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Arsenic and uranium in the settling particulate matter and sediments of Alfonso Basin, La Paz Bay

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ABSTRACT: Arsenic and uranium contents in surface sediments of La Paz Bay, in a sediment core and settling particulate matter collected in Alfonso Basin are presented. Arsenic is most enriched in sediments of the southwestern bay, probably associated with terrigenous supply. Uranium accumulates in sediments of the deeper part of the embayment. The profile of uranium in the core is characterized by higher concentrations near the surface and lower contents below 40 mm. Uranium concentration maximum at 35 mm is probably related to low oxygen in the water column at the deposition time. The contents of As and U in settling particles from 2002–2008 were greatest in late spring-early summer (May-July 2002, 2007 and 2008). The accumulation timing corresponds with the intrusion of oxygen-depleted waters from the Equatorial Pacific Ocean into the Gulf of California. Maximum uranium and arsenic contents in the settling particles coincide with moderate "El Niño" of 2002–2003.

1 INTRODUCTION

Arsenic and uranium concentrations are commonly studied by the scientific community, because high contents of these elements are common in anthropogenically contaminated sediments. However, enrichments of As and U also can be the product of natural processes (Anderson 1981; Klinkhammer & Palmer 1991).

Some redox-sensitive elements are known to be enriched in reducing sedimentary environments of continental margins with low dissolved oxygen (Böning et al. 2004, 2009). Arsenic is such a redox-sensitive element, occurring as (hydr)oxoanions under oxic conditions, but can be adsorbed to metal oxides and other particles (Böning et al. 2004, 2009; Brumsack 1989; McManus et al. 2006).

Uranium, in oxygenated seawater is typically dissolved as an uranil-tricarbonate anion $[UO_2(CO_3)_3]^{4-}$ (McManus et al. 2006). However, the reducing conditions in oxygen depleted water may favor the reduction of uranium (+6) to much less soluble hydrolyzed species of uranium (+4), that tend to form particles and accumulate in sediments (Klinkhammer & Palmer 1991).

In addition to arsenic and uranium dissolved in sea water, these elements can be supplied to the ocean from the surrounding land masses. Arsenic is a component of a variety of continental and marine rocks. Uranium is frequently found in deep marine sedimentary formations, such as black shales (Brumsack 1989). Other sedimentary rocks enriched in U and As are phosphorites and phosphatic sandstones (Piper 1994).

The temporal variability of U contents recorded in sediment cores could be used in order to interpret redox conditions of the past. The distinction between authigenic and lithogenic U one can be made using a crustal uranium/scandium ratio. This evaluation is important to validate the use of this element as a proxy for paleoclimatic and paleoceanographic reconstructions (McManus et al. 2006).

The main objective of this work is to describe the spatial distribution (seafloor sediments) and small scale (settling particulate matter) versus large scale (sediment core) temporal variability of arsenic and uranium concentrations, in order to establish the processes controlling their behavior in the southern Gulf of California.

2 MATERIALS AND METHODS

2.1 *Study area and sampling*

La Paz Bay is located in the southern part of the Baja California Peninsula, near the city of

La Paz (Fig. 1). This embayment has a variable depth, ranging from less than 200 m beneath most of the Bay to a maximum depth of 410 m in a tectonic depression called Alfonso Basin.

A variety of rock types are exposed around La Paz Bay (Hausback 1984). The volcanoclastic rocks of the Comondú Formation include basaltic-andesitic volcanic breccias, sandstones and tuffs, that outcrop in the south-western part of the bay. The El Cien Formation includes marine mudstones, sandstones, phosphorites and conglomerates on the western coast of the embayment. Intrusive granitic-tonalitic complex of Sierra Las Cruces and the terrestrial (non volcanic influenced) Lomas de la Virgen Formation are rock formations distant from the Bay, but are still important. Sediment from the eroded rock units are episodically carried through arroyos into the bay, mainly during the passage of tropical cyclones.

Settling particulate matter was obtained with a Technicap® PPS 3/3 sedimentary trap, positioned at a depth of 300to 350 m (50–100 m above the sea floor). The time series represent a record between 2002 and 2009 with most samples collected with a periodicity of 7–15 days. Surface sediments were obtained from across the bay in August 1998 using a Van Veen grab. A sediment core was collected using a box corer in August 2008 (Fig. 1).

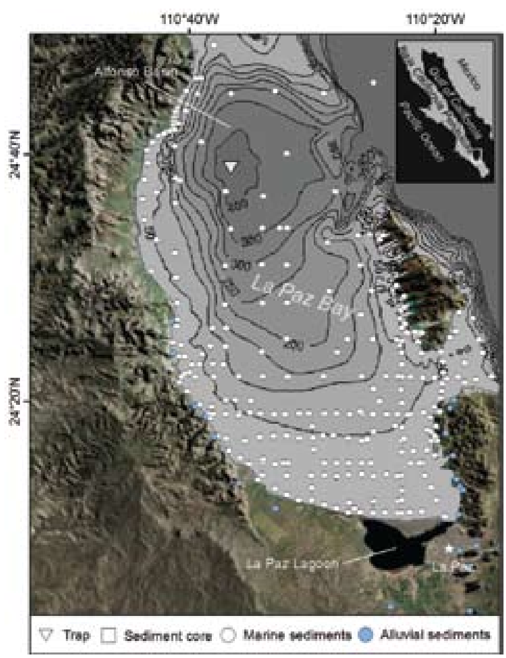

Figure 1. Location of the study area and sampling stations.

2.2 *Analyses and data treatment*

All samples, after their pretreatment, as described in Shumilin et al. (2001) and Silverberg et al. (2007), were analyzed for major and trace elements using instrumental neutron activation analysis (neutron flux 2.8×10^{13} n s^{-1} cm^{-2}). The accuracy and precision of the method was checked using certified reference materials of estuarine and marine sediments: NIST 1346, IAEA-356 and SD-N-1/2.

The linear sedimentation rate of the CA core was measured using the ^{210}Pb radiometric dating technique, as this core showed a normal exponential drop in ^{210}Pb activity as a function of depth. A regression model that assumed a constant input rate of ^{210}Pb yielded a sedimentation rate of 0.61 mm yr^{-1}.

The following software were used in order to obtain the presented results: STATISTICA 7, MatLab R2009b, Surfer 7, Global Mapper 10 and ArcGIS 9.3.

3 RESULTS AND DISCUSSION

The data on the elemental composition of the sediments and settling particulate matter is partially presented in Rodríguez Castañeda (2002, 2008) and will be provided on request from the first author.

General information on uranium and arsenic mean concentrations, standard deviations and ranges are presented in Table 1.

3.1 *Arsenic and uranium in surficial marine sediments*

Elevated contents of arsenic in sediment were found in the southern and southwestern part of the bay (Fig. 2).

This pattern is attributed to west to east littoral and nearshore transport of sediment along the southern coast. These are the product of eroded marine rocks of the El Cien Formation with

Table 1. Arsenic and uranium concentrations (mg kg^{-1}) in different sedimentary material from the La Paz Bay (in the numerator: ranges; in the denominator: average ± standard deviation).

Sedimentary material	Arsenic	Uranium
Alluvial sediments (n = 21)	1.0–27.0 11.0 ± 6.8	0.3–4.5 1.6 ± 1.3
Settling particulate matter (n = 182)	0.4–47.5 8.7 ± 7.1	0.4–42.8 4.8 ± 5.7
Surface marine sediments (n = 261)	0.5–43.4 11.0 ± 7.8	0.3–19.5 4.8 ± 3.0
Fine sediments of the CA core (n = 34)	0.4–9.7 4.4 ± 3.0	0.7–19.1 6.2 ± 4.6

elevated phosphate content (Rodriguez-Meza 1999; Rodriguez-Castañeda 2002). Similar accumulation of As was reported in the sediments of the northern part of the La Paz Lagoon (Rodriguez-Meza 1999; Shumilin et al. 2001).

Uranium presents a different spatial distribution than As. It is most abundant in the sediments of the northern part of the La Paz Bay.

The distribution of uranium contents seems to follow the bathymetry (Fig. 1), the highest concentration coinciding with the deepest part of the bay, Alfonso Basin. This location is distal from terrigenous input. These deep sediments consist mainly of fine-grained material high in organic carbon (Rodriguez-Castañeda 2002). Uranium could be enriched by its transfer from the dissolved to the particulate phase, due to the very low oxygen content in the lower part of the water column (de Diego & Douglas 1999).

3.2 *Arsenic and uranium in the sediment core*

Variations of arsenic and uranium concentrations with depth in the CA core of the finely-laminated Alfonso Basin sediments are shown in Figure 4.

Concentrations of both elements vary. For As, there is a concave shaped curve with a minimum near 75 mm. Uranium is characterized by higher contents above 40 mm and much lower contents below this level. There is a prominent U maximum at 35 mm core depth.

La Paz Bay may display variable oxygen concentrations (de Diego & Douglas 1999). Reducing conditions would presumably increase the uranium

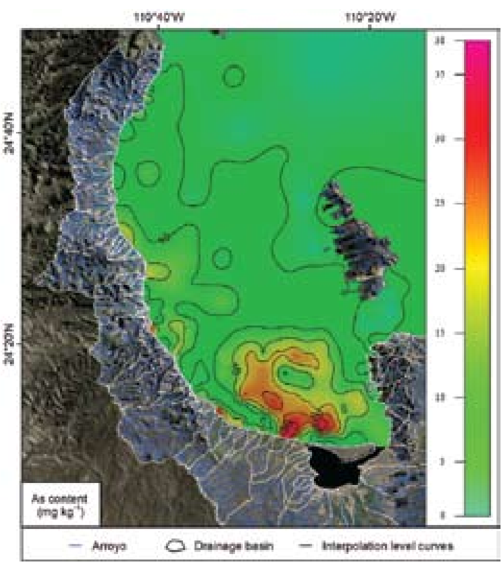

Figure 2. Arsenic content distribution in the surface sediments of La Paz Bay.

content in the sediment, which makes this element a suitable indicator of past changes in the oxygen content of the deeper water column. Accordingly to the ^{210}Pb dating results (0.61 mm yr^{-1}) we could suppose that the high levels of uranium point to low dissolved oxygen contents in the deep water between 1930 and 2008. The highest influence of the OMZ on U in Alfonso Basin would correspond to the period from 1945 to 1960.

3.3 *Arsenic and uranium in the sedimenting particulate matter*

The time-series of As and U contents in the sediment-trap-collected settling particulate matter, are displayed in Figure 5.

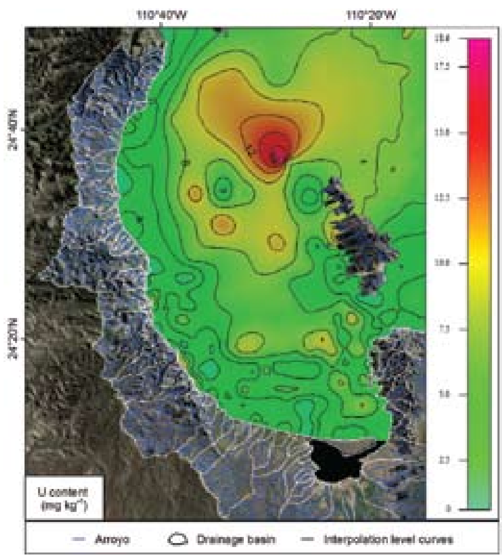

Figure 3. Uranium content distribution in the surface sediments of La Paz Bay.

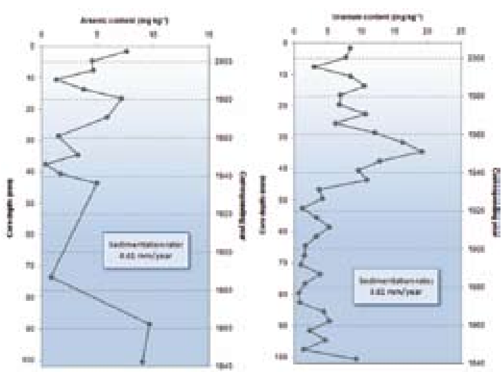

Figure 4. Vertical distribution of As and U contents in the CA core.

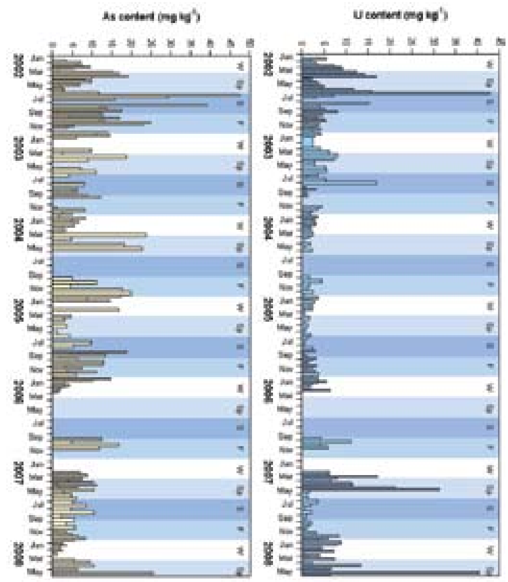

Figure 5. Arsenic and uranium content in settling particulate matter from the Alfonso Basin, during January 2002–May 2008 observation period.

Similarly to the sediment core, contents of both elements vary greatly in the settling particles (Fig. 5 and Table 1). However this data set has a much higher resolution and is exactly time-calibrated. It is clear that there is no evident periodicity, although maximum concentrations of both elements are typically favored in late spring—early summer. This effect was more evident in May–July of 2002 and occurred with lower intensity in late spring of 2007 and 2008. The intrusion of oxygen-depleted Superficial Equatorial Waters and Subsuperficial Subtropical Waters from the Equatorial Pacific Ocean into the Gulf of California, during late spring and summer, may be responsible for the observed enrichments. The entry of such waters into the Gulf of California may be enhanced during "El Niño" (Thunnel et al. 1998). For example, a moderate strength "El Niño" was reported for 2002–2003 (McPhaden 2004), which coincide with the highest As and U contents in particles of the Alfonso Basin.

3.4 *Further plans*

For better understanding of As and U behavior in the La Paz Bay additional studies are needed. It is planned to estimate the role of terrigenous sources that supply As and other elements into the bay. Another need is to ensure a continuous monitoring of oxygen vertical profiles near the sedimentary trap location in the Alfonso Basin, in order to explain the uranium and other redox-sensitive element behavior in the water column of this embayment.

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