

Migration of As, Hg, Pb, and Zn in arroyo sediments from a semiarid coastal system influenced by the abandoned gold mining district at El Triunfo, Baja California Sur, Mexico

Ana Judith Marmolejo-Rodríguez,* Martha Alicia Sánchez-Martínez, Juan Armando Romero-Guadarrama, Alberto Sánchez-González and Víctor René Magallanes-Ordóñez

Received 25th January 2011, Accepted 1st June 2011

DOI: 10.1039/c1em10058k

Extensive waste deposits (tailings) and ash from the ignition oven of the abandoned gold mine of mining district El Triunfo (MD-ET) in Baja California Sur, Mexico have released trace elements into the sediments of the Hondo-Las Gallinas–El Carrizal arroyo, which connects to the Pacific Ocean through an evaporitic basin. Migration of these elements through the arroyo is mainly caused by winds or tropical hurricanes that occur sporadically during the summer and cause the otherwise dry arroyo to overflow. To evaluate the concentration and distribution of the elements As, Hg, Pb, and Zn along the 48 km arroyo, surface sediments were collected from 26 sites, ranging from close to the MD-ET to the mouth of the arroyo at the Pacific Ocean. Concentrations in tailings and ash were for As 8890 and 505 000 mg kg⁻¹; for Hg 0.336 and 54.9 mg kg⁻¹; for Pb 92 700 and 19 300 mg kg⁻¹; and for Zn 49 600 and 1380 mg kg⁻¹. The average of the Normalized Enrichment Factor (Av-NEF) in surface sediments, calculated using background levels, indicates that the sediments are severely contaminated with As and Zn (Av-NEF = 22), Pb (Av-NEF = 24) and with a moderate contamination of Hg (Av-NEF = 7.5). **The anthropogenic influence of those elements is reflected in the arroyo sediments as far as 18 km away from the MD-ET, whereas the samples closest to the discharge into the Pacific Ocean show a natural to moderate enrichment for As and Zn and low or no enrichment for Hg and Pb.** A principal components analysis identified four principal components that explained 90% of the total variance. Factor 1 was characterized by a high positive contribution of the anthropogenic source elements, especially As, Pb, and Zn (37%), whereas Factor 2 was strongly correlated with the oxy-hydroxides of Fe and Mn (27%). Factor 3 was correlated with Li (16%) and Factor 4 with Al (10%), which indicates more than one source of lithogenic composition, though they played a minor role in the distribution of the elements.

1. Introduction

Mining for gold and other precious metals causes the release and accumulation of toxic quantities of other elements, such as As,

Hg, Pb, and Zn, into the surroundings. The extraction of gold from rocks with average assays of up to 1 g t⁻¹ of Au produces millions of tonnes of tailings around the world. As a consequence, naturally occurring metals and metalloids, such as As, Hg, Pb, and Zn, are accumulated in abandoned tailings close to the mines where they are exposed to weathering and consequently scattered in soils and sediments adjacent to the mining areas.^{1–4} Presently, artisanal mining (consisting of rudimentary

Centro Interdisciplinario de Ciencias Marinas – Instituto Politécnico Nacional, Av. IPN s/n Col. Playa Palo de Sta. Rita, 23096 La Paz, BCS, Mexico. E-mail: amarmole@ipn.mx

Environmental impact

This semiarid area is influenced by an abandoned gold mine. Consequently, conspicuous piles of tailings are scattered in the area. Tropical storms and hurricanes create sporadic large floods. Moreover, the tailing piles increase the concentrations of As, Hg, Pb, and Zn along the arroyo sediments that are potentially toxic for human health. The contributions of this research to be considered by future international workers are (i) to assess the importance of calculating the normalized enrichment factors by using regional background levels in areas greatly polluted to determine the areas affected, (ii) to clearly discriminate the origin of pollutants, anthropogenic or natural, and (iii) to assess the distance most influenced by these elements.

branches of the mining sector using basic tools with limited capital investments) is practiced mainly in poor countries where the regulation of mining and the waste produced do not exist or have become less strict than in developed countries. To avoid soil and sediment pollution in coastal areas some mining areas are now disposing of the tailings into the deep ocean, where elements such as As and Hg are subsequently bioaccumulated by marine organisms.⁵

Sediments act as a sink for elements and those sediments with a finer grain size can adsorb a larger quantity of trace elements compared to sediments with coarser grains.^{6,7} Tailings from the gold extraction process generally have a fine grain size (<38 μm)⁸ and as a consequence have high elemental mobility. Their influence in river basins can be seen in the sediments enriched in trace elements.^{2,9} Changing environmental conditions can cause the release of elements such as As from the sediments so that the polluted sediments can therefore act as chemical time bombs (CTBs).¹⁰ The inclusion of other elements, such as Hg, Pb or Zn, further increases the potential damage of the CTBs.

Arsenic compounds can be found in more than 245 different minerals.¹¹ In minerals from gold mines, As is associated with pyrite and arsenopyrite and its mobilization has been favored by past gold-mining activities.¹² Arsenic exists in four oxidation states, with the possible processes in biogeochemical cycling of arsenic seen in Reisinger *et al.*¹³ This element comes from either geological sources or from human activities such as mining, the burning of fossil fuels, and pesticide use.¹⁴ Although recent studies show that As may be essential to some organisms,¹⁵ it is toxic in small doses with stimulatory and carcinogenic effects reported.¹⁶ Its mobility from gold mining areas to groundwater has negative implications for human health.¹⁷ The relation between arsenic content in drinking water and in human urine has been measured in many countries ($r > 0.65$; $P < 0.022$).¹⁸

Mercury is an environmental pollutant that is mainly supplied to the soil *via* anthropogenic sources. It is harmful because of its toxicity, mobility, bioaccumulation, methylation process, and transport by hydrometeorological processes.¹⁹ Elemental mercury is obtained by roasting cinnabar (HgS), is stable in air and water, and unreactive with acids, except HNO_3 , and alkalis. Mercury has three oxidation states: Hg(I), which forms fluorides and chlorides; Hg(II), which mainly forms oxides and sulfides; and Hg(0) that is the predominant oxidation state in sediment samples from gold mining areas.²⁰ The most toxic mercury compound is methyl mercury (HgCH_3^+) which is teratogenic.¹⁶ Studies of mercury in dissolved and solid phases have shown that mercury appears to be bound mainly to organic matter, and only a minor fraction is associated with Mn or Fe oxides close to the redox boundary, adsorbed to or coprecipitated with acid volatile sulfides, or incorporated into pyrite.^{21,22}

The majority of gold mines are in rocks with galena.¹ Consequently, the Pb is obtained from galena (PbS) during gold mining. The main oxidation states of Pb are Pb(II) and Pb(IV), both of which form oxides, sulfides, fluorides, and chlorides. Lead is toxic, teratogenic, and carcinogenic. It is less labile in river sediments than other elements^{23,24} though even small quantities may affect the immune system of an organism.¹⁶

Zinc is present in high quantities in rivers influenced by gold mining.¹⁸ It is an essential trace element and nontoxic except in large excess when it is carcinogenic. The main oxidation state is

Zn(II), which forms oxides, sulfides, hydroxides, and many organic and inorganic complexes.²⁵ Zinc is labile in river sediments²⁶ and has an increased mobility at $\text{pH} < 5$.²⁷

Gold forms in composite minerals with sulfur (arsenopyrite, cinnabar, galena, and sphalerite). In the rainy season there may be changes in the pH so a fraction of the sulfides may be oxidized forming iron oxides and trace element (TE) oxides and give off the gas SO_2 . The elements could be dissolved, caused by changes in the pH,^{3,28} and contaminate aquifers. Atmospheric processes, such as tropical hurricanes, may accelerate their incorporation into aquifers and also into the ocean. Because of this weathering and intake into the water table, these metal compounds are incorporated into the food chain.^{18,29}

Previous studies in Mexico have found high concentrations of these elements in sediments close to tailings produced by mining, with the further consequent evidence of environmental problems.^{30–33} Our aim is to establish the influence of past gold mining on elements such as As, Hg, Pb, and Zn and to determine their concentration and distribution along the Hondo—Las Gallinas—El Carrizal arroyo, which leads from the now abandoned mining district of El Triunfo to the Pacific Ocean. This in turn will allow us to determine the normalized enrichment factors (NEFs) and background levels (BLs) of those elements in this semiarid system.

1.2. Study area

The abandoned gold mines at El Triunfo (MD-ET) are located in the mountainous portion of the El Carrizal drainage basin, in the southernmost part of the Baja California peninsula, Mexico ($24^\circ 09' 02''\text{N}$, $110^\circ 06' 22''\text{W}$, Fig. 1). The main ore deposits are epithermal veins with sulfide mineralization. They are in the central part of the tectonic block of Cabo San Lucas, which is influenced by Tertiary volcanic rocks and upper Tertiary sedimentary sequences.¹ So the origin of sediments is from past volcanic activity.

The Hondo-Las Gallinas-El Carrizal arroyo connects the MD-ET to the Pacific Ocean. The climate in the area is semiarid and influenced by tropical storms, particularly in the late summer.

Artisanal gold exploitation began in 1748 and has continued intermittently up until the end of the last century.³⁴ Extensive waste deposits (around 30 tailing piles) have been left in the open in the mining area. There are small cyanide-heap leaching pools with no environmental control and ash from the ignition oven that have been concentrated into arsenolite. Both tailing piles and ash remaining in the abandoned ovens are subject to the erosive effects of seasonal rains and wind-transport processes. Previous studies on soils and flora in the area have found high contents of As, Pb, and Zn.^{35,36} Tailings have been studied by Carrillo,¹ who reported concentrations of 35% of As, and Volke-Sepúlveda *et al.*⁸ who characterized the tailings and found them extremely contaminated with As, Hg, Pb, and Zn.

Independent of the anthropogenic influences caused by past mining, a geological map of the study area (Fig. 1) shows the type of rocks that predominate. This is useful to determine their influence on the composition of the sediments. Close to the mining district, the rocks are granite and granodiorite (Cretaceous), schists, and metasedimentary rocks (Jurassic). About 20 km down the arroyo there are influences of sandstone

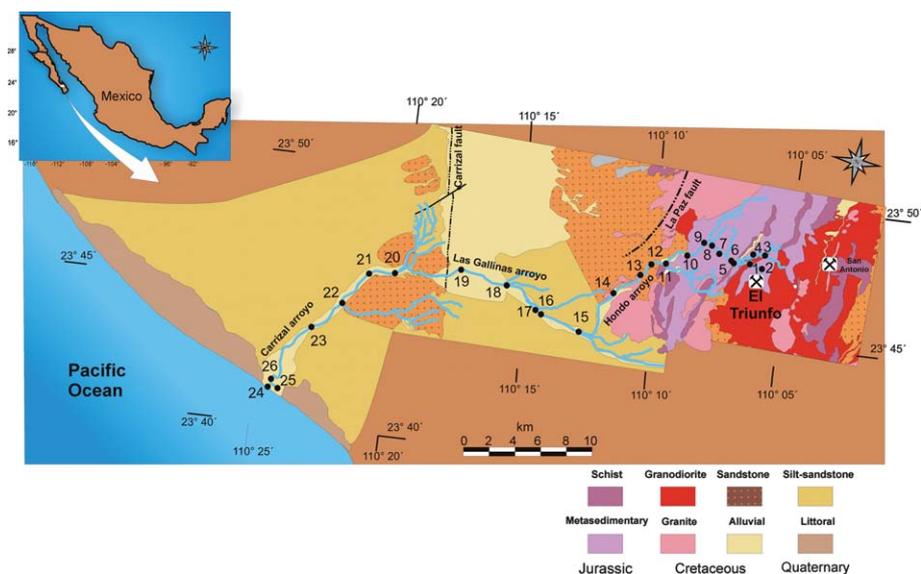


Fig. 1 Study area. Geologic map with the location of sampling sites in the main arroyo (Hondo—Las Gallinas—El Carrizal).

(Quaternary). The next 10 km are predominantly silt-sandstone. The silt-sandstone and sandstone sediments from the Quaternary are in the last 18 km close to the mouth of the arroyo at the Pacific Ocean.

2. Material and methods

Twenty-six samples were collected along 48 km of the main Hondo-Las Gallinas-El Carrizal arroyo (Fig. 1), from close to the MD-ET to an evaporitic basin connected to the Pacific Ocean. Polyethylene bottles previously cleaned separately with HNO₃ (15%) and HCl (10%) were used to collect the samples. Ash samples were collected from the abandoned oven with a plastic spoon and saved in the cleaned polyethylene bottles. Samples were dried and powdered with an agate mortar and a sieved fraction (<2000 μm) was used for analysis.

The textural composition of the sediments was determined using the granulometric method of Folk.³⁷ The sample (0.5 g) was digested with aqua regia to leach out soluble compounds. Mercury was determined by absorption at 253.7 nm using the flow-injection cold-vapour mercury technique, FIMS (Flow injection Mercury System—Model 100 Perkin Elmer). For As, Al, Fe, Li, Mn, Pb, and Zn, 0.25 g of sediment was completely digested using four acids, HF, HCl, HNO₃, and HClO₄, evaporated to dryness after which the residues were diluted with HCl. Briefly, the sample is digested with four acids beginning with hydrofluoric, followed by a mixture of nitric and perchloric acids, heated using precise programmed-controlled heating in several ramping and holding cycles that take the samples to dryness. After dryness is attained, samples are brought back into solution using hydrochloric and nitric acids. Elements (Al, As, Fe, Li, Mn, Pb, and Zn) were determined by an magnetic-element sector inductively coupled-plasma mass spectrometer (ICP-MS) using a microconcentric nebulizer with a standard double-pass condensing spray chamber for sample introduction and determined by using a Perkin Elmer Sciex ELAN 9000 ICP-MS (Actlabs, Ontario Canada). The methods were validated by using certified reference materials of marine sediments

(PACS-2, MESS-3; National Research Council Canada Institute for National Measurement Standards). Arsenic was also measured by Neutron Activation (INAA); Pb > 5000 mg kg⁻¹ and Zn > 10 000 mg kg⁻¹ determined by ICP-OES. Method validations were done using the certified reference materials of marine sediments intercalated into the set of samples. The results are shown in Fig. 2. The recovery percentages show accuracy close to 100% in almost all elements measured.

The Normalized Enrichment Factors (NEFs) were calculated using the average of the Upper Continental Crust (UCC)³⁸ to be compared with regional published papers (Table 1). However, to get a better appreciation of the contents and enrichment of the arroyo, the NEFs were also calculated using local background levels (BLs). Aluminium was selected as the normalizing element according to Marmolejo-Rodríguez *et al.*²³ The background levels were determined using an average of the samples that are considered the cleanest samples because their contents were less concentrated than the UCC for the majority of the elements.

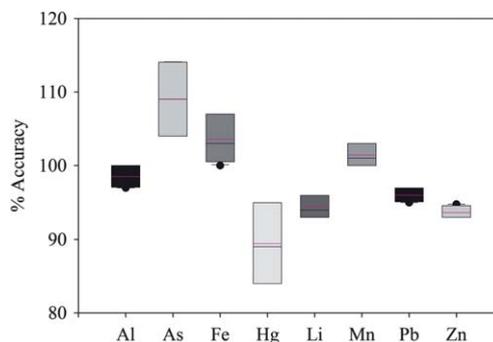


Fig. 2 Method validations for the determination of Al, As, Fe, Hg, Li, Pb, and Zn concentrations were made using two certified reference materials of marine sediments, PACS 2 and MESS3. Determinations were made in duplicate for each standard and the percentage of recovery was calculated from the results obtained, considering the certificated results as 100%. Boxes represent the range (5–95% percentiles of confidence) of the results obtained.

Table 1 Ranges of elements determined, means and standard deviation (*s*) of background levels (BLs), normalized enrichment factors (NEFs) in the gold mining district and its main arroyo. Regional contents and other world systems impacted by gold ore mines^a

	As (mg kg ⁻¹)	Hg (ng g ⁻¹)	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Al (mg g ⁻¹)	Fe (mg g ⁻¹)	Li (mg kg ⁻¹)	Mn (mg kg ⁻¹)
Range (<i>n</i> = 26) ^b	2.8–412	<5 to 217	10.7–1230	14–1950	42.3–92.9	5.5–153	7.3–27.8	97–3390
Background value ^b (mean ± <i>s</i>)	7.9 ± 2.7	10.5 ± 5.3	19.2 ± 9.2	28.9 ± 10.5	78.6 ± 8.1	41.7 ± 16.0	9.9 ± 2.4	900 ± 645
NEF (1–17 stations) UCC ^b (mean ± <i>s</i>)	85 ± 52	2.1 ± 1.5	27 ± 22	12.6 ± 7.7	—	—	—	—
NEF (1–17 stations) BL ^b (mean ± <i>s</i>)	22 ± 13	7.5 ± 5.2	24 ± 19	22 ± 21	—	0.96 ± 0.43	—	—
NEF (18–26 stations) UCC ^b (mean ± <i>s</i>)	5.1 ± 2.3	0.4 ± 0.5	2.5 ± 1.7	0.8 ± 0.3	—	—	—	—
NEF (18–26 stations) BL ^b (mean ± <i>s</i>)	3.2 ± 3.9	1.24 ± 1.67	2.8 ± 2.7	3.0 ± 2.6	—	1.2 ± 2.1	—	—
Tailing ^b	8890	336	92 700	49 600	17.6	173	7.1	1390
Ashes ^b (range)	363 000–505 000	2250–54 900	2170–19 300	565–1380	1.5–3.2	6.9–12.6	<0.5–2	15–137
<i>Regional contents</i>								
Tailing different grain sizes ⁸	4229–18 360	310–2100	1203–5722	1094–3399	n.d.	22.2–66.1	n.d.	466–1004
Ashes ⁸	5229–24 468	2000–8100	19 170–122 838	8635–79 308	n.d.	71–190	n.d.	811–2109
Alluvial soils ⁸	12–675	470–1220	179–641	123–1205	n.d.	45.9–83.2	n.d.	681–1137
La Paz Lagoon (sediments) ⁴¹	10 ± 7	n.d.	50 ± 14	45 ± 28	n.d.	20	n.d.	n.d.
La Paz Bay (sediments) ⁴³	11 ± 7.8	n.d.	n.d.	37 ± 24	n.d.	18	n.d.	n.d.
Santa Rosalia (sedimentary cores) ⁴²	7.5 ± 3.6	n.d.	n.d.	171 ± 61	n.d.	31 ± 3.3	n.d.	n.d.
Santa Rosalia mining zone (sediments) ⁴⁴	7.0	n.d.	60	521	n.d.	35	n.d.	n.d.
Loreto (sedimentary core) ⁴²	12.6 ± 3.1	n.d.	n.d.	776 ± 13	n.d.	29.7 ± 1.2	n.d.	n.d.
Sn Juan dela Costa (sedimentary core) ⁴²	7.6 ± 4.0	n.d.	n.d.	16.3 ± 12.7	n.d.	22.3 ± 1.5	n.d.	n.d.
El Coyote (sedimentary core) ⁴²	4.1 ± 3.3	n.d.	n.d.	19.2 ± 7.04	n.d.	28.1 ± 3.6	n.d.	n.d.
Ojo de Liebre (lagoon sediments) ⁴⁵	4.4	n.d.	n.d.	22.3	n.d.	12	n.d.	n.d.
Guerrero Negro (lagoon sediments) ⁴⁵	2.7	n.d.	n.d.	21.4	n.d.	12	n.d.	n.d.
<i>Systems impacted by gold mining in Mexico</i>								
El Fraile, Taxco, México (tailing) ³³	1838 ± 803	n.d.	3610 ± 1310	6079 ± 7373	n.d.	n.d.	n.d.	n.d.
Zimapán, Hidalgo, México (tailing) ⁴⁶	15 260	n.d.	6570	8700	n.d.	142	n.d.	n.d.
<i>Other coastal areas impacted by gold mining</i>								
Rudnaya River, Russia (sediments) ⁵¹	n.d.	n.d.	106	4227	n.d.	n.d.	n.d.	3534
Río Loa, Chile (sediments) ⁴⁷	26–2000	n.d.	n.d.	9–160	n.d.	0.5–95	10–120	n.d.
Ria de Huelva, España (sediments) ¹¹	139–499	n.d.	232–447	227–3998	n.d.	82–130	n.d.	n.d.
Zlotystok, Poland., tailing ⁴⁹	8500–17 200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Alluvial soils ⁴⁹	11 500	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Leichhardt River, Australia (sediment) ⁴	n.d.	n.d.	724	807	n.d.	n.d.	n.d.	n.d.
East Rand, South Africa (river sediment) ³	6.4–130.7	0–5800	7.4–38.7	35.8–423.5	n.d.	11.7–58.3	n.d.	68–3488
Upper continental crust ³⁸	2.0	56	17	52	77.4	30.8	22	527

^a n.d. = not determined; UCC = upper continental crust. ^b This study.

$$NEF_{(UCC)} = (TE_S/Al_S)/(TE_{UCC}/Al_{UCC}) \quad (1)$$

$$NEF_{(BL)} = (TE_S/Al_S)/(TE_{BL}/Al_{BL}) \quad (2)$$

Eqn (1): NEF_(UCC) is the NEF calculated as a ratio to the UCC where TE_S and Al_S are the trace element and Al concentrations in the sample and TE_{UCC} and Al_{UCC} are the trace element and Al in the UCC.

Eqn (2): NEF_(BL) is the NEF calculated using the background levels where TE_S and Al_S are the concentrations of the trace element and the aluminium in the samples (the same as in eqn (1)), and TE_{BL} and Al_{BL} are the background levels of the system for the trace element and aluminium.

For interpretation of the NEF results, the contamination criteria used were NEF = 1–3 zero or low contamination; 3–10 moderate; 10–25 severe; 25–50 very severe; >50 extremely severe (adapted from Hakanson;³⁹ Cobelo-Garcia and Prego;⁴⁰ Mar-molejo-Rodríguez *et al.*²³).

3. Results and discussion

3.1. Textural composition of sediments

The sand fraction (0.063–2 mm) was the most abundant (>98%) in the arroyo sites (Fig. 3). The fraction <2 mm was used for the

chemical analyses. The fraction <63 μm was found in a greater percentage in the tailings (20%) and in the ash (90%). The organic matter concentration was not determined because this system is in an arid zone with scarce vegetation in the arroyo sediments.

3.2. Influence of sources on trace element distribution and background levels

Tailing and ash samples were treated separately from the arroyo sediments to evaluate the general trend of element distribution in the study area. Ranges of contents in tailings and ash samples and averages and standard deviation of background levels, NEF_{UCC} and NEF_{BL} from sediments are shown in Table 1. Multivariate techniques were used to assess the element association. The comparisons between regional^{41–45} and international areas^{3,4,47–51} were made in the following sections.

In this study, As, Pb, and Zn showed a clear enrichment in their distribution with the highest concentrations found close to the MD-ET (Fig. 4 and Table 1). None of the samples in this study had As in a lesser concentration than the UCC (2 mg kg⁻¹).³⁸ A considerable As contamination was determined in tailings, ash, and arroyo sediments. Lead had a high concentration close to the MD-ET though its background level (19.2 mg kg⁻¹, this study) was similar to the average calculated for the UCC (17 mg kg⁻¹).³⁸ For Zn the regional background levels were

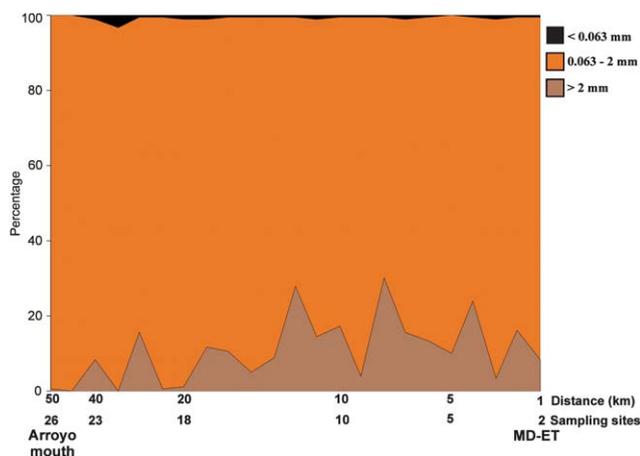


Fig. 3 Distribution of grain size in sediments in the arroyo from the mining district (MD-ET) to the mouth of the arroyo.

low (28.9 mg kg^{-1}) compared to the UCC (52 mg kg^{-1}),³⁸ which is why it is important to calculate the background levels of the system in addition to the global averages. When Zn is normalized to the UCC, a depletion is measured (Fig. 4), though zinc normalized to the regional background levels indicates a high enrichment close to the mining district (samples 1–17) and a moderate enrichment (NEF > 3) in the samples near the arroyo discharge into the Pacific Ocean (samples 18–26).

Mercury concentrations were less concentrated than the UCC values in more than 45% of the samples (Fig. 4 and Table 1) and in 30% of the samples Hg concentrations were below the detection limit ($<5 \text{ ng g}^{-1}$). The concentration in 45% of the surface sediments from the arroyo with detectable Hg concentrations varied from <5 to 17 ng g^{-1} , which are the background levels from soil and sediments according to Gray *et al.*⁵² and Willerer *et al.*⁵³ The background level of Hg in this semiarid system is $10.5 \pm 5.3 \text{ ng g}^{-1}$ (Table 1), which is less concentrated than the mean of the Earth's crust (56 ng g^{-1}).³⁸

Previous studies on different grain sizes⁸ in one tailing pile and from two samples of natural soils in the surrounding area of the MD-ET (Table 1) found As, Hg, Pb, and Zn contents within the

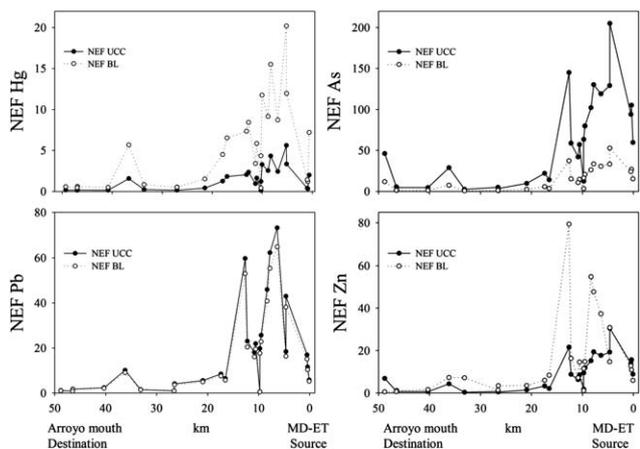


Fig. 4 The Normalized Enrichment Factor (NEF) along the arroyo. Black circles represent NEFs calculated using the upper continental crust (UCC), and white circles are regional background levels (BLs) of the studied system.

range of this study. The arsenic, Hg, Fe, Mn, Pb, and Zn concentrations are high in the tailings, but in ash from the abandoned oven the As, Hg, Pb, and Zn were enriched and the Al, Fe, Li, and Mn were considerably depleted.

The results of this study reflect contamination as a function of the distance. In the first 18 km there is direct evidence of an anthropogenic influence from the mining. Farther on (toward the mouth of arroyo and the evaporitic basin) the concentration and mean of the NEFs of these elements are at natural levels (background level).

3.3. Behaviour of lithogenic elements

The contents of the lithogenic elements Al, Fe, Li, and Mn and their distribution in the surface sediments along the arroyo are shown in Fig. 5. Here, Al shows a homogeneous behaviour compared to Li, Fe, and Mn. For this reason Al was selected as a normalizer element. The Fe and Mn cannot be normalizers because they are redox sensitive and were enriched in the tailings. In tailings and ash, Al and Li were depleted compared to the background levels of the system and the UCC (Table 1). Because of the fine grain size of the sediment and the red sediments in the tailings, accumulation of iron oxyhydroxides was seen, which promotes an enrichment of elements associated with the gold extraction processes.

3.4. Normalized enrichment factor distribution using upper continental crust and background levels

The NEF using the UCC values for calculation generally gives a good approximation of contamination, however using the local background levels (to calculate the NEF) is a useful tool to evaluate the environmental remediation processes to be used

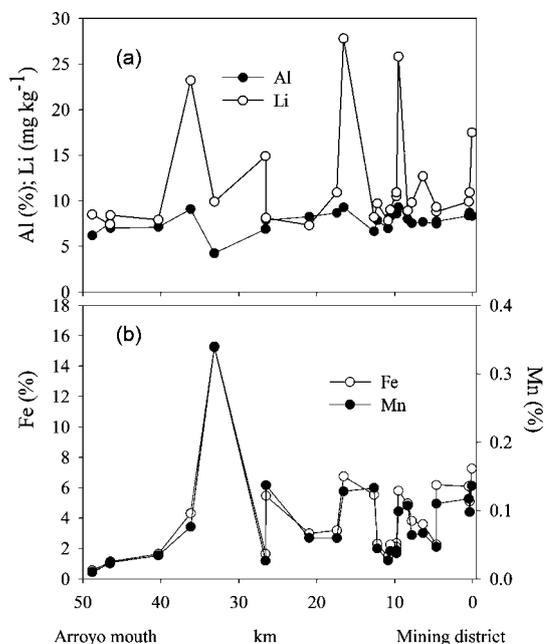


Fig. 5 Distribution of Al and Li (a) and Fe and Mn (b) in the surface sediment along the arroyo from the source (MD-ET) to the destination (arroyo mouth).

locally. The average values of the NEF (Av-NEF) were calculated using the UCC and BL (mean and *s* are shown in Table 1). The distribution of the NEFs along the arroyo can be seen in Fig. 4 for stations 1 to 17 (close to the MD-ET). The Av-NEF values of 85 and 22 for As indicate extremely severe and very severe contamination (UCC and BL), for Hg the Av-NEFs of 2 and 7.5, UCC and BL, indicate low and moderate contamination, the Av-NEFs of 27 and 24 for Pb indicate very severe and severe contamination, and the Av-NEFs of 13 and 22 for Zn indicate severe contamination for both UCC and BL. Close to the discharge into the Pacific Ocean (NEF_{UCC} and NEF_{BL}; Stations 18 to 26) the Av-NEFs for As (5.11 and 3.2, moderate contamination), Hg (0.35 and 1.24, nil or low contamination), Pb (2.45 and 2.8, nil or low contamination), and Zn (0.76 and 3.0, depleted and moderate contamination) indicate that concentrations have been considerably diluted at the discharge. These values of the Av-NEFs for As and Zn are comparable to other regional coastal systems that are not anthropogenically contaminated (Table 1). Mercury concentrations in some sampling sites (<5 ng g⁻¹; St 1 to 17 in the MD-ET) are less than the Earth's crust. The NEF_{UCC} reduces the contamination interpretation compared to the NEF_{BL} and the sampling sites closest to the arroyo mouth are considerably diluted (Fig. 4). The tailings and ash (Table 1) from melting extraction and some sampling sites (St 1, 4–10, 12–16, and 22) along the drainage system are severely contaminated with Hg (Fig. 4). Sample 22 reflects a change in lithology and the arrival of another arroyo.

3.5. Anthropogenic or natural contamination: multivariate analysis from arroyo sediments

A Pearson correlation matrix for the sediment components was made to group the elements according to their association with the gold mine (Table 2). As, Pb, and Zn were well-correlated ($r > 0.7$; $P < 0.001$). The high correlation between these three elements indicates a common contamination source. Mercury is enriched in tailings and ash, and it is less correlated with As, Pb, and Zn ($r < 0.5$; $P < 0.05$). This (and the concentrations <5 ng g⁻¹ along the arroyo sediments described in Section 3.2) indicates a different source of Hg, probably intermittently generated amalgamation, being only of anthropogenic origin. The iron and manganese are well-correlated ($r < 0.99$; $P < 0.001$). In uncontaminated systems they are well-correlated to Al and Li. In contrast Li and Al are not correlated, which indicates that there are more than two lithogenic sources in the system. Conversely, Li and oxyhydroxides of Fe and Mn are more sensitive to lithology changes than Al (Fig. 5a and b).

These findings are supported by the results from the principal component analysis of the dataset (Fig. 6). Four principal components were identified that explained 89% of the total variance. Factor 1 was characterized by a high positive contribution of the anthropogenic source elements, especially As, Pb, and Zn (37% of the variance). The elements with the highest contamination in the arroyo showed a stronger relationship with Factor 1, whereas Factor 2 was strongly correlated with the oxyhydroxides of Fe and Mn (27% of the variance). Factor 3 (Li and Hg, 16% of the variance) and Factor 4 (Al, 10% of the variance) played a minor role in the distribution of the elements.

Table 2 Pearson correlation matrix, for the elements of the arroyo sediments (total fraction)

	Al	As	Fe	Hg	Li	Mn	Pb	Zn
Al	1							
As	0.17	1						
Fe	-0.25	0.13	1					
Hg	0.21	0.51	-0.01	1				
Li	0.21	-0.14	0.05	0.30	1			
Mn	0.09	0.07	0.99	-0.03	0.04	1		
Pb	-0.34	0.78	0.07	0.34	-0.13	0.03	1	
Zn	-0.01	0.71	0.16	0.42	-0.13	0.16	0.89	1

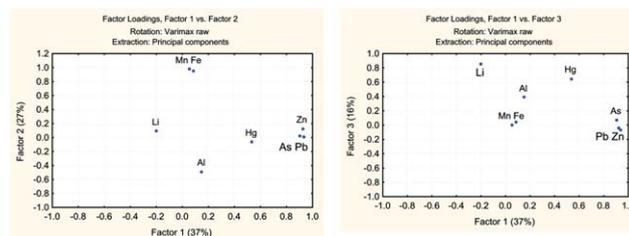


Fig. 6 Multivariate analysis of the elements in the arroyo sediments. A principal component analysis (PCA) was done to evaluate the association of elements to distinguish between a natural and/or anthropogenic origin (a) Factor 1 explains 37% of the variance represented by the enriched elements As, Pb, and Zn, and Factor 2 where Fe and Mn explain 27% of the variance, and (b) Factor 3 is represented by Li with 16% of the variance.

3.6. Natural enrichment of As, Pb, and Zn and their comparison with regional concentrations

This section was included because the contents of the region (around 800 km from the study area) are rich in As. The results are similar to our data using the NEF_{UCC} in coastal sediment samples close to the Pacific Ocean (St 18 to 26; Table 1) found in regional studies. Sediment cores from pristine fan deltas 200 km from the study area, such as the El Coyote sediments, have a natural enrichment in As and depletion in Zn.⁴² However, with the NEFs recalculated using the local background levels in this study, the enrichments of As and Zinc are both moderate. The natural enrichment of As (BL in this study 7.9 ± 2.7 mg kg⁻¹ in relation to 2 mg kg⁻¹ Wedepohl³⁸) is caused by geological processes, most likely volcanism and high tectonic activity in the region in the past. In Santa Rosalía, at the mining zone in Loreto located about 800 km from the study area, at San Juan de La Costa (60 km from the study area), and at the Ojo de Liebre Lagoon and the Guerrero Negro (800 km from the study area), the As contents are diluted (range 0.05 to 17 mg kg⁻¹),^{42,44,45} see Table 1.

The comparison between concentrations from this study area (Volke-Sepúlveda *et al.*,⁸ this study) shows that the results of the El Triunfo tailings are in a range between the minimum of El Fraile and the extreme of Zimapán (Table 1), which was more enriched in As and associated elements.³³

3.7. Comparison with sediments influenced by gold mining in other world systems

Our results were compared with other impacted coastal systems with Au and Ag mines that are also contaminated by As, Hg, Pb,

and Zn. In our study the presence of arsenic from As-rich riverbed sediments is associated with pyrite and arsenopyrite minerals observed *in situ*, whose mobilization has been favored by past gold mining, such as at the Rio Anllóns, Spain.⁹ The coastal river sediment influenced by an Au mine in Chile (maximum concentration of As 2000 mg kg⁻¹),⁴⁷ Spain (max. concentration of 499 mg kg⁻¹),⁵⁰ and As, Hg, Pb, and Zn in South African mining areas (maximum concentrations of 130.7, 5.8, 38.7 and 423.5 mg kg⁻¹)³ are highly enriched and serious problems of environmental contamination have been reported. Concentrations in tailings left from artisanal mining such as at Zloty stock, Poland⁴⁹ were also comparable with this study area and with other gold mining areas³³ that showed evidence of soil contamination that could negatively influence agriculture and farming and consequently humans.

To assess the high concentration of Pb in tailings and ash analyzed in our study, we compared the Pb/Zn ratio (tailings 1.9; ash 14) with the Earth's crust (0.33) calculated from Wedepohl.³⁸ The high concentration is caused by a considerable, relative accumulation of Pb compared to the contents in the arroyo (arroyo sediments Pb/Zn = 0.66). In other coastal sediments influenced by mines (referenced in Table 1), such as in Russia (Pb/Zn ratio of 0.02, with 106 and 4227 mg kg⁻¹ of Pb and Zn)⁵¹ and Spain (Pb/Zn ratio of 0.11, with 447 and 3998 mg kg⁻¹ of Pb and Zn),⁴⁸ only Australia (Pb/Zn ratio of 0.9 with 724 and 807 mg kg⁻¹ of Pb and Zn)⁴ reflects a Pb enrichment with respect to Zn.

Most studies that have found high concentration of Hg are referring to Hg mines, though there are also reports of abandoned gold mines with high contents of Hg in soils and tailings.² The results for mercury in this study and in a previous study⁸ also reported extremely high concentrations in tailings and ash. Although there has been no report in the literature that the Hg-amalgam extraction method has been used, a significant Hg enrichment (max. 217 ng g⁻¹) was found in the arroyo sediments in the first 18 km after the alteration zone.

In permanent river sediments, the release of As is greatly influenced by the effect of pH and phosphorus concentrations, and the kinetics of the As release process. Rubinos *et al.*⁹ found that at acid pH (4) the major oxidation states of As in solution were As(III) and As(V), representing 45% to 69% and 29% to 51% of As released. In contrast, at pH 10 almost all the released arsenic was As(V) (99%). In this study, the arroyo is dry and water to measure pH is only available during the sporadic rainy season. The major content of arsenic could be in the form of As (V), which is more stable and predominant under oxidizing environmental conditions, whereas under reducing conditions As (III) is predominant.⁵⁴ However, more studies are necessary to evaluate the As speciation along the arroyo sediment to determine how much As is released from the tailings, ash, and polluted sediments and its wind-borne transport, and also to understand the release of Pb and Zn. It is well-known that Pb is less labile and bioavailable than Zn. Studies have shown high total concentrations of Pb with only a small percentage of bioavailable lead.^{23,24,26} In this studied area, Pb and Zn do not travel longer distances than As.

Tailings and ash in the system were extremely enriched in As, Hg, Pb, and Zn (Table 1) and weathering by wind and rain promotes their distribution along the arroyo. Water is scarce in this arid (desert) zone and As concentrations in regional aquifers

of 400 µg L⁻¹ have been reported,⁵⁵ whereas concentrations in most of the aquifers are up to the Mexican legal limit⁵⁶ of <25 µg L⁻¹. According to Rubinos *et al.*,¹² As(V) forms oxides in sediments and this is probably the dominant oxidation state. However As(V) may reach the aquifers converted to As(III), which is easily incorporated into the food chain and which is also the toxic oxidation state with carcinogen effects. Reexploitation of tailings followed by soil remediation is necessary to avoid exposure of contaminants in this system and other systems around the world.

4. Conclusions

The present study of arroyo sediments influenced by an Au mine shows a significant enrichment of As, Hg, Pb, and Zn in tailings and ash from the melting extraction within the mining district and in some sampling sites along the principal arroyo to its discharge into the Pacific Ocean. The enrichment of As, Pb, and Zn in rocks is probably caused by geological volcanism. The Hg enrichment in the sediments and contents in ash and tailings indicates a clear anthropogenic influence, introduced into the system from past artisanal gold extraction processes. The enrichment, in the first 18 km of the arroyo path from the mining district, in the sediments is likely a result of seasonal erosion caused by rainfall and winds. Arsenic and Zn are severely enriched, however their concentrations along the arroyo specifically from the 20 km mark to the arroyo mouth close to the Pacific Ocean decreased considerably to moderate and low contamination. Lead was enriched in the samples closest to the mining district, however the Pb content was diluted to low NEF values in samples closest to the Pacific Ocean.

Acknowledgements

This research was funded by a grant from the SIP: 20090092, 20100692, 20110874. Instituto Politécnico Nacional, Mexico. Marmolejo-Rodríguez thanks the *Comisión de Operaciones y Fomento de las Actividades Académicas del Instituto Politécnico Nacional*. Sánchez-Martínez and Romero-Guadarrama thank the *Consejo Nacional de Ciencia y Tecnología*. The authors thank Dr Elisabeth Svensson and Dr Ellis Glazier for editing this English-language text.

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