



# Trace elements in two wetland plants (*Maytenus phyllanthoides* and *Salicornia subterminalis*) and sediment in a semiarid area influenced by gold mining

Martha A. Sánchez-Martínez<sup>a,\*</sup>, Rafael Riosmena-Rodríguez<sup>a</sup>,  
Ana J. Marmolejo-Rodríguez<sup>b</sup>, Alberto Sánchez-González<sup>b</sup>

<sup>a</sup> Programa de Investigación en Botánica Marina, Departamento de Ciencias Marinas y Costeras, Universidad Autónoma de Baja California Sur, Km 5.5 carretera al sur, La Paz, BCS 23080, Mexico

<sup>b</sup> Centro Interdisciplinario de Ciencias Marinas del Instituto Politécnico Nacional, Av. IPN s/n, Col. Playa Palo de Sta. Rita, 23096 La Paz, Baja California Sur, Mexico

## HIGHLIGHTS

- Based on quality guidelines, basin sediments may cause harmful effects on biota.
- Element concentrations in plants were smaller than in sediments.
- Trace element contents were greater in root than in aerial parts of plants.
- *M. phyllanthoides* can be considered not efficient for bioaccumulation of elements.
- The roots of *S. subterminalis* can be considered accumulator of Cu and Zn.

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## ABSTRACT

Trace element (TE) concentrations were determined in sediments and plants collected from an evaporite basin near the mining district of El Triunfo, Baja California Sur. The elements were measured using ICP-MS. The TE concentrations in arroyo banks and beach sediments are close to background levels. According to the criteria of toxicity (ERL and ERM), the evaporite basin sediments may cause harmful effects on marine biota due to high average concentrations of As (233 mg kg<sup>-1</sup>), Cd (10.5 mg kg<sup>-1</sup>), Pb (970 mg kg<sup>-1</sup>) and Zn (598 mg kg<sup>-1</sup>). In general, the TE concentrations in tissues of *M. phyllanthoides* and *Salicornia subterminalis*, are less than sediment concentrations and follow the pattern: Zn > Cu > Cd > Pb > As > Sb. The average bioconcentration factor (BCF) values for almost all elements are very low (<1), except for Cu and Zn in root of *S. subterminalis* (BCF > 1). The translocation factor (TF) values were <1 except for Cd in *S. subterminalis*.

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## 1. Introduction

Mining activities in semi-arid areas have generated tons of unconfined mine tailings, which are characterized by being formed of fine particles with traces of sulfide minerals such as pyrite (FeS<sub>2</sub>), galena (PbS), sphalerite (ZnS), chalcopyrite (CuFeS<sub>2</sub>) and arsenopyrite (FeAsS) (Carrillo, 1996; Bhattacharya et al., 2006; Krysiak and Karczewska, 2007; Pulford et al., 2009). Other

minerals commonly present in mine tailings are oxidized sulfide ores like arsenolite (As<sub>2</sub>O<sub>3</sub>), greenockite (CdS), covellite (CuS), anglesite (PbSO<sub>4</sub>), cerussite (PbCO<sub>3</sub>), smithsonite (ZnCO<sub>3</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>) which mostly are associated with fine particles of iron oxyhydroxides (Moncur et al., 2005; Navarro-Flores and Doménech-Rubio, 2010). The easy dispersion of fine particles by wind action and rain cause the migration of trace elements (TE) (i.e. As, Cd, Cu, Pb, and Zn), also known as potentially toxic elements (PTE), which can be toxic to organisms at high concentrations (Castro-Larragoitia et al., 1997; Moncur et al., 2005; Krysiak and Karczewska, 2007; Taylor and Hudson-Edwards, 2008; Espinosa et al., 2009; Navarro-Flores and Doménech-Rubio, 2010; Armienta et al., 2010; Marmolejo-Rodríguez et al., 2011; Sánchez-Martínez et al., 2013). Eventually, the water and the polluted sediments

\* Correspondence to: Marine and Coastal Sciences Department, Universidad Autónoma de Baja California Sur, Km 5.5 carretera al sur, La Paz BCS 23080, Mexico.  
E-mail address: [masm\\_quimica@yahoo.com.mx](mailto:masm_quimica@yahoo.com.mx) (M.A. Sánchez-Martínez).

coming from mining sites are displaced towards the mouths of river systems, where they may affect estuaries and coastal areas (Osher et al., 2006; Filgueiras et al., 2002; Audry et al., 2004).

The mining zone of El Triunfo in Baja California Sur, Mexico, was exploited for Au and Ag from the middle of the 18th century until 1983 (Carrillo, 1996; Volke-Sepúlveda et al., 2003). The main source of pollution with PTE (As, Cd, Pb, Sb and Zn) of the surface sediments of the Hondo-Las Gallinas-El Carrizal arroyo and an evaporite basin that is at the mouth of this arroyo are unconfined mining wastes and tailings of this mining district (Marmolejo-Rodríguez et al., 2011; Sánchez-Martínez et al., 2013).

The interaction of PTE with biota has wide applications mainly as an indicator of the bioavailability of PTE in sediment as well as the potential for organisms to accumulate elements in their tissues (Williams et al., 1994). Mangrove ecosystems (water, sediments and biota) may efficiently retain TE and prevent movement of TE to adjacent aquatic systems (MacFarlane et al., 2003; Bayen, 2012; Usman et al., 2013). The contents of TE have been reported for different mangrove systems around the world (MacFarlane et al., 2003; Defew et al., 2005; Qiu et al., 2011; Bayen, 2012; Usman et al., 2013). The TE accumulation in mangrove plants depends on a combination of several factors: mangrove species, bioavailability of elements in sediment, exclusion in the root or physiological adaptation of mangrove plants to prevent bioaccumulation (Bayen, 2012).

Marsh grasses, such *Salicornia spp.* are used as bioindicators of sediment quality because they can grow in extreme conditions of salinity and TE content, and may accumulate high levels of As, Cd, Cu, Pb and Zn, without presenting phytotoxicity (Sharma et al., 2010; Smillie, 2015; Van Oosten and Albino, 2015). Halophytes are able to survive in saline environments by excluding salt from their tissues. Many of these grasses restrict entry of TEs to the aerial portion whilst hyper-accumulating elements within roots (Thurman, 1981).

Though previous studies have shown that mine wastes of El Triunfo have contaminated sediments of the evaporite basin with As, Cd, Pb and Sb (Sánchez-Martínez et al., 2013), there are no studies that evaluate the content and accumulation of PTE in sediments around the evaporite basin and in plants growing in these sediments affected by mining activities. Thus the objectives of this study were: (1) To determine the concentration of PTE (As, Cd, Cu, Pb, Sb and Zn) in surface sediments of the evaporite basin, frontal dunes and beach adjacent to this basin, (2) To determine sediment quality according to guideline values suggested by Long et al. (1995), (3) To determine the concentration of PTE (As, Cd, Cu, Pb, Sb and Zn) in *Maytenus phyllanthoides* and *Salicornia subterminalis* that grow on the periphery of the evaporite basin, and (4) To calculate bioconcentration and translocation factors. Due to the fact that the discharge zone of contaminated sediments coming from El Triunfo area is the Pacific Ocean coastal zone, this work examines anthropogenic influence on the deposition and dispersion of PTE in coastal sediments adjacent to the basin. This study also provides information on the capacity of *M. phyllanthoides* and *S. subterminalis* to accumulate PTE in their tissues, thereby inferring the relative bioavailability of PTE in evaporite basin sediments.

## 2. Materials and methods

### 2.1. Study area

The evaporite basin is a small hypersaline lagoon located at the mouth of the Hondo-Las Gallinas-El Carrizal arroyo towards the Pacific Ocean, in the municipality of La Paz, Baja California Sur, (23°37'53.07"N, 110°26'48.74"W to 23°37'32.56"N, 110°26'1.19"W) (Fig. 1). In periods of tropical storms or hurricanes

the basin accumulates water and extends along the coast. There is also seawater infiltration especially during high tides. The climate is very dry with a temperature range between 8 °C and 22 °C, and annual rainfall of 100–150 mm (Report of the Geological Mining Charter, La Paz G12-10-11, 1999). Summer winds have a south-east–northwest direction and are reversed for the winter (Troyo-Diequez, 2003). In late summer and autumn the influence of tropical cyclones is received, with most activity between August and September; late September trade winds produce occasional rain (Troyo-Diequez, 2003). In the arroyos of Baja California Sur most of the surface water is in the form of seasonal streams, which are fast-flowing and only active during stormy weather. Previous regional studies in the evaporite basin have measured the PTE concentrations in two sedimentary cores. The normalized enrichment factors (NEF) showed that the sediment cores had a high enrichment of As, Pb, and Zn (Sánchez-Martínez et al., 2013).

### 2.2. Sampling methods

#### 2.2.1. Sediment sampling

Sediment samples were collected in polyethylene containers, previously washed with 15% HNO<sub>3</sub> and rinsed with distilled water. The sediments were collected in February and March 2015 at three sampling sites: (i) evaporite basin sediments, (ii) frontal dunes and beach sediments adjacent to the evaporite basin, and (iii) El Conchalito beach sediments. Three surface sediment samples were collected in the periphery of the evaporite basin (MS1 23°37'39.82"N, 110°26'33.09"W) on which plants *S. subterminalis* and *M. phyllanthoides* grow (Fig. 2). Surface sediments were also collected from arroyo banks of El Palmarito (MS2 23°35'14.88"N, 110°21'50.28"W), La Bocanita (MS3 23°34'11.82"N, 110°20'24.06"W) and La Muela (MS4 23°30'46.2"N, 110°17'19.26"W) southeast of the evaporite basin (Fig. 2). The clastic material from MS2, MS3, and MS4 comes from arroyos without influence by the El Triunfo mining district. We also collected four surface samples from coastal dunes (SD 23°37'36.7"N, 110°26'35.0"W to 23°37'30.9"N, 110°26'19.8"W) and four surface samples of beach sand in the intertidal zone adjacent to the evaporite basin (SI 23°37'35.4"N, 110°26'36.1"W to 23°37'29.1"N, 110°26'20.4"W). Beach sediments were also collected from a test pit (PVI 23°37'38.1"N, 110°26'41.6"W) of approximately 50 cm depth (Fig. 2); the sediment was taken every 10 cm starting from the base to the surface. El Conchalito is located in Playa Palo de Santa Rita colony, in the city of La Paz, Baja California Sur and is not influenced by mining activities. A sample of surface sediment (SL) was collected in the peripheral part of La Paz Lagoon (24°08'32.7"N, 110°21'19.4"W) in the mangroves of El Conchalito.

#### 2.2.2. Sampling plants

In February, March and April 2015, two samples (1 kg) of *S. subterminalis* shoots and roots (VS1) and leaves and roots from the mangrove *M. phyllanthoides* (VM1) were collected from the periphery of the evaporite basin (23°37'38.6"N, 110°26'34.9"W) (Fig. 2). A 1 kg sample of *S. subterminalis* shoots and roots (VS2) and 0.5 kg of mangrove leaves from *M. phyllanthoides* (VM2) was collected from El Conchalito beach (24°08'32.7"N, 110°21'19.4"W). Sample plants were placed in plastic bags and refrigerated until processed in the laboratory.

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