along the transect (Figure 9). The preformed ratio is lowest in the immediate subsurface (57 ± 50 pmol:µmol for observations at 100–250 m depth), associated with local Tropical Water ($\sigma_0 < 25 \text{ kg/m}^3$) that dominates waters above 250 m and has a preformed Cd:PO₄³⁻ ratio of 42 ± 42 pmol:µmol (Figure 8b). The preformed Cd:PO₄³⁻ ratio increases between 250 m and 1,000 m depth, associated with a transition to denser water masses formed in the higher latitudes (Figure 9a). Between 500 and 1,000 m depth, AAIW dominates with a preformed Cd:PO₄³⁻ ratio of 142 ± 12 pmol:µmol (Figure 8b). Below about 1,000 m the preformed Cd:PO₄³⁻ ratio is relatively constant at ~200 ± 10 pmol:µmol, reflecting the average of a diverse mixture of water masses, the most dominant being AABW with a preformed Cd:PO₄³⁻ ratio of 252 ± 12 pmol:µmol (Figure 8b).

Like the preformed Cd:PO₄³⁻ ratio, the regenerated Cd:PO₄³⁻ ratio is also low in the immediate subsurface (~65 ± 53 pmol:µmol for observations at 100–250 m, Figure 9b). This low ratio is associated with regeneration of locally derived organic matter, which reflects the low Cd:PO₄³⁻ concentration ratio locally in the surface



Figure 9. Ratio of transect-averaged (a) regenerated and (b) preformed Cd to those of PO_4^{3-} . (c) Ratio of regenerated to preformed Cd: PO_4^{3-} ratios. These ratio profiles were calculated after summation of individual preformed and regenerated components along the horizontal layers of our ocean circulation model.

ocean. A rapid jump to regenerated $Cd:PO_4^{3-}$ ratios of ~300 pmol:µmol at 350 m depth indicates the influence of particles regenerated from production in more distal regions, where surface $Cd:PO_4^{3-}$ ratios, and therefore $Cd:PO_4^{3-}$ uptake ratios, are higher (Figure 9b). The deepest parts of the transect below ~2,000 m collect deep waters that have traversed both the North and South Pacific (Talley et al., 2011), suggesting that the deep regenerated $Cd:PO_4^{3-}$ ratio of ~370 pmol:µmol reflects a basin-averaged ratio for the Pacific Ocean.

3.3. Controls on Cd-PO₄³⁻ Uptake Systematics

Assuming that the regeneration length scales of Cd and PO_4^{3-} are similar, then the regenerated Cd: PO_4^{3-} ratio is determined by the Cd: PO_4^{3-} uptake ratio in the surface ocean, which determines the Cd: PO_4^{3-} ratio of sinking particles. Thus, the approximately twofold higher regenerated Cd: PO_4^{3-} ratio compared to preformed Cd: PO_4^{3-} ratio in the deep ocean of our transect (~370 versus 200 pmol:µmol) reflects the average Cd: PO_4^{3-} biological fractionation factor (the ratio of Cd: PO_4^{3-} in biogenic particles to dissolved Cd: PO_4^{3-} in surface waters) throughout most of the Pacific Ocean's surface waters. Elderfield and Rickaby (2000) estimated this ratio at 2 for the global ocean, which is very similar to the ratio we derived for the most of the water column along our transect in the South Pacific (1.8 ± 0.06 as the average for depths >1,000 m; Figure 8c). Fe-limited regions in high-productivity areas of the sub-Antarctic Southern Ocean, North Pacific, and Eastern Equatorial Pacific (Moore et al., 2013) are likely the major factor that leads to the basin-wide fractionation factor of ~2, since low iron availability has been shown to enhance the incorporation of Cd into phytoplankton cells (Baars et al., 2014; Cullen et al., 2003; Cullen & Sherrell, 2005). Indeed, a recent study suggests that iron limitation in the Pacific Ocean is the dominant factor contributing to twofold higher Cd: PO_4^{3-} uptake ratios in the Pacific Ocean as compared to the Atlantic Ocean (Quay et al., 2015).

Nonetheless, our analysis also shows that the regenerated $Cd:PO_4^{3-}$ ratio along our transect is about same as the surface preformed ratio for observations between 100 and 250 m, where the fractionation factor of 1.1 ± 0.6 reflects the local surface $Cd:PO_4^{3-}$ uptake ratio (Figure 8c). Since Fe concentrations are very low in the surface along our transect (Resing et al., 2015), this observation does not follow the expectation based on enhancement of Cd uptake under low Fe conditions (Baars et al., 2014; Cullen et al., 2003; Cullen & Sherrell, 2005; Ellwood, 2004; Ellwood, 2008). It also runs counter to the expectation based on the observed low

surface zinc (Zn) concentrations in this region (Roshan et al., 2016), which could enhance the uptake of Cd relative to PO_4^{3-} since Cd can replace zinc (Zn) in phytoplankton cells (Baars et al., 2014; Lane & Morel, 2000; Sunda & Huntsman, 2000). What, then, leads to the low Cd: PO_4^{3-} fractionation factor in surface waters of the study region? One possibility is that the Cd and PO_4^{3-} ratios are too low for this calculation to accurately capture the mean fractionation factor in the surface. Indeed, the uncertainties on ratio of regenerated Cd: PO_4^{3-} to preformed Cd: PO_4^{3-} approach 100% in the shallow water column of our transect. Nonetheless, there appears to be a significant shift in the Cd: PO_4^{3-} ratio above and below 250 m along our transect (Figure 4b), which is captured in the relative ratios of regenerated and preformed Cd and PO_4^{3-} (Figure 9c). Taking the calculated values at face value, the low fractionation factor in shallow waters of our transect requires an explanation.

One possible explanation lies in the fact that dissolved Cd itself can occur as both "free" Cd ion (Cd²⁺) and as Cd bound to organic ligands (Bruland, 1992). There is no way to distinguish these forms in our total dissolved Cd pool, but ligand-binding chemistry shows that the proportion of Cd²⁺ to total Cd will decrease with decreasing Cd concentrations. If phytoplankton take up only free Cd²⁺, as has been hypothesized for other trace metals such as Fe (Sunda & Huntsman, 2000; Twining & Baines, 2013), then their rate of Cd uptake will decrease with decreasing Cd concentrations. At low concentrations of dissolved Cd, the concentration of Cd²⁺ varies dramatically with the concentration of organic ligand, which can eventually lead to a large-scale variability of Cd:PO₄³⁻ uptake ratio in marine algae (Sunda & Huntsman, 2000). This renders the chemical speciation of Cd particularly important for surface regions with low dissolved Cd concentrations such as our transect.

Another possible explanation is that the plankton community in our study region has a lower efficiency of Cd bioassimilation than other plankton communities in low Fe regions. Relationships between pigments specific to particular phytoplankton functional groups and satellite-derived surface Chl *a* concentrations (Hirata et al., 2011) predict that >95% of the phytoplankton community in the local Tropical Water region (Figure 8a) is picoplankton and nanoplankton. On the other hand, studies demonstrating enhance Cd uptake under low Fe and Zn availability have focused mainly on diatom-dominated communities (Cullen et al., 2003; Cullen & Sherrell, 2005; Sunda & Huntsman, 2000). Thus, our results could indicate a lower Cd:PO₄³⁻ uptake ratio for picoplankton and nanoplankton compared to diatoms under similar conditions. Indeed, a low Cd: PO₄³⁻ stoichiometry in small plankton compared to diatoms has been documented in previous studies (Finkel et al., 2007; Lane et al., 2009; Quigg et al., 2011). For example, Finkel et al. (2007) found that cells of *Cyanobacteria* and nanoplankton green algae had approximately tenfold lower Cd:P ratios than diatoms. Ohnemus et al. (2017) have also found that the Cd:P ratio in the particles sampled along our transect is highest near shore, where diatoms dominate, and decreases significantly seaward where smaller plankton are found (Hirata et al., 2011).

4. Conclusion

Our study measured Cd concentrations along the GEOTRACES GP16 transect in the tropical South Pacific, a region lacking historical Cd observations. The dissolved Cd distribution in the region shows an expectedly nutrient shape and falls between the reported concentrations in the North Atlantic and North Pacific, which is consistent with the general concept of nutrient tracers increasing along the great ocean conveyor belt. Nevertheless, examination of the Cd-PO₄³⁻ plot along the transect demonstrates that Cd and PO₄³⁻ follow two distinct lines above and below 250 m. Observations above 250 m depth which are impacted by local water masses show a shallow $Cd:PO_4^{3-}$ slope, and observations below 250 m which are impacted by distal water masses display a twofold to fourfold steeper Cd:PO4³⁻ slope. Analysis of the preformed and regenerated Cd and PO_4^{3-} concentrations in the context of a global ocean circulation model shows that the ratio of regenerated Cd:PO₄³⁻ to preformed Cd:PO₄³⁻ shows similar variations, with low regenerated:preformed ratios above 250 m and high regenerated:preformed ratios in the deeper ocean. We infer that the average $Cd:PO_4^{3-}$ assimilation ratio in the Pacific Ocean is about twice the preformed $Cd:PO_4^{3-}$ ratio. This is similar to the $Cd:PO_4^{3-}$ biological fractionation factor derived for the global ocean by Elderfield and Rickaby (2000) and attributed to the numerous iron-limited areas in the Pacific Ocean (Cullen et al., 2003). However, the water column shallower than 250 m shows similar regenerated Cd:PO₄³⁻ ratio to the ambient seawater dissolved Cd:PO $_4^{3-}$ ratio. We suggest that this locally lower biological fractionation factor is caused either by the chemical speciation of Cd or by a lower Cd uptake efficiency of picoplankton and nanoplankton living in the region of our transect.

Our findings suggest three recommendations for future studies. First, given the insights that can be derived from analyzing the concentrations of preformed and regenerated tracer metals, it is important to perform sampling and analysis of trace metals in the surface ocean more frequently. Knowing the surface distribution enables estimating the effects of regeneration processes on already-available full-depth profiles. This analysis in turn can shed light on the optimal locations of full-depth sampling. In our case, the knowledge of surface dissolved Cd distribution in the South Pacific and Pacific sectors of the Southern Ocean might help to better resolve processes controlling the Cd-PO₄³⁻ systematic along the entire water column of our study region. Second, our study suggests a possible dependence of $Cd:PO_4^{3-}$ uptake ratios on phytoplankton type, which should be considered in global models and interpretation of $Cd:PO_4^{3-}$ ratios. Finally, the abundance and distribution of Cd-binding organic ligands should be better resolved, in order to determine the effect of ligand concentration on $Cd:PO_4^{3-}$ uptake ratios in the ocean.

Acknowledgments

We are thankful to the captain and crew of R/V Thompson and chief scientists: J. Moffett, C. German, and G. Cutter. This work was possible by the tireless efforts of the U.S. GEOTRACES sampling team. We are grateful to the U.S. National Science Foundation (NSF) for their financial support awarded to J. Wu (OCE-1233155). T. D. acknowledges support from a Hellman Family Faculty Fellowship and the U.S. NSF grant OCE-1658392. We also thank P. Quay for help in data compilation. The data produced in this study are appended to this paper as supporting information.

References

Anderson, L. A., & Sarmiento, J. L. (1994). Redfield ratios of remineralization determined by nutrient data analysis. *Global Biogeochemical Cycles*, 8(1), 65–80.

- Baars, O., Abouchami, W., Galer, S. J., Boye, M., & Croot, P. (2014). Dissolved cadmium in the Southern Ocean: Distribution, speciation, and relation to phosphate. *Limnology and Oceanography*, 59(2), 385–399.
- Bowman, K. L., Hammerschmidt, C. R., Lamborg, C. H., Swarr, G. J., & Agather, A. M. (2016). Distribution of mercury species across a zonal section of the eastern tropical South Pacific Ocean (US GEOTRACES GP16). *Marine Chemistry*, 186, 156–166.

Boyle, E. A. (1988). Cadmium: Chemical tracer of deepwater paleoceanography. Paleoceanography, 3(4), 471-489.

Boyle, E. A., Sclater, F., & Edmond, J. M. (1976). On the marine geochemistry of cadmium. Nature, 263(5572), 42-44.

Bruland, K. W. (1980). Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific. Earth and Planetary Science Letters, 47(2), 176–198.

Bruland, K. W. (1992). Complexation of cadmium by natural organic ligands in the central North Pacific. *Limnology and Oceanography*, 37(5), 1008–1017.

Conway, T. M., & John, S. G. (2015). Biogeochemical cycling of cadmium isotopes along a high-resolution section through the North Atlantic Ocean. *Geochimica et Cosmochimica Acta*, 148, 269–283.

Cullen, J. T., & Sherrell, R. M. (2005). Effects of dissolved carbon dioxide, zinc, and manganese on the cadmium to phosphorus ratio in natural phytoplankton assemblages. *Limnology and Oceanography*, 50(4), 1193–1204.

Cullen, J. T., Chase, Z., Coale, K. H., Fitzwater, S. E., & Sherrell, R. M. (2003). Effect of iron limitation on the cadmium to phosphorus ratio of natural phytoplankton assemblages from the Southern Ocean. *Limnology and Oceanography*, 48(3), 1079–1087.

Cutter, G. A., & Bruland, K. W. (2012). Rapid and noncontaminating sampling system for trace elements in global ocean surveys. *Limnology* and Oceanography: Methods, 10, 425–436.

de Baar, H. J., Saager, P. M., Nolting, R. F., & van der Meer, J. (1994). Cadmium versus phosphate in the world ocean. *Marine Chemistry*, 46(3), 261–281.

DeVries, T. (2014). The oceanic anthropogenic CO2 sink: Storage, air-sea fluxes, and transports over the industrial era. *Global Biogeochemical Cycles*, 28, 631–647. https://doi.org/10.1002/2013GB004739

DeVries, T., & Deutsch, C. (2014). Large-scale variations in the stoichiometry of marine organic matter respiration. *Nature Geoscience*, 7(12), 890–894.

DeVries, T., & Primeau, F. (2011). Dynamically and observationally constrained estimates of water-mass distributions and ages in the global ocean. *Journal of Physical Oceanography*, 41(12).

Elderfield, H., & Rickaby, R. E. M. (2000). Oceanic Cd/P ratio and nutrient utilization in the glacial Southern Ocean. *Nature*, 405(6784), 305–310. Ellwood, M. J. (2004). Zinc and cadmium speciation in subantarctic waters east of New Zealand. *Marine Chemistry*, 87(1), 37–58.

Ellwood, M. J. (2008). Wintertime trace metal (Zn, Cu, Ni, Cd, Pb and Co) and nutrient distributions in the Subantarctic zone between 40–52 S; 155–160 E. Marine Chemistry, 112(1), 107–117.

Finkel, Z. V., Quigg, A. S., Chiampi, R. K., Schofield, O. E., & Falkowski, P. G. (2007). Phylogenetic diversity in cadmium: Phosphorus ratio regulation by marine phytoplankton. *Limnology and Oceanography*, *52*(3), 1131–1138.

Fitzwater, S. E., Johnson, K. S., Gordon, R. M., Coale, K. H., & Smith, W. O. (2000). Trace metal concentrations in the Ross Sea and their relationship with nutrients and phytoplankton growth. Deep Sea Research Part II: Topical Studies in Oceanography, 47(15), 3159–3179.

Franck, V. M., Brzezinski, M. A., Coale, K. H., & Nelson, D. M. (2000). Iron and silicic acid concentrations regulate Si uptake north and south of the Polar Frontal Zone in the Pacific Sector of the Southern Ocean. Deep Sea Research Part II: Topical Studies in Oceanography, 47(15), 3315–3338.

Frew, R. D., & Hunter, K. A. (1992). Influence of Southern Ocean waters on the cadmium-phosphate properties of the global ocean. *Nature*, 360, 144–146.

- Garcia, H. E., Locarnini, R. A., Boyer, T. P., Antonov, J. I., Baranova, O. K., Zweng, M. M., ... Johnson, D. R. (2014a). In S. Levitus & A. Mishonov (Eds.), World ocean atlas 2013, volume 4: Dissolved inorganic nutrients (phosphate, nitrate, silicate) (NOAA Atlas NESDIS, Vol. 76, 25 pp.). Silver Spring, MD: US Governent Printing Office.
- Garcia, H. E., Locarnini, R. A., Boyer, T. P., Antonov, J. I., Baranova, O. K., Zweng, M. M., ... Johnson, D. R. (2014b). In S. Levitus & A. Mishonov (Eds.), *World ocean atlas 2013, volume 3: Dissolved oxygen, apparent oxygen utilization, and oxygen saturation* (NOAA Atlas NESDIS, Vol. 75, 27 pp.). Silver Spring, MD: US Goverment Printing Office.
- Gordon, L. I., Jennings Jr, J. C., Ross, A. A., & Krest, J. M. (1993). A suggested protocol for continuous flow automated analysis of seawater nutrients (phosphate, nitrate, nitrite and silicic acid) in the WOCE hydrographic program and the joint Global Ocean fluxes study. WOCE Operations Manual, Part, 3(3), 91-1.

Hirata, T., Hardman-Mountford, N. J., Brewin, R. J. W., Aiken, J., Barlow, R., Suzuki, K., ... Yamanaka, Y. (2011). Synoptic relationships between surface chlorophyll-*a* and diagnostic pigments specific to phytoplankton functional types. *Biogeosciences*, 8(2), 311.

Horner, T. J., Lee, R. B., Henderson, G. M., & Rickaby, R. E. (2013). Nonspecific uptake and homeostasis drive the oceanic cadmium cycle. Proceedings of the National Academy of Sciences, 110(7), 2500–2505.

Hutchins, D. A., & Bruland, K. W. (1998). Iron-limited diatom growth and Si: N uptake ratios in a coastal upwelling regime. *Nature*, 393(6685), 561–564.

Ito, T., Follows, M. J., & Boyle, E. A. (2004). Is AOU a good measure of respiration in the oceans? Geophysical Research Letters, 31, L17305. https://doi.org/10.1029/2004GL020900

Janssen, D. J., Conway, T. M., John, S. G., Christian, J. R., Kramer, D. I., Pedersen, T. F., & Cullen, J. T. (2014). Undocumented water column sink for cadmium in open ocean oxygen-deficient zones. *Proceedings of the National Academy of Sciences*, 111(19), 6888–6893.

- Lane, E. S., Semeniuk, D. M., Strzepek, R. F., Cullen, J. T., & Maldonado, M. T. (2009). Effects of iron limitation on intracellular cadmium of cultured phytoplankton: Implications for surface dissolved cadmium to phosphate ratios. *Marine Chemistry*, 115(3), 155–162.
- Lane, T. W., & Morel, F. M. (2000). A biological function for cadmium in marine diatoms. Proceedings of the National Academy of Sciences, 97(9), 4627–4631.

Mawji, E., Schlitzer, R., Masferrer Dodas, E., Abadie, C., Abouchami, W., Anderson, R. F., ... Bluhm, K. (2015). The GEOTRACES intermediate data product 2014. *Marine Chemistry*, 177, 1–8.

Moore, C. M., Mills, M. M., Arrigo, K. R., Berman-Frank, I., Bopp, L., Boyd, P. W., ... Jickells, T. D. (2013). Processes and patterns of oceanic nutrient limitation. *Nature Geoscience*, 6(9), 701–710.

Morel, F. M. (2013). The oceanic cadmium cycle: Biological mistake or utilization? Proceedings of the National Academy of Sciences of the United States of America, 110(21), E1877–E1877.

Ohnemus, D. C., Rauschenberg, S., Cutter, G. A., Fitzsimmons, J. N., Sherrell, R. M., & Twining, B. S. (2017). Elevated trace metal content of prokaryotic communities associated with marine oxygen deficient zones. *Limnology and Oceanography*, *62*, 3–25. https://doi.org/10.1002/ lno.10363

Quay, P., Cullen, J., Landing, W., & Morton, P. (2015). Processes controlling the distributions of Cd and PO₄ in the ocean. *Global Biogeochemical Cycles*, *29*, 830–841. https://doi.org/10.1002/2014GB004998

Quigg, A., Irwin, A. J., & Finkel, Z. V. (2011). Evolutionary inheritance of elemental stoichiometry in phytoplankton. Proceedings of the Royal Society of London B: Biological Sciences, 278(1705), 526–534.

Resing, J. A., Sedwick, P. N., German, C. R., Jenkins, W. J., Moffett, J. W., Sohst, B. M., & Tagliabue, A. (2015). Basin-scale transport of hydrothermal dissolved metals across the South Pacific Ocean. *Nature*, 523(7559), 200–203.

Roshan, S., & Wu, J. (2015). Cadmium regeneration within the North Atlantic. Global Biogeochemical Cycles, 29, 2082–2094. https://doi.org/ 10.1002/2015GB005215

Roshan, S., Wu, J., & Jenkins, W. J. (2016). Long-range transport of hydrothermal dissolved Zn in the tropical South Pacific. *Marine Chemistry*, 183, 25–32.

Sunda, W. G., & Huntsman, S. A. (2000). Effect of Zn, Mn, and Fe on cd accumulation in phytoplankton: Implications for oceanic cd cycling. *Limnology and Oceanography*, 45(7), 1501–1516.

Talley, D. L., Pickard, G. L., Emery, W. J., & Swift, J. H. (2011). Descriptive Physical Oceanography: An Introduction (6th ed.). London: Academic Press.

Twining, B. S., & Baines, S. B. (2013). The trace metal composition of marine phytoplankton. *Annual Review of Marine Science*, *5*, 191–215.
Wu, J., & Boyle, E. A. (1997). Low blank preconcentration technique for the determination of lead, copper, and cadmium in small-volume seawater samples by isotope dilution ICPMS. *Analytical Chemistry*, *69*(13), 2464–2470.

Wu, J., & Roshan, S. (2015). Cadmium in the North Atlantic: Implication for global cadmium–phosphorus relationship. Deep Sea Research Part II: Topical Studies in Oceanography, 116, 226–239.

Xie, R. C., Galer, S. J., Abouchami, W., Rijkenberg, M. J., De Jong, J., de Baar, H. J., & Andreae, M. O. (2015). The cadmium-phosphate relationship in the western South Atlantic—The importance of mode and intermediate waters on the global systematics. *Marine Chemistry*, 177, 110–123.