

# Assessment of contamination levels of watercourses and streambed sediments downstream the Capillitas Mine, Catamarca, Argentina

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## ABSTRACT

The present study evaluates the degree of contamination by heavy metals and metalloids of streams affected by upstream mining activities in Capillitas Mine (Catamarca, Argentina), an epithermal precious- and base-metal vein deposit previously mined for copper, gold and silver and currently exploited for rhodochrosite. Geochemical water analyses were performed on three streams (Ortíz, Acid and Capillitas) and a small pond that shows a very thin layer of turquoise-colored precipitates at its bottom. Additionally, the environmental risk factor was calculated. Moreover, the concentrations of potential toxic elements in sediments from the Ortíz and Capillitas streams were determined by ICP-OES and the Index of geoaccumulation (*Igeo*) for As, Cd, Zn, Cu, Mn and Pb was computed.

According to their major ions concentration, the four water samples correspond to calcium SO<sub>4</sub> waters. The Acid and Ortíz streams and the turquoise pond show concentrations of Al, Mn, Cd, Zn, Cu, Cr, Ni and Pb that largely exceed the permissible limits for the protection of aquatic life and irrigation waters according to the legislation of Argentina. The Capillitas stream has a lower content of heavy metals but shows concentrations of Mn, Zn, Cu and Pb exceeding the limit values for protection of aquatic life.

According to the obtained *Igeo*, the three streambed sediments from the Ortíz creek are extremely polluted with Cd, Zn and Pb, whereas they range from strongly to extremely polluted with Cu, As and Mn. The sediments from Capillitas creek show lower contents of metals and metalloids; though it is strongly polluted with Cd, moderately polluted with Cu and unpolluted to moderately polluted with Pb and Zn.

The pollution generated by the long-lasting mining activities in the Capillitas Mine highlights the need to implement Government initiatives leading to improve mine tailings management.

Key words: AMD; heavy metals; polluted sediments; contaminated site; mining environmental impact; geoaccumulation indexes.

## RESUMEN

El objetivo de este estudio es determinar el grado de contaminación por metales pesados y metaloides en varios arroyos ubicados aguas abajo de la Mina Capillitas (Catamarca, Argentina), un depósito vetiforme epitermal que en el pasado fue explotado por Cu, Au y Ag, y del que actualmente se extrae rodocrosita. Se realizaron análisis químicos de iones mayoritarios y elementos traza para tres arroyos (Ortíz, Ácido y Capillitas) y un pequeño estanque, ubicado pocos metros por encima del cauce del arroyo Ortíz, que presenta una delgada capa color turquesa en su fondo. Por otra parte, se determinó la concentración de elementos pesados y metaloides en sedimentos de fondo de los arroyos Ortíz y Capillitas por ICP-OES y se calcularon los índices de geoacumulación (*Igeo*) para As, Cd, Zn, Cu, Mn y Pb.

De acuerdo con su contenido de iones mayoritarios las aguas analizadas son de tipo sulfatadas-cálcicas. Los arroyos Ácido y Ortíz así como el 'estanque turquesa' presentan concentraciones de Al, Mn, Cd, Zn, Cu, Cr, Ni y Pb que exceden largamente los niveles guía establecidos en la legislación argentina tanto para protección de vida acuática como para aguas de irrigación. Antes de su confluencia con el arroyo Ortíz el arroyo Capillitas presenta menores concentraciones de metales pesados que los otros arroyos analizados. Sin embargo, sus contenidos de Mn, Zn, Cu y Pb exceden los niveles guía de protección de vida acuática.

De acuerdo con los valores de *Igeo* obtenidos los sedimentos de lecho del arroyo Ortíz se encuentran extremadamente contaminados por Cd, Zn y Pb, en tanto que varían entre fuerte a extremadamente contaminados por Cu, As y Mn en los tres puntos de muestreo. Los sedimentos de lecho del arroyo Capillitas presentan contenidos más bajos de metales y metaloides que los del arroyo Ortíz pero se encuentran fuertemente contaminados por Cd, moderadamente contaminados por Cu y no contaminados a moderadamente contaminados por Pb y Zn.

La contaminación generada por las actividades mineras desarrolladas desde mediados del siglo XIX en la Mina Capillitas evidencia la necesidad de tomar medidas tendientes a mejorar el manejo de los desechos mineros, para adecuarlo a los estándares actuales.

*Palabras clave:* drenaje ácido de mina; metales pesados; sedimentos contaminados; impacto ambiental de actividades mineras; índices de geoacumulación.

## INTRODUCTION

Acid mine drainage (AMD) is a complex process originated under oxidizing conditions when mining activities expose sulfur-bearing rocks to moisture and surface waters, giving rise to acid-SO<sub>4</sub> waters with high contents of metals (Bighman and Nordstrom, 2000). This phenomenon has been extensively studied in the last decades as it is considered the most serious pollution problem affecting lotic and lentic systems (Younger *et al.* 2002, 2004, Johnson and Hallberg, 2005; Jennings *et al.*, 2008, Jain *et al.*, 2016). The chemical reactions that generate AMD trigger a cyclical process that perpetuates the continual creation of AMD (Johnson and Hallberg, 2005, Larios *et al.*, 2012). As a consequence, acid mine drainage can persist during all the life of an active mine and long after it has been shut down (Jain *et al.*, 2016). However, acid drainage may also originate in mineralized areas unaffected by mining, in a process known as acid rock drainage (ARD). Due to the common occurrence of ARD processes in mineralized areas, the natural baseline conditions should be characterized before any mining activity (Nordstrom, 2015). In many cases, mining activities began decades or even centuries before any scientific study were carried out. In such cases, when there are no previous hydrogeochemical studies from pre-mining times, the baseline conditions of a mine site are difficult to assess. Even in such cases, discriminating between water pollution caused by ARD from that derived from oxidation of sulfurs exposed in underground excavations, open pits, waste piles, and tailings arising from mining operations, is crucial to establish plausible environmental restoration goals (Nordstrom, 2015).

This is the case of many small and medium size mines in Latin America that have ceased its activities leaving behind waste piles,

tailings or flooded underground tunnels, whose impact in the surrounding rivers and groundwater has been rarely determined (Kirschbaum *et al.*, 2012, Méndez-Ramírez and Armienta Hernández, 2012, Ramos *et al.*, 2012, Murray *et al.*, 2014, Nieva *et al.*, 2016). Moreover, in Latin America, the exploitation of metallic minerals has often been done in regions of water scarcity, and with little to no environmental controls (Responsible Mining Foundation and Centro Vincular-PUCV, 2020).

Nevertheless, water courses pollution is not the unique threat to the environment associated with mining operations, as they can also pollute streambed sediments, littoral sediments and soils (*i.e.* DelValls *et al.*, 1998; Fernández-Turiel *et al.*, 2001; Navarro *et al.*, 2004; Sarmiento *et al.*, 2011; Resongles *et al.*, 2014; Stefanowicz *et al.*, 2014; Rack *et al.*, 2017, Galuszka, *et al.*, 2018; Do Campo *et al.*, 2020). In the case of sediments it is also difficult to estimate pre-mining background metal concentrations when mining activities began in historical times, previous to any geochemical survey (Kossoff *et al.* 2016).

This is the case of the Capillitas Mine deposit (Catamarca, Argentina) that was intermittently mined, initially for copper and later for gold and silver between 1855 and 1930, when the richest veins were exhausted. Afterwards, copper mining was gradually replaced by the extraction of rhodochrosite (Delfino *et al.* 2014), a semiprecious stone widely employed in jewelry, the national stone of Argentina. In the former period, the ore containing copper bearing sulfurs was processed in the Muschaca smelting plant. A recent study shows the existence of contamination by Cu, Zn, As and Sn in the soil located ~80 m south of the old smelting plant (Do Campo *et al.* 2020). According to the remaining documents, 6818 tons of copper could have been produced from 1860 to 1881.

Nowadays Capillitas Mine is operated by a state-owned company and the mining of rhodochrosite is an important economic activity of Catamarca province. In the area located downstream the current border of the Capillitas Mine property, there are several watercourses: Ortiz, Capillitas and an unnamed tributary of the Ortiz stream (Figure 1). The unnamed stream runs SW-NE through the mineralized zone and

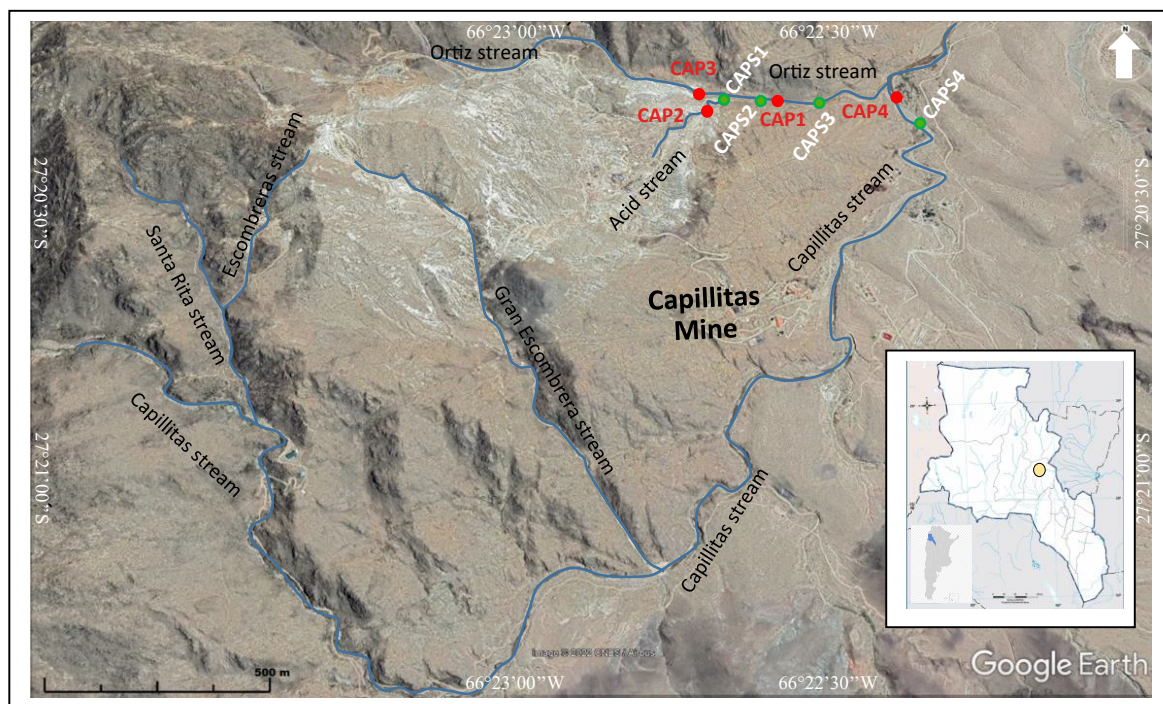


Figure 1. Satellite image of the study area with the location of sampling stations. Samples of streambed sediments: green points, water samples: red points.

stockpiles, whereas the Ortíz stream also drains the mineralized area and crosses tailings dams. Moreover, along the Ortíz stream, several remains of the old mining activities can still be observed. The most conspicuous are stockpiles of fine-grained material and longitudinal channels at both sides of the valley whose inner walls preserved the old sealing with tar (Figure 2a, 2b). These channels seem to be used to process the copper ore during the first stage of the mining operation. Moreover, ochre deposits including hardpan crusts are widespread at both sides of the channels and also cover the Ortíz stream riverbed (Figure 2c). There are few previous geochemical studies of this area, Ferpozzi *et al.*, (2003) presented a geochemical chart compiling metal contents of streambed sediments at regional scale. More recently, Yaciuk *et al.*, (2022) studied the water and streambed sediment composition in the upper and middle basin of the Capillitas stream and analyzed Cd mobility. However, the impact of mining activities on the watershed and streambed sediments downstream Capillitas Mine has not been evaluated so far.

The aim of the present study is to assess the level of contamination produced by the dispersion of heavy metals and metalloids by streams that flow through spoil heaps and tailings dams of the Capillitas Mine. For this purpose, chemical analyses of waters and streambed sediments sampled from several water courses downstream Capillitas Mine were performed. Furthermore, the pollution degree by heavy metals was quantified applying the environmental risk factor (Riba *et al.*, 2002; Sarmiento *et al.*, 2011) to waters and the geo accumulation index to sediments (Müller, 1981).

## STUDY AREA

Capillitas Mine is an epithermal precious and base metal vein deposit, located along the western slope of the Sierra de Capillitas, in Catamarca province (Argentina). This polymetallic epithermal deposit is part of the Farallón Negro Volcanic Complex (FNVC) that comprises numerous veins hosted in volcanic rocks and granites (Márquez-Zavalía, 2002; Putz *et al.*, 2009). Putz *et al.* (2009) studied the mineralogy of this deposit and distinguished high and intermediate sulfuration events overprinted by supergene alteration. The main primary ore minerals are: pyrite (FeS<sub>2</sub>), sphalerite (ZnS), galena (PbS), chalcocite (Cu<sub>2</sub>S), bornite (Cu<sub>5</sub>FeS<sub>4</sub>), malachite (Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>), tennantite (Cu<sub>6</sub>Cu<sub>4</sub>(Fe<sup>2+</sup>, Zn)<sub>2</sub>As<sub>4</sub>S<sub>12</sub>S), enargite (Cu<sub>3</sub>AsS<sub>4</sub>), bornite (Cu<sub>5</sub>FeS<sub>4</sub>), stannite (Cu<sub>2</sub>FeSnS<sub>4</sub>) and gold (Márquez-Zavalía, 2002). Rhodochrosite and quartz are the predominant gangue minerals.

The Sierra de Capillitas belongs to the Northwestern Sierras Pampeanas morphotectonic region (Ramos, 1999). The basement of the area is represented by metamorphic and plutonic rocks of Proterozoic to Lower Paleozoic age. This basement is unconformably overlain by continental conglomerates, sandstones and claystones deposited in fluvial environments corresponding to the Hualfín Formation (Muruaga, 1998; 2001a, b; Bossi *et al.*, 1999). In the study area this unit is unconformably overlain by red sandstone and pelites deposited in fluvial environments assigned to the Morterito Formation (Turner, 1973) middle to upper Miocene in age (Márquez-Zavalía, 2006). The FNVC is composed of volcanic, volcanoclastic and hypabyssal rocks from upper Miocene to lower Pliocene, that unconformably overlain the older units (Llambías 1972; Sasso, 1997; Sasso and Clark, 1998). In the Capillitas area the FNVC developed a diatreme filled by fragmented volcanic rocks that were later intruded by a volcanic dome (Morro Pan de Azúcar, Márquez-Zavalía, 1988, 1999). Seggiaro *et al.* (2014) distinguished three main volcanic facies assemblages in the FNVC: volcanic rocks ranging in composition from basalt to rhyolite, reworked volcanoclastic rocks and intrusive hypabyssal rocks.

The study area is located to the NE of the Capillitas Mine, where two streams, Ortíz and its unnamed affluent, drain spoil heaps and tailings dams that contain materials produced by old mining operations, that took place between 1855 and 1930, and recent mining activity. The Ortíz stream is an affluent of the Capillitas stream that discharges in Campo del Arenal. The Capillitas stream originates in an unmineralized area with no mining activities. However, along its upper course, it receives the water from the Santa Rita stream, which originates near the Rhodochrosite Mine and, in turn, has the Escombreras stream as a tributary. According to Yaciuk *et al.* (2022) the Escombreras stream, which flows through a sulfide mine dump, exhibits a pH ranging between 2.26 and 2.70 and therefore they classified it as an acid mine drainage. After its confluence with the Escombreras stream the pH of the Santa Rita stream decreases from 5.83 to 3.09 in a few meters (Yaciuk *et al.*, 2022).

The climate of the study area corresponds to a height desert with annual average precipitation < 200 mm as the region lies in the rain shadow of the Sierra del Aconquija. On a regional scale, rainfall has a monsoon regime characterized by wet summers and dry winters, heavier rains are very frequent during southern summers (December to March) (Banchig *et al.*, 2009). Yaciuk *et al.* (2022) indicated that even though the hydrological balance of the Capillitas region is markedly negative, several low-flow (0.05–14.5 L·s<sup>-1</sup>) streams exist.

## MATERIAL AND METHODS

During the sampling campaign, carried out in January of 2018, four samples of water and four samples of streambed sediments were collected in a small area (~0.8 km<sup>2</sup>) downstream the Capillitas Mine (Figure 1). Water sample CAP2 corresponds to the unnamed stream, a tributary of the Ortíz stream, and sample CAP3 to the Ortíz stream; these samples were collected ~0.5 km downstream the active mining operations of Capillitas Mine, just before their confluence. The amount of suspended sediments is insignificant in both streams. Sample CAP1 was taken in a small pond situated a few meters above the riverbed level of the Ortíz stream and 100 m to the NE of its confluence with its unnamed tributary. This pond receives a low shallow groundwater flow from the NW, presumably infiltrated through the Ortíz stream bed. At the same time, it discharges into the Ortíz stream through a narrow short channel on its eastern border (Figure 2d). This pond has a very thin layer of turquoise-colored mineral precipitates at the bottom, and thus it will be called 'turquoise pond' hereafter (Figure 2e). Water sample CAP4 corresponds to the Capillitas stream, and it was taken a few meters before its confluence with the Ortíz stream (Figure 2f). During the sampling campaign, the flow rate of the Ortíz and the unnamed streams was several times greater than that of the Capillitas stream, where water flowed from a small spring coming from the bottom of the dry creek.

Electrical conductivity (EC), pH, and temperature were determined *in situ* in each sampling point employing a portable multi meter Lutron with calibrated probes. Each water sample was collected in two 200mL PVC bottles, one to determine anions and the other one to analyze major and minor cations. All the water samples were vacuum-filtered using 0.45-µm cellulose nitrate filters, whereas the sub samples for cations determination were acidified with nitric acid until pH < 2, to prevent precipitation during the transport to the laboratory. All the samples were stored at 4 °C until analysis. Alkalinity was determined by titration with 0.02 M HCl and phenolphthalein-bromocresol green-methyl red as colorimetric indicators, while the other major anions (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, F<sup>-</sup>) were determined by ion chromatography at the Department of Geology Chemical Laboratory (FCEyN, UBA) employing a



Figure 2. Field photographs of the study area. a) View of the Ortiz stream valley upstream its confluence with the Capillitas stream. b) Longitudinal channel parallel to the Ortiz stream that would have been used for the processing of the copper ore until 1930. c) Ochre deposits and hardpan crust at the northern bank of the Ortiz stream. d) Discharge of the 'turquoise pond' into the Ortiz stream. e) View of the small pond containing a thin layer of turquoise-colored mineral precipitates at its bottom. The narrow discharge channel situated on its E border can also be observed. f) View of the valley of the Capillitas stream before its confluence with the Ortiz stream.

Thermo Scientific Dionex Aquion, using the pre-column AG18 4-microns and the column AS18-4 microns, and KOH 35 mM as eluent. The concentration analysis of dissolved major cations and trace elements (Na, K, Ca, Mg, Mn, As, Cd, Zn, Cu, Fe, Al, Se, Sr, Cr, Ni, Mo, Pb and Ba) was performed on the acidified samples by Inductively Coupled Plasma Optic Emission Spectrometry (ICP-OES) PERKIN ELMER OPTIMA-8300 in the chemical laboratory of the 'Servicio Geológico

Minero Argentino' (SEGEMAR). Certified standards supplied by NWRI - CANADA were employed for calibration. Method detection levels (M.D.L.) and Practical quantification levels (P.Q.L.) informed for the chemical laboratory were: 0.41–1.2 mg·L<sup>-1</sup> for Na<sup>+</sup>, 0.38–1.1 mg·L<sup>-1</sup> for K, 0.45–1.3 mg·L<sup>-1</sup> for Ca<sup>2+</sup>, 0.24–0.74 mg·L<sup>-1</sup> for Mg<sup>2+</sup>, 1.3–4 mg·L<sup>-1</sup> for Mn, 2–10 µg·L<sup>-1</sup> for As, 0.8–2.4 µg·L<sup>-1</sup> for Cd, 0.2–0.7 µg·L<sup>-1</sup> for Zn, 1.2–3.6 µg·L<sup>-1</sup> for Cu, 0.4–1.1 µg·L<sup>-1</sup> for Fe, 0.4–1.1 µg·L<sup>-1</sup> for Al,

3–9  $\mu\text{g}\cdot\text{L}^{-1}$  for Se, 10–25  $\mu\text{g}\cdot\text{L}^{-1}$  for Sr, 0.5–1.5  $\mu\text{g}\cdot\text{L}^{-1}$  for Cr, 0.3–0.9  $\mu\text{g}\cdot\text{L}^{-1}$  for N, 0.4–1.2  $\mu\text{g}\cdot\text{L}^{-1}$  for Mo, 2.5–7.5  $\mu\text{g}\cdot\text{L}^{-1}$  for Pb and 0.8–2.4  $\mu\text{g}\cdot\text{L}^{-1}$  for Ba.

Active stream sediments in contact with stream water were collected in plastic bags. Samples were taken from the first centimeter of the riverbed surface, avoiding deeper sediments because they show significant changes in color and texture compared to the superficial material. CAPS1 was taken from the bed of the Ortíz stream just at the confluence with the unnamed stream, whereas CAPS2 and CAPS3 were taken from the Ortíz creek bed, respectively, ~80 and 250 m downstream from its confluence with the Acid stream (Figure 1). Sample CAPS4 corresponds to the streambed sediments of the Capillitas stream. The four sediment samples were milled in a Herzog tungsten carbide grinder and then the material <150  $\mu\text{m}$  was subjected to total acid digestion in a microwave oven based on the EPA 3052 method (0.5 g is digested in 9 ml of  $\text{HNO}_3$  + 3 ml of  $\text{HF}$  + 2 ml of  $\text{HCl}$  at 180 °C for 9.5 min). The contents of Cu, Zn, As, Se, Mo, Cd, Sb, Pb, Bi, Sn and W in the extracted sediments were determined by ICP-OES PERKIN ELMER OPTIMA-8300 in the chemical laboratory of the ‘Servicio Geológico Minero Argentino’ (SEGEMAR). The contents of Al, Fe and Mn were determined by X-ray fluorescence (EDFRX-SHIMADZU) on sub samples not submitted to digestion. Certified standards supplied by NWRI – CANADA were employed for calibration.

## RESULTS

### Hydro geochemistry

Physicochemical results are summarized in Table 1, where reference values for protection of aquatic life (PAL, Law N° 24051

Appendix IV, Argentina), and irrigation water (IW: Law N° 24051 Appendix IV, Argentina) are also included. According to the major ions concentration, the four samples correspond to calcium  $\text{SO}_4$  waters; however their pH, conductivity and contents of major (Figure 3) and minor cations are markedly different. The waters of the Ortíz stream and its unnamed tributary are acidic and depict high conductivities and high  $\text{SO}_4$  contents. The unnamed stream (CAP2) depicts pH ~3 and high contents of As (30  $\mu\text{g}\cdot\text{L}^{-1}$ ), Mn (104500  $\mu\text{g}\cdot\text{L}^{-1}$ ), Al (18698  $\mu\text{g}\cdot\text{L}^{-1}$ ) and heavy metals (Cd: 378  $\mu\text{g}\cdot\text{L}^{-1}$ , Zn: 53790  $\mu\text{g}\cdot\text{L}^{-1}$ , Cu: 11110  $\mu\text{g}\cdot\text{L}^{-1}$ , Cr: 32  $\mu\text{g}\cdot\text{L}^{-1}$ , Ni: 118  $\mu\text{g}\cdot\text{L}^{-1}$ , Pb: 427  $\mu\text{g}\cdot\text{L}^{-1}$ ); thus it constitutes an AMD, so it will be designated as the ‘Acid stream’ hereafter. This stream also shows the highest content of Fe (14500  $\mu\text{g}\cdot\text{L}^{-1}$ ), what is consistent with the high solubility of Fe(III) under low pH oxidant waters (Brookins 1988). The Ortíz stream (CAP3) depicts pH ~5, slightly lower EC and extremely lower concentration of Fe than the Acid stream. The lower Fe content is accordant with the Fe(III) insolubility in moderately acidic and well-oxygenated waters (Brookins, 1988). Despite its higher pH, the Ortíz stream also shows high contents of Al, Mn, Cd (738  $\mu\text{g}\cdot\text{L}^{-1}$ ), Zn (52410  $\mu\text{g}\cdot\text{L}^{-1}$ ), Cu (7848  $\mu\text{g}\cdot\text{L}^{-1}$ ), Cr (16  $\mu\text{g}\cdot\text{L}^{-1}$ ), Ni (127  $\mu\text{g}\cdot\text{L}^{-1}$ ) and Pb (1897  $\mu\text{g}\cdot\text{L}^{-1}$ )

The Capillitas stream and the turquoise pond (CAP4 and CAP1) are slightly alkaline; present lower conductivities and higher contents of bicarbonate. The turquoise pond shows concentrations of  $\text{SO}_4$  (458.8  $\text{mg}\cdot\text{L}^{-1}$ ), Cd (96  $\mu\text{g}\cdot\text{L}^{-1}$ ), Zn (19310  $\mu\text{g}\cdot\text{L}^{-1}$ ), Cu (215  $\mu\text{g}\cdot\text{L}^{-1}$ ), Fe (37  $\mu\text{g}\cdot\text{L}^{-1}$ ), Mn (29580  $\mu\text{g}\cdot\text{L}^{-1}$ ), Al (120  $\mu\text{g}\cdot\text{L}^{-1}$ ), Cr (7.5  $\mu\text{g}\cdot\text{L}^{-1}$ ), Ni (36  $\mu\text{g}\cdot\text{L}^{-1}$ ) and Pb (30  $\mu\text{g}\cdot\text{L}^{-1}$ ) substantially lower than the nearby Ortíz stream, whereas the As concentration was below the detection limit. The low content of metals in these waters is in accordance with the occurrence of a thin layer of secondary Cu-bearing sulfates precipitates at the bottom of the pond, probably associated with other metal-bearing phases (Figure 2e).

Table 1. Main physicochemical parameters, major ions, and some trace element concentrations of the water samples. M.D.L: Method detection level, P.Q.L.: Practical quantification level, PAL: Protection of aquatic life (Law N° 24051 Appendix IV, Argentina), IW: Water for irrigation (Law N° 24051 Appendix IV, Argentina), CCC: criteria continuous concentration (US-EPA 2002). Geographic coordinates of sampling points: CAP1: 27°20'12", 66°22'32.3", CAP2: 27°20'12.4", 66°22'35.9", CAP3: 27°20'8.7", 66°22'14.7", CAP4: 27°20'14.2", 66°22'14.5".

		M.D.L.	P.Q.L.	CAP1	CAP2	CAP3	CAP4	PAL	IW
CE	$\text{ms}\cdot\text{cm}^{-1}$			1.022	1.94	1.75	0.97		
pH				7.4	3.14	5.15	7.9		
$\text{HCO}_3^-$	$\text{mg}\cdot\text{L}^{-1}$			68.28	0.00	1.22	200.57		
$\text{SO}_4^{2-}$	$\text{mg}\cdot\text{L}^{-1}$			458.8	1454.3	1085.7	265.1		
Cl <sup>-</sup>	$\text{mg}\cdot\text{L}^{-1}$			29.7	30	38.9	53.9		
F <sup>-</sup>	$\text{mg}\cdot\text{L}^{-1}$			0.4	0.7	0.3	0.7		
Na <sup>+</sup>	$\text{mg}\cdot\text{L}^{-1}$	0.41	1.2	42	40	35	54		
K <sup>+</sup>	$\text{mg}\cdot\text{L}^{-1}$	0.38	1.1	ND	ND	ND	ND		
Ca <sup>2+</sup>	$\text{mg}\cdot\text{L}^{-1}$	0.45	1.3	95	184	180	97		
Mg <sup>2+</sup>	$\text{mg}\cdot\text{L}^{-1}$	0.24	0.74	26	48	51	24		
Mn	$\mu\text{g}\cdot\text{L}^{-1}$	1.3	4	29580	104500	65170	105	100	200
As	$\mu\text{g}\cdot\text{L}^{-1}$	2	6	ND	30	14	17	50	100
Cd	$\mu\text{g}\cdot\text{L}^{-1}$	0.8	2.4	96	378	738	ND	0.2	10
Zn	$\mu\text{g}\cdot\text{L}^{-1}$	0.2	0.7	19310	53790	52410	115	30	2000
Cu	$\mu\text{g}\cdot\text{L}^{-1}$	1.2	3.6	215	11110	7848	12	2	200
Fe	$\mu\text{g}\cdot\text{L}^{-1}$	0.4	1.1	37	14500	99	61	5	5000
Al	$\mu\text{g}\cdot\text{L}^{-1}$	0.4	1.1	120	18698	537	63	5	5000
Se	$\mu\text{g}\cdot\text{L}^{-1}$	3	9	ND	ND	ND	ND	1	20
Sr	$\mu\text{g}\cdot\text{L}^{-1}$	10	25	244	557	309	412		
Cr	$\mu\text{g}\cdot\text{L}^{-1}$	0.5	1.5	7.5	32	16	1.5	2	100
Ni	$\mu\text{g}\cdot\text{L}^{-1}$	0.3	0.9	36	118	127	ND	25	200
Mo	$\mu\text{g}\cdot\text{L}^{-1}$	0.4	1.2	ND	ND	ND	2.4		10
Pb	$\mu\text{g}\cdot\text{L}^{-1}$	2.5	7.5	30	427	1897	8.7	1	200
Ba	$\mu\text{g}\cdot\text{L}^{-1}$	0.8	2.4	13	7.8	8.8	11		

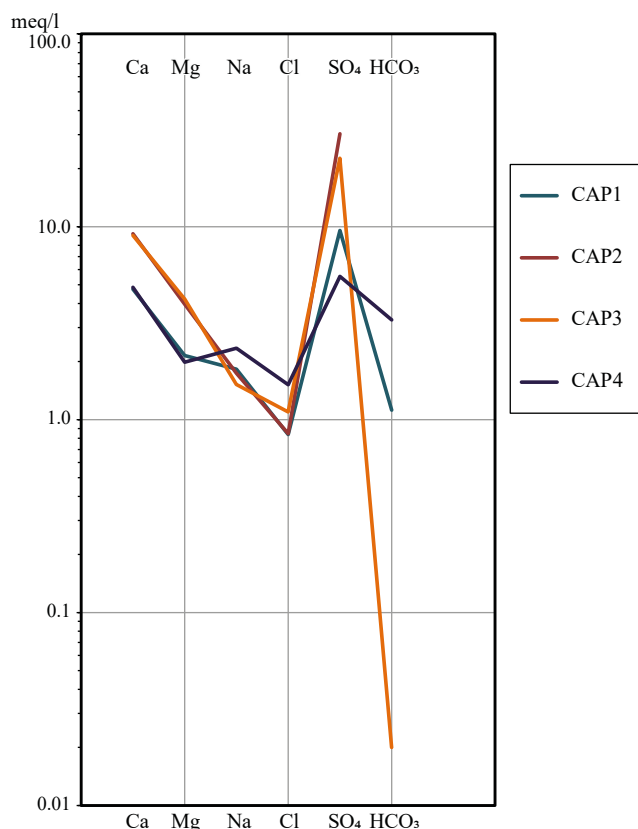


Figure 3. Schoeller-Berkaloff diagram of the analyzed waters.

The pond is located on the hillside, above the riverbed level of the Ortiz stream, consequently the slight alkalinity of this water is probably caused by dilution with locally infiltrated rainwater that was not in contact with mine wastes. Therefore, the precipitation of the newly formed phases should be mainly driven by the pH increase.

The waters of the Capillitas stream (CAP4) are alkaline and show lower EC and the lowest contents of Al ( $63 \mu\text{g}\cdot\text{L}^{-1}$ ), Mn ( $105 \mu\text{g}\cdot\text{L}^{-1}$ ), Zn ( $115 \mu\text{g}\cdot\text{L}^{-1}$ ), Cu ( $12 \mu\text{g}\cdot\text{L}^{-1}$ ), Cr ( $1.5 \mu\text{g}\cdot\text{L}^{-1}$ ), and Pb ( $8.7 \mu\text{g}\cdot\text{L}^{-1}$ ). Whereas Ni and Cd were below detection limits the concentrations of Mn, Zn, Cu and Pb at this sampling point exceed the limiting values for the protection of aquatic life in Argentina (Table 1). On the contrary, it shows a slightly higher content of As ( $17 \mu\text{g}\cdot\text{L}^{-1}$ ) than the Ortiz stream. Upstream its confluence with the Ortiz stream the waters of the Capillitas stream are suitable for irrigation according to the environmental legislation of Argentina. This might seem unlikely at first because a few kilometers upstream of the sampling point, the Capillitas stream receives the waters from Santa Rita stream, which has a small mine at its source (Santa Rita Mine) and a tributary that originates in a sulfide mine and flows through the mineralized area. However, a recent study of the upper and middle sections of the Capillitas basin has found that, in the area of Santa Rita Mine, the acidity arising from pyrite oxidation is partially neutralized by the weathering of ubiquitous rhodochrosite (Yaciuk *et al.*, 2022).

The waters of the Acid and Ortiz streams and the turquoise pond show concentrations of Al, Mn, Cd, Zn, Cu, and Pb that exceed one hundred to five thousand times the limiting concentrations for the protection of aquatic life and from five to sixteen times in the cases of Cr and Ni. Moreover, the concentrations of Mn, Cd, Zn, Cu, and Pb of these watercourses also exceed, in different degrees (2 to 2900) the allowable maximum values for irrigation waters (Table 1).

Table 2. Environmental risk factor for potential toxic metals in water samples (Riba *et al.*, 2002), CCC values (US-EPA 2002) were employed in calculations.

	CAP1	CAP2	CAP3	CAP4
As	ND	- 0.8	- 0.91	- 0.89
Cd	383.0	1511.0	2951.0	ND
Zn	159.9	447.3	435.8	0.0
Cu	22.9	1233.4	871.0	0.3
Cr	- 0.32	1.91	0.45	- 0.86
Ni	- 0.21	1.27	1.44	ND
Pb	11	169.8	757.8	2.48

In order to rank the pollution degree of the studied watercourses we employed the environmental risk factor proposed by Riba *et al.* (2002) for sediments that was later extended by Sarmiento *et al.* (2011) to waters. This factor was defined as,

$$\text{ERF} = (C_n - C_{\text{SQV}}) / C_{\text{SQV}}$$

Where  $C_n$  is the concentration of the metal in water and  $C_{\text{SQV}}$  is the highest concentration measure of an element in the sampling site, not related with biological effects. In order to apply the ERF to waters,  $C_{\text{SQV}}$  was replaced by the continuous concentration criteria (CCC), estimated by the Environmental Protection Agency (USEPA), following Sarmiento *et al.* (2011). According to the USEPA definition, CCC represent the highest concentration of an element in surface water to which an aquatic community can be indefinitely exposed without resulting in unacceptable effects (US-EPA 2002). This implies that positive ERF values indicate environmental risk, specifically for aquatic life. The ERF was calculated for As, Cd, Zn, Cu, Cr, Ni and Pb (Table 2). CCC values were not included in US-EPA (2002) for the other determined metals. The ERF obtained for the Acid and Ortiz streams and for the turquoise pond indicates that Cd, Cu, Zn and Pb represent a considerable environmental risk for these watercourses. Namely, an ERF from 383 to 2951 was obtained for Cd, from 23 to 1233 for Cu, from 160 to 447 for Zn, and from 11 to 758 for Pb. In the case of Cr and Ni, they only represent a risk in the Ortiz and Acid streams; although the ERF values are considerably lower (0.45 to 1.92) than those calculated for the other heavy metals. On the contrary, As does not represent an environmental risk in these watercourses according with this criterion. Regarding the Capillitas stream, only Pb and minimally Cu represent an environmental risk according to the computed ERF (Table 2).

### Streambed sediments

The results of the chemical analyses of streambed sediments are shown in Table 3. The three samples of sediments taken from the Ortiz stream are ochre-colored or virtually orange in the case of CAPS1 (Figure 4), they have in common a high content of heavy metals and metalloids. However, the pattern of variation of metal and metalloids contents downstream the Ortiz creek is not the same for all the elements (Figure 5). The highest contents of Cd ( $79 \mu\text{g}\cdot\text{g}^{-1}$ ) were registered in the streambed sediments taken at the nearest sampling point to the Capillitas Mine (CAPS1). On the contrary, the highest concentrations of As ( $1291 \mu\text{g}\cdot\text{g}^{-1}$ ), Cu ( $7802 \mu\text{g}\cdot\text{g}^{-1}$ ), Fe (5.5 %), Mn (2.6 %) and Pb ( $4596 \mu\text{g}\cdot\text{g}^{-1}$ ) were registered in the streambed sediments taken at the sampling point located ~ 250 m from the joint between both streams. It is worth noting that, in the case of Pb and Fe, the concentrations obtained at this point were very similar to those registered at the nearest sampling point to Capillitas Mine (CAPS1). Moreover the maximum concentration of Zn ( $38768 \mu\text{g}\cdot\text{g}^{-1}$ ) and Sn ( $36 \mu\text{g}\cdot\text{g}^{-1}$ ) and Mo ( $13 \mu\text{g}\cdot\text{g}^{-1}$ ) was registered 80 m away from the point where the Ortiz the Acid

Table 3. Near-total composition (total acid digestion) of streambed sediments of the Ortiz creek. PEL: probable effect level, Canadian freshwater quality sediment guidelines for protection of aquatic life (CCME, 2001).  $B_n$  values were calculated from data for unpolluted streambed sediments reported in the geochemical chart of the region (samples 5004, 5008, 5015, 5022, 5026, 5033, 5037 for Cd, Cr, Cu, Pb and Zn, and samples 2952, 2957, 2962 and 2964 for As (Ferrozzi *et al.*, 2003).

	M.D.L.	P.Q.L.	CAPS1	CAPS2	CAPS3	CAPS4	PEL	$B_n$
Al	%	0.04	5.2	5.6	6.7	6.9		
As	$\mu\text{g}\cdot\text{g}^{-1}$	0.4	1.2	851	616	1291	17	41.81
Bi	$\mu\text{g}\cdot\text{g}^{-1}$	1	2	<2	<2	<2	17	
Cd	$\mu\text{g}\cdot\text{g}^{-1}$	0.16	0.5	79	36	40	6.5	0.34
Zn	$\mu\text{g}\cdot\text{g}^{-1}$	0.04	0.14	26031	38768	15722	206	315
Cu	$\mu\text{g}\cdot\text{g}^{-1}$	0.24	0.72	806	5737	7802	130	197
Sn	$\mu\text{g}\cdot\text{g}^{-1}$	2	4	38	69	54	36	
Fe	%	0.03	0.08	4.7	3.1	5.5	2.7	
Mn	%	0.06	0.19	1.4	1.2	2.6	0.1	0.09
Mo	$\mu\text{g}\cdot\text{g}^{-1}$	0.08	0.24	1.7	0.46	<0.24	13	
Pb	$\mu\text{g}\cdot\text{g}^{-1}$	0.2	1.5	4515	3268	4596	75	91.3
Se	$\mu\text{g}\cdot\text{g}^{-1}$	0.6	1.8	<1.8	<1.8	<1.8	<1.8	

streams meet. This suggests that the metal-bearing particles have been transported downstream by water currents, probably in combination with chemical processes such as precipitation and adsorption.

To distinguish metal(oids) coming from mining activities from the natural geochemical background we considered the average composition of As, Cd, Zn, Cu, Mn and Pb for unpolluted streambed sediments based on data from the geochemical chart of the region (Ferrozzi *et al.*, 2003). Additionally, the index of geoaccumulation ( $I_{geo}$ ) proposed by Müller (1981) was computed in order to assess the metal pollution in the analyzed sediments. This index is defined as,

$$I_{geo} = \log_2 (C_n/1.5B_n)$$

where  $C_n$  is the concentration of the toxic element in the sediment and  $B_n$  is the concentration of the same element in unpolluted sediments. The values of  $B_n$  employed in the  $I_{geo}$  calculation were the average composition of As, Cd, Zn, Cu, Mn and Pb for unpolluted streambed sediments according to data from the geochemical chart of the region (Ferrozzi *et al.*, 2003). This geochemical chart does not include results of Bi, Mo and Sn, thus  $I_{geo}$  could not be computed for these elements.

According to the obtained  $I_{geo}$ , the three streambed sediment samples from the Ortiz creek are extremely polluted with Cd, Zn and Pb, whereas they range from strongly to extremely polluted with Cu, As and Mn (Figure 6). The streambed sediment from Capillitas creek (CAPS4) depicts lower contents of metals and metalloids; however, it is strongly polluted with Cd, moderately polluted with Cu and unpolluted to moderately polluted with Pb and Zn (Figure 6).

The three stream sediment samples from the Ortiz creek depict levels of As, Cd, Zn, Cu and Pb exceeding the Canadian freshwater quality sediment guidelines (PEL, probable effect level, As:  $17 \mu\text{g}\cdot\text{g}^{-1}$ , Cd:  $3.5 \mu\text{g}\cdot\text{g}^{-1}$ , Zn:  $315 \mu\text{g}\cdot\text{g}^{-1}$ , Cu:  $197 \mu\text{g}\cdot\text{g}^{-1}$ , Pb:  $91.3 \mu\text{g}\cdot\text{g}^{-1}$ ).

## DISCUSSION

The Acid stream that drains the mineralized area and the stockpile of the Capillitas Mine constitutes an AMD as it shows pH  $\sim$ 3, high EC, high contents of  $\text{SO}_4$ , As and heavy metals. However, in comparison with the nearby Escombreras stream, that also represents an AMD (Yaciuk *et al.*, 2022), it presents significantly lower contents of  $\text{SO}_4$ ,

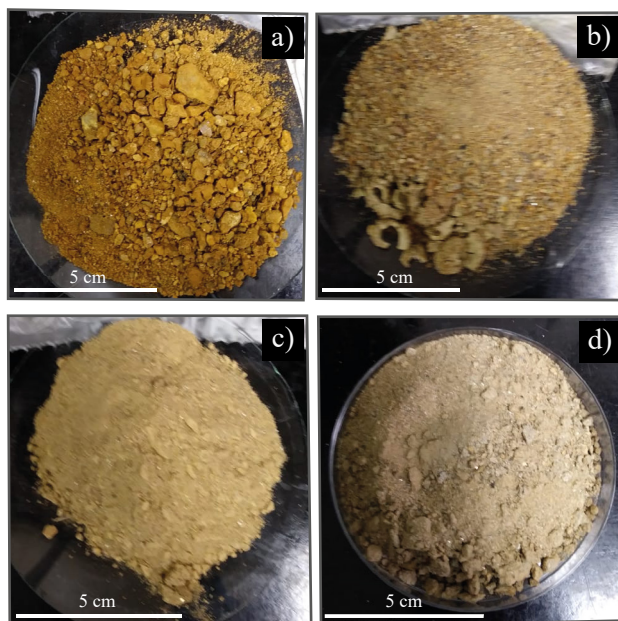


Figure 4. a) Orange-colored sediment of the Ortiz stream at the point of its confluence with the Acid stream (CAPS1). b) and c) Ochre-colored streambed sediments taken  $\sim$ 80 (CAPS2) and 250 m (CAPS3) downstream of CAPS1 in the Ortiz creek. d) Light brown-colored sediment of Capillitas stream (CAPS4) before its confluence with the Ortiz stream.

Cu, Fe, Zn and Cd, and a slightly higher pH. On the contrary, the Acid stream shows higher contents of Pb than the Escombreras stream. These differences could be due to the fact that the Escombreras stream was sampled in close proximity to a sulfide mine dump of large dimensions comprising chalcopyrite, sphalerite, galena and pyrite (Yaciuk *et al.*, 2022). Moreover, the lower pH of the Escombreras stream, as well as its higher EC, indicate stronger dissolution, lixiviation and metal mobility processes. Furthermore, the higher content of Pb in the Acid stream could be due to several reasons: 1) a higher proportion of galena in the stockpile that is drained by the Acid stream; 2) Pb could have been removed from the solution by co-precipitation or adsorption onto the metal sulfates that appear as efflorescent salts along the course of the Escombreras stream (Yaciuk *et al.*, 2022).

The Ortiz stream shows a higher pH and lower EC than the Acid stream; but higher concentrations of Cd, Ni and Pb. Heavy metals should mainly derive from alteration of metal sulfides, mainly galena and sphalerite, occurring in the tailings dam that the Ortiz stream crosses. In relation to Cd, Yaciuk *et al.* (2022) found that sphalerite is the main carrier of this element in the veins of the sulfide mine that crosses the Escombreras stream. Besides, a minor contribution arising from dissolution of metal bearing sulfurs of the mineralized area to the Ortiz stream could not be discarded. The differences in heavy metal and As contents between the Acid and Ortiz streams should be mainly controlled by the contrasting mineralogy of the mine dumps that they cross.

The metal content of the Ortiz and Acid streams imply a considerable environmental risk, since it is known that dissolved heavy metals such as Zn, Pb, Cd and Cu are highly toxic to many aquatic organisms (Verma and Dwivedi, 2013; Jain *et al.*, 2016; Masindi and Muedi, 2018). The Ortiz stream also represents a potential threat to groundwater resources as significant water infiltration occurs in its channel near the confluence with the Capillitas stream, which is evidenced by a considerable reduction of flow rate.

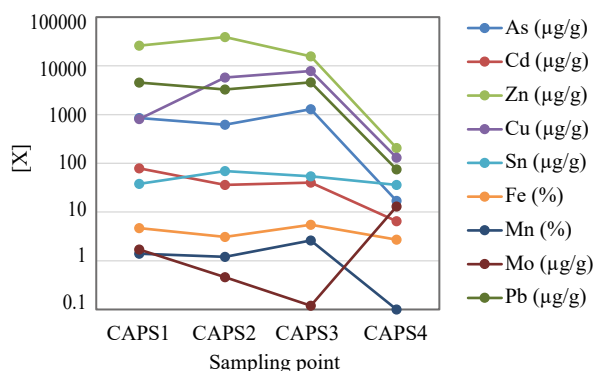


Figure 5. Concentration of some toxic metals and metalloids in the streambed sediments sampled along the Ortiz creek.

In the case of the Capillitas stream, only Pb, and minimally Cu, represent an environmental risk according to the ERF index. However, it is worth noting that the concentration of Mn, Zn, Cu, Fe, Al and Pb shown by Capillitas stream before its joint with the Ortiz stream are markedly higher than those obtained around one kilometer upstream by Yaciuk *et al.* (2022). This suggests that the attenuation processes proven by these authors in the upper section of the Capillitas basin are counterbalanced downstream by the input of toxic elements, probably lixiviated from the mine wastes stacked along the south bank of the Ortiz creek. A specific concern is that the Capillitas stream shows similar As contents than the Ortiz stream, even though the sampling point CAP4 is located far away from the mine dumps that affected the tributaries of the Capillitas stream in its upper course. A similar case of alkaline waters showing high contents of dissolved As was reported downstream the La Soterreña mine by Larios *et al.* (2012). It is worth noting that in both cases As and Fe contents are not correlated, indicating that As cannot arise from dissolution of Fe(III) oxy-hydroxides. In the case of the La Soterreña mine, the high level of As in the alkaline waters was related with the dissolution of arsenates (Larios *et al.*, 2012). Unfortunately, in the case of the Capillitas stream, there was not enough data to identify the processes controlling As mobilization.

It is interesting to compare the contents of heavy metals between the waters of the Acid stream with those of the streambed sediments at the confluence with the Ortiz stream (CAPS1). The water shows contents of Cd, Zn, Cu and Mn markedly higher than those of the streambed sediments, indicating that these potentially toxic elements remain in great part dissolved. On the contrary, the contents of Fe, As, and Pb are extremely higher in the sediment than in the water. This means that the pH increase, caused by the mixing of the Acid and Ortiz streams, promotes the precipitation of authigenic phases that capture a significant part of the dissolved heavy metals and metalloids. The intense ochre color of these streambed sediments, as well as their high content of Fe and As, evidence the presence of iron oxy-hydroxides. The high affinity of As for newly-formed Fe(III) precipitates is well established and is regarded as the main attenuation mechanism of As migration (Smedley and Kinniburgh, 2002, Asta *et al.*, 2010, Larios *et al.*, 2012). It is known that these ochre sediments can stifle the stream bed and benthic habitat (Jain *et al.* 2016). Downstream the contents of heavy metals and As in the sediments of the Ortiz creek vary in a complex way. The highest content of Cd was found in CAPS1, whereas Zn and Sn show higher concentrations in CAPS2. The highest content of As, Cu, Fe, Mn and Pb was observed in the sediments taken ~250 m downstream (CAPS3). Thus, the polluted sediments have been dispersed by water currents, probably in combination with dissolution/precipitation, adsorption and other chemical processes.

The  $I_{geo}$  obtained for stream sediments from the Ortiz creek indicates that the contents of Cd, Zn, Cu, Mn, Pb and As largely exceed the average values computed for the unpolluted sediments of the study area. It is well known that the total metal content in sediments is not a reliable indicator of toxicity, as contaminants can be allocated in numerous phases with different bioavailability degrees (Landrum and Robbins, 1990). However, the water in contact with these streambed sediments shows contents of Cd, Zn, Cu and Mn remarkably higher than the sediments, indicating the need for a remediation program leading to the isolation of potentially toxic metal(oids) in order to meet environmental regulations and international standards of the mining industry.

The water courses that drain materials from the Capillitas Mine, as well as their streambed sediments, show high contents of potentially toxic elements that can affect the hydrochemical water quality of the Capillitas stream, which is used by the rural population. Thus, effective actions are needed in the Capillitas Mine in order to avoid the dispersion of toxic elements into the watershed of this area.

The issues raised by the pollution related with Capillitas Mine is not unique in Argentina. In the case of NW Argentina, a study demonstrated the deleterious effect of Aguilar Mine on the water quality of Casa Grande stream and Yacoraite River, displaying high concentrations of Mo, Pb, Zn and Cd (Kirschbaum *et al.*, 2012). La Concordia mine (Salta province, Argentina) represents another worrying case. It was closed in the mid '80, leaving sulfide-rich residues accumulated in tailing dams in the valley of the Concordia stream, a 14 km long watercourse that is a tributary of the San Antonio River, which constitutes the main water supply of San Antonio de los Cobres, the main city of the region (~6000 inhabitants). Chemical analysis of the stream water close to the mine demonstrate the occurrence of highly acidic waters ( $3 < \text{pH} < 4$ ) with concentrations of As, B, Cd, Mn, Pb, and Zn that largely exceed the guideline values for drinking water in Argentina (Kirschbaum *et al.*, 2012). A later study demonstrates the high mobility of the As retained in secondary (hydrated)sulfate forming large saline crusts or aggregates disseminated within the matrix of the oxidized levels of La Concordia mine tailings (Nieva *et al.*, 2016). The high concentration of As observed in a sampling site of the Capillitas stream, located far away from the mine dumps that affected its upper basin tributaries, indicates a high mobility of As, in accordance with the behavior observed in La Concordia mine tailings (Nieva *et al.*, 2016).

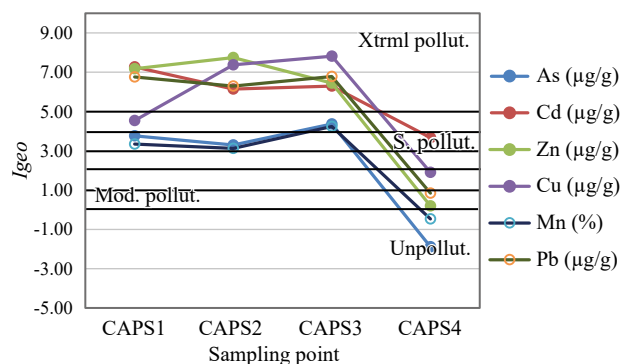


Figure 6. Variation of the streambed sediments  $I_{geo}$  along the Ortiz creek between sampling stations. Horizontal bold lines indicate the threshold values for the different categories of  $I_{geo}$  (Unpollut.: unpolluted, Mod. pollut.: moderately polluted, strongly pollut.: S. pollut.: strongly polluted, Xtrml pollut.: extremely polluted). The values of  $B_n$  employed in the  $I_{geo}$  calculation were the average composition of As, Cd, Zn, Cu, Mn and Pb in unpolluted streambed sediments reported in the geochemical chart of the region (Ferpozzi *et al.* 2003).

## CONCLUSIONS

Sulfide oxidation from the tailings and spoil heaps at Capillitas Mine originated a typical acid mine drainage, rich in dissolved metal(oids) and  $\text{SO}_4$ , that leaks into the Ortíz and Acid streams which cross the site. As a result, the water quality is strongly affected, as it shows acidic pH values (*i.e.*,  $\text{pH} < 4$ ) and concentrations of metals and As that highly exceed the guideline values for the protection of aquatic life and irrigation specified in the legislation of Argentina. Moreover, the high concentration of As depicted by the Capillitas stream in a sampling point located far away from the mine dumps, that affected its upper basin, evidences the high mobility of this element and represents an environmental concern. The increase of pH resulting from the mixing of the Acid stream and the Ortíz stream promotes the precipitation of Fe oxy-hydroxides that adsorb part of the dissolved As onto their surfaces and also provokes the precipitation of Pb-bearing phases, probably sulfates. The content of heavy metals and As in the sediments of the Ortíz creek varies in a complex pattern. The highest content of Cd was found where the Ortíz and Acid streams join, whereas Zn and Sn show higher concentrations in the sediments sampled ~80 m downstream. The highest content of As, Cu, Fe, Mn and Pb was observed in the sediments taken ~250 m downstream. Thus, the polluted sediments are being dispersed by water currents probably in combination with dissolution/precipitation and adsorption processes. According to the obtained *Igeo*, the three streambed sediment samples from the Ortíz creek are extremely polluted with Cd, Zn and Pb, and range from strongly to extremely polluted with Cu, As and Mn. Whereas the sediments from Capillitas creek are strongly polluted with Cd, moderately polluted for Cu and unpolluted to moderately polluted with Pb and Zn.

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