Bull. Environ. Contam. Toxicol. (2005) 74:493–500
© 2005 Springer Science+Business Media, Inc.
DOI: 10.1007/s00128-005-0612-4

Bulletin of Environmental Contamination and Toxicology

Arsenic Concentrations in the Surface Sediments of the Magdalena–Almejas Lagoon Complex, Baja California Peninsula, Mexico

E. Shumilin,[1] G. D. Rodríguez Meza,[1] D. Sapozhnikov,[2] S. Lutsarev,[3] J. Murrillo de Nava[1]

[1] Interdisciplinary Center of Marine Sciences, National Polytechnic Institute, Post Office Box 592, La Paz 23096, B. C. S., Mexico
[2] V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow, Russia
[3] P. P. Shirshov Institute of Oceanology, Russian Academy of Sciences, Moscow, Russia

Received: 15 September 2004/Accepted: 7 January 2005

Arsenic is an environmentally important trace element (Goessler et al.1997; Kubota et al. 2001; Millward et al.1997) since its inorganic species are highly toxic (Whalley et al. 1999). In oxidized marine sediments As(V) is associated with iron oxyhydroxides and marine phosphates, while in reducing sediments As(III) is coprecipitated with sulphide minerals (Neff 1997).

Arsenic biogeochemistry in the Magdalena-Almejas lagoon complex, located along the southwestern coast of the Baja California Peninsula, merits special attention as its high biological productivity supports a fishery and aquaculture industry. It is also the reproduction and nesting area for a number of protected species (e.g. marine mammals and sea turtles). The adjacent drainage basin is predominantly composed of Upper Tertiary and Quaternary sandstones, shale-sandstones, conglomerates, limestones and aeolian deposits, sometimes enriched in phosphate minerals (Piper 1991). Episodic inputs of particulate arsenic into this coastal marine ecosystem may occur from the adjacent land including a phosphate-rich San Gregorio Formation, mainly via the Las Bramonas arroyo and wind-driven transport from Magdalena island into the channeled northern part of Magdalena Bay, from the eastern land through the La Presa arroyo at the southern portion of the Almejas Bay, and from the western land through the arroyos from Magdalena and Margarita islands. Seasonal coastal upwelling on the adjacent shelf and slope in the Pacific Ocean in front of the Magdalena–Almejas lagoon complex could also carry some dissolved arsenic along with other nutrients through the La Bocana, La Rehusa and Flor de Malva channels into this coastal embayment. Anthropogenic contribution of arsenic from the port of San Carlos and from the fertilizers used in the agricultural zone further inland may be important in the shallow northern part of Magdalena Bay. The geochemical behavior of arsenic in the lagoon environment may also be affected by mangrove groves, which are abundant in northern Magdalena Bay (San Gil Channel, Estero Banderitas and Estero San Buto). The aim of the present study is to characterize the spatial distribution of this element in the surface sediments of Magdalena and Almejas Bays so as to create a base for future geochemical studies and for the monitoring of arsenic bioaccumulation in the marine food chain of this ecologically important lagoon complex.

Correspondence to: E. Shumilin

MATERIALS AND METHODS

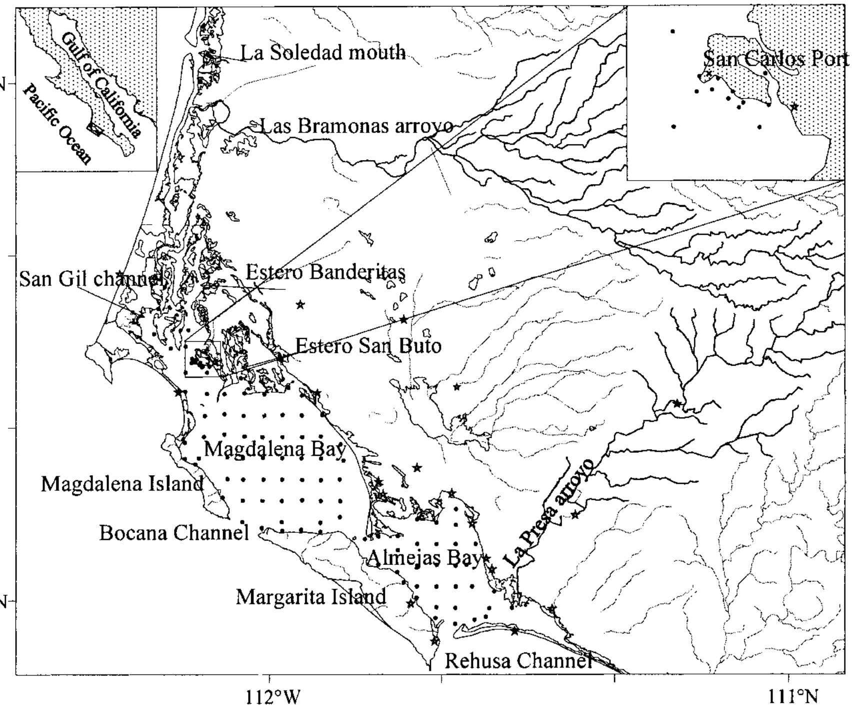

Figure 1. A chart of the study area, showing drainage basin (INEGI, 1996) and the location of the sampling sites in the Magdalena-Almejas lagoon complex. Stars represent soil sample locations.

Surface sediment samples were collected from a small motor boat during August 1998 using a Van Veen grab sampler. Locations of sampling stations of the study area and principal arroyos of drainage basin are shown in Figure 1.
The entire depth of sampling was about 10 cm of the sediment mixed together. The samples were spooned off the grab into the pre-cleaned polyethylene packets and were stored in a freezer until to be processed. They were thawed before the treatment and split in subsamples for different kinds of the analysis. Grain-size analysis of the sediments was done by standard sieving procedure (Folk 1974). The determination of total carbon and organic carbon in sediments was based on the rapid combustion of two subsamples (with and without treatment by hydrochloric acid) in a tubular furnace at 850 ^{o}C using oxygen as the carrier gas. The resulting carbon dioxide was carried away by the oxygen flow into a coulomb cell of the Express-analyzer AN-7529, where it was absorbed by a solution of barium hydroxide at a controlled pH. The carbon content of each subsample was calculated from the titration data of the final Ba hydroxide solution and carbonate carbon was found by difference between total carbon and organic carbon contents (Ljutsarev 1987).

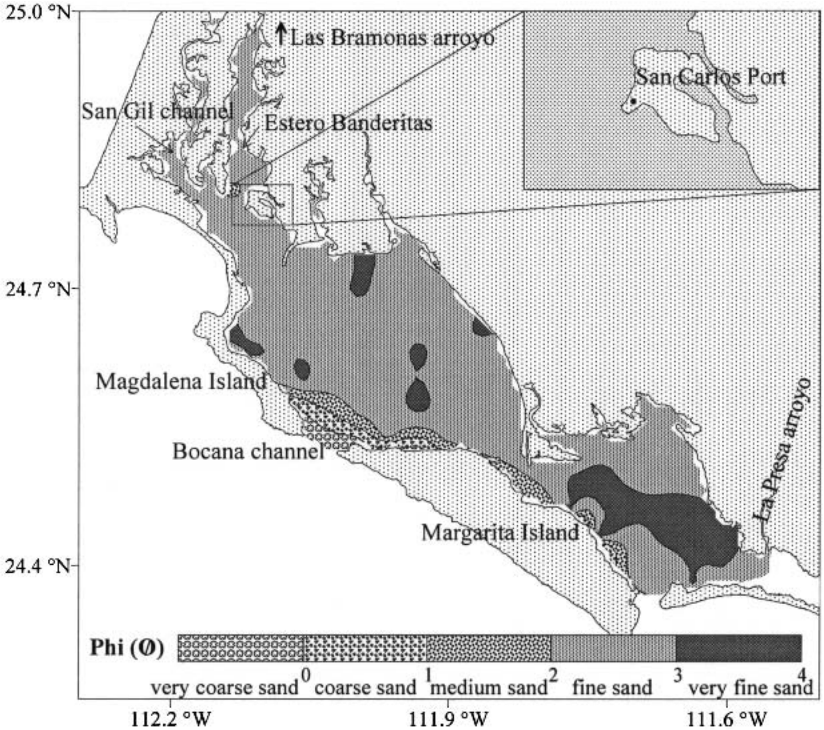

Figure 2. Spatial distribution of grain-size of surficial sediments of Magdalena-Almejas complex. The fine sediments in the inner part of Almejas Bay are enriched in organic carbon (Figure 3b), possibly influenced by discharge from La Presa arroyo and the material input from the mangroves, while the coarsest sediments are mainly biogenic carbonates (Figure 3a) with some admixture of heavy minerals and rock fragments.

Arsenic contents of subsamples of finely-ground dried sediment were determined using instrumental neutron activation analysis (Shumilin et al. 2001). Standard reference materials SRM 1646a "Estuarine sediment", IAEA-356 "Polluted marine sediment" and SD-N-1/2 "Contaminated marine sediment" (IAEA) have provided reliable precision and exactitude. Standard error was 8% to As and less than 1 % for total and inorganic carbon.

RESULTS AND DISCUSSION

The distribution of grain sizes (expressed as "phi" units) of the surface sediments is shown in Figure 2. Fine sands prevail, with some areas of the floor covered by very fine sands, mainly in the central portions of both lagoons, with coarse and very coarse sands indicating more dynamic environments near the Bocana channel.

Table 1. Arsenic concentrations (mg kg^{-1}) and enrichment factors (EF= $(As/Sc)_{sample}$:$(As/Sc)_{crust}$) in soil samples from the drainage basin and in surface sediments of the Magdalena-Almejas lagoon: range underlined; average ± S.D (below)

Sedimentary material	As concentrations	Enrichment factor
Earth's crust - average abundance (Li & Schoonmaker, 2003)	1.6	1
Soil material (31 samples)	0.13 - 22.9 5.0 ± 5.0	1 - 62 13 ± 17
Marine sediments (110 samples)	1 - 34 11 ± 7	1 - 82 19 ± 14

Arsenic concentrations in the surface sediments and soil samples are shown in the Table 1.

These levels of arsenic in the sediments are higher than that of the earth's crust average (1.6 mg kg^{-1}), but the range is comparable with a that reported for uncontaminated marine and estuarine sediments (5 - 15 mg kg^{-1}), and the 23 mg kg^{-1} average for marine phosphorites (Li & Schoonmaker 2003; Neff 1997; Whalley et al. 1999). This difference also was observed with the enrichment factors (average EF= 19 for the marine sediments and average EF= 13 for the soil samples).
The spatial distribution of the arsenic contents in surface sediments is presented in Figure 4. High values (> 20 mg kg^{-1}) were found mainly in the sediments collected in front of San Carlos Port, in the zone adjacent to San Gil Channel, off the northeastern part of Magdalena Island, as well as in some areas in the central portions of Magdalena and Almejas Bays (> 10 mg kg^{-1}) (Fig. 4). This element is presumably associated with the accumulation of phosphate mineral fragments, supplied from phosphate-rich sedimentary rocks in the drainage area via Las Bramonas arroyo during episodic heavy runoff from tropical storms in late summer and fall (Fig. 1).Phosphorite-enriched sedimentary unit, exposed in the local drainage basins, was formed during late Oligocene to early Miocene age under conditions of high primary productivity driven by coastal upwelling (Piper 1991). Deposits of this mineral in the northeastern sector the drainage basin were subjected to the mining during the last decades of the XXth century but are presently abandoned (Secretaría de Comercio y Fomento Industrial 1999). Phosphorites from these deposits are composed mainly of calcium phosphates, all of which are varieties of apatite. Phosphorites contain high levels of phosphorus, silicon, calcium, and elevated levels of trace elements, often exceeding their average concentrations in the earth's crust (Boggs 1995). Arsenic is a common substitute for phosphorous in apatite minerals.

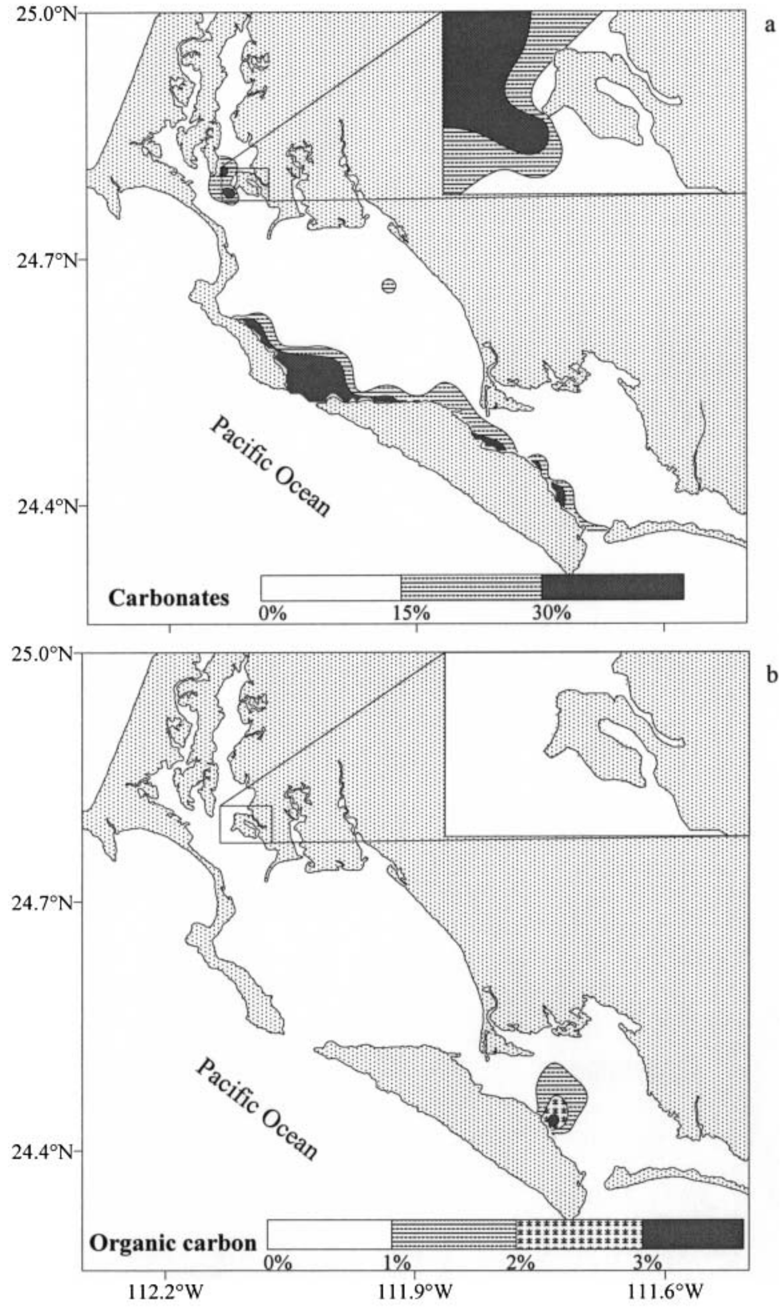

Figure 3. Spatial distribution of carbonates (a) and organic carbon (b) in surficial sediments of Magdalena-Almejas lagoon complex.

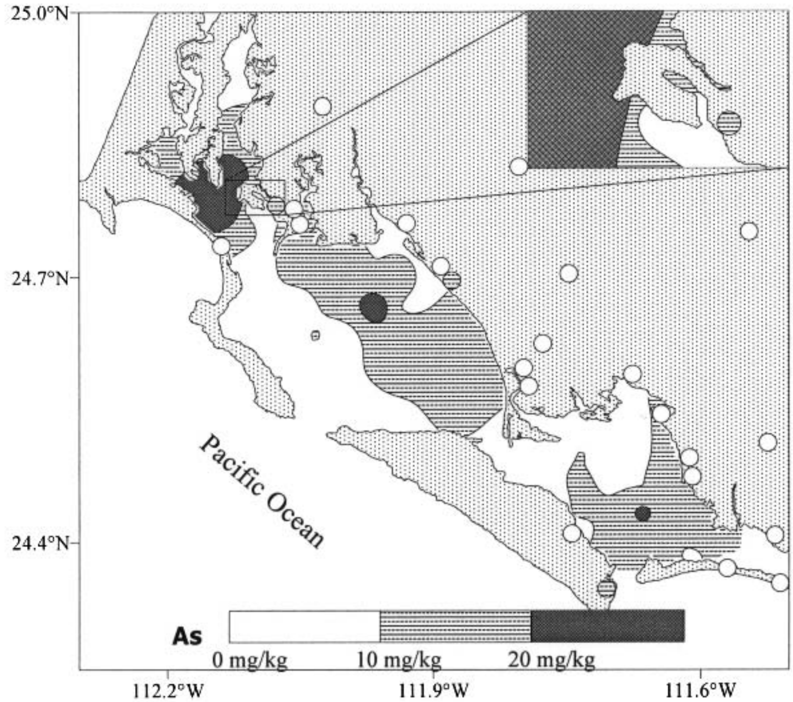

Figure 4. Spatial distribution of As concentrations in surficial sediments of Magdalena-Almejas lagoon complex.

The spatial distribution of arsenic concentrations in the lagoon sediments does not coincide with either of the two principal patterns found for other elements. The first pattern, found for Sc, Cr, Co, U, Zr, Zn, Cd, and rare earth elements, is controlled mainly by finer grain-size and higher organic matter content associated with the sediments of the deeper portions of both lagoons and the channel zones (Bocana and Rehusa channels). The second pattern, displayed by Fe, Pb, Ni, and Cu, is associated with high abundance of calcareous material (mainly mollusc shells and fragments) together with rock fragments derived from the erosion of the sedimentary and ultramafic igneous rocks of Magdalena and Margarita islands (Shumilin et al. in preparation).

The correspondance between these distributions of high arsenic and the high phosphorus contents found by Alvarez-Arellano (1995) is, however, not perfect.The observed differences could be caused by the use of different sets of sample stations in the two studies. An alternative possibility is the influx of arsenic along with seasonal Ekman-driven upwellings of nutrient-rich waters along the Pacific coast, its incorporation into the plankton followed by its deposition or adsorption onto sediment particles. This is not supported by our data, since low As values are encountered close to the main entrance to the bay, Bocana Channel.

Other aspects of the arsenic geochemical cycle in the Magdalena-Almejas lagoon complex have yet to be examined. Apart from the simple lithodynamic transport of phosphate minerals enriched in arsenic, some arsenic solubilization, especially through diagenetic processes in organic-rich mangrove sediments can be expected. Diffusion along concentration gradients in the interstitial water and secondary accumulation of arsenic on the seafloor via coprecipitation with iron oxyhydroxides or with insoluble sulphides in the reducing environment below the sediment surface cannot be excluded (Belzile & Tessier 1990; Caetano & Vale 2002).
The uptake of dissolved inorganic arsenic by phytoplankton was shown to be the dominant arsenic removal process in the Humber plume (Millward et al. 1997). This phenomenon could be also important in the highly productive waters of the lagoon complex, at least during blooms. Seaweeds are also abundant in the lagoons and they can also contribute to the arsenic cycle by accumulating dissolved inorganic arsenic species from seawater and converting it them arsenosugars, followed by further transformation through the marine food chain (Francesconi & Edmonds 1997).

The observed arsenic enrichment of sediments in the northern part of Magdalena Bay suggests the need for more detailed further investigation in Estero Banderitas and San Gil Channel to better understand the role of natural terrestrial and anthropogenic sources of this element. The latter would include the waste water discharge from the town of Puerto San Carlos and particularly of its cannery (sardine processing plant)

Acknowledgments. This study was supported by a grant (Project no. 966614) from the Coordinación General del Posgrado e Investigación (CGPI) of the Instituto Politécnico Nacional of Mexico).

REFERENCES

Álvarez-Arellano A (1995) Estudio geoquímico y de procedencia de arenas fosfáticas. Tesis Doctoral. Universidad Autónoma Nacional de México. México, D.F. (in Spanish)

Belzile N.,Tessier A. (1990) Interaction between arsenic and iron oxyhydroxides in lacustrine sediments. Geochim Cosmochim Acta 54: 103-109

Caetano M, Vale C (2002) Retention of arsenic and phosphorus in iron-rich concretions of Tagus salt marches. Mar Chem 79: 261-271

Francesconi KA, Edmonds JS. (1997) Arsenic and marine organisms. Adv Inorg Chem 44: 147-189

Goessler W, Maher W, Irgolic KJ, Kuehnelt D, Schlagenhaufen C, Kaise T. (1997) Arsenic compounds in a marine food chain. Fresenius J Anal Chem. 359: 434-437.

Instituto Nacional de Estadística, Geografía e Informatica (1996) Carta topográfica, Ciudad Constitución G11-12-13. (Scale: 1:250 000) INEGI Agascalientes, Ags. (in Spanish)

Kubota R, Kunito T,Tanabe S (2001) Arsenic accumulation in the liver tissue of marine mammals. Environ Pollut 115: 303-312.

Li Y.-H., J.E.Schoonmaker (2003). Chemical composition and mineralogy of marine sediments.pp.1-35. *In*:Treatise on Geochemistry. Vol.7. Sediments, Diagenesis, and Sedimentary Rocks. *Editor*, F.T. Mackenzie. Elsevier Publishing, Amsterdam

Ljutsarev AV (1987) Determination of organic carbon in sea-bottom sediments by dry combustion. Oceanology 26: 533-536

Millward GE, Kitts HJ, Ebdon L, Allen JI, Morris AW (1997). Arsenic species in the Humber Plume, U.K. Continental Shelf Res 17: 435-454.

Monografía geológico-minera del estado de Baja California Sur (1999) Secretaría de Comercio y Fomento Industrial, Consejo de Recursos Minerales, Pachuca, Hidalgo. México (in Spanish)

Murillo de Nava J.M. (1997). Sedimentary characteristics and chronology of Holocene aeolian deposits of the southern portion of Baja California Sur, México.Ph. D. Theses. University of Southern California, Los Angeles

Neff J (1997) Ecotoxicology of arsenic in the marine environment. A review. Environ Toxicol Chem 16: 917-927.

Piper D Z (1991) Geochemistry of a Tertiary sedimentary phosphate deposit: Baja California Sur, Mexico. Chem Geol 92: 283-316

Shumilin E, Páez-Osuna F, Green-Ruiz C., Sapozhnikov D, Rodríguez-Meza G., Godínez-Orta L (2001) Arsenic, antimony, selenium and other trace elements in sediments of the La Paz Lagoon, Peninsula of Baja California, Mexico. Mar Pollut Bull 42: 174-178

Shumilin E, Kalmykov St, Sapozhnikov D, Nava-Sanchez E, Gorsline D, Godínez-Orta L, Sapozhnikov Yu, Holguin-Quiñónez O, Rodríguez-Castañeda A (2000) Major and trace element accumulation in coastal sediments along southeastern Baja California studied by instrumental neutron activation analysis and ^{210}Pb age-dating. J Radioanal Nucl Chem 246: 533-541.

Whalley C, Rowlatt S, Bennet M, Lovell D (1999) Total arsenic in sediments from the western North Sea and the Humber Estuary. Mar Pollut Bull 38: 394-400.