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Environmental Assessment of an Active Tailings Pile in the State of Mexico (Central Mexico)

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Abstract: As part of the assessment of an active tailings pile, water and sediment samples were collected in different locations (10 in water, 8 in tailings and 5 in sediments across the El Ahogado River) in dry and wet season of the years 2005, 2006 and 2007 to determine acid mine drainage pollution (AMD). Chemical composition of water differentiate between two zones: 1) Zone of influence of AMD (inner zone), where water is highly acidic (pH 2.5), metals (in mg L⁻¹) such as As (0.095-0.1), Cd (0.04-0.2), Fe (0.35-88.56), Mn (0.06-12.81), Pb (1.47-5.6), Zn (0.48-46.2), as well as sulfates (up to 4880 mg L⁻¹) are above the maximum permissible limits (MPL) for human consumption and 2) zone out of influence of AMD (outer zone), where waters are from less acidic to alkaline (pH 3.54-8.76) and metals such as As (0.1-0.2), Cd (0.36-0.9), Fe (0.03-18.8), Mn (0.03-39.5), Pb (0.13-5.02), Zn (0.06-307), as well as sulfates (up to 4650 mg L⁻¹) still exceed the MPL also. In the outer zone, chemical pollution can be related to natural weathering of rocks in the study area. On the other hand, two methods were applied to calculate sediment pollution: 1) Enrichment Factor (EF), which indicates that Fe and Ba were the metals in pollutant levels, while As, Zn, Cu and Pb were in lower concentrations in unpolluted sediments (P1, P2, P3 and P4) located upstream the tailings pile. 2) The geoaccumulation index (I_{geo}), indicates that there is null pollution with respect to Ba, while metals such as As, Cu, Pb and Zn showed null to moderate capacity to pollute superficial water. Only Fe showed to be consistent with the first method (EF) and has moderately capacity to pollute. This method is more reliable than the former, due to the fact that it considers local background levels.

Key words: Sediment pollution, enrichment factor, geoaccumulation index, El Ahogado River

INTRODUCTION

Sulfide mine waste disposal constitutes an important environmental threat, either in extensively mineralized areas or in localized spot sites (Ferreira da Silva *et al.*, 2006). The mining wastes contain high metal concentrations and represent a source of metal pollution for a long time after extraction (Alvarez *et al.*, 2006; Ferreira da Silva *et al.*, 2006). The oxidation of sulfides such as pyrite, is an acid producing reaction, which affects the weathering of other minerals, leading to the formation of Acid Mine Drainage (AMD), often with high concentration of metals (Hudson Edwards *et al.*, 1999; Alakangas and Öhlander, 2006). Iron sulfates are common weathering products of Fe sulfide oxidation in mining environments and some have the potential to form acid drainage (Cravotta, 1994; Jennings *et al.*, 2000). As the metals are transported away from their source, their concentrations in surface and ground waters may be controlled by precipitation-dissolution and co-precipitation

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reactions, adsorption-desorption reactions and solid-solution substitutions (Blowes and Jambor, 1990; Anderson *et al.*, 1991; Levy *et al.*, 1997). The accumulation of metals in sediments is controlled by a number of environmental factors that include pH, redox potential (Eh), anthropogenic input, type and concentration of organic and inorganic ligands, hydraulic processes within the stream and available surface area for adsorption caused by the variation in grain size distribution (Atxmann and Luoma, 1991; Davies *et al.*, 1991; Sondi *et al.*, 1994; Wakida *et al.*, 2007).

This study aims to assess the metal concentrations in soils and surface waters around the active tailings pile located in the town of San Juan Zacazonapan (central Mexico) and the proximal El Ahogado River. The objectives of this study are: (1) To investigate the hydrogeochemical characteristics of the AMD originated at the tailings pile and (2) to evaluate the polluting extent of AMD.

MATERIALS AND METHODS

Location

The study area is located south west of the State of Mexico in the town of San Juan Zacazonapan (Fig. 1a). It is at an altitude of 1200 m.a.s.l. and the predominant climate is from temperate to warm with dry winter and rainy summer. During the months of July, August and September the region receives the maximum precipitations. The annual average precipitation is of 1500 mm. The temperature in summer exceeds 30°C and the temperature in winter oscillates between 10 to 16°C.

Study Area

The mining company in the study area is in operation since 1994. It exploits zinc, lead and copper from a volcano sedimentary massive sulfide deposit. The extracted mineral is put under a process of crushing and milling until the size of 200 µm. The concentrated minerals, that contain zinc sulfides, lead and copper, are recovered in the surface and the remnant, around 95% of the mineral (rich in pyrite, FeS₂), called tailings, is pumped as a slurry to the tailings pile. Studies have been made on the generation of acid leachates of these tailings which confirmed the potential of acid drainage generation due to its high pyrite content and the absence of neutralizing material (González Sandoval *et al.*, 2007). Currently, the tailings pile surface is of 132,800 m² and contains around five million tons of tailings deposited. On the other hand, to the east of the tailings pile, at 1300 m, El Ahogado River is located, which transports water through all the year. Water downstream to the east and to the south east of this river must be affected by the AMD.

Water Samples

Sampling of water, tailings and sediments (across the El Ahogado River upstream and downstream) were made during different times of the year, through several years (November 2004, April, August and September of the 2005, January of the 2006 and March of the 2007). Figure 1b and c show the location of sampling sites. Accuracy of the chemical analysis was verified by calculating the ionic balance error (Hem, 1970) and the values obtained were lower than 10% and with the certified reference material (for natural water) from the National Research Council of Canada (SRLS-1).

Samples ca. 1L, were collected in previously acid washed bottles, leaving a space of around 1% of their capacity to allow the thermal expansion (PROY-NMX-AA-003-SCFI, 2006). The collected water samples were measured for physical parameters such as: pH, temperature, electrical conductivity, total dissolved solids, dissolved oxygen and salinity, using the field equipment Corning Checkmate II Model. The samples were acidified with nitric acid until pH was equal or less than 2. The metals such as Al, Ag, As, B, Cd, Cr, Cu, Fe, Li, Mg, Mn, Pb, Si, Sr and Zn, were analyzed in ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer, Perkin Elmer 2002 model Optima 4300 DV) in superficial waters as well as in sediments.

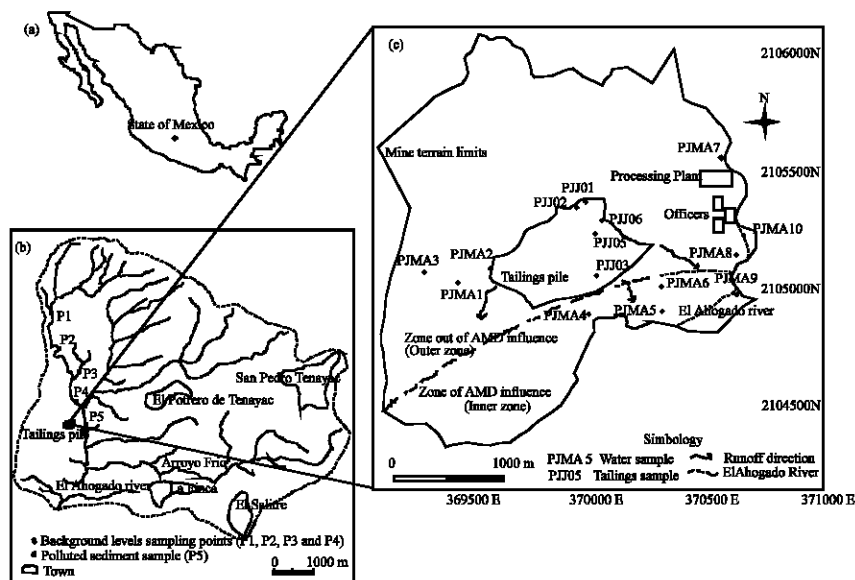


Fig. 1: (a) Location of the study area in the State of Mexico (central Mexico), (b) hydrological basin and sediment sampling location through El Ahogado River (P1, P2, P3, P4 and P5) and (c) water (PJMA) and tailings (PJJ) sampling locations in and around the tailings pile

Total metals concentrations were determined in the Faculty of Chemistry, Department of Chemistry-Metallurgy, UNAM. The samples were digested by triplicate modifying methodologies of the EPA 3051 (1991) by total digestion in microwave, following the fabricant instructions. Sulfates were quantified by triplicate in each sample and analyzed by turbidimetry according to the methodology proposed by the norm NOM-141-SEMARNAT-2003 (2004) and the method EPA 9038 (1986). The results obtained were compared with several environmental norms to determine its quality for human use (Table 1a, b).

Tailings Samples and Mineralogical Composition

Mixed tailings samples were done following the methodology accepted by the Mexican norm NOM-141-SEMARNAT-2003 (2004) as sampling preparation previous to mineralogical analysis. Mixed tailings samples are taken in different locations across the tailings pile at 0 to 50 cm in depth and size less than 200 micrometers (Fig. 1c). The mineralogical composition of tailings was determined through a semi-quantitative analysis by X Ray diffraction (XRD) in the laboratory of the mine company (X Ray Spectrophotometer, Rigaku, RIX 3100). The minerals identified helps to evaluate which minerals could be solubilized and mixed with superficial and groundwater, as well as which of them could be oxidized and generate acid drainage (Table 2, Fig. 1c).

Methods for Estimating Pollutant Impact

Surface soils have been sampled at a depth of 0-50 cm and size less than 200 micrometers following established methodologies of Canadian Soil Quality Guidelines, (1996) (P1 to P5). Local sediment background concentrations have been determined in samples collected in areas not affected by the mine wastes and mine drainage (P1 to P4, Fig. 1b), while polluted sediment (P5) located near the tailings pile was analyzed also. Soil samples were dried in an oven for 48 h at a temperature below 40°C to minimize volatility of elements (Alloway, 1995). It is commonly accepted that the

Table 1a: Water chemistry results obtained from samples taken in superficial waters around the tailings pile (inner zone)

Zone of influence of AMD																	
Parameters	PML	PJMA4 ²	PJMA4 ⁴	PJMA4 ⁵	PJMA4 ⁶	PJMA5 ²	PJMA5 ⁴	PJMA5 ⁵	PJMA5 ⁶	PJMA6 ²	PJMA6 ⁴	PJMA6 ⁵	PJMA6 ⁶	PJMA9 ²	PJMA9 ⁴	PJMA9 ⁵	SRLS-1
a		150.00				400.00				350.00				1300.00			
pH	6.5-8.5	4.55	6.78	4.08	6.81	4.76	5.03	6.24	3.57	3.98	5.01	6.19	7.62	2.50	7.32	7.60	7.71
EC	100	5800.00	5640.00	5420.00	450.00	5930.00	5190.00	6260.00	450.00	6000.00	5180.00	6500.00	450.00	6800.00	8660.00	205.00	278.00
($\mu\text{S cm}^{-1}$)																	
Alcalinity		55.00	67.00	10.00	80.00	75.00	98.00	35.00	47.00	67.00	80.00	100.00	106.00	110.00	85.00	90.00	102.00
(CaCO_3)																	
Al		0.016	0.036	0.085		0.067	0.083	0.053			0.077	0.09		0.097	0.026	0.036	
As	0.025			0.10						0.095							
B		0.60	1.10		2.02	2.00	1.80		3.24	1.90	1.80		3.19	3.00			0.31
C					29.12				30.09				38.423				47.07
Ca		507.20	501.00		560.00	560.00	722.40		721.00	576.40	709.00		723.00	588.20	9.20		25.30
Cd	0.005			0.04	0.06	0.08			0.20	0.11			0.19				
Cl	250	56.70	50.10	64.00	109.02	47.60	98.00	186.50	98.26	153.00	200.00	235.00	96.11	228.00	216.00	245.00	10.47
Cu	1.0			0.09	0.05	0.02			0.04		0.03		0.04				
Fe	0.3			4.10	0.48	48.80	5.90	6.40	9.56	7.03	6.00	5.60	9.57	88.56	0.46	3.80	0.35
H					10.543				13.856				10.42				10.23
HCO ₃ ⁻		90.00	75.00	100.00	100.00	110.00	105.00	90.00	80.00	65.00	34.00	110.00	75.00				120.00
K		1.31	5.21	5.33	118.00	2.65	1.45	3.26	265.00	2.54	2.33	1.15	277.00	2.33	2.54	2.15	5.80
Li		0.13	0.15		0.27	1.98	1.59		1.58	1.69	1.49		1.63	2.06			
Mg		600.00	596.40		678.20	251.00	274.80		592.40	252.00	271.00		600.60	303.20	3.20		13.56
Mn	0.05	4.50	8.16		7.29	3.18	5.96		12.01	3.18	6.12		12.81	7.35	0.06		0.17
Na		11.00	10.00	12.10	386.00	20.00	22.50	19.50	724.40	19.70	15.65	25.70	732.00	30.50	25.70	39.00	18.70
Pb	0.01					2.98	3.29	3.60	4.60	3.57	3.44	5.60	4.50	1.47			
Si		39.00	35.02		39.27	3.59	4.30	2594.02	7.25	3348.82	4.38		7.05	24.73	12.50		24.03
SO ₄ ²⁻	250	2883.06	3830.00	3467.16	3730.00	2806.55	4350.00		4660.00	5.00	4250.00	1504.47	4880.00	3786.85	20.00	2594.03	
Sr		2.50	3.20		3.43	1.80	2.10		2.23	2.20	1.90		2.15	2.70	0.10		0.23
Zn	5.0	4.06	10.68	17.80	10.31	7.42	17.92	46.20	34.04	7.13	18.21	45.60	35.45	8.15		5.00	0.48

a: Distance (in m) from the tailings dam, Blank spaces indicate that concentrations could not be quantified, PML: Permissible maximum limits established by environmental norms, (Mexican official norm NOM-127-SSA1-1994; US National Primary Drinking Water Standards, 2003), Concentrations are in mg L⁻¹, ¹: April 2004, ²: April 2005, ³: August 2005, ⁴: September 2005 ⁵: January 2006, ⁶: March 2007, Values in bold indicate exceeding the PML for human consume, SRLS-1: Certified Reference Material (natural water) from the National Research Council of Canada

Table 1b: Water chemistry results obtained from samples taken in superficial waters around the tailings pile (Outer zone)

Zone out of influence of AMD																	
Parameters	PML	PJMA1 ²	PJMA1 ⁴	PJMA1 ⁵	PJMA2 ²	PJMA2 ⁴	PJMA2 ⁵	PJMA3 ²	PJMA7 ⁴	PJMA7 ⁵	PJMA7 ⁶	PJMA8 ²	PJMA8 ⁴	PJMA8 ⁵	PJMA8 ⁶	PJMA10 ⁵	SRLS-1
a		250.00			50.00			700.00	1500.00			1000.00				950.00	
pH	6.5-8.5	8.76	7.71	7.27	7.76	5.19	9.35	6.73	7.19	7.54	6.90	5.78	6.20	6.08	3.54	7.79	7.70
EC	100	97.70	79.60	132.10	85.70	92.90	94.30	120.70	146.00	141.00	152.30	6250.00	5320.00	5030.00	749.00	205.00	352.00
($\mu\text{S cm}^{-1}$)																	
Alcalinity (CaCO_3)		110.00	90.00	76.00	83.00	25.00	45.00	106.00	98.00	100.00	100.00				100.00	98.00	106.00
Al		0.40	0.33	0.045	0.025	0.018	0.05	0.015	0.04	0.044		0.064	0.024	0.023			
As	0.025						0.10							0.20			
B											0.33	4.10	3.10		3.10		0.27
C											34.447				16.78		23.078
Ca		9.60	20.20		5.80	7.80		9.40	13.80		9.70	296.00	301.00		723.80		56.60
Cd	0.005											0.75	0.51	0.90	0.36		
Cl	250	65.00	77.00	52.00	58.00	78.00	53.20	48.30	242.00	164.00	4.45	236.00	225.00	217.00	98.26	245.00	7.03
Cu	1.0		0.03										0.16		0.07		
Fe	0.3	0.54	1.20	4.20	1.93	0.46	5.20	5.13		4.00	0.03	5.10	7.25	18.80	8.30	3.40	0.05
H											14.435				16.34		14.559
HCO_3^-											120.00					900.00	130.00
K		2.30	2.43	1.23	1.15	1.62	2.51	1.62	2.18	2.11	3.30	1.85	2.75	2.88	274.00	2.92	4.50
Li								0.02				2.15	1.62		1.58		
Mg		3.00	4.80		4.00	4.40		5.80	10.80		10.56	570.40	484.60		607.20		8.79
Mn	0.05	0.03	0.05		0.04	0.05		0.26	0.03			15.20	11.50		12.78	39.50	
Na		2.50	4.30	2.51	4.33	4.55	10.00	10.50	30.20	33.60	11.00	37.90	27.50	34.70	762.40		14.40
Pb	0.01												0.13	0.60	5.02		
Si		1.97	5.02		7.60	5.97		9.99	26.75		28.67	17.56	17.30		6.24	20.00	14.85
SO_4^{2-}	250	10.47		11.39			11.88	21.12		20.74		3691.55	3470.00	2216.39	4650.00		
Sr		0.10	0.10		0.10	0.10		0.10	0.10		0.13	1.70	1.50		2.57		0.36
Zn	5.0	0.62	2.50	4.99	2.42	1.27	5.08	7.46	0.31	4.81	0.07	107.67	68.39	56.82	37.50	4.15	0.06

a: Distance (in m) from the tailings dam, Blank spaces indicate that concentrations could not be quantified, PML: Permissible maximum limits established by environmental norms (Mexican official norm NOM-127-SSA1-1994; US National Primary Drinking Water Standards, 2003), Concentrations are in mg L^{-1} , ¹: April 2004, ²: April 2005, ³: August 2005, ⁴: September 2005 ⁵: January 2006, ⁶: March 2007, Values in bold indicate exceeding the PML for human consume, SRLS-1: Certified Reference Material (natural water) from the National Research Council of Canada

Table 2: Mineralogical composition in tailings samples taken from different zones in the tailings pile

Sample mineral	PJJ01 ¹	PJJ01 ²	PJJ02 ¹	PJJ02 ²	PJJ03 ²	PJJ05 ²	PJJ06 ²	PJMC ³
	(%)							
FeS ₂ (Pyrite)	73	74	67	91	67	75	70	71
ZnS (Sphalerite)	5	5	5	3	5	5	5	5
CuFeS ₂ (Chalcopyrite)				1			1	
SiO ₂ (Quartz)	5	5	8	5	5	5	5	5
SiO ₂ (Cristobalite)			2		2			2
(K,Na)(Al,Mg,Fe)(Si _{3.1} Al _{0.09})O ₁₀ (OH) ₂ (Muscovite)	5	5	5		5	5	5	5
(Mg,Fe) ₆ (Si,Al) ₄ (OH) ₈ (Clinocllore)	5	5	5		5	5	8	5
NaAlSi ₃ O ₈ (Albite)	3	3	3		3	3	3	3
CaSO ₄ · 2H ₂ O (Gypsum)	3	3			8	2		
CaSO ₄ · ½H ₂ O (Bassanite)	1		5				3	4

¹April 2004, ²: April 2005, ³: August 2005, PJMC: Composite sample (PJJ01², PJJ02², PJJ03²)

Table 3: Metal concentrations in unpolluted (background level) and polluted sediment samples. These background values were taken from the El Ahogado River, which can be considered reference concentrations, or unpolluted values

Sediment (mg kg ⁻¹)							
Background (Unpolluted)					Polluted	Background average ^a	EF study area
Metals	P1	P2	P3	P4	P5		
As	31.00	10.00	21.00	33.00	33.00	23.75	0.42
Ba	na	na	na	49.40	70.10	12.35	1.72
Cr	78.00	187.00	149.00	113.00	na	131.75	na
Cu	46.00	19.00	182.00	64.00	16.00	77.75	0.06
Fe	2.31	1.14	3.66	1.22	40.01	2.08	5.84
Pb	20.00	na	63.00	73.00	36.00	39.00	0.28
Zn	51.00	79.00	159.00	83.00	214.00	93.00	0.69

(Fig. 1b for location). na: not available, EF: Enrichment Factor a: Wedepohl (1995)

concentration of soil contaminants increases with decreasing particle size due to the large surface area of all the particles combined (Wilber and Hunter, 1979). Hence, the usual emphasis is on the finer fraction such as silts and clays, which have negative surface charges (Striegl, 1987). Chemical characterization of soil samples was performed by multi-elemental analysis of the soluble fraction resulting from a strong acid attack of the sample. Soil samples were separated in the fine fraction (size less than 200 µm). Samples of 0.5 g were digested with 3 mL of 3:1:2 HCl-HNO₃-H₂O at 95°C for 1 h and then diluted to 10 mL with distilled water. In all soil samples concentrations of metals such as As, Ba, Cr, Cu, Fe, Pb and Zn were determined by ICP-OES (Table 3).

The more recent approach to establish reference values is to compare concentrations of the target metals in contaminated and uncontaminated sediments that are mineralogically and texturally similar or identical (Salomons and Förstner, 1984; Hornung *et al.*, 1989). This method is much more reasonable than comparisons with average crustal values due to the textural, mineralogical and bulk chemical similarity between the compared sediment samples.

Enrichment Factor (EF)

A common approach to estimate the anthropogenic impact on sediments is to calculate an Enrichment Factor (EF) for metal concentrations above uncontaminated background levels (Salomons and Förstner, 1984; Dickinson *et al.*, 1996; Hornung *et al.*, 1989). The EF method normalizes the measured heavy metal content with respect to a sample reference metal such as Fe, Al or Zn (Ravichandran *et al.*, 1995). In this approach the Fe, Al, or Zn is considered to act as a proxy for the clay content. The EF is calculated according to the following equation: $EF = (M_x)(Fe_b) / (M_b)(Fe_x)$, where M_x and Fe_x are the concentrations of the heavy metal and Fe in the sediment sample (or other reference metal), while M_b and Fe_b are their concentrations in a suitable background or baseline reference material (Salomons and Förstner, 1984).

Geoaccumulation Index (I_{geo})

A common approach to estimate the enrichment of metal concentrations above background or baseline concentrations is to calculate the geoaccumulation index (I_{geo}) as proposed by Müller (1969). The method assesses the degree of metal pollution in terms of seven enrichment classes, based on the increasing numerical value of the index. This index is calculated as follows: $I_{geo} = \log_2 C_n / 1.5 B_n$, where C_n is the concentration of the element in the enriched samples and the B_n is the background or pristine value of the element. The factor 1.5 is introduced to minimize the effect of possible variations in the background values, which may be attributed to lithologic variations in the sediments (Stoffers *et al.*, 1986).

RESULTS AND DISCUSSION

Water

Based on the chemical composition of water samples analyzed (Fig. 1c), it is possible to differentiate between two zones: 1) Zone of influence of acid mine drainage contamination (inner zone) at the South and Southeastern part of the tailings pile, where the sampling points PJMA4, PJMA5, PJMA6 and PJMA9 (El Ahogado River downstream) are located and 2) zone out of influence of acid mine drainage contamination (outer zone) at the west and eastern part of the tailings pile, where the sampling points PJMA1, PJMA2, PJMA3, PJMA7, PJMA8 and PJMA10 (El Ahogado River upstream) were collected. It was observed that between these two zones there are some elements that exceeded the Permissible Maximum Limits (PML) established by the environmental norms (NOM-127-SSA1, 1994; US National Primary Drinking Water Standards, 2003) for human consumption.

The chemical characterization of sampling points indicate that in the inner zone, waters are highly acidic, with pH values ranging from 2.5 to 4.08, Electrical Conductivities (EC) up to 8660 $\mu\text{S cm}^{-1}$ and also have several elements in high concentrations (exceeding the PML), such as As (0.095 to 0.1 mg L^{-1}), Cd (0.04 to 0.2 mg L^{-1}), Fe (0.35 to 88.56 mg L^{-1}), Mn (0.06 to 12.81 mg L^{-1}), Pb (1.47 to 5.6 mg L^{-1}), SO_4^{2-} (5 to 4880 mg L^{-1}) and Zn (0.48 to 46.2 mg L^{-1}), during the dry season (Table 1a). The results indicate that low pH values together with high concentrations of sulfate and iron and other metals are indicators of AMD. These metals can be transported through superficial water, polluting the environment. This can occur because of the secondary permeability of rocks (rock fracturing) could allow the migration of the acid leachates formed in the tailings pile, in combination of gravity, reaching the superficial waters near to this site.

On the other hand, the chemical characterization of sampling points indicate that in the outer zone water is still acidic, (pH 3.54), but alkaline water (pH 8.76) also exists in the western side of the tailings pile. With respect to Electrical Conductivities (EC) values are medium to high (79.6 to 6250 $\mu\text{S cm}^{-1}$), with high metal concentrations that exceeded the PML in this zone were: As (0.1 to 0.2 mg L^{-1}), Cd (0.36 to 0.9 mg L^{-1}), Fe (0.03 to 18.8 mg L^{-1}), Mn (0.03 to 39.5 mg L^{-1}), Pb (0.13 to 5.02 mg L^{-1}), SO_4^{2-} (10.47 to 4650 mg L^{-1}) and Zn (0.06 to 307 mg L^{-1}), respectively (Table 1b). Observing the topographical location of these sampling points with respect to the tailings pile, it is no possible to expect an AMD pollution of these superficial waters, because all of them are located upward to this site, but the high values in this area could be due to natural rocks weathering.

Tailings Mineralogy

Eight samples taken from the tailings pile were analyzed for mineralogical composition (Fig. 1c). Pyrite is the predominant mineral (65 to 91%), followed by sphalerite (5%), galena (5%), chalcopyrite (1%), quartz (5%), muscovite (5%), clinocllore (5%), albite (3%), gypsum (from 2 to 8%) and bassanite (from 1 to 5%) (Table 2). The chemical composition of tailings indicates that high concentrations of elements such as Mn, Cu, Fe and Zn, are similar to those that have been liberated

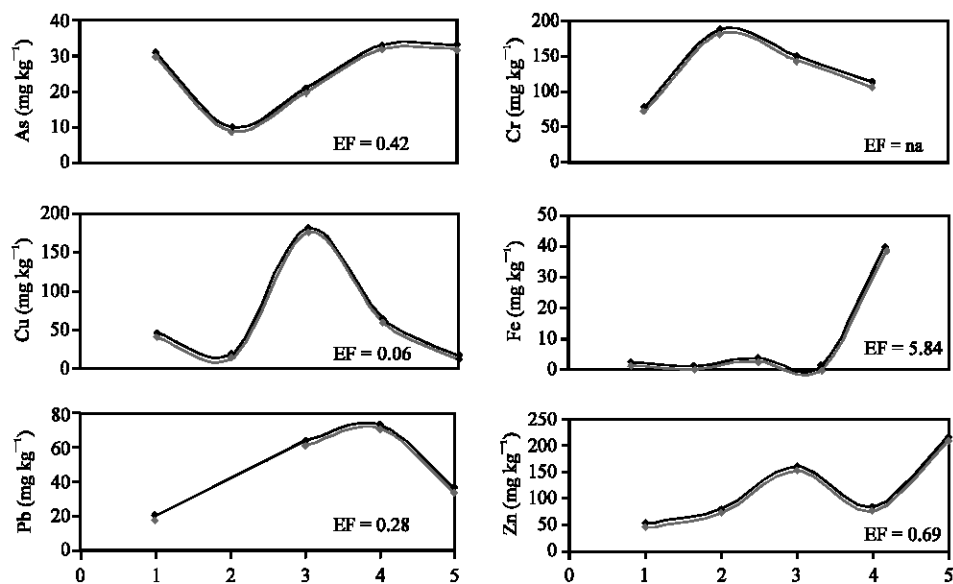


Fig. 2: Variation of metal concentrations with respect to unpolluted sediments (1, 2, 3 and 4) and polluted sediment (5) (Fig. 1b). EF represents the enrichment factor calculated for each metal (Table 3). na means not available

by the AMD, when in contact with superficial waters (in the outer zone). Vega *et al.* (2004) mentioned that the extraction of metal ores causes generally a multi-elemental contamination (Mn, Fe, Cd and Zn) of the environment, especially those located near to tailings piles. It can be expected that in the study area a multi-elemental contamination could be due to acid leachates generated from tailings.

Tailings mineralogy depends not only on the ore deposit mineralogy, but on the mineralogy of rocks as well. When sulfides are weathered, the presence of sulfates predominates. According to González Sandoval *et al.* (2007), tailings taken from the tailings pile in the study area were submitted to static and kinetic laboratory tests and showed no neutralizing potential with high capacity to generate acid leachates (pH<2.5). This indicates the potential of the tailings pile to generate AMD and to lixiviate through the rocks and reach the superficial waters near to the site. These mobilized metal-bearing tailings and waste, can be stored in alluvial sediment for considerable periods of time (tens to thousands of years) and constitute a long-term threat to river quality (Salomons and Förstner, 1984).

Heavy Metal Enrichment Enrichment Factor (EF)

In the study of polluted sample (P5), the determination of the extent or degree of pollution by a given heavy metal, requires that the pollutant metal concentration be compared with an unpolluted reference material (P1, P2, P3 and P4). Pollution will be measured as the amount (or ratio) of the sample metal enrichment above the concentrations present in the reference material (unpolluted) against the polluted material (P5) (Abraham and Parker, 2007) (Table 3, Fig. 2).

In calculating the Enrichment Factors (EF), the original Salomons and Förstner (1984) equation was substituted in the present study by Zn, because Al data was not available. For comparison, normalized EF values were calculated using the continental crust abundance of Zn (65%) (Wedepohl, 1995), as well as using the average concentration of Zn in the lower part of the studied

Table 4: Index of geoaccumulation (I_{geo}) in sediments of the El Ahogado River; the background average values (P1, P2, P3 and P4) were taken from four different samples in unpolluted sediments

Metals	River sediment	Background average ^a	I_{geo}	I_{geo} class	Sediment quality
As	33.00	23.75	0.14	0-1	Uncontaminated to moderately contaminated
Ba	70.10	12.35	-0.18	0	Uncontaminated
Cu	16.00	77.75	0.08	0-1	Uncontaminated to moderately contaminated
Fe	40.01	2.08	1.70	1-2	Moderately contaminated
Pb	36.00	39.00	0.03	0-1	Uncontaminated to moderately contaminated
Zn	214.00	93.00	0.05	0-1	Uncontaminated to moderately contaminated

(Fig. 1b for location), a: $(P1+P2+P3+P4)/4$

sediments (Table 3). According to Sinex and Helz (1981) the EF is generally not very sensitive to the choice of baseline. It is observed both Ba and Fe present an enrichment with respect to background level (1.72 and 5.84, respectively), while elements such as Cu, Pb, As and Zn indicate minor enrichment than background levels ($0.06 < 0.28 < 0.42 < 0.69$, respectively) (Table 3). From Fig. 2, we can mention that elements such as As, Fe and Zn were found in higher concentrations in polluted sediment (P5), possibly due to mining activities and the weathering of tailings (which predominant minerals content is pyrite). Elements such as Cr, Cu and Pb were present in higher concentrations in unpolluted sediments ($P2 > 3 > 4$, respectively). But this simple observation is not conclusive, because we have not taken into account the natural weathering of rocks through time. Another factor that can influence the composition of sediments is the wind transportation of very fine sediments.

Using the average continental crust Zn concentration as a normalizer, results are significantly higher than EF values (average = 5.84 for Fe), while for the rest of the metals evaluated, all of them were lower than 1, indicating that no heavy metal pollution (except Fe). In view of these features it is clear that normalized EF values calculated using the average concentration in continental crust, concentrations need to be interpreted with caution.

Geoaccumulation Index (I_{geo})

The geoaccumulation index (I_{geo}) method was used to calculate the metal contamination levels for the recovered sediments from the El Ahogado River (Table 4). The negative I_{geo} values found indicate low levels of contamination for Ba. The I_{geo} factor is not readily comparable to the Enrichment Factor (EF) due to the nature of the I_{geo} calculation, which involves a log function and a background multiplication of 1.5. It was found that exist several degrees of pollution, concerning to the classification for each metal evaluated (Abraham and Parker, 2007). Comparing the river sediment concentration (P5) with respect to the background average, it is observed that river sediment concentrations are higher for As, Ba, Fe and Zn than their respective background level (P1, P2, P3 and P4). But considering the I_{geo} values calculated, it is observed that it is moderately contaminated with respect to Fe, but for As, Cu, Pb and Zn it falls in uncontaminated to moderately contaminated classification. Only Ba was the element that showed no pollution capacity.

This can be explained because pyrite (FeS_2) is the predominant mineral in tailings (Table 2) and due to the fact that these tailings were classified as the potential source for acidity (González Sandoval *et al.*, 2007). Therefore, acid leachates are formed and can liberate heavy metals when pH is acid. The acid leachates are transported through secondary fracturing to superficial waters and they do affect their quality.

CONCLUSIONS

The Enrichment Factor (EF) calculations showed no reliable results because the comparison of background levels and polluted sediment concentrations. But it must be taken into account that every zone has variations in background levels. From these results, Fe and Ba showed to be the metals

causing pollution problems, while As, Zn, Cu and Pb showed to be in lower concentrations. The geoaccumulation index (I_{geo}) was used as a second method to evaluate the pollution capacity of some metals present in the study area. We observed that null pollution exists with respect to Ba, while metals such as As, Cu, Pb and Zn showed null to moderate capacity to pollute the superficial waters. Only Fe showed to be consistent with the first method applied (EF) and has moderately capacity to pollute superficial waters.

From the chemical characterization of superficial waters, it was concluded that there are two zones in the study area: 1) Zone of influence of AMD (inner zone) that is possibly polluted due to the AMD formed in the tailings pile and 2) zone out of influence of the AMD (outer zone). Topographical location of inner zone influences migration of AMD pollution through El Ahogado River downstream, while natural weathering of rocks is related to chemical pollution on the same river upstream of the study area.

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