



# 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 (PO<sub>4</sub>) is observed in the Cd vs. PO<sub>4</sub> plot, but the relative Cd depletion is not present in the plot of Cd:PO<sub>4</sub> ratio vs depth. The apparent relative Cd depletion at the Cd maximum appears to reflect a depth-dependent variation of Cd:PO<sub>4</sub> ratio commonly observed in the world ocean. Such depth dependent variation of Cd:PO<sub>4</sub> 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:PO<sub>4</sub> 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.

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## 1. Introduction

Cadmium (Cd) occurs in oceanic waters at picomolar to nanomolar concentrations and has a oceanic distribution similar to phosphate (PO<sub>4</sub>) (Boyle et al., 1976; Bruland, 1980). The similarity between Cd and PO<sub>4</sub> 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 PO<sub>4</sub> (Boyle et al., 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 PO<sub>4</sub> 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 PO<sub>4</sub> 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 PO<sub>4</sub> has a ‘kink’ at 1.3 μM PO<sub>4</sub> (Boyle, 1988; de Baar et al., 1994; Löscher et al., 1997; Cullen, 2006), and that the Cd:PO<sub>4</sub> ratio increases with depth in the upper thermocline, reaches a maximum at or above the individual dissolved maxima of Cd and PO<sub>4</sub> 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) (Löscher et al., 1997; Elderfield and Rickaby, 2000). The mechanism responsible for such Cd–PO<sub>4</sub> relationships is not well understood. While the coincidence of Cd and PO<sub>4</sub> maxima observed in the global ocean argues against the suggestion that Cd has a deeper regeneration cycle relative to PO<sub>4</sub> (Boyle, 1988), the different deep water Cd:PO<sub>4</sub> 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 PO<sub>4</sub> from surface waters (Boyle et al., 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 PO<sub>4</sub> 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:PO<sub>4</sub> ratio between the North Atlantic and North Pacific is likely to result mainly from the different ratios of Cd and PO<sub>4</sub> regenerated from sinking particles between the two oceans.

In this paper, we present the distribution of Cd and PO<sub>4</sub> across a large gradient of surface productivity and subsurface dissolved

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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:PO<sub>4</sub> 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:PO<sub>4</sub> 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.

## 2. 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 (Fig. 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 h 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 h 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)<sub>2</sub> 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 (3σ) 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. PO<sub>4</sub> was analyzed with spectrophotometry (Strickland and Parsons, 1972).

## 3. Results and discussion

The distribution of dissolved Cd and PO<sub>4</sub> is shown in Fig. 1B and C and the data are listed in Table 1. Dissolved Cd and PO<sub>4</sub> 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 (Fig. 1B). The Cd maximum coincides with PO<sub>4</sub> and AOU maximum at the thermocline depths (100–800 m) at stations USGT10-09–USGT10-12 (Fig. 1C and D). These stations lie in the oxygen minimum zone (OMZ) (Fig. 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, PO<sub>4</sub> and AOU maxima and dissolved O<sub>2</sub> minimum reflects

the concurrent Cd and PO<sub>4</sub> regeneration and dissolved oxygen consumption in the OMZ.

When Cd is plotted against PO<sub>4</sub> (Fig. 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–PO<sub>4</sub> 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 PO<sub>4</sub> 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:PO<sub>4</sub> ratio in the OMZ than outside the OMZ would be expected because of the excessive Cd removal relative to PO<sub>4</sub> by particle scavenging at the subsurface depths. However, when Cd:PO<sub>4</sub> ratio is plotted vs depth (Fig. 3), such lower Cd:PO<sub>4</sub> ratio is not observed in the OMZ (station USGT10-09–USGT10-12). In contrast, the Cd:PO<sub>4</sub> ratio in this region is similar to those outside the OMZ at similar depths (Fig. 3), suggesting that the apparent relative Cd depletion in the OMZ may reflect a common depth dependent variation of Cd:PO<sub>4</sub> ratio, rather than a preferential Cd removal by particle scavenging.

As shown in Fig. 3, Cd:PO<sub>4</sub> ratio at stations in the OMZ increases with depth. Such depth dependent variation of Cd:PO<sub>4</sub> 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 (Fig. 2) is the commonly observed depth-dependent variation of Cd:PO<sub>4</sub> ratio showing as an artefact of Cd depletion in the Cd–PO<sub>4</sub> plot. The Cd concentration at upper thermocline depths of the OMZ falls below that predicted from the linear Cd–PO<sub>4</sub> trend observed for stations outside the OMZ because of the low Cd:PO<sub>4</sub> ratios commonly observed at shallow depths combining with the high Cd and PO<sub>4</sub> concentrations resulting from the enhanced regeneration of Cd and PO<sub>4</sub> in the OMZ. As the data points at the upper thermocline depths of the OMZ have high Cd and PO<sub>4</sub> concentration and low Cd:PO<sub>4</sub> ratio, they tend to fall below those observed in the deep oceanic waters that have similar Cd and PO<sub>4</sub> concentrations but higher Cd:PO<sub>4</sub> ratios. As shown in Fig. 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:PO<sub>4</sub> ratios observed at 100–500 m depth at stations outside the OMZ, suggesting similar Cd:PO<sub>4</sub> 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–PO<sub>4</sub> plot. Such depth dependent variation of Cd:PO<sub>4</sub> ratio may also be responsible for the “kink” observed in the global Cd–PO<sub>4</sub> plots (Boyle, 1988; de Baar et al., 1994) as the transition from low Cd:PO<sub>4</sub> ratio in the upper water column to high Cd:PO<sub>4</sub> ratio in the deep ocean would produce this ‘kink’.

The depth-dependent variation of Cd:PO<sub>4</sub> 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 PO<sub>4</sub>, increase Cd:PO<sub>4</sub> ratio with depth, and result in the coincident Cd and PO<sub>4</sub> maxima observed in the global ocean (de Baar et al., 1994). This mechanism can be illustrated by simulating vertical profiles of Cd and Cd:PO<sub>4</sub>

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