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Arsenic and Mercury Contamination of Sediments of Geothermal Springs, Mangrove Lagoon and the Santispac Bight, Bahía Concepción, Baja California Peninsula

María Luisa Leal-Acosta · Evgueni Shumilin · Nicolai Mirlean · Dmitry Sapozhnikov · Vyacheslav Gordeev

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Abstract In order to find out the environmental impact on the coastal zone, the composition of sediments of the intertidal geothermal hot spring zone and adjacent area of Playa Santispac in the pristine Bahía Concepción (Baja California peninsula) was studied. High concentrations of As (13–111 mg kg^{-1}) and Hg (0.55–25.2 mg kg^{-1}) were found in the sediments of the geothermal sources. Arsenic and Hg concentrations decrease rapidly in the adjacent small mangrove lagoon sediments and reach background levels (0.7–2.6 mg kg^{-1} and 6–60 µg kg^{-1} respectively) in the marine sediments collected in front of Playa Santispac.

Keywords Geothermal hot spring sediments · Arsenic and mercury contents · Bahía Concepción · Baja California Peninsula

The biogeochemical cycles of arsenic and mercury in the coastal environment need special attention due to the interaction of these elements with different components of marine ecosystems and the toxicity of high concentrations of As and Hg to the marine biota (Clark 2001; Davis et al. 2008; Brinkmann and Rasmussen 2010). The levels of these elements in the environment depend on the existence and closeness of natural sources or on the intensity of human activities (Gerlach 1981; Polyakov et al. 1992). They can naturally appear in the areas of elevated tectonic and volcanic activity, particularly during the discharges of geothermal or hydrothermal fluids (Shiikawa 1983). Important anthropogenic sources of these elements to the marine environment are the mining and smelting activities, especially those occurring in the coastal zone (Nriagu 1994). As an example, in the Boleo mining district (central Baja California peninsula) the coastal marine sediment composition is strongly influenced by Hg—containing material, carried by arroyos of the drainage basin (Kot et al. 2009). In the Magdalena Bay, on the western part of Baja California peninsula, arsenic is introduced to the sediments from Puerto San Carlos harbor discharges, out washed fertilizers from the adjacent agricultural fields, as well as from the eroded material of local phosfatic deposits (Shumilin et al. 2005). Extremely high levels of As are also reported for solid wastes and arroyo bed sediments from the drainage basins of the El Triunfo-San Antonio mining district (southern Baja California peninsula) as a consequence of the mining and smelting of sulfidic ores during gold, silver and lead extraction which occurred there for

M. L. Leal-Acosta (✉) · E. Shumilin
Centro Interdisciplinario de Ciencias Marinas-Instituto Politécnico Nacional, Av. IPN s/n, colonia Playa Palo de Santa Rita, Apdo postal 592, 23096 La Paz, Baja California Sur, Mexico
e-mail: maluleal40@yahoo.com.mx

E. Shumilin
e-mail: eshumili@ipn.mx

N. Mirlean
Oceanography Geological Laboratory, Oceanography Institute, Federal University of Rio Grande, Rio Grande, Brazil
e-mail: dgeonmir@furg.br

D. Sapozhnikov
V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow, Russia
e-mail: sapozz@yandex.ru

V. Gordeev
P. P. Shirshov Institute of Oceanology, Russian Academy of Sciences, Moscow, Russia
e-mail: gord_vv@mail.ru

almost two centuries (Carrillo-Chavez et al. 2000). However, in Bahía Concepción, As and Hg are supplied to the pristine environment (mangroves, lagoon and adjacent Santispac Bight) by natural sources, such as intertidal geothermal hot spring waters, highly enriched in both elements and some other components (Prol-Ledesma et al. 2004). The origin of these geothermal springs presumably is the result of the action of the tectonically active El Requesón fault system and the weathering of the host rocks during crustal circulation of a mixture of ground water and sea water near heat sources (McFall 1968; Villanueva-Estrada 2007). The affected sediments and solid deposits of these intertidal geothermal springs are constituted by aggregates of opal, calcite, barite and Ba-rich Mn oxides, covered by silica-carbonate stromatolitic sinters (Camprubí et al. 2008). The sediments of the geothermal springs and the adjacent marine environment presumably may be naturally contaminated by As, Hg and some other elements, adsorbed or coprecipitated by freshly formed Mn and Fe oxyhydroxides or strongly hydrated silica (Canet et al. 2005). The objective of this study is to characterize the elemental composition of the surface sediments collected in the hot spring discharge points and adjacent area of Playa Santispac, in the northwestern part of Bahía Concepción, with emphasis on As and Hg as potential natural contaminants of mangroves and their adjacent marine ecosystem, as well as Santispac Bight itself, actively used by tourists as an all seasons recreation area.

Materials and Methods

Bahía Concepción is located in the Baja California peninsula, Mexico (Fig. 1). Three principal geothermal hot springs are located several meters above the mangrove lagoon near Playa Santispac, Bahía Concepción embayment. The temperature of the spring water varied in the range of 39–56°C and the pH values were between 6.9 and 7.3. Three samples of spring sediments, one sample of the crust wall of the second spring, four sediment samples of the mangrove lagoon and 19 marine sediment samples were collected in the study area directly or by scuba diving. The sampling stations are shown in Fig. 1. The sediment samples were put into pre-cleaned polyethylene bags and were stored in the freezer until treatment. They were defrozen, dried at 60°C, homogenized and split in subsamples. For the determination of arsenic about 0.2 g of sediment sample was extracted with a mixture of 5 ml of 33% H_2O_2 and 15 ml of Analar grade 14 M HNO_3 in a water bath (60°C) for 5 h. After acid treatment, the solutions were filtered and diluted with 2 M HCl to 100 ml. An aliquot of the solution was pre-reduced with potassium iodide during 3 h for As analysis. The final KI concentration in the analyzed solutions was 10%. Arsenic was measured by flame atomic absorption spectrophotometry coupled with a hydride generator using 1% $NaBH_4$ with 0.1 M NaOH and 2 M HCl. All samples were analyzed in triplicate. Coefficients of variation for all triplicates were <6%. The detection limit for As was 25 μg kg^{-1}. For mercury determination about 0.5 g of each sediment subsamples were placed in 125-ml digestion flasks, and 15 ml of a mixture (1:3) of concentrated nitric and sulfuric acids, together with 2 ml of concentrated perchloric acid were slowly added into each flask. These sediment-acid mixtures were left overnight and then digested at 120°C for 3 h in a block digester. After cooling, the flask solutions were filtered through Whatman # 44 filter paper, and the volume of the filtrates was adjusted in the 50 ml volumetric flasks using Milli-Q water. Total mercury concentrations were measured using a cold vapor system, coupled with an atomic absorption spectrophotometer (GBC 932AA). Each sample was analyzed three times, and the mean value was calculated. Maximum values of relative standard deviation (RSD) of individual samples were less than 4%. The detection limit for Hg in the sediments was 5 μg kg^{-1}. The accuracy of all analyses was ensured by digestion and analysis of PACS-2 and MESS-3 sediment Certified Reference Materials (National Research Council of Canada). Results obtained from these analyses were in agreement (±5%) with the certified values. Barium, iron, scandium and uranium content in sedimentary material were determined by instrumental neutron activation analysis. The

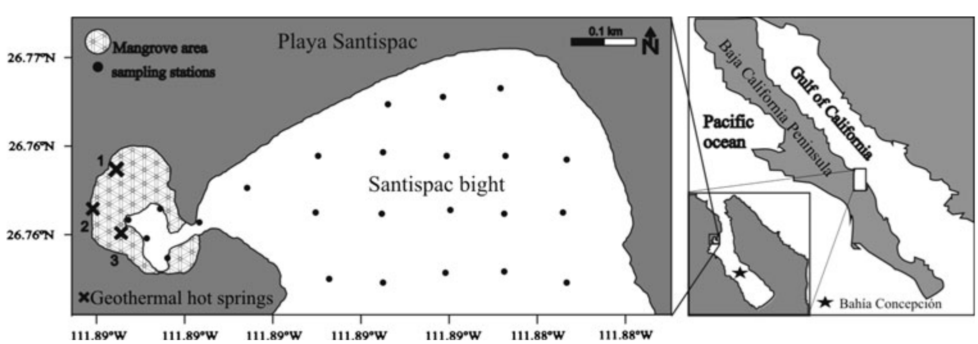

Fig. 1 Location of study area and sampling stations of surficial sediments

detection limits for this method were 80 mg kg^{-1} (Ba), 100 mg kg^{-1} (Fe), 0.05 mg kg^{-1} (Sc) and 0.2 mg kg^{-1} (U). Copper, manganese, nickel, and zinc contents were measured after complete strong acid digestion of the sediments by a flame atomic absorption spectrophotometer "Quantum-2A" (flame: air-acetylene) at the analytical laboratory of P.P. Shirshov Institute of Oceanology of the Russian Academy of Sciences. The detection limits in these analyses were 0.2 mg kg^{-1} (Cu), 0.6 mg kg^{-1} (Mn and Ni) and 0.1 mg kg^{-1} (Zn). Total and inorganic carbon contents were measured with total carbon analyzers TOC-VCPH (Combustion catalytic oxidation INDR method, PC-controlled, high-sensitivity model). Marine sediment samples were pulverized, dried, pre-treated with phosphoric acid, pH-adjusted to 2 or less and followed by a C_{org} content measurement. The total carbon (TC) was determined directly in the analyzer without chemical pre-treatment. The inorganic carbon content was calculated by difference between TC and C_{org}.

Results and Discussion

The trace element concentrations, inorganic carbon, organic carbon, major elements and carbonates in Santispac Bight's sediments: range underlined; average ± S. D. are shown in Table 1 and they were compared with upper crust average abundances (Wedepohl 1995). The contents of As and Hg in the sediments of the geothermal springs are the highest in all the dataset, exceeding their earth's crust average abundances. This could be due to the elevated concentrations of As and Hg in the geothermal fluids (280 mg kg^{-1} and 24 μg kg^{-1}, respectively) (Prol-Ledesma et al. 2004). The sediments of the geothermal springs are quite terrigenous with 9.1 mg kg^{-1} of Sc, while the lagoon's and Santispac Bight's sediments show lower average concentration of this element (1.8 and 2.4 mg kg^{-1}) respectively (Table 1).

The adjacent to geothermal hot springs sediments are predominantly biogenic with the range of 67.5–90.7% of $CaCO_3$ for the mangrove lagoon sediments and the range of 62.2 to 94.3% of $CaCO_3$ estimated from the determinations of inorganic carbon. However, for the third hot spring source sediments, which are constituted mainly by amorphous strongly hydrated freshly precipitated amorphous authigenic silica, have low contents of $CaCO_3$ (4.9%). On the other hand, the levels of organic carbon in these sediments (averaging 1.5%) are slightly higher than that the adjacent sediments with 1% of mean value for lagoon mangrove sediments and 0.6% for Santispac Bight sediments. The geothermal hot spring sediments have high concentrations of major components, principally MnO, Fe_2O_3 and Al_2O_3 (Table 1). Furthermore, the high contribution of SiO_2 (50% on average) is remarkable because its content is eight times higher than the found for the sediments of the adjacent to geothermal hot spring area

Table 1 Contents of trace elements (mg kg^{-1}) except Hg (μg kg^{-1}), inorganic carbon, organic carbon, major elements and carbonates (%) in Santispac area sediments: range underlined; average ± S. D. (below)

Elements	Geothermal hot springs	Mangrove Lagoon	Santispac Bight	Upper crust average abundance
As	13–111	0.7–2.8	0.5–4	2.0
	74 ± 53	1.5 ± 1	1.4 ± 1	
Hg	549–25200	14.8–233	6–60	56
	11130 ± 12700	83 ± 95	19 ± 14	
Mn	460–9120	102–255	31–125	527
	4027 ± 4527	173 ± 67	70 ± 27	
Sc	7.7–11	0.8–2.8	0.5–5.7	7
	9 ± 2	1.8 ± 0.8	2.4 ± 1.6	
C_{inorg}	0.6–10.2	8.1–10.9	8.1–11.3	
	4 ± 6	10 ± 1	10 ± 11	
C_{org}	0.3–2.2	0.02–2.3	0.01–4	
	1.5 ± 1.1	1 ± 0.9	0.6 ± 0.9	
$CaCO_3$	4.9–85.2	67.5–90.7	67.2–94.3	
	31.8 ± 46.2	80 ± 10	81 ± 9	
Al_2O_3	1.6–10.6	0.9–2.6	0.5–3.4	14
	6.6 ± 3.7	1.7 ± 0.8	1.8 ± 1.0	
SiO_2	39.2–56.1	3.1–12.3	1.6–10.4	64.9
	50 ± 8	7 ± 4	5.7 ± 3.2	
Fe_2O_3	0.8–4.3	0.4–1.2	0.2–1.5	4.3
	2.7 ± 1.5	0.7 ± 0.3	0.8 ± 0.5	

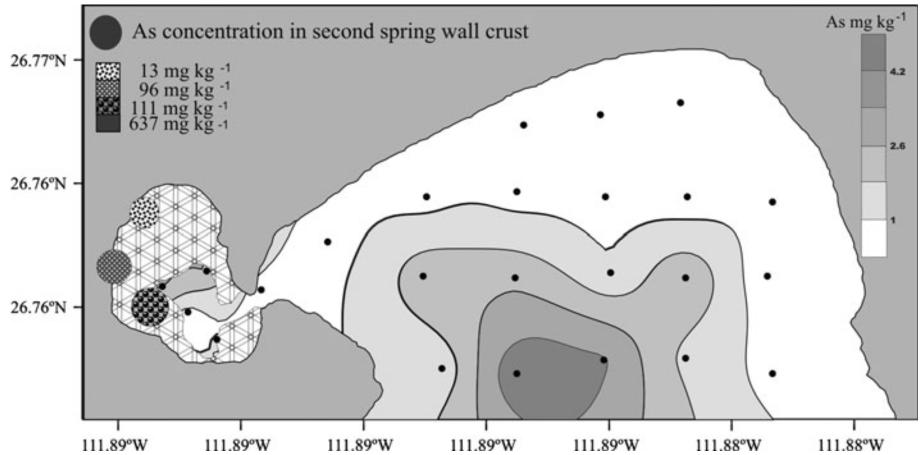

Fig. 2 Spatial distribution of the concentration of As (mg kg^{-1}) in the sediments of geothermal hot springs and Santispac area's sediments

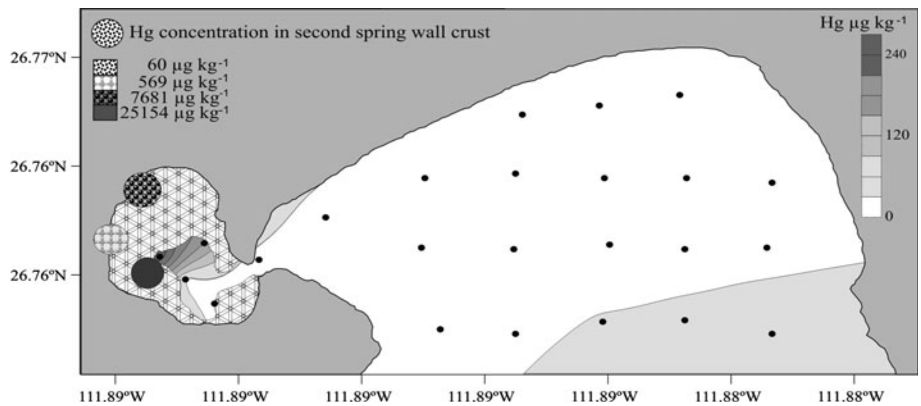

Fig. 3 Spatial distribution of the concentration of Hg (µg kg^{-1}) in the sediments of geothermal hot springs and Santispac area's sediments

(Table 1). Arsenic displays elevated contents in the sediments of the geothermal springs (13.4–111.2 mg kg^{-1}), low levels in the sediments of the mangrove lagoon (0.7–2.6 mg kg^{-1}) and somewhat lower contents in the marine sediments of the zone adjacent to Playa Santispac (0.5–4 mg kg^{-1}) (Fig. 2). The spatial distribution of mercury (Fig. 3) shows that the sediments of the geothermal springs of the mangroves of Playa Santispac are strongly enriched in Hg (0.55–25.2 mg kg^{-1}). The concentrations of this element decrease rapidly in the sediments of the mangrove lagoon (14.8–233 µg kg^{-1}) and vary in the range of 6–60 µg kg^{-1} in the marine sediments.

The geothermal hot springs located in Playa Santispac are important sources of As and Hg for the sediments of the mangrove lagoon and the adjacent part of Bahía Concepcion. However, due to the decrease of temperature and/or oxygenated sea water conditions these elements are rapidly incorporated in the solid phase near to hot springs, probably into the freshly forming Mn-oxides and silica (Canet et al. 2005). Elevated manganese contents (9,120 mg kg^{-1} and 2,500 mg kg^{-1}) were found in the sediments of the second and third geothermal springs, only 460 mg kg^{-1} in the first geothermal spring, decreasing till 106–255 mg kg^{-1} in the sediments of the mangrove lagoon and lower contents of 31–125 mg kg^{-1} in the marine sediments, collected in the Bahía Concepción in front of Playa Santispac. Even thought, the crust of the wall of the second geothermal spring on the mangrove area of Playa Santispac is characterized by very high contents of Mn (10.35%), As (637 mg kg^{-1}) and others components if compare with their upper crust average abundances, with the sediments of the proper hot spring and with the surficial sediments of the studied area (Tables 1 and 2).

Table 2 Crust wall composition of second spring (mg kg^{-1}), except Fe and Mn (%)

Element	Crust wall	Upper crust average abundance[a]
As	635	2.0
Ba	840	668
Cu	5.2	14.3
Fe	0.74	3.08
Hg	60.3	0.056
Mn	10.35	0.0527
Ni	7.5	18.6
U	4.65	2.5
Zn	21.8	52

[a] Average values for upper continental crust (Wedepohl 1995)

These hot geothermal springs are probably affecting the marine ecosystem of the adjacent part of Bahía Concepción. However, the evaluation of the accumulation of As and Hg in the marine biota and the effects on edible marine organisms is necessary in this area for further biogeochemical and ecotoxicological studies.

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