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# Sediment accumulation of Ag, Cu, and Ni through a semi-arid basin as a by-product of the El Triunfo gold mine, Baja California Sur, Mexico

# Acumulación de Ag, Cu y Ni en sedimentos en una cuenca semiárida como sub-producto de la mina de oro El Triunfo, Baja California Sur, México

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# Abstract

The dispersal of Ag, Cu, and Ni in mine wastes (tailings and ash) was studied from the source of an abandoned gold mine at El Triunfo (Baja California Sur, Mexico) to the adjacent coast of the Pacific Ocean. The highest contamination levels of the studied elements were measured in one sample of the tailings (Ag: 247 mg kg<sup>-1</sup>; Cu: 1660 mg kg<sup>-1</sup>; Ni: 111 mg kg<sup>-1</sup>). Horizontal and vertical distributions of these elements were obtained from the analysis of surface sediments, tailings, a test pit, a sediment core, and dunes. The background levels of these elements were estimated from independent methods. Then, these regional background level calculations were used to determine the normalised enrichment factors (NEFs). Relatively high NEF values (averages of Ag, Cu, and Ni were 24.0, 3.0, and 1.4, respectively) indicated that the area close to the mine waste zone (up to about 18 km from the source area) was moderately to severely polluted. Moderate to null pollution (average NEFs of Ag, Cu, and Ni were 7, 2 and 1, respectively) was interpreted for the area at about 18-49 km from the mine waste zone. Vertical distributions of the elements in sediments of the overbank, the test pit in the mine zone, and the sediment core (at the discharge of the main arroyo Hondo–Las Gallinas–El Carrizal), also revealed enrichment of Ag, Cu, and Ni relative to the surface sediments. This study indicated that historic and contemporary contamination continues to impact the fluvial environment.

Keywords: silver, copper, metals, contamination, tailings, arroyo

# Resumen

Se estudió la dispersión de Ag, Cu, y Ni, en desechos mineros (jales y cenizas) desde su origen en la mina de oro abandonada de El Triunfo (Baja California Sur, México) hasta su desembocadura en la costa adyacente al Océano Pacífico. Los mayores niveles de la contaminación de los elementos estudiados se presentan en los jales (Ag: 247 mg kg<sup>-1</sup>; Cu: 1660 mg kg<sup>-1</sup>; Ni: 111 mg kg<sup>-1</sup>). Se obtuvieron distribuciones horizontales y verticales de estos elementos a partir de los análisis de sedimentos superficiales, de un jale, de un pozo de ensayo, de un testigo y en las dunas adyacentes a la desembocadura del arroyo. Los niveles de fondo fueron calculados considerando varios métodos independientes. Luego, con estos cálculos de niveles de fondo se determinaron los Factores de Enriquecimiento Normalizados (NEFs). Los valores relativamente altos de NEF (promedios de Ag, Cu and Ni de 24.0, 3.0 y 1.4, respectivamente) indicaron que el área situada cerca de la zona minera (aproximadamente 18 km de los desechos mineros abandonados) se encuentra de moderada a severamente contaminada. Una contaminación moderada a nula (NEFs promedio de Ag, Cu y Ni: 7, 2 y 1, respectivamente) fue determinada en el área comprendida entre los 18 y los 49 km medidos desde el distrito minero. Las distribuciones verticales de los elementos en los sedimentos de los jales y el pozo de ensayo en la zona minera, así como en el testigo analizado en la desembocadura del arroyo principal (Arroyo Hondo – Las Gallinas – El Carrizal), muestran mayor enriquecimiento de Ag, Cu y Ni, que los sedimentos superficiales adyacentes. Este estudio indica que la contaminación histórica y contemporánea está impactando el ambiente fluvial.

Palabras clave: plata, cobre, metales, contaminación, jales, arroyo

# 1. Introduction

Large quantities of mineral residues that are rich in Ag and other associated elements, such as Cu and Ni, are produced when artisanal mining techniques are used to mine for Au. As a result of these residues, environmental contamination has been reported (Rampe and Runnells, 1989; Ramírez-Requelme et al., 2003), requiring costly remediation processes for the deteriorated environment. Mining residues (tailings and ash) can be scattered by winds and transported by water during the rainy season. This movement of residues may remobilise trace elements in adjacent areas, thereby increasing their concentrations in sediments and soil, which act as sinks for contaminants (Hudson-Edwards et al., 1999). Sediment quality has been recognised as an important indicator of the input of anthropogenic pollutants (Chester, 2003). Trace metals are also introduced to sediments through massive tailing dams via the atmospheric fallout of fine particles. Studies on silver sorption in soils show that silver is controlled by the organic matter in the soil, either through exchange or complexation (Jacobson et al., 2005). Thus, changes in geochemical conditions can easily remobilise sequestered trace metals, making the metal-rich sediment repositories a potential long-term source of pollution, from which the genotoxic metals can move through the food chain in living organisms (Ward et al., 1977; Peplow and Edmonds, 2005).

Gold mines contain many sulphide minerals, with the predominant minerals being pyrite and arsenopyrite (Rubinos *et al.*, 2003). The Fe of the pyrite captures such elements as Ni and Cu (and others) in the form of leachable oxides. The gold found in Pb–(Ag)–Zn ore deposits are of high-sulphidation veins and stockwork types, such as the gold found in Mazarrón, Spain (Oyarzun *et al.*, 2011). Because of the high concentrations of Pb and Ag (500 mg kg<sup>-1</sup> Ag in galena) at the Ag-mining site on the crest of Medvednica mountain near Zagreb (Croatia), high concentrations of associated elements, such as Cu and Ni, have been generated, which have been attributed

to the oxidation of sulphides in the weathering environment (Durn *et al.*, 1999).

Trace element studies around abandoned mines reflect instrumental limitations and a lack of stringent regulatory guidelines in the past (Kim and Jung, 2004; Ahn *et al.*, 2005; Bhattacharya *et al.*, 2006). Effluents of gold mines contain elements at toxic concentrations, producing metal enrichment in the sediments of various types of aquatic systems, such as arid river sediments (Australia; Taylor and Hudson-Edwards, 2008) and tropical systems (Brazil; de Andrade Lima *et al.*, 2008), where these effluents have been shown to exceed background concentrations of Cu significantly.

Abandoned mine sites with high contents of accumulated tailings can also be found close to towns or cities. The accumulation of trace elements needs to be investigated because of the risk of exposure of the population to the toxic elements. The presence of Ag, Cu, and Ni from abandoned mines in small towns may have environmental effects, because Ag is toxic to microorganisms and is a suspected carcinogen for humans (Emsley, 1990; Rodgers et al., 1996). Copper is an essential element, and humans require approximately 2-5 mg of Cu per day (Merian, 1991). However, copper is toxic in high amounts, as are other nonessential heavy metals, even at low concentrations, e.g., Hg and Pb (Emsley, 1990). Exposure to Ni in humans produces adverse effects upon skin contact. An increased risk of respiratory-tract cancers may occur via the inhalation of dust or fumes from mining with minor effects of respiratory tract irritation and asthma (Merian, 1991). Corrective actions to avoid the dispersion of contaminants must be achieved by considering the analytical data and characteristics of each site (Loredo et al., 2005).

Thus, the aims of our research were two-fold: 1) to assess the enrichment processes of the main arroyo that is adjacent to the mining district where Ag, Cu, and Ni have been found in tailings, test pits, surface sediments, sediment cores, and dunes from the source (El Triunfo mining district: ET-MD) to the destination (Fig. 1), the arroyo's discharge into the Pacific Ocean; and 2) to deter-



mine the influence of those elements from the abandoned gold mines. For this purpose, the regional background levels and the normalised enrichment factors were calculated to determine the horizontal and vertical distributions along the pathway to the arroyo's discharge into the Pacific Ocean.

#### 2. Study Area

The ET-MD is located at 24°09'02"N and 110°06'22"W. The system covers the main arroyo, which changes its name to: Hondo - Las Gallinas - El Carrizal, and runs from the mining district to the Pacific Ocean (Fig. 1). This arroyo discharges into an evaporitic basin that has a marine influence (salinity = 60-140 ‰, and pH = 7.98). Abandoned tailings are dispersed into the environment, mainly by the wind, though this desert zone occasionally experiences tropical storms and hurricanes. The average annual precipitation ranges from 400 mm in the Sierra La Laguna to less than 200 mm in the greater part of the system. Previous studies, predominantly of the soils and flora, have found high contents of As, Pb, and Zn (Carrillo-Chávez et al., 2000, Naranjo, 2004). The aquifers have been studied by Carrillo (1996), who reported 0.21 mgL<sup>-1</sup> of As in groundwater. On the other hand, elevated concentrations of As, Hg, Pb, and Zn in both tailings and sediments have been reported (Marmolejo-Rodríguez et al., 2011, Romero Guadarrama et al., 2010). Volke-Sepúlveda et al. (2003) reported concentrations of Ag, Cu, and Ni in grain size fractions (from <1700 to  $<38 \mu m$ ) of one tailing sample (< 4 to 86.2, 99-447, and 21.5-60 mg kg<sup>-1</sup>, respectively), one ash sample (<4-123, 492-2155, 9-94, mg kg<sup>-1</sup> respectively) and two alluvial soil samples (<4, 150-682, and 113-266 mg kg<sup>-1</sup> respectively). Nevertheless, their analyses were conducted at the mine wastes (approximately 200 m from the abandoned installations of the mine).

Stockwork and dispersed deposits consist of gold associated with pyrite and arsenopyrite. The average grade (average assay) of Au and Ag ranges from 0.7 to 3.3 and 131 to 436 grams per tonne (g t<sup>-1</sup>) respectively, in rocks from the exploitation zone (COREMI, 1999). Extensive waste deposits in tailings and ash from the ignition oven at the abandoned mine have been left in the surroundings and have been concentrated into arsenolite. The abandoned mine installations are located in the small town of El Triunfo (around 500 inhabitants); therefore, these inhabitants are likely to be exposed to the tailings. Moreover, because tourists often visit this region, they also could be exposed to inhalation of metal dust, because there are no restrictions on access to the abandoned mine.

#### 3. Material and Methods

Samples from tailings (T1), the overbank tailings pile (T2 station 4), the test pit (station 4), and ash (residues from the walls of the abandoned mining installations, station 1) were collected from the zone of El Triunfo (Fig. 1). The overbank samples were obtained from the base of the exposures toward the surface every 10 cm using a plastic spoon. Samples at 10 cm interval from the upper 1 m of the excavated section (of a test pit were collected (4 m of distance from the overbank). Ash samples were collected from the surface of the abandoned installations. One sediment core (station 25) was obtained from the middle of the evaporitic basin (a small lagoon) using a

plastic tube with a plastic trap. Three dunes were sampled at the mouth of the El Carrizal arroyo (1 sample every 50 m) at its connection to the Pacific Ocean. Surface sediments were collected along the 49-km length of the arroyo (stations 1 to 26), from the ET–MD to the Pacific Ocean. Clean polyethylene bottles and plastic spoons (acid-washed with 15% HNO<sub>3</sub> and 10% HCl separately) were used to collect the samples.

Sediments were dried and pulverised with an agate mortar. The < 2000-µm fraction was used for analysis. Briefly, the sediments (0.25 g) were completely dissolved with HCl, HF, HClO<sub>4</sub> and HNO<sub>3</sub>. The samples were digested with the four acids, beginning with hydrofluoric acid and followed by a mixture of nitric and perchloric acids while undergoing heating through a precisely controlled heating programme in several ramping and holding cycles that brought the samples to dryness. After the samples were completely dried, they were dissolved again using hydrochloric and nitric acids. Metals (Al, Ag, Cu, and Ni) were determined using a Perkin Elmer Sciex ELAN 9000 ICP-MS (Actlabs, Canada). The analytical methods were validated using certified reference materials of marine sediments (PACS-2 and MESS-3). The results of the method validation are included in Table 1.

Linear regressions and their respective 95% prediction limits on Al were performed for Ag, Cu, and Ni, allowing us to obtain the background values from the lithogenic element content of the sediments following the method



Fig. 2.- Spatial distribution of the concentrations of Ag, Cu, and Ni as a function of distance from the source. Filled circles–Ag, triangles–Cu, and open circles–Ni. In the upper continental crust, the average values for Ag, Cu, and Ni are 0.055, 14.3, and 18.6 mg kg<sup>-1</sup>, respectively (Wedepohl, 1995).

Fig. 2.- Distribución espacial de las concentraciones de Ag, Cu, y Ni, en función de la distancia. Círculos llenos = Ag, triángulos = Cu, y círculos vacíos = Ni. En la corteza continental superior los promedios para Ag, Cu, y Ni, son 0.055, 14.3 y 18.6 mg kg<sup>-1</sup> respectivamente (Wedepohl, 1995).

	mean ± one standard deviation						
Certificate Materials	Al (%)	Ag (mg kg <sup>-1</sup> )	Cu (mg kg <sup>-1</sup> )	Ni (mg kg <sup>-1</sup> )			
PACS-2 Certified This work (n=3)	$8.59 \pm 0.23$ $8.30 \pm 0.30$	$0.18 \pm 0.02$ $0.16 \pm 0.02$	$33.9 \pm 1.6$ $34.2 \pm 1.0$	$46.9 \pm 2.2$ $45.6 \pm 1.2$			
MESS-3 Certified This work (n=3)	$6.62 \pm 0.32$ $6.47 \pm 0.24$	$1.22 \pm 0.14$ $1.28 \pm 0.23$	$\begin{array}{r} 310\pm12\\ 315\pm5\end{array}$	$39.5 \pm 2.3$ $40.1 \pm 1.4$			

Table 1. Method validation of results from certified reference materials (CRMs) of marine sediments (PACS-2 and MESS-3). Averages and standard deviations of the certified (Berman *et al.*, 1997) and obtained results from triplicate determinations of the CRM (this work) are presented.

Tabla 1. Resultados de la validación de los métodos con material de referencia certificado (CRMs) de sedimento marino (PACS-2 y MESS-3). Promedios y desviaciones estándar del material certificado (Berman *et al.*, 1997) y obtenido por triplicado del CRMs (este trabajo).

of Marmolejo-Rodriguez *et al.* (2007a,b). Alternative methods were according by Marmolejo-Rodríguez *et al.* (2011) and for univariate data based on the multiple-test method proposed by Verma (1997) was also used for estimating background concentrations under the assumption that the arroyo sediments far away from the pollution sites represent the background values.

Normalised enrichment factors (NEFs) were calculated as a function of background levels from the following equations:

$$NEF_{Metal} = [Metal] / [Metal]_{BL}$$
(1)

where

$$[Metal]_{BL} = a \cdot [Al] + b \tag{2}$$

To calculate the NEF<sub>Metal</sub>, it was necessary to divide the enriched metal (natural and/or anthropogenic) of the collected sample by the calculated metal containing the lithogenic element (Metal<sub>BI</sub>) (equation 1). To calculate equation 2, it was necessary to know the Al concentrations in the least contaminated samples. In this case, we used only some surface sediment samples considered as unpolluted to calculate the correlation. Coefficients a and b resulted from the correlation equation for each element according to the metal content in samples from surface sediments that had not been polluted. Equation 2 was applied for each element and for each sampling site, and the Al concentration in the contaminated samples was not changed in the system. Therefore, in equation 2, [Metal]<sub>PI</sub> is the concentration of metal in the sediment if there had been no contamination. For interpretation of the NEFs results, the contamination criteria used in this study were NEFs <1: no contamination; 1–3: zero or low contamination; 3-10: moderate; 10-25: severe; 25-50: very severe; and >50: extremely severe (Marmolejo-Rodríguez et al., 2011).

	km	Al (%)	Ag mg kg-1	Cu mg kg-1	Ni mg kg-1
		Surface	e sediments	<u> </u>	
1	0.01	8.32	4.62	75.8	111.0
$\frac{2}{2}$	0.39	8.70	3.31	28.4	25.0
5	0.50	8.35 7 73	35.10 36.10	27.7	23.0
5	4.05	7.73	1 95	17.1	11.8
6	6.39	7.66	8.70	40.0	14.9
7	7.81	7.53	4.87	43.8	13.8
8	8.34	7.98	4.38	52.6	17.2
9	9.53	9.29	2.72	47.8	30.1
10	9.77	8.66	2.59	19.7	11.8
11	9.97	8.55	0.08	13.5	11.1
12	10.39	6.22 6.95	2 33	21.9	8.9
14	12.23	7.84	2.83	23.6	12.1
15	12.65	6.63	4.17	52.1	14.1
16	16.53	9.27	0.74	47.2	33.8
17	17.41	8.66	0.79	16.5	16.0
18	20.95	8.25	0.38	10.3	13.1
19	25.51	7.88	0.24	12.0	16.4
20	30.00	6.87	0.07	9.6	8.9
∠1 22	36.18	4.23	0.09	19.0 29.4	1/./ 24 A
22	40.30	7.10	0.10	74	84
24	46.44	6.99	0.11	4.9	5.7
25	46.50	7.53	0.05	4.0	5.6
26	48.78	6.17	0.05	4.2	4.6
		Backgrou	nd level (BL)		
Regression method		$7.77 \pm 1.09$	$0.28\pm0.27$	$20.7\pm12.1$	$16.0\pm7.2$
Outlier based method		(n=20) 7 30+1 40	(n=9) 0.101+0.065	(n=18)	(n=23)
(A)		(n=12)	(n=7)	8.61±4.37 (n=8)	(n=10)
Outlier-based method		$6.08\pm1.40$ (n=8)	0.0783±0.0256	11.3±8.9	11.5±7.2
(B)		0.98±1.40 (11-8)	(n=6)	(n=8)	(n=8)
T 1	I	1.70	ailing	1((0	111.0
1-1 T 2		1.76	247	1660	111.0
Ash		5.05	82.8-247	588.0	32.2
A-1		0.15	37.60	42.9	2.4
A-2		0.32	89.30	117.0	3.4
Test pit					
TP-1cm		7.71	12.90	65.2	27.1
TP-10cm		6.90	11.90	89.1	24.4
TP-20cm		7.04	23.10	157.0	22.8
TP-40cm		7.62	6.95	32.9	21.3
TP-50cm		7.32	2.98	52.7	25.3
TP-60cm		7.82	5.47	28.0	23.0
TP-70cm		7.45	57.00	44.2	20.7
TP-80cm		2.76	6.42	27.4	15.5
C Jam	1	5 42	Lore 1.75	26.5	16.0
C-2cm		5.45 6.02	1./5	20.3 32.8	10.0
C-6cm		6.96	2.19	33.8	20.5
C-8cm		7.03	1.19	26.2	21.5
C-10cm		7.29	2.07	33.6	20.3
C-12cm		7.20	2.23	34.7	50.5
C-14cm		7.09	0.89	33.4	24.6
C-16cm		7.87	1.80	34.4	23.7
C-18cm		8.40 0.51	2.33	38.0 57.5	24.1 32.8
C-20011		9.31	3.31	57.5	32.0
C-24cm		7.83	3.55	56.7	32.1
C-26cm		8.50	3.55	58.9	32.4
C-28cm		8.59	3.17	50.0	28.7
C-30cm		8.40	2.41	45.3	26.6
C-32cm		9.10	1.54	42.2	25.3
C-34cm		8.38	1.63	37.4	23.7
D 1	I	6.43 L	2 57	26.6	21.0
D-1 D-2		6 74	3.20	37.4	21.9
D-3		8 46	10.70	74.8	25.6

- Table 2. Concentrations of Al, Ag, Cu, and Ni in the surface sediments of the Hondo-Las Gallinas-El Carrizal arroyo in addition to the tailings, ash, test pit (near the mining district) and sediment results from the core and dunes at the arroyo mouth.
- Tabla 2. Concentraciones de Al, Ag, Cu, y Ni en sedimento superficial del arroyo Hondo - Las Gallinas -El Carrizal. Además los resultados de las muestras de jales, cenizas, pozo de ensayo (cerca del distrito minero) y resultados de los testigos y las dunas en la desembocadura del arroyo.

	NEF Ag	NEF Ag*	NEF Ag**	NEF Cu	NEF Cu*	NEF Cu**	NEF Ni	NEF Ni*	NEF Ni**
Surface sediments									
1	12.8	15.4	15.8	3.4	3.4	3.5	6.1	6.5	6.7
2	8.1	10.6	10.9	1.1	1.2	1.3	1.2	1.4	1.4
3	90.7	110.1	113.1	1.2	1.2	1.3	1.5	1.5	1.4
4	77	73	155.5 7 A	2.0	2.2	1.7	1.5	1.4	1.4
6	31.2	31.5	32.4	2.6	2.0	2.0	1.0	0.0	1.0
7	18.6	18.0	18.5	3.2	2.2	2.2	1.1	0.9	0.9
8	13.8	15.2	15.7	2.8	2.5	2.5	1.1	1.0	1.1
9	5.6	8.1	8.4	1.4	1.9	2.0	1.2	1.6	1.6
10	6.4	8.3	8.5	0.7	0.9	0.9	0.6	0.7	0.7
11	0.2	0.3	0.3	0.5	0.6	0.6	0.6	0.6	0.6
12	8.9	10.5	10.8	1.0	1.0	1.0	0.6	0.6	0.7
13	12.3	9.3	9.6	2.0	0.8	0.8	1.0	0.6	0.6
14	9.4	10.0	10.3	1.4	1.1	1.2	0.8	0.7	0.8
15	27.8	17.5	17.9	15.1	2.9	3.0	2.2	1.0	1.1
10	2.0	2.2	2.5	1.4	0.7	2.0	1.4	1.8	1.8
18	1.1	1.3	1.3	0.0	0.7	0.7	0.8	0.9	0.9
19	0.8	0.8	0.9	0.7	0.6	0.6	1.1	1.0	1.0
20	0.4	0.3	0.3	1.6	0.5	0.5	1.1	0.6	0.6
21	-0.6	0.6	0.6	-0.8	1.7	1.7	-1.8	2.0	2.1
22	3.2	4.5	4.6	0.9	1.2	1.3	1.1	1.3	1.3
23	0.5	0.4	0.4	0.8	0.4	0.4	0.9	0.6	0.6
24	0.6	0.4	0.4	0.6	0.3	0.3	0.6	0.4	0.4
25	0.2	0.2	0.2	0.3	0.2	0.2	0.4	0.4	0.4
26	0.5	0.2	0.2	-2.4	0.3	0.3	1.4	0.4	0.4
т 1	5201	2000 1	2256.2		(12111ng	264.1	4.1	20.6	21.5
T-1 T-2	-550.1	2020.4 207 1	418 2	-52.1	145.6	26.5	-4.1	2.8	28
Ash	5050.5	407.1	410.2	50.7	145.0	20.5	120.0	2.0	2.0
A-1	-56.9	6963	7153.0	-0.6	107.4	110.4	-0.1	7.8	8.0
A-2	-139.7	7752	7963.2	-1.7	137.2	141.1	-0.1	5.2	5.3
				Test	pit				
TP-1cm	45.3	46.5	47.7	4.2	3.2	3.3	2.0	1.7	1.8
TP-10cm	64.9	47.9	49.2	13.7	4.8	5.0	2.9	1.7	1.8
TP-20cm	114.9	91.1	93.6	19.4	8.4	8.6	2.5	1.6	1.6
TP-30cm	10.5	14.3	14./	4.0	2.2	2.2	1.9	1.5	1.4
TP-40cm	12.6	23.5	20.0	2.2 1 7	1.0	1.7	2.3	1.4	1.4
TP-60cm	18.3	19.4	20.0	17	13	1.4	1.6	1.7	1.7
TP-70cm	226.0	212.5	218.3	3.5	2.2	2.3	1.7	1.3	1.4
TP-80cm	-19.2	64.6	66.4	-0.7	3.7	3.8	-0.8	2.7	2.8
				Coi	re				
C-2cm	0.00	9.0	14.7	-2.6	1.8	2.2	-9.1	1.4	1.4
C-4cm	29.8	10.1	26.0	-9.5	2.0	1.7	8.4	1.5	1.4
C-6cm	11.0	8.4	11.6	4.7	1.8	2.8	2.3	1.4	1.7
C-8cm	6.0	4.7	20.0	3.3	1.4	1.4	2.3	1.5	1.5
C-10cm	8.9	7.9	218.3	3.1	1./	2.3	1.8	1.4	1.4
C-12cm	10.1	0.0 3.5	00.4 0.2	3.5	1.0	5.8 1.9	4.9	5.4 1.7	2.0
C-16cm	59	6.4	10.4	2.0	1.6	2.1	1.6	1.7	1.5
C-18cm	6.7	8.4	8.6	1.6	1.7	1.9	1.3	1.4	1.5
C-20cm	6.9	10.3	4.8	1.6	2.3	1.4	1.3	1.7	1.5
C-22cm	7.2	10.3	8.1	1.7	2.2	1.8	1.3	1.6	1.4
C-24cm	11.8	12.6	8.8	3.3	2.7	1.9	2.2	2.0	3.5
C-26cm	9.3	11.6	3.6	2.4	2.6	1.8	1.7	1.9	1.7
C-28cm	8.0	10.3	6.5	1.9	2.2	1.7	1.4	1.6	1.5
C-30cm	6.5	8.0	8.6	1.9	2.0	1.8	1.4	1.5	1.4
C-32cm	3.4	4.7	10.5	1.3	1.7	2.3	1.1	1.4	1.7
C-34cm	4.4	5.4	10.6	1.0 D	1./	2.5	1.5	1.4	1./
D-1	20.6	11.1	11.9	30.7	2.1	27	43	17	19
D-2	19.6	13.2	10.5	7.9	2.1	2.2	3.4	1.8	1.7
D-3	28.3	35.1	8.2	3.1	3.3	2.1	1.3	1.5	1.6

Table 3. Normalised enrichment factors calculated by three methods. Linear regression, \*NEF= (Me/Al)sample/(Me/Al)BL, and \*\*DODESSYS method. Values in italics are anomalous.

Tabla 3. Factores de enriquecimiento normalizado calculado con tres métodos: Regresión lineal, \*NEF= (Me/Al) muestra/(Me/Al)BL, y DODESSYS. Valores en itálicas son anómalos.

#### 4. Results

# 4.1. Spatial distribution of Ag, Cu, and Ni in surface sediments

The concentrations versus distance are presented in Fig. 2 and Table 2. The ranged concentrations that were measured in the surface sediments were Ag, 0.05–36 mg kg<sup>-1</sup>; Cu, 4–76 mg kg<sup>-1</sup>; and Ni, 4.6–34 mg kg<sup>-1</sup>, thereby revealing a wide variation of concentrations over the approximately 49 km of the arroyo. The concentrations in the surface sediments decreased along the length of the arroyo from the abandoned installations that were rich in tailings and ash (i.e., the source) to the arroyo mouth adjacent to the Pacific Ocean (i.e., the destination). The measured concentrations in the dunes showed an accumulation of Ag (2.6-10.7 mg kg<sup>-1</sup>) and Cu (37-75 mg kg<sup>-1</sup>) relative to the sediments of the arroyo discharge (Ag and Cu concentrations were 0.05 and 4 mg kg<sup>-1</sup>, respectively).

# 4.2. Vertical distribution of Ag, Cu, and Ni in the overbank tailings, test pit and the core

The results from locations near the abandoned mining wastes of the overbank and the test pit and the results of the sediment core at the discharge are presented in Fig. 3. The concentrations in the overbank tailings sampled were ranged (T1 and T2) close to the alteration zone were rather high (in mg kg<sup>-1</sup> about 83 and 247 for Ag, 388 and 1660 for Cu, and 32 and 111 for Ni: Table 2). The test pit also showed an accumulation of up to 57 and 157 mg kg<sup>-1</sup> for Ag and Cu, respectively; for Ni, the maximum concentration was only about 27 mg kg<sup>-1</sup> (Table 2). In the arrovo mouth, sediment core results indicated that the sediments were deposited as a trap, and vertical accumulation of Ag, Cu, and Ni was evident (see open inverted triangles in Fig. 4). Silver, despite having a low concentrations in stations 25 and 26 (0.05 mg kg<sup>-1</sup>), which were close to the evaporitic basin, showed significant accumulation in the

	Al	Ag	Си	Ni
	%	mg kg-1	mg kg <sup>-1</sup>	mg kg-1
Arroyo Sediments Range (n=26)*	4.2 - 9.3	0.05 - 36.1	4-75.8	4.6-33.8
Background value (mean $+ s$ )*	$7.99 \pm 0.75$	$0.28\pm0.27$	$21 \pm 12$	16 ±7
Dackground value (mean ± 3)	1.99 ± 0.15	n=9	n=18	n=23*
NEF (1-17 km) BL*	-	0.2 - 126	0.6 - 15	0.8 - 2
NEF (17-45 km) BL*	-	0.2 - 3.2	0.3 - 1.6	0.4 - 1.4
Tailings (Overbank) Range (n=9)*	16-56	83 - 247	6.6 - 1660	12.7 - 111
NEF Tailings (Overbank)	1.0 - 5.0	407 - 3898	146 - 623	2.8 - 30
Ashes Range (n=2)*	0.15 - 0.32	37.6 - 89.3	42.9 - 117	2.4 - 3.4
Test pit Range (n=9)*	2.76 - 7.82	2.98 - 57	27.4 -157	15.5 - 27.1
Test pit NEFs*	-	13 - 226	1.7 - 19	1.6 - 2.9
Core Range* (n=17)*	5.4 - 9.5	0.89 - 3.6	26.2 - 58.9	16 - 50.5
Core sediments NEFs*	-	3 - 30	1.3 - 5	1.1 - 8
Dune sands Range (n=3)*	6.4 - 8.4	2.6 - 10.7	36.6 - 74.8	21.9 - 25.6
Dune Sands NEFs*	-	20 - 28	3 – 31	1.3 - 4
Regional contents				
Tailing different grain size <sup>1</sup>	n.d.	<4-86.2	99 - 447	21.5 - 60
Ashes <sup>1</sup>	n.d.	<4-123	492 - 2155	9 - 99
Alluvial Soils <sup>1</sup>	n.d.	<4	194 - 682	113 - 266
System impacted by gold mining in Mexico				
Tailing Nacozari Sonora, México <sup>2</sup>	n.d.	$48 \pm 2.3$	$400 \pm 16$	$70 \pm 16$
Santa Barbara Chihuahua <sup>3</sup>				
Tailings	n.d.	n.d.	472 - 2415	n.d.
Sediment	n.d.	n.d.	190	n.d.
Other sediments impacted by gold mining				
Vaal river Blesbokspruit South Africa <sup>4</sup>	_	0.3 - 10.2	144-362	16.2 - 438
NEFs	_	14.8 - 887	1.9 - 53	1.7 - 36.2
The Leichhardt River Australia <sup>5</sup>				1
Channel (arroyo)	_	n.d.	4 - 8500	n.a.
Overbank (sediments)	-	n.d.	19 - 1820	11.u.
Upper Continental Crust <sup>6</sup>	7.74	0.055	14.3	18.6
Upper Continental Crust <sup>7</sup>	8.15	0.053	28	47

\* This study

<sup>1</sup> Volke-Sepúlveda et al. (2003); <sup>2</sup> Meza-Figueroa et al. (2009); <sup>3</sup> Gutiérrez-Ruíz et al. (2007); <sup>4</sup> Roychundhury and Starke (2006); <sup>5</sup> Taylor and Hudson-Edwards (2008); <sup>6</sup> Wedepohl (1995); <sup>7</sup> Rudnick and Gao (2003).

Table 4. Average regional background levels and standard deviations of Ag, Cu, and Ni (mg kg<sup>-1</sup>) concentrations, as determined in surface sediments, the overbank, ash, the test pit, the core and dune sands from the El Triunfo mining district to their discharge into the Pacific Ocean. The NEFs are unitless. Ranges are compared to those reported in other mining-impacted systems around the world.

Tabla 4. Valores de fondo regionales de Ag, Cu, y Ni, en mg kg<sup>-1</sup>(promedio y desviación estándar). Concentraciones determinadas en sedimento superficial, la trinchera, ceniza, el pozo de arroyo, el núcleo y las dunas desde el distrito minero El Triunfo hasta su desembocadura en el Océano Pacífico. Los NEFs no tienen unidades. Los rangos son comparados con otros reportados en otros sistemas impactados por minas.



Fig. 3.- Vertical profiles of Ag, Cu, and Ni in the overbank (2 m height), test pit (1 m depth) and the core (34 cm depth). Filled circles = Ag, triangles = Cu, and open circles = Ni.

Fig. 3.- Perfiles verticales de la distribución de Ag, Cu, y Ni, en la terraza aluvial antigua influenciada por jales (2 metros de altura a partir de la superficie); el pozo de ensayo (1m de profundidad), y el testigo (34 cm de profundidad). Círculos llenos = Ag, triángulos = Cu, y círculos vacíos = Ni.

core (about 0.9-3.6; Table 2). Additionally, in the sediment core samples, Cu (26-58 mg kg<sup>-1</sup> in sediment core versus 4.0-4.9 mg kg<sup>-1</sup> at stations 24-26; Table 2) and Ni (16-50 mg kg<sup>-1</sup> versus 4.6-5.7 mg kg<sup>-1</sup>) also showed accumulation relative to the surface sediments of the arroyo mouth (see Fig. 1 for location).

4.3. Background level equation, prediction intervals, NEFs and the differences in the concentrations of Ag, Cu and Ni in ashes, overbank tailings, test pit, core and dunes

4.3.1. Linear regression method of Hanson et al. (1993), Cobelo-García and Prego (2003) and Marmolejo-Rodriguez et al. (2007a, b)

To calculate the linear regression equation and the background levels for each element, surface sediment results were used. The filled circles in Fig. 4 represent the non-polluted samples of the arroyo surface sediment, and those concentrations were used when constructing the linear regression. The criteria for classifying the samples as non-polluted is considering only the samples which are inside the prediction intervals and are well correlated to lithogenic element (Aluminium for this case). The averages with their respective standard deviations are shown in Table 2. Because Ag was found at higher concentrations in this system, fewer points were used to calculate its concentration than for Cu or Ni (Fig. 4). In this figure can be seen the points inside the prediction intervals. The averages of them are the Background Levels. For Ag, the open circles represent the levels of Ag in the sediments of the same arroyo (n=9). For Cu n= 18. In contrast, the Ni equation was calculated with n=23 sampling site results. The Ni concentrations fell within the confidence intervals, suggesting no evidence of anthropogenic enrichment in the arroyo surface sediments. The average background levels (Metal<sub>BI</sub>) calculated from the results of non-polluted samples (filled circles in Fig. 4) was 0.28  $\pm$  0.27 mg kg<sup>-1</sup> (Table 4) for Ag. NEF's results calculated with this method are presented in Table 3. At most stations, the Ag concentrations were greater than the average found in the Earth's crust (0.053; Rudnick and Gao, 2003; Table 4); therefore, the Metal<sub>BL</sub> was higher for Ag in this system than the average concentration found in the crust. However, for Cu and Ni, the results indicated the opposite with lower BLs ( $20.6 \pm 12.1$  and  $16.0 \pm 7.2$  mg kg<sup>-1</sup>, respectively) than the average concentrations found in the Earth's crust (Cu = 28 mg kg<sup>-1</sup>, Ni = 47 mg kg<sup>-1</sup>; Rudnick and Gao, 2003).

Aluminium concentrations of the surface sediments (average  $\pm$  standard deviation, about 7.8%  $\pm$  1.1%; from 26 surface sediment data in Table 4.) were similar to the average for the Earth's crust (8.15%; Rudnick and Gao, 2003) and were consequently within the range reported for many systems. It was useful to characterise the system, including the matrices that were anthropogenically altered (Fig. 4). Aluminium concentrations are consider-



Fig. 4.- Linear regression of the metal concentrations vs. Al at the least contaminated site (arroyo surface sediment) identified with the filled circles. Dashed lines represent the 95% prediction intervals. For the remainder of the stations of the arroyo, open circles = contaminated sites, filled triangles = tailings, open triangles = ash, filled crosses = the test pit, open upside down triangles = core samples, and the hexagon = dune samples. The solid horizontal line represents the average of the background level that was calculated (Table 4) for this system. This line is the regional average background level.

Fig. 4.- Regresión lineal de la concentración de los metales vs. Aluminio realizada con los resultados del sedimento superficial de las estaciones no contaminadas (identificadas por los círculos llenos). Las líneas discontinuas representan el 95 % de los intervalos de predicción. Para el resto de las estaciones: las muestras de arroyo contaminadas son los círculos vacíos, los jales son los triángulos llenos, los triángulos vacíos corresponden a las cenizas, las cruces al pozo de ensayo; los triángulos vacíos invertidos corresponden al testigo de sondeo y los hexágonos a las muestras de dunas. La línea horizontal es el valor de fondo promedio calculado (Tabla 4) para este sistema. ably lower in the tailing (1.76 and 5.65% in Table 2) and ash samples (0.15 and 0.32% in Table 2). The Al concentrations in the test pit are about 6.9-7.8% except one sample with 2.8%. Sediment core and dune samples display Al concentrations of about 5.4-9.5% and 6.4-8.5%, respectively (Fig. 4, Table 2).

# 4.3.2. Outlier-based method of univariate data using the multiple-test method proposed by Verma (1997)

An alternative method to estimate the background level for Ag, Cu and Zn would be to assume that the arroyo sediment samples far away from the pollution source (see tailing sites T-1 and T-2 in Fig. 1) are likely to be non-polluted. This method does not assume any significant correlation of Ag, Cu or Zn with Al in the background level samples, but does rely on a systematic behaviour (negative correlation) of these elements with the distance from the tailing sites (Fig. 1). Exploratory regression analysis of the abundance of these elements with distance (data of Table 2) supports this assumption, because even without the detection of discordant outliers (Verma and Díaz-González, 2012) it shows statistically significant correlation (at 95% confidence level) of each element with the distance (all linear regression coefficients were negative, implying decreasing concentration with increasing distance, n=26 for all cases,  $r_{Distance-Ag} =$ -0.437;  $r_{Distance-Cu} = -0.617$ ;  $r_{Distance-Zn} = -0.385$ ; all absolute r values are greater than the critical value of r at 95% confidence level about 0.375, see Table A20 in Verma, 2005). Therefore, we can estimate the background levels from the sediment data of samples relatively far from the tailing sites (Fig. 1). However, for the unbiased final estimations, the compositional data for these sites should be normally distributed, because any discordant outliers are likely to originate from the pollution process. This can be easily achieved through the computer program DODESSYS (Verma and Díaz-González, 2012), which uses the most recent precise critical values (Verma et al., 2008) for the evaluationWe present two different estimates of the background levels (Table 2) using the computer program DODESSYS. (A): the data for twelve sediment samples from sites 15 to 26 away from the tailing sites (Fig. 1, Table 2) were processed for discordant outliers from multiple-outlier type tests at 95% confidence level. (B): the data for only eight sediment samples from sites 19 to 26 much farther away from the tailing sites were used and processed from single-outlier tests at more strict 99% confidence level.

Both sets of background levels presented in Table 2 show good agreement between them. NEFs values calculated by this program are presented in Table 3.

#### 5. Discussion

# 5.1. Normalised Enrichment Factor calculations by different methods.

The NEF results calculated by three different methods are presented in Table 3. For natural sediments any of them can be used to further explore the implications of the entire dataset, although we have attempted in this paper the interpretation from the regression method by Hanson et al., (1993); Cobelo-García and Prego, (2003); and Marmolejo-Rodriguez et al. (2007a,b) for natural sediment. Nevertheless, although the linear regression method is recommended because it considers the specific value of Al for each sample -not an average of lithogenic element in all the system- to calculate NEFs; in order to evaluate anthropogenic influence such as the great contamination of tailings and ashes, with anomalous values of lithogenic element (Table 2 and Table 3), the linear regression method is limited, because in natural sediments, the linear model must not be forced to pass through the origin. NEFs results in tailings and ashes were different.

# 5.2. Alteration zone near the abandoned Au mine (source)

Concentrations of Ag and Cu in the tailings of the study area are higher compared to other geographic systems, such as in Ticapampa, Peru (Schippers et al., 2008) and some Au mines in parts of Australia (Mudd, 2007). In our study, the overbank tailings had high concentrations that decreased with depth, probably due to their proximity to a large tailings pile and the fact that they were deposited over time, thereby creating the overbank. A similar phenomenon was observed in the Leichhardt River, Australia (Taylor and Hudson-Edwards, 2008). The tailings are dispersed by the wind and thereby contaminated the adjacent region. The concentrations suggested that tailings from the El Triunfo mining district (Ag concentrations greater than 200 mg kg<sup>-1</sup>; Table 2 and Fig. 3) could be reprocessed with new biohydrometallurgical technologies (Schippers et al., 2008) to extract those elements.

The opposite behaviour occurred with Ag, Cu, and Ni concentrations in the test pit (Fig. 3), where the vertical concentrations increased with depth (Ag NEFs 13-226; Fig. 3), probably reflecting extreme events from both mining activities and the rainy season. Copper and Ni also showed an increase with depth (NEFs 1.7-19 and 1.6-2.9, respectively). These results allowed us to infer about the extreme events that carried sediments from the scattered tailings and the lixiviation processes.

Because of the potential effect on the population in the town of El Triunfo and other small towns in the nearby region, it is necessary that the tailings are removed or reme-





Fig. 5.- Distribución de los Factores de Enriquecimiento Normalizado (NEFs) a lo largo del arroyo desde la fuente (ET-MD) hasta el destino (desembocadura del arroyo). Los círculos llenos representan las muestras del arroyo. Se graficaron los promedios de los factores de enriquecimiento normalizado: para el pozo de ensayo (cruz), el núcleo (triángulos vacíos) y las dunas (triángulos llenos). La distancia entre el origen (ET-MD) y el destino (desembocadura del arroyo) es 49 km.

diated. The old structures of the abandoned mine containing ash (Ag 36.7-89.3 mg kg<sup>-1</sup> and Cu 42.9-117 mg kg<sup>-1</sup>) and tailings are visited by tourists that have direct access to the contaminated areas. If the Ag is extracted from the tail-



ings, it must be done under strict environmental control. The concentrations of these and other associated elements could be a risk to the population because of the proximity of the aquifers that support the local towns and cities.

#### 5.3. Arroyo sediments (transport of elements)

In the Hondo-Las Gallinas-El Carrizal arroyo, the sediments are dry during most of the year. The Ag and Cu are mostly dispersed by winds, and they have not been exposed to acid dissolution that is often experienced in temperate systems with low-pH water (Borrego *et al.*, 2004). Moreover, the Cu content was lower in this arid system than in other systems affected by Ag and Au mines, such as the sediments of the Leichhardt River, Australia (Taylor and Hudson-Edwards, 2008) and sediments of the Vaal River (Blesbokspruit, South Africa; Roychoudhury and Starke, 2006), where Cu and Ni are significantly enriched.

The enrichment calculated from the BL as a function of distance from the source is shown in Figure 5. It is evident that the Ag levels (NEF = 126) were enriched in the sediments near the mine and up to 18 km away. These concentrations were higher than those previously reported (Ward *et al.*, 1977) in soil and sediments near silver mines. The next section of the arroyo (18 to 49 km from the ET-MD) was not enriched with Ag, Cu and Ni (Ag NEFs = 0.2-3.2 and Cu and Ni NEFs <1.6).

#### 5.4. Arroyo mouth (destination) and dunes

The arroyo discharges into an evaporite basin (stations 24-26; Fig. 1). At this location, the vertical distribution of elements in the sediment core showed increased

- Fig. 6.- NEFs calculated for Ag, Cu, and Ni from the various samples of the system. A = arroyo surface sediment samples, TP = test pit samples, C = core samples, and D = dune samples. Boxes represent 95% of prediction intervals.
- Fig. 6.- Factores de Enriquecimiento Normalizado (NEFs) para Ag, Cu y Ni en las muestras del sistema. A= sedimento superficial del arroyo; TP = sedimento del pozo de ensayo, C= sedimento del testigo de sondeo y D = sedimento de las dunas. Las cajas grises corresponden al 95% del intervalo de predicción.

metal concentrations compared to the surface sediments (maximum Cu concentration was 58.9 mg kg<sup>-1</sup>; Tables 2 and 3). This finding could be related to the grain-size of sediment in the core, which was finer compared to the predominantly sandy sediments of the arroyo. It cannot be explained by the pH values, because sediment cores from acidic environments are known to concentrate metals such as Cu (Cu 1677 to 5712 mg kg<sup>-1</sup>; Borrego *et al.*, 2004). Because the water in the evaporitic basin was of pH 7.98 (basic or alkaline) and the surface sediments did not concentrate the metal concentrations, the higher concentrations in the core may be due to finer grain-size.

After determining that arroyo surface sediments near the arroyo mouth contained low concentrations of Ag, Cu, and Ni, the dunes at the arroyo mouth unexpectedly revealed an enrichment of these metals with NEFs of 20-28 for Ag, 3-31 for Cu, and 1.3-4 for Ni (Fig.5). This finding could be due to accumulation processes from the evaporitic basin sediments that are caused by old discharges from extreme rainy events or wind-borne transport, similar to observations made in other dunes contaminated by mining activities (Conesa *et al.*, 2011).

# 5.5. Comparison of enrichments between the natural sediments of the environments studied

The calculation of the 5th/95th percentiles of the NEFs of the test pit, arroyo sediments, sediment core, and dunes (Fig. 6) showed a clear enrichment of Ag in the test pit and in certain arroyo sediments (NEFs >100). Copper had NEFs greater than 10 in the surface sediments of the arroyo, sediment core, and dunes, while the Ni NEF was 1 (i.e., not enriched).

#### 5.6. Similar studies in other parts of Mexico

Studies on the distribution of silver (horizontal and/ or vertical) in tailings, soils and sediment of Mexico have been scarce. Some studies have been conducted to assess the anthropogenic impacts of heavy metal discharges. As an example, water treatment plants from the border region between California, USA and Baja California, Mexico, have been shown to release Ag (e.g., mean total fraction of  $Ag = 0.025 \text{ mg kg}^{-1}$ ), and Ag has been associated with iron oxy-hydroxides and organic matter in sediments (Villaescusa-Celava et al., 1997). These authors mentioned that Ag is useful for the determination of the origin of the anthropogenic impact using their concentrations according with Ruiz-Fernández et al., (2003), after an exhaustive geochemical and geochronological analysis. Agricultural development and urban growth in Sinaloa began 50 years ago, which confirmed that Ag was considered as a good indicator of allochthonous organic matter (Ruiz-Fernández et al., 2003). However, surface sediments that were influenced by mining were studied in the Rio Conchos basin (Chihuahua, Mexico; Gutiérrez et al., 2008). Although these authors did not report levels of Ag, it was correlated to potentially toxic elements (PTE). A statistical analysis of 540 samples of arroyo surface sediments showed significant correlations of Ag to Cu, toxic metalloids, and associated elements. High concentrations of Cu (472 -2415 mg kg<sup>-1</sup>) in tailings and sediments (190 mg kg<sup>-1</sup>) from the Santa Barbara mine zone (Chihuahua) were associated with such elements as As, Sb, and Pb at potentially toxic concentrations (Gutiérrez-Ruiz et al., 2007). A similar association in vertical distributions was found between Cu and PTE in sediments that were influenced by the Ag-Pb-Zn-Cu-Au mining district of Santa María, San Luis Potosí (Central Mexico; Castro-Larragoitia et al., 1997).

In the El Triunfo tailings, punctual research with detailed laboratory work is necessary such as that performed by Volke-Sepúlveda *et al.* (2003). However, these researchers did not measure the sediment distribution as a function of distance nor they determined which sediments were more polluted. These researchers found maximum concentrations in the fine fraction (<38  $\mu$ m) of Ag, Cu, and Ni in one tailing sample (86.2, 447, and 60 mg kg<sup>-1</sup>, respectively), one ash sample (123, 2155, and 99 mg kg<sup>-1</sup>, respectively), and in two samples of alluvial soils (<4, 682, and 266 mg kg<sup>-1</sup>, respectively). The results of this study and other similar studies are necessary to analyse the distribution of Ag and other toxic elements in enriched sediments and other matrices that are influenced by ore mines.

#### 6. Conclusions

Severe contamination of Ag was determined in surface sediments from the tailings, ash, arroyo surface sediments, test pit, sediment core, and dunes in the El Triunfo mining area. Copper was highly enriched in the tailings, sediment core, and dune sediments. Nickel was a smaller risk to the system. The tailings were dispersed in the small town of El Triunfo, where people, flora, and fauna are exposed to its contamination. Remediation studies to protect the nearby environment by treating the tailings are necessary to reduce the influence of the dispersal of the pollutants. Treatment of the abandoned installations (chimneys) is also necessary to lower the risk of metals' exposure to nearby residents and tourists.

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