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Anomalous Trace Element Composition of Coastal Sediments near the Copper Mining District of Santa Rosalía, Peninsula of Baja California, Mexico

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The ecological consequences of mining activities close to the ocean shore are a subject of great concern to the local populations and were explored in several studies carried out mainly in temporate climates (e.g. Canada and Western Europe: Achtenberg et al. 1999; Elbaz-Poulichet and Leblanc 1996; Macdonald and Crecelius 1994; Macdonald et al. 1991). Recently these have also become the object of biogeochemical investigation within an area characterized by a semi-desertic, hot climate (Wray 1998).

To extend our knowledge in this field of study, the Santa Rosalía mining district, situated on the east coast of the central part of the peninsula of Baja California was selected. The abundant copper carbonate mineral found there is supposedly of marine hydrothermal origin (Escandon 1995). The adjacent environment seems to have been strongly affected by former mining and ore processing.This activity was initiated by the French company "El Boleo" (1896–1954) and continued until 1984 by the Mexican enterprise "Santa Rosalía" (Rodríguez-Figueroa et al. 1998).

The drainage basin belongs to a zone of active tectonic deformation due to collisions of plates of the earth's crust, with marked signs of ancient volcanism and present day hydrothermal activity. The rocks of the study area are part of the Commondú Formation of the geological subprovince of the Sierra de La Giganta. The copper mines were abandoned during the 1980's for economic reasons. However, given more modern methods of mineral extraction and processing technology, they might be reopened.

The objective of our work was to elucidate the distributions of heavy metal concentrations (total Cu, Zn, Co and Pb) in sedimentary materials from the area.

MATERIALS AND METHODS

About 200 g of sediment were taken using a clean plastic shovel and sealable clean plastic bags during October 1997 from: 1) the beds of the principal ephemeral water courses ("arroyos") which cut across the zone of former mining operations, 2) tailing deposits on land, 3) beach sands, and 4)the adjacent sea floor (Fig. 1).

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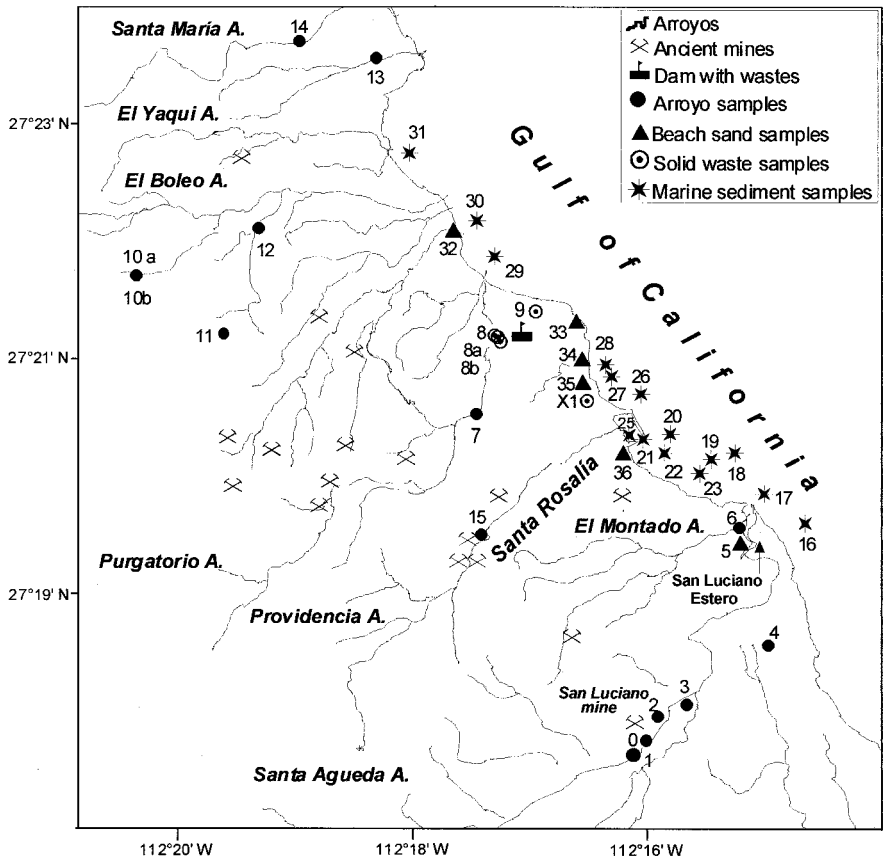

Figure 1. Location of sampling sites in the mining district of Santa Rosalía

In the laboratory, 100 mg of dried finely-ground sample was digested in Teflon beakers using a mixture of concentrated HNO_3, HF and HCl in a microwave oven at controlled pressure (120 PSI). The resulting solutions were analyzed by ICP-MS using a VG Elemental model PQ3 instrument and procedures recommended by Jarvis et al. (1996). Detection limits were better than 50 ppt. The calibration of the apparatus was performed with a multi-elemental standard solution (SPEX- High Purity). Matrix effects and instrumental drift were eliminated by the use of ^{115}In (10 ppb) as an internal standard. The validity of the analytical procedure was assessed by accuracy and precision tests comparing measured and certified reference values (MAG-1). All element determinations had a precision better than 3%. Statistical treatment of the data was accomplished by standard statistical software for personal computers (Statistica). Surfer-32 was used to draw the spatial distributions of the four elements in the coastal sediments.

RESULTS AND DISCUSSION

The data on heavy metal concentrations in different sedimentary materials of the Santa Rosalía mining district are presented in generalized form in Table 1. They support the conclusion of our previous report that marine sediments here have anomalously high contents of several elements (Rodríguez-Figueroa et al. 1998).

Table 1. Concentrations of Cu, Zn, Co and Pb in ppm of dry weight (ranges underlined; average ± S.D. below) in various deposits from the Santa Rosalía mining district

Element	Arroyo bed samples	Solid wastes	Beach sands	Coastal marine sediments
Cu	150-5760 2400±1800	790-33200 11000±11550	3100-30380 13420±12090	46-1950 420±609
Zn	83-3700 1500±1220	444-3350 1954±970	3141-26970 11670±10800	72-2750 510±710
Co	0.03-960 209±260	46-1250 436±440	680-6870 2840±2860	12-450 66±105
Pb	13-1620 360±440	37-610 320±230	460-2100 1100±720	12 -220 54±52

The distribution pattern of copper in samples taken from the arroyo beds, solid wastes, beach sands and coastal sediments is presented in Fig. 2a. The lowest contents of copper were found in the sample from the El Yaqui arroyo (St. 13, 169

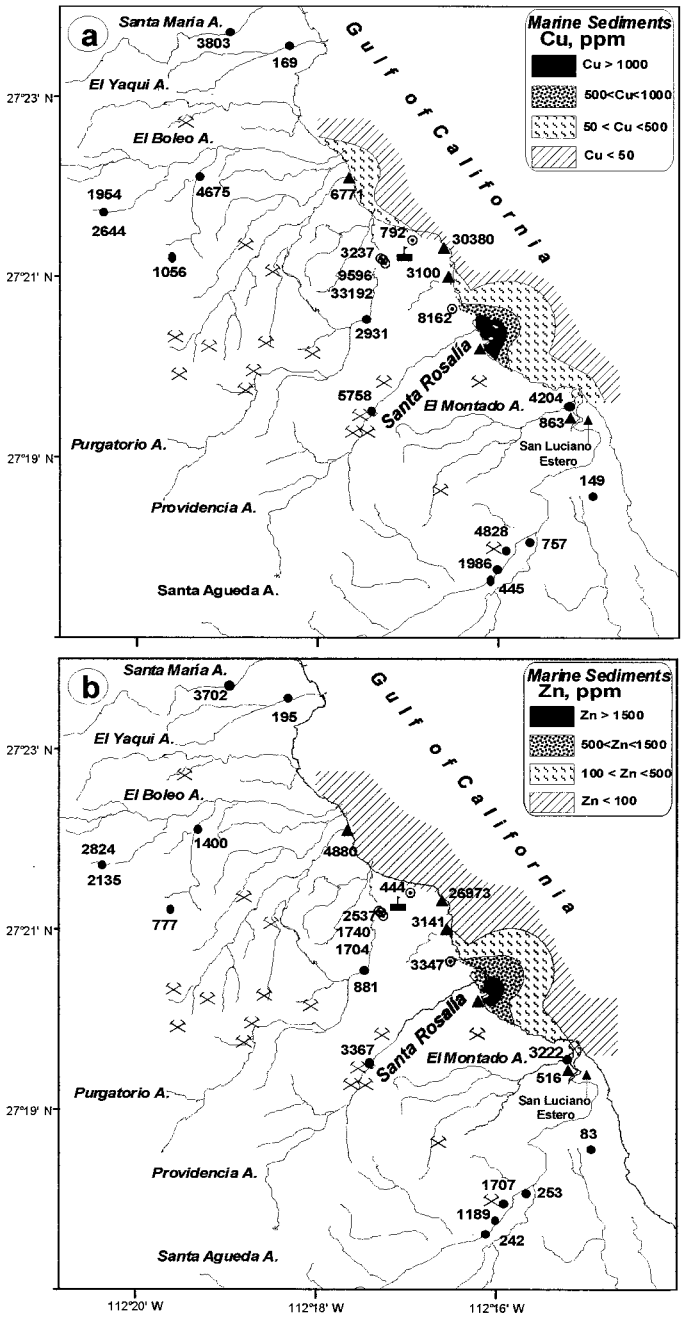

Figure 2. Spatial distribution of copper (a) and zinc (b) in continental and marine sediments in the mining district of Santa Rosalía.

ppm) and in the lower part of the Santa Agueda arroyo (St. 4, 149 ppm). These values probably represent the regional background contents of Cu in the arroyos not affected by copper mining, but they are still quite high (Cu content in the arroyos of the catchment basin of the La Paz Lagoon in southern part of the Baja California Peninsula amounted to only 10±9 ppm (Shumilin et al., in press). Copper is highly enriched in almost all samples of the Santa Agueda, Santa Rosalía, El Purgatorio and El Boleo arroyos, collected near or downstream of copper mines (445-5785 ppm) and deposits of solid wastes produced by ore processing (792-33192 ppm).

Numerous samples of beach and coastal sediments of the area near Santa Rosalía also display very high contents of copper. These exceed levels reported in many studies of the disposal of copper-rich tailings to adjacent coastal waters (Macdonald et al. 1991), as well as values found in other industrial zones and ports (Tkalin et al. 1996). They are much higher than values typically registered for the coastal sediments of the Gulf of California (Shumilin et al., in press) and of other coastal areas of marginal seas (Macdonald and Crecelius 1994; Páez-Osuna et al. 1986; Páez-Osuna and Osuna-López 1992). Maximum contents of copper for marine sediments were found in samples of St.21 (1859 ppm) and St.25 (1953 ppm), near the mouth of Santa Rosalía harbor. These are one or two orders of magnitude greater than maximal copper concentration recorded in sediments of the Mancha, Llano and Salada Lagoons in the state of Verazcuz, Mexico (50-70 ppm) (Villanueva and Botello 1998) and in the heavily polluted sediments of the industrialized zone (181 ppm in Golden Horn Bay, Vladivostok, Russia) (Tkalin et al. 1996). This "hot spot" of copper in Santa Rosalía harbor sediments seems to be limited in extent because sediments at the margins show much lower contents (48 ppm, St.16 and 46 ppm, St.31). The observed spatial distribution of copper in sediments indicates not only the position of the sites of largest inputs of copper-containing material on the shore, but reveals also the principal direction of transport of contaminated sedimentary material in the adjacent sea. Transport probably occurs toward the east and south (Fig. 2a), coinciding with the circulation scheme in these waters.

Contents of zinc in the samples of St.4 and St.13 (83 and 195 ppm , respectively) of the most pristine arroyos, as in the case of copper, can be accepted as regional background values. Samples of the arroyos of the mining zones reveal Zn contents as high as 3367 ppm at St.15 at the Santa Rosalía arroyo, 3222 ppm at St.5 in the mouth of the Santa Agueda arroyo, and 2824 ppm at St. 10 in the upper part of the El Boleo arroyo. Samples of solid wastes also display very high contents of Zn (up to 2537 ppm at St.8 in old solid wastes north of Santa Rosalía and up to 3347 ppm for the sample X1 in wastes within the village itself. Samples of beach sands in front of Santa Rosalía can have as much Zn as waste samples (e.g. 26973 ppm at St.33, collected on the shore directly in front of a broken dam which had been used to retain solid wastes). The pattern of Zn concentrations in surface sediments (Fig. 2b) is similar to that found for copper, with maximum contents in samples St.21 (2746 ppm) and St.25 (1516 ppm) collected near the mouth of Santa Rosalía harbor and minimum values outside the "hot spot "(72 ppm for the sample St.16 at

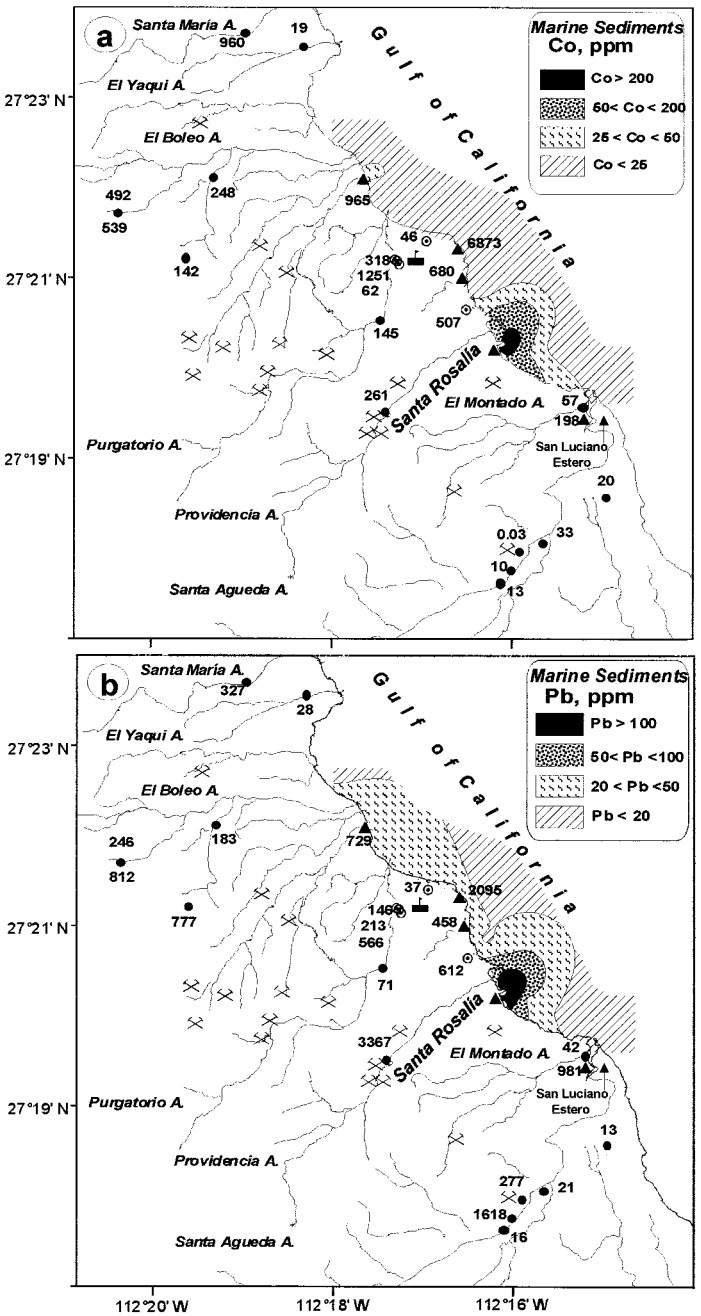

Figure 3. Spatial distribution of cobalt (a) and lead (b) in continental and marine sediments in the mining district of Santa Rosalía.

the southern end and 100 ppm for the sample St.16 at the northern end of the study area). As in the case of copper, zinc contents in sediments near Santa Rosalía are higher than concentrations of this element in polluted sediments near other industrialized zones (e.g. 362 ppm in Golden Horn Bay, Vladivostok, Russia) (Tkalin et al. 1996).

Background levels of cobalt were found in El Yaqui arroyo (10.3 ppm) and along the Santa Agueda arroyo (0.03-32.6 ppm). The Co levels in sedimentary materials from the El Boleo arroyo and El Purgatorio arroyo were considerably higher, amounting to several hundred ppm. The copper-bearing minerals of these areas of the mining district are probably enriched in cobalt, in contrast to the minerals extracted from the San Luciano mine. Almost all samples of solid wastes revealed high contents of cobalt (507-1251 ppm). It is remarkable that beach samples generally had values higher or comparable to those of solid wastes (from 689 ppm up to 6873 ppm). It is possible that processed ores have had different contents of cobalt, some very high. Sands, highly enriched in Co, were probably concentrated in the beach zone and in the sediments of the adjacent sea floor near the entrance to the Santa Rosalia harbor (Fig. 3a) as a result of the sorting by wave action of particles of different grain size and density. In any case, these values of Co in surface sediments exceed significantly the highest concentrations of Co found in Mexico, in coastal sediments of the state of Veracruz (29.5 ppm) (Villanueva and Botello 1998).

Lead is distributed heterogeneously in the samples of the arroyos. Extremely high content of this element (1618 ppm) was found in an arroyo sample collected from St.0 near the San Luciano mine. Sedimentary materials from El Boleo arroyo and some other arroyo samples were also significantly enriched in lead, at levels between 200 and 800 ppm. Low background contents of this element were found in El Yaqui arroyo: St.13 - 27 ppm, and from St.4 and St.3 along the Santa Agueda arroyo (13 and 21 ppm, respectively). Levels of lead in waste samples were highly variable-from 37 ppm up to 612 ppm and in general fall within the range of concentrations found for arroyo samples. Lead in samples of beach material collected near Santa Rosalía (St.32, St.33 and St.34) displayed high contents, ranging from 458 to 2095 ppm. This may be due to the same processes responsible for concentrating cobalt in beach material. Maximum values of lead in marine sediments are much lower (Fig. 3b): from 12 ppm in baseline marginal samples (e.g. St.16, St.17 , St.18) to 218 ppm in sample St.21 of the highly impacted, but quite small area near Santa Rosalía harbor. Here, Pb concentrations in sediments are comparable with the highest Pb values recorded previously in Mexico: in coastal sediments of the Ilusiones Lagoon, Tabasco (159 ppm, Villanueva and Botello 1998) and in heavily polluted (214 ppm) sediments of the industrialized zone in Golden Horn Bay, Vladivostok, Russia (Tkalin et al. 1996).

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