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Mercury Dispersal to Arroyo and Coastal Sediments from Abandoned Copper Mine Operations, El Boléo, Baja California

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Abstract Evidence for mercury dispersal in an arid coastal region of central Baja California (Mexico) suggests that abandoned copper mining operations are a noticeable source of mercury in the environment. There is a generally elevated level of mercury in alluvium of arroyos throughout the mining district (0.14–0.18 mg kg^{-1}). In the first several dozen meters surrounding two of the biggest mines, mercury levels range from 0.26 to 3.16 mg kg^{-1}, forming a halo of anomalously high concentrations. The coastal marine sediments, particularly those close to the copper smelter in the town of Santa Rosalía, also display some mercury enrichment.

Keywords Mercury halo · Abandoned mines · El Boléo mining district · Coastal marine sediments

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Mercury has long been recognized as a potentially valuable tracer when prospecting for various types of mineralization, primarily because many of its forms naturally display high vapor pressure. Saukov (1946) was the main early proponent, recognizing that this attribute could produce anomalies around certain types of mineral deposits. Since the 1960s, Hg has become an important geochemical exploration tool for water, vegetation, soil, bog, stream sediment, and rock studies (Lentz 2005). Weathering of abandoned metal ore mines may produce a noticeable Hg halo that can be traced by examination of the sediments in the local drainage basin. While metal mine pollution has been extensively studied in temperate and cold regions, the impact of mining activities on terrestrial and marine ecosystems of arid and semi-arid regions has received much less attention (Shumilin et al. 2000).

The aim of the present study was to trace the Hg dissipation halo of copper mines under arid conditions, namely at the abandoned mines of the El Boléo mining district near Santa Rosalía, east-central Baja California (Mexico). Intensive copper mining and smelting were carried out there between 1885 and 1985. According to Wilson and Rocha (1955) and Conly et al. (2005), the copper deposits were formed within geologic formations related to Miocene continental rifting (approx. 11 Ma) during the early stages of the opening of the Gulf of California. The area is characterized by laterally extensive strata of laminated claystone and claystone breccia that contain finely disseminated Cu–Co–Zn sulfides and oxidized sulfides (Conly et al. 2005).

The marine sediments near Santa Rosalía are affected by material discharged by arroyos and may serve as a relevant indicator of mine metal dissipation. The alluvium in the arroyo below the town includes waste products from the smelter.

Materials and Methods

The study area is shown in Fig. 1. For most of the year, the area is hot and arid and there are no permanent streams. Most precipitation occurs during summer and fall, typically in the form of torrential rains that result in flash flooding, following which the arroyos dry out quickly. The heavy runoff crosses the old mining plots and tailings, causing extensive erosion, gullying and high sediment transport that eventually reaches the sea.

Anomalously high metal contents have been reported for the coastal sediments, including elements representing both the regionally elevated background concentration of Cu and the anthropogenic components associated with the mining activity (Co, Cu, Mn, Pb and Zn) (Rodríguez Figueroa 2004; Rodríguez-Figueroa et al. 1998; Shumilin et al. 2000).

The arroyo sediments, abandoned mine waste heaps, and beach sands were sampled in October 1997 using plastic tools. The coastal marine sediments were sampled using a Van Veen grab. Sampling locations are shown in Fig. 2. The samples were air-dried, homogenized using an agate mortar, and subsampled for analysis. Details concerning the methodology and the lithologic and chemical composition of the material are given in Shumilin et al. (2000) and Rodríguez Figueroa (2004).

The laboratory glassware and equipment that came in contact with the samples were pre-leached of metals by soaking in 2% HNO_3 for 48 h and then rinsing with

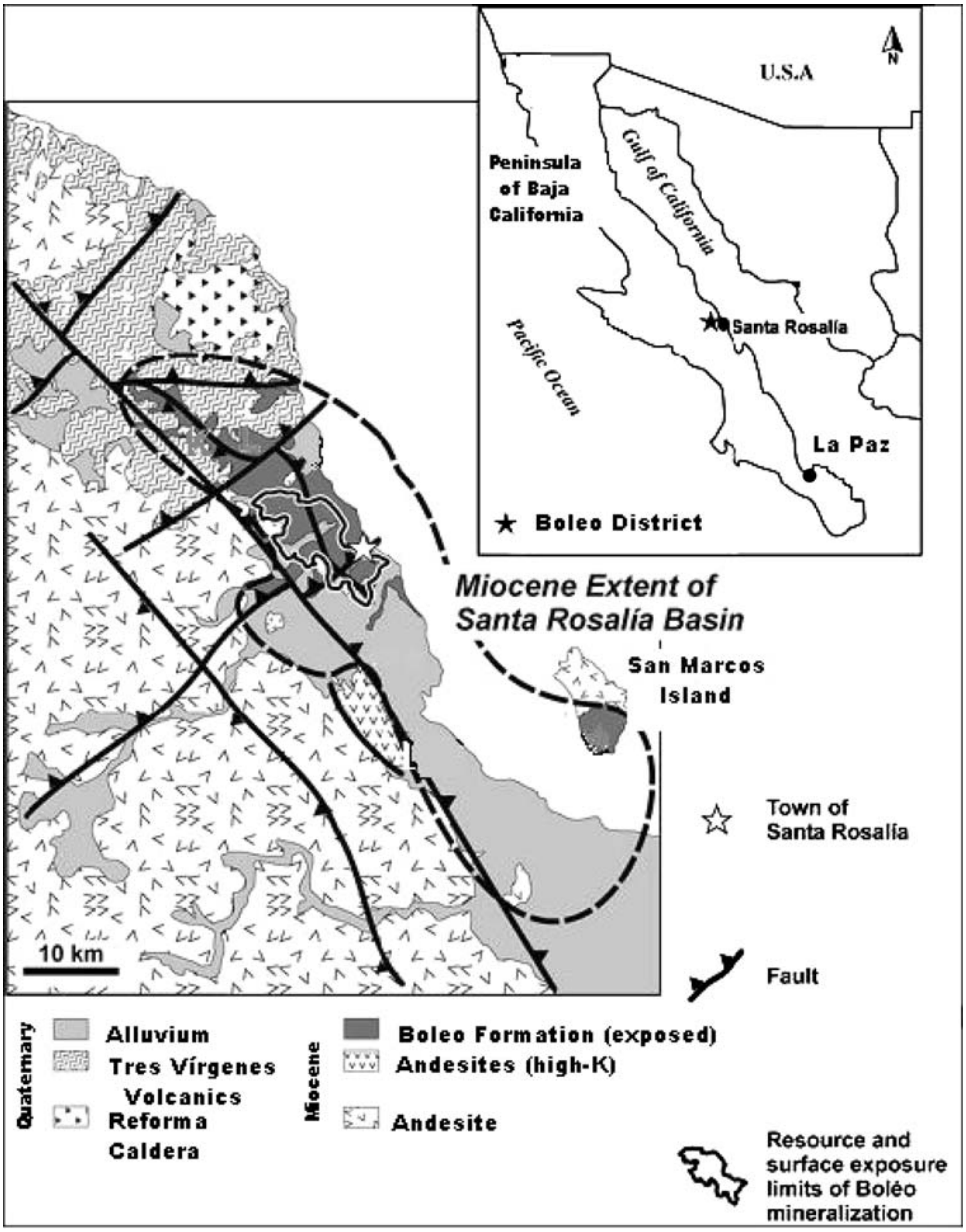

Fig. 1 Location and simplified geological map of the El Boléo mining district, east-central Baja California peninsula (modified from Conly et al. 2006)

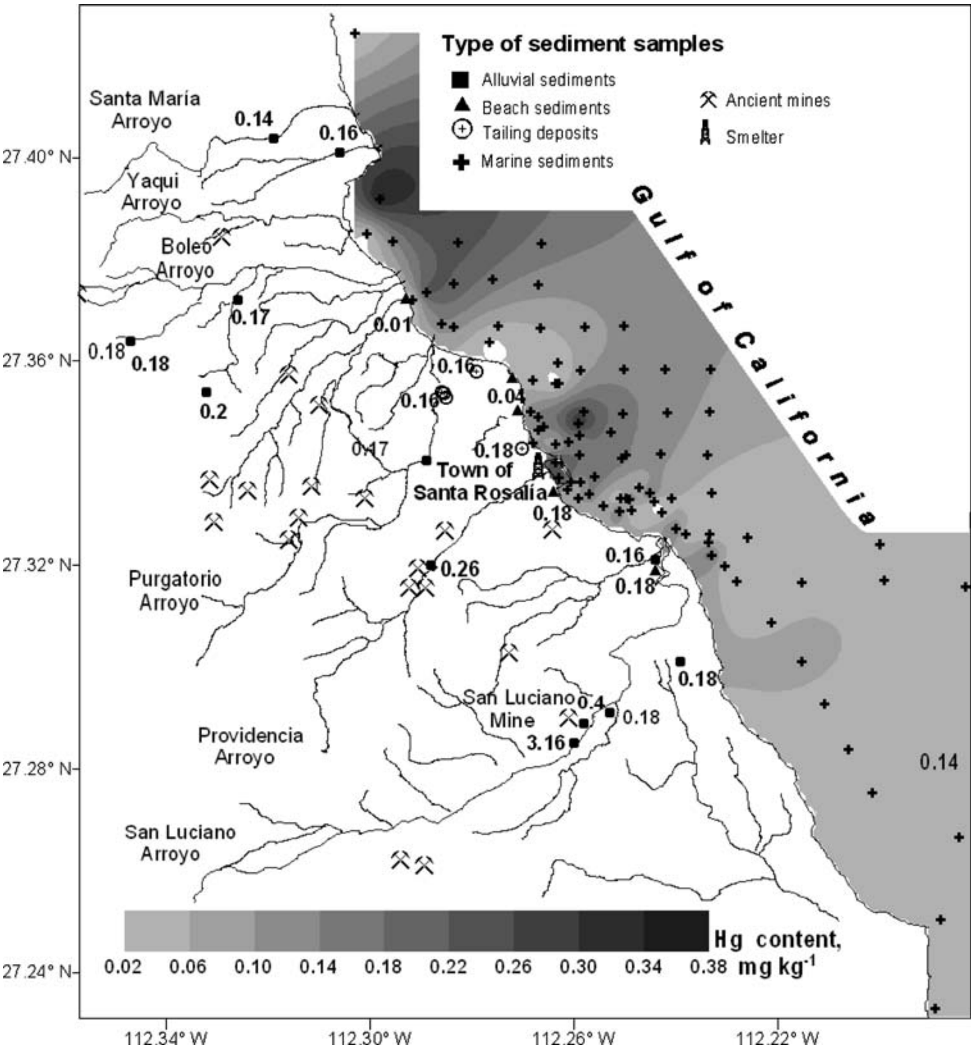

Fig. 2 Mercury distribution in arroyo sediments, beach sands, mining waste heaps and coastal marine sediments

demineralized water. All of the reagents were tested for Hg content. The analytical precision was controlled by duplicate determinations and the accuracy by using standards for Hg from the Ukrainian Physico-Chemical Institute, NAS (Odesa). Hg concentration in the samples was measured using the cold vapor technique in a "Yuliya-2"-"Hitachi" device with a combined unit (spectrophotometer and Hg reduction). Details about the analysis can be found in Kot (2004). Briefly, preliminarily wetted 1 g aliquots were soaked with 1 ml of HNO_3(c) overnight, following which, 1 ml H_2SO_4(c) was added. The mix was simmered cautiously for 15 min in a Kjeldahl flask with a reflux condenser. 10% $SnCl_2$ in HCl (1:1) was then used to reduce the Hg in the digested sample. The detection limit, defined as three times the standard deviation of the procedural blank expressed per unit sample analyzed, was 0.005 mg kg^{-1}. The corresponding reproducibility from replicate analysis was better than ±10% for samples with Hg content >0.10 mg kg^{-1}, while for samples with lower Hg content, the precision decreased to between ±10% and ±25%.

Fe and Sc were determined by neutron activation analysis. The analyses of the National Bureau of Standards reference material, NBS 1646 "Estuarine sediments", fell within the 15% standard deviation limit recommended by the United States Environmental Protection Agency. Organic carbon (C_{org}) and total carbon content were determined coulometrically, as described in Shumilin et al. (2005).

Results and Discussion

Data on the Hg content and other components of mine and smelter wastes, and in arroyo, beach and coastal sediments are summarized in Table 1.

Arroyo sediments enriched in Hg were found in the immediate vicinity of the abandoned San Luciano copper mine. Sample 0, taken directly at the mine, and sample 2, taken 100 m downstream, contained 3.16 and 0.40 mg kg^{-1} Hg, respectively (Fig. 2). Site 3, sampled 300 m further

Table 1 Mean, standard deviation and concentration range of some major and trace constituents in mine wastes and arroyo, beach and coastal marine sediments in the El Boléo mining region (number of samples in square brackets [ ])

Material	$CaCO_3$, %	C_{org}, %	Fe, %	Sc, mg kg^{-1}	Hg, mg kg^{-1}
Arroyo sediments [14]	9.0 ± 5.9	0.16 ± 0.26	6.33 ± 3.86	12.8 ± 4.0	0.18 ± 0.03
	(1.7–20.9)	(0.00–0.98)	(3.00–17.2)	(6.0–18.3)	(0.14–0.26)
Beach sands [3]	(9.0–20.5)	(0.06–0.38)	(3.32–6.49)	(8.0–14.2)	(0.01–0.16)
Mine and smelter wastes [4]	(6.5–11.1)	(0.11–0.38)	(4.70–25.2)	(4.4–11.9)	(0.16–0.18)
Marine coastal sediments [51]	21.6 ± 14.3	0.30 ± 0.20	3.07 ± 1.02	10.7 ± 3.5	0.10 ± 0.09
	(4.1–76.2)	(0.11–1.06)	(0.78–5.55)	(2.5–20.7)	(0.01–0.35)

downstream, contained 0.18 mg kg^{-1} Hg, which corresponds to the average Hg content in the arroyo alluvium over the entire area sampled. Sample 1, 100 m upstream of the mine, contained 0.14 mg kg^{-1} Hg.

There is clear evidence of Hg dispersion from the abandoned mines within the arroyo sediments. The revealed halo was of a local character, evident up to a few dozen meters from the source (Fig. 2). Except for the two extremes found near San Luciano mine and in the Providencia Arroyo, the Hg concentrations further away in San Luciano Arroyo were close to the regional average (Fig. 2, Table 1). This background level, however, was one order of magnitude greater than that of lagoon and arroyo sediments found beyond the known mineralization zones. La Paz Lagoon and local arroyo sediments, for example, presented levels of 0.020 ± 0.011 and 0.016 ± 0.009 mg kg^{-1} Hg, respectively (Kot et al. 1999), even though they had higher contents of organic matter and iron oxyhydroxides, which are known for their efficient trapping capacity for Hg. Thus, one can conclude that the El Boléo mining area, including the town of Santa Rosalía, lies within a primary Hg contact mineralization halo. Azzaria and Carrier (1976) investigated Hg contents in rocks associated with the copper deposits at Murdochville, Québec, Canada and showed that the deposits are located inside a low alteration Hg halo, while no Hg enrichment appeared in the surrounding unaltered rocks. Many authors stressed that mineral-bound Hg occurs worldwide in metal deposits (Smirnov 1946; Kerfoot et al. 2002; Koski et al. 2008; Navarro 2008).

From the above, one can construe the existence of a local Hg anomaly with respect to the regional mineralization, i.e. the primary Hg halo (Matschullat et al. 2000). Moreover, the high regional Hg background may mask the influence of the former mining operations on the environment. Even the concentrations in the municipal tailing and smelting waste dumps around Santa Rosalía (0.16–0.18 mg kg^{-1} Hg) do not exceed this local Hg background.

The coastal marine sediments adjacent to the affected area have been found to be Hg-enriched by an order of magnitude compared with the smaller concentrations found in the carbonate diluted sediments to the south (Fig. 2). The highest Hg concentrations were found in the semi-enclosed man-made harbor, probably the result of contamination with slag material from the smelter.

The very sharp inflection of the cumulative frequency curve (Fig. 3) separates the two types of coastal sediments: (1) those with low background levels of Hg – average of 0.03 mg kg^{-1}, n = 30; and (2) Hg-enriched sediments – averaging 0.18 mg kg^{-1}, n = 21. The latter corresponds to the average concentrations found in the arroyo sediments.

The two groups are also distinguishable based upon their content of carbonates, iron and C_{org} (Table 2). The Hg-enriched sediments contain higher concentrations of C_{org} and iron, but lower calcium carbonate. Turekian and Wedepohl (1961) reported an average Hg content in calcareous sediments of 0.04 mg kg^{-1}.

It is difficult to know for certain what the major sources of Hg to the terrigenous and marine sediments were. These might be: (1) the local dispersion halos; (2) physical transport during flash floods away from the abandoned mines, tailing deposits or slag heaps; (3) anthropogenic transport of slag and tailings and refined metals near the port and along the coast.

The degree of association of Hg with the sedimentary material i.e., its concentration compared with that of organic matter (C_{org}), $CaCO_3$, Fe and Sc (a component of

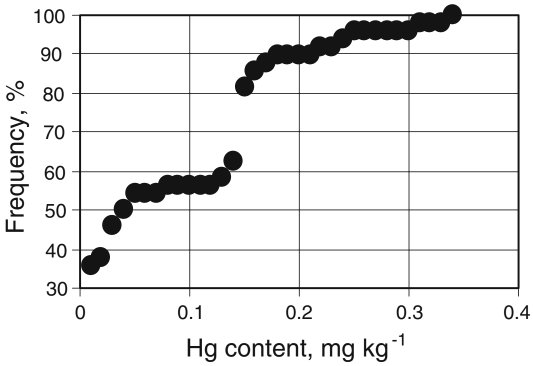

Fig. 3 Cumulative frequency curve of Hg content in coastal marine sediments near Santa Rosalía

Table 2 Two groups of coastal sediments – low background and Hg-enriched

Parameters	Coastal marine sediments	
	Poor in Hg (n = 30)	Enriched in Hg (n = 21)
Hg, mg kg^{-1}	0.03 ± 0.03 (<0.01–0.13)	0.18 ± 0.07 (0.14–0.35)
C_{org}, %	0.25 ± 0.09 (0.11–0.48)	0.37 ± 0.29 (0.12–1.06)
Fe, %	2.67 ± 0.95 (0.78–4.85)	3.70 ± 0.81 (2.46–5.55)
$CaCO_3$, %	24.9 ± 16.4 (4.1–76.2)	17.0 ± 8.8 (6.7–44.5)

Table 3 Correlation coefficients between Hg with other geochemical components

Parameters	Arroyo sediments	Marine coastal sediments
C_{org}	0.91	0.49
$CaCO_3$	0.37	−0.32
Fe	0.30	0.42
Sc	0.29	−0.36

clays and refractory terrigenous minerals; Zhang 1999) was evaluated by correlation analysis (Table 3). The correlation coefficients reveal a strong association of Hg with organic matter, particularly for the arroyo sediments. For the marine deposits, Hg displays similar positive correlation levels with C_{org} and Fe, but is negatively correlated with $CaCO_3$ and Sc.

The abandoned copper mines within the El Boléo mining district, as well as the products of the ore processing, are sources of Hg dispersion in the environment. The following dispersal mechanisms can be presumed to be involved: (1) Hg migration, together with weathered material washed down from the immediate area of the abandoned mines, via runoff from punctually intense torrential rains; (2) oxidation of Hg sulfides typically resulting in the formation of soluble organic and chloride complexes (Koski et al. 2008; Navarro 2008) – such dissolved Hg compounds are easily trapped and immobilized by co-precipitation with (roentgen-)amorphous iron sulfides (probably, hydrotroilite) and amorphous aluminum oxides (Yelpatyevsky and Kot 2000). Given the arid climate (i.e., lack of humidity and low microbial activity), transport of particulate forms of Hg must have been much more significant, since the solubility of Hg sulfides is extremely low, even compared with common soil matrix minerals such as quartz and feldspar (3×10^{-25} g L^{-1} for cinnabar – Saukov 1946). It has been observed that Hg concentrations in mine waters of sulfide and even cinnabar ores are extremely low (Laredo et al. 1999; Mastrine et al. 1999; Ganguli et al. 2000).

The Hg dispersal is quite local in character – detectable over the first several dozens of meters. The extent of the halo, however, may be masked by the high background concentrations typical for zones of sulfide mineralization (Saukov 1946).

Two groups of sediments have been distinguished in the coastal marine environment: (1) those with low background Hg levels and higher carbonate content, and (2) those enriched with Hg, often finer grained and with higher iron and organic matter contents. The marine sediments are influenced both by the Hg-containing material carried to the coast via the arroyos, as well as by the handling of tailings and smelter debris within the town of Santa Rosalía which are dumped at sea.

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