

Environmental risk assessment of watercourses and streambed sediments downstream the Capillitas Mine, Catamarca, Argentina

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Abstract

The present study assessed the environmental risk associated with the dispersion of heavy metals and metalloids by streams that flow through Capillitas Mine (Catamarca, Argentina), an epithermal precious- and base-metal vein deposit previously mined for copper along with gold and silver; and subsequently for rodochrosite. Geochemical analyses of water of three streams (Ortíz, Acid and Capillitas) and a small pond depicting a very thin layer of turquoise-colored precipitates in its bottom were performed and 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_4 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 limiting concentrations for protection of aquatic life, as well as for irrigation waters. The Capillitas stream has a lower content of heavy metal but shows concentrations of Mn, Zn, Cu and Pb exceeding the limiting values for protection of aquatic life.

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

Introduction

Acid mine drainage (AMD) is a complex process originated when mining activities exposed sulfur-bearing rocks to moisture and surface waters under oxidizing condition given place to acid- SO_4 waters with high contents of metals. This phenomenon has been extensively studied in the last decades as it is considered the most serious pollution problem affecting lotic and lentic systems. Because the chemical reactions that generates AMD give place to a cyclical process that perpetuates the continual creation of AMD. 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 for 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 would be characterized before to any mining activity (Nordstrom 2015). However, in many cases mining activities began decades or even centuries before any scientific study had been carried out. In such cases, when there are no hydro geochemical study for 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 for constrain plausible environmental restoration goals (Nordstrom 2015).

Nevertheless, water courses pollution is not the unique threat to the environment related with mining activities, 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; Gałuszka, 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, first for copper along with gold and silver, from 1855 until 1930, when the richest veins were exhausted. Afterwards, mining of copper was gradually replaced by the extraction of rodochrosite (Delfino et al. 2014), a semiprecious stone widely employed in jewelry, that is the national stone of Argentina. In the first period the ore containing copper bearing sulfurs was processed in the Muschaca smelting plant. A recent study shown the existence of contamination by Cu, Zn, As and Sn in the soils located ~ 80 m towards the south of the old smelting plant (Do Campo et al. 2020). According to the documents that have been preserved 6,818 tons of copper would be produced from 1860 to 1881.

Nowadays Capillitas Mine is operated by a state-owned company and the mining of rodochrosite is an important economic activity of the Catamarca province. In the area located downstream the current border of the property of Capillitas Mine there are several watercourses: Ortíz, Capillitas and an unnamed stream tributary of the Ortíz stream (Fig. 1). The unnamed stream runs SW-NE through the mineralized zone and stockpiles, whereas the Ortíz stream also drains the mineralized zone and cross a tails damp. 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 (Fig. 2a, b). These channels seems to be used to the processing of the copper ore during the first period of mining operation. Moreover, ochre deposits including hardpan crusts are widespread at the sides of the channels and also cover the riberbed of the Ortíz stream (Fig. 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 composition of the waters and streambed sediments 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 constrain the environmental risk associated with the dispersion of heavy metals and metalloids by streams that flow through spoil heaps and tails dam of the Capillitas Mine. With this objective chemical analyses of waters and streambed sediments from several water courses downstream Capillitas Mine were performed. Furthermore, the degree of pollution 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 for sediments (Muller 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 (SFe), sphalerite (SZn), galena (SPb), calchopyrite (CuFeS₂), marcasite (FeS₂), pyrrhotite (Fe₇S₈), tennantite (Cu₆Cu₄(Fe²⁺,Zn)₂As₄S₁₂S), enargite (Cu₃AsS₄), bornite (Cu₅FeS₄), stannite (Cu₂FeSnS₄) 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 (Marquez Zabalía 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 studied area is located to the NE of the Capillitas Mine, where two streams, Ortíz and its unnamed affluent, drains spoil heaps and tails dam, containing material from recent and old mining operations. The Ortíz stream is an affluent of the Capillitas stream that discharge in the Campo del Arenal. The Capillitas stream has its headwaters in an unmineralized area with no mining activities. However, in its upper course it receives the contribution of the Santa Rita stream, which in turn originates near the Rhodochrosite Mine and has the Escombreras stream which originates in the Galena Mine as a tributary. According to Yaciuk et al. (2022) the Escombreras stream exhibits pH ranging between 2.26 and 2.70 and thus is classified as an acid mine drainage. After its confluence with the Escombreras stream the pH of the Santa Rita stream decrease from 5.83 to 3.09 in a few meters (Yaciuk et al. 2022).

The climate of the study area correspond to a height desert with annual average precipitation < 200 mm as the region lie in the rain shadow of the Sierra del Aconquija. At regional scale rainfall have a monsoon regime characterized by wet summers and dry winters, heaviest rains are very frequent during southern summers (December to March) (Banchig et al. 2009). Yaciuk et al. (2022) indicate that even though the hydrological balance of the Capillitas region is markedly negative, several low-flow (0.05–14.5 L s⁻¹) 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 ($\sim 0.8 \text{ Km}^2$) downstream the Capillitas Mine (Fig. 1). Water sample CAP2 corresponds to the unnamed stream tributary of the Ortíz stream, and sample CAP3 to the Ortíz stream; these samples were collected $\sim 0.5 \text{ km}$ downstream of the active mining works of Capillitas Mine, just before their confluence. The amounts of suspended sediments are insignificant in the two streams. Sample Cap1 was taken in a small pond situated 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 received a low flow of shallow groundwater flowing from NW and discharge into the Ortíz stream through a narrow channel situated in its E border (Fig. 2d). This pond depicts a very thin layer of turquoise-colored mineral precipitates in its bottom, and thus will be called 'turquoise pond' hereafter (Fig. 2e). Water sample CAP4 corresponds to the Capillitas stream, and was taken few meters before its confluence with the Ortíz stream (Fig. 2f). During the sampling campaign the flow rate of the Ortíz and unnamed streams were considerable greater than this of the Capillitas stream, where water flowed from a little 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 to analyze major and minor cations. All the water samples were vacuum-filtered using 0.45-cellulose nitrate filters, whereas that sub samples for cations determination were acidified with nitric acid until $\text{pH} < 2$, to prevent the metals precipitation during the transport to the laboratory. All the samples were stored at 4°C until analysis. Major anions (HCO_3^- , SO_4^{2-} , Cl^- , F^-) were analyzed by ion chromatography at the Department of Geology Chemical Laboratory (FCEyN, UBA) employing a Thermo Scientific Dionex Aquion, using the pre-column AG18 4-microns and the column AS18-4 microns, and KOH 35 mM as eluent. Analytical determinations of major and minor cations and trace elements (Na, K, Ca, Mg, Mn, As, Cd, Zn, Cu, Fe, Al, Se, Sr, Cr, Ni, Mo, Pb and Ba) were performed in the acidified samples by ICP-OES in the chemical laboratory of the Servicio Geológico Minero Argentino (SEGEMAR).

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 sediment because they depict marked changes in color and texture with the superficial material. CAPS1 was taken in the bed of the Ortíz stream just in the point of its confluence with the unnamed stream, whereas CAPS2 and CAPS3 were taken, respectively, ~ 80 and 250 m downstream in the Ortíz creek (Fig. 1). Sample CAPS4 correspond to the streambed sediments of the Capillitas stream. The four samples of sediment were grinded 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 (0.5g a 100ml, HNO_3 9ml + HF 3ml + HCl 2ml, 180°C , 9.5min). The contents of Al, Fe and Mn in the sediment extract were analyzed by FRX whereas their Cu,

Zn, As, Se, Mo, Cd, Sb, Pb, Bi, Sn and W contents were determined by ICP-OES in the chemical laboratory of the Servicio Geológico Minero Argentino (SEGEMAR).

Results

Hydro geochemistry

Physicochemical results are summarized in Table 1. According to their major ions concentration the four samples correspond to calcium SO_4 waters; however their pH, conductivity and contents of major (Fig. 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 SO_4 contents. The unnamed stream (CAP2) depicts pH \sim 3, along with a high contents of heavy metals; thus it constitutes and AMD, and so it will be hereafter designated as the 'Acid stream'. This stream also shows the highest content of Fe, what is in agreement with the high solubility of Fe^{+3} under low pH oxidant waters (Brookins 1988). The Ortíz stream (CAP3) depicts pH \sim 5, slightly low EC and extremely lower concentration of Fe than the Acid stream. The low Fe content is in agreement with the insolubility of Fe^{+3} in moderately acidic and well-oxygenated waters (Brookins 1988). Despite its higher pH the Ortíz stream also depict high contents of Al, Mn, Cd, Zn, Cu, Cr, Ni and Pb.

Table 1

		M.D.L.	P.Q.L.	CAP 1	CAP 2	CAP 3	CAP 4	PAL	IW	CCC
CE	ms cm^{-1}			1.022	1.94	1.75	0.97			
pH				7.4	3.14	5.15	7.9			
HCO_3^-	mg L^{-1}			68.28	0.00	1.22	200.57			
SO_4^{2-}	mg L^{-1}			458.8	1454.3	1085.7	265.1			
Cl^-	mg L^{-1}			29.7	30	38.9	53.9			
F^-	mg L^{-1}			0.4	0.7	0.3	0.7			
Na^+	mg L^{-1}	0.41	1.2	42	40	35	54			
K^+	mg L^{-1}	0.38	1.1	ND	ND	ND	ND			
Ca^{2+}	mg L^{-1}	0.45	1.3	95	184	180	97			
Mg^{2+}	mg L^{-1}	0.24	0.74	26	48	51	24			
Mn	$\mu\text{g L}^{-1}$	1.3	4	29580	104500	65170	105	100	200	
As	$\mu\text{g L}^{-1}$	2	6	ND	30	14	17	50	100	150
Cd	$\mu\text{g L}^{-1}$	0.8	2.4	96	378	738	ND	0.2	10	0.25
Zn	$\mu\text{g L}^{-1}$	0.2	0.7	19310	53790	52410	115	30	2000	120.0
Cu	$\mu\text{g L}^{-1}$	1.2	3.6	215	11110	7848	12	2	200	9.0
Fe	$\mu\text{g L}^{-1}$	0.4	1.1	37	14500	99	61		5000	
Al	$\mu\text{g L}^{-1}$	0.4	1.1	120	18698	537	63	5	5000	
Se	$\mu\text{g L}^{-1}$	3	9	ND	ND	ND	ND	1	20	
Sr	$\mu\text{g L}^{-1}$	10	25	244	557	309	412			
Cr	$\mu\text{g L}^{-1}$	0.5	1.5	7.5	32	16	1.5	2	100	
Ni	$\mu\text{g L}^{-1}$	0.3	0.9	36	118	127	ND	25	200	
Mo	$\mu\text{g L}^{-1}$	0.4	1.2	ND	ND	ND	2.4		10	
Pb	$\mu\text{g L}^{-1}$	2.5	7.5	30	427	1897	8.7	1	200	2.5
Ba	$\mu\text{g L}^{-1}$	0.8	2.4	13	7.8	8.8	11			

PAL: Protection of aquatic life

IW: Water for irrigation

ccc

On the other side, the Capillitas stream and the turquoise pond (CAP4 and CAP1) are slightly alkaline; depict lower conductivities, and higher contents of bicarbonate. The turquoise pond shows concentration of SO_4 , Cd, Zn, Cu, Fe, Mn, Al, Cr, Ni and Pb substantially lower than the nearby Ortíz stream. The low content of metals in these waters is in agreement with the occurrence of a thin layer of secondary Cu-bearing sulfates precipitates in the bottom of the pond, probably associated with other metal-bearing phases (Fig. 2e). In turn, precipitation should be mainly driven by the almost neutral pH. The slight alkalinity of this water should be caused by dilution with locally infiltrated rainwater that were not in contact with mine wastes; as the pond is located nearby the hillside, above the riverbed level of the Ortíz stream.

The waters of the Capillitas stream (CAP4) are alkaline and show lower EC and the lowest contents of Al, Mn, Cd, Zn, Cu, Cr, Ni and Pb. Even though the concentrations of Mn, Zn, Cu and Pb in this sampling point exceed the limiting values for protection of aquatic life in Argentine. On the other side, according to the environmental legislation of Argentina the waters of the Capillitas stream before it confluence with the Ortíz stream are suitable for irrigation. This might seem unlikely at first because few kilometers upstream of the sampling point the Capillitas stream receives the Santa Rita stream, that has a small mine in its headwaters (Santa Rita Mine) and, in turn has a tributary that originates in a sulfide mine and go through the mineralized area. However, a recent study of the upper and middle section of the Capillitas basin has founded 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).

On the other side, the waters of 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 limiting concentrations for protection of aquatic life, as well as for irrigation waters.

In order to rank the degree of pollution in the studied watercourses we employed the environmental risk factor proposed by Riba et al. (2002) for sediments that was later extended for 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_{SQV} is the highest concentration measure for an element in the studied site not related with biological effects. In order to apply ERF to waters C_{SQV} was replaced for the criteria continuous concentration (CCC) estimated for USEPA, following Sarmiento et al. (2011). According to the definition of USEPA CCC represent the highest concentration of an element in surface water to which an aquatic community can be exposed indefinitely without resulting in unacceptable effects (USEPA 2002). This implies that positive ERF values indicate risk for the environment and specifically for aquatic life. ERF was calculated for As, Cd, Zn, Cu, Cr, Ni and Pb (Table

2), as for the other analyzed metals CCC values were not estimated by USEPA. The ERF obtained for the Acid and Ortíz streams and for the turquoise pound indicate that Cd, Cu, Zn and Pb represent a considerable environmental risks in these watercourses. Namely ERF from 383 to 2951 were 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 Ortíz and Acid streams; although the ERF values are considerable lower (0.45 to 1.92) than those calculated for the other heavy metals. On the contrary As do not represent an environmental risk in these watercourses according with this criteria. On the other side, in the case of Capillitas stream only Pb and minimally Cu represent an environmental risk according with the computed ERF (Table 2).

Table 2
Environmental risk factor for potential toxic metals in water samples (Riba et. Al., 2002), CCC values (USEPA 2002) were employed in calculation.

	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

Streambed Sediments

The results of the chemical analyses of streambed sediments are shown in Table 3. The three samples of sediments taken in the Ortíz stream are ochre-colored, or virtually orange in the case of CAPS1 (Fig. 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 Ortíz creek is not the same for all the elements (Fig. 5). The highest contents of Cd and Mo were registered in the streambed sediments taken in the point nearest to the Capillitas Mine (CAPS1). On the contrary, the highest concentrations of As, Cu, Fe, Mn and Pb were registered in the streambed sediments taken in 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 concentration obtained in this point were very similar to those registered in the point nearest to the Capillitas Mine (CAPS1). On the other hand, the maximum concentration of Zn and Sn were registered 80 m of the point where the Ortíz the

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

Table 3

Near-total composition (total acid digestion) of streambed sediments of the Ortíz creek. PEL: probable effect level, Canadian fresh water quality sediment guidelines for protection of aquatic life (Canadian Council of Ministers of the Environment 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 (Ferpozzi et al. 2003).

		M.D.L.	P.Q.L.	CAPS1	CAPS2	CAPS3	CAPS4	PEL	B_n
Al	%	0.04	0.12	5.2	5.6	6.7	6.9		
As	$\mu\text{g g}^{-1}$	0.4	1.2	851	616	1291	17	17	41.81
Bi	$\mu\text{g g}^{-1}$	1	2	<2	<2	<2	17		
Cd	$\mu\text{g g}^{-1}$	0.16	0.5	79	36	40	6.5	3.5	0.34
Zn	$\mu\text{g g}^{-1}$	0.04	0.14	26031	38768	15722	206	315	119.78
Cu	$\mu\text{g g}^{-1}$	0.24	0.72	806	5737	7802	130	197	23.05
Sn	$\mu\text{g g}^{-1}$	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	$\mu\text{g g}^{-1}$	0.08	0.24	1.7	0.46	< 0.24	13		
Pb	$\mu\text{g g}^{-1}$	0.2	1.5	4515	3268	4596	75	91.3	27.7
Se	$\mu\text{g g}^{-1}$	0.6	1.8	< 1.8	< 1.8	< 1.8	< 1.8		

In order to distinguish metal(loids) coming from mining activities from 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 (Ferpozzi et al. 2003). Thus, the index of geoaccumulation (I_{geo}) proposed by Müller (1981) was computed in order to constrain 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 measure in the sediment and B_n is the concentration of the same element in unpolluted sediments. The values of B_n employed in 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 (Ferpozzi et al. 2003). This geochemical chart do not contain results for Bi, Mo and Sn, thus *Igeo* could not be computed for these elements.

According to the obtained *Igeo* the three streambed sediments from the Ortíz creek are extremely polluted for Cd, Zn and Pb, they range from strongly to extremely polluted for Cu and and from strongly to extremely polluted for As and Mn (Fig. 6). The streambed sediment from Capillitas creek (CAPS4) depicts lower contents of metals and metalloids; however it is strongly polluted for Cd, moderately polluted for Cu and unpolluted to moderately polluted for Pb and Zn (Fig. 6).

The three stream sediments corresponding to the Ortíz creek depict levels of As, Cd, Zn, Cu and Pb exceeding the Canadian fresh water quality sediment guidelines (PEL, probable effect level).

Discussion

The Acid stream that drains the mineralized area and the stockpile of the Capillitas Mine constitutes an AMD as it shows pH ~ 3, high EC, high contents of SO₄ and heavy metals. Its composition differs from that of the Escombreras stream, a nearby watercourse that flows through galena-rich wastes and also represent an AMD (Yaciuk et al. 2022). Namely, the Acid stream depicts contents of SO₄, Cu, Fe, Zn and Cd significantly lower than those of the Escombreras stream, whereas its Pb contents are higher (Yaciuk et al. 2022).

The Ortíz 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 the tails dam that the Ortíz stream crosses. Although, a small contribution arising from dissolution of metal bearing sulfurs of the mineralized area could not be discarded. The metal content of both watercourses imply a considerable environmental risk, as 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 Khathutshelo 2018). The Ortíz stream also represent a potential risk for groundwater resources because significant water infiltration occurs in its channel near its confluence with the Capillitas stream, evidenced by a considerable reduction of flow rate.

In the case of the Capillitas stream only Pb, and minimally Cu, represent an environmental risk according with 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 join with the Ortíz stream are markedly higher than those obtained around one kilometer upstream for Yaciuk et al. (2022). This suggests that the attenuation processes proven for these authors in the upper section of the Capillitas basin are counterbalanced downstream by input of toxic elements probably arisen from lixiviation of the mine wastes stacked along the south bank of the Ortíz creek.

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 point of its confluence with the Ortíz stream (CAPS1). The water shows contents of Cd, Zn, Cu and Mn markedly higher than 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. Thus in this case the mobility of the metal(loid)s are $As \ll Pb \ll Zn < Cd < Cu < Mn$. This is in agreement with the intense ochre color of this streambed sediments that indicates the occurrence of iron oxi-hydroxides precipitates that are frequently associated with As (Smedley and Kinniburgh 2002). It is known that these ochre sediments can stifle the stream bed and benthic habitat (Jain et al. 2016). The observed partition of metal(loids) between water and sediments are to some degree coincident with potential mobility determined by sequential extractions: $As < Zn < Pb < Cd$ (Resongles et al 2014). Downstream the contents of heavy metals and As in the sediments of the Ortíz creek varies in a complex way. Namely, only Cd depicts the highest contents in CAPS1, whereas Zn and Sn show higher concentrations in CAPS2, and the highest contents of As, Cu, Fe, Mn and Pb were observed in the sediments taken ~ 250m downstream (CAPS3). Thus, the polluted sediments are being dispersed by water currents probably in combination with dilution/precipitation, adsorption and other chemical processes.

The *Igeo* obtained for stream sediments from the Ortíz creek indicate that their contents of Cd, Zn, Cu, Mn, Pb and As largely exceed the average values computed for unpolluted sediments of the study area. It is 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 degrees of bioavailability (Landrum and Robbins 1990). However, the water in contact with this streambed sediments shows contents of Cd, Zn, Cu and Mn markedly higher than the sediments evidencing the need for a remediation program leading to insulate potentially toxic metal(loids) in order to meet environmental regulation and international standards of the mining industry.

The water courses that drains materials from the Capillitas Mine as well as their streambed sediments show high contents of potentially toxic metals and metalloids that can affect the hydro chemical quality of the waters of the Capillitas stream that flow towards the Campo del Arenal.

Conclusions

Sulfide oxidation from the tailings and spoil heaps at Capillitas Mine originated a typical acid mine drainage, rich in dissolved metal(oid)s and SO_4 , that leaks into the Ortíz and Acid streams that crosses the site. As a result, the water quality is strongly affected, as it shows acidic pH values (i.e., $pH < 4$) and concentrations of metals and As that highly exceed the guidelines values for protection of aquatic life and irrigation. The contents of Cd, Zn, Cu, Mn, Pb and As shown by streambed sediments from the Ortíz creek largely exceed the average values computed for unpolluted sediments of the study area, as reflected by values of *Igeo* between 3 and 7.8.

Declarations

Author Contributions

All authors contributed to the study conception and design and field work. Material preparation for analysis were performed by Margarita Do Campo. The first draft of the manuscript was written by Margarita Do Campo and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Figures

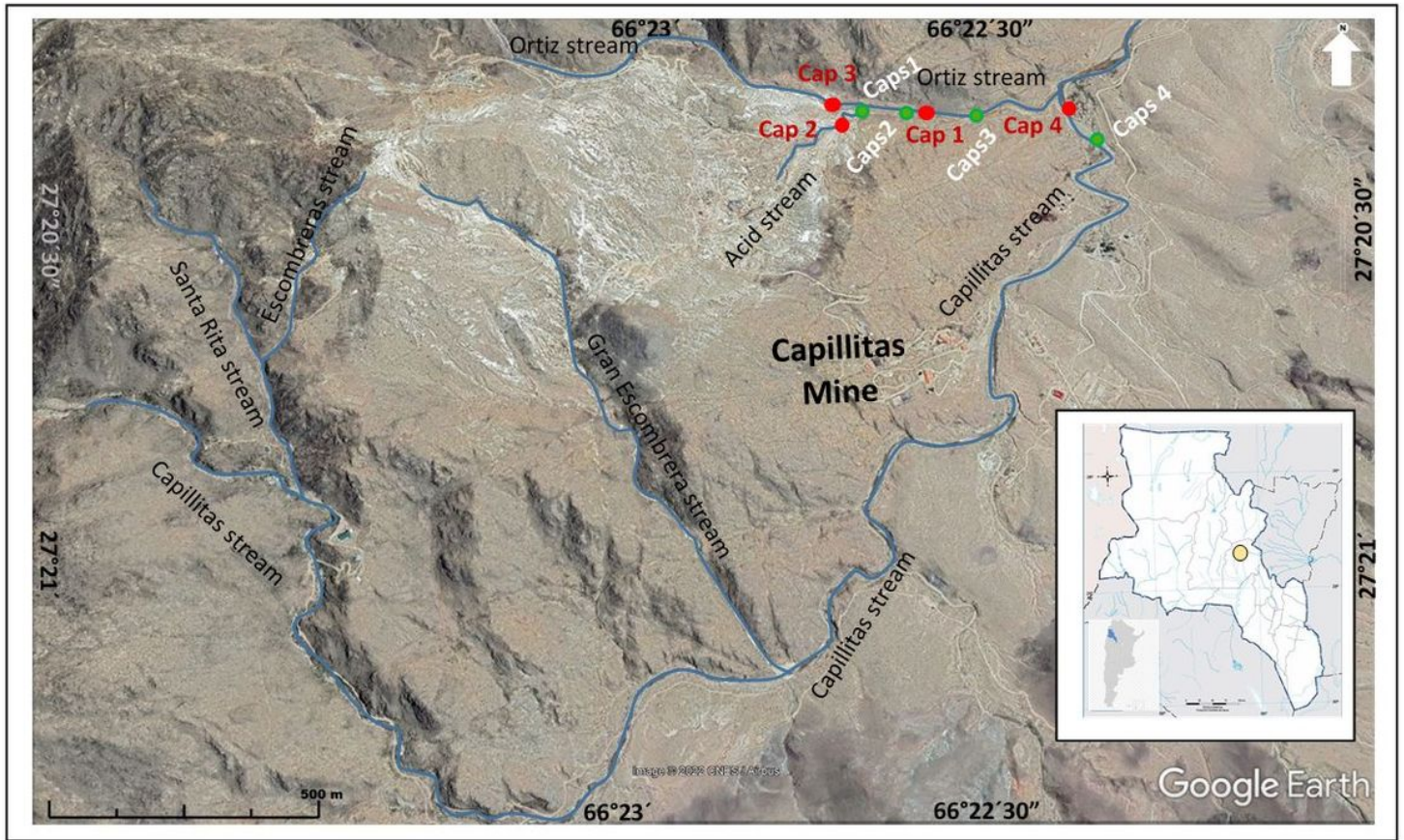


Figure 1

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



Figure 2

Field photographs of the study area. a. View of the Ortiz stream valley before 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 pound' into the Ortiz stream. e. View of the small pond containing a thin layer of turquoise-colored mineral precipitates in its bottom. The narrow discharge

channel situated in its E border could also be observed. f. View of the valley of the Capillitas stream before its confluence with the Ortíz stream.

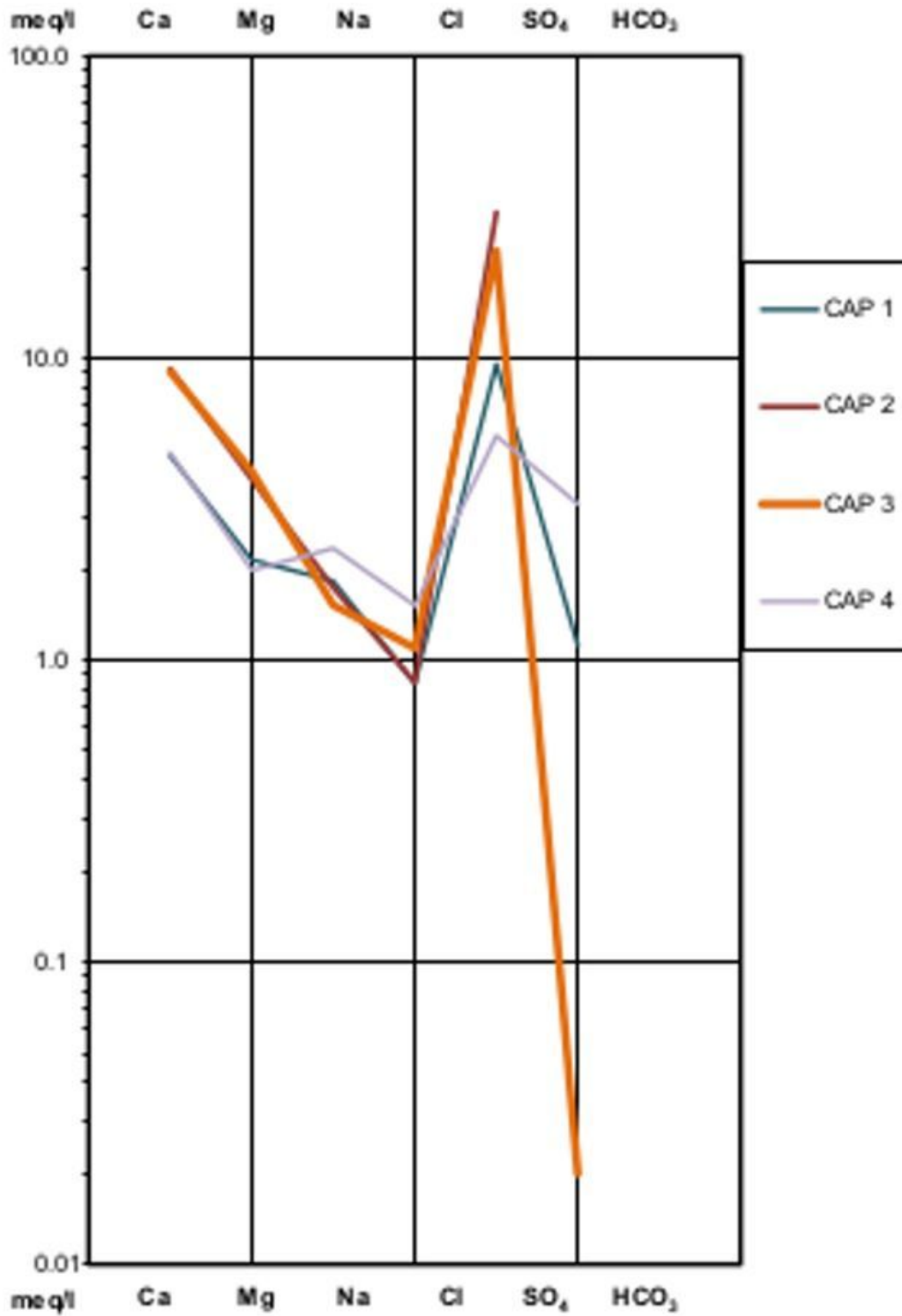


Figure 3

Schoeller-Berkaloff diagram of the analyzed waters.

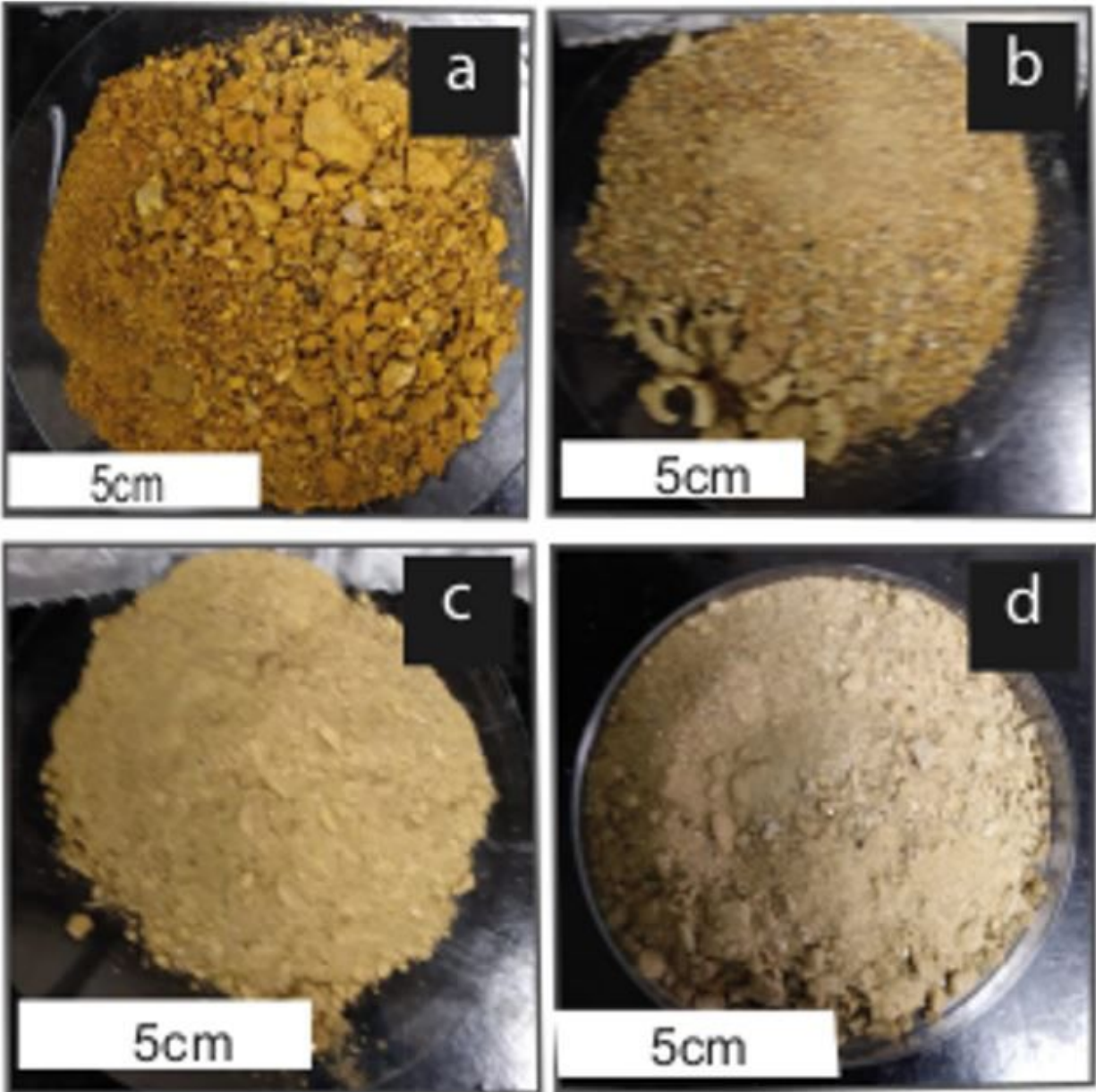


Figure 4

a. Orange-colored sediment of the Ortíz stream at the point of its confluence with the Acid stream (CAPSS1). B and C. Ochre-colored streambed sediments taken ~80 (CAPSS2) and 250 m (CAPSS3) downstream of CAPS1 in the Ortíz creek. D. Light brown-colored sediment of Capillitas stream (CAPSS4) before its confluence with the Ortíz stream.

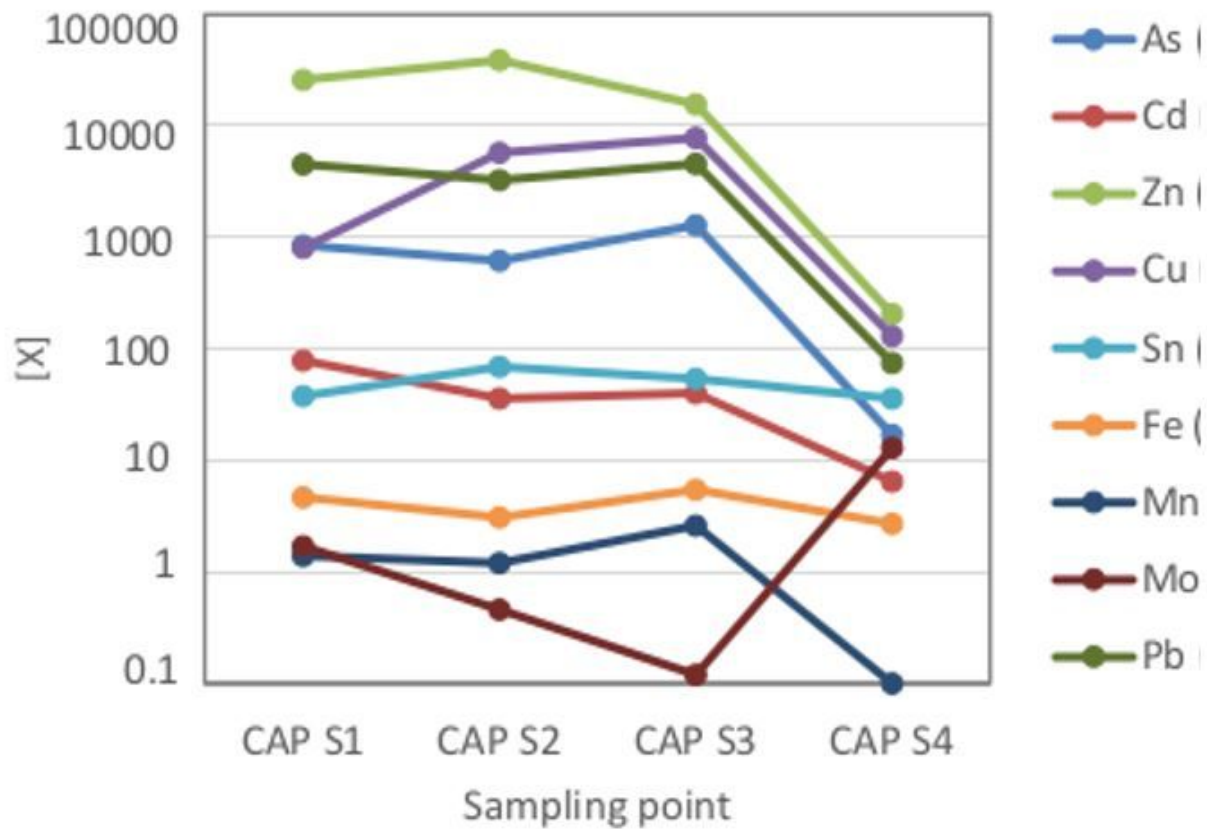


Figure 5

Concentration of some toxic metals and metalloids in the streambed sediments sampled along the Ortíz creek.

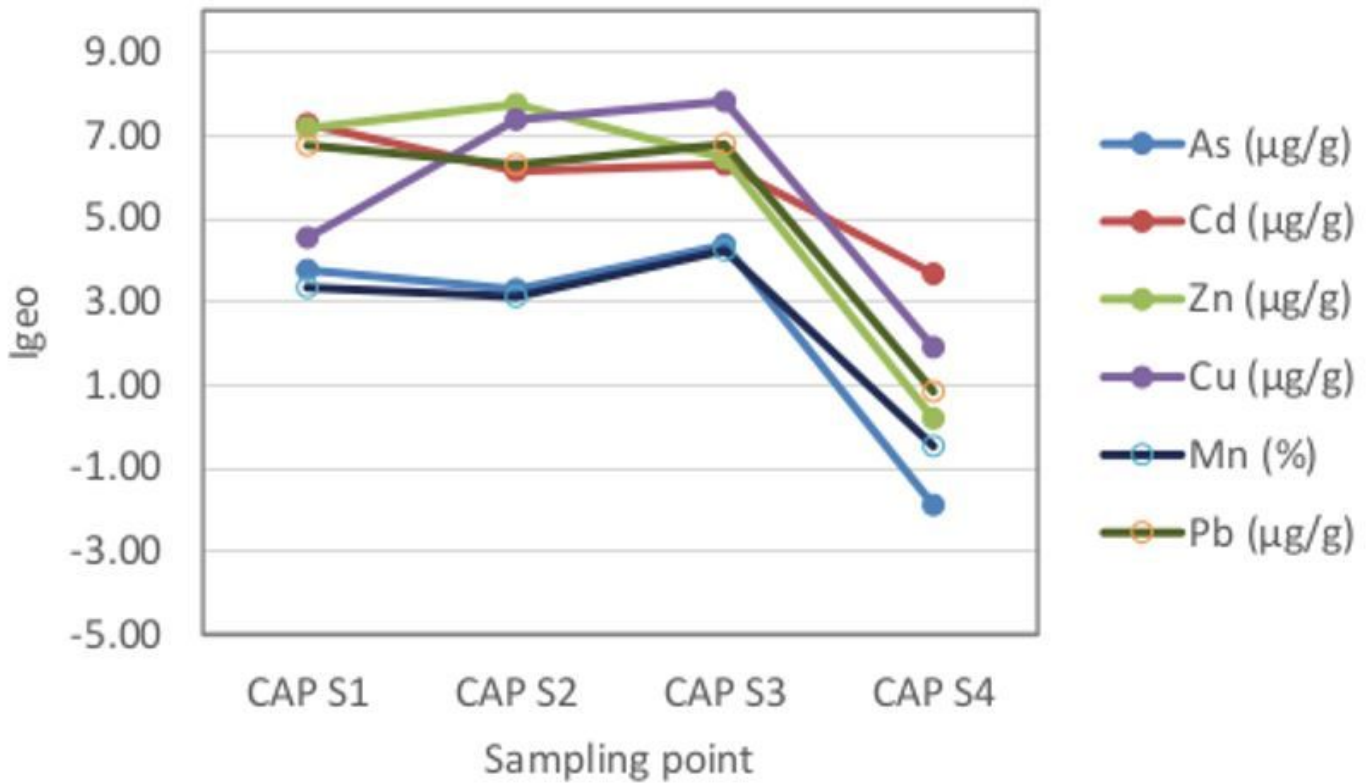


Figure 6

Variation of I_{geo} of streambed sediments of the Ortíz creek between sampling stations. The values of B_n employed in I_{geo} calculation were the average composition of As, Cd, Zn, Cu, Mn and Pb for unpolluted streambed sediments reported in geochemical chart of the region (Ferpozzi et al. 2003).