Bull. Environ. Contam. Toxicol. (2006) 76:327–333
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DOI: 10.1007/s00128-006-0925-y

Bulletin of Environmental Contamination and Toxicology

Trace Metal Concentrations in Different Primary Producers from Altata-Ensenada del Pabellón and Guaymas Bay (Gulf of California)

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Received: 30 June 2005/Accepted: 12 December 2005

In the last decades, the rate of population growth in coastal areas has increased in comparison to inland areas; the demand for goods and services in such urban settlements means an extra stress over the surrounding environment. Contaminants, such as trace metals, are extensively used and released from diverse sources into water bodies. In order to assess the degree of contamination by trace metals in a given area it is necessary to make analyses of environmental samples, i.e. water, sediments or biota. The approach of water and sediment analyses does not supply information on the bioavailability (Phillips 1977; Bryan et al. 1985); these problems can be resolved by using organisms, which by definition reflect the bioavailability of contaminants (Villares et al. 2001). In the specific case of macroalgae, it is known that they concentrate trace metals several times higher than in the surrounding waters; it is possible by the presence of active and passive processes responding essentially to metals present in solution (Bryan 1969; Seeliger and Edwards 1977; Leal et al. 1997). This work was elaborated with the objective of establishing concentrations of Cd, Cu, Fe, Mn, Pb and Zn in three different types of primary producers from two coastal areas of the Gulf of California, namely phytoplankton, macroalgae and mangroves.

MATERIALS AND METHODS

Sampling occurred between April 1998 and February 1999. The sites where specimens were collected were Altata-Ensenada del Pabellón lagoon (AEP) and Guaymas Bay (GUB). Altata-Ensenada del Pabellón lagoon is located in the central part of Sinaloa state (24° 20' and 24° 40' N; 107° 30' and 107° 58' W) and has an area of 300 km^2 and an average depth of 2 m; the major source of pollution is waste effluents from the intensive agriculture (140,000 ha) which border the lagoon system and consists mostly of vegetables, grains and sugar cane. Another source of pollution is urban sewage from Costa Rica, Las Puentes, Villa Juárez, El Castillo, El Molino and Sataya towns (overall estimated population of 100,000); and the cities of Culiacán (population 750,000) and Navolato (population 50,000) which are located 40 and 20 km away from the main lagoon, respectively, on the margin of the Culiacán River (Páez-Osuna et al. 1998). Guaymas harbor is located in central Gulf of California (27° 54' and 27° 59' N; 110° 48' and 110° 55' W); the system has an area of 28 km^2 and an average depth of 2.3 m. Potential sources of pollution include domestic effluents from Guaymas (population >150,000), oil

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residues from transport operations, effluents from a cement industry and cooling waters from a thermo electrical plant (Green-Ruiz 2000).

In order to avoid contamination of samples, glassware and other plastic utensils were previously washed according to Moody and Lindstrom (1977). Phytoplankton was collected in Altata-Ensenada del Pabellón using a plankton net (118 μm); macroalgae and mangrove specimens were collected by hand at low tide. Mangroves were sampled from a site in Altata-Ensenada del Pabellón lagoon; Guaymas Bay does not have significant mangroves in its margins. Macroalgae species from Guaymas Bay were: *Codium amplivesciculatum* Setchell and Gardner (Codiaceae), *Enteromorpha clathrata* Greville, 1830 (27° 54.04'N; 110° 33.96'W) and *Ulva lactuca* Linnaeus, 1753 (Ulvaceae) and *Gracilaria subsecundata* Setchell and Gardner, 1924 (Gracilariaceae) (27° 54.07'N; 110° 53.89'W).

Concerning specimens from Altata-Ensenada del Pabellón, predominant species of phytoplankton was *Coscinodiscus centralis* Grant and Angst 1931 (24° 30.02'N; 107° 42.44'W); macroalgae were *Gracilaria sp.* (Gracilariaceae) and *Polysiphonia sp.* (Rhodomelaceae) (24° 28.00'N; 107° 37.71'W); and mangroves were *Rhizophora mangle* Linnaeus (Rhizophoraceae), *Avicennia germinans* Stearnes (Vervenaceae) and *Laguncularia racemosa* Gaertner (Cambrelaceae) (24° 29.74'N; 107.33.85'W). Macroalgae and mangrove materials were rinsed repeatedly with seawater in-situ. The phytoplankton material, was separated individually under the microscope, where was selected the species more abundant. After taxonomic identification of organisms, leaves and twigs were dissected from mangroves samples and samples were pooled (40 leaves/twigs). Macroalgae fronds were used for analyses. Two or 4 homogenized replicates for each species were examined.

Samples were freeze-dried for 72 hours (-49°C and $133x10^{-3}$ mBar) then ground in an automatic agate mortar (Retsch) for 10 min. Powdered samples were acid digested (5 ml of quartz distilled concentrated nitric acid) using a microwave digestion unit (CEM MDS-2000) under the following conditions (MESL 1997): step 1, 20 psi for 10 min; step 2, 40 psi for 10 min; step 3, 90 psi for 30 min. Digested samples were stored in polyethylene containers for further analysis. Two aliquots of each tissue were analyzed. Analyses of Cu, Fe, Mn and Zn were made by flame atomic absorption spectrophotometry (FAAS); Cd and Pb were detected by graphite furnace atomic absorption spectrophotometry (GFAAS) in a Varian SpectrAA220 equipment (Rothery 1988). Precision and accuracy of the analytical method were assessed by using reference material IAEA-331 (spinach). A satisfactory agreement between the analytical results and the certified values was obtained (86-113%). Blanks were run with every batch of eleven samples. For a given element, significant differences ($p < 0.05$) between two species of macroalgae were defined by a Student's t-test; in the case of the mangrove species, differences were defined by a one-way ANOVA and a Bonferroni post test using GraphPad Prism 2.1 (Graph Pad Software, San Diego, CA).

Table 1. Levels ($\mu g\ g^{-1}$ dry weight) of analyzed trace metals in macroalgae from Guaymas bay (GUB) and macroalgae and phytoplankton from Altata-Ensenada del Pabellón (AEP).

Species	N	Site	Cd	Cu	Fe	Mn	Pb	Zn
U. lactuca	4	GUB	0.54± 0.07[a]	13.4± 0.4[b]	2131± 5.1[c]	120± 0.3	0.35± 0.05	40± 1.3
G. subsecundata	4	GUB	0.28± 0.11	14.7± 0.1	1751± 10	57± 0.4	0.29± 0.04	33± 1.1
C. amplivesciculatum	4	GUB	0.32± 0.1	24.6± 0.6	508± 35	10± 1.1	8.7± 1.8	103± 4.2
E. clathrata	4	GUB	0.13± 0.01[a]	7.5± 0.7[b]	1450± 280[c]	88± 5.1	0.97± 0.4	26.2± 2.6
Gracilaria sp.	2	AEP	0.23± 0.01	9.3± 0.2	504± 318	29± 0.3	4.9± 0.4	36± 2.2
Polysiphonia sp.	2	AEP	0.87± 0.3	14.4± 0.3	2264± 82	48± 34	3.1± 0.7	34± 2.9
Phytoplankton	2	AEP	0.27± 0.06	30± 0.5	889± 18	289± 13	23± 0.3	117± 3.2

For each element, the same literal denotes significant differences ($p < 0.05$) between species; N is the number of pools or groups that were analyzed.

RESULTS AND DISCUSSION

Although different species probably accumulate varying amounts of metals, it is interesting to compare the concentrations between macroalgae specimens from AEP and GUB; the results are shown on Table 1, where significant differences are indicated.

The only collected species belonging to the same family were *Ulva lactuca* and *Enteromorpha clathrata*; a comparison between these species would be more objective considering taxonomic similarities, the same date of sampling and the same site of collection. With the exception of Pb, all trace metals were more concentrated in *Ulva lactuca* than in *E. clathrata,* this is in concordance with the study of Wahbeh et al. (1985) where Cu, Mn, and Zn were in higher levels in *U. lactuca*.

High cadmium levels in *Polysiphonia* sp. from AEP might indicate an enhanced ability of this species to concentrate this metal as well as the natural enrichment with Cd of the Pacific waters from upwelling (Segovia-Zavala et al. 1998). In the case of Cu and Fe, elevated levels in GUB and AEP might be due to effluent discharges from urban and agricultural activities; in the specific case of AEP, intensive agriculture makes use of pesticides that contain Cu and Mn (Páez-Osuna et al. 1993).

In the case of mangroves, Cd concentrations in twigs of *R. mangle* were significantly ($p<0.05$) higher than in twigs of *A. germinans* and *L. racemosa*. Regarding Cu, leaves in twigs of *A. germinans* were significantly ($p<0.05$) higher than in twigs of *R. mangle* and *L. racemosa*. Levels of Fe in leaves of *A.*

Table 2. Levels ($\mu g\ g^{-1}$ dry weight) of analyzed trace metals in three mangrove species from Altata-Ensenada del Pabellón (AEP).

Species	N*	Tissue	Cd	Cu	Fe	Mn	Pb	Zn
R. mangle	3	twigs	0.59 ± 0.17[a,b]	3.0 ± 0.1[a,b]	41 ± 12[a]	47 ± 28[a]	0.9 ± 0.2[a,b]	10.1 ± 1.4
		leaves	0.17 ± 0.04	7.4 ± 0.2[d,e]	115 ± 44	30 ± 14	2.1 ± 1.2	8.7 ± 1.3[a,b]
A. germinans	4	twigs	0.12 ± 0.01[a]	18.1 ± 0.1[b,c]	77 ± 2.0[a,b]	11.1 ± 0.5[b]	0.4 ± 0.1[a]	11 ± 0.3
		leaves	0.10 ± 0.01[c]	4.6 ± 0.11[d,f]	171 ± 0.7[c]	64 ± 0.6[c]	2.2 ± 1.0	21 ± 0.3[a,c]
L. racemosa	4	twigs	0.29 ± 0.07[b]	5.0 ± 0.1[a,c]	28.8 ± 1.9[b]	106 ± 0.7[a,b]	0.4 ± 0.07[b]	11 ± 0.4
		leaves	0.25 ± 0.07[c]	2.3 ± 0.2[e,f]	97 ± 1.5[c]	28 ± 0.5[c]	0.94 ± 0.3	15 ± 0.6[b,c]

*pooled samples of 40 leaves/twigs; for each element, same literals denote significant differences ($p < 0.05$) among species.

germinans were significantly higher than in leaves of *L. racemosa*. With respect to Mn, concentrations in twigs of *L. racemosa* were significantly ($p<0.05$) higher than in twigs of *R. mangle* and *A. germinans*. Zinc accumulation in leaves of *A. germinans* was significantly ($p<0.05$) higher than in leaves of *R. mangle* and *L. racemosa* (Table 2).

From the decreasing order of trace metal concentrations in macroalgae, it can be seen that Fe was the element with the highest values while Cd (with the exception of *U. lactuca*) was the metal with the lowest values. Concerning mangroves, Fe and Mn were the elements with the highest levels, while Cd was the metal with the lowest concentrations in all the analyzed species. Diverse authors (Untawale et al. 1980; Talbot and Chegwidden, 1982; Karez et al. 1994) have mentioned that Fe and Mn are some of the metals with elevated concentrations in macroalgae and mangroves; despite the elevated concentration of such elements, organisms are able to cope with their presence through biochemical processes (Shiber and Washburn 1978; Ho 1990).

Though published data on diverse elements in the literature can vary due to factors such as seasonal variation, salinity in the sampling area and the amount of contaminants in the environment (Villares et al. 2001), comparison of trace metals levels (in $\mu g\ g^{-1}$ dry weight) in the analyzed macroalgae species with specimens of the same genus from diverse sites resulted as follows: *Enteromorpha clathrata* from GUB had lower values of Cu (7.5), Pb (0.9) and Zn (26.2) than *E. intestinalis* Cu (120), Pb (2.2) and Zn (425) from Kuwait (Buo-Olayan and Subrahmanyam 1996). *Ulva lactuca* from GUB had higher levels of Fe (2131), Mn (120) and Zn (40) than *U. lactuca* from Mazatlán Fe (670), Mn (58) and Zn (8.8) (Páez-Osuna et al. 2000); but lower values of Cu (13.4) and Zn (40) than *U. lactuca* (Cu 445 and Zn 130) from Kuwait (Buo-Olayan and Subrahmanyam 1996). *Codium amplivesciculatum* from GUB had higher levels of Cu (24.6) and Zn (103) than *C.*

amplivesciculatum from Lobos lagoon (Cu 4.3, Zn 10.5); but lower values of Cd (0.32 and 1.9, respectively) (Páez-Osuna et al. 2000). Cd and Mn in *G. subsecundata* (this study) were an order of magnitude lower than in *G. subsecundata* (Cd 1.6, Mn 163) from Ceuta (Páez-Osuna et al. 2000).

In the case of mangroves, concentrations of Cu, Fe, Mn, Pb and Zn in leaves of *Rhizophora mangle* and *Laguncularia racemosa* from AEP were comparable to values reported (De Lacerda et al. 1986) in leaves of *R. mangle* and *L. racemosa* from areas with no pollution sources in the south-eastern coast of Brazil. Similarly, levels of Cu, Fe, Mn, Pb and Zn in twigs of *Avicennia germinans* from AEP were comparable or lower than values reported in twigs of *A. officinalis* from an uncontaminated area in Kerala, India (Thomas and Fernández 1997).

Concerning phytoplankton, the predominant species was *Coscinodiscus centralis* var. *Pacifica*; studies in this group of organisms are scarce, comparison of Cd (7 $\mu g\ g^{-1}$), Cu (50 $\mu g\ g^{-1}$) and Pb (40 $\mu g\ g^{-1}$) levels in phytoplankton from Monterey Bay, California (Knauer and Martin 1976) with concentrations in *C. centralis* (this study) were of the same magnitude order. In phytoplankton from South Texas continental shelf (Horowitz and Presley 1977) levels of Fe (624 $\mu g\ g^{-1}$) were in the same magnitude order, but levels of Mn (21.7 $\mu g\ g^{-1}$) and Zn (90.8 $\mu g\ g^{-1}$) were lower than values in *C. centralis* from AEP. Recently, it has been demonstrated that trace metal accumulation in phytoplankton can be affected by nutrient enrichment (Rijstenbil et al. 1998); such could be the case of this lagoon system.

More studies concerning trace metal accumulation in phytoplankton, macroalgae and mangrove species from the Gulf of California are needed; mainly related to field work (seasonal variations, metal interactions and surveys for gradients according to point sources of pollutants) and laboratory experiments (metal distribution in diverse tissues of specimens, biochemical processes against metal toxicology, concentration factors of metals in relation to sediments).

Acknowledgments. Special thanks are due to A. Núñez-Pastén for plankton sampling, R. Cortés-Altamirano for plankton identification, C. Agraz for the identification of mangroves, J. Ochoa-Izaguirre for the identification of macroalgae, H. Bojórquez-Leyva for the laboratory assistance, and C. Ramírez-Jáuregui for the bibliographical support.

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