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Cadmium enriched stable isotope uptake and addition experiments with natural phytoplankton assemblages in the Costa Rica Upwelling Dome

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ABSTRACT

Cadmium (Cd) can function as either a nutrient or toxin in the marine environment. This duality has been demonstrated in phytoplankton cultures where Cd has been shown to have toxic effects to cyanobacteria, but acts as a nutrient in the marine diatom *Thalassiosira weissflogii* by biochemically replacing zinc (Zn). In July of 2005, Cd bioavailability and uptake in the Costa Rica Upwelling Dome in the eastern Pacific Ocean were examined using Cd addition and enriched stable isotope uptake experiments. This dome is known to support particularly high densities of the cyanobacterium, *Synechococcus*. Bottle incubation experiments with Cd additions ranging from 0.5 to 5 nM resulted in reduced chlorophyll *a* outside and at the edge of the dome relative to control treatments, but showed no reduction in chlorophyll *a* inside the dome. Total dissolved Cd showed depletion of Cd in the surface waters and increased concentrations with depth. ^{110}Cd stable isotope tracer uptake experiments were conducted at stations inside and outside the dome, in which variations with depth and time were examined. Cd uptake was greatest within the upper 40 m of water inside the dome, decreased with depth, and increased with time. Uptake trended positively with chlorophyll *a* concentrations. Together, these experiments demonstrate Cd uptake into the microbial loop in the upper water column both inside and outside of the dome, but show that Cd toxicity was not induced within the dome. This greater Cd tolerance within the Costa Rica Dome relative to oligotrophic waters was likely due to a combination of higher quantities of biomass, resultant greater ligand production inside the dome, metallothionein production by *Synechococcus*, and different toxicity thresholds and coping mechanisms of the microbial communities.

1. Introduction

Cadmium (Cd) is a biogeochemical enigma: it is toxic to most organisms, but also has been shown to be a cofactor in a class of enzymes in some diatoms and exhibits nutrient-like distribution in the ocean, implying biological uptake and regeneration at depth. Cd concentrations range from 1 to 1100 pM in the open ocean (Bruland, 1980). Cd distributions resemble those of phosphate; concentrations are depleted in surface waters, increase with depth, and are fairly constant in deep waters (Boyle, 1988; Boyle et al., 1976, 1981; Bruland, 1980).

Like most other trace metals in surface waters, Cd is complexed by strong organic ligands (Bruland, 1980, 1992; Ellwood, 2004; Morel et al., 2003). The speciation of a metal is vital to determining its bioavailability (Hunter et al., 1997), where complexation by strong complexes can reduce the ability of a substance to be taken up into a cell, thus preventing it from being either a nutrient or a toxin, but the bioavailability of organically complexed metals is becoming increasingly apparent. Due to the dissociation of trace metal complexes, however, bioavailability may ultimately be considered a kinetic concept as discussed by Morel et al. (2003), but knowledge of which chemical species are bioavailable is still lacking for most metals. Inorganic Cd may be more bioavailable than organically complexed Cd, although the bioavailability of organically complexed Cd is not known. Also, different chemical species can be more or less bioavailable to different microorganisms. Toxic effects in culture have been observed to be proportional to the summation of inorganic species (Sunda, 1988), although for copper and iron, organic ligands have been shown to be bioavailable (Hutchins et al., 1999b; Maldonado and Price, 1999; Quigg et al., 2006 and Semeniuk et al., 2009).

Abbreviations: ASV, anodic stripping voltammetry; Cd, cadmium; chl a, chlorophyll *a*; Cu, copper; Fe, iron; ICP-MS, inductively coupled plasma mass spectrometry; PO_4^{3-}, phosphate; RDE, rotating disc electrode; Zn, zinc.

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Cd has toxic effects to eukaryotic organisms in culture (Lee and Morel, 1995), but in some instances of Zn limitation in the marine diatom *Thalassiosira weissflogii* and other species, low level Cd additions restored the growth rate (Lee and Morel, 1995; Price and Morel, 1990; Sunda and Huntsman, 2000). It follows that Cd at low concentrations (pM) may act as a nutrient by replacing Zn (Lee and Morel, 1995), with Cd replacing Zn in the active site of carbonic anhydrase (Lane and Morel, 2000; Lane et al., 2005; Lee et al., 1995; Morel et al., 1994; Xu et al., 2008).

Synechococcus species have lower toxicity thresholds relative to eukaryotic organisms by approximately two orders of magnitude (Brand et al., 1986; Payne and Price, 1999; Saito et al., 2003). The presence of Zn has been previously noted to have an effect on Cd toxicity in marine cyanobacteria (Saito et al., 2003) and the presence of Zn 'buffers' the proteomic response of *Synechococcus* cultures to short-term, pM free Cd additions (Cox, 2011; Cox and Saito, 2013). Other studies examining copper effects on open ocean cyanobacteria show *Prochlorococcus* were inhibited at free Cu^{2+} that did not affect *Synechococcus*, although high-light adapted *Prochlorococcus* were more copper resistant than low-light adapted *Prochlorococcus* (Mann et al., 2002). In addition, *Prochlorococcus* has fewer genes annotated that cope with metal stress than *Synechococcus*, including fewer metal efflux pumps (Palenik et al., 2003) and no known genes for metallothionein (Cox, 2011), a small protein known to detoxify metals.

The Costa Rica Upwelling dome is a tropical thermocline dome located near 9°N 90°W, with a diameter ranging from 100 to 1000 km. Uniquely fed by a coastal wind jet, it is seasonably predictable, characterized by a shoaling of the thermocline by local cyclonic wind stress curl off of the coast during February and March. It separates from the coast during May–June and expands to the west during July-November. The dome produces a habitat with high phytoplankton and zooplankton biomass relative to that of surrounding tropical waters (Fiedler, 2002) (Fig. 1). The wind generation, productivity and phytoplankton assemblages continue to intrigue scientists (Broenkow, 1965; Fiedler, 2002; Franck et al., 2003; Hofmann et al., 1981; Li et al., 1983; Saito et al., 2005). The highest reported cell densities of *Synechococcus* have been recorded in the dome, varying from 1.2×10^6 to 3.7×10^6 cells mL^{-1} (Saito et al., 2005), making the dome an ideal place to observe microbial community processes dominated by *Synechococcus*.

In this study, ^{110}Cd, with a natural abundance of 12.5%, was used as a tracer of Cd uptake into the particulate fraction (>0.2 μm). ^{110}Cd can be traced by an increase in concentration and deviation of samples from natural isotope abundance ratios (Table 1). Previously, uptake and adsorption experiments have utilized radiotracers such as ^{65}Zn, ^{55}Fe, ^{59}Fe, or ^{109}Cd (Cullen et al., 1999; Hutchins et al., 1999a; Morel et al., 1994; Sunda and Huntsman, 1995), as well as low abundance stable isotopes (Croteau et al., 2007; Gee and Bruland, 2002; Hurst and Bruland, 2007; Pickhardt et al., 2002). Using stable isotopes over radiotracers is advantageous due to increased safety, ease of shipboard use clearance, and waste disposal.

^{110}Cd can be used to trace the movement of dissolved $^{110}Cd^{2+}$ to the particulate phase, where transfer would represent biological uptake of bioavailable Cd. Yet it can be difficult to discern between i) Cd absorption into cells, ii) Cd adsorption to the surface of cells, iii) Cd adsorption to non-living particulate organic matter, and iv) Cd adsorption to particulate inorganic matter. We use the word "uptake" to refer to the absorption of dissolved Cd into the particulate fraction, presumably into the cells of the phytoplankton community which likely dominates the signal due to the abundance of actively growing autotrophic cells in the photic zone.

The disparity in toxicity thresholds between eukaryotic diatoms and among Cyanobacteria, the reported nutritive use of Cd in a eukaryotic

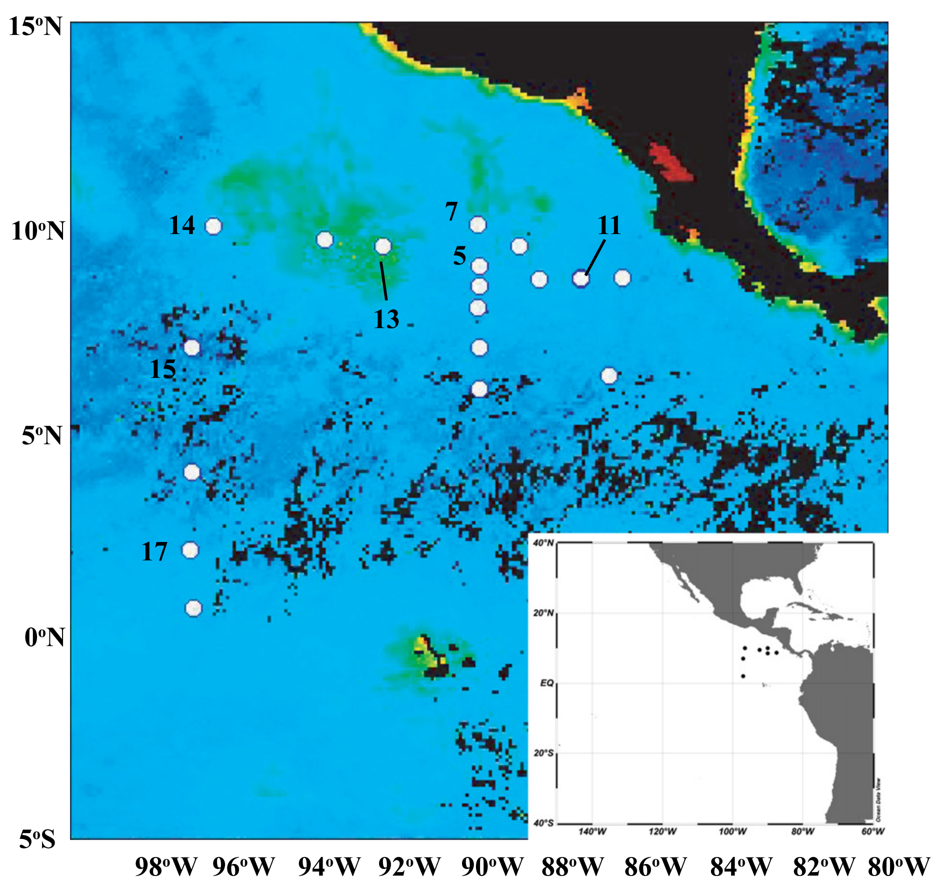

Fig. 1. Costa Rica upwelling dome stations, July-August 2005. Stations superimposed on time-averaged SeaWiFs satellite imagery. See Supplementary Table 1.