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Cadmium, Copper, Lead and Zinc in Cultured Oysters Under two Contrasting Climatic Conditions in Coastal Lagoons from SE Gulf of California, Mexico

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Abstract In order to determine the metal concentrations in cultured oysters from four coastal lagoons from SE Gulf of California, several individuals of *Crassostrea gigas* and *C. corteziensis* were collected and their cadmium, copper, lead and zinc levels were measured by atomic absorption spectrometry after acid digestion. The concentration of metals in oyster soft tissue was Zn > Cu > Cd > Pb. In two lagoons, Cd concentrations (10.1–13.5 μg g^{-1} dw) exceeded the maximum level allowed according to the Official Mexican Standard (NOM-031-SSA1-1993), which is equivalent to the WHO recommended Cd levels in organisms used for human consumption.

Keywords Metals · Coastal lagoons · *Crassostrea* oysters · Gulf of California

Cadmium, copper, lead and zinc, accumulate in the tissues of aquatic organisms at concentrations higher than in water, may be biomagnified in the food chain and cause physiological impairment at higher trophic levels and in human consumers. For the purposes of assessing coastal water quality, oysters of *Crassostrea* genus have already been proposed as sentinel organisms for marine ecotoxicological tests, because they are very sensitive to pollutants and provide a rapid response (Zhou et al. 2008). The Pacific and the mangrove oysters (*C. gigas* and *C. corteziensis*, respectively), are cultivated inside coastal lagoons, hence the oysters are susceptible to contamination by metals and other chemicals (Osuna-Martínez et al. 2010). Therefore, this study was conducted to determine and compare the concentration of Cd, Cu, Pb and Zn in the soft tissue of *C. gigas* and *C. corteziensis* specimens from four coastal lagoons (SE Gulf of California, Mexico).

Materials and Methods

This study was performed at four oyster farms located in four coastal lagoons from Sinaloa state, SE Gulf of California, Mexico: El Colorado (EC), Santa María-La Reforma (SMLR), Altata (ALT) and Ceuta (CEU) (Fig. 1). A total of six samples of cultured oysters *C. gigas* and two samples of *C. corteziensis* (species restricted to only one farm) were collected during the dry and rainy season in duplicate. Once cleaned, the oyster shells were measured (mm) and weighed (total and soft tissue, g). The condition index (CI) was determined by: CI = [soft tissue dry wt (g) × 1,000]/shell dry wt (g). The soft tissue of the groups (each batch of 25 oysters) was extracted, homogenized, freeze-dried over 72 h (−49°C and 133 × 10^{-3} mbar) and then ground in an automatic agate mortar. Finally, they were kept frozen until their digestion (<3 months) (Osuna-Martínez et al. 2010). Analyses were carried out by atomic absorption spectrometry with flame detection (Cd, Cu and Zn) and grafite furnace (Pb) (Jara-Marini et al. 2008). For metal quality control purposes, certified mussel material (Standard Reference Material® 2976, from NIST) was analyzed (recoveries from 113.9 to 119.6%). The limits of detection were 0.06, 3.6, 0.44 and 11.3 μg g^{-1}, for Cd, Cu, Pb and Zn, respectively.

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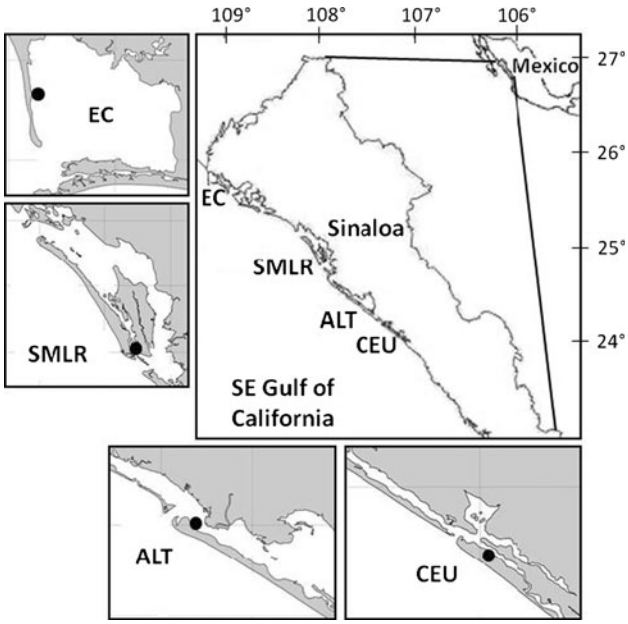

Fig. 1 Location of the study area: coastal lagoons from Sinaloa, where cultured oysters were collected. The point (*filled circle*) indicates the approximate position of the farms

Additionally, one blank was included per each set of 14 samples. One-way analysis of variance (ANOVA) was performed, which showed significant differences between the mean concentrations, and correlation analysis (bivariate correlations) were used in order to find the relationships among the concentrations of these metals in the oysters.

Results and Discussion

In spite that organisms had similar sizes, the mean weights were different from one season to another, therefore, the soft tissue weight was higher in samples from the dry season, when the condition index is greater (Table 1 from Osuna-Martínez et al. 2010). The concentration of metals in oyster soft tissues were Zn > Cu > Cd > Pb, and their global mean concentrations for *C. gigas* for the rainy and dry season were 8.05 ± 2.60 and 11.30 ± 2.70 $\mu g\ g^{-1}$ (dw) for Cd, 35.1 ± 16.1 and 16.0 ± 10.3 for Cu, 1.52 ± 0.43 and 0.92 ± 0.45 for Pb, and 342 ± 116 and 156 ± 41 for Zn, respectively. For this species, higher mean concentrations of Cd were found during the dry season, as well as for *C. corteziensis* in CEU lagoon. This increase on the bioavailability of Cd during dry season could be explained by the presence of upwelling regime during this season, since the Gulf of California is characterized by the upwellings events along its eastern coast, normally from February to April (Staines-Urías et al. 2009). The average Cd concentration trend for the *C. gigas* specimens were SMLR > CEU > EC and SMLR > ALT > CEU, during the rainy and dry seasons, respectively. At both cases, the oysters from SMLR had the highest concentrations. This could be related to the extension of the lagoon mouth at SMLR (which has two big mouths) and its closer distance from the farm location. For Cu, Pb and Zn, the highest concentrations were found during the rainy season in all the lagoons, for both species, which is in agreement with Frías-Espericueta et al. (1999), who found the highest concentrations of Cu, Pb

Table 1 Range of metal concentrations ($\mu g\ g^{-1}$ dry wt) in *Crassostrea* oysters species from Mexico and other world regions

Species	Cd	Cu	Pb	Zn	Study area
C. gigas	0.6–9.4	3.6–42.1	1.2–7.4	28–672	Oualidia Lagoon, Morocco[a]
C. gigas	1.3–2.3	18.0–39.0	ND	967–2028	Potengi Estuary, Brazil[b]
C. gigas	4.7–27.2	250–6576	4.1–36.0	1683–7262	Ussuriyskiy Bay, Japan[c]
C. gigas	4.9–13.9	9.1–58.0	0.5–2.1	113–478	Coastal lagoons, SE Gulf of California, Mexico[g]
C. corteziensis	1.5–7.4	17.5–166.3	4.1–9.4	245–2304	Coastal lagoons, SE Gulf of California, México[d]
C. corteziensis	ND	15.4–216	3.6–7.6	442–1595	Pacific Coast, Mexico[e]
C. corteziensis	0.2–0.6	33.6–44.9	0.3–1.9	263–382	Urías Lagoon, Mexico[f]
C. corteziensis	4.2–5.5	5.5–18.4	0.2–0.7	114–226	Coastal lagoons, SE Gulf of California, Mexico[g]

ND, not determined

[a] Maanan (2008)

[b] Silva et al. (2006)

[c] Shulkin et al. (2003)

[d] Frías-Espericueta et al. (2009)

[e] Páez-Osuna et al. (2002)

[f] Jara-Marini et al. (2008)

[g] This study

and Zn in autumn, when the oysters were in resting phase. Besides, this pattern implies a higher input of these metals from the watershed. These three metals showed the same trend among the concentration levels of the different lagoons at both seasons (Rainy: EC > CEU > SMLR; Dry: ALT > CEU > SMLR), except for Zn during rainy season (CEU > EC > SMLR). However; in all cases SMLR had the lowest concentrations in contrast to the Cd results. Again, its position farthest from the inlet could be playing an important role in the availability of these three metals (Fig. 2).

A linear model was applied in which the Cd, Cu, Pb and Zn concentrations in the tissues of *C. gigas* were plotted as a function of the CI; the results showed only a good correlation coefficient for Zn, which was negatively correlated to the CI ($r = -0.86$; $p < 0.05$); which is in agreement with the analyses made in mussels (*Mytilus edulis*) by Mubiana et al. (2006) and in the same oysters for Hg (Osuna-Martínez et al. 2010). Bivariate correlation analyses (with Pearson correlation coefficient) among these four metals were made; the results showed a significant correlation just for Cu-Pb ($r = 0.93$; $p < 0.05$), while Pb showed to be closely related to Zn, but it did not reached a significant correlation ($r = 0.80$; $p > 0.05$). These results differ from the ones found for *C. iridescens* (Frías-Espericueta et al. 1999), which show no correlation for Cu-Pb and a negative correlation for Pb–Zn. Nevertheless, they are in agreement to the correlations found for the mussels *Mytilus galloprovincialis* (Szefer et al. 2004). Such correlations indicate that the metals involved have similar physical/chemical properties of the involved elements (Szefer et al. 1994).

According to the WHO (1982) and the Official Mexican Standard (NOM-031-SSA1-1993), the maximum permissible levels for these metals are equivalent to 10, 50, 5 and 500 µg g^{-1}, dry wt (ca. 80% humidity) for Cd, Cu, Pb and Zn, respectively. Cd levels exceeded the permitted levels in ALT during the dry season and in SMLR during both seasons; Cu concentration was higher than the permitted level in EC only during dry season; while Pb and Zn showed levels lower than the permitted limit (Fig. 2). The Expert Committee on Food Additives (WHO, 2003) has established regulatory guidelines regarding the dietary intake of metals, it recommends for Cd (a metal of concern), a provisional tolerable weekly intake (PTWI) of 7 µg kg^{-1} body weight. Such concentration is equivalent to 490 µg Cd/week for a 70 kg person. According to the results of this study, during the dry season, the mean concentration of Cd in both cultured species was 8.5 µg g^{-1} dry wt, equivalent to 42.5 µg g^{-1} wet wt. Therefore, ca. 11.53 g wet wt is the total weekly maximum amount of oysters harvested from this region that could be consumed by a 70 kg person without exceeding a body cadmium concentration of 7 µg kg^{-1} on a weekly basis. Normally, the persons consume 6 or until 12 oysters, consequently, such PTWI may be easily reached. From these results is evident the risk of Cd by consumption of these

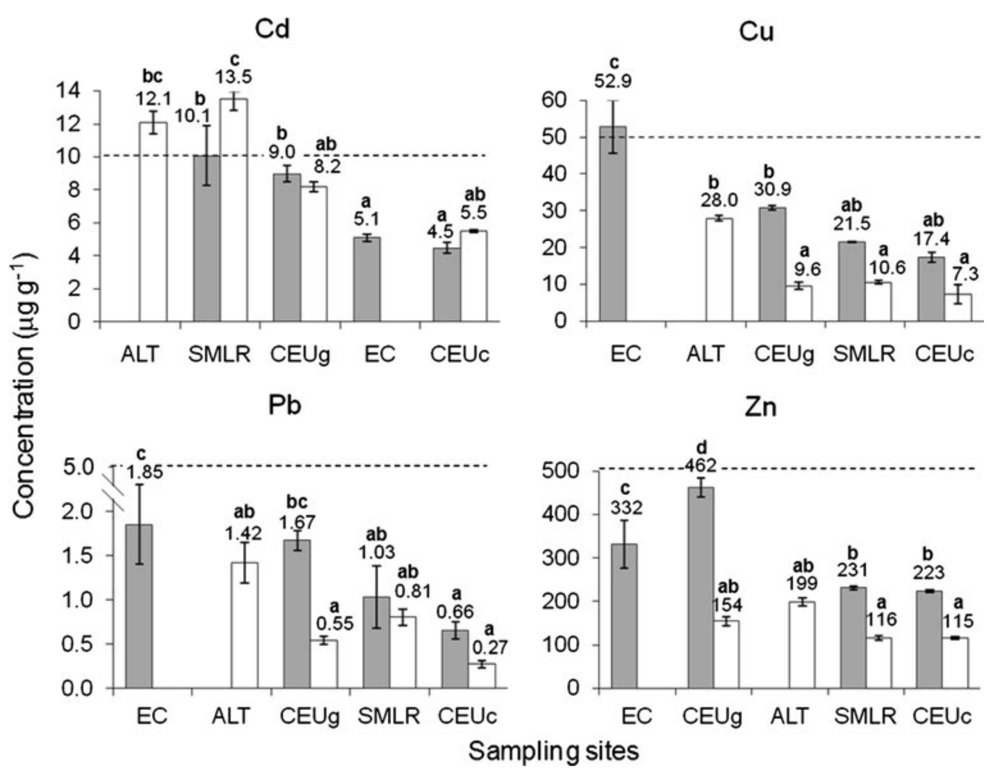

Fig. 2 Metal concentrations in the oysters from the coastal lagoons (mean ± SD, µg g^{-1}, dry wt). The maximum tolerable values are indicated by *dashed lines*, rainy and dry season data are represented by *filled* and *unfilled bars*, respectively. Different *letters* for a particular metal show significant differences ($p < 0.05$) among sites

oysters and the need of more research in this context is justified.

In the case of the CEU samples, both species were collected from the same farm (site and depth); therefore, they were exposed under the same water conditions and levels of metals. Although there were a limited number of samples collected (n = 8), the analysis of correlation of metal content between the two species: *C. corteziensis* (x) and *C. gigas* (y) revealed a significant correlation ($p < 0.05$) for Cu, y = 0.484, x + 2.514 ($r = 0.97$); Pb, y = 0.348, x + 0.079 ($r = 0.98$); and Zn, y = 0.349, x + 62.213 ($r = 0.99$). These equations may be useful in the intercomparison of metals levels among different sites involving these two species in monitoring programs. In the case of Cd, although was obtained a $r = 0.89$, it was not statistically significant ($p > 0.05$). Clearly a higher number of samples are required to examine reliably such correlations.

Table 1 shows a comparison between metal concentrations in *C. gigas* and *C. corteziensis* from different sites around the world and the values found in this study. In the case of Cd for both species, the determined concentrations in this study are higher than the registered for other sites of the world. But for *C. corteziensis* they are comparable with the results of studies done in the same region (Páez-Osuna et al. 2002; Frías-Espericueta et al. 2009). The Cu and Pb concentrations are comparable (for *C. gigas*) or less (for *C. corteziensis*) and the Zn levels are less, for both species, than the levels found in other regions. From this work, emerge the need of research the mechanisms and sources of metals associated with the enrichment of such metals in cultured oysters in both seasons; which apparently for Cu, Pb and Zn is connected in rainy months with transported material from the watershed, while in dry season the higher availability of Cd is related to upwellings in the Gulf of California.

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