

Monitoring of chemical elements in soils, waters and plants near the active mine tailing dam in the central zone, Chile

Y Tapia (✉ yasnatapiafernandez@uchile.cl)

Universidad de Chile

A Joven

Universidad de Chile

O Salazar

Universidad de Chile

M Casanova

Universidad de Chile

F Najera

Universidad de Chile

C Kremer

Universidad de Chile

B Castillo

Universidad de Chile

O Diaz

Universidad de Santiago de Chile

Ruben Pastene

Universidad de Santiago de Chile

Edouard Acuña

Pontificia Universidad Católica de Chile

Monica Antilen

Pontificia Universidad Católica de Chile

P Comejo

Universidad de La Frontera, CIMYSA

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Abstract

Chile, the world's largest copper producer, generates massive amounts of mine tailings that are a source of ongoing environmental concern for local communities. The main objective of this work is to evaluate the concentration of elements: As, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Zn and SO_4^{2-} in soils, water, and vegetation in the communities surrounding a mine tailings dam in central Chile. Soils, waters and plants samples were collected from the towns of Chacabuco, Huechún, Huertos Familiares, Punta Peuco and Santa Matilde, which are located at 3 to 8 km from the Ovejería mine tailings site, operated by CODELCO in operation since 1999. The results showed that the levels of metals/metalloids and SO_4^{2-} in water (pH 6.69–7.95) met both WHO limits and Chilean water quality standards for miscellaneous uses. In soil (pH 7.67–8.39), total and available concentrations of metals/metalloids did not exceed common international reference values. Plants with acceptable levels of metals and S were *Citrus limon*, *Eucalyptus*, *Schinus molle*, *Prunus persica*, *Medicago sativa*, *Citrus sinensis*, and *Ficus carica*. The only species with a content of one metal (Fe) well above the reference value and high concentrations of other metals (Cu, Mn, Mo, and Pb) was *Acacia caven*. The concentrations of chemical elements determined between 2015–2018, in soils, water and plants in different locations near the active copper tailings dam Ovejería, in Central Chile, allow us to conclude that in general the levels are comparable to national and international references and do not indicate contamination.

1. Introduction

Chile is the world's top producer of copper, churning out about 5.6 million tons per year (U.S. Geological Survey, 2020). This massive production generates an enormous amount of mine tailings, estimated at 30 tons per ton of copper mined. There are approximately 757 tailings storage sites in the country (SERNAGEOMIN, 2021), located mainly in arid and semi-arid regions and spread over large areas of land. Acidification of mine tailings by pyrite oxidation (FeS_2) increases metal mobility, and values of pH 3.5–4.5 have already been reported in deactivated mine tailings in Piuquenes, central Chile (Dold and Fontobé, 2001). Chalcopyrite (CuFeS_2) is one of the main source minerals of Cu in Chile (Alloway, 2010; Dold and Fontboté, 2001), and consequently, high concentrations of Cu, Fe and SO_4^{2-} are to be expected in mine tailings.

Mine tailings deposits significantly impact landscape aesthetics and are a source of metals, metalloids and sulphates (SO_4^{2-}) that can enrich and/or contaminate the air, water, soils and plants. There is concern in the scientific community regarding methods to assess the risk of exposure to mine tailings in different environmental, social and economic settings (Werner et al., 2019). However, elements or compounds released from mining wastes may be of low availability, and even when elements are bioavailable, they are not necessarily taken up by plants and animals, and in cases where uptake of elements does occur, such uptake does not necessarily lead to toxicity (Lottermoser, 2010). The dispersion of chemical elements in soluble or particulate form to soils, water, and vegetation from tailings depends mainly on climatic factors (Meza-Figueroa et al., 2009). In semiarid areas, the transport of chemical elements from tailings to groundwater does not seem to be significant; however, there is transport by surface runoff and winds in these areas that can favour transport (Meza-Figueroa et al., 2009). The possible inhalation or ingestion of airborne particulate matter from tailings is dependent on the season of the year and wind erosion, which determine the associated risk levels (Meza-Figueroa et al., 2009).

Plants growing in mining soils have been used as indicators of metal bioavailability and to assess the transfer of metals in the food chain (Qin et al., 2021). In the mining locality of Valle de Alcudia (Spain) in the species *Quercus ilex*, the levels of Pb and Zn metals exceeded toxicity levels determined to be safe in plants (Higuera et al., 2017). In the Morila Gold mine (Mali), As levels in plants are two hundred times higher than those in the soil background (Bokar et al., 2020). However, in plants, metal/metalloid uptake is a complex process because it depends on several factors (Higuera et al., 2017) mainly related to soil chemistry (organic matter) and climate; therefore, the assessment is specific to each plant and geographical area and dependent on mining activity. Other studies point out that it is the species assemblage, and not soil properties, that determines the element content in plant tissues (Gagnon et al., 2020).

The communities of people living in mine tailings areas have expressed consistent concern regarding soil and water contamination. The active mine tailings Ovejería (CODELCO Company) in the central zone of Chile (Chacabuco Province) cover vast areas of land (850 ha) affecting the aesthetics of the landscape. Recently a study has been published in the area (Chacabuco Province) where it is reported that the water consumed by the population appears to be free of metal contamination, according to WHO guidelines, however, there is no known scientific data on the geochemical background of the area (Le Goff et al., 2022) and there are no published studies of mining influence related to levels of metals (loids) and sulphur in soils and plants. Therefore, it is necessary to monitor the concentration of chemical elements that can serve as background levels for future results in soils, water and plants around Ovejería mine tailings. In this study background definition is the concentration of an element or a substance characteristic of a soil type in an area or region arising from both natural sources and anthropogenic diffuse sources such as atmospheric deposition (ISO 19258, 2018).

The objectives of this work are 1) to determinate the concentration of metals (loids) and S, in soils, water and plants in towns near the active mine tailings of the Ovejería dam located in the central zone of Chile 2) Relate the concentrations of metals (loides) and S in soil and water to the proximity of the Ovejería tailings dam.

2. Materials And Methods

2.1 Study area. Analysis of mine tailings and tailings waters

The study area includes the towns of Chacabuco (CH), Huechún (HU), Huertos Familiares (HF), Punta Peuco (PP) and Santa Matilde (SM), which are located between 3-8 km the active mine tailings Ovejería (CODELCO Company) and Las Tórtolas (Anglo American Sur S. A Company), a copper mining operation, in the central zone of Chile (Fig. 1). The communities are mostly rural, and their population is engaged in mining, agricultural and commerce activities. The populations of CH, HU, HF, PP and SM are 472, 239, 4186, 165 and 822 inhabitants, respectively (INE, 2019). Currently, the Ovejería tailings dam (19 H 332190 m E; 6341395 m S; 580 m.a.s.l) covers an area of 850 ha and stores approximately 453,000,000 tons of mine tailings with a mine water volume of 7,500,000

m³ (Fig. 2). Ovejería dam operations began in 1999 and are projected to continue until 2054 with an estimated total tailing of 1,930,000,000 tons and a surface area of 1900 ha (Mining Council, 2021). Mine tailings are transported 85 km by surface and underground canals from the South-South and Rio Blanco mines to be deposited in the Ovejería dam. The copper extraction process is by flotation. The tailings dam is deposited on soil (Mollisols) of the Rungue series classification, which is formed at the base of the hills as a piedmont of colluvial origin. This soil is very clayey and with a significant carbonate content at a depth of one metre (CIREN, 1996). The area has a semiarid climate, an altitude of 630 masl, and the average annual climatic conditions are characterised by a minimum temperature of 6.7 °C, a maximum temperature of 25 °C, a relative humidity of 68.8% and precipitation of 218 mm (Tapia et al., 2020). The average wind speed is 1.91 m s⁻¹ (range of 0.06-14.4 m s⁻¹) and the predominant direction is NW. The Chacabuco and Quilapilún estuaries are located in the area of influence of the active mine tailings Ovejería (García, 2007). Important rivers are the Aconcagua, Rio Blanco and El Juncal (Fierro et al., 2020).

Mine tailings samples were collected from the wall in 2018 for chemical characterisation in quadruplicate. In the tailings, the pH in aqueous suspension (1:2.5, W/V) and electrical conductivity (EC) in a saturated extract were determined using Hanna HI 3222 and 4321 equipment (Woonsocket, Rhode Island, USA), respectively. The sulphate concentration was determined in the saturated extract and by colorimetric determination with BaCrO₄ (Dewis and Freitas, 1970), and the available S was determined by extraction with 0.01 M Ca(H₂PO₄)₂ and turbidimetry using a Hatch DR500 spectrophotometer (Loveland, Colorado, USA) (Sing et al., 1995). For the determination of the total concentration of the chemical elements As, Cd, Cr, Fe, Mn, Mo, Ni, Pb and Zn, the samples of mine tailings were digested with HF-HClO₄-HCl-HNO₃ (Dold and Fontboté, 2001), and metal levels were determined by atomic absorption spectrophotometry (AAS) of PerkinElmer (Boston, Massachusetts, USA) and As by flow-injection hydride generation atomic absorption spectrophotometry (FIHG-AAS) using a Perkin Elmer FIAS 100. The Hg was determined by atomic fluorescence. The distribution of Cu, Fe, Mn and Zn (%) in fractions in mine tailings: FI, water soluble; FII, exchangeable; FIII, Fe(III) oxyhydroxides; FIV, Fe(III) oxides; FV, organics and secondary Cu sulfides; FVI, primary sulfides; FVII, residual fractions were performed according Dold and Fontboté (2001). The chemical characteristics of the tailings water (Table 1) are in the public registry National Information System of National Control Information (<https://snifa.sma.gob.cl/SeguimientoAmbiental>).

2.2 Drinking, irrigation and estuary water analysis

A total of 27 water samples from different uses, including drinking, irrigation and estuary waters (Table 2), were collected from places where the inhabitants indicated. Water for agricultural irrigation is water obtained from groundwater and water from estuaries is natural water from canals. The samples were obtained from CH: 3 samples, HU: 7 samples, HF: 6 samples, PP: 6 samples and SM: 5 samples. The criterion for the number of agreements was according to the according to the interest and possibilities of the inhabitants of each locality. The samples were analysed in triplicate at the Soil and Water Chemistry Laboratory of the Faculty of Agricultural Sciences of the University of Chile. pH and EC were determined directly in the samples using a pH metre and conductivity metre Hanna (Woonsocket, Rhode Island, USA) model HI 3222 and 4321 equipment, respectively. To determine the total metals, the water samples were digested in HNO₃ on Thermolyne® Cimarec® hot plates (Darmstadt, Germany) model HP131530-33. The measurement of As was quantified by FIHG-AAS and Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn by AAS. Colorimetry was used for the determination of SO₄²⁻ with BaCrO₄ (Dewis and Freitas, 1970) by a Hatch DR500 spectrophotometer (Loveland, Colorado, USA).

2.3 Soil analysis

A total of 12 soil samples of different uses, rural and agricultural, were collected from locations indicated by the inhabitants of the localities CH: 1 sample; HU: 5 samples; HF: 2 samples; PP 2 samples and SM: 2 samples (Table 3) according to the interest and possibilities of the inhabitants of each locality. The soils were collected at a depth of 0-20 cm. For all analyses, 3 replicates were performed. Samples were air-dried and sieved at 2 mm. The pH was determined in a 1:5 (w/v) aqueous suspension. The EC was determined in saturated paste. Organic matter was determined by calcination at 360 °C for 16 h (Sadzawka et al., 2006). Available N was determined using KCl extraction followed by NH₄ distillation and titration (Mulvaney, 1996). The available P was extracted with sodium hydrogen carbonate (0.5 M, pH 8.5) by the Olsen method (Kuo, 1996). The available K was extracted with ammonium acetate and determined by AAS. The available S was determined by extraction with 0.01 M Ca(H₂PO₄)₂ and turbidimetry (Sing et al., 1995). For the determination of total concentrations of As, Cd, Cr, Fe, Mn, Mo, Ni, Pb and Zn, the soil samples were digested with HNO₃ and H₂O₂ (Wenzel et al., 2001) using an autoclave, and metal levels were determined using AAS and As was determined by FIHG-AAS. For the determination of available metals, DTPA-CaCl₂-TEA at pH 7.3 (Baker and Amacher, 1982) and for available As, NH₄SO₄ 0.05 M were used (Ascar et al., 2008). The concentration of elements is expressed in mg kg⁻¹ of dry matter.

2.4. Plant analysis

A total of ten leaf samples of shrub and tree plants were collected from locations indicated by the inhabitants of the different localities HU: 2 samples (*Acacia caven*, *Citrus limon*), HF: 2 samples (*Eucalytus*, *Schinus molle*); PP: 2 samples (*Prunus persica*, *Medicago sativa*) and SM: 4 samples (*Citrus sinensis*, *Ficus carica*, *Citrus limon*, *Schinus molle*) (Table 4). The samples were carefully washed with distilled water and dried at 60 °C until a constant weight was achieved. For all analyses, 3 replicates were performed. Subsequently, 0.5 g of sample was digested with HNO₃ and H₂O₂ (Wenzel et al., 2001) in an autoclave Speedy WM-341 (MinChuan W. Rd. Taipei, Taiwan), and metal levels were determined using AAS. To determine the amount of S in plant tissue, the samples were calcined with Mg(NO₃)₂ and dissolved in HCl (AOAC, 1995), and the turbidity produced by the addition of BaSO₄ was measured (Lachica et al., 1973). The concentration of elements is expressed in mg kg⁻¹ of dry matter.

2.5. Reagents and quality assurance

Deionized water (18.2 MΩ.cm at 25 °C) obtained using a Milli-Q system (Merck, Darmstadt, Germany) was used for the preparation of reagents and standards. All reagents used correspond to Merck brand analysis quality. The detection limits of the FIHG-AAS Perkin Elmer measuring equipment (model

PinAAcle 500) for As are 0.0005 mg L^{-1} , and those for metals are 0.0001 mg L^{-1} . The Soil and Water Chemistry Laboratory, Faculty of Agronomic Sciences, Universidad de Chile, is accredited by the Servicio Agrícola Ganadero (SAG), an official organization of Chile (RE 7849, 2020). Internal references of the Soil and Water Chemistry Laboratory of the U. de Chile were used to verify the quality of the measurements. For copper-enriched samples (tailings, soils, and waters) the recovery rate is in the order of 98-102%.

2.6 Isoline map

In order to relate the concentration of metals (lloides) and S in soils and water to the proximity of the active mine tailings Ovejería isoline maps were plotted by SURFER 16 software. In waters, the georeferenced points (Table 2) and concentrations Cu, Fe, Mo and SO_4^{2-} (Table 6) were plotted. In soil, the georeferenced points (Table 3) and the total concentrations Cu, Fe, Mo and available S (Table 8) were plotted. The elements concentration in active mine tailings Ovejería (top of the map) and different locations were marked by points (black circles). If the colour distribution is consistent with the isolines (no isolated colours) then the interpretation was that the points are relation to the source (active mine tailings Ovejería) according to concentration and proximity.

3. Results

3.1 Tailings and mine waters

The active mine tailings Ovejería have neutral pH and higher total concentrations of Cu and Mo (Table 5) than normal concentrations in soils, which are up to 250 and 40 mg kg^{-1} , respectively (Sparks, 2003). In mine tailings the total Cu concentration can vary between $1\text{-}750 \text{ mg kg}^{-1}$ and Mo between $100\text{-}800 \text{ mg kg}^{-1}$ (Hossner and Shahandeh, 2005). However, according to the sequential extraction (Fig. 3), the available metal concentrations of Cu, Fe and Mn are low because they are mainly associated with fractions that are not absorbed by plants as sulfides (Lottermoser, 2010). The Cu, Fe and Mn were found associated mainly residual fraction with 307 mg kg^{-1} , 9561 mg kg^{-1} and 262 mg kg^{-1} respectively whereas Zn associated to Fe (III) oxides (5.48 mg kg^{-1}). The total concentrations of toxic metals such as As, Cd, Cr, Hg and Pb are low in these mine tailings.

The water from the mine tailings (Table 1), which has an alkaline pH, does not have concentrations of toxic metals that exceed Chilean water quality standards for different uses or standards for discharge into aquifers, only Mo and SO_4^{2-} exceed water quality standards for different uses (73 times and 10 times, respectively).

3.2 Drinking, irrigation and estuary waters

Water samples, including drinking, estuarine and irrigation water, presented a pH range of 6.69-7.95, in accordance with Chilean regulations for drinking and irrigation water including the WHO (2004) guidelines (Table 6). The electrical conductivity did not exceed $1000 \mu\text{S cm}^{-1}$. The metals (lloides) evaluated in drinking, estuarine and irrigation water complied with Chilean quality standards for different uses (NCh 1333, 1987), Chilean drinking water standards (NCh 409/1, 2005) and the WHO (2004) guidelines for drinking water (Table 6). The highest water concentrations of Cu, Fe and Mn were found in the Quilapilún estuary in the town of Huechún; however, these concentrations are in line with the rivers in the area (Fierro et al., 2020) except for Fe. Molybdenum was detected only in two localities, CH and HU. The concentrations of Mo, Ni and Zn are significantly lower than the limits allowed by Chilean regulations for irrigation water and by the WHO (2004) guidelines for drinking water. The SO_4^{2-} concentration did not exceed the limits of 250 and 500 mg L^{-1} indicated for Chilean regulations for irrigation water and drinking water, respectively.

The isoline map of metal concentrations in drinking, estuarine and irrigation water (Fig. 4) shows that the distribution of Cu concentration is not related to the proximity to active Ovejería mine tailings because the concentrations are not distributed in isolines in relation to the location of dam. The highest Cu concentration in the water ($133 \mu\text{g L}^{-1}$) was found in the Punta Peuco drinking water sample from point 19 H 330982 m E 6284328 m S, which is the farthest point from the active mine tailings Ovejería (19 H 332190 m E; 6341395 m S). For the Fe in water, the distribution of the concentration is not related with distance to the dam. However, for Mn and SO_4^{2-} , the isolines show a relationship with the proximity to active mine tailings Ovejería is observed. The highest concentrations of Mn and SO_4^{2-} in water are observed at points near the tailings, and the lowest concentrations are observed at points farther away.

3.3 Soils

The pH of the soils from the different localities, CH, HU, HF, PP and SM (Table 7), presented a range of 7.67-8.39, which are normal values for the Central Valley of Chile, a semiarid zone, with pH values between 6.00 and ≥ 7.90 (Casanova et al., 2013). The soils of these localities correspond to the order Mollisol which forms in semi-arid to semi-humid areas, typically under pasture cover, the parent material is generally calcite, loess, or sandstone (Soil Taxonomy, 1999).

Electrical conductivity ranged between $0.50\text{-}2.00 \text{ dS m}^{-1}$, indicating nonsaline soils ($<4.0 \text{ dS m}^{-1}$). The lowest level of organic matter was found in HU (2.59%), while in the rest of the localities, the levels were within the medium range of soil fertility (3.1-8.0%). The available concentrations of N, P, K, and S were within the medium range of fertility, except for HU, where the concentration of K was low (43.5 mg kg^{-1}). The total concentration of metals/metalloids in the soils (Table 8) fit the range of levels commonly found in soils (Sparks, 2003) and uncontaminated soils (Kelly, 1979); however, they exceeded the average levels of metal concentrations in soils in the world (Alloway, 2010). The available concentration of metals/metalloids (Table 9), for all locations, in general, was less than 10% of the total concentration, except Cd (17%) and Zn (15%) for CH.

Isoline maps of agricultural and rural soils (Fig. 5) show that the distribution of Cu and Mo concentrations and available S concentrations are higher as the distance from active mine tailings Ovejería decreases. For the total Fe concentration in soils, no distribution was found in relation to the location of active mine tailings Ovejería.

3.4 Plants

In tree, shrub and fruit plants from the different localities (HU, HF, PP and SM), the concentrations of metals and S did not exceed the reference levels for plants (Kabata-Pendias, 2011; Havlin et al., 2013), nor did they exceed the references for animal consumption (NRC, 2005). An exception is for the high concentration of Fe in *Acacia caven* from the locality of HU (Table 10), the closest locality to the active mine tailings Ovejería. Additionally, with respect to the other species, the highest concentrations of Cu, Mn, Mo and Pb were found in *Acacia caven*. The highest concentration of Cu was found in *Schinus molle* from SM, followed by *Acacia caven* from HU, while *Citrus limon* HU and SM and *Acacia caven* from HU presented the highest levels of S, however, these values were within the normal range.

4. Discussion

4.1 Mine tailings in Central zone of Chile

In Chile, there is little published information on the concentrations of metals/metalloids and other elements in soils, waters and plants in areas near active mine tailings dams. Mine tailings contain pyrite (FeS_2), which oxidises and generates acidity (acid drainage) in the presence of O_2 and H_2O , increasing the mobility of metals, which is a constant concern for the scientific community (Lottermosser, 2010; Abraham and Susan, 2017). Tapia et al. (2019) reported an FeS_2 concentration of 0.77% for the active Ovejería mine tailings. Most likely, the low FeS_2 content, the arid-semiarid conditions and the condition of active tailings currently do not allow acidification processes. However, in nonactive Piuquenes mine tailings (1.7% FeS_2) in central Chile, which have not been in operation for more than 40 years, strong acidic pH values of 2.1–3.5 have been found (Dold and Fontboté, 2001). Currently, the pH value of active mine tailings Ovejería is near neutral to alkaline, which does not favour the mobility of cationic metals. However, the extensive surface of soils currently covered by these tailings makes it likely that the dispersion of particles by wind action is currently the most important mechanism of chemical impact on soils, water and plants. On the other hand, the water from the mine tailings, which is stored in the basin and mostly evaporates, meets the quality standards for different uses, except for the levels of Mo and SO_4^{2-} . In view of the water shortage declared by Chile in the Til Til Commune (Decreto 27, 2021), where active mine tailings Ovejería is located, it is necessary to investigate sustainable technologies for the treatment of mining water and its potential use in agricultural irrigation. In this case, mining water could be treated using sulphate bioreactors (Neculita and Zagury, 2007).

4.2 Waters surrounding mine tailings

Samples of drinking water, irrigation water and estuaries waters from localities near the active mine tailings Ovejería indicate pH close to neutral-alkaline, which is not an anomaly for the area. Recently, Fierro et al. (2020) reported that the pH of the waters of different rivers (Aconcagua, Blanco, El Juncal and Putaendo) located in the area of the present study, with and without the influence of mining activities, varies in a pH range of 6.0–8.6. These pH conditions favour Al and Fe precipitation reactions and have limited their higher concentrations in mining area waters (Abraham and Susan, 2017). In Uganda, in areas surrounding the Kilembe Cu mine (operation time 1956–1982), values between pH 5.28–6.65 were found in waters of the Nyamwanba River, while the mean of the control sample was pH 6.53 (Abraham and Susan, 2017). This criteria was included: Considering the pH values of the present study, the natural pH of the soils (6.00 and ≥ 7.90 , Casanova et al., 2013), the pH of the natural waters of rivers and estuaries in the area (6.9–8.2, Fierro et al., 2020) and, that the mobility of cationic metals, particularly Al, is favoured under acidic conditions, a pH value ≤ 5.5 could be recommended as a pollution warning value for waters around Ovejería mining tailings. In relation to the electrical conductivity (EC) of the waters, it is a highly variable value that depends on the season of the year and the chemical characteristics of each area. The values obtained in the present study are in accordance with EC values between 204 and 1122 $\mu\text{g L}^{-1}$ that have been reported for waters of different rivers (Aconcagua, Blanco, El Juncal and Putaendo), adjacent to the area of the present study (Fierro et al., 2020). In Chile, as in most countries, one of the important water quality parameters for irrigation is salinity, whose degree of use restriction is light to moderate in the range 700–3000 $\mu\text{S cm}^{-1}$ (Ayers and Westcot, 1989), while EC values $< 1000 \mu\text{S cm}^{-1}$ are recommended by Australia and New Zealand to protect aquatic life (Boyd, 2015). The concentrations of metals/metalloids in river waters where mining activity takes place depend on the geological and geographical characteristics of each area and the ore being extracted. Recently, Sun et al. (2020), in the city of Potosi (Bolivia) with five centuries of silver mining activity, reported that in the Pilcomayo River the concentrations of metals and SO_4^{2-} increased by several orders of magnitude and decreased the pH with respect to the waters of the Cayara River (river without mining influence). The concentrations in Rio Pilcomayo waters (pH 6.69) for some metals/metalloids were (mg L^{-1}) As: 5.97; Cr: 0.026; Cu: 2.60; Fe:171 and Pb:5.0, while in Rio Cayara (pH 9.04), they were (mg L^{-1}) As: 0.01; Cr: 0.0005; Cu: 0.003; Fe:0.52 and Pb 0.006. In the case of this study, where the Ovejería tailings dam has been operating for 22 years, Fe, Mn and Mo in the Quilapilun and Chacabuco streams of the Huechun locality do not exceed the Chilean water quality standard for different uses (NCh 1333, 1987) but are higher respect to values (without mining activity) published for the Juncal river (Fierro et al., 2020). However, the elements concentrations published by Fierro et al. (2020) from the Juncal river are soluble (Fe: 22 $\mu\text{g L}^{-1}$; Mn: 28 $\mu\text{g L}^{-1}$; Mo: 3.3 $\mu\text{g L}^{-1}$ Zn: 19 $\mu\text{g L}^{-1}$ and SO_4^{2-} : 71 mg L^{-1}) whereas in this study from the Huechun estuaries the elements concentrations are total (Fe: 2380 $\mu\text{g L}^{-1}$; Mn: 90 $\mu\text{g L}^{-1}$; Mo: 10 $\mu\text{g L}^{-1}$ Zn: 25 $\mu\text{g L}^{-1}$ and SO_4^{2-} : 116 mg L^{-1} , Table 6). Nevertheless, it is necessary to monitor Fe, Mn and Mo in the waters of these estuaries, particularly the SO_4^{2-} as a species that usually increases the concentration in mining areas. The isoline map also showed that the concentrations of Mn and SO_4^{2-} in waters increased in relation to the proximity to the active mine tailings Ovejería.

4.3 Soils surrounding mine tailings

The pH of the soils around active mine tailings Ovejería are values within an alkaline range, which indicates that there are no acidification processes in the area after 22 years of mine tailings deposits. However, changes are observed with respect to organic matter in soils of the Huechun locality. According to a publication by CNR (1981) in agricultural soils of Huechun, the organic matter presented values of 3.4% and in the present study of 2.59%, which is a decrease; however, in the study of CNR (1981), the points are not georeferenced. The decrease in organic matter is an indicator of the loss of soil quality, and currently, in the context of climate change, all soil management measures should aim to fix carbon. The levels of macronutrients in soils generally occur at high

concentrations. In the locality of Huechun, 3 km from active mine tailings Ovejería, export agriculture is developed with plum and walnut trees (Fundo Huechun) and has recently introduced new grape varieties (Red Agrícola, 2017), which indicates that soil quality for agricultural use is not a problem. However, monitoring of Cu and Mo concentrations in soils is recommended because a relationship of increasing concentrations of these metals was found as the distance to active mine tailings Ovejería decreases. In the central valleys of Chile, Cu and Mo concentrations are naturally high in soils (Alloway, 2010), and these levels exceed world references; consequently, Chile is a world producer of these elements (U.S. Geological Survey, 2020). Cu and Mo are micronutrients for plants but can be toxic when they exceed 40 and 5.0 mg kg⁻¹, respectively (Kabata-Pendias, 2011). In the case of S is a macronutrient that does not have toxicological scopes as metals but is an element that must be controlled in soils, water and plants in areas of metal extraction from metal sulphides. The form of S as SO₄²⁻ increases the electrical conductivity of water and soil solution and may hinder the growth of roots. The concentration of available elements in soils is a parameter that should be evaluated for mining impact studies because it is the chemical form in which it is absorbed by plants and microflora. When the total concentration of an element exceeds 10% of the total concentration, there is a risk of mobility (Mileusnić et al., 2014). However, although the available concentrations of Cd and Zn in the CH locality exceeded 10% of the total concentration, the available levels were very low. In Chile, the lack of legislation on soil contamination (Neaman et al., 2020) is a difficulty in establishing monitoring and control plans for active tailings.

4.3 Plants surrounding mine tailings

Plants (trees, shrubs) sampled in the different locations of influence of active mine tailings Ovejería indicate that metals available in the soils are not transferred in high concentrations to the aerial part. This is attributable to the alkaline pH of the soils in the area and/or high organic matter content (pH 7.6–9.4 and 2.6–5.1%, respectively), factors that cause the low availability of metals in the soils. In this study, the high level of Fe in the aerial part of *Acacia caven* tree (1981 ± 396 mg kg⁻¹) is comparable to the Fe concentration in the aerial part of *Dactylis glomerata* (1220–5820 mg kg⁻¹) from soils (pH 3.31–7.21) of the Moiel haematite mine (Iran), which operated from 2003 to 2013 (Hosseini et al., 2018). The *Acacia caven* species that was collected in Huechun, the closest locality active mine tailings Ovejería, showed in general a higher concentration of metals and S. Particularly, the element Fe is of interest for monitoring in plants because the main ore for Cu extraction in Chile is chalcopyrite (CuFeS₂). Pyrite (FeS₂) mineral oxidises over time and releases Fe²⁺ and SO₄²⁻ species related to the exposure of inactive mine tailings to oxygen and water. Therefore, *Acacia caven* can be recommended for monitoring concentrations of chemical elements related to this tailings dam, such as Cu, Fe, Mn, Mo and S. *Acacia caven* is a tree native to central Chile that grows in semiarid areas and soils of low fertility (Riedemann and Aldunate, 2000) and has shown high synchrony with environmental factors (Raab et al., 2015). This tree has been described as a continuous and ecologically well-defined unit within the Mediterranean climate vegetation of Chile (Olivares, 2016). The concentration of chemical elements in vegetation (shrubs, trees) is a main indicator used to assess soil and water contamination in areas surrounding mining activities. Vegetation acts as a chemical and physical barrier to the dispersion of pollutants. Given the large areas of land occupied by mine tailings dams in central Chile, mitigation measures should prioritise the conservation and/or increase in vegetation. Mine tailings are reflect the properties of sand, lacking organic matter, and therefore retain low humidity and have a low buffering capacity to temperature changes.

The data generated in this study allow us to recommend the levels of metals and S in water, soil and plants as reference values (background) for future monitoring studies in the active mine tailings of the Ovejería area. The diagnosis of metal- and S-contaminated soils in mine tailings area is recommended when the following three characteristics are met: a) the total element concentration in soils is three times higher than the background concentration (Bern et al., 2019), b) the available element concentration in soils is higher than 10% of the total concentration (Mileusnić et al., 2014), and c) the element concentration in the aerial part of plants in the mining area exceeds the levels established by Kabata-Pendias (2011).

Conclusions

The concentrations of chemical elements determined between 2015–2018, in soils, water and plants in different locations near the active copper tailings dam Ovejería, in Central Chile, allow us to conclude that in general the levels are comparable to national and international references and do not indicate contamination. Some elements require monitoring, such as Cu, Fe, Mn, Mo and SO₄²⁻, which in general, showed a tendency to increase in concentration in soils or water as the distance to the tailings dam decreased. *Acacia caven* tree can be used as an indicator plant to assess metal (loids) and sulphur uptake in areas around mine tailings dams.

Conclusions

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Declarations

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Tables

Table 1. Chemical composition of tailings water of Ovejería dam (range of values January-March 2018) and comparison with Chilean water quality regulations for different uses (NCh 1333, 1987) and regulations for the discharge of liquid waste into marine and continental surface waters.

	Tailing water Ovejería	NCh 1333, 1987	DS90, 2001
pH	7.9-8.7	5.5-9.0	6.0-8.5
EC (mS cm ⁻¹)	3.37-3.65	0.75-7.5	-
TDS (mg L ⁻¹)	2664-3220	2000	-
Al (mg L ⁻¹)	0.16-0.55	5.0	5.0
As (mg L ⁻¹)	0.0064-0.0113	0.10	0.50
B (mg L ⁻¹)	0.22-0.38	0.75	0.75
Cd (mg L ⁻¹)	0.0027-0.0042	0.010	0.010
Cl ⁻ (mg L ⁻¹)	58-112	200	400
Cr (mg L ⁻¹)	0.0011-0.0028	0.10	0.05
Cu (mg L ⁻¹)	<0.014-0.658	0.20	1.00
Fe (mg L ⁻¹)	<0.02-0.36	5.00	5.00
Hg (mg L ⁻¹)	<0.00013-0.00020	0.001	0.001
Mn (mg L ⁻¹)	0.065-0.360	0.20	0.30
Mo (mg L ⁻¹)	0.560-0.725	0.010	1.0
Na (%)	11.5-13.6	35	-
SO ₄ ²⁻ (mg L ⁻¹)	1985-2390	250	1000
Pb (mg L ⁻¹)	<0.00045-0.00083	5.00	0.05
Zn (mg L ⁻¹)	<0.022-0.045	2.00	3.0

Table 2. Waters samples of village of Chacabuco (CH, n=3), Huechun (HU, n=7), Huertos Familiares (HF, n=6), Punta Peuco (PP, n=6), Santa Matilde (SM, n=5)

Towns	Water use	Identification place	Geographical coordinates (UTM) 19 H		Data
			E	S	
			m		
CH	Drinking water (rural)	Chacabuco College	341985	6344066	November 19, 2018
CH	Drinking water (rural)	Nursery School	341954	6344019	November 19, 2018
CH	Drinking water (rural)	Don Javier's grocery	342080	6344259	November 19, 2018
HU	Irrigation water (agricultural)	Water well Mr. Osvaldo Barrera	334307	6338719	January 7, 2015
HU	Irrigation water (agricultural)	Well Water N° 3 plot Alessandrini	335056	6338803	January 7, 2015
HU	Estuary waters	Quilapilún Estuary	337384	6338314	January 7, 2015
HU	Estuary waters	Chacabuco Estuary	336681	6338056	January 7, 2015
HU	Drinking water (rural)	Rural drinking water tank tap	334629	6333835	August 1, 2018
HU	Drinking water (rural)	Medical care centre	334722	6338872	August 1, 2018
HU	Drinking water (rural)	School kitchen	334609	6338757	August 1, 2018
HF	Drinking water (rural)	Berta Bugueño's house	331595	6332088	November 8, 2017
HF	Drinking water (rural)	Jorge Araya's house	332353	6332748	November 8, 2017
HF	Drinking water (rural)	Alto del Huerto School	332072	6332672	November 8, 2017
HF	Drinking water (rural)	School Casino	331889	6332782	August 9, 2018
HF	Drinking water (rural)	CESFAM Bathroom	331690	6332819	August 9, 2018
HF	Drinking water (rural)	Bathroom Liceo Huertos Familiares	332139	6332217	August 9, 2018
PP	Irrigation water (agricultural)	Well water house of Sergio Retamales	330028	6334168	October 25, 2017
PP	Irrigation water (agricultural)	Canal carrot patch	329300	6335230	October 25, 2017
PP	Drinking water (rural)	Rural drinking water tank tap	329819	6334424	October 25, 2017
PP	Drinking water (rural)	Yasna Gómez's house	348354	6284328	July 05, 2017
PP	Drinking water (rural)	Jessica Cornejo's house	329923	6334229	July 05, 2017
PP	Drinking water (rural)	Grace Riquelme's house	330982	6284328	July 05, 2017
SM	Irrigation water (agricultural)	90 m deep well	333021	6335165	October 25, 2017
SM	Irrigation water (agricultural)	Well for rural drinking water	332635	6335475	October 25, 2017
SM	Drinking water (rural)	Ana Navarro hardware spanner	332707	6334961	July 05, 2018
SM	Drinking water (rural)	School	322638	6335521	July 05, 2018
SM	Drinking water (rural)	Nicole Rojas's house	332237	6337300	July 05, 2018

Table 3. Soil samples recolected in Chacabuco (CH, n= 1), Huechun (HU, n= 5), Huertos Familiares (HF, n=2), Punta Peuco (PP, n=2) and Santa Matilde (SM, n=2), towns of Central Valley of Chile

Soil use	Village	Identification place	Geographical coordinates		Data
			(UTM) 19H		
			E	S	
			m		
CH	Rural soil	Playground Nursery School	341959	6344013	November 19, 2018
HU	Agricultural soil	On Kadin	334378	6339040	July 1, 2015
HU	Agricultural soil	Plum sector (Alessandrini)	335030	6339400	July 1, 2015
HU	Rural soil	Courtyard of José Salinas	333796	6338757	August 17, 2018
HU	Rural soil	Courtyard of Teresa Castillo	334857	6338901	August 1, 2018
HU	Rural soil	Basic School	334606	6338908	January 7, 2015
HF	Agricultural soil	Jorge Araya's house	332353	6332748	November 8, 2017
HF	Rural soil	Patricia Campos's house	332637	6332558	November 8, 2017
PP	Agricultural soil	Enrique Ulloa's plot	329137	6335468	October 25, 2017
PP	Rural soil	Veronica Livesey's house	329744	6334508	October 25, 2017
SM	Rural soil	Courtyard Judith Molina's house	332566	6335413	October 25, 2017
SM	Rural soil	Courtyard of Rosa Meneses	332722	6334604	October 25, 2017

Table 4. Plants samples recolected in Huechun (HU, n=2), Huertos Familiares (HF, n=2), Punta Peuco (PP, n=2) and Santa Matilde (SM), towns of Central Valley of Chile

Towns	Vegetal specie	Type	Identification place	Geographical coordinates		Data
				(UTM) 19H		
				E	S	
HU	<i>Acacia caven</i>	Tree	José Salinas' house	333796	6338757	August 1, 2018
HU	<i>Citrus limon</i>	Fruit tree	Teresa Castillo's house	334844	6338896	August 1, 2018
HF	<i>Eucalytus</i>	Tree	neighbourhood Centre	332121	6332657	November 8, 2017
HF	<i>Schinus molle</i>	Tree	Central street	332046	6332872	November 8, 2017
PP	<i>Prunus persica</i>	Fruit tree	Veronica Livesey's house	329744	6334508	October 25, 2017
PP	<i>Medicago sativa</i>	Grass animal feed	Propiedad de Agrícola Bauza	329452	6335067	October 25, 2017
SM	<i>Citrus sinensis</i>	Fruit tree	Hortensia Hurtado's house	332879	6335163	October 25, 2017
SM	<i>Ficus carica</i>	Fruit tree	Judith Molina's house	332566	6335413	October 25, 2017
SM	<i>Citrus limon</i>	Fruit tree	Judith Molina's house	332566	6335413	October 25, 2017
SM	<i>Schinus molle</i>	Tree	Sample of the square	332710	6335096	October 25, 2017

Table 5. Chemical composition of mine tailings of Ovejera dam (values are average $\pm$ standard deviation, n=4)

	Mine tailings
	Ovejera ¹
pH	7.03±0.08
EC (µS cm ⁻¹)	6.16±0.46
S available (mg kg ⁻¹)	2209 ± 102
SO ₄ ²⁻ (mg L ⁻¹)	1243±27.8
Total As (mg kg ⁻¹)	19.7±0.01
Total Cd (mg kg ⁻¹)	2.17±0.56
Total Cr (mg kg ⁻¹)	85.6±16.7
Total Cu (mg kg ⁻¹)	1999±223
Total Fe (mg kg ⁻¹)	46,300±2,500
Total Mn (mg kg ⁻¹)	647±76
Total Mo (mg kg ⁻¹)	164±22
Total Ni (mg kg ⁻¹)	24.5±9.20
Total Pb (mg kg ⁻¹)	19.3±3.0
Total Zn (mg kg ⁻¹)	109±7.8

Table 6. Average concentration of pH, EC (electrical conductivity) metals (loid) (µg L⁻¹) and sulphates (mg L⁻¹) in waters of different uses from the localities of Chacabuco (CH), Huechún (HU), Huertos Familiares (HF), Punta Peuco (PP) and Santa Matilde (SM). (values are average ± standard deviation, , n=3).

Towns	Water use	pH	EC	As	Cd	Cr	Cu	Fe	Mn	Mo	Ni
			uS cm ⁻¹					µg L ⁻¹			
CH	Drinking water	7.51±0.16	773±31	4.57±0.69	1.33±0.58	1.00±0.01	16.7±5.8	16.7±1.50	40.0±17.3	2.00±0.01	nd
HU	Irrigation water	6.69±0.54	641±120	3.00±0.01	6.00±0.01	10.0±0.01	<dl	1085±0.54	10.0±0.01	<dl	nd
	Estuary waters	7.15±0.16	475±209	5.00±4.24	6.00±0.01	10.0±0.01	90.0±0.01	2380±1.00	90.0±0.01	10.0±0.01	nd
	Drinking water	7.95±0.11	387±5.49	6.08±4.91	1.67±0.58	<dl	73.3±15.3	106±19.0	4.67±0.58	<dl	1.00±0.01
HF	Irrigation water	7.87±0.14	504±28	4.81±1.37	3.17±1.50	1.67±0.58	28.2±15.2	71.0±39.9	4.50±1.76	<dl	1.50±0.01
PP	Irrigation water	7.71±0.15	473±239	6.04±4.29	1.00±0.01	<dl	29.5±27.6	110±0.01	42.0±0.01	<dl	2.00±0.01
	Drinking water	7.71±0.15	664±9.05	4.78±2.37	2.00±0.82	1.00±0.01	70.0±49.1	111±54.4	6.50±4.51	<dl	3.00±0.01
SM	Irrigation water	7.76±0.08	566±35.3	6.12±2.81	2.50±0.71	1.00±0.01	22.5±2.12	320±0.01	50.0±0.01	<dl	2.00±0.01
	Drinking water	7.88±0.12	465±101	3.80±1.67	1.67±1.41	<dl	27.0±9.54	180±0.01	3.33±1.53	<dl	1.67±0.01

References

Drinking water (Chile) ¹	6.5-8.5	-	10	10	50	2000	300	1000	-	-
Irrigation water (Chile) ²	5.5-9.0	500-1000	100	10	100	200	5000	200	10	200
Drinking water (WHO) ³	-	-	10	3.0	50	2000	-	-	-	70
Estuary waters (Chile) ⁴	6.9-8.2	303-938	0.70-4.30	-	-	3.5-182.4	11.8-30.3	4.5-235	1.3-20.3	-

nd: no determinated; dl: detection limited ¹ NCh 409/1, 2005 ² NCh 1333, 1987. ³ WHO, 2004. ⁴ For dissolved element (Fierro et al.2020).

Table 7. Fertility parameters in soil of Chacabuco (CH), Huechún (HU), Huertos Familiares (HF), Punta Peuco (PP) and Santa Matilde (SM). (values are average ± standard deviation, n=3).

Village	Soil use	pH	EC	OM	N	P	K	S
			dS m ⁻¹	%	Available (mg kg ⁻¹)			
CH	Rural soil	7.90±0.40	1.87±0.47	4.66±0.93	26.6±5.32	30.1±6.01	253±50.6	101±20.2
HU	Agricultural soil	7.67±0.11	0.53±0.22	2.59±0.25	32.5±5.35	17.7±10.4	43.5±30.8	nd
	Rural soil	7.83±0.06	2.00±0.60	5.13±3.03	59.1±4.29	103±10.2	405±209	69.5±12.2
HF	Agricultural soil	8.39±0.42	0.50±0.10	4.73±1.18	24.3±6.07	29.2±7.29	899±225	38.3±9.57
	Rural soil	8.25±0.41	0.89±0.18	4.89±1.22	32.2±8.05	25.8±6.44	705±176	45.7±11.4
PP	Agricultural soil	7.94±0.40	0.39±0.08	4.23±1.06	60.2±15.1	31.9±7.98	593±148	86.0±21.5
	Rural soil	8.02±0.40	0.83±0.17	5.13±1.28	67.2±16.8	84.3±21.1	877±219	69.7±17.4
SM	Rural soil	7.96±0.40	1.39±0.28	4.88±0.55	75.1±50.8	43.8±37.7	700±549	153±46.3
Soil fertility medium levels (Rodríguez, 1993)		6.5-8.0	<4.0	3.1-8.0	21-35	11-15	101-150	8.1-12

nd: no determinated

Table 8. Total metals(loids) in soil (mg kg⁻¹) of Chacabuco (CH), Huechún (HU), Huertos Familiares (HF), Punta Peuco (PP) and Santa Matilde (SM). (values are average ± standard deviation; n=3).

Towns	Soil use	As	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Z
Total (mg kg ⁻¹)											
CH	Rural soil	6.64±1.99	0.30±0.28	78.9±23.7	32.3±9.69	42,400±12,720	408±122	4.75±1.43	36.4±10.9	4.75±1.43	3
HU	Agricultural soil	5.80±4.26	nd	27.5±2.12	51.5±3.54	33,333±9,999	765±92.0	nd	nd	22.2±6.66	4
	Rural soil	1.88±0.33	0.94±0.25	16.0±5.40	70.0±15.6	48,562±15,488	751±41.9	8.24±0.49	23.0±8.63	26.5±6.07	7
HF	Agricultural soil	3.46±1.07	1.08±0.33	93.3±28.9	101±31.3	80,500±24,955	808±250	15.8±4.90	60.8±18.8	48.5±15.0	1
	Rural soil	4.55±1.46	0.84±0.27	87.0±27.8	91.3±29.2	75,042±24,013	709±227	11.0±3.52	61.3±19.6	40.7±13.0	1
PP	Agricultural soil	7.94±2.62	0.84±0.28	78.2±25.8	57.8±19.1	30,725±10,139	511±169	7.37±2.43	31.5±10.4	18.3±6.04	5
	Rural soil	8.02±2.73	0.84±0.29	50.5±17.2	93.8±31.9	46,300±15,742	460±156	5.72±1.94	31.3±10.6	26.2±8.91	1
SM	Rural soil	8.02±1.29	1.68±0.85	32.5±3.89	52.4±2.32	37,225±5,660	453±18.3	5.08±0.60	30.3±4.95	20.4±2.00	6

References

Soil in world (Sparks, 2003)	0.1-40	0.01-2.0	5.0-1,500	2.0-250	2,000-550,000	20-10,000	0.1-40	2.0-750	2.0-300	1
Soil in world (Alloway, 2010)	4.7	1.1	42	14	-	418	1.8	18	25	6
Contaminated soil (Kelly, 1979)	50-100	3-10	200-500	-	-	1,000-2,000	-	-	1,000-2,000	-

nd: no determinated

Table 9. Available metals(oids) in soil (mg kg⁻¹) of Chacabuco (CH), Huechún (HU), Huertos Familiares (HF), Punta Peuco (PP) and Santa Matilde (SM). (values are average ± standard deviation; n=3).

Towns	Soil use	As	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
Available (mg kg ⁻¹)											
CH	Rural soil	<dl	0.050±0.015	0.01±0.003	2.79±0.84	7.48±	6.70±	0.19±0.06	0.18±0.05	0.46±0.14	5.50±1.64
HU	Agricultural soil	<dl	nd	0.32±0.110	2.81±1.84	9.10±3.54	15.2±11.0	nd	nd	0.01±0.003	0.37±0.17
	Rural soil	<dl	0.027±0.020	0.01±0.003	5.98±1.39	12.3±1.12	19.9±17.7	0.01±0.003	0.17±0.03	1.73±1.00	2.53±1.36
HF	Agricultural soil	<dl	0.004±0.001	<dl	2.23±0.67	7.53±2.26	12.5±3.75	0.51±0.153	0.12±0.04	0.21±0.06	1.69±0.57
	Rural soil	<dl	0.003±0.001	<dl	2.17±0.65	7.12±2.14	15.5±4.65	0.59±0.177	0.19±0.06	0.04±0.01	0.23±0.07
PP	Agricultural soil	<dl	0.006±0.002	<dl	3.81±1.14	12.2±3.66	14.6±4.38	0.42±0.139	0.24±0.07	0.03±0.01	0.21±0.06
	Rural soil	<dl	0.002±0.001	<dl	4.83±1.449	7.05±2.12	17.2±5.16	0.41±0.123	0.15±0.05	0.04±0.01	0.68±0.26
SM	Rural soil	<dl	0.010±0.003	<dl	2.12±0.11	7.58±0.17	16.9±1.96	0.47±0.06	0.16±0.05	<dl	0.42±0.36
Soil contaminated (Kelly, 1979)		-	-	-	200-500	-	-	-	50-200	500-1,000	500-1,000

nd: no determinated; dl: detection limited.

Table 10. Metals in leaves of plant (mg kg⁻¹) recolected in Huechún (HU), Huertos Familiares (HF), Punta Peuco (PP) and Santa Matilde (SM). (values are average ± standard deviation; n=3).

Town	Plant specie	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn	S
		mg kg ⁻¹									%
HU	<i>Acacia caven</i>	0.38±0.076	2.00±0.40	19.3±3.86	1981±396	62.6±12.5	2.00±0.4	6.40±1.28	3.00±0.60	20.4±4.1	0.84±0.1
HU	<i>Citrus limon</i>	0.36±0.072	2.40±0.48	6.10±1.22	547±109	23.8±4.76	<dl	6.80±1.36	1.40±0.28	33.6±6.72	0.91±0.1
HF	<i>Eucalyptus</i>	0.40±0.080	<dl	1.90±0.38	170±34.0	49.6±9.92	0.12±0.02	<dl	0.20±0.04	15.7±3.14	0.25±0.0
HF	<i>Schinus molle</i>	0.60±0.12	1.00±0.20	4.20±0.84	184±36.8	17.8±3.56	<dl	0.40±0.08	1.80±0.36	22.4±4.48	0.63±0.1
PP	<i>Prunus persica</i>	0.65±0.13	0.40±0.08	5.70±1.14	189±37.8	11.2±2.24	<dl	0.60±0.12	1.40±0.28	26.2±5.24	0.81±0.1
PP	<i>Medicago sativa</i>	0.60±0.12	2.80±0.56	6.80±1.36	86.0±17.3	13.6±2.72	0.79±0.16	2.20±0.44	1.40±0.28	42.8±8.56	0.75±0.1
SM	<i>Citrus sinensis</i>	0.40±0.08	<dl	11.0±2.20	119±23.8	6.90±1.38	<dl	<dl	1.60±0.32	35.0±7.00	0.33±0.0
SM	<i>Ficus carica</i>	0.60±0.12	0.20±0.04	9.20±1.84	284±56.8	48.3±9.66	<dl	<dl	1.80±0.36	24.0±4.80	0.21±0.0
SM	<i>Citrus limon</i>	0.60±0.12	1.60±0.32	5.60±1.12	145±29.0	10.7±2.14	<dl	1.10±0.22	1.20±0.24	16.6±3.32	0.99±0.1
SM	<i>Schinus molle</i>	0.80±0.16	1.00±0.20	26.6±5.32	341±68.2	48.0±9.60	0.05±0.01	1.00±0.20	1.00±0.20	21.3±4.26	0.43±0.0
Leaf concentration references		0.05-0.20 ^a	0.1-0.50 ^a	5-30 ^a	50-250 ^b	30-300 ^a	0.2-5.0 ^a	0.1-5.0 ^a	5.0-10 ^a	27-150 ^a	0.2-0.5
Concentration for feed livestock		10 ^c	100 ^c	40 ^c	500 ^c	2,000 ^c	5.0 ^c	100 ^c	100 ^c	500 ^c	0.40

^aKabata-Pendias 2011, plant leaf sufficient or normal

^bHavlin et al. 2013, plant leaf sufficient or normal

^cNRC. 2005, livestock toxicity limits (cattle)

Figures

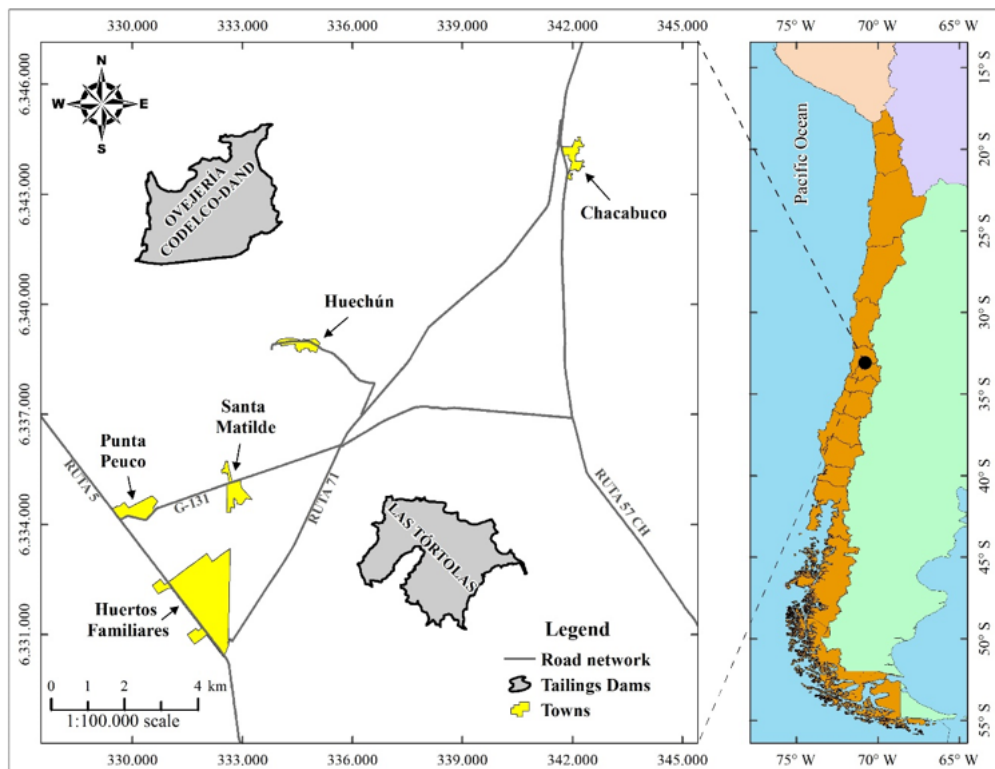


Figure 1



Figure 2

Active mine tailings Ovejera (CODELCO DAND) of 850 hectares of surface located in the central area of Chile

(see location in Fig 1)

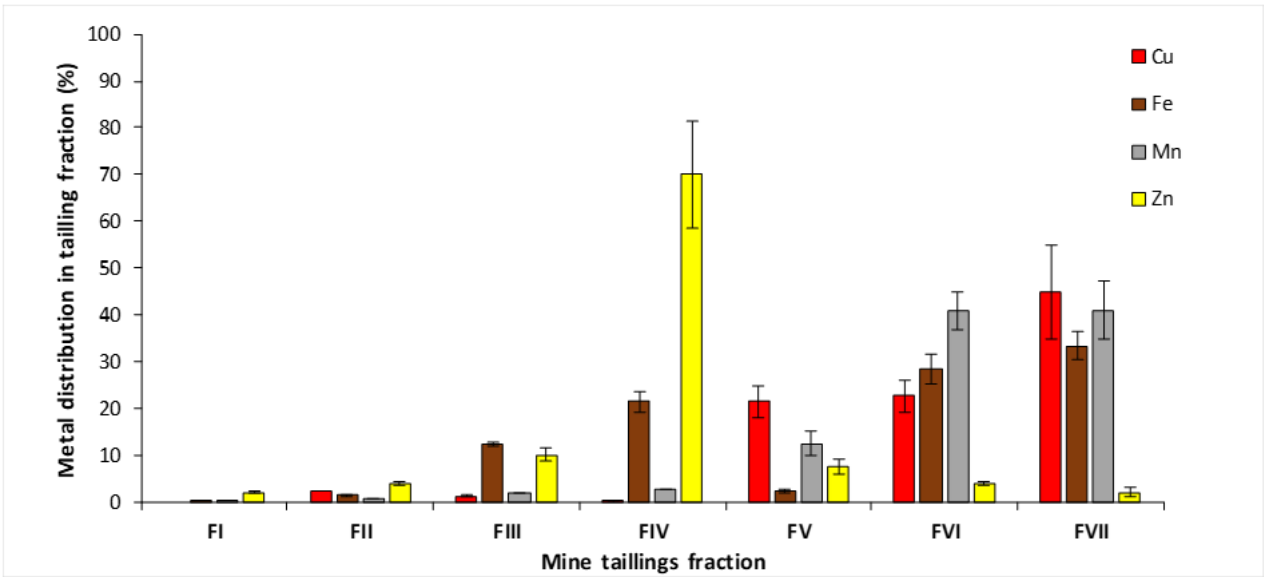


Figure 3

Distribution of metals (%) in mine tailings fractions. FI: water soluble; FII: exchangeable; FIII: Fe(III) oxyhydroxides; FIV: Fe(III) oxides; FV: organics and secondary Cu sulfides; FVI: primary sulfides; FVII: residual fractions. The lines within the bars indicate the standard deviation; n = 4.

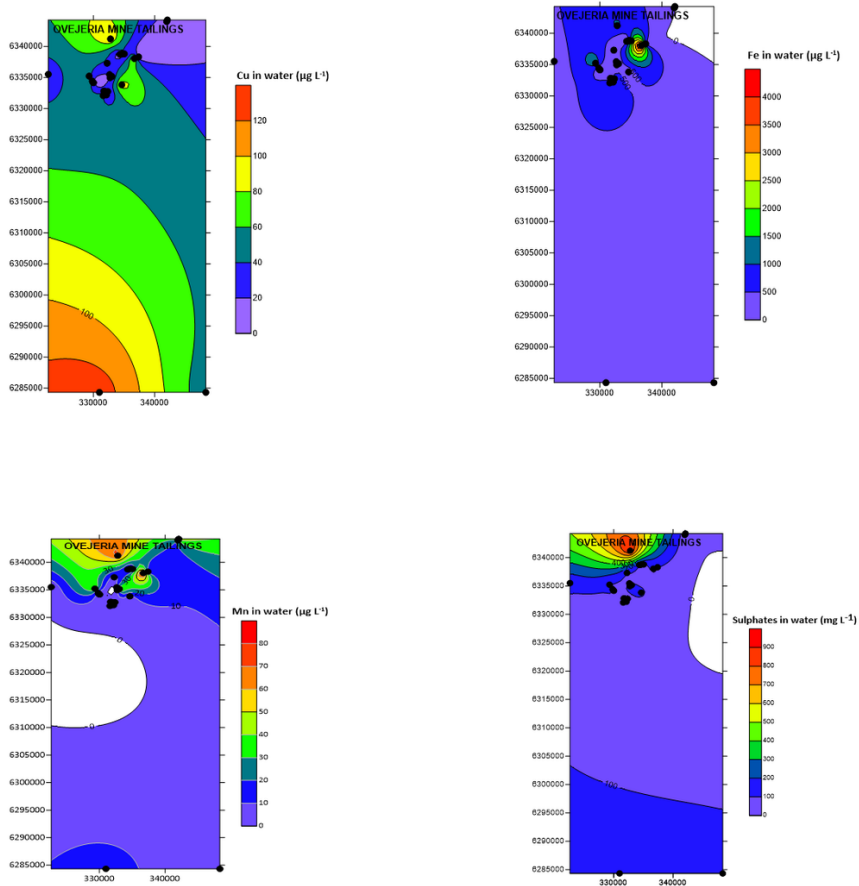


Figure 4

Isoline map for the concentration of metals and S in water (drinking water, irrigation water, estuaries) in relation to the active tailings dam Ovejería (Chile).

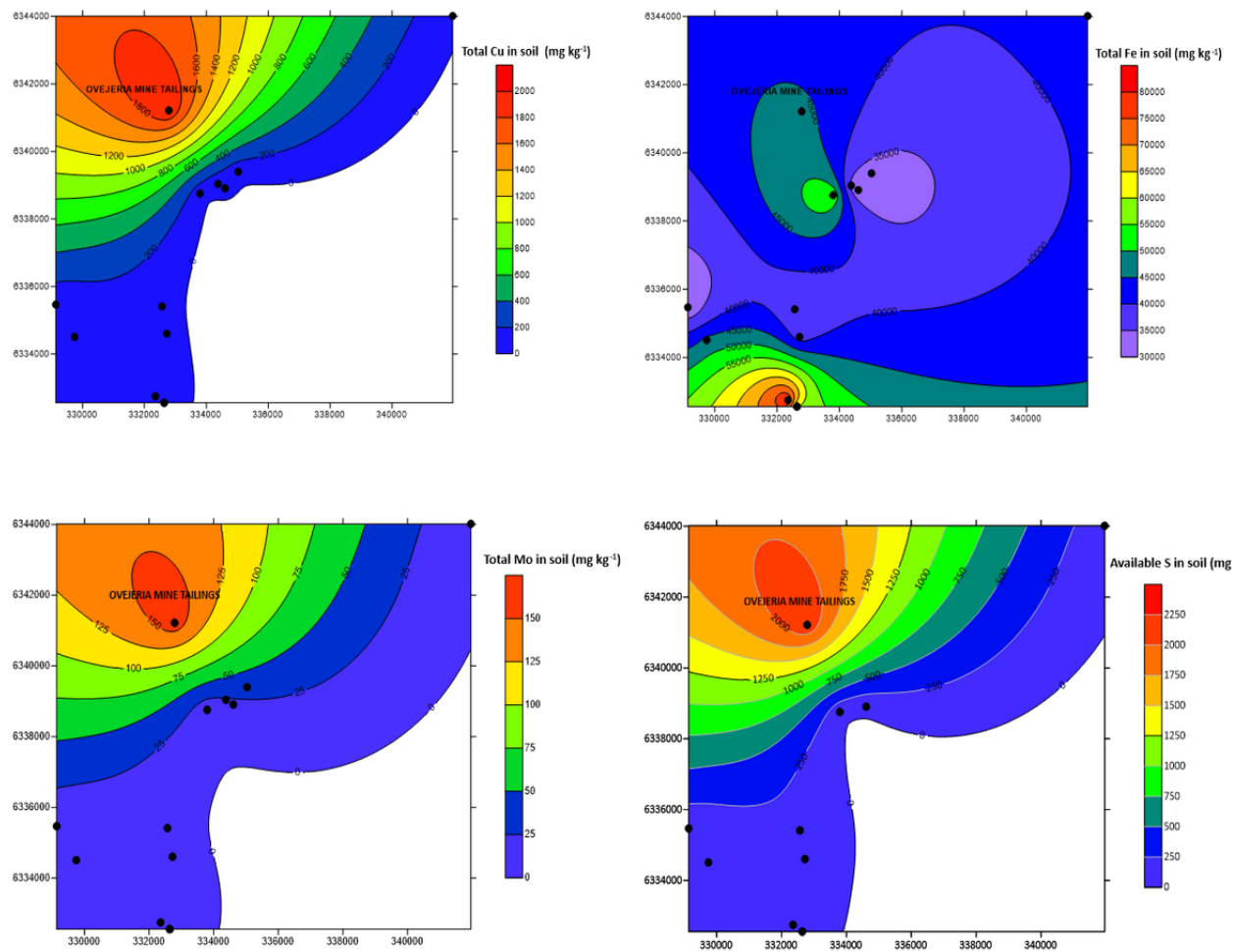


Figure 5

isoline map for the concentration of metals in soils in relation to the active tailings dam Ovejera (Chile).