Arch Environ Contam Toxicol (2009) 57:96–102
DOI 10.1007/s00244-008-9236-0

Heavy Metal Levels in Marine Mollusks from Areas With, or Without, Mining Activities Along the Gulf of California, Mexico

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Received: 1 May 2008 / Accepted: 5 September 2008 / Published online: 30 September 2008

Abstract To assess the safety for human consumption of commercially important bivalves harvested from areas with or without mining activities, we compared the levels of heavy metals in mollusks collected from different coastal environments along the Gulf of California. We sampled the mussel *Mytilus edulis* and the clams *Laevicardium elatum* and *Megapitaria squalida* (June 2004) and the clam *Chione californiensis* (November 2006). Concentrations of cadmium, lead, nickel, zinc, iron, copper, and manganese in the soft tissue of the mollusks were measured by atomic absorption spectrophotometry. Based on dry weight, the highest average concentrations of iron, copper, and cadmium were found in clams from Loreto (572, 181, and 4.66 mg/kg, respectively); that of nickel, in mussels from San Luquitas (12.2 mg/kg); that of zinc, both in mussels from San Luquitas and in clams from Golfo de Santa Clara (94.3 and 91.8 mg/kg, respectively); and those of lead and manganese in clams from the Golfo de Santa Clara (9.2 and 3.68 mg/kg, respectively). Although mollusks were taken from coastal areas of the Gulf of California, which are considered to be contaminated by mining activities, the heavy metals in the sediments apparently were in a chemical form that had low bioavailability for the bivalves feeding in those areas. The interplay of oceanographic conditions and the chemical composition of anthropogenic inputs into the environment is not well understood. Thus, these factors or their interaction could potentially result in increased concentration and bioavailability of such metals in areas without effluent generated by mining activities.

Mollusks, specifically bivalves, have been widely used as indicators of aquatic contaminants due to their characteristic type of feeding (filtration of dissolved particles) and the consequent bioaccumulation of such contaminants in their tissues. Species such as the chocolate clam (*Megapitaria squalida*), blue mussel (*Mytilus edilus*), white clam (*Laevicardium elatum*), and Venus clam (*Chione californiensis*) are distributed in various littoral zones of the Gulf of California and are commercially exploited for human consumption (Anónimo 1994).

The Baja California peninsula has what is considered to be one of the two largest deposits of phosphorite in the world (Riley 1989). In addition to other elements, this mineral is a rich source of calcium and phosphorous, with cadmium (Cd) being a common impurity (Maanan and Ritchie 1995; Shumilin et al. 2001). There are two large, active mining complexes located in the south of the Baja California peninsula, which possibly have an impact on the Gulf of California. The first, a phosphorite mine located near La Paz Bay, has been in operation for about 25 years. Méndez et al. (2006) found concentrations of lead up to 7.8 mg/kg dry weight (dw) in the soft tissue of *M. squalida* taken from a site near (~200 m from) the mining complex and concentrations of Cd up to 11 mg/kg (dw) in those from a site far (~4 km) from the mine; the latter site had no anthropogenic activities in the area to serve as a source

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of contamination. The second, a copper (Cu) mine located near Santa Rosalia (SR), has metal deposits that are of marine hydrothermal origin (Escandon 1995). The extraction of Cu from this mine for over a century (Shumilin et al. 2000) has resulted in such a high accumulation of mine waste in marine sediments that the beaches located near the mine have turned black, levels up to 7078 mg Cu/kg (dw) having been found in samples of the sand (Rodríguez-Figueroa et al. 1998). Shumilin et al. (2000) reported elevated levels of Pb (220 mg/kg dw) and zinc (Zn; 2750 mg/kg dw) in marine sediments near SR. Because San Luquitas (SL), Mulege (MU), and Loreto (LO) are not located near mines and have no industries other than tourism-related activities, these areas are considered to have no, or low, impact by humans (Shumilin et al. 2000). In sediment samples taken from sites near these population centers, Rodríguez-Figueroa et al. (1998) found that the concentrations of trace elements, such as iron (Fe; 24,000 mg/kg dw), Zn (50 mg/kg dw), and nickel (Ni; 50 mg/kg dw), were at levels considered typical of sediments in unperturbed environments.

No information is available concerning the concentrations of heavy metals in mollusks from these areas or from the Golfo de Santa Clara (GSC), which is located in the extreme upper Gulf and which is affected by nautical and agricultural activities (García-Hernández et al. 2001). However, several studies of samples taken from coastal areas surrounding the mouth of the gulf have reported high concentrations of heavy metals such as Fe, Cu, Pb, Cd, and manganese (Mn) in oysters *(Crassostrea corteziensis, C. iridescens,* and *C. palmula*), mussels (*Mytella strigata*, *M. edulis*), and clams (*Ch. subrugusa*, *Ch. californiensis*, and *Tellina* sp.) (Páez-Osuna et al. 1988, 1991, 1993, 1995). These increased concentrations were attributed to the runoff of agricultural activities and domestic residues (Ruelas-Insunza and Páez-Osuna 2000). Because mollusks are an integral part of the diet of the humans living in towns and cities along the Gulf of California, information concerning the levels of heavy metals that are ingested through the consumption of mollusks harvested in these areas is important to human health.

The objective of this study was to evaluate the safety of commercially important bivalve mollusks harvested in the Gulf of California for consumption by humans. To that end, we compared the levels of heavy metals (Fe, Cu, Zn, Ni, Pb, Cd, and Mn) in mollusks which had been harvested along coast of the Gulf of California at sites associated with mining activities or high metal content in sediments with the levels in mollusks taken from areas affected by nautical, tourist, or agricultural industries. We assessed the resulting data by comparison with international guidelines.

Materials and Methods

Six areas were sampled (Fig. 1). In June 2004, mollusks were taken from the following five sites, designated by the name of the nearby urban center: Loreto (LO); Mulege (MU); San Luquitas (SL); and two sites (a and b) in Santa Rosalia (SR), approximately 0.5 and 3 km, respectively, from the town. In November 2006, samples were collected from the sixth site, the Golfo de Santa Clara (GSC), which is located in the northernmost part of the Gulf of California.

In legislation concerning the levels of heavy metals, in mollusks, which are considered to be safe for human consumption, no distinction is made between species. For this reason and because not all species are found throughout the Gulf of California, the mollusk species included in this study were chosen based on their presence and relative abundance in the areas of interest and on their commercial importance to the local human population in each area. *M. squalida* was collected in LO; *L. elatum*, in MU; *M. edulis,* in SL, SR(a), and SR(b); and *Ch. californiensis,* in GSC. Twenty individuals of each species were manually collected at each site at depths between 6 and 10 m. Each mollusk was weighed and its dimensions were recorded before the soft tissue was removed, weighted, and dried to constant weight in an oven (Precision Science 18 EM; Chicago, IL, USA) at 70°C (36 h). Each dried sample was transferred to an individual acid-washed Teflon tube, digested with concentrated nitric acid in a microwave oven (CEM model Mars 5X; Matthews, NC, USA), and then dissolved in 1 mL concentrated HCl and 24 mL deionized water in a volumetric flask. The concentrations of Fe, Cu, Zn, Ni, Pb, Cd, and Mn in the samples were analyzed using an atomic absorption spectrometer (AVANTA; GBC Scientific Equipment, Dandenong, Australia) with an air-acetylene flame. Certified standard reference material TORT-2 (National Research Council of Canada, Ottawa) was used to check the accuracy of the instrument; the analytical values were within the range of certified values. Recoveries of all metals studied were >95%. To calculate the amount of each metal per mollusk in an average human meal, the dw was converted to wet weight (ww) using a factor of 0.20, the dw/ww ratio (Mendez et al. 2002). ANOVA was used to determine the statistical difference in trace element concentrations between each locality using Statistica for Windows software (Starsoft, Inc., Tulsa, OK, USA).

Results

The average concentrations of the heavy metals in mollusks sampled in this study are listed in Table 1. The statistically highest concentrations of Fe in clams

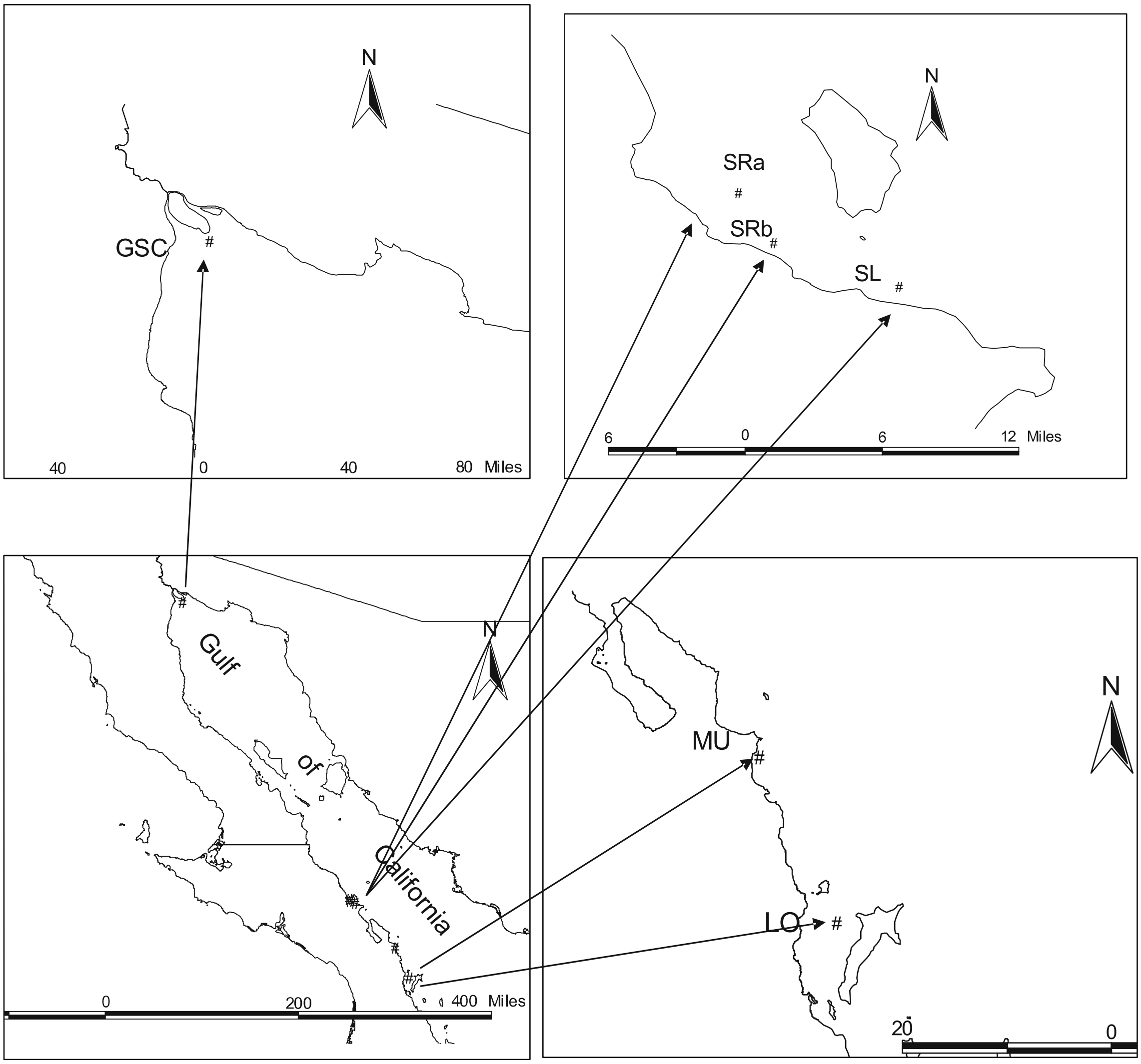

Fig. 1 Map of the Gulf of California, Mexico, indicating locations of mollusk sampling sites. # GSC—Golfo de Santa Clara; SR(a) and SR(b)—two sites at Santa Rosalia; SL—San Luquitas; MU—Mulege; LO—Loreto

Table 1 Heavy metal concentrations in clams and mussels in different localities of the Gulf of California

Mollusk	Locality	Fe	Cu	Zn	Ni	Pb	Cd	Mn
Clam								
Ch. californiensis	GSC	189 ± 20^{a}	5.70 ± 0.84^{a}	91.8 ± 7.8^{a}	4.4 ± 0.9^{a}	9.2 ± 1.5^{c}	0.42 ± 0.14^{a}	3.68 ± 0.48^{b}
M. squalida	LO	572 ± 132^{c}	181 ± 20^{c}	49.8 ± 2.3^{b}	5.6 ± 0.5^{a}	$<0.03^{d}$	4.66 ± 0.53^{c}	2.93 ± 0.34^{b}
L. elatum	MU	408 ± 52^{b}	3.9 ± 0.99^{a}	62.4 ± 4.2^{b}	7.6 ± 1.3^{a}	$<0.03^{d}$	1.70 ± 0.47^{b}	1.21 ± 0.54^{a}
Mussel								
M. edulis	SL	200 ± 30^{a}	6.10 ± 0.96^{a}	94.3 ± 4.2^{a}	12.2 ± 1.8^{b}	0.27 ± 0.06^{a}	2.42 ± 0.34^{b}	3.12 ± 0.48^{b}
M. edulis	SR(a)	369 ± 125^{b}	49.6 ± 9.82^{b}	47.9 ± 3.4^{b}	7.8 ± 0.6^{a}	5.8 ± 0.4^{b}	4.05 ± 0.44^{c}	0.53 ± 0.18^{a}
M. edulis	SR(b)	150 ± 24^{a}	17.1 ± 3.86^{a}	52.9 ± 4.8^{b}	6.4 ± 0.70^{a}	4.8 ± 0.5^{b}	3.51 ± 0.23^{bc}	0.84 ± 0.23^{a}

Note: GSC (Golfo de Santa Clara, 2006); LO (Bahía de Loreto, 2004); MU (Mulege, 2004); SL (San Luquitas, 2004); SR(a) (Santa Rosalia a, 2004); SR(b) (Santa Rosalia b, 2004). Concentrations are milligram per kilogram dry weight. Values are mean ± SD. Different superscript letters in the same column denote statistical significance ($p < 0.05$) between concentrations

($p < 0.05$) were found in LO, and the lowest in GSC, with a threefold difference between these values. The locality with the statistically highest concentration of Fe in mussels was SR(a), compared with SL and SR(b) ($p < 0.05$), with an approximately 2.2–fold difference between the highest and the other two average concentrations.

By site, the Cu concentrations in clams varied in the order, LO >> GSC > MU, with a statistical difference ($p < 0.001$). The highest value was 46.4-fold greater than the lowest value. The highest Cu values for mussels were found in SR(a) in comparison to that recorded in SL ($pp < 0.001$), where Cu levels were 8.1-fold lower.

Zn concentrations in clams at the different locations varied between sites in the order GSC > MU > LO, with a statistical difference of 1.8-fold between the highest and the lowest value ($p < 0.001$). Mussels from SL showed the highest significant ($p < 0.005$) concentrations in relation to those collected in SR(a) and SR(b), with an almost-twofold difference between the highest and the lowest concentrations.

No statistically significant differences in the levels of Ni were found for clams, whereas for mussels almost twofold higher concentrations ($p < 0.005$) were recorded for organisms from SL compared to those from sites SR(a) and SR(b).

The highest statistical concentration of Pb was recorded for clams from GSC (9.62 ± 1.5 mg/kg; $p < 0.001$). Levels of Pb in LO and MU were below the detection limit (0.03 mg/kg) of the analytical technique; therefore, the Pb concentration in clams from GSC was at least 320-fold that in clams from LO or MU. For mussels, the highest concentrations of Pb were recorded in those from SR(a) and SR(b), with those from SL ($p < 0.005$) having ~20-fold less than the average value of the other two sites.

The concentration gradient of Cd in clams at the different sites was LO > MU > GSC. There was a statistical difference ($p < 0.001$) between the highest and the lowest, with almost an 11-fold difference in concentrations between these two sites. The highest statistical concentrations of Cd ($p < 0.001$) in mussels were recorded for both sites in SR. The difference between the highest (SR[a]) and the lowest (SL) concentrations of Cd was 1.7-fold.

Manganese concentrations in clams decreased in the following order: GSC > LO >MU. The Mn concentration for GSC was threefold higher and statistically different ($p < 0.05$) than that for MU. In mussels, Mn concentrations were SL > SR(b) > SR(a), with the highest concentration of Mn approximately sixfold higher than, and statistically different ($p < 0.01$) from, the lowest concentration.

Discussion

As part of an ongoing biogeochemical project evaluating the effect of heavy metal contamination on the marine environment, we compared the levels of heavy metals in commercially important bivalves collected from different coastal environments, with or without mining activities, along the Gulf of California. Note that in the Discussion, all values are expressed as milligrams per kilogram dry weight, unless otherwise noted.

The levels of Fe in clams and mussels recorded in this study were within the ranges reported in previous studies for samples taken in the Gulf of California. Méndez et al. (2006) found Fe concentrations of from 323 to 438 mg/kg (before and after the rainy season, respectively) in areas near the phosphorite mine in La Paz, whereas in areas distant from the mine which are apparently pristine, they found Fe levels ranging from 154 to 558 mg/kg (before and after the rainy season, respectively). No significant difference was found between these values. At Guaymas Bay, Sonora, Mexico, which is considered to have been contaminated for many years by sewage from the fisheries industry and by urban waste (Arreola-Lizárraga et al. 2001), Fe concentrations for two species of clams, *C. gnidia* and *L. elatum*, were reported to be between 85.6 and 397 mg/kg (Méndez et al. 2002). For the clams *Ch. subrugosa* and *Tellina* sp. from the southern Gulf of California in the Pabellón-Altata wetland system in Sinaloa, Mexico, Páez-Osuna et al. (1993) found concentrations of up to 2231 and 2311 mg/kg, respectively. Ruelas-Inzunza and Paéz-Osuna (2000) recorded Fe concentrations of between 150 and 700 mg/kg in the mussel *M. strigata* from the Estero de Urias, east of Mazatlan, Sinaloa, which is affected by urban sewage. In northeast England, concentrations of 402 to 623 mg Fe/kg were recorded in *M. edulis* from nonimpacted sites, whereas in areas affected by the mining industry, concentrations between 636 and 1032 mg Fe/kg were registered (Giusti et al. 1999). Results from Estero de Urias showed concentrations up to 3000 mg Fe/kg dw in the oyster *C. corteziensis*, whereas the Fe concentration in sediments ranged from 700 to 9500 mg/kg dw (Soto-Jiménez and Páez-Osuna 2001). In the present study, the major significant ($p < 0.005$) concentration of Fe in mollusks was found in LO, a pristine area. In sediments taken from this area, Shumilin et al. (1998) found Fe concentrations (24,000 mg/kg) that were lower than those (41,600 mg/kg) in sediments from SR(a). Taken together, these findings indicate that a higher fraction of Fe was bioavailable in sediments in LO than in those in SR(a). From this, we conclude that high concentrations of an element in sediment do not necessarily indicate that the organisms present in the area will accumulate high concentrations of that metal.

Studies carried out in organisms collected in the southern Gulf of California reported Zn concentrations from 25 to 1247 mg/kg in *Ch. californiensis*, 64 to 1218 mg/kg in *Ch. subrugosa*, and 64 to 1944 mg/kg in *Tellina* sp. (Páez-Osuna et al. 1993). The authors ascribed the high levels of Zn to the use, in the 1980s, of agrochemicals such as organophosphate pesticides, carbamates, and some metallic fungicides, e.g., Maneb, Zineb, and Cupravit, that contain Mn, Zn, and Cu in their formulas, respectively (Páez-Osuna et al. 1993). In the same region, Ruelas-Insunza and Páez-Osuna (2000) recorded levels of 200 mg Zn/kg of the mussel *M. strigata* and 3500 mg Zn/kg of the oyster *C. corteziensis*. Studies done in Guaymas Bay reported levels of Zn in clams, *C. gnidia* and *L. elatum,* from 92.4 to 246.0 mg/kg; these values are considered typical of pristine environments (Méndez et al. 2002). Clams *M. squalida* from La Paz Bay had Zn concentrations up to 64.6 mg/kg (Méndez et al. 2006), a concentration well below the "general expected levels" (GELS; ~650 mg/kg (130 mg/kg ww), established by Food Standards of Australia New Zealand (ANZFA 2000). Otchere (2003) recorded Zn levels of 87 mg/kg for the mussel *P. perna* in a nonpolluted area in Ghana during a wet season. Maanan (2007) obtained an average concentration of 292 mg Zn/kg for *M. galloprovincialis* from an industrial area of Jorf Lasfar on the Morocco coast. The highest levels of Zn in mollusks were not necessarily found in the same areas for which the highest concentration of the element had been reported for sediments. This can be seen in the following findings: (1) in the present study, the highest Zn concentration was found in organisms from the GSC, where the mean level of Zn in sediments was 43.5 mg/kg (Shumilin et al. 2002); and (2) one of the lowest mean concentrations of Zn was found in organisms off SR, where Shumilin et al. (2000) reported up to 2100 mg Zn/kg in sediments. These findings are further indication that the bioaccumulation of heavy metals depends on several factors, with chemical speciation being the main one.

Background levels of Cu in mollusks of between 4 and 5 mg/kg have been reported for some areas along the Gulf of California, which are influenced by agriculture (Páez-Osuna et al. 1993). Concentrations up to 82 mg Cu/kg have been detected in oysters (*C. corteziensis* and *C. palmula*), mussels (*M. strygata*), and clams (*Ch. subrugusa*, *Ch. californiensis*, and *Tellina* sp. (Páez-Osuna et al. 1993). In areas such as Guaymas Bay, contaminated by the fisheries industry, normal concentrations of Cu, ranging from 15 to 23 mg/kg, have been reported for the clams, *C. gnidia* and *L. elatum* (Méndez et al. 2002). In La Paz Bay, concentrations of Cu up to 8.0 mg/kg have been found in the clam *M. squalida* (Méndez et al. 2006), the same species that was collected in LO. A concentration of 13.4 mg Cu/kg was reported in clams from the upper Gulf of California (García-Hernández et al. 2001). Otchere (2003) reported 16 mg Cu/kg for *P. perna* from uncontaminated lagoons in Ghana. Maanan (2007) recorded a mean concentration of 26.8 mg Cu/kg in *M. galloprovincialis* collected near an industrial area of the Moroccan coast; these values are lower than those recorded in the present study for mollusks from LO (181 mg/kg) and SR(a) (49.6 mg/kg). Previous studies reported mean Cu levels in sediments off LO (131 ± 23 mg/kg) (Méndez et al. 1998) and the extremely anomalous Cu concentrations off SR (7078 ± 3294 mg/kg) (Shumilin et al. 2001); these are, respectively, 3-fold and >100-fold higher than values (up to 50 mg/kg) reported in other areas also located along the west coast of the Gulf of California, which have not been contaminated with Cu. In SR, the Cu concentrations in sediments (Shumilin et al. 2000) were found to be higher than those in polluted industrialized zones such as Golden Horn Bay in Vladivostok, Russia (Tkalin et al. 1996). These results suggest that the local composition of the sediments from the area near SR, rich in Cu-containing minerals, is probably the result of contamination by mine waste from old mining activities (from 1896 to 1984) (Rodríguez-Figueroa et al. 1998). According to the literature (Yap et al. 2004), the bioavailable fraction of Cu which was accumulated by marine organisms sampled in the present study was well within the limits (350 mg/kg) established by the Australian Legal Requirements for mollusks to be fit for human consumption; however, these same mollusks would be considered unfit according to the guidelines of Thailand and Malaysia (150 mg/kg).

In the Gulf of California, Ni concentrations of 13.3 mg/kg in *Ch. californiensis*, 11.1 mg/kg in *Ch. subrugosa*, and 6.5 mg/kg in *Tellina* sp. have been detected in areas like Pabellon-Altata lagoon that are influenced by agriculture (Páez-Osuna et al. 1993). Páez-Osuna et al. (1995) also recorded 4.4 mg Ni/kg in *C. iridescens* from San Cristobal, Nayarit, México. Méndez et al. (2002) found up to 23.65 mg Ni/kg in *C. gnidia* and *L. elatum* from Guaymas Bay, a fisheries industry zone. Méndez et al. (2006) recorded up to 8.8 mg Ni/kg in *M. squalida* from La Paz Bay; however, the highest value was found for specimens taken from in front of a gasoline storage depot. Maanan (2007) detected 32.8 mg Ni/kg for *M. galloprovincialis* from the Moroccan coast near an industrial zone. The Food and Drug Administration (FDA 2003) established 400 mg Ni/kg (80 mg/kg ww) in mollusks as the safety limit for human consumption. According to the results of the present study, the levels of Ni for all mollusks sampled were found to be within acceptable limits, thus making the mollusks fit for human consumption.

Pb is generally taken as being indicative of pollution from industrial sources, in particular, from fuel use (Anónimo 2002). Méndez et al. (2002) determined the Pb concentrations in *C. gnidia* and *L. elatum* from Guaymas Bay to be up to 4.03 mg/kg. This bay is considered to be impacted by industrial and harbor activities because, at any given time, ~1000 boats can be found within its limits (Arreola-Lizárraga et al. 2001). Méndez et al. (2006) recorded concentrations up to 7.8 mg Pb/kg in *M. squalida* collected in La Paz Bay, which the authors associated with the fuel used in nautical activities. Pb concentrations similar to those reported in this study were detected by Maanan (2008) in *M. galloprovincialis* (9.6 mg Pb/kg) from the Moroccan coastal region. The FDA (2003) established 1.7 mg Pb/kg (8.5 mg Pb/kg dw) as a safe concentration in mollusks for human consumption. Shumilin et al. (2000) found Pb concentrations in marine sediments in the SR area to be comparable with high levels in sediments at the Ilusiones lagoons in Tabasco, México, and the industrialized zone in Golden Horn Bay, Vladivostok. However, although the Pb concentrations in the sediment were high, the mussels collected near SR were fit for human consumption, based on the permissible limits outlined by the FDA and Non Observed Adverse Effects Level (NOAEL). Only the clams collected in the upper Gulf at GSC were not fit for human consumption due to their high Pb concentration. To our knowledge, there are no studies of Pb concentrations in marine sediments in the GSC. However, the region of GSC from which our specimens were taken is known to have high activity from shrimp-fishing vessels (~200 outboard boats and ships) from August to April (Anónimo 2002). Therefore, the Pb levels found in the clams from GSC may be explained by this activity could explain the presence of Pb in the sediments as a consequence of fuel combustion and occasional gasoline spill from small boats.

Background concentrations of Cd in clams from the Pabellon-Altata lagoon system, an area influenced by agriculture activities, were 8.7 mg/kg for *Tellina* sp., 3.8 mg/kg for *Ch. californiensis*, and 3.5 mg/kg for *Ch. subrugusa* (Páez-Osuna et al. 1993). Temporal variations of Cd concentrations in oysters (*C. iridescens*) were observed in other studies and were explained as changes in gonadic maturation, with the highest concentration (3.4 mg Cd/kg) in mature organisms (Páez-Osuna et al. 1995). The Cd concentration in sediments from Mazatlan has been reported to be 1.8 mg/kg (Soto-Jiménez and Páez-Osuna 2001) and 0.92 mg/kg (Frías-Espericueta et al. 2004). In Guaymas, an industrial area, the maximum Cd concentration observed in two species of clams, *C. gnidia* and *L. elatum*, was 1.28 mg/kg (Méndez et al. 2002). None of the areas sampled for the present study reached the maximum Cd concentration of 11.1 mg/kg found by Méndez et al. (2006) in *M. squalida* from an apparently pristine area, without anthropogenic activities, located in La Paz Bay. No published data are available for the concentration of Cd in sediments from GSC, SR, or La Paz. An alternate explanation for the highest levels of Cd in LO and SR(a) found in the present study could be the upwelling processes in the area, which have been documented by Segovia-Zavala et al. (1998). In the present study, the average Cd concentration obtained for each site sampled was well below 20 mg Cd/kg (4 mg/kg ww), the value established by the FDA as the Cd limit for mollusks to be fit for human consumption. In addition, Cd in mollusks binds to metallothioneins, proteins of low molecular weight that decrease metal toxicity (Vahter et al. 1996); however, they would not reduce the potential risk for consumption.

Páez-Osuna et al. (1993) reported the background concentration of Mn to be 69 mg/kg in *Ch. californiensis*, 80 mg/kg in *Ch. subrugosa*, and 43 mg/kg in *Tellina* sp. from the Pabellon-Altata lagoon system, an environment affected by agricultural and urban activities. Páez-Osuna et al. (1995) detected a maximum value of 15.8 mg Mn/kg in soft tissue of *C. iridescens* from San Cristobal estuary, which is considered to be an area not impacted by anthropogenic activities. García-Hernández et al. (2001) reported 12 mg Mn/kg in marine clams from GSC. Méndez et al. (2002) recorded a maximum of 26.9 Mn mg/kg in *C. gnidia* and *L. elatum* from Guaymas Bay, and Méndez et al. (2006) registered a mean of 14.1 mg Mn/kg in *M. squalida* from La Paz. Maanan (2007) detected 20.8 mg Mn/kg in *M. galloprovincialis* from an area affected by urban and industrial activities in the Moroccan coastal environment; the Mn concentrations found in this study are close to those reported as background levels in oysters (*C. gigas*) by Paez-osuna et al. (1995). The highest level of Mn in the present study was found at GSC (3.68 mg/kg); this could be due to the influence of surficial sediments from the Colorado River (Daessle et al. 2002), which empties into GSC. The origin of the Mn in the sediments can be related to a biogenic fraction in the geology of this area (Daesslé et al. 2002; Maanan 2007).

In conclusion, our work shows that, although the Gulf of California has a long history both of mining activities and of natural enrichment of heavy metals in sediments, the bioavailability of these metals is, apparently, low. Areas that are apparently pristine or that have few anthropogenic activities showed higher concentrations of heavy metals such as Pb, Fe, and Cu in the soft tissue of mollusks than did areas near mining, heavy industry, or other anthropogenic activities. This finding should be considered in environmental studies. In this study, with the exception of clams from the GSC, which had high levels of Pb, all mollusks sampled along the Gulf of California were found, in general, to be fit for human consumption, as the levels of heavy metals were within the limits set by international legislation.

Acknowledgments This work was carried out with the financial support of (Grant C01-1425) from the Mixed Fund of the Secretaría del Medio Ambiente and the Consejo Nacional de Tecnología of Mexico for the project, "Biogeochemical Evaluation of the Heavy Metals in the Marine Environment of the Santa Rosalia Mining District (B.C.S.)." This project is under the direction of Eugene Choumiline. The authors thank Melania Lopez-Castro and Veronica Yakoleff for editing the manuscript.

References

Anónimo (1994) Carta Nacional Pesquera de México, Instituto Nacional de la Pesca, Ciudad de México

Anónimo (2002) Carta Nacional Pesquera de México, Instituto Nacional de la Pesca, Ciudad de México

ANZFA (2000) Generally expected levels (GELs) for metal contaminants: guidelines for retailers and enforcement officers. Australia New Zealand Food Authority, Canberra

Arreola-Lizárraga JA, Padilla-Arredondo G, Burrola-Sánchez MS, Urias-Laborin D, Dorado-Villanueva F, Hernández-Ibarra A, López-Tapia MR, Méndez-Rodríguez LC, Acosta B (2001) Diagnóstico de la contaminación marina de la bahía de Guaymas, Sonora y proximidades. Informe técnico Secretaria de Marina-CIBNOR, Guaymas, México

Daesslé LW, Ramos SE, Carriquiry JD, Camacho-Ibar VF (2002) Clay dispersal and the geochemestry of manganese in the Northen Gulf of California. Cont Shelf Res 22:1311–1323. doi:10.1016/S0278-4343(02)00007-9

Escandon VF (1995) Génesis de los yacimientos polimetálicos del boleo, Santa Rosalía, Baja California Sur. Academia Mexicana de Ingeniería, México

FDA (2003) Guide for the control of molluscan shellfish. Chapter II Growing areas. U.S. Food and Drug Administration, Center for Food Safety and Applied Nutrition, Washington, DC

Frías-Espericueta MG, Osuna-López JI, López-Saenz PJ, López-López G, Izaguerre-Fierro G (2004) Heavy metals in surface sediments from Huizache-Caimanero lagoon, Northwest coast of México. Bull Environ Contam Toxicol 73:749–755. doi:10.1007/s00128-004-0489-7

García-Hernández J, King AK, Velazco LA, Shumilin E, Mora AM, Glenn EP (2001) Selenium, selected inorganic elements, and organochlorine pesticides in bottom material and biota from the Colorado River Delta. J Arid Environ 49:65–89. doi:10.1006/jare.2001.0836

Giusti L, Wiliamson AC, Mistry A (1999) Biologically available trace metals in *Mytilus edulis* from the coast of northeast England. Environ Inter 25(8):969–981. doi:10.1016/S0160-4120(99)00066-5

Maanan M (2007) Heavy metal concentration in marine molluscs from the Moroccan coastal region. Environ Pollut 153:173–186

Maanan SS, Ritchie GSP (1995) Forms of cadmium in sandy soils after amendment with soils of higher fixing capacity. Environ Pollut 87:23–29. doi:10.1016/S0269-7491(99)80004-9

Méndez L, Acosta B, Alvarez-Castañeda ST, Lechuga-Devéze CH (1998) Trace metal distribution along the southern coast of Bahía de La Paz (Gulf of California), México. Bull Environ Contam Toxicol 61:616–620. doi:10.1007/s001289900805

Méndez L, Salas-Flores M, Arreola-Lizárraga A, Alvarez-Castañeda ST, Acosta B (2002) Heavy metals in clams from Guaymas Bay, Mexico. Bull Environ Contam Toxicol 68:217–223. doi:10.1007/s001280241

Méndez L, Palacios E, Acosta B, Monsalvo-Espencer P, Alvarez-Castañeda T (2006) Heavy metals in the clam *Megapitariaa squalida* from wild and phosphorite mine impacted sites in Baja California, Mexico. Biol Trace Element 110:1–13. doi:10.1385/BTER:110:1:1

Otchere FA (2003) Heavy metals concentrations and burden in the bivalves (*Anadara (Senilia) seniles*; *Crassostrea tulipa* and *Perna perna*) from lagoons in Ghana: model to describe mechanisms of accumulation/excretion. Afr J Biotechnol 2:280–287

Páez-Osuna F, Izaguerre-Fierro G, Godoy-Meza RI, Gonzáles-Farias F, Osuna-López JI (1988) Metales pesados en cuatro especies de organismos filtradores de la región costera de Mazatlán: Técnicas de extracción y niveles de concentración. Contam Ambient 4:33–41

Páez-Osuna F, Zazueta-Padila MH, Izaguerre Fierro G (1991) Trace metals in bivalves from Navachiste Lagoon, Mexico. Mar Pollut Bull 22:305–307. doi:10.1016/0025-326X(91)90809-7

Páez-Osuna F, Osuna-Lopez JI, Izaguerre-Fierro G, Zazueta-Padilla HM (1993) Heavy metals in clams from subtropical coastal lagoon associated with an agricultural drainage basin. Bull Environ Contam Toxicol 50:915–921

Páez-Osuna F, Frías-Espericueta MG, Osuna-López JI (1995) Trace metal concentration in relation to seasonal and gonadal maturation in the oyster *Cassostrea iridescens*. Marine Env Res 1:19–31. doi:10.1016/0141-1136(94)00004-9

Riley JP (1989) Los elementos mas abundantes y menores en el agua de mar. In: Riley JP, Chester R (eds) Introducción a la química marina. AGT SA, México, p 459

Rodríguez-Figueroa G, Shumilin E, Páez-Osuna F, Nava-Sánchez E, Sapozhnikov D (1998) Ocurrencia de metales y metaloides en sedimentos superficiales de cuatro abanicos-deltas de la costa oriental de Baja California Sur. Actas INAGEQ 4:43–50

Ruelas-Insunza JR, Páez-Osuna F (2000) Comparative bioavailability of trace metals using three filter-feeder organisms in a subtropical coastal environment (Southeast Gulf of California). Environ Pollut 107:437–444. doi:10.1016/S0269-7491(99)00157-8

Segovia-Zavala JA, Delgadillo-Hinojosa F, Vidal-Talamantes R, Muñoz-Barbosa A, Gutierrez-Galindo EA (1998) *Mytilus californianus* transplanted as upwelling bioindicators to two areas off Baja California, México. Ciencias Mar 29:665–675

Shumilin EN, Green-Ruiz D, Sapozhnikov D, Rodríguez-Meza D, Páez-Osuna F (1998) Asociaciones geoquímicas y patrones de distribución espacial de metales y metaloides en los sedimentos superficiales de la laguna de La Paz, Baja California Sur. Actas INAGEQ 4:23–32

Shumilin EN, Rodríguez-Figueroa G, Morton-Bermea O, Lounejeva-Baturina E, Hernández E, Rodríguez-Meza D (2000) Anomalous trace element composition of coastal sediments near the copper mining district of Santa Rosalia, peninsula of Baja California, Mexico. Bull Environ Contam Toxicol 65:261–268. doi:10.1007/s001280000123

Shumilin E, Páez-Osuna F, Green-Ruiz C, Sapozhnikov D, Rodríguez-Meza GD, Godínez-Orta L (2001) Arsenic, Antimony, Selenium and other trace elements in sediments of the La Paz lagoon, peninsula of Baja California México. Mar Poll Bull 42(3):174–178. doi:10.1016/S0025-326X(00)00123-5

Shumilin EN, Carriquiry JD, Camacho-Ibar VF, Sapozhnikov D, Kalmykov S, Sánchez A, Aguiñiga-García S, Sapozhnikov YA (2002) Spatial and vertical distributions of elements in sediments of the Colorado River delta and Upper Gulf of California. Mar Chem 79:113–131. doi:10.1016/S0304-4203(02)00059-2

Soto-Jiménez MF, Páez-Osuna F (2001) Distribution and normalization of heavy metal concentrations in mangrove and lagoonal sediments from Mazatlán harbor (SE Gulf of California). Est Coastal Shelf Sci 53:259–274. doi:10.1006/ecss.2000.0814

Tkalin AV, Presley BJ, Boothe PN (1996) Spatial and temporal variations of trace metals in bottom sediments of Peter the Great Bay, the Sea of Japan. Environ Pollut 92:73–78. doi:10.1016/0269-7491(95)00083-6

Vahter M, Berglund M, Nermell B, Akesson A (1996) Bioavailability of cadmium from shellfish and mixed diet in women. Toxicol Appl Pharmacol 136:332–341. doi:10.1006/taap.1996.0040

Yap CK, Ismail A, Tan SG (2004) Heavy metal (Cd, Cu, Pb and Zn) concentrations in green-lipped mussel *Perna pirividis* (Linnaeus) collected from some wild and aquacultural sites in the west coast of peninsular Malaysia. Food Chem 84:569–575. doi:10.1016/S0308-8146(03)00280-2