



# Geochemical processes controlling the distribution and concentration of metals in soils from a Patagonian (Argentina) salt marsh affected by mining residues



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## ABSTRACT

Heavy metal pollution that affects salt marshes is a major environmental concern due to its toxic nature, persistence, and potential risk to organisms and to human health. Mining waste deposits originated four decades ago, by the metallurgical extraction of heavy metals, are found near to the San Antonio salt marsh in Patagonia. The aim of the work was to determine the geochemical processes that control the distribution and concentration of Cu, Fe, Pb and Zn in the soils of this Patagonian salt marsh. A survey of the mining waste deposits was carried out where three dumps were identified. Samples were collected to determine soil texture, Eh pH, organic matter and metal contents and the soil mineralogical composition. The results shows that the soils developed over the mining waste deposits are predominantly reddish constituted mainly by iron oxide, hydroxide and highly soluble minerals such as Zn and Cu sulphates. The drainage from these deposits tends to move towards the salt marsh. Within the salt marsh, the highest concentrations of Cu, Pb and Zn occur in the sectors closest to the mining wastes deposits. The sulphide oxidation and the dissolution of the Cu, Pb and Zn sulphates could be the mainly source of these metals in the drainage water. The metals in solution that reach the salt marsh, are adsorbed by the organic matter and the fine fraction of the soils. These adsorbed metals are then remobilized by tides in the lower sectors of the marsh by desorption from the cations present in the tidal flow. On the other hand, Fe tends to form non soluble oxides, hydroxides and sulphates which remain as altering material within the mining waste deposit. Finally, the heavy metal pollutants recorded in the San Antonio salt marsh shows that the mining waste deposits that were abandoned four decades ago are still a source metal contamination.

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## 1. Introduction

Soils play an important role in the mobility of trace metals in coastal systems, acting occasionally as sink and/or source (Du Laing et al., 2009). The presence of metals in coastal and marine environments, caused both by natural processes and anthropogenic activities, is a major environmental concern worldwide due to its toxic nature, persistence, and potential risk to human health and to organisms (Rainbow et al., 2006). Several studies of metal accumulation rates in salt marshes, with different impact levels of human activities, have been carried out in different regions of the world (e.g., Lee and Cundy, 2001; Duarte et al., 2010; Suntornvongsagul et al., 2007; Hung and Chmura, 2007; Sundaramanickam et al., 2016).

Soil pollution associated with heavy metals from mining residues still being an important problem worldwide (Sheoran and Sheoran, 2006). Dumps and foundry slags of polymetallic rich-sulphide deposits are sources of acid drainage in which high concentrations of metals are mobilized (Nash, 2005). The metal load is of greater concern than the acidity in the terms of environmental damage (Kuyucak, 2002). An insidious feature of acid mine drainage (AMD) is that its sources may remain active for decades or even centuries after mine closure (Modis et al., 1998). Both operating and abandoned polymetallic sulphide mining sites are often active sources of metal.

Slags originated four decades ago, by the metallurgical extraction of heavy metals from an ore mainly composed by galena, sphalerite, pyrite and chalcopyrite, are found in deposits near to the San Antonio salt marsh in Patagonia (Fig. 1). The aim of the work was to determine the geochemical processes that control the distribution and concentration of Cu, Fe, Pb and Zn in soils of the above mentioned salt marsh.

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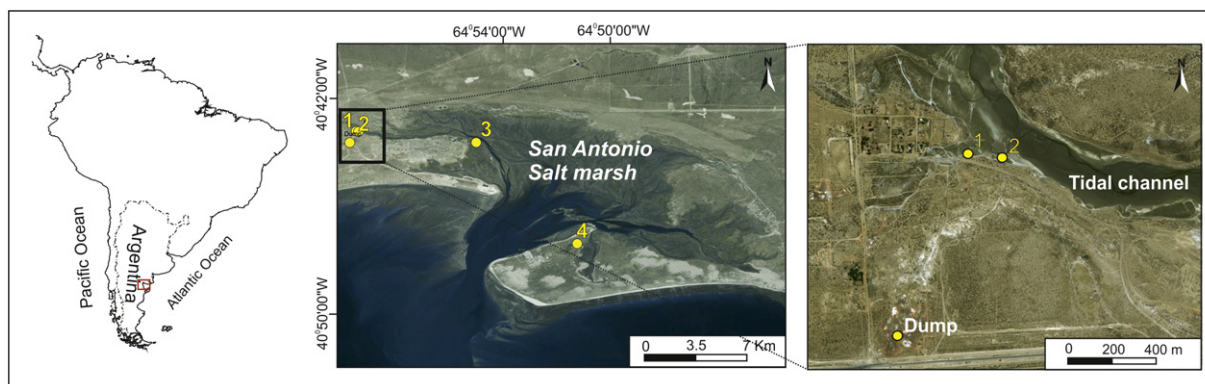


Fig. 1. Location map showing the study area and the sampling sites.

## 2. Materials and methods

### 2.1. Study area

The study was carried out in the salt marsh located surrounding the San Antonio Bay ( $40^{\circ}44'S$ ,  $54^{\circ}68'W$ ), in a Natural Protected Area (Río Negro, Argentina; Fig. 1). This is a strictly marine salt marsh with a semi-diurnal macro-tidal regime (tidal amplitude:  $\sim 9$  m) crossed by several tidal channels. The climate is semi-arid, the mean annual precipitation is around 250 mm, and the mean annual air temperature is  $15.1^{\circ}C$ , fluctuating between mean extremes of  $-7.7^{\circ}C$  in July to  $41.4^{\circ}C$  in February (Firstater et al., 2016). The mean annual wind speed is  $18\text{ km h}^{-1}$ , reaching an average of  $25\text{ km h}^{-1}$  in the hotter seasons (Firstater et al., 2016). The vegetation is characterized by *Spartina alterniflora* in the lower marsh zone, and the higher zones are commonly dominated by *Spartina densiflora*, accompanied by the shrubs *Limonium brasiliense*, *Sarcocornia perennis* and *Atriplex* spp. (Bortolus et al., 2009; Idaszkin et al., 2015). The outcropping geology that limits the marsh area, it is constituted by quaternary deposits. These deposits are mostly represented by beach ridges and coastal spits, composed by sands and gravels with mollusc shells. Overlaying them some aeolian landforms constituted by dunes and sandy layers are developed (Angulo et al., 1978).

### 2.2. Methodology

A survey of the mining waste deposits located in the vicinity of the San Antonio salt marsh was carried out, where samples were collected to measure pH in saturated soil-paste and to determinate the mineralogy. The mineralogical composition was determined by X-ray diffraction analysis (DRX) using a Phillips X'pert Pro. According to the surface runoff and the drainage from the waste dump deposits area recognized in the field, soil samples were extracted at four points within the marsh (Fig. 1). Site 1 is located in the higher topographic sector of the salt marsh that receives the surface runoff from the mining deposits drainage. Site 2 is located nearest the above site but in a topographically lower sector of the salt marsh. Site 3 is located in the same channel than sites 1 and 2, but in an external sector of the salt marsh with marked tidal influence. Finally, site 4 is located in the northern sector of the salt marsh where does not receive drainage from mining deposits, with tidal characteristics similar to site 3.

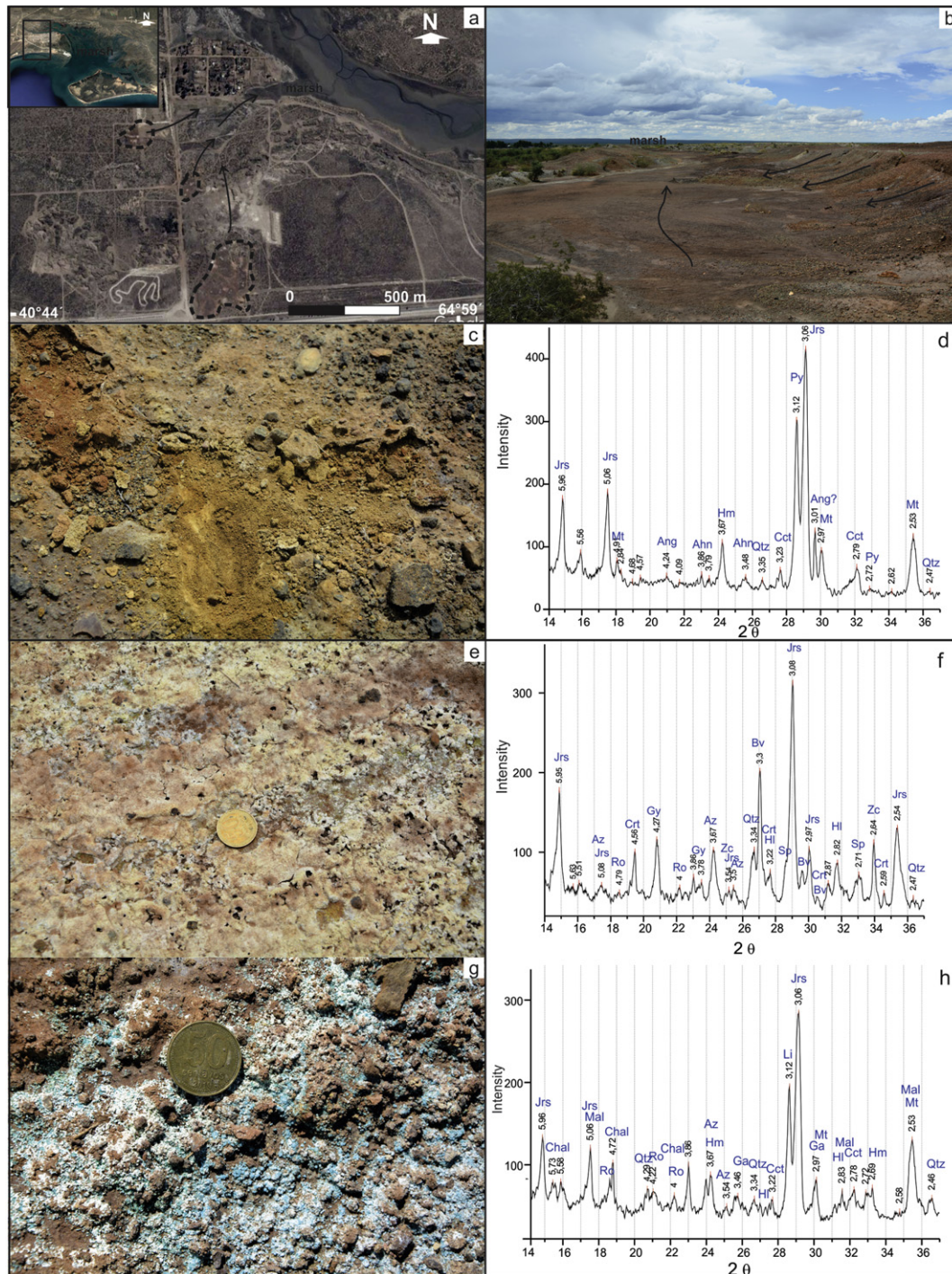
At each site ten soil samples from the upper 15 cm were collected, always at low tide. The redox potential (Eh) and pH of the soil samples were determined in the field using a portable pH/Eh (ORP) meter and an electrode system Termo/pH meter Altronix TPA-IV. Samples were stored in polyethylene bags, transported to the laboratory, and frozen to  $-20^{\circ}C$  until analyzed. The soil samples were dried at  $80^{\circ}C$  until constant weight and sieved through a 2 mm mesh to remove large stones and dead plant material. Electrical conductivity (EC) was measured

with a conductivity meter after diluting 10 g of dried and sieved soil with 50 ml of distilled water. Organic matter (OM) was determined by the loss on ignition method (4 h at  $450^{\circ}C$ ) (Davies, 1974). Percentage of sand, silt, and clay were estimated using the Pipette method (Day, 1965). For the analysis of metals, 1 g of dried and sieved soil was digested in 2 ml of  $HNO_3$  (Merck) ultrapure using microwave oven MARS-5, CEM Corporation, USA (2011) and was then diluted to a final volume of 15 ml with nitric acid (EPA, 2000). Copper (Cu), iron (Fe), lead (Pb), and zinc (Zn), in both matrixes were then measured by inductively coupled plasma (ICP-AES) spectroscopy (Shimadzu 9000). In all cases, the average uncertainty of metal ion determination was  $<2\%$ . All extractions were carried out in duplicate and blanks were processed as the samples. Results were reported on a dry weight. Reagents of analytical grade were used for the blanks and for calibration curves. Quality assurance of soils was done through analysis of standard reference freshwater sediment CNS392-050. The recovery was 87% for Zn, 89% for Pb, 90% for Cu, and 98% for Fe. Also in these soil sample mineralogical composition was determined by X-ray (DRX) diffraction analysis using a Phillips X'pert Pro were determined.

## 3. Results

Three mining waste deposits were identified, which showed abundant erosion and drainage features identified mainly in the higher sectors where the gully development dominates (Fig. 2a and b). The drainage from these three deposits tends to move towards the salt marsh. Although locally the surface runoff also accumulates in the lower sectors within these areas. The soils developed over the mining waste deposits are predominantly reddish (Fig. 2b), with acid pH values between 4.0 and 5.7. The DRX mineralogical determinations showed that soils are composed mainly by iron oxides and hydroxides such as hematite (Hm), magnetite (Mt) and iron sulphates of jarosite (Jrs) type. Superficially, the formation of yellowish to whitish crusts, consisting of gypsum (Gy), carminite (Crt), roemerite (Ro), anglesite (Ang), beaverite (Bv), zincosite (Zc), halite (HI) (Fig. 2 e and f) was observed. Locally, blue to greenish aggregates composed of malachite (Mal), chalcantite (Chal), azurite (Az) and linarite (Li) (Fig. 2 g and h) were also observed. Within the residues some ore minerals such as pyrite (Py), sphalerite (Sph), chalcocite (Chlc) and quartz (Qtz) were identified. On the other hand, salt marsh soils are composed mainly by quartz (Qtz), plagioclase (Pl), feldspar (F and KF), dolomite (Dol) and calcite (Cal) (Fig. 3). Within sites 1 and 2 the presence of gypsum (Gy), hematite (Hm) and halite (HI) were identified, being this last one more abundant in site 1 (Fig. 3).

Table 1 resume texture, Eh, pH, EC, OM, and metals content in the soils samples from the four salt marsh sampled sites. In site 1, which is located in the topographically higher part of the salt marsh, nearest to the mining waste deposits, the soil is dominated by fine textures,



**Fig. 2.** (a) Location of mining waste deposits, (b) photograph indicating, with arrows, the development of gullies and drainage to the salt marsh area; (c, d) photograph and X-ray diffractograms of sulphates and iron oxides, (e, f) photograph and X-ray diffractograms of iron and zinc sulphates, (g, h) photograph and X-ray diffractograms of copper, lead and zinc sulphates.

with OM content rounding the 6%, slightly basic pH (between 7.5 and 7.6) and values of EC varied from 5.8 to 13.4 mmhos  $\text{cm}^{-1}$ . Regarding the mean metal contents in soils from this site, they were of 38.8  $\mu\text{g g}^{-1}$  for Cu, 14,385  $\mu\text{g g}^{-1}$  for Fe, 65.1  $\mu\text{g g}^{-1}$  for Pb, and 222  $\mu\text{g g}^{-1}$  for Zn.

In site 2, located near to site 1, but in a topographically lower sector of the salt marsh, both texture and pH were similar to site 1, but OM and EC of some samples showed a slight decrease. Likewise, soil metals also showed a decrease, being the mean metal contents in

soils of site 2 12.2  $\mu\text{g g}^{-1}$  for Cu, 12,283  $\mu\text{g g}^{-1}$  for Fe, 14.2  $\mu\text{g g}^{-1}$  for Pb and 55.7  $\mu\text{g g}^{-1}$  for Zn.

In site 3, located in the external sector of the salt marsh and far of the mining waste deposits, soils were predominantly sandy, with sand percentages above 65%. In this site, a decrease in OM content (with values generally below 3%) and EC (with values between 3.6 and 4.3 mmhos  $\text{cm}^{-1}$ ) were recorded. The content of Cu ( $<7 \mu\text{g g}^{-1}$ ), Pb ( $<9 \mu\text{g g}^{-1}$ ) and Zn ( $<22 \mu\text{g g}^{-1}$ ) also decreases, while the Fe content was in some cases higher than in soils from sites 1 and 2.

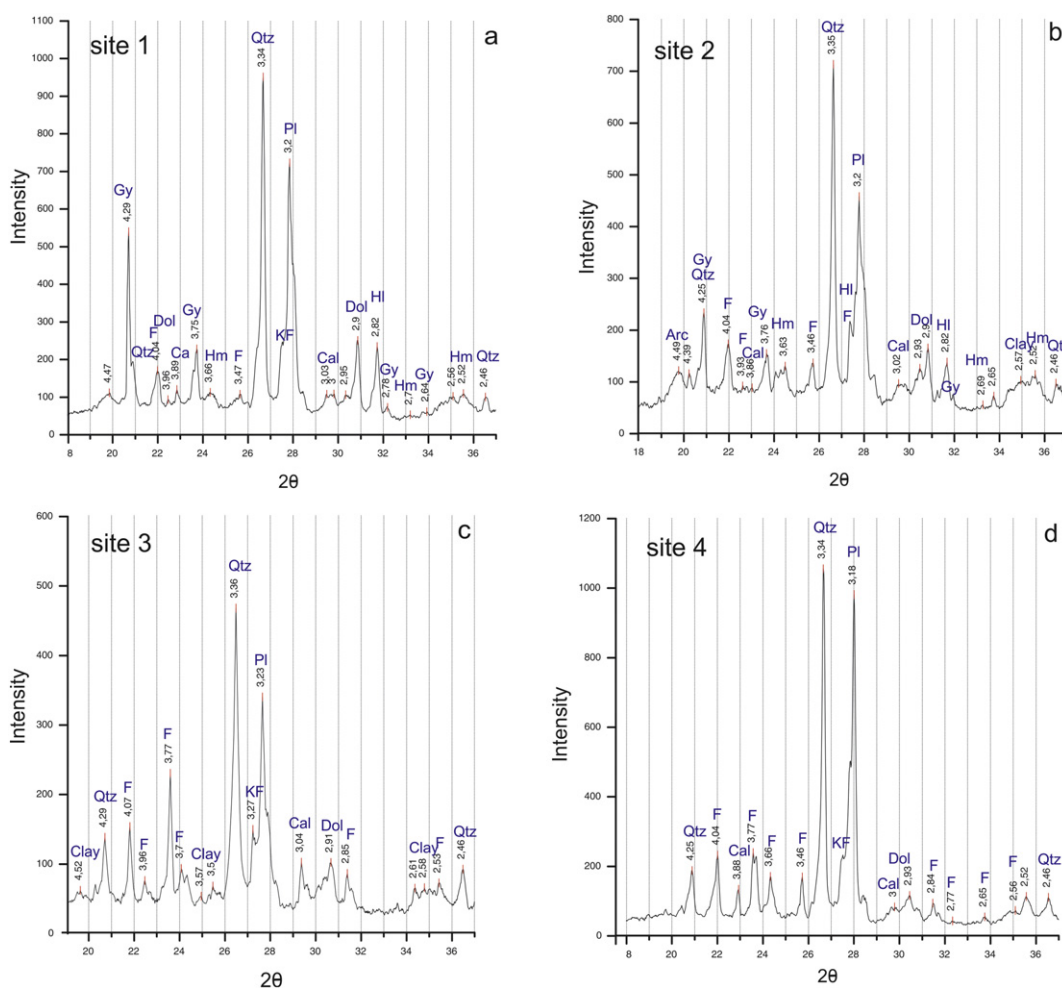


Fig. 3. X-Ray diffractograms of representative samples of each sampling site in the salt marsh sector.

Analyzing the data together for these three sites a decrease from site 1 to site 3 was observed for the fine fraction, OM and EC, as well as for Cu, Pb and Zn content. On the other hand, at site 4, textural features as such as pH, OM and metal contents were similar to site 3. Regarding Eh, all recorded values indicated oxidant conditions in the sampled soils (Table 1).

When the relation among the metals was analyzed using bivariate graphs, a linear relation between the increase in the Cu, Pb and Zn concentrations were observed for the four sampled sites (Fig. 4). However,

for Fe, this linear trend is only recorded with the metals previously mentioned at site 1.

#### 4. Discussion

The obtained results show that the mining waste deposits that were abandoned four decades ago still being a source metal contamination. Although mean annual precipitation in the region is 250 mm (Firstater et al., 2016), the exposure of these residues to the atmospheric

Table 1  
Soil parameters in the San Antonio salt marsh (n = 10).

Soil parameters	Site 1		Site 2		Site 3		Site 4	
	Mean ± S.E.	(min – max)	Mean ± S.E.	(min – max)	Mean ± S.E.	(min – max)	Mean ± S.E.	(min – max)
EC (mmhos cm <sup>-1</sup> )	(8.5 ± 0.7)	(5.8 ± 13.4)	(6.9 ± 0.3)	(5.3 ± 8)	(3.9 ± 0.1)	(3.6 ± 4.3)	(3.5 ± 0.3)	(2.4 ± 4.6)
Eh (mV)	(141.2 ± 4.8)	(122 ± 165)	(154.7 ± 9.3)	(119 ± 187)	(157.1 ± 6.3)	(116 ± 180)	(177.7 ± 9)	(148 ± 225)
pH	(7.6 ± 0)	(7.5 ± 7.8)	(7.6 ± 0)	(7.5 ± 7.9)	(7.6 ± 0)	(7.4 ± 7.7)	(7.7 ± 0)	(7.5 ± 7.9)
OM (%)	(6.2 ± 0.2)	(5.2 ± 7.3)	(5.2 ± 0.4)	(3.9 ± 7.3)	(3 ± 0.1)	(2.7 ± 3.4)	(2.5 ± 0.2)	(1.6 ± 3.3)
Clay (%)	(20.7 ± 2.7)	(11.9 ± 34.4)	(17.2 ± 1.4)	(12.2 ± 24.2)	(3.9 ± 0.3)	(2.5 ± 5.3)	(5.6 ± 0.5)	(3.1 ± 7.5)
Silt (%)	(53.8 ± 3.5)	(35.1 ± 69.4)	(51.6 ± 3.4)	(40.1 ± 68.4)	(28.8 ± 0.8)	(22 ± 33.5)	(25 ± 1.9)	(14 ± 32)
Fine silt (%)	(26.1 ± 2.4)	(14.7 ± 36.8)	(28.6 ± 2.8)	(15.9 ± 41.1)	(13.9 ± 0.9)	(10.4 ± 20.7)	(10 ± 1.3)	(3.9 ± 16.8)
Coarse silt (%)	(27.7 ± 1.3)	(19.6 ± 34.0)	(23.1 ± 1.0)	(16.4 ± 27.2)	(14.9 ± 0.6)	(11.9 ± 18.3)	(15 ± 1.1)	(10.1 ± 20.6)
Fine fraction (%)	(74.6 ± 3)	(50.8 ± 82.4)	(68.9 ± 4.2)	(53.6 ± 85.7)	(32.5 ± 6.3)	(29.1 ± 37.2)	(30.6 ± 2)	(18.5 ± 38.1)
Sand (%)	(25.4 ± 3)	(17.6 ± 49.1)	(31.1 ± 4.2)	(14.3 ± 46.4)	(67.3 ± 0.8)	(62.8 ± 70.9)	(69.4 ± 2)	(61.9 ± 81.4)
Cu (µg g <sup>-1</sup> )	(38.8 ± 2)	(26.1 ± 51.3)	(12.2 ± 1.2)	(8.1 ± 17.8)	(5.3 ± 0.2)	(4.4 ± 6.1)	(5.6 ± 0.7)	(3 ± 7.8)
Fe (µg g <sup>-1</sup> )	(14,385 ± 360)	(12,750 ± 16,138)	(12,282 ± 580)	(10,060 ± 14,860)	(13,493 ± 345)	(11,364 ± 14,938)	(14,174 ± 1102)	(10,023 ± 18,132)
Pb (µg g <sup>-1</sup> )	(65.1 ± 3.8)	(49.2 ± 86.7)	(14.2 ± 1.5)	(8.1 ± 19.8)	(7.9 ± 0.2)	(6.8 ± 8.8)	(4.7 ± 0.7)	(2.2 ± 7.1)
Zn (µg g <sup>-1</sup> )	(222 ± 11.9)	(135 ± 287)	(55.7 ± 6.7)	(29 ± 83)	(18.4 ± 0.6)	(15.3 ± 21.4)	(18.9 ± 0.8)	(16 ± 21.7)

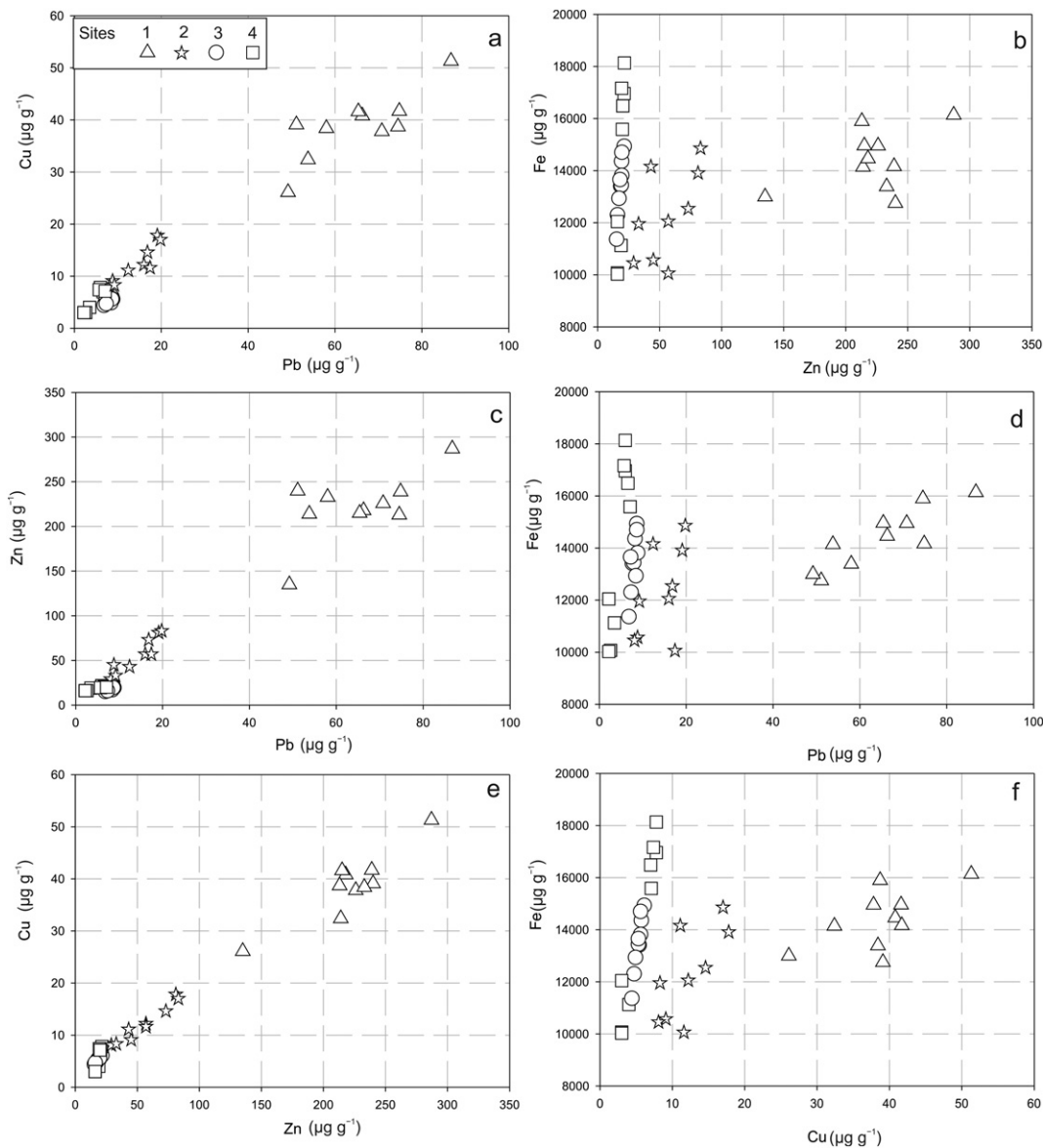


Fig. 4. Bivariate graph showing the relationship among the metals.

conditions for more than four decades allowed to occur a strong alteration. This is in agreement with the high content of the Fe hydr(oxides) and sulphate minerals that constitute the deposits, where only a little amount of slag scraps without alteration are recognized. Furthermore, the arid climate characterized by high evaporation rates allows the formation of highly soluble minerals such as Cu and Zn sulphates (chalcantite:  $\text{CuSO}_4 \cdot 5(\text{H}_2\text{O})$  and zincocite:  $\text{ZnSO}_4$  respectively). These sulphates are observed mainly as crusts above the surfaces of the mining waste deposit and some ones are the result of evaporation of the drainage water that is accumulated in the endorheic areas within this deposit (Fig. 2).

During rain events and favoured by the increasing of the pH, the heavy metals of these minerals are mobilized by the drainage towards the salt marsh in their soluble form or as a particulate material. Two main processes are the responsible of the soluble forms generation: the oxidation of sulphides and the dissolution of high solubility minerals. The oxidation of sulphides such as pyrite (SFe) and calcopirite ( $\text{CuFeS}_2$ ) lead to the formation of sulphate ions and metals in their soluble forms. In the other hand the dissolution of Cu, Pb and Zn sulphates such as chalcantite ( $\text{CuSO}_4 \cdot 5(\text{H}_2\text{O})$ ), anglesite ( $\text{PbSO}_4$ ) and zincocite ( $\text{ZnSO}_4$ ) are also a source of these metals to the drainage water. This is

supported by the lineal relationship observed between Cu vs. Pb, Pb vs. Zn and Zn vs. Cu (Fig. 4 a, c and e) that could indicate that these three metals are related with the lixiviation from a common source. When the drainage water flows the salt marsh the metals in solution are adsorbed by the organic matter and the fine fraction of the soils (Muller, 1988). These determine that the main Cu, Zn, and Pb concentrations occur in the samples with higher clay and organic matter percentages (Table 1). On the other hand, it should be noted that the higher concentrations of Cu, Zn, and Pb occur in the soils with higher salinities (Table 1, sites 1 and 2). This high salinity could be related to the contribution of sulphate ions from the drainage water from the mining residues which also lead, by evaporation, to the formation of gypsum crust. However, the presence of halite precipitated together (Fig. 3) with gypsum in sites 1 and 2 soils indicate that the high salinity is also due to the sea water evaporation. This evaporation of the tidal flow take place in the most marginal and elevated sectors of the salt marsh (sites 1 and 2) due to the shorter flood period (Carol and Alvarez, 2016). Even though groundwater was not analyzed in this study, it should be considered that some of the soluble forms can reach the water table by infiltration (Kumpiene et al., 2008) and then flow towards the salt marsh.

Regarding to the metals distribution within the salt marsh, it should be noted that in site 2, which is close to site 1 but in a topographically lower sector of the salt marsh, the concentrations of Cu, Pb and Zn were considerably lower than in site 1 (Table 1). This could be related with the fact that in site 2 may be smaller adsorption sites or that some process is taking place that remobilises the adsorbed metals. Given that the OM and fine fraction contents within both sites are similar (Table 1), then the absorptions sites should be equal too. This rules out the hypothesis that the variations in the metal contents among the different sites could be exclusively defined by the OM and fine fraction percentages. Therefore a process of desorption it should be occurring preferentially in the topographically lower sectors of the salt marsh. In this sense, the tidal flow, that is more frequent in site 2 due to the fact of their minor height, could be the causal process. The tidal flow with high ionic strength favours the metal desorption because the seawater major cations (Na, K, Mg and Ca) compete with metals for the adsorption sites (Tam and Wong, 1999) due to fact that they are in greater concentration, displacing them. In this way the metals goes into solution again and are remobilized with the tides (Teuchies et al., 2008; Du Laing et al., 2009).

This desorption and removal of metals in solution by the tidal flow could also explain the fact that in site 3, located in a sector of the salt marsh with greatest tidal influence, Cu, Pb and Zn occur in low concentrations and similar to those of site 4, where there are no contributions from the mining residues. Also, it is important to consider that the soils from sites 3 and 4 are predominantly sandy and that this decrease in the fine fraction and organic matter contents lead to a smaller existence of adsorption sites to retain the metals.

On the other hand, Fe shows a different behavior, which tends to form insoluble compounds by hydrolysis and/or oxidation, leading to the development of a great variety of oxides, oxyhydroxides, hydroxides and sulphates (Woulds and Ngwenya, 2004). These could explain the abundance of these types of minerals in the mining residues such as hematite, magnetite and jarosite. However, Fe may be mobilized as particulate material or suspended colloids in the drainage water, which would explain the presence of hematite at sites 1 and 2 of the marsh (Fig. 3a and b). Nevertheless, there are no variations in Fe concentrations among the different sites of the studied salt marsh. This could be due to the fact that this metal is naturally abundant in the salt marsh soils and therefore the influence from the mining waste deposits is low.

## 5. Conclusion

The heavy metal pollutants recorded in the San Antonio salt marsh (Patagonia, Argentina) shows that the mining waste deposits and smelting slags are sources of heavy metal pollution that may be active for almost half a century. Control of acid drainage of these deposits is a measure of utmost importance to minimize the overall impact in the surrounding environments.

Among the alteration minerals formed in the deposits, Cu, Pb and Zn sulphates are the most polluting because they enter in solution and they are easily mobilized with the drainage during the rains due to their high solubility. On the other hand, Fe tends to form non soluble oxides, hydroxides and sulphates which remain as altering material within the mining waste deposit.

Within the salt marsh, the highest concentrations of Cu, Pb and Zn occur in the sectors closest to the mining wastes deposits, being the adsorption in the organic matter and fine fraction the principal process of retention of the metals in the soil. These adsorbed metals are remobilized by tides in the lower sectors of the salt marsh by desorption from the cations present in the tidal flow. Therefore, the topographically higher sectors of the salt marsh are the most affected and where the metals tend to be accumulated for long periods.

Heavy metal pollution is a problem that affects many salt marshes worldwide. The obtained results helps to understand the geochemical processes that control the distribution and concentration of metals in

salt marshes affected by mining wastes. These results are not only useful for the study area but also for other salt marshes in the world where this type of pollution sources act. The understanding of the geochemical processes has a vital importance for the development of environmental management guidelines and the implementation of mitigation measures for these environments.

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