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Comparative bioaccumulation of trace metals using six filter feeder organisms in a coastal lagoon ecosystem (of the central-east Gulf of California)

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Abstract The Tobari Lagoon, located in the central-east coast of the Gulf of California, receives effluents from the Yaqui Valley, one of the most extensive agricultural areas of México. The Tobari Lagoon also receives effluents from nearby shrimp farms and untreated municipal sewage. Surface sediment samples and six different species of filter feeders (*Crassostrea corteziensis*, *Crassostrea gigas*, *Chione gnidia*, *Anadara tuberculosa*, *Chione fluctifraga*, and *Fistulobalanus dentivarians*) were collected during the dry and the rainy seasons and analyzed to determine concentrations of cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), and zinc (Zn). Seasonal variations in metal concentrations in sediment were evident, especially for Cd, Cu, Hg, and Zn. The total and bioavailable concentrations of the five metals are not elevated in comparison to other areas around the world. The percentages of bioavailable respect to total concentrations of the metals varied from 0.6 % in Hg to 50.2 % for Cu. In the organisms, Hg showed the lowest concentrations (ranged from 0.22 to 0.65 μg/g) while Zn showed the highest (ranged from 36.6 to 1,702 μg/g). Linear correlations between the levels of Cu, Pb, and Zn in the soft tissues of *C. fluctifraga* and *C. gnidia*, and *A. tuberculosa* and *C. gnidia* were found. Seasonal and interspecies variations in the metal levels in filter feeders were found; *F. dentivarians*, *C. corteziensis*, and *C. gigas* exhibited the highest levels, could be used as biomonitors of metals contamination in this area.

Keywords Coastal lagoon · Heavy metals · Bioaccumulation · Bioavailable fraction · Biomonitor organism · Filter feeders · Gulf of California

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Introduction

There are numerous coastal lagoons along the Gulf of California. From the Colorado River in Sonora to San Blas in Nayarit state, there are approximately 35 lagoon systems (Lankford 1977). An important feature of coastal lagoons is a great variety of habitats they support, including mangrove forest, salt-marshes, swamps, brackish, and seawater systems; all of these habitats have a high biological diversity and rich and complex food chains (Flores-Verdugo 1990). These ecosystems constitute important fishery and nursery grounds and some human settlements are within or near them. Untreated or partially treated sewage and agricultural and aquaculture effluents that are discharged in these ecosystems are an important contamination issue (Páez-Osuna et al. 2002). The Tobari lagoon (TL) is an area that receives agricultural and aquacultural effluents, and, occasionally, rain runoffs and untreated municipal sewage. All of these effluents may contain toxic substances, such as heavy metals. In a previous work in the TL, García-Hernández (2004) found elevated levels of cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), and zinc (Zn) in sediment and biota.

Biomonitors are species that accumulate bioavailable chemical forms of contaminants (Phillips and Rainbow 1994). Individual biomonitor species respond differently to various sources of bioavailable metals. However, to obtain a complete description of the total metals bioavailability in coastal ecosystems, it is necessary to use a suite of biomonitor species that can reflect the metal bioavailability of all available sources (Phillips and Rainbow 1994; Luoma and Rainbow 2005). In the present study, sediment samples and six different species of filter feeders (the oysters *Crassostrea corteziensis* and *Crassostrea gigas*, the clams *Chione gnidia*, *Anadara tuberculosa* and *Chione fluctifraga*, and the barnacle *Fistulobalanus dentivarians*) were collected from the TL. The aim was to determine the seasonal and spatial accumulation of Cd, Cu, Hg, Pb, and Zn in filter feeders organisms and evaluate its potential as biomonitors of metals contamination.

Materials and methods

Study area

The TL is located in the Sonora state Mexico, along the central-east coast of the Gulf of California (Fig. 1). TL has a surface area of 64.2 km^2, an average depth of 1.4 m, and its axis is parallel to the coast. It is a type IIA coastal lagoon, with differential terrigenous sedimentation and two mouths (Lankford 1977). The predominant climatic condition is a semi-arid warm-dry, with an average annual precipitation of 259 mm. The TL receives freshwater inputs from land runoffs, some streams, and is subject to regular effluents discharges from ten drainage basins in the Yaqui Valley agricultural area. The TL also receives effluents from nearby shrimp farm (1,190 ha) and untreated municipal sewage from Obregón and surrounding towns. The TL supports a variety of organisms including mangroves, macroalgaes, mollusks, fishes and birds. The hydrodynamics of TL was affected 35 years ago, by an artificially constructed inner-stone, increased its susceptibility to contaminant accumulation (García-Hernández 2004).

Sampling and data processing

Sediment and biological samples were collected from 12 stations in the lagoon system during June and November of 2009. These dates correspond to the rainy–hot and dry–cold seasons, respectively. Triplicate surface sediment samples (0–2.5 cm from the top of sedimentary column) were taken at each station using a Van Veen dredge. Sediment samples were dried at 55°C for 24 h and organic carbon (Loring and Rantala 1992) and carbonates (Rauret et al. 1988) content were determined. For bulk metal analysis, dried sediments were digested in a MARS-X microwave system (CEM Co) using a previously reported method (Jara-Marini et al. 2009). Sediment samples were subjected to the Huerta-Díaz and Morse (1990) chemical sequential extraction scheme, but only the levels of bioavailable fractions metals (reactive plus pyrite) are reported. Briefly, 20 mL of 1 M HCl was added to 2.5 g of dry sediment and agitated at room temperature for 16 h (reactive fraction). The residue was treated at room temperature with two successive additions of 10 M HF for 1 and 10 h, respectively (silicates fraction). Finally, 10 mL of concentrated HNO_3 was added to the resulting residue and agitated for 2 h at room temperature (pyrite fraction). After each sequential step, samples were centrifuged at 3,000 rpm for 15 min. The supernatant was decanted and stored in polyethylene bottles for metal analysis. The bulk, reactive, and pyrite extracts were analyzed for Cd, Cu, Pb, and Zn using a flame atomic absorption spectrophotometer (VARIAN, SpectrAA-240-FS). Mercury was analyzed using a cold-vapor system (VARIAN, VGA-77). Marine sediment certified reference material (PACS-2 from the National Research Council Canada) and blanks were analyzed for quality

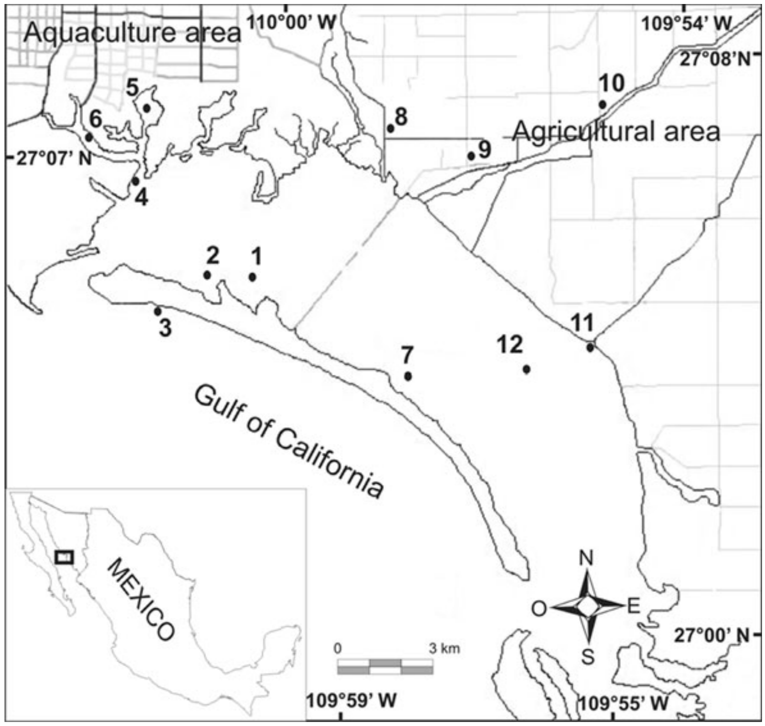


Fig. 1 Study area and sampling stations in the "El Tobari" Lagoon system (central-east Gulf of California)

control purposes. The limits of detection for bulk metal analyses were (in µg/g, except Hg in ng/g): Cd=0.063, Cu=0.057, Hg=0.119, Pb=0.360, and Zn=0.073. For the reactive metal fraction analysis, the limits of detection were as follows (in µg/g, except Hg in ng/g): Cd=0.029, Cu=0.017, Hg=0.022, Pb=0.280, and Zn=0.029. The limits of detection for the pyrite fraction metal analyses were as follows (in µg/g, except Hg in ng/g): Cd=0.018, Cu=0.025, Hg=0.018, Pb=0.170, and Zn=0.020.

For the biological samples and accordance with abundance, 12–15 individuals of similar size of each filter feeder species were collected from stations specified in Table 3. The organisms sampled were two species of oyster, *C. corteziensis* (3.1–5.4 cm shell length (SL)) and *C. gigas* (7.2–10.6 cm SL); three species of clams, *C. gnidia* (5.2–6.8 cm SL), *A. tuberculosa* (3.0–4.2 cm SL), and *C. fluctifraga* (3.1–4.8 cm SL); and the barnacle, *F. dentivarians* (0.7–1.1 cm SL). These organisms were separated, cleaned and the total edible tissue was transferred to pre-cleaned (2 M HNO_3 for 3 days) polyethylene containers. The samples were then stored at −20°C, freeze-dried (−48°C and 32×10^{-3} mbar) for 48 h and manually homogenized with an agate mortar for 10 min. They were then digested in concentrated HNO_3 using the MARS-X microwave system (Jara-Marini et al. 2009). Lead levels were determined with graphite-furnace-atomic absorption spectrophotometer (VARIAN, GTA-120). Cadmium, Cu and Zn were measured with a flame-furnace-atomic absorption spectrophotometer and Hg was analyzed with a cold-vapor-atomic absorption spectrophotometer. Data are reported on dry weight basis. Certified reference materials (Dogfish muscle, DORM-2 National Research Council, Canada; oyster tissue 1566-b, National Institute of Standards and Technology, USA) and blanks were analyzed for quality control purposes. The coefficients of variation for the analyzed materials were ≤12.5 %, with a relative error of 1.41 to 13.6 %. The limits of detection were as follows (in µg/g, except Hg in ng/g): Cd=0.126, Cu=0.163, Hg=0.260, Pb=0.159, and Zn=0.084.

Normality and variance of homogeneity tests for total physical and chemical properties, bioavailable metal concentrations in the sediments, and metal concentrations in the organisms were performed using Kolmogorov-Smirnov D and Bartlett tests (Zar 1999). The mean concentrations were compared using the Kruskal–Wallis and Student–Newman–Keuls tests (Glantz 2002). Correlations between metal concentrations in the sediments and organisms were evaluated using Spearman's correlations. All statistical analyses were performed with the NCSS software (version 6.0; NCSS 2007).

Results and discussion

Physical and chemical composition of sediments

The average physical and chemical parameters measured in surface sediments from TL sites are presented in Tables 1 and 2. The organic matter ranged from 0.57 (±0.08) to 1.76 % (±0.01) during the hot–rainy season and from 0.36 (±0.06) to 1.40 % (±0.09) during the cold–dry season. There was not a seasonal pattern in the organic matter content and sites 2, 5, and 11 showed the highest ($p<0.05$) levels of during both season. There is a spatial pattern in organic matter content for sites close to mangroves and areas of shrimp aquaculture (2, 4, 5, and 6) and sites receive agricultural and semi-urban effluents (11 and 12). However, the percentages of organic matter found in this study were lower than expected considering the levels of anthropogenic activities in the TL. The values were similar to the Altata-Ensenada del Pabellón Lagoon, an agricultural and municipal discharge-impacted ecosystem (range, 0.8 to 2.4 %; Green-Ruiz and Páez-Osuna 2003) but lower than the Urías Lagoon, a small urbanized ecosystem, affected by fish and shrimp processing industries, fishing and merchant fleets, and untreated domestic effluents (range, 0.6 to 11.4 %; Soto-Jiménez and Páez-Osuna 2001). Respect to heavy metals, significant correlations between organic matter content and bioavailable levels of Cd ($r=0.79$), Cu ($r=0.60$), and Pb ($r=0.80$) were found, indicative that act as a metal carrier in relation with its ability of complexation and adsorption. These metals have a high affinity for humic substances present in organic matter (Brown et al. 1999; Clemente and Bernal 2006).

The carbonates content was significantly higher ($p<0.05$) during hot rainy season in sites 4 and 6, whereas during the cold–dry season in sites 5 and 12. Moreover, there was a seasonal pattern in carbonate contents because cold–dry season showed significant higher values. Sites 4, 5, and 6 include a mangrove area, where shell organisms are abundant, and reflected the high carbonates content in sediments. The highest carbonates contents during cold–dry season may be related to sediment-suspension event derived of storm occurred in October 2009. Respect to heavy metals, no significant correlations ($p>0.05$) between carbonates and total and bioavailable metals concentrations were determined, indicative of its minimal role in the mobilization the studied metals. Similar results were reported in estuarine ecosystems (e.g., Green-Ruiz and Páez-Osuna 2003; Soto-Jiménez and Páez-Osuna 2001).

The total and bioavailable metal contents are also presented in Tables 1 and 2. There are spatial and seasonal variations in total and bioavailable Cd concentrations. In the hot–rainy season, the highest significant ($p<0.05$) total concentrations of Cd were detected in sites 7 and 8 but in sites 2, 3, 4, 5, and 6 for the bioavailable fraction; during the cold–dry season, the highest total concentrations of Cd were detected in sites 11 and 12, and in sites 4, 5, and 12 for the bioavailable fraction. The spatial and seasonal variations in Cd concentrations reflected the percentages of bioavailable metal respect to total metal (ranges, 7.3 % in site 7 to 18.2 % in site 6 during the hot–rainy season, and 6.1 % in site 6 to 18.4 % in site 1 during the cold–dry season). Other sites showed similar Cd bioavailability during both seasons, but the percentage in sites 6 and 11 decreased significantly in the cold–dry season respect to the hot–rainy season (range, 18.4 to 6.13 % and from 10.2 to 5.27 %, respectively). Anthropogenic sources of Cd include urban, suburban and agricultural effluents (Segovia-Zavala et al. 2004). The TL receives discharges from ten Yaqui Valley drains (García-Hernández 2004) that are associated with an extensive (~450,000 ha) agricultural area (SAGARPA 2010). However, other sources of Cd exist (Sañudo-Wilhelmy and Flegal 1991; Van Geen and Husby 1996; Segovia-Zavala et al. 1998). Dissolved Cd enrichment in coastal waters off the border area and Southern California have been attributed to water advection; approximately 95–97 % of the Cd influx is estimated to come from upwelling processes (Sañudo-Wilhelmy and Flegal 1991; Segovia-Zavala et al. 1998).

Sites 2, 5, 8, 10, and 11 showed the highest ($p<0.05$) total Cu concentrations during the hot–rainy season while sites 2, 5, 7, and 9 showed the highest ($p<0.05$) total Cu concentrations during the cold–dry season (Tables 1 and 2). However, the highest total Cu concentrations were detected during the cold–dry season, ranging between 1.5 to 6.7 times that of values obtain from the hot–rainy season samples. In contrast, the highest Cu bioavailable concentrations were detected during the hot–rainy season, ranging between 1.1 and 3.9 times that observed in cold–dry season. Sites 1, 2, 4, 5, and 8 during the hot–rainy season and sites 1, 5, and 12 during the cold–dry season showed the highest bioavailable Cu concentrations. Among these sites, only site 8 is located in an area that is influenced by agricultural

Table 1 Physical and chemical composition (mean±standard deviation in micrograms per gram of dry weight) of superficial sediments during the hot–rainy season

Station	Organic matter (%)	Carbonates (%)	Total Cd Bioavailable Cd	Total Cu Bioavailable Cu	Total Hg Bioavailable Hg	Total Pb Bioavailable Pb	Total Zn Bioavailable Zn
1	$0.89^{a,b}\pm0.08$	$2.84^{a}\pm0.14$	$2.43^{c}\pm0.06$	$12.06^{a}\pm0.66$	$0.89^{b}\pm0.07$	$45.78^{a,b}\pm0.57$	$50.57^{b}\pm2.31$
			$0.31^{c}\pm0.03$	$6.06^{b}\pm0.22$	$0.16^{b}\pm0.01$	$0.51^{a}\pm0.07$	$9.02^{b,c}\pm0.48$
2	$1.34^{b}\pm0.02$	$3.67^{a,b}\pm0.15$	$2.69^{c,d}\pm0.08$	$15.94^{b}\pm0.09$	$0.91^{b}\pm0.01$	$78.30^{c}\pm2.54$	$116.91^{d,e}\pm3.39$
			$0.44^{e}\pm0.03$	$7.45^{c}\pm0.10$	$0.15^{b}\pm0.01$	$0.85^{c}\pm0.07$	$26.17^{d}\pm4.07$
3	$0.79^{a,b}\pm0.02$	$2.74^{a}\pm0.01$	$2.16^{a}\pm0.21$	$12.12^{a}\pm0.58$	$1.02^{b,c}\pm0.30$	$42.74^{a}\pm0.21$	$47.04^{a,b}\pm2.00$
			$0.38^{d}\pm0.04$	$5.88^{b}\pm0.17$	$0.17^{b}\pm0.02$	$0.76^{a}\pm0.17$	$10.14^{b,c}\pm0.25$
4	$1.11^{b}\pm0.06$	$4.45^{b}\pm0.41$	$2.27^{c}\pm0.10$	$13.30^{a,b}\pm0.46$	$0.87^{b}\pm0.05$	$54.76^{b}\pm0.20$	$57.48^{b}\pm1.74$
			$0.37^{d}\pm0.01$	$6.00^{b}\pm0.46$	$0.09^{a}\pm0.01$	$0.71^{a}\pm0.01$	$6.64^{a,b}\pm0.21$
5	$1.25^{c}\pm0.02$	$4.08^{a,b}\pm0.14$	$2.54^{c}\pm0.03$	$19.18^{c}\pm0.22$	$0.62^{a}\pm0.01$	$71.37^{c}\pm4.59$	$104.40^{d}\pm3.43$
			$0.43^{a}\pm0.01$	$6.48^{b,c}\pm0.13$	$0.10^{a}\pm0.01$	$0.94^{d,e}\pm0.14$	$20.97^{c,d}\pm1.04$
6	$1.14^{b}\pm0.03$	$14.23^{c}\pm1.45$	$2.00^{b}\pm0.02$	$11.42^{a}\pm0.28$	$0.80^{b}\pm0.01$	$54.06^{b}\pm1.47$	$75.59^{c}\pm3.51$
			$0.37^{d}\pm0.01$	$4.65^{a}\pm0.03$	$0.09^{a}\pm0.02$	$0.97^{d,e}\pm0.06$	$17.57^{c,d}\pm1.81$
7	$0.90^{a,b}\pm0.10$	$4.37^{a}\pm0.14$	$3.33^{e}\pm0.04$	$13.10^{a,b}\pm0.01$	$1.10^{c}\pm0.01$	$43.15^{a}\pm1.86$	$52.45^{b}\pm1.90$
			$0.24^{a,b}\pm0.03$	$5.24^{a,b}\pm0.04$	$0.15^{b}\pm0.02$	$1.14^{e}\pm0.03$	$13.58^{c}\pm0.56$
8	$0.71^{a,b}\pm0.04$	$3.23^{a,b}\pm0.01$	$3.00^{d}\pm0.16$	$18.74^{c}\pm0.07$	$1.34^{d}\pm0.01$	$75.37^{c}\pm0.33$	$124.07^{e}\pm4.13$
			$0.27^{b,c}\pm0.01$	$7.07^{c}\pm0.08$	$0.07^{a}\pm0.01$	$0.84^{c,d}\pm0.01$	$31.48^{e}\pm4.66$
9	$0.57^{a}\pm0.08$	$2.72^{a,b}\pm0.14$	$1.64^{a}\pm0.08$	$12.76^{a}\pm0.57$	$0.92^{b}\pm0.01$	$41.25^{a}\pm5.86$	$38.93^{a}\pm3.75$
			$0.20^{a}\pm0.01$	$4.56^{a}\pm0.32$	$0.10^{a}\pm0.01$	$0.85^{c,d}\pm0.02$	$4.42^{a}\pm0.63$
10	$0.58^{a}\pm0.08$	$2.41^{a,b}\pm0.01$	$1.59^{a}\pm0.02$	$14.78^{b}\pm0.48$	$0.98^{b,c}\pm0.01$	$40.80^{a}\pm3.03$	$42.77^{a,b}\pm0.96$
			$0.24^{a,b}\pm0.01$	$5.32^{a,b}\pm0.15$	$0.11^{a}\pm0.02$	$0.77^{b,c}\pm0.01$	$5.17^{a,b}\pm0.42$
11	$1.76^{b}\pm0.01$	$2.05^{a}\pm0.05$	$1.93^{a,b}\pm0.02$	$14.28^{a,b}\pm0.12$	$0.92^{b}\pm0.04$	$51.43^{b}\pm0.52$	$50.20^{b}\pm0.30$
			$0.20^{a}\pm0.01$	$4.88^{a}\pm0.17$	$0.08^{a}\pm0.01$	$0.58^{a,b}\pm0.01$	$9.39^{b,c}\pm1.06$
12	$1.14^{b}\pm0.02$	$1.87^{a}\pm0.06$	$1.79^{a,b}\pm0.01$	$13.84^{a,b}\pm0.08$	$0.83^{b}\pm0.01$	$46.70^{a,b}\pm1.08$	$55.41^{b}\pm0.73$
			$0.24^{a,b}\pm0.01$	$4.76^{a}\pm0.41$	$0.09^{a}\pm0.01$	$0.75^{b,c}\pm0.01$	$11.98^{c}\pm1.79$

n=3 at each station; different letters by column denote significant differences (p<0.05)

Table 2 Physical and chemical composition (mean±standard deviation in micrograms per gram of dry weight) of superficial sediments during the cold–dry season

Station	Organic matter (%)	Carbonates (%)	Total Cd Bioavailable Cd	Total Cu Bioavailable Cu	Total Hg Bioavailable Hg	Total Pb Bioavailable Pb	Total Zn Bioavailable Zn
1	$0.36^{a}\pm0.06$	$6.29^{b,c}\pm0.30$	$2.37^{a,b}\pm0.13$	$30.52^{b}\pm2.96$	$0.47^{c}\pm0.11$	$53.58^{a,b}\pm2.93$	$89.10^{d}\pm5.06$
			$0.43^{c,d}\pm0.12$	$3.02^{b}\pm0.13$	$0.15^{a}\pm0.03$	$0.74^{b,c}\pm0.14$	$13.14^{b}\pm1.95$
2	$1.06^{b}\pm0.04$	$6.65^{b,c}\pm0.01$	$3.36^{c,d}\pm0.32$	$81.81^{e}\pm2.80$	$0.66^{d}\pm0.04$	$51.26^{a,b}\pm3.06$	$78.99^{c}\pm1.06$
			$0.33^{b}\pm0.03$	$1.93^{a}\pm0.12$	$0.10^{a}\pm0.02$	$0.60^{a,b}\pm0.08$	$11.45^{b}\pm1.47$
3	$0.70^{a,b}\pm0.06$	$5.62^{b,c}\pm0.01$	$2.71^{b}\pm0.23$	$36.14^{b,c}\pm0.82$	$0.45^{c}\pm0.12$	$56.38^{a}\pm4.69$	$103.65^{f}\pm4.53$
			$0.36^{b,c}\pm0.02$	$2.38^{a,b}\pm0.12$	$0.11^{a}\pm0.02$	$0.70^{b}\pm0.16$	$14.81^{b}\pm1.03$
4	$1.02^{a,b}\pm0.06$	$3.67^{a,b}\pm0.15$	$2.96^{b}\pm0.09$	$27.30^{b}\pm1.25$	$0.23^{a}\pm0.02$	$54.47^{a,b}\pm0.89$	$53.52^{b}\pm1.72$
			$0.48^{d,e}\pm0.03$	$2.24^{a}\pm0.13$	$0.06^{a}\pm0.01$	$0.57^{a,b}\pm0.16$	$2.85^{a}\pm0.41$
5	$1.40^{b}\pm0.09$	$10.63^{d}\pm0.15$	$3.81^{d,e}\pm0.16$	$65.59^{d}\pm4.48$	$0.37^{b,c}\pm0.03$	$56.40^{a,b}\pm2.72$	$139.75^{g}\pm9.33$
			$0.63^{e}\pm0.05$	$4.34^{c}\pm0.14$	$0.15^{a}\pm0.02$	$1.16^{d}\pm0.17$	$21.29^{c}\pm4.16$
6	$0.66^{a,b}\pm0.08$	$7.87^{c,d}\pm0.05$	$3.53^{c,d}\pm0.16$	$13.62^{a}\pm1.27$	$0.32^{b}\pm0.02$	$50.79^{b}\pm4.08$	$53.64^{b}\pm1.27$
			$0.22^{a}\pm0.03$	$2.73^{a,b}\pm0.17$	$0.14^{a}\pm0.03$	$0.46^{a}\pm0.15$	$8.29^{a,b}\pm1.03$
7	$1.25^{a,b}\pm0.03$	$7.97^{c,d}\pm0.15$	$3.58^{c,d}\pm0.28$	$66.48^{d}\pm11.45$	$0.48^{c}\pm0.03$	$67.92^{a,b}\pm4.77$	$101.21^{e,f}\pm9.32$
			$0.22^{a}\pm0.04$	$2.53^{a,b}\pm0.15$	$0.10^{a}\pm0.02$	$0.53^{a}\pm0.14$	$17.15^{b,c}\pm1.40$
8	$0.74^{a}\pm0.08$	$6.63^{b,c}\pm1.45$	$3.21^{c}\pm0.08$	$31.08^{b}\pm1.53$	$0.30^{b}\pm0.03$	$71.33^{a,b}\pm1.62$	$140.44^{g}\pm1.96$
			$0.42^{c,d}\pm0.07$	$2.21^{a}\pm0.13$	$0.07^{a}\pm0.01$	$0.71^{b}\pm0.11$	$21.34^{c}\pm1.56$
9	$0.73^{a}\pm0.06$	$2.32^{a}\pm0.30$	$2.14^{a}\pm0.11$	$64.55^{d}\pm2.16$	$0.32^{a}\pm0.03$	$55.87^{a}\pm1.38$	$88.96^{c,d}\pm1.74$
			$0.33^{b}\pm0.03$	$2.63^{a,b}\pm0.11$	$0.11^{a}\pm0.01$	$0.75^{b,c}\pm0.22$	$3.18^{a}\pm0.38$
10	$0.83^{a}\pm0.08$	$2.33^{a}\pm0.04$	$3.21^{c}\pm0.21$	$40.08^{c}\pm1.88$	$0.52^{c}\pm0.03$	$47.07^{a}\pm2.66$	$34.49^{a}\pm1.09$
			$0.42^{c,d}\pm0.07$	$2.40^{a}\pm0.18$	$0.08^{a}\pm0.02$	$0.82^{c}\pm0.13$	$2.56^{a}\pm0.35$
11	$1.33^{b}\pm0.10$	$5.20^{b,c}\pm0.08$	$6.53^{f}\pm0.23$	$30.55^{b}\pm1.53$	$0.49^{c}\pm0.04$	$91.81^{c}\pm4.22$	$90.20^{d,e}\pm1.40$
			$0.34^{b}\pm0.03$	$2.67^{a,b}\pm0.10$	$0.07^{a}\pm0.02$	$0.54^{a}\pm0.14$	$8.78^{a,b}\pm0.38$
12	$0.79^{a}\pm0.02$	$12.95^{d}\pm0.11$	$4.07^{e}\pm0.12$	$28.39^{b}\pm2.45$	$0.49^{c}\pm0.04$	$56.79^{a}\pm0.48$	$144.88^{g}\pm1.97$
			$0.54^{e}\pm0.04$	$3.31^{b}\pm0.11$	$0.11^{a}\pm0.02$	$0.53^{a}\pm0.10$	$36.42^{d}\pm1.05$

n=3 at each station; different letters by column denote significant differences ($p<0.05$)

discharges. Seasonal variation in the total Cu concentrations could be associated with sediment re-suspension events; the minimum metal bioavailability ranged from 40.7 % during the hot–rainy season to 2.4 % during the cold–dry season. The levels of bioavailable metals are linked to fine mineral (<63-µm fractions) (Wang et al. 1997), while immobile metal are associated with coarse minerals that have been re-suspended from deeper sediment layers (Brown et al. 1999).

Seasonal variations in the total Hg concentrations were detected, with the highest ($p<0.05$) values occurring during the hot–rainy season; these values were 2.0 to 5.8 times higher than those observed during the cold–dry season (Tables 1 and 2). However, there was not a spatial pattern in the total Hg concentrations; sites 3, 7, 8, and 10 showed the highest total concentrations during the hot–rainy season while sites 1, 2, 3, 7, 10, 11, and 12 showed the highest concentrations during the cold–dry season. No significant seasonal variations were detected in the levels of bioavailable Hg (range, 0.07 to 0.16 µg/g during the hot–rainy season and 0.06 to 0.15 µg/g during the cold–dry season). However, the percentage of bioavailable Hg varied from 5.2 to 18.0 % during the hot–rainy season and from 14.3 to 43.8 % during the cold–dry season. When compared with Cu, there was a decrease in total Hg concentrations during the cold–dry season; this finding suggests that these two metals behave differently. It is possible that these metals released from different sources, such as atmospheric deposition for Hg (Fitzgerald and Lamborg 2005). This hypothesis is supported by the negative correlation between the total concentration of Hg and Cu ($r=-0.52$, $p<0.05$). Indeed, Komárek and Zeman (2004) found that both metals are released under different conditions: Cu under strongly acidic reducing conditions and Hg under acidic oxidizing conditions.

The total concentrations of Pb were similar in samples obtained from both seasons, but the sites with the highest ($p<0.05$) levels were different: sites 2, 5, and 8 were highest during the hot–rainy season and sites 7, 8, and 11 were highest during the cold–dry season (Tables 1 and 2). Site 11 showed an anomalous level of Pb during the cold–dry season, exhibiting 1.8 fold elevation over concentration measured during the hot–rainy season. Otherwise, the bioavailable Pb concentrations were similar in both seasons; they varied from 0.51 to 1.14 µg/g during the hot–rainy season and 0.46 to 1.16 µg/g during the cold–dry season. The highest Pb levels were observed in sites 5, 6, and 7 during the hot–rainy season, and sites 5 and 10 during the cold–dry season. Lead is frequently positively correlated with Cu, suggesting these metals have similar sources and/or geochemical characteristics (Brown et al. 1999; Luoma and Rainbow 2005; Yuan et al. 2011). In this study, we found a significant positive correlation between Pb and Cu ($r=0.41$) within the bioavailable metals fractions, but this relationship was not significant ($r=0.14$) within the total metal concentrations.

The total concentration of Zn ranged from 38.9 (site 9) to 124.1 µg/g (site 8) during the hot–rainy season, and 34.5 (site 10) to 144.9 µg/g (site 12) during the cold–dry season (Tables 1 and 2). The bioavailable fraction in the sediments ranged from 4.4 (site 9) to 31.5 µg/g (site 8) during the hot–rainy season, and 2.6 (site 10) to 36.4 µg/g (site 12) during the cold–dry season. Sites 2, 5, and 8 during hot–rainy season and sites 3, 5, 7, 8, and 12 during cold–dry season showed the highest ($p<0.05$) total and bioavailable Zn concentrations. There was not a seasonal pattern in the total Zn concentrations, but there was a spatial pattern; most of the sites with the highest total and bioavailable concentrations are located near the TL coast line. Significant correlations were found between Zn and Cu in bioavailable and total concentrations ($r=0.38$ in both cases), indicating common source and/or similar geochemical pathways (Brown et al. 1999; Luoma and Rainbow 2005; Yuan et al. 2011). Possible sources of Zn and Cu are discharges from agricultural areas. Both metals are present in fertilizers and fungicides that are used in agriculture (Cao and Hu 2000; Green-Ruíz and Páez-Osuna 2001).

Heavy metals in filter feeders

The average concentrations of heavy metals in different filter feeder organisms are presented in Table 3. There is not a consistent seasonal pattern in the Cd concentrations of filter feeders. Some species showed elevated Cd concentrations during the cold–dry season. This elevation was not significant ($p>0.05$) for the two oyster species in sites 4, 5, and 6, and *C. fluctifraga* in site 4, but significant ($p<0.05$) for *C. gnidia* in sites 7 and 12. Other organisms showed elevated Cd concentrations during the hot–rainy season with respect to the cold–dry season. These elevations were significant for *F. dentivarians* in sites 5 and 6, for *A. tuberculosa* in sites 4 and 6, and for *C. gnidia* in site 4. The Cd concentrations in filter feeders species ranged from 0.28 to

0.90 μg/g. There was not a significant correlation between the Cd levels of different filter feeder species collected at single site in TL. This finding could be due to interspecies differences in Cd accumulation and detoxifying mechanisms. Other studies in filter feeders obtained from the Gulf of California showed that Cd levels were associated with anthropogenic activities. For example, Páez-Osuna et al. (1993) reported a range of 0.70 to 3.8 μg/g in *Chione* sp. clams, and Ruelas-Inzunza and Páez-Osuna (2008) reported means of 7.2 μg/g in *C. corteziensis* and 1.1 μg/g in *Balanus eburneus*. Both studies obtained samples from in the Pabellón-Altata Lagoon, an area that is influenced by agricultural activities. Méndez et al. (2002) found a Cd range of 0.21 to 1.7 μg/g in *C. gnidia* samples from Guaymas, an industrialized harbor area. Méndez et al. (2006) reported a Cd range of 1.5 to 11.1 μg/g for clams collected from a mining impacted area. The concentrations of Cd found in this study for many organisms are according with those found in the bioavailable sediment fraction (Tables 1 and 2) because highest tissue concentrations were related with sites with highest bioavailable Cd concentrations. In this sense, only *A. tuberculosa* showed a significant correlation with Cd in bioavailable fraction (r=0.70); the others filter feeder showed a tendency but was not significant ($0.15 \geq p \geq 0.08$). There are several different sources of Cd in the Gulf of California. Delgadillo-Hinojosa et al. (2001) reported that Cd enrichments in superficial open water masses in the Gulf of California were associated with organic matter production and remineralization. Dynamic Cd levels in lagoon ecosystems may differ from those in open waters. First, primary productivity may be driven by organic matter from anthropogenic discharges, and its transfer can be linked to dominant species in the phytoplankton. Second, sediment resuspension events may produce a rapidly remineralization of metal. Third, filter feeder organisms may acts as a trap, accumulating high levels of metal because they have low excretion rates (Phillips and Rainbow 1994; Luoma and Rainbow 2005). When consumed, filter feeders my also transfer accumulated concentrations of Cd to higher trophic levels.

Cooper concentrations in filter feeder organisms varied from 2.4 to 91.7 μg/g. The order of accumulation was as follows: *C. corteziensis*>*C. gigas*>*F. dentivarians*>*C. gnidia*>*C. fluctifraga*>*A. tuberculosa* (Table 3). The Cu levels in *C. corteziensis* were higher during the cold–dry season than the hot–rainy season, but this difference only was significant (p<0.05) in site 6. Cooper concentrations in *F. dentivarians* and *C. gnidia*, however, decreased significantly (range, 1.6 to 3.6 times) between the hot–rainy to cold–dry seasons. The hot–rainy season also showed the highest bioavailable Cu levels in sediments (Tables 1 and 2). The differences in seasonal accumulation of Cu by the two oyster species in this study may be related their spawning period; lower Cu levels in adult oysters are expected following the spawn event (Berthelin et al. 2000). Frías-Espericueta et al. (1999) studied metal concentrations and gonadal maturation of *C. corteziensis* and found that Cu concentrations ranged 2.0 to 32.2 μg/g, with the highest levels occurring during the post-spawning phase in October and November. Frequently, barnacles accumulate the highest concentrations of Cu when compared with other filter feeders (Páez-Osuna et al. 1993; Phillips and Rainbow 1994; Luoma and Rainbow 2005; Ruelas-Inzunza and Páez-Osuna 2008). Figure 2 shows the variations in the concentrations of Cu in three clam species collected in same sites from the TL. There was a negative significant correlation (y=−2.09x+22.6; r=0.46; n=16) between the levels of Cu in the soft tissues of *C. fluctifraga* (x) and *C. gnidia*. This finding implies that the body burden of Cu in one organism varies in a manner that is inversely proportional to the other. However, a positive significant correlation (y=4.60x−5.26; r=0.67; n=16) between *A. tuberculosa* (x) and *C. gnidia* (y) was found. Moreover, significant correlations (p<0.05) between biovailable Cu fraction in sediments and concentrations of Cu in filter feeder were determined: r=0.76 for *C. corteziensis*, r=0.53 for *C. gigas*, r=0.82 for *F. dentivarians*, r=0.71 for *A. tuberculosa*, r=0.64 for *C. fluctifraga*, and r=0.85 for *C. gnidia*. This suggests similar ways of accumulation and/or ingestion for Cu in the studied organisms. Wang (2002) discussed data of the accumulation of metals in filter feeders from different studies and according to simple kinetic model; the higher Cu concentrations found in oysters compared with other species are explained by higher assimilation efficiencies, the higher influx rate from the dissolved phase and the lower efflux rate. Many studies of filter feeder in the Gulf of California have shown a wide Cu concentration range. In the Urías Lagoon the oyster *C. corteziensis*, showed higher Cu accumulation (approximately 13.6 times) than the barnacle, *F. dentivarians*; both were collected in the same site (Ruelas-Inzunza and Páez-Osuna 2000). In Guaymas Bay, a range of 8.9–23.0 μg/g was found in the clam, *C. gnidia*, with the highest levels associated

Table 3 Metal concentrations (mean±standard deviation in micrograms per dry weight) in filter-feeding organisms

Organism	Station	Cd hot–rainy Cd cold–dry	Cu hot–rainy Cu cold–dry	Hg hot–rainy Hg cold–dry	Pb hot–rainy Pb cold–dry	Zn hot–rainy Zn cold–dry
Crassostrea corteziensis	4	$0.29^{a}\pm0.02$	$68.18^{f}\pm1.70$	$0.49^{c}\pm0.02$	$3.43^{b}\pm0.32$	$86.20^{b}\pm4.04$
		$0.55^{a,b}\pm0.12$	$80.67^{f}\pm4.63$	$0.38^{b}\pm0.07$	$2.74^{b}\pm0.24$	$684.2^{g}\pm65.84$
	5	$0.32^{a}\pm0.05$	$66.09^{f}\pm1.70$	$0.45^{c}\pm0.02$	$3.29^{b}\pm0.23$	$81.85^{b}\pm5.29$
		$0.53^{a,b}\pm0.15$	$77.15^{f}\pm7.66$	$0.35^{b}\pm0.05$	$2.57^{b}\pm0.32$	$616.9^{g}\pm45.80$
	6	$0.33^{a}\pm0.02$	$71.71^{f}\pm0.82$	$0.53^{c}\pm0.03$	$4.12^{d,e}\pm0.04$	$86.90^{b}\pm1.86$
		$0.53^{a,b}\pm0.06$	$91.65^{g}\pm5.11$	$0.41^{c}\pm0.05$	$3.04^{b}\pm0.73$	$676.2^{g}\pm50.17$
Crassostrea gigas	4	$0.27^{a}\pm0.06$	$39.16^{e}\pm3.61$	$0.49^{c}\pm0.04$	$2.45^{b}\pm0.74$	$214.2^{e}\pm23.37$
		$0.49^{a,b}\pm0.17$	$34.18^{d}\pm5.40$	$0.27^{a,b}\pm0.03$	$3.08^{b,c}\pm0.70$	$1{,}702.5^{h}\pm174.4$
	5	$0.29^{a}\pm0.06$	$42.69^{e}\pm5.22$	$0.44^{b}\pm0.06$	$2.28^{b}\pm0.27$	$237.56^{b}\pm26.57$
		$0.45^{a,b}\pm0.13$	$32.72^{d}\pm3.74$	$0.28^{a,b}\pm0.03$	$1.84^{a}\pm0.72$	$1{,}628.5^{h}\pm150.4$
	6	$0.28^{a}\pm0.05$	$44.40^{e}\pm5.47$	$0.60^{c}\pm0.17$	$2.54^{b}\pm0.24$	$229.29^{e}\pm10.00$
		$0.53^{a,b}\pm0.05$	$33.17^{d}\pm3.08$	$0.33^{b,c}\pm0.04$	$1.42^{b}\pm0.04$	$1{,}554.8^{h}\pm24.16$
Fistulobalanus dentivarians	4	$0.85^{c}\pm0.16$	$26.63^{d}\pm4.03$	$0.59^{c,d}\pm0.02$	$4.10^{d,e}\pm0.49$	$163.6^{c,d}\pm3.73$
		$0.80^{c}\pm0.02$	$10.35^{b}\pm1.51$	$0.29^{b}\pm0.05$	$1.48^{a}\pm0.34$	$236.9^{e}\pm16.91$
	5	$0.82^{c}\pm0.04$	$27.12^{d}\pm0.46$	$0.68^{d}\pm0.01$	$4.24^{d,e}\pm0.38$	$163.6^{c}\pm1.87$
		$0.50^{a,b}\pm0.16$	$14.31^{c}\pm1.82$	$0.38^{b}\pm0.03$	$1.56^{a}\pm0.48$	$487.9^{f}\pm73.0$
	6	$0.90^{c}\pm0.05$	$26.34^{d}\pm1.26$	$0.58^{c}\pm0.02$	$4.95^{e}\pm0.09$	$155.1^{c,d}\pm2.22$
		$0.48^{a,b}\pm0.05$	$16.93^{c}\pm2.17$	$0.45^{b}\pm0.03$	$1.73^{a}\pm0.40$	$1{,}133.4^{h}\pm355.4$
Anadara tuberculosa	2	$0.62^{b}\pm0.03$	$4.59^{a}\pm0.20$	$0.20^{a}\pm0.06$	$4.14^{d,e}\pm0.42$	$55.72^{a,b}\pm2.58$
		$0.68^{b,c}\pm0.20$	$3.32^{a}\pm0.30$	$0.14^{a}\pm0.09$	$2.60^{b}\pm0.17$	$46.23^{a}\pm1.01$
	4	$0.65^{b}\pm0.09$	$4.33^{a}\pm0.38$	$0.24^{a,b}\pm0.03$	$4.18^{d,e}\pm0.14$	$61.26^{a,b}\pm1.38$
		$0.36^{a}\pm0.06$	$3.44^{a}\pm0.16$	$0.22^{a,b}\pm0.07$	$3.75^{c,d}\pm0.21$	$39.27^{a}\pm0.77$
	5	$0.44^{a}\pm0.12$	$3.99^{a}\pm0.25$	$0.24^{a,b}\pm0.07$	$3.94^{c,d}\pm0.29$	$55.91^{a,b}\pm1.87$
		$0.39^{a,c}\pm0.15$	$3.10^{a,c}\pm0.41$	$0.18^{a}\pm0.05$	$3.79^{c,d}\pm0.15$	$37.24^{a}\pm0.90$
	6	$0.84^{c}\pm0.17$	$4.60^{a}\pm0.15$	$0.19^{a}\pm0.04$	$3.99^{c,d}\pm0.22$	$57.44^{a,b}\pm1.10$
		$0.69^{a}\pm0.11$	$2.42^{a}\pm0.24$	$0.23^{a,b}\pm0.05$	$2.38^{a}\pm0.09$	$35.52^{a}\pm1.03$
Chione fluctifraga	4	$0.48^{a,b}\pm0.12$	$3.99^{a}\pm0.13$	$0.24^{a,b}\pm0.05$	$2.58^{b}\pm0.15$	$62.65^{a,b}\pm1.14$
		$0.70^{b,c}\pm0.03$	$4.18^{a}\pm0.21$	$0.27^{a,b}\pm0.04$	$1.39^{a}\pm0.24$	$90.00^{b}\pm3.79$
	5	$0.53^{a,b}\pm0.08$	$4.32^{a}\pm0.29$	$0.23^{a,b}\pm0.08$	$2.43^{a}\pm0.11$	$57.88^{a,b}\pm1.55$
		$0.49^{a,b}\pm0.05$	$6.67^{a,b}\pm0.80$	$0.32^{b,c}\pm0.03$	$2.49^{a}\pm0.34$	$93.12^{b,c}\pm5.00$
	6	$0.5\ 4,^{a,b}\pm0.03$	$4.00^{a}\pm0.12$	$0.26^{a,b}\pm0.01$	$2.72^{b}\pm0.16$	$59.57^{a,b}\pm0.63$
		$0.43^{a}\pm0.07$	$4.42^{a}\pm1.19$	$0.33^{b,c}\pm0.05$	$1.40^{a}\pm0.10$	$90.29^{b}\pm8.92$
	12	$0.61^{b}\pm0.10$	$4.27^{a}\pm0.22$	$0.21^{a}\pm0.09$	$2.76^{b}\pm0.18$	$60.90^{a,b}\pm3.92$
		$0.56^{b}\pm0.06$	$6.30^{a,b}\pm1.12$	$0.39^{b}\pm0.10$	$1.72^{a,b}\pm0.15$	$90.87^{b,c}\pm5.09$
Chione gnidia	1	$0.58^{b}\pm0.04$	$14.90^{c}\pm0.73$	$0.77^{e}\pm0.03$	$2.29^{a,b}\pm0.04$	$124.6^{c,d}\pm9.69$
		$0.51^{a,b}\pm0.05$	$9.27^{b,c}\pm0.86$	$0.40^{b}\pm0.02$	$4.70^{d,e}\pm0.19$	$44.27^{a}\pm4.16$
	2	$0.55^{b}\pm0.02$	$14.47^{c}\pm1.62$	$0.75^{e}\pm0.19$	$2.07^{a,b}\pm0.71$	$115.0^{c,d}\pm28.0$
		$0.50^{a,b}\pm0.05$	$5.03^{b}\pm0.90$	$0.43^{b}\pm0.08$	$3.46^{c}\pm0.12$	$36.64^{a}\pm1.70$
	4	$0.55^{b}\pm0.18$	$15.95^{c}\pm0.18$	$0.65^{d}\pm0.09$	$2.85^{b,c}\pm0.09$	$108.9^{c}\pm10.0$
		$0.33^{a}\pm0.05$	$4.41^{a}\pm0.38$	$0.41^{c}\pm0.03$	$3.58^{c}\pm0.18$	$44.67^{a}\pm1.48$
	5	$0.69^{b}\pm0.17$	$19.64^{c}\pm2.51$	$0.57^{c}\pm0.13$	$2.19^{a,b}\pm0.22$	$179.6^{d,e}\pm53.4$
		$0.53^{a,b}\pm0.12$	$8.82^{a,b}\pm0.28$	$0.29^{b}\pm0.03$	$4.57^{d}\pm0.19$	$47.74^{a}\pm1.48$
	6	$0.46^{a}\pm0.05$	$17.67^{c}\pm1.15$	$0.47^{c}\pm0.13$	$2.23^{a,b}\pm0.56$	$117.9^{c,d}\pm3.61$
		$0.58^{b}\pm0.14$	$10.07^{b}\pm0.05$	$0.39^{c}\pm0.01$	$4.58^{d}\pm0.03$	$48.90^{a}\pm0.59$

Table 3 (continued)

Organism	Station	Cd hot–rainy Cd cold–dry	Cu hot–rainy Cu cold–dry	Hg hot–rainy Hg cold–dry	Pb hot–rainy Pb cold–dry	Zn hot–rainy Zn cold–dry
	7	$0.45^{a}\pm0.05$	$14.87^{c}\pm0.30$	$0.32^{b}\pm0.02$	$1.79^{a,b}\pm0.15$	$132.2^{c,d}\pm2.50$
		$0.65^{b}\pm0.23$	$9.17^{b}\pm0.02$	$0.32^{b}\pm0.\ 70$	$4.18^{d}\pm0.26$	$44.73^{a}\pm2.97$
	12	$0.58^{b}\pm0.02$	$17.00^{c}\pm0.17$	$0.44^{c}\pm0.05$	$1.93^{a,b}\pm0.08$	$125.82^{c,d}\pm1.55$
		$0.83^{c}\pm0.11$	$8.49^{a,b}\pm0.02$	$0.39^{c}\pm0.02$	$4.19^{d,e}\pm0.24$	$42.18^{a}\pm1.36$

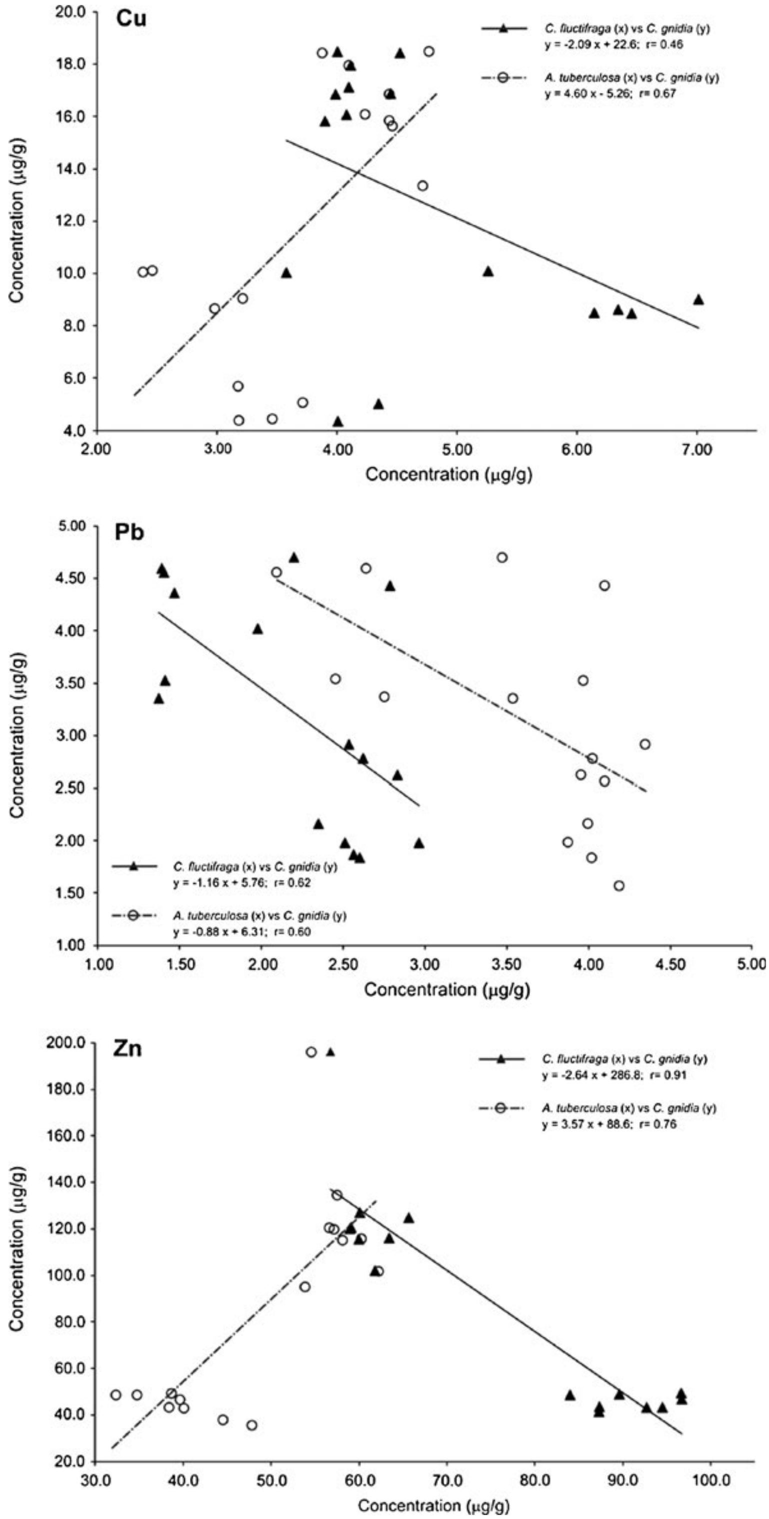
Different letters by column denote significant differences ($p<0.05$)

with industrialized and urbanized areas (Méndez et al. 2002). In an agricultural and shrimp aquaculture impacted area, Frías-Espericueta et al. (2008) found Cu concentrations ranged from 38.9 to 107.5 μg/g in *C. corteziensis*, with slight variations between the rainy and dry seasons. Cadena-Cárdenas et al. (2009) found a wide range of Cu levels (3.9 to 181 μg/g) in three clam species collected from three Gulf of California ecosystems with different anthropogenic activities; the highest values were associated with anomalous Cu concentrations in sediments. Because Cu is used in many fungicides and fertilizers (Cao and Hu 2000; Páez-Osuna et al. 2002), the relatively elevated levels of Cu found here can probably be attributed to agricultural activities from the Yaqui Valley, an area adjacent to TL, that is one of the most productive agricultural regions in México (SAGARPA 2010).

Mercury concentrations in *C. corteziensis*, *C. gigas*, *F. dentivarians*, and *C. gnidia* decreased significantly ($p<0.05$) from the hot–rainy to the cold–dry season (Table 3). Because the lowest percentage of bioavailable Hg occurred during the hot–rainy season (from 5.2 to 18.0 %), filter feeders showed high Hg accumulation efficiency and/or low Hg excretion rates during that season. Accumulation of non-essential metals can be related to physiological mechanisms, physicochemical environments (Wang 2002; Luoma and Rainbow 2005), and/or preexposure to another metals, such as Cd and Cu (Wang and Rainbow 2005). The metal levels in filter feeders ranged from 0.14 to 0.77 μg/g. The order of concentration was as follows: *C. corteziensis*≈*C. gigas*≈*F. dentivarians*>*C. gnidia*>*C. fluctifraga*>*A. tuberculosa*. There was no significant ($p>0.05$) correlations between the Hg levels of different filter feeder species collected from the same sites. However, only *C. fluctifraga* showed a significant correlation ($p<0.05$) with Hg in bioavailable fraction ($r=0.54$); the others filter feeder showed a tendency but was not significant ($0.22\geq p\geq0.14$). This finding may be due to interspecies differences in Hg accumulation and detoxifying mechanisms. The Hg concentrations in the present study were similar to those found in other areas of the Gulf of California. Green-Ruiz et al. (2005) reported Hg levels of 0.063 μg/g in *Chione subrugosa* and 0.23 μg/g in *C. gigas* collected in Guaymas, an industrial and harbor area in the Gulf of California. Jara-Marini et al. (2010) reported a range of Hg from 0.031 to 0.083 μg/g in *C. corteziensis*, collected in the Urias Lagoon an area that receives industrial, municipal, and aquaculture run-offs. The most important anthropogenic sources of Hg in coastal ecosystems are combustion of coal and municipal wastes; however, also Hg can be deposited via atmospheric transport (Fitzgerald and Lamborg 2005). In the TL ecosystem, the primary sources of Hg may be from municipal wastes and agricultural and aquaculture run-offs. However, atmospheric dispersion of Hg may reach long distances and result in deposition in apparently non-impacted ecosystems (Hobson and Welch 1992; Dehn et al. 2006). Importantly, of Hg undergoes biomagnification in marine food webs (Hobson and Welch 1992; Dehn et al. 2006; Jara-Marini et al. 2010).

The Pb concentrations in filter feeders ranged from 1.4 to 4.9 μg/g but did not exhibit a defined order of accumulation among species (Table 3). The seasonal behavior of Pb varied with the organisms: (a) no significant ($p>0.05$) seasonal variations were found for the two oyster species; (b) a significant ($p<0.05$) elevation in concentrations in the hot–rainy season was found with respect to the cold–dry season for *F. dentivarians* in all sites, *A. tuberculosa* in sites 2 and 6, and *C. fluctifraga* in sites 4 and 6; and (c) a significant elevation in concentration during the cold–dry season with respect to the hot–rainy season was found in sites 1, 5, 6, 7, and 12 for *C. gnidia*. This contrasts with the ranges of bioavailable Pb concentrations that were similar across both seasons (Tables 1 and 2). There was a significant

Fig. 2 Relationships between three clam species (*C. gnidia*, *C. fluctifraga*, and *A. tuberculosa*) collected in same sites, for Cu, Pb, and Zn levels in the soft tissues



negative correlation in the Pb levels found in *C. fluctifraga* (x) and *C. gnidia* (y) ($y=-1.16x+5.76$; $r=0.62$, $n=16$) (Fig. 2) and *A. tuberculosa* (x) and *C. gnidia* (y) ($y=-0.88\,x+6.31$; $r=0.60$, $n=16$). Thus, Pb levels in the soft tissue of *C. fluctifraga* and *A. tuberculosa* vary in a manner that is inversely proportional to the metal levels in *C. gnidia*. In addition, significant correlations between bioavailable Pb fraction in sediments and concentrations of Pb in *A. tuberculosa* (r=0.60) and *C. fluctifraga* (r=0.71) were determined. Even among closely related taxa, aquatic invertebrates living in the same habitat may have very different body burden of trace metals; interspecific differences in concentrations suggest that these organisms display a varying capacities for the net accumulation of metals, ranging from weak net accumulators for certain elements to very strong net accumulators for others (Luoma and Rainbow 2005). The range of Pb concentrations reported for areas of Gulf of California with different anthropogenic activities vary widely. For example, Méndez et al. (2002) found a range of 0.51 to 4.0 μg/g of Pb in *C. gnidia* and *Laevicardium elatum* collected from the industrial impacted sites of Guaymas Bay. Páez-Osuna et al. (2002) reported a range of 2.2 to 7.8 μg/g in two species of oysters collected from 14 lagoons in the Gulf of California; the highest levels were associated with proximity to fisheries, shrimp farming, agriculture and urban sewage activities. Frías-Espericueta et al. (2008) reported Pb concentrations in the range of 4.5 to 8.8 μg/g in filter feeders gathered from an agriculturally impacted lagoon. Jara-Marini et al. (2009) reported Pb concentrations ranging from 0.37 to 7.3 μg/g in filter feeders from an urbanized lagoon. Across all studies in Gulf of California, there are common anthropogenic activities that explain Pb levels, i.e., agricultural and urban sewage run-offs. However, high levels of Pb in the region have been associated with the combustion of leaded gasoline in Mexico (Soto-Jiménez et al. 2006), a source that is more clearly attributed to urban and suburban development.

Contrasting seasonal behavior of Zn between filter feeder species was detected (Table 3). A significant (p<0.05) increase between the hot–rainy and cold–dry seasons was observed for the two oyster species and for the barnacle, *F. dentivarians*; this tendency, however, was not significant (p>0.05) for the clam *C. fluctifraga*. The concentrations of Zn decreased from the hot–rainy season to the cold–dry season in a no significant and significant manner for clam *A. tuberculosa* and *C. gnidia*, respectively. The range of Zn in filter feeders was wide (35.5 to 1,634.5 μg/g), with the highest levels occurring in *C. corteziensis*, *C. gigas*, and *F. dentivarians*. There is not a seasonal pattern in total Zn concentrations but a pattern of spatial behavior was clear; in general, the sites with the highest Zn total and bioavailable levels were located near the TL coast. However, no significant correlations between Zn in bioavailable fraction and levels of metal in organism were determined. There was a significant negative correlation between *C. fluctifraga* (x) and *C. gnidia* (y) (y=−2.64x+286.8; r=0.91; n=16) but a positive correlation between *A. tuberculosa* (x) and *C. gnidia* (y) (y=3.57x+88.6; r=0.76; n=16) obtained from the same TL sites. These interspecies differences in the Zn concentrations, suggest that different species display a range of capacities for the net accumulation of this essential metal. Cadena-Cárdenas et al. (2009) reported a Zn range of 49.8 to 91.8 μg/g in clams from areas with and without nearby mining activities, and Méndez et al. (2002) found levels of Zn in clams, *C. gnidia* and *L. elatum*, ranging from 92.4 to 246.0 μg/g in an area affected by harbor and industrial activities. Ruelas-Inzunza and Páez-Osuna (2008) presented Zn concentrations ranging from 1,182 to 1,529 μg/g in *B. eburneus* and *C. corteziensis* from the Altata-Ensenada del Pabellón Lagoon. These high levels were attributed to the nearby agricultural activities; in another study in the same lagoon, Frías-Espericueta et al. (2008) reported a Zn range of 849–1,049 μg/g in *C. corteziensis*. Interestingly, the highest values were detected during the hot–rainy season. This is due that zinc is often used in fertilizers and fungicides (Páez-Osuna et al. 2002). The TL may have seasonal differences in the composition of agricultural run-offs that may explain the observation that differences in Zn accumulation between organisms are related to reproductive cycles (Frías-Espericueta et al. 1999) and/or physiological strategies (Luoma and Rainbow 2005). The high concentrations of Zn in oysters and barnacles may largely be attributable to their much lower efflux rates than other filter feeders species (Wang 2002).

Conclusions

The metal behavior in TL sediments varied. Spatial and seasonal variations in total and bioavailable Cd content were detected. Cooper was different in that high levels were detected during cold–dry season, but the bioavailable fraction was significantly higher in the hot–rainy season. Total Hg concentrations also exhibited a seasonal pattern, with the highest levels detected during the hot–rainy season although the bioavailable fraction was higher during the cold–dry season. With respect to Pb, neither seasonal or spatial variation were detected; the total and bioavailable concentrations were similar in both seasons. Zinc showed spatial and seasonal variations in the total and bioavailable concentrations. Most of sites with the highest Zn levels were located along the TL coastline. In general, sites 2, 5, and 8 showed high concentrations of metals in bioavailable fraction and high accumulation in filter feeder. This evidence the impacts of effluents from agricultural activities in the ecosystem in specific sites due to reduction of currents by the inner-stone. Significant correlations between the bioavailable fraction for Cu and Pb and for Zn and Cu were found. This finding suggests that these metals either have common sources and/or similar geochemical pathways. The total and bioavailable concentrations of the five metals included in this study are not elevated in comparison to other areas around the world.

The order of accumulation of metals differed among filter feeder species. The highest concentrations of the different metals were accumulated as follows: Cd, *F. dentivarians* followed by *A. tuberculosa*; Cu, *C. corteziensis* and *C. gigas*, followed by *F. dentivarians*; Hg, *F. dentivarians* followed by *C. corteziensis* and *C. gigas*; Pb by *C. corteziensis* and *C. gigas*, with slightly lower levels found in all other filter feeders except *C. fluctifraga*; and Zn, *F. dentivarians* and *C. gigas*, followed by *C. corteziensis*. Among filter feeder organisms, *F. dentivarians*, *C. corteziensis*, and *C. gigas* contained the highest levels of metals and may be useful for monitoring as metals contamination. Importantly, the spatial distribution and bioavailability of metals in the TL is heterogeneous, thus, it is necessary to study other organisms thoroughly to evaluate the bioavailable fraction of heavy metals.

Although correlations in heavy metals concentrations between bioavailable fraction and some organisms were founds, data collected from filter feeder do not reflect the conventional bioavailable metal fractions found in sediments. These organisms employ regulatory and detoxification processes that modify their net accumulation. In summary, metal bioaccumulation within an organism results from complex interactions between physiological factors (growth, weight loss, absorption, and accumulation), chemical factors (metal concentration, speciation, and bioavailability) and environmental factors (temperature and food availability). In the biomonitoring studies, it is important include different species to assess better estimations on heavy metals accumulation in ecosystems.

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