

Cadmium—Copper Antagonism in Seaweeds Inhabiting Coastal Areas Affected by Copper Mine Waste Disposals

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Cadmium and copper accumulation by macroalgae was studied in a coastal area exposed to upwelling events and high levels of Cu, the latter resulting from mine disposals. Eight species were studied, and all had very high concentrations of Cd outside of the Cu-contaminated area. Cu in algal tissues was much higher in contaminated than in reference sites. High Cu appeared to suppress Cd bioaccumulation; Cd in algal tissues was much lower in the Cu-contaminated area than in the reference sites. Transplant experiments with *Lessonia nigrescens* revealed a depuration of Cd in individuals transplanted to areas with high Cu. However, Cd depuration occurs more slowly than Cu uptake. These differences suggest that while Cd and Cu are linked mechanistically, it is not a simple substitution. Overall, the work confirms that macroalgae are useful indicators of metal contamination and may be used as in situ biomonitors for labile forms of metals, like free Cu²⁺. However, antagonistic relationships between metals must be clearly understood in order to properly interpret their concentrations in macroalgae.

Introduction

Cadmium is an important contaminant in coastal environments (1); it is actively accumulated by macroalgae and invertebrates (2, 3) and, over certain levels, becomes highly toxic to organisms. Cd is not considered a biologically essential element, though it can be utilized in carbonic anhydrate by phytoplankton (4). Furthermore, Cd bioaccumulation in bivalves poses a potential health hazard to humans and has important economic consequences for the shellfish industry (5). High levels of Cd in marine organisms are associated with both natural and anthropogenic sources (6). The latter cases include mines and industries processing minerals as well as urban and agricultural runoffs. The main natural sources of Cd in seawater are upwelling events (7, 8). Coastal upwelling areas are highly productive and have an impact on the ecological relationships regulating the structure

of benthic organisms (9), a number of which are also economically important resources exploited by humans (10), so elevated Cd levels are of general interest. Bioaccumulation in Cd-rich upwelled water off Baja California accounts for high levels of Cd in phytoplankton (11) and macroalgae (12). Coastal upwellings in northern Chile are similar to those in Baja California (13), but to date there have been no reports of metal enrichment and bioaccumulation of Cd in marine macroalgae from the Chilean coast.

In contrast, and as a result of the concentration of copper mining operations in northern Chile, considerable work has been done on the bioaccumulation of Cu in macroalgae in the vicinity of the coastal mine impacted areas, including Chañaral (26°15'S; 70°40'W), where wastes from the El Salvador copper mine have been dumped for more than 60 years, leading to excessive contamination (14). Chañaral is characterized by high levels of dissolved Cu (15), a severe reduction in species richness with a complete modification of the intertidal community structure (16), and high Cu concentrations in macroalgae (14).

Despite the common occurrence of the two metals in natural and impacted aquatic environments, the potential relationships between Cu and Cd in macroalgae have not been reported. On the contrary, there are numerous examples of competitive interactions between different metals for uptake, storage, and utilization documented in marine phytoplankton (17–19), and an antagonistic relationship between Cd and Cu uptake was recently reported (20).

In this study, we investigated the bioaccumulation of Cu and Cd simultaneously on several species of macroalgae at study sites subjected to upwelling events, within and outside the highly Cu-contaminated Chañaral region. Thus, the study presents an ideal opportunity to study the (i) accumulation of both metals over a large range of Cu concentrations in the water and (ii) Cd:Cu ratios in macroalgae. Furthermore, we assessed the dynamics of metal accumulation using transplants of the ecologically key brown kelp *Lessonia nigrescens* (*L. nigrescens*).

Materials and Methods

Sample Collection. Samples of macroalgae and coastal seawater were collected simultaneously between April 2003 and January 2004, at three sites in northern Chile. Among sampling stations (Figure 1), Zenteno (26°54.1'S; 70°48.5'W) and Guanillo (25°53.7'S; 70°41.5'W) were considered reference sites because they are located outside the area influenced by the mine tailings discharge at Chañaral bay (15). Caleta Palito (26°15.8'S; 70°40.6'W), on the other hand, is located close (<200 m) to the site where wastes are currently discharged and high levels of total dissolved Cu have been measured (15).

At low tide, samples of red (*Ahnfeltiopsis* sp., *Chondrus* sp., *Porphyra* sp.), brown (*Glossophora kuntii* (*G. kuntii*), *Lessonia nigrescens*, *Scytosiphon lomentaria* (*S. lomentaria*)), and green (*Ulva compressa* (*U. compressa*) and *Ulva* sp.) macroalgal species were randomly collected at several places in each site. Samples were separated by species and immediately allocated in acid-clean plastic bags at 4 °C until metal analysis. Due to seasonality, algae were collected every time they were present during the period of sampling, which included a visit to each site every other month (see Table 2). Each sample consists of pieces of different individuals of the same species and was gathered along the coast in a single site, pooled together.

Seawater samples were collected monthly during the period of the transplant experiment (see below). Duplicate

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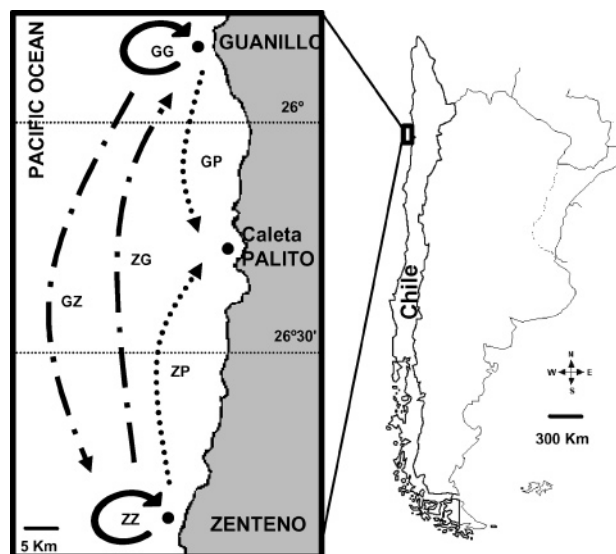


FIGURE 1. Study area and location of the three sampling sites (●). Arrows indicate the transplant experiment using the brown kelp *Lessonia nigrescens*. Experimental plants were identified according to the site of detachment and fastening: from Zenteno to Zenteno (ZZ), Guanillo (ZG), and Caleta Palito (ZP) and from Guanillo to Guanillo (GG), Zenteno (GZ), and Caleta Palito (GP).

samples were taken from the shore using acid-washed low-density polyethylene bottles (1 L) secured to a 3-m non-metallic pole sampler according to Andrade et al. (21). After collection, bottles were placed in a double plastic bag and kept at 4 °C until analysis.

Transplant Experiment. Transplantation of the brown kelp *L. nigrescens* was set up in three steps using the methodology described by Correa et al. (22). First, *L. nigrescens* individuals of 4–8 cm holdfast diameter and up to 120 cm frond length were simultaneously collected from natural stands at both reference sites (Figure 1). Forty-five plants were detached from each site and immediately labeled with plastic tags fastened to their holdfast. Thirty individuals were stored in tanks with seawater from the place of collection to minimize physiological stress during transportation to the receiving sites (see below). The remaining 15 plants were fastened to the rocky platform near the place where they were detached, as control for manipulation. These auto-transplant groups were labeled as GG (Guanillo to Guanillo) or ZZ (Zenteno to Zenteno), depending on the site of collection (first letter) and site of destination (second letter).

The second step was executed within the next 24 h. From the 30 individuals of each site kept in tanks, a group of 15 plants from Guanillo and 15 from Zenteno were transported to Caleta Palito. During low tide, these plants were fastened to the rock at their natural position in the intertidal zone. These groups were labeled as GP (Guanillo to Palito) or ZP (Zenteno to Palito).

The last step started 48 h after plants were removed from their site of origin. The remaining 15 individuals from Guanillo and 15 individuals from Zenteno were cross-transplanted and fastened in the other site (i.e. Z and G, respectively). Between detachment and fastening of plants, the water in the tanks was renewed every half-hour to reduce the physiological stress of algae. These two groups were labeled as GZ (Guanillo to Zenteno) and ZG (Zenteno to Guanillo) (Figure 1).

Immediately after fastening to the rock, six individuals of *L. nigrescens* from each group were sampled for metal analysis to determine the basal (t_0) levels of Cd and Cu. At Caleta Palito, three to six different individuals per group (GP and ZP) were also sampled after 36 h and 1 and 2 months of

TABLE 1. Salinity and Total Dissolved Concentration of Cd and Cu in Seawater (Mean Values $\pm$ Standard Deviation ($n = 6$))^a

site	code	salinity (psu)	Cd ($\mu\text{g L}^{-1}$)	Cu ($\mu\text{g L}^{-1}$)
Guanillo	G	33.9 $\pm$ 0.5	ND	2.40 $\pm$ 1.52
Caleta Palito	P	33.7 $\pm$ 0.4	ND	10.69 $\pm$ 2.05
Zenteno	Z	33.3 $\pm$ 0.8	0.17 $\pm$ 0.11	4.30 $\pm$ 2.43

^a ND: below detection limits.

transplantation. In the sites of origin, fastened individuals were sampled 1 and 2 months after transplantation only. Samples consisted of 10 cm of frond tissue taken from each plant and were maintained separately in acid-clean plastic bags at 4 °C until analysis. The entire transplant experiment took place from May to July 2003.

Analytical Procedure. Samples of algal tissue reached the laboratory within 72 h of collection. Upon arrival, the tissue was washed three times with filtered seawater, sonicated for 30 s and oven-dried to constant weight at 45 ± 5 °C. Three subsamples of ≈ 0.3 g of dry alga were digested with a concentrated Suprapur nitric acid (Merck) and hydrogen peroxide p.a. (Merck) mixture (6:1), using a microwave oven (Milestone MLS 1200 Mega). Determination of Cd and Cu were conducted by inductively coupled plasma mass spectrometry (ICP-MS) in a Perkin-Elmer ELAN 6100 ICP-MS with an autosampler AS90. Metal concentration was calculated from five replicate readings of each subsample. The detection limits were 0.01 and 0.03 μg of metal g^{-1} of dry wt for Cd and Cu, respectively. Analytical grade reagents were used to prepare relevant blanks and calibration curves. Spinach leaves (NIST-CRM-1570a) provided by the National Institute of Science and Technology, USA, were used to check the accuracy of the digestion and analysis procedures during determination of total metals in algae. In both cases, the metal contents were not significantly different from expected values (t test, $P > 0.05$).

Seawater samples were filtered through acid-washed 0.45 μm cellulose acetate Millipore membrane filters, with a polycarbonate filter unit. Samples were fixed with 0.5 mL of concentrated nitric acid ($\text{pH} < 2$) per liter of sample and UV-irradiated using a Metrohm 705 UV digester. Dissolved Cu and Cd concentrations were determined by differential pulse anodic stripping voltammetry analysis (DPASV) using a Metrohm 757 VA processor, following the methodology described by Metrohm (23). The detection limits were 0.1 and 0.5 μg of metal L^{-1} for Cd and Cu, respectively. Accuracy of the measurement procedure was checked against the reference material TMDA 62, provided by The National Water Research Institute, Canada. The metal contents were not significantly different from expected values (t test, $P > 0.05$). All pretreatment and analyses of seawater samples were conducted at room temperature (25 °C) in a Class-100 vertical flow hood.

Statistical Analysis. Data were checked for normal distribution and homogeneity of variance by application of the Kolmogorov-Smirnov test and the Levene's test, respectively. Statistical comparisons were performed using t tests and ANOVA procedures. In the latter, significant differences between groups were assessed by the application of the post-hoc Tukey's multiple comparison tests (24).

Results

Metal Concentration in Seawater. Salinity and total dissolved Cd and Cu concentrations in seawater of the three study sites are shown in Table 1. Data show that dissolved Cd levels varied from below detection limits in Guanillo and Caleta Palito to almost 0.2 $\mu\text{g L}^{-1}$ in Zenteno. Dissolved Cu concentrations, on the other hand, were significantly different

among sites (one way ANOVA $F_{(2,5)} = 49.996$, $P < 0.05$). The post-hoc Tukey's multiple comparison tests showed that dissolved Cu levels in Caleta Palito were significantly higher than both Guanillo and Zenteno, which did not differ from each other.

Metal Concentration in Macroalgae. Algal Cd and Cu data are shown in Table 2. The most significant finding was that Cd in algae from Caleta Palito was, in general, one order of magnitude lower than in algae from the reference sites (Zenteno and Guanillo). At this site, the lowest and highest amounts of Cd were found in *U. compressa* and *G. kunthii*, respectively, while the lowest Cd concentration at the reference sites was recorded in *Ulva* sp. and the highest in *Ahnfeltiopsis* sp.

All macroalgal species collected at Caleta Palito showed Cu concentrations higher than those from reference sites, ranging from 93.5 $\mu\text{g g}^{-1}$ of dry wt in *U. compressa* to 1600 $\mu\text{g g}^{-1}$ of dry wt in *G. kunthii*. The Cu content of algae from the reference sites varied from 1.6 $\mu\text{g g}^{-1}$ dry wt in *Ahnfeltiopsis* sp. to 27.1 $\mu\text{g g}^{-1}$ of dry wt in *Porphyra* sp. It is necessary to indicate that species common to both contaminated and reference sites displayed intermediate levels of Cu.

The Cu-to-Cd ratio varied between 0.4 and 2.6 in algae from the reference sites and between 203 and 1052 in those from the contaminated site (Table 2). This big range reflected much higher Cu values in Caleta Palito combined with much lower Cd values at that site compared with those at the reference sites.

Transplant Experiment. Cd concentrations in *L. nigrescens* transplanted within (autotransplants) and between reference sites (cross-transplants) and to Caleta Palito are shown in Figure 2A. No significant differences in Cd levels at t_0 were found between plants from Guanillo and Zenteno ($t_{10} = 0.485$, $P > 0.05$). At this time, the average Cd concentration in these plants was $7.27 \pm 1.59 \mu\text{g g}^{-1}$ of dry wt. After 36 h of being transplanted and exposed to the Cu-enriched environment of Caleta Palito, Cd levels in these plants were still not significantly different from that in plants maintained as controls at the reference sites ($t_{15} = 1.46$, $P > 0.05$). However, after 1 month of transplantation, a significant decline in Cd content was observed in relation to their basal level ($t_{13} = 6.94$, $P < 0.001$). After this period, mean Cd values of plants maintained at Zenteno (ZZ and GZ) and Guanillo (GG and ZG) were 8.59 and 7.45 $\mu\text{g g}^{-1}$ of dry wt respectively,

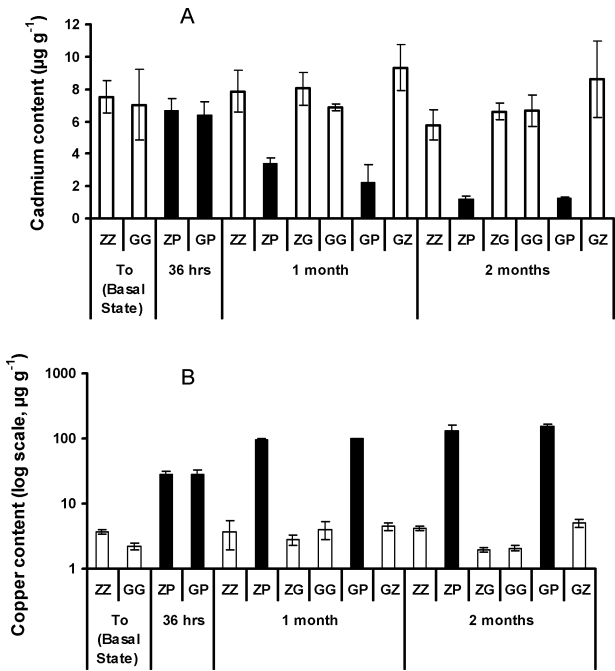


FIGURE 2. Cd (A) and Cu (B) content in *Lessonia nigrescens* fronds determined in individuals transplanted from Zenteno to Zenteno (ZZ), Guanillo (ZG), and Caleta Palito (ZP) and from Guanillo to Guanillo (GG), Zenteno (GZ), and Caleta Palito (GP).

whereas in Caleta Palito the levels of the metal dropped to 3.4 $\mu\text{g g}^{-1}$ of dry wt in plants from Zenteno (ZP) and to 2.19 $\mu\text{g g}^{-1}$ of dry wt in plants from Guanillo (GP). Two months after the beginning of the experiment, the Cd concentration in these plants was only 20% of their basal level and 17–20% of the level recorded in plants maintained at the reference sites.

In general, Cu in *L. nigrescens* behaved in an opposite manner to Cd (Figure 2B). In Zenteno and Guanillo the Cu content was $<4.3 \mu\text{g g}^{-1}$ of dry wt at t_0 but increased significantly ($t_{12} = 22.23$, $P < 0.001$) 36 h after transplantation to Caleta Palito. After this period, the Cu concentrations in plants from Zenteno and Guanillo reached mean concentrations 7.3 and 12.7 times higher than their respective basal

TABLE 2. Ranges of Cd and Cu Content in Macroalgal Samples from the Studied Sites^a

site	algal species	N	Cd ($\mu\text{g g}^{-1}$ dry wt)	Cu ($\mu\text{g g}^{-1}$ dry wt)	Cu/Cd	
reference	Guanillo	<i>Ahnfeltiopsis</i> sp.	7	5.1–17.5	1.6–17.9	0.9
		<i>Chondrus</i> sp.	4	5.4–6.9	1.7–8.7	0.7
		<i>Lessonia nigrescens</i>	17	5.1–13.6	1.7–5.8	0.4
		<i>Porphyra</i> sp.	7	6.1–13.2	5.9–16.6	1.2
	Zenteno	<i>Glossophora kunthii</i>	2	15.4–17.2	6.1–6.8	0.4
		<i>Ulva compressa</i>	4	6.6–7.8	4.2–6.1	0.7
		<i>Ulva</i> sp.	7	2.8–7.8	4.4–17.4	2.1
		<i>Ahnfeltiopsis</i> sp.	8	5.2–17.8	1.8–10.7	0.7
		<i>Chondrus</i> sp.	6	4.1–16.8	3.2–12.9	0.7
		<i>Lessonia nigrescens</i>	17	5.1–12.2	2.2–6.9	0.5
		<i>Porphyra</i> sp.	7	3.9–14.6	4.2–27.1	1.7
contaminated	Caleta Palito	<i>Scytosiphon lomentaria</i>	2	4.8–7.6	4.3–8.1	0.9
		<i>Ulva</i> sp.	7	2.5–6.2	4.2–18.8	2.6
	Caleta Palito	<i>Glossophora kunthii</i>	4	0.4–1.9	811.1–1609.2	1052.3
		<i>Scytosiphon lomentaria</i>	19	0.3–1.7	120.3–720.4	420.3
		<i>Ulva compressa</i>	18	0.1–1.8	93.5–790.6	465.3
		<i>Ulva</i> sp.	2	0.4–1.5	128.4–256.6	202.6

^a Metal ratios, calculated from mean concentration values, are also indicated.

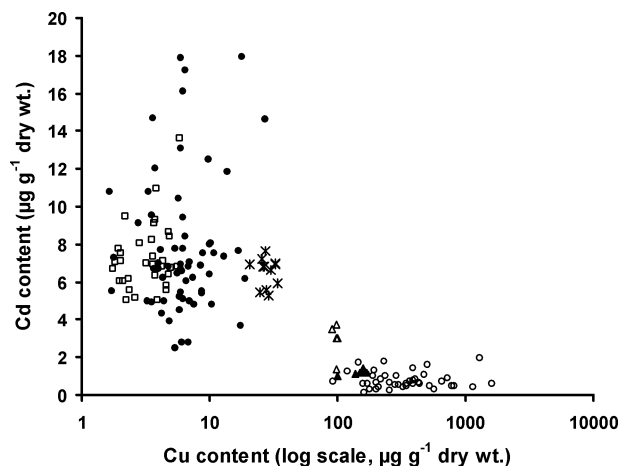


FIGURE 3. Correlation between Cd and Cu content in the eight species of naturally occurring macroalgae from Z and G (●) and from P (○). The figure also includes *Lessonia nigrescens* individuals fastened in Z and G (□) and transplanted to Caleta Palito: after 36 h (*); 1 month (Δ), and 2 months (▲). ($n = 159$).

levels. These differences became even more evident after 1 month of exposure to the Cu-enriched environment of Caleta Palito ($t_4 = 56.10$, $P < 0.01$). In this case, transplants from Guanillo and Zenteno displayed levels of Cu 24.1 and 25.5 times higher than those plants maintained at their original, reference sites. This increase in Cu accumulation continued, and after 2 months of exposure, transplants from Zenteno and Guanillo accumulated 31.4 and 74.8 times more Cu than their autotransplant controls. Cross-transplants between reference sites, on the other hand, did not result in significant changes in Cu accumulation, even after 2 months of experimentation.

When metal contents of all algae analyzed in this study were pooled (including the transplants), a significant negative correlation ($r = 0.857$, $P < 0.01$) was found between Cd and Cu in their tissues (Figure 3).

Discussion

The results suggest that the concentrations of Cu and Cd in the macroalgae are determined by two factors, the dissolved phase concentrations of the metals as well as their relative concentrations. Evidently, the uptake and/or sequestration pathways are mechanistically linked in order to account for these observations. In the following section, we argue that while there are little data to provide a molecular understanding of these processes in macroalgae, research in unicellular algae provides some insight and guidelines for future research in the former group.

Cd and Cu Concentration in Macroalgae. The range of Cd in the eight species of macroalgae from the reference sites, including *L. nigrescens*, were higher than those reported for algae in non-upwelling areas (25–28) but were within the range reported for species within upwelling regions (12). On the other hand, the levels of Cu found in the study species were in agreement with values previously reported in macroalgae from different parts of the world (26, 29, 30). However, the high concentration of this metal measured in algae native to Caleta Palito, and in *L. nigrescens* transplanted for 2 months to this site, agree only with what has been reported in marine algae from other contaminated coastal systems (29, 31, 32).

Relationship between Dissolved Cu and Cd Concentrations and Algal Metal Content. Data show a clear relationship between dissolved Cu and the concentration of the metal in the algal tissues. However, while dissolved Cu increases up to four times (2.5–4 times) in contaminated sites, algal Cu

increases by as much as 200-fold. The most likely explanation is that Cu accumulation is proportional to the free Cu^{2+} ion and simple inorganic complexes, rather than the total dissolved concentration, which includes many complexes that are non-bioavailable. This mechanism, included in the so-called free ion model, has been shown to be a valuable predictive tool for toxicity to many marine organisms, including unicellular phytoplankton (33). Recently, we studied the speciation of Cu at these sites using anodic stripping voltammetry (21), and results indicated an almost 60-fold increase in free Cu^{2+} between the pristine ($0.01 - 0.006 \mu\text{g L}^{-1}$ copper in Guanillo and Zenteno, respectively) and contaminated sites ($0.33 \mu\text{g L}^{-1}$ in Caleta Palito). This increase reflects saturation of ambient Cu complexing ligands by the elevated Cu at the contaminated site. Taking into consideration the average values of free Cu^{2+} (21) together with copper levels in *L. nigrescens* from the transplant experiment, harvested after 2 months of exposure to the contaminated environment, it was found a 43-fold increase in Cu over the initial values of the metal in the plants, comparable to the difference in free Cu^{2+} .

Our data suggest that the Cu content in macroalgae may be a useful indicator of the biologically available fraction of Cu in seawater. The rapid accumulation of Cu observed in transplanted *L. nigrescens* suggests that macroalgal metal data may also be a useful integrative probe of episodic events such as storms, floods, and dredging where large fluctuations in metal inputs may be difficult to detect with conventional metal sampling strategies. Clearly, a calibration would need to be performed with any given species to determine the relationship between Cu content in the algae and dissolved concentrations, but the trends, as well as the concentrations in the reference sites, are remarkably similar.

For Cd, we have no speciation data, and our study sites show that the Cd concentration in the water was below detection limits. However, it is highly unlikely that the decrease of Cd in algae from Caleta Palito is due to stronger complexation in the aqueous phase. In general Cd is weakly complexed by organic matter, and there is no reason to suspect that Cd-binding ligands are more abundant in Caleta Palito or anywhere else along this arid coast. As noted above, there was no significant difference in Cu binding ligands between sites (21). Therefore, the most plausible explanation for Cd decrease in the algae is an antagonistic interaction at the molecular level. This is supported by the work of Wei et al. (20), who experimentally demonstrated that metals such as Cu, Cd, and Zn had different effects on phytochelatin production in *Thalassiosira pseudonana* (*T. pseudonana*), depending upon the free metal concentration in the water. These authors suggested antagonistic relationships as the bases for the observed results. Antagonistic relationships were also reported for Cu uptake and liberation of exudates by the marine microalga *Emiliana huxleyi* (*E. huxleyi*) when exposed to Cd and/or Pb in laboratory assays (34).

Variations of Cadmium and Copper Concentrations in Macroalgae. The transplant experiment revealed that individuals exposed to the Cu-enriched environment of Caleta Palito experience an increase in Cu content, in agreement with other transplant studies (31, 35), even though this study is the first demonstration of a concomitant decrease in Cd content. However, Cu increase and Cd loss occurred over very different time scales, with Cu increasing over the course of hours, while Cd decreased over a course of weeks to months. Therefore it is not a simple displacement of one metal for another at binding sites associated with sequestration, for example intracellular chelators such as phytochelators or metallothioneins. There are several plausible explanations. Both metals may be sequestered by phytochelators, as has been observed in marine phytoplankton (36). Oxidative stress associated with Cu toxicity may

consume glutathione (37), a useful intracellular antioxidant that is also a phytochelatin precursor, leading to a gradual decrease in phytochelatin. Cu(I) forms stronger complexes with phytochelatin than Cd(II) (38) so, if phytochelatin levels gradually decline, Cd would be affected first. In support of this hypothesis the activation of an antioxidant metabolism has been reported in macroalgae inhabiting sites within the influence of the mine tailing discharge at Chañaral bay (i.e. *U. compressa* and *S. lomentaria*) in response to the oxidative stress caused by elevated dissolved Cu levels (37, 39). Alternatively, Cd may be continuously effluxed from *L. nigrescens*, with a turnover time on the order of months, as demonstrated by Lee et al. (40) in *Thalassiosira weissflogii* (*T. weissflogii*). Competition between Cu and Cd at uptake sites would lead to an overall decrease as efflux exceeds uptake. Although antagonistic interactions have been demonstrated between several pairs of metals during uptake and accumulation in *Thalassiosira pseudonana* (*T. pseudonana*), including Mn–Cu (17), Mn–Cd and Cd–Zn (18, 41) and most recently Cd–Cu antagonism (20), at present, these mechanisms are impossible to distinguish.

Another potential mechanism of metal sequestration involves the polyphosphate bodies (PPB), which serve a dual purpose in cells by providing a storage site for essential metals and acting as a detoxification mechanism of toxic metals (42). Cd sequestration by PPB has been described as an important mechanism for Cd uptake in *Macrocystis pyrifera* (*M. pyrifera*) (25). Moreover, PPB may be a means of storing phosphate containing high-energy chemical bonds similar to those in ATP, therefore representing a rich source of energy useful to the cells during periods of stress (25). If so, the energy demand to cope with the toxic effects associated with Cu-mediated oxidative stress could lead to degradation of the PPB with the subsequent liberation of Cd.

Cu:Cd Ratios. Comparison between different species suggests that there are probably aspects of the mechanism of bioaccumulation common to all macroalgae. Cu bioaccumulation at levels comparable to bioavailable Cu, and the depuration of Cd in high Cu waters were common to all studied species.

The most noteworthy difference between species is the Cu:Cd ratio. It is noteworthy that for the four species that grow in both pristine and contaminated waters, the trends in Cu:Cd ratios are exactly the opposite between stations. For instance, *G. kunthii* has the lowest Cu:Cd ratio in the reference site but the highest Cu:Cd ratio in the contaminated site. These data suggest that, despite similarities between species, there are significant differences that probably reflect mechanistic differences in storage and detoxification strategies.

Overall, our work suggests that macroalgae–metal interactions may have many characteristics in common with unicellular phytoplankton–metal interactions. This is highly promising because it suggests that robust relationships between biomass content, physiology, and aqueous phase speciation can be identified that will provide insight into the ecology of metal–macroalgal interactions and further their value to the community as contaminant indicators.

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