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# Intertidal geothermal hot springs as a source of trace elements to the coastal zone: A case study from Bahía Concepción, Gulf of California

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ABSTRACT

We investigated the influence of the intertidal geothermal hot spring (GHS) on the biogeochemistry of trace elements in Santispac Bight, Bahía Concepción (Gulf of California). The geothermal fluids were enriched in As and Hg mainly in ionic form. The suspended particulate matter of the GHS had elevated enrichment factor (EF) > 1 of As, Bi, Cd, Co, Cu, Mn, Mo, Sb, Sn, Sr, Ti, U and Zn. The sediment core from GHS1 had high concentration of As, Hg, $C_{org}$, S, V, Mo, and U and the extremely high EF of these elements at 8 cm of the core. The maximum bioaccumulation of As and Hg was in seaweeds *Sargassum sinicola* collected near the GHS2. The results confirm the input of trace elements to the coastal zone in Bahía Concepción from geothermal fluids and the evident modification of the chemical composition of the adjacent marine environment.

## 1. Introduction

Trace elements play important roles in the ocean as nutrients, as tracers of processes and as contaminants. However, the knowledge about their sources, sinks, internal cycling and chemical speciation within the ocean is limited (GEOTRACES, 2006). The supplies of trace elements to the coastal zones from the continent across rivers, atmospheric deposition and anthropogenic activities have been studied over the last decades (Chester and Jickells, 2012). Others sources such as submarine groundwater discharges (SGD) and shallow submarine hydrothermal vents have been assessed recently (Santos et al., 2011; Pichler et al., 1999). However, the influence of intertidal geothermal hot springs on the biogeochemistry of trace elements in the adjacent marine environment is still poorly understood. The presence of the intertidal geothermal springs in the coastal zones is related to tectonically active plate boundaries (Tarasov et al., 2005). The geothermal fluids generally are a mixture of meteoric water with heated, acidic and anoxic seawater enriched in some major and trace elements such as Si, Fe, Mn, Ba, Ca, and As, products of the water-rock interaction (Vidal et al., 1978; Pichler et al., 1999; Wheat and Mottl, 2000; Dias et al., 2010). When the geothermal fluids are discharged to the adjacent marine environment, the biogeochemical processes in these zones may be complex also because they occur in the euphotic zone. Typically, when the fluids are discharged to the seawater, the Fe/Mn oxides and sulfide minerals precipitate and the adjacent sediments are enriched in several trace elements, especially arsenic (Canet et al., 2005; Pichler and Veizer, 1999). Potentially, if the precipitates are formed in anoxic conditions, they can be a source of dissolved trace elements including potentially toxic elements (PTEs) to the seawater by diffusion in the water-sediment interface (Santos et al., 2011). Therefore both geothermal fluids and pore water from the sediments could be sources of trace elements, which remain in the neighboring seawater and are available to local biota (Price et al., 2013; Leal-Acosta et al., 2013). The effects of the intertidal geothermal fluids discharged in mangroves areas are even less known. These ecosystems are typically sink of organic matter in the marine sediments and its oxidation could generate anoxic conditions in the sedimentary column. It is unknown actually how the geothermal fluids mixed with seawater influence the distribution and biogeochemical transformation of trace elements in the water column (dissolved and particulate fractions) and in the

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sedimentary environment adjacent to the intertidal geothermal hot springs in mangrove areas.

The goal of this study is to evaluate the biogeochemical fate of trace elements including the potentially toxic elements (As and Hg) in the water and sedimentary columns near to intertidal hot springs in the mangrove area of Santispac Bight, Bahía Concepción (Gulf of California). Another objective is to know the effect of the fluids on the biota adjacent to the intertidal hot springs using the brown seaweed *Sargasum sinicola* as a bioindicator.

### 1.1. Intertidal geothermal hot springs in Bahía Concepción, Gulf of California

The intertidal geothermal hot springs in the Bahía Concepción are part of the numerous sites identified in the western coast of the Gulf of California (GC), recognized as a tectonically active region (Ledesma-Vázquez and Johnson, 2001; Barragán et al., 2001). The origin of geothermal springs is presumably a result of the action of the El Requesón fault system and the weathering of the host rocks during crustal circulation of a mixture of groundwater and seawater near to the heat sources (McFall, 1968; Villanueva-Estrada et al., 2012). The outflowing waters in the adjacent zone of the Bahía Concepción were identified using $^{222}$Rn radioactivity as a tracer (Santos et al., 2011). The intertidal geothermal hot springs are related to a reservoir composed by meteoric water mixed with seawater, according with their isotopic composition (Barragán et al., 2001). Shallow submarine hydrothermal vents exist in the same bay located at 5 m depth in Mapachitos at 10 km south of the Santispac Bight (Prol-Ledesma et al., 2004). Such hydrothermal vents have been characterized as a source of arsenic as a potentially toxic element (Villanueva-Estrada et al., 2013). The intertidal geothermal hot springs of Santispac Bight is a different scenario because the fluids are discharging in a small lagoon surrounded by mangrove trees. However, it is unknown about the dispersion of fluids in the area. Our previous results related to the geochemistry of the surficial marine sediments of Santispac Bight have shown an accumulation of the PTE As and Hg, especially in the surficial sediments of mangrove lagoon enriched in organic carbon (Leal-Acosta et al., 2010). Elevated As (635 mg kg$^{-1}$), Mn (10.3%), Hg (60.3 mg kg$^{-1}$), Ba (840 mg kg$^{-1}$), and U (4.65 mg kg$^{-1}$) contents were detected in the wall crust of the hot springs adjacent to the lagoon (Leal-Acosta et al., 2010).

## 2. Material and methods

### 2.1. Study area

Bahía Concepción is located in the Gulf of California (26° 33′ to 26°53′ N and 111° 42′ to 112° 56′ W) and has 40 km longitude. It is a semiarid region with an annual precipitation range of 200 to 731 mm and an annual temperature range of 6.5 to 45 °C, classified as semiwarm climate (García, 1973). The bathymetry is characterized by the maximum depth of 38 m to the south of the bay and the average depth in the central part of the bay is of 30 m (Ponte et al., 2012). The type of the tides in the bay is semidiurnal ranging from 59 cm at the entrance and 75 cm at the head (Obeso-Nieblas et al., 1996). The water dynamic showed some spots of cyclonic circulation in the head and central part of the bay, the water current follows the wind direction in the surface and a recirculation pattern in opposite way (Ponte et al., 2012). The drainage basin of Bahía Concepción is dominated by volcanic and volcanoclastic rocks, marine and continental sedimentary rocks, lava flows, domes and recent pyroclastic rocks (Pliocene-Quaternary) also occur, and the basement consists of a series of Cretaceous granitic rocks (Camprubí et al., 2008). The intertidal hot springs are located in the north-western part of the bay, and they are surrounded by a mangrove environment (Forrest et al., 2005; Prol-Ledesma et al., 2004).

**Table 1**
Samples description, location and physicochemical parameters.

| Sample | Sampling depth, m | Description | T, °C | S, ‰ | pH | $O_2$, mg L$^{-1}$ |
|---|---|---|---|---|---|---|
| GHS1 | 0.3 | Geothermal hot spring in mangrove area | 56 | 40 | 7.7 | 0 |
| SWL | 3 | Seawater collected in small lagoon | 29 | 40 | 8.1 | 2.7 |
| GHS2 | 0 | Geothermal hot spring in the beach | 58 | 35 | 7.7 | 2 |
| MW1 | | Site of reference (middle of the bay) | | | | |
| | 2 | | 20 | 35.76 | 9.2 | 7.1 |
| | 15 | | 19.4 | 35.71 | Nd | Nd |
| | 24 | | 18.3 | 35.79 | Nd | Nd |
| RW | | Site of reference (south of the bay) | | | | |
| | 2 | | 20 | 35.76 | 9.3 | 7.1 |
| | 14 | | 19.9 | 35.71 | Nd | Nd |
| | 26 | | 18.8 | 35.79 | Nd | Nd |

Nd means not determined.

### 2.2. Sampling

Our sampling was carried out in June of 2010 and includes the collection of water samples from two intertidal hot springs, the first one located in the mangrove area (GHS1) and the second from the beach located 500 m to the south (GHS2) (Table 1). Another water sample (SWL) was collected adjacent to GHS1 from a small lagoon surrounded by mangroves trees. The reference samples MW1 and RW were collected from the middle and south of the bay respectively, far from the intertidal hot spring (Fig. 1). The water samples were collected by hand with polyethylene gloves into precleaned 0.5-L high-density polyethylene bottles, or from a boat using a Niskin bottle and transported on ice to the laboratory for subsequent analysis. The samples were filtered through 0.45 μm Nuclepore filters as soon as possible after collection. The pH values, temperature, and dissolved oxygen concentrations were registered "in situ" at each station using a portable "Horiba U-10 Water Quality Checker" (Horiba Instrument Inc., Ann Arbor, MI, USA) and the salinity values were measured by a "Sea-Bird 911 *plus*" CTD probe. A sediment core was collected from the mangrove area near GHS1 (1 m) during a low tide by pushing a polypropylene tube manually into the sediments (Fig. 1). The extracted sediment core was cut with a plastic knife into 1 cm thick sub-samples, stored in plastic bags and transported on ice to the laboratory. Some samples of brown seaweed (*Sargassum sinicola*) specimens were collected manually by scuba divers at the Santispac Bight and outside it. They were rinsed several times in local seawater and the sand and epiphytes were removed by hand. Then the samples were placed in plastic bags and transported on ice to the laboratory.

### 2.3. Sample treatment and analytical procedures

#### 2.3.1. Dissolved trace elements

Dissolved trace elements As, Cu, Fe, Hg and Mn were determined in the filtered water samples using Whatman Nuclepore Polycarbonate Membranes (0.45 μm). Mercury was analyzed using a TECRAN® instrument with a cold-vapor atomic fluorescence spectrophotometer (CVAFS) method according to USEPA recommendations (EPA, 2002). The analysis procedure for determination of mercury was described in Leal-Acosta et al. (2013). The detection limit of the analysis of Hg in water was 0.2 ng L$^{-1}$, and the system blank demonstrated as much as 0.44 ± 0.1 ng L$^{-1}$. The analysis includes the determination of dissolved reactive mercury ($Hg_R$), which is mostly ionic ($Hg^{2+}$) plus elemental Hg, as well as the labile Hg found in weakly bound inorganic and organic complexes. The total dissolved mercury ($Hg_T$), including all