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Short communication

Potential toxicity of chemical elements in beach sediments near Santa Rosalía copper mine, Baja California Peninsula, Mexico

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ABSTRACT

A total of 17 beach sediment samples were analyzed for the determination of thirty-one chemical elements to generate a geochemical data set from the Santa Rosalía mining area in the State of Baja California Sur (south), Mexico. Results indicate that the beach sediments were enriched in Cu, Zn, Co, Pb, Cd (3856, 2599, 635, 236, 240 mg kg^{-1}, respectively) and in Mn (2.01%) due to a century of mining and smelting activities. Comparison of these concentration with ecotoxicological sediment quality criteria (ERL, ERM, LEL, SEL) indicated the values of As, Cd, Co, Cr, Cu, Ni, Pb, Sr, Zn and Mn were higher than the permissible limits. Average values of the calculated geoaccumulation index (I_{geo}) suggest that the key elements such as Mn, Ba, Cd, Co, Mo, Pb, Sr, Zn are categorized in class 4 to 6 encompassing the strongly polluted to extremely polluted groups. The association and enrichment of the above elements are also well supported statistically (factor analysis) which points to the role of Fe-Mn oxides as the main scavengers for retaining these chemical elements.

1. Introduction

Trace metals are often transported into the coastal and marine environment by the local rivers, streams (*arroyos*) due to the influence of regular inputs of waste products generated by human activities. Studies on the concentration pattern of metals in sediments along beaches prove to provide direct evidence of the impact of various anthropogenic activities from adjacent terrestrial areas (Radenac et al., 2001; Uluturhan et al., 2011). Since many anthropogenic activities takes place in coastal marine environments, considerations of historic and ongoing sediment contamination by trace elements are needed to establish spatial and temporal monitoring programs for the implementation of suitable remedial actions to prevent the enrichment of toxic elements (Balls et al., 1997; Chapman and Wang, 2001).

Santa Rosalía in the State of Baja California Sur, Mexico is well known for its historical mining activities especially for Cu. A striking feature in the beach sediments of the present study is the impact of extensive mining of Cu and related elements during the past 100 years (1856–1965 in the "*El Boleo*" deposit; 1984 in the "*Santa Rosalia*" deposit). The Santa Rosalía smelter was said to be one of the leading procedures of metallic Cu during those periods (Wilson and Rocha, 1955; Conly et al., 2011). During the mining activities and ore processing periods various types of materials (industrial and mining wastes) were deposited in the beaches, which were subsequently transported by ocean currents as this drainage basin is tectonically active. Earlier reports indicate approximately 370 million tons of solid wastes were generated due to the mining and smelting activities. Previous studies stated that these beach sediments comprised nearly 3×10^6 tons of furnace slag that had been transferred from the dam site in the land to the adjacent local beaches and nearly 1.4×10^6 tons of mine tailings were disseminated from the dam region (Romero Gil, 1991; Huerta-Diaz et al., 2014). The region is also dominated by short-lived streams ("*arroyos*"), which flow between the mineralized zones that were mined for copper for more than a century. It is believed that the mining and processing of copper in the Santa Rosalía area has resulted in strong enrichment of trace metals in terrestrial zones and as well as in the sediments of Gulf of California

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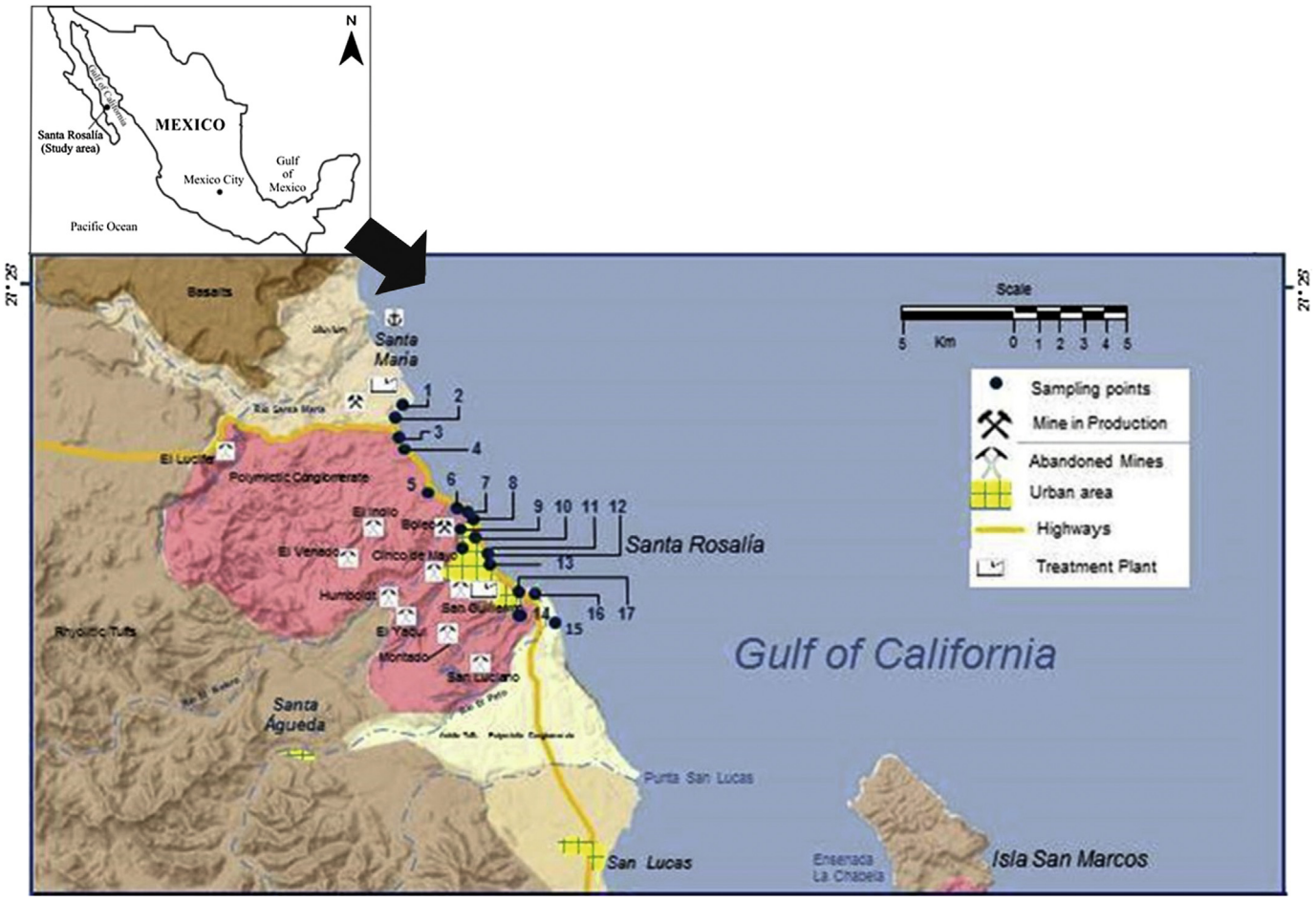

Fig. 1. Study area map with sampling locations in Santa Rosalía, Baja California, NW Mexico.

(Rodríguez-Figueroa, 2010; Shumilin et al., 2000, 2011, 2012, 2013). Geologically, rocks of Miocene age Comondu formation underlie the region and marine sedimentary rocks of the Infierno and Santa Rosalía formations of Pliocene and Pleistocene ages are also found here (Hausback, 1984).

In spite of several reports about the potential contamination of land and marine sediment resources from the prevalent trace metals of this region, new construction has been initiated in an effort to extend the mining activity in the northern region of Santa Rosalía. In order to understand the degree of enrichment and pollution, this study aims to identify the concentration pattern of major (Si, Al, Fe, Ca, Mg, Ca, Mg, Na, K, Mn) and trace elements (Ag, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Ho, Mo, Ni, Pb, Rb, Sb, Sc, Se, Sn, Sr, V, Y, Zn, Zr) in the inter-tidal beach sediments of the present study which is the impact of Cu mining and associated elements during the past 100 years in Santa Rosalía region of Baja California Sur, Mexico. This study focused on the variations in concentration of trace metals would suggest better strategic plans for a long term monitoring program in controlling the enrichment of trace elements in the beach sediment quality (see Fig. 1).

2. Materials and methods

Seventeen surface sediment samples were collected from the intertidal zones of Santa Rosalía beach front during the month of April 2011. In addition, mineral ore sample (2 samples) and mineral slag sample (2 samples) were analyzed to estimate their elemental concentration and for its utility in comparison studies. The top five centimeters of the sediment layers were collected using a plastic spatula and transported to the laboratory for further processing. Prior to the chemical analysis, sediment samples were dried at low temperature (below 40 °C) and powdered to 200 μm particle size. Sediment samples (0.25 g) were digested in teflon vials (acid washed prior to use) with HNO_3, HCl, $HClO_4$ and HF by using a programmable hot plate and heated to incipient dryness. Samples were redissolved in agua regia and the concentrations were determined using ICP-AES (Agilent 735 ICP) and ICP-MS (Perkin Elmer Sciex ELAN 6000) (Wei and Haraguchi, 1999). Standard reference materials PACS-2, MESS-3, and NIST-164a were used to determine the accuracy of the analysis and the reference values varied from 0.28 to 4.78% for major and 0.21–6.97% for trace elements.

Factor analysis was performed in order to identify the dominance of different element groups. Five factors (Factor 1, Factor 2, Factor 3, Factor 4 & Factor 5) were generated using Statistica software (Version 7.0). The factors were generated after normalization with the p value at 0.5 for better association and only significant values are included in the table. Likewise, the Müller's geo-accumulation indexes (I_{geo}) were calculated using the formula: $I_{geo} = \log_2 [(C_n/1.5B_n)]$, where North American Shale Composite (NASC) values and average Upper Continental Crust abundances (for values which were not present in NASC) were used as baseline concentrations B_n to define the classes of pollution for each element (Müller, 1979). The I_{geo} classification is classified as follows: Class 0: