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ECOLOGICA RISK ASSESSMENT OF TRACE ELEMENTS IN THE TAILINGS FROM ANDACOLLO CITY, NORTHEN CHILE

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ABSTRACT

In Chile, metal mining is concentrated between the Administrative Regions IV and VI (which includes the Metropolitan Region). The northern and central zones of the country have abundant copper as well as mineral iodine and iron. Today, these residues are stored in tailing dams. Mine tailings constitute the toxic residues composed of trace elements, which in many occasions are deposited in areas neighboring human settlements and are a health hazard for the inhabitants

In this work, the concentrations of trace elements such as: Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Zn were studied in 6 sites of the tailings located within Andacollo city, Northern Chile.

The sampling points were recorded using GPS geographic coordinates and, in the laboratory, they were characterized determining: pH, electrical conductivity, soluble organic carbon, total organic carbon, available phosphorus, boron, total nitrogen and capacity cation exchange. The concentrations of trace elements in tailings samples, were quantified by atomic absorption spectrophotometry (AAS).

Potential anthropogenic hotspots were assessed using indices including enrichment factor (EF), geoaccumulation index (Igeo), contamination factor (CF), Pollution load index, (PLI), ecological risk (Ei) and potential ecological risk (PERI) index. These indexes are used to assess the presence and intensity of anthropogenic contaminant deposition on surface soil.

The physicochemical characterization of the tailings allowed establishing a profile of the environmental conditions of the sampled sites. The sites that presented a higher concentration of metals correspond to sites 4 and 6.

The polluted index values than indicated, high degree of contamination for Cu, Hg and Mo by other hand PLI and Ri index indicated the sites more polluted are 4,5 and 6.

Keywords: Tailings, trace elements; geo accumulation index (Igeo); enrichment factor (EF), contamination factor (CF), Pollution load index (PLI), Potential Ecological Risk (PERI).

1. INTRODUCTION

Mining environmental liabilities (MEL) are elements such as facilities, infrastructures, surfaces affected by spills, disturbed watercourses, machine shops, tool storages, storages, mining waste deposits or stockpiles currently located in abandoned mines that pose a permanent potential risk for human health and the environment [1–3].

The absence of clear regulations has led the accumulation of MEL in mining zones worldwide. There are polluted areas due to the mining activities that have been carried out for centuries in different countries such as Peru [1–4], Mexico [5], Chile [6], South Africa [7], Ghana [8], Slovakia [9], Korea [10], Spain [11], and Ecuador [12–16]. Moreover, numerous MEL have been reported in Latin American countries such as Bolivia, Chile, Colombia, and Peru [17].

In most cases, tailings dams are MEL that represents significant ecological risk because it is feasible that they release potentially toxic elements (PTE) such as As, Cd, Cu, Zn, and Mn into the nearby water sources. These contaminated water resources are often used for crop irrigation or for human consumption, creating a serious pollution issue.

Tailing dams pose a potential risk to the environment and the safety of people due to the characteristics of the wastes and the intensive storage [18]. The poor management of mining waste has triggered the failure of dams with catastrophic consequences for the environment, as reported in Minas Gerais-Brazil [19, 20], Aznalcóllar-Spain [21], and Karamken-Russia [22].

In Chile, metal mining is concentrated between the Administrative Regions IV and VI (which includes the Metropolitan Region). The northern and central zones of the country have abundant copper as well as mineral iodine and iron [23]. Of the entire mineral extracted from a copper mine, only 2 % is used; the rest is cast off as different types of waste: 50 % sterile, 44 % tailings and 4 % slag [24]. These residues are deposited directly in the rivers, ravines of the ocean, causing negative effects on the ecosystems. Today, these residues are stored in tailing dams. Mine tailings constitute the toxic residues composed of trace elements, which in many occasions are deposited in areas neighboring human settlements and are a health hazard for the inhabitants [25].

Copper sulphide mining extracts large amounts of material from the deposit being exploited. A smaller percentage corresponds to the mineral and the rest is sterile material, which is called "tailing" and must be deposited in a safe and environmentally responsible manner [26]. The amount of waste that must be disposed of, both in dams and reservoirs has high concentrations of elements and chemical compounds, which irreparably transform the environment [27]. A tailing corresponds to the residue, a mixture of ground mineral with water and other compounds, which remains as a result of having extracted the sulphide minerals in the flotation process. This residue, also known as glue, is transported through gutters or pipes to specially prepared places or dams, where the water is recovered or evaporated to be finally disposed of as a stratified deposit of fine materials (sand and silt) [28].

The physical and chemical characteristics of tailings vary with the type of ore. Process effluents may contain metallic and acidic trace elements that must be neutralized before disposal, even so, solid tailings generally have remnants of sulphide minerals that remain after the mining process and, therefore, constitute a potential environmental problem [29]. In tailings deposition, pyrite can oxidize in the presence of water to produce sulfuric acid and leach the metals contained in said structures, becoming available to the environment and in turn affecting the populations close to said waste [30].

Currently, there are around 740 mining tailings deposits in Chile, distributed in 65 of the country's 346 communes (between the Arica and Parinacota regions and the Aysen region). However the most of the deposits are found in the Atacama and Coquimbo regions, with 21.8% and 52.2%, respectively [31].

Among the main compounds that tailings have, there are various toxic metals, such as arsenic, cadmium, chromium, copper, mercury and lead, among others. Its availability varies depending on the type of mining extraction and the years of accumulation. In the older tailings deposits, there is a greater presence of contaminating compounds, such as metals and reagents from the flotation processes, due to the fact that the metal extraction techniques were less efficient and, therefore, more polluting [32].

The registry of tailings deposits in Chile considers three types of status: Active, Inactive and Abandoned. From this inventory, there are: 101 active deposits, 170 abandoned deposits and 469 inactive deposits. The Coquimbo region has the largest number of inactive (250) and abandoned (106) deposits; the active deposits are 30, the same as the Atacama Region, increasing the historical problems [24].

There are various risks and impacts related to the operation and closure of mining tailings, among the main risks to which people and the environment are exposed are: failures in the dam wall, the dragging of dams due to the effect of rains, the filtration of tailings water into the environment and infiltration into the

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underground layers, and the lifting and dragging of fine material by the action of the wind, among others. Among the main causes identified when establishing the various risks associated with mining tailings, are earthquakes, hydrogeological risks, alternative land use, and water consumption and failures in the disposal system. Consequently, active and/or inactive tailings deposits - some being abandoned - can be considered risky because they generate various impacts on health and the environment, both in their solid phase (deeply settled solids) and in their solid phase, aqueous (the water that comes off the tailings dam) [33-35].

Among the main physiological functions of living beings are: the absorption of food, among the main mechanisms for transporting pollutants to surface and groundwater are: the direct discharge of water from the production process mining, mine waters, surface runoff and infiltration. The adverse impacts that occur in surface waters also include the discharge of contaminated sediments, reduction of the pH, the destruction or degradation of water ecosystems and the contamination of drinking water. The so-called "acid mine drainage" or "acid waters" It is produced by the oxidation of sulfur minerals - such as pyrite - that come into contact with air, water and bacteria. Pyrite is one of the most abundant sulfides in hydrothermal mineralization and forms part of the tailings content. The oxidation of this element (pyrite) produces sulfuric acid and iron oxides, which form "acid waters" that help transport other toxic elements (for example: trace elements) into the environment. Regarding the contamination of surface waters, these can be affected by erosion and discharge of sediments and materials from pits or open pits, leach pads, tailings dams, clearings, among others, to aquatic bodies. On the other hand, groundwater can be contaminated by the penetration of acidic liquids from poorly sealed tailings, or when its structure gives way, contaminating the adjacent water table. These last points are the main environmental problem in the case of sulphide mining [36].

In the case of the environmental impacts of tailings deposits in the soil, it can be mentioned that the adverse effects on it can be due to erosion and degradation, product of the exposure of rem oved and processed materials, the destruction of the protective vegetal layer and also by the disposal of mining waste on the surface. On the other hand, the impacts of tailings in the air are related to the dust, or coarse and fine particulate matter, coming from the surface sediments of the tailings deposits. This dust contains toxic elements, such as trace elements, and can cover large areas of the territory where the deposits are located and their surroundings [37, 38].

Surface and groundwater contamination is considered one of the main environmental impacts of mining processes, especially mining tailings. Also considering that on certain occasions and as a result of natural phenomena, mining activity can modify the local hydrological and/or hydrogeological regime. In this sense, water pollution resulting from mining activity is directly related to the release of pollutants toxins used in production processes and that are also contained in their waste (tailings). Among the main polluting sources are the substances and/or elements that occur naturally in ore and those that are used in the processing of minerals, considering among these cyanide, sulfuric acid and nitrates, among others. Among the main mechanisms for transporting pollutants to surface and groundwater are: the direct discharge of water from the mining production process, mine water, surface runoff and infiltration. The adverse impacts that occur in surface waters also include the discharge of contaminated sediments, reduction of the pH, the destruction or degradation of water ecosystems and the contamination of drinking water [39, 40].

Of the almost importance in evaluating the site and deciding how to approach soil management is quantifying the ecological risk of soil pollution. Using soil pollution indices, such as enrichment factor (EF), geoaccumulation index (Igeo) and pollution load index (PLI), gives information on the soil quality, and the degree of contamination for each sample, based on individual metals [41-47]. The potential ecological risk can be estimated based on the risk index (RI) for each sample. Also, the risks from individual metals, which contribute to the ecological risk, can be identified [43, 48-49].

The main objectives of this study were to evaluate the trace elements concentration in the tailings and estimate the level of pollution using different index.

2. MATHERALS AND METHODS

2.1 Description of the study site

Andacollo is a commune of the IV region of Chile (Coquimbo), Elqui province, which is located approximately 50 km southeast of La Serena. It has an area of 310 km^2, an altitude of 1,017 meters above sea level. The economy of the commune has historically depended on mining activity, where copper and gold exploitations stand out. This productive activity had its greatest peak between the years 1933 and 1939, being in this period, the main activity of Andacollo and an important support in the national economy.

Currently, Andacollo is in a decontamination plan due to the large number of Mining Environmental Liabilities (MELs) present in the area. These correspond to those abandoned or paralyzed mining operations, including their residues, which constitute a significant risk to the life or health of people or to the environment. These facilities or waste can be: mines, treatment plants, massive mining waste, non-massive mining waste, industrial mining waste and related infrastructure, classifying the tailings within the massive mining waste. This is why several options such as transfer, containment and extraction are considered, and thus be able to reduce the toxicity of these tailings present within the same commune [50-53].

2.2 Sampling area

The analyzed tailings are located in the center of the city of Andacollo; its characteristics are described in table 1. Sampling was carried out in the summer period, collecting six sites throughout the entire tailings as shown in the in figure 1.

Figure 1. Sampling sites of Andacollo city.

Table 1. Coordinates of sampling sites

Sites	Coordinates WGS-84	
1	30° 14’ 9,726’’ S	71° 5’ 3,361’’ O
2	30° 14’ 10,961’’ S	71° 5’ 1,658’’ O
3	30° 14’ 13,268’’ S	71° 5’ 1,355’’ O
4	30° 14’ 16,148’’ S	71° 5’ 1,481’’ O
5	30° 14’ 17,131’’ S	71° 4’ 59,437’’ O
6	30° 14’ 18,755’’ S	71° 5’ 0,722’’ O

2.3 Material preparation

The material used, both for the sampling and for the analysis of the samples in the laboratory, was pre-treated, to avoid and rule out possible contamination. This was made for both polyethylene plastic materials and glassware. It was washed with potable water and Extran® detergent (Merck), then rinsed with plenty of potable water and distilled water. A 2% solution of nitric acid (HNO_3) Suprapur® (Merck) was added, allowing it to stand for 48 hours. It was subsequently rinsed with distilled water and then with Milli-Q grade deionized water. It was left to dry until later use.

2.4 Reagents and solvents

All the reagents solids were Merck p.a. acid HNO_3, HCl and HF suprapur Merck; metals standards were tritisol Merck.

2.5 Physicochemical Characterization of soils from tailings [54]

2.5.1 Sample Preparation

The collected samples were sieved to two different fractions, fraction < 2 mm. For the physical-chemical characterization and fraction < 63 μm, for the determination of metals.

2.5.2 pH and Electrical Conductivity

10.00 ± 0.01 g of each samples were mashed into 50 mL plastic bottles. Then 25 mL of deionized water was added to each flask and subsequently left on an orbital shaker for 2 hours at 150 rpm (Already Enterprise Inc, DSR-2800A model). The pH and electrical conductivity of the suspension were recorded with the previously calibrated multiparameter equipment (HANNA, HI 9813 model).

2.5.3 Total Organic Carbon (TOC)

The crucibles dried at 105.0 ± 0.1 ° C were put into the flask and calcined at 550.0 ± 0.1 ° C for in an oven for 6 hours (Barnstead International, FB 1300 model). The sample was then allowed to cool to room temperature in a desiccator and then be massed. The previous steps were repeated until constant mass.

2.5.4 Soluble Organic Carbon (SOC)

For the preparation of the digestion with potassium dichromate, the Walkley and Black **[**54], procedure was followed, which involves a wet combustion of organic matter with a mixture of potassium dichromate and sulfuric acid. After the reaction, the dichromate solution that did not react was titrated with iron (II) sulfate. 0.50 ± 0.01 g of each sample was transferred to a 250 mL Erlenmeyer flask along with a duplicate and two blanks to standardize the iron (II) sulfate solution. 10 mL of 0.1667 $molL^{-1}$ potassium dichromate was added under a hood and with caution 20 mL of concentrated sulfuric acid. Samples were allowed to stand for 30 minutes. Later, 180 mL of deionized water and 10 mL of concentrated phosphoric acid were added. Finally, it was titrated with $FeSO_4$ 1.0 $mol\cdot L^{-1}$ using a platinum electrode (Hanna HI 3831 B).

2.5.5 Available Phosphorus

For the determination of available phosphorus in acidic soils, the Bray and Kurtz [54] procedure was followed, where the readily acid-soluble forms of phosphorus are extracted with a combination of HCl and NH_4F (Bray solution). The phosphorus in the extract was determined calorimetrically by the ammonium molybdate method with ascorbic acid as reducing agent. In conjunction with the preparation of the mixed reagent for the determination of phosphorous in the soil samples, a calibration curve was made based on a series of phosphorus standards to determine the phosphate concentration. Then 14 mL of Bray extracting solution was added; it was shaken manually for 1 min and filtered with a syringe filter. Next, 3 mL of the standard series, blank, and sample extracts were pipetted into test tubes along with 3 mL of mixed reagent into each tube. It was left to stand for 2 hours until the blue hue developed to its maximum. The absorbance was measured at 880 nm in a spectrophotometer (Shimadzu, Pharmaspec 1700 model).

2.5 6 Kjeldahl Nitrogen

For the determination of total nitrogen, the Kjeldahl digestion procedure1 **[**54]**,** was followed, which consists of digestion, distillation and subsequent titration. In digestion with sulfuric acid, all organic nitrogen is converted to ammonium sulfate. Then the solution becomes alkaline, so the ammonia becomes ammonia which is distilled. This is trapped in boric acid and titrated with hydrochloric acid. Then 1.00 ± 0.01 g of samples was mashed into a digestion tube along with a duplicate and two blanks. 1 g of Devarda catalyst (Merck p.a.), 8 mL of concentrated sulfuric acid were added, mixed well and digested for 90 min at 420 ° C. At the end of the time, the tubes were allowed to cool to take them to the distillation equipment, where an Erlenmeyer flask with 25 mL of boric acid-indicator solution was placed at the end of the condenser and in the other the digested sample, which was distilled for 7 minutes. After receiving the final solution in the flask, it was titrated with 0.01 $mol\cdot L^{-1}$ HCl until the color changes from green to pink (Digetro VELP® Scientifica, modelo DK 6; Destilador (VELP® Scienfica model UDK 127).

2.5.7 Boron

Boron is obtained by means of the technique proposed by Berger and Truog **[**54]**,** which consists of the extraction of boron by means of the continuous boiling of the sample with hot water. The boron in the extract forms the boric acid-azomethine colorimetric complex for later measurement by spectrophotometry. Each solution, subsequently, measure the absorbance at a length of 420 nm in a spectrophotometer (Shimadzu, Pharmaspec 1700 model).

2.5.8 Cation Exchange Capacity (CEC)

For the determination of the CEC, in tailings and clays, the method was used by saturation with sodium acetate, washing with ethanol, and displacement of the adsorbed sodium with ammonium acetate. In this way in the obtained extract, the sodium displaced by EEA (Shimadzu atomic absorption spectrometer; model AA-6800) was measured **[**54].

2.6 Analysis of trace elements in the Tailings

The digestion of the samples for the determination of metals was carried out by microwaves in tubes covered with Teflon PFA, 250 mg of soil with 1 mL HNO_3, 3 mL HCl and 3 mL HF were added to each tube. This was done for all sites along with one duplicate and ten blanks. Once the tubes were sealed and placed on the turntable, the digestion process was started according to the following conditions.

Table 2. Microwave conditions for tailings samples digestion.

Parameter	Stege 1	Stege 2
Máximum power	800 W	400 W
Power	80 %	80 %
Ramp	4 min	4 min
Temperature	175 °C	175 °C
Cooling	4 min	4 min

After digestion was complete, the samples were allowed to cool covered at room temperature for 30 minutes. Then, 12 mL of 5% m / v H_3BO_3 was added to neutralize the solution, it was filtered with syringe filters of pore size 0.45 µm and the solutions were stored refrigerated in centrifuge tubes until their subsequent analysis by EAA (Shimadzu atomic absorption spectrometer; AA-6800 model).

2.6.2 Chemical determination of trace elements

It was carried out by EAA, on a Shimadzu atomic absorption spectrometer; model AA-6800, equipped with ASC-6100 auto sampler and wizAArd software. To analyze each metal, prepared before were measured, using hollow cathode lamps of the inversion type with neon gas inside, each one with a specific wavelength and intensity: Al(309.3 nm); As (193.7nm); Cd (228.8 nm); Cr (357.9 nm); Cu (324.8 nm); Fe (248.3 nm); Hg (2534.7 nm); Mn (279.5 nm); Mo (313.3 nm); Ni(232.0 nm); Pb (217.0 nm); Zn (213. 9 nm).

2.7 Assessment of soil tailings quality

2.7.1 Geoacumulation index (I_{geo})

The geoaccumulation index (I_{geo}) was developed by Müller (1979) [42]. It compares the measured concentration of the elements in tailings; with geochemical background [55] The Igeo expression is show in Equation (1).

$$I_{geo} = \log 2\ Cn/1.5\ Bn \qquad \text{(Eq. 1)}$$

where C_n is the measured concentration of metal *"n"* in soil, B_n is the geochemical background value for the metal "*n*" in soil, while the 1.5 factor accounts for the possible variation in background data caused by lithology effects [56]. I_{geo} is divided seven classes. The classes are: $0 \leq I_{geo}$ unpolluted; $0 \leq I_{geo} \leq 1$ unpolluted to moderately polluted; $1 \leq I_{geo} \leq 2$ moderately polluted; $2 \leq I_{geo} \leq 3$ moderately to strongly polluted; $3 \leq I_{geo} \leq 4$ strongly polluted; $4 \leq I_{geo} \leq 5$ strongly to extremely polluted; and $I_{geo} \geq 5$ extremely polluted [57].

2.7.2 Enrichment factor, *EF*

The enrichment factor (*EF*) is an indicator used to evaluate the availability and intensity of anthropogenic contamination in sediments or soil surface [57]. Fe is normally selected for material reference due to its abundance in the earth's crust. The enrichment factor expression is show in Equation (2):

$$EF = \frac{[Metal/Fe]_{Sample}}{[Metal/Fe]_{UCC}} \qquad \text{(Eq. 2)}$$

where $[Metal]_{sample}$ is the amount of metal in soil and $[Metal]_{UCC}$ refers to the concentration of the same metal in the upper continental crust (UCC). Using EF values, the contamination can be classified as follows: $EF \leq 1$ no enrichment; $1 < EF \leq 3$ minor enrichment; $3 < EF \leq 5$ moderate enrichment; $5 < EF \leq 10$ moderately severe enrichment; $10 < EF \leq 25$ severe enrichment; $25 < EF \leq 50$ very severe enrichment; and $EF > 50$ extremely severe enrichment [58].

2.7.3 Contamination factor, CF

The contamination factor (*CF*) was used to determine the overall contamination of trace elements in soil samples [59]. The contamination factor (*CF*) was calculated by Equation (3):

$$CF=\frac{M_c}{B_c} \qquad \text{(Eq. 3)}$$

Where M_c and B_c are the metals' measured concentration and background values, respectively. The contamination factor is categorized into four classes The classifications are as follows: low contamination ($CF < 1$); moderate contamination ($1 \leq CF < 3$); considerable contamination ($3 \leq CF < 6$); and $CF \geq 6$ for very high contamination [60].

2.7.4 Pollution load index, PLI

The pollution load index (*PLI*) indicates the number of trace elements concentrations in soil, which exceeds that of the background concentration in the study area [61]. The PLI is represented by the following Equation (4):

$$PLI_{site}=\sqrt[n]{CF_1 \times CF_2, \ldots, \times CF_n} \qquad \text{(Eq. 4)}$$

Where "*n*" is the number of metals under investigation and "*CF*" is a contamination factor [41]. When the value of $PLI > 1$, it indicates that pollution exists, whereas the values of $PLI < 1$ indicate a no-pollution status of the assessed soil [62].

2.7.5 Potential Ecological Risk

The potential ecological risk (PERI) was proposed by Hakanson (1980) [63]. This index emphasizes the toxicology response to trace elements. The PERI for an individual metal (E_i) is defined by the following Equation (5):

$$\mathrm{Ei} = \mathrm{Ti} \times \mathrm{CF} \qquad \text{(Eq. 5)}$$

The risk index (RI) of sampling sites was calculated using the following Equation (6):

$$\mathrm{RI} = \sum \mathrm{Ti} \times \mathrm{CF} \qquad \text{(Eq. 6)}$$

T_i is the toxic-response factor for the given trace elements (Cd = 30, Cu = Pb = Ni = 5, Cr = 2, Hg = 40 and Zn = 1) [63], [64].

2.8 Statistical analysis

2.8.1 Principal component analysis

The ACP provides a method of constructing new uncorrelated and mutually independent variables; it is a statistical technique of information synthesis, or reduction of the dimension of the number of variables.

2.8.2 Pearson's correlation

The trace elements concentrations were related to the physicochemical characteristics of tailings samples using Pearson's correlations. Parameters showing a value of $r > 0.7$ were considered strongly correlated, while values of $0.7 \geq r \geq 0.5$ were considered to exhibit a moderate correlation [65].

3. RESULTS Y DISCUSSION

3.1. Physicochemical characterization of tailings samples

Table 3 show the results obtained for the physicochemical characterization of the tailings samples present in the Andacollo center from the methods described in the experimental part. Each measurement was performed in duplicate.

Table 3. Physical chemical parameters of tailings samples. Each value is the average of two replicates

Site	pH (H_2O1:2.5)	CE ($dS \cdot m^{-1}$)	OC (%)	TOC (%)	P ($mg \cdot kg^{-1}$)	N (%)	B ($mg \cdot kg^{-1}$)	CEC ($cmol(+)kg^{-1}$)
1	2.8	3.1	3.1	5.5	16.5	< LOD	0.8	17.1
2	2.3	3.9	2.3	5.1	15.2	0.01	0.9	12.0
3	3.2	1.2	1.1	2.0	16.8	0.05	< LOD	12.2
4	3.2	2.0	1.6	3.0	16.8	0.11	0.4	9.3
5	2.8	1.3	0.9	2,.1	2.2	0.14	0.2	1.6
6	2.9	7.2	2.4	6.0	38.9	< LOD	1.7	15.1

According to table 3, all the sample sites have an extremely acidic pH; compared to the classification given by the Soil Science Society of America. Regarding electrical conductivity, the values obtained in the soil: water ratio (1: 2.5) were found within 1.2 to 7.2 dS m^{-1}, being classified as non-saline for sites 3, 4 and 5, low saline for sites 1 and 2, and moderately saline for site 6.

Numerous studies indicate that electrical conductivity is directly proportional to the concentration of dissolved salts, so its contribution comes mainly from easily oxidizable minerals which remain in solution as metal cations ($Cu^{2+,}$ $Zn^{2+,}$ $Pb^{2}+$, $Al^{3+,}$ etc.) or anions that accompany these structures (SO_4^{2-}, CO_3^{2-}, PO_4^{3-}). According to this, it could be inferred that in the places with higher electrical conductivity a higher concentration of dissolved salts should be found because heavy metals tend to be in solution when the pH of the medium decreases [66].

Table 3 shows that the highest amount of OC was found in site 1 with 3.1% followed by site 2 and 6 with 2.4%. These values would indicate a low content in the amount of "available" carbon and biologically resistant carbon that binds to the finest mineral fractions. On the other hand, the total carbon content (TOC) is not higher than the previous parameter, indicating that the carbon content, both organic and inorganic, which decomposes into CO_2 above 800 ° C, is in low quantity.

Regarding the amounts of phosphorus, and observing table 3, the highest concentration was found in site 6 with 38.9 $mgkg^{-1}$, followed by sites 1, 2, 3 and 4 with very similar values between them. The mineral concentration processes result in the tailings containing between 1.6% to 1.8% of phosphorus may be in the form of the apatite compound ($Ca_5 (PO_4)_{3)}$ (F, Cl, OH)) or also as phosphorus oxides (P_2O_5).

The nitrogen results are all similar and close to the LOD, which would indicate a low availability of this nutrient in the tailings sites. Nitrogen is required by microorganisms and acts as a limiting nutrient controlling the production of ecosystems. The low concentration of nitrogen is one of the main problems to be able to reuse the soil as reforestation sites, due to the fact that they do not present a considerable microbial activity, which prevents a self-sustaining ecosystem from being generated there, the organic matter does not degrade and the soil under the first layers are still intact and therefore the nutrients are not recycled [67].

Finally, the boron content fluctuates with values lower than LOD, for site 3, and a maximum of 1.7 $mgkg^{-1}$ for site 6. These concentrations are low because, in that particular area, the concentration is low specially because the pH acid.

CEC is related to the ability of a solid, in this case soil to absorb cations. This capacity varies depending on multiple factors. The highest CEC values were found in sites 1 and 6 and the lowest in sites 4 and 5, even so, all the values obtained for the soil are low due to the null amount of organic matter, especially humic substances, and also to the possible lack of expandable clay minerals, such as those of the smectics group [39].

On the other hand, in some mining soils an inverse relationship has been found between the low CEC of these sites with the high concentration of heavy metals, in addition to mentioning that mining activity generates strong degradation of the soils especially with regard to their CEC values [68].

3.2 Trace elements concentration in tailings.

Twelve trace elements were determined in tailings in six sites of Andacollo.

Table 4: Trace elements concentration (mg/kg), in tailings samples. Total fraction. Each value is the average of three replicates

Sites	**Al**	**As**	**Cd**	**Cr**	**Cu**	**Fe**	**Hg**	**Mn**	**Mo**	**Ni**	**Pb**	**Zn**
1	22444	0.7	0.3	1.9	574.9	12726	2.0	40.8	16.6	3.4	14.9	34.1
2	22420	0.4	0.2	1.4	776.2	21602	3.1	27.5	64.9	5.1	17.3	34.2
3	24966	1.0	0.3	5.5	558.3	40279	3.2	49.0	102.0	4.9	14.3	35.5
4	24460	0.7	0.4	9.5	803.5	33739	4.9	50.7	64.78	6.5	32.3	58.4
5	24442	0.6	0.3	1.9	294.6	37210	6.8	33.1	225.8	5.2	25.2	43.3
6	27702	0.7	0.9	4.2	6650.1	17311	7.0	309.8	68.0	11.4	17.4	115.8

LOD of the elements (mgL^{-1}): Al: 0.63; As: 0.40; Cd: 0.01; Cr: 0.08; Cu: 0.04; Fe: 0.08; Hg: 0.14; Ni: 0.08; Mn: 0.03; Mo: 0.50; Pb: 0.10; Zn: 0.01.

Table 4 shows that both Al and Fe remain relatively uniform in the different sampled sites of the tailings, due to the fact that both metals are known to be found mostly in the earth's crust. The concentration of aluminum was found in a higher quantity at site 6 and in a lower quantity at site 2. Although the concentrations do not vary significantly from site to site, this can be explained by the lithogenic character of this element, which is it is located with an approximate 7.45% of abundance in the earth's crust, occupying the third place. On the other hand, the highest concentration of iron was found at site 3 and the lowest at site 1. These high concentrations found also support the great lithogenic contribution of this element, which is why it should always be found in quantities of this magnitude. Its abundance corresponds to 4.20%, leaving it in fourth place.

On the other hand, Cu varies with each sampled site; the place with the highest concentration corresponds to site 6 and the lowest to site 5. In soils, this element occurs in its divalent state and between the range of 2 to 100 $mgkg^{-1}$, when it is not contaminated or rich in said mineral. The large amount of copper found in the tailings is due to the fact that several deposits of this mineral are located in Andacollo, so the concentrations found in mining waste become significant [69].

According to the Canadian soil quality guide (CCME) [70], the metal that would be above the norm to be found within an industrial and urban area, and that is found in its database, would be copper, since its average would correspond to 91 $mgkg^{-1}$, value exceeded in all six sites.

The highest concentration of manganese was found at site 6 and the lowest at site 2. The content of this metal can be related to a natural contribution, since this element has an abundance of 0.10% in the earth's crust. In addition, in the Andacollo commune there is a mining site that extracts manganese minerals, a product of which the waste in the area may contain mineral remains from the extractive processes [71]. In terms of zinc concentration, the highest amount was found at site 6 and the lowest at site. Copper mining, in general, is also associated with zinc minerals, which may be present in the smelting processes, finally reaching mining waste [72].

The largest amount of molybdenum was found on site 5 and the minor on site 1. This element is, between the trace elements, the scarce in nature. In some floors it has come to find values close to 30 $mgkg^{-1}$. The copper deposits in Andacollo are of the porphid type, which are, in addition to copper, an important source of molybdenum [73], which by extractive processes could reach the abandoned tailings of the area.

According to the Canadian Floor Quality Guide (CCME) [70], the metal that would be over the rule to be within an industrial and urban area, and that it is in its database, would be molybdenum, since its average would correspond to 40 $mgkg^{-1}$, value exceeded for 5 of the 6 sites studied.

Nickel amounts were quite similar, finding the highest concentration on site 6 and the lower value on site 1. Mercury had the highest concentration on site 6 and the lower concentration on site 1. This metal can be found naturally on the ground or be the result of human activity, specifically gold mines [74]. Andacollo at a beginning extracted gold in an artisanal and less scale, amalgamating said metal with mercury in the extraction processes. These processes of greater scale would favor Hg's increase in soil, and specifically in tailings of the Commune.

The most lead corresponds to the site 4 and the lower than the site 3. The amount of lead is relatively similar between the sites so it can be inferred that the concentration depends on a geogenic contribution due to the amount of minerals with this element in the zone. According to the Canadian Floor Quality Guide (CCME) [70], none of these three metals would exceed the average value delivered by the database of this organization, but, even so, mercury is one of the most toxic metals so it should be monitory continuously.

The amount of cadmium was relatively similar for all sites. The highest concentration was found on site 6 and the minor on site 2. This metal is scarce in the terrestrial cortex, so its low values would be consistent with this. The chromium concentration had its higher content on site 4 and less on site 2. Like cadmium, chromium is not very abundant in terrestrial cortex. Finally, arsenic concentration is relatively similar at all sites, with the highest value for site 3 and lower for Site 2.

3.3 Assessment of soil tailings quality

3.3.1 Geo accumulation index

The geo accumulation index obtained by site and metal is summarized in Table 5.

Table 5. Geo accumulation index values of the tailings studied Igeo were calculated in according eq. 1.

Sites	**Al**	**As**	**Cd**	**Cr**	**Cu**	**Fe**	**Hg**	**Mn**	**Mo**	**Ni**	**Pb**	**Zn**
1	0.06	0.01	0.21	0.01	2.56	0.05	1.02	9.6×10^{-3}	1.27	0.01	0.15	0.07
2	0.05	0.01	0.13	0.11	3.45	0.14	1.53	6.5×10^{-3}	4.99	0.02	0.17	0.07
3	0.06	0.02	0.21	0.03	2.46	0.26	1.62	1.0×10^{-2}	7.85	0.01	0.14	0.07
4	0.06	0.01	0.27	0.05	3.57	0.21	2.44	1.0×10^{-2}	4.98	0.02	0.32	0.12
5	0.06	0.01	0.21	0.01	1.31	0.24	3.38	$7.8 \times 10^{--3}$	17.36	0.02	0.23	0.09
6	0.07	0.01	0.78	0.02	29.56	0.11	3.49	7.0×10^{-2}	5.22	0.03	0.17	0.24

For Al, As, Cd, Cr, Mn, Ni, Fe, Pb and Zn, Igeo indicated unpolluted to moderately polluted; in all the sites. While for Cu, indicate, moderately polluted in site 5; moderately to strongly polluted; in sites 1 and 3, strongly polluted in sites 2 and 4: 5 and extremely polluted in site 6. For Mo indicated moderately to strongly pollute in site 1 and extremely polluted in the others sites. Hg indicates moderately polluted in sites 1, 2, 3 and moderately and strongly polluted in sites 4, 5 and 6.

3.4 Enrichment factor, *EF*

The enrichment factor obtained by site and metal is summarized in Table 6 according eq. 2.

Table 6. Enrichment factor values of the tailings studied. EF was calculated in according eq. 2.

Sites	**Al**	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Mn x 10^{-3}**	**Mo**	**Ni**	**Pb**	**Zn**
1	0.73	39.3	1.5	0.009	63	114	0.002	43	0.002	2.0	1.4
2	0.43	13.6	0.5	0.025	50	101	0.002	100	0.002	1,6	0.8
3	0.25	17.1	0.4	0.526	25	56	0.001	83	0.092	0.8	0.5
4	0.30	13.6	0.6	0.105	25	103	0.001	63	0.146	2.0	0.9
5	0.28	11.4	0.5	0.020	10	130	0.008	203	0.107	1.4	0.6
6	0.66	29.3	2.5	0.099	500	287	0.034	130	0.507	2.0	3.5

The range of EF values found for the metals in the 6 sites of Andacollo tailings are shown in the next table

Table 7. Metals classification in relation with EF values [75].

Range	Origen	Elements
EF < 1	Natural, Litogenic	Al, Cr, Mn, Ni all the sites; Cd and Zn sites 2, 3, 4 and 5; Pb site 3
1<EF<10	Natural and antropic	Cd and Zn sites 1 and 6; Pb sites 1, 2, 4, 5 and 6
EF>10	Important antropogenic contribution	As, Cu, Hg and Mo all the sites

The computed *EF* values in the present study indicate that the Andacollo tailings were very highly to extremely enrich with respect to As, Cu, Mo and Hg in all the sites (table 7).

3.5 Contamination factor, *CF*

The Contamination factor obtained by site and metal is summarized in Table 8 according eq. 3.

Table 8. Contamination factor values of the tailings studied. CF was calculated in according eq. 3.

Sites	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	Zn
1	0.28	0.05	1.07	0.02	12.78	0.27	5.08	0.05	6.37	0.05	0.75	0.36
2	0.29	0.03	0.67	0.02	17.24	0.46	7.65	0.08	24.95	0.07	0.86	0.36
3	0.31	0.08	1.07	0.06	12.41	0.85	8.08	0.12	39.23	0.07	0.71	0.37
4	0.31	0.05	1.37	0.11	17.36	0.71	12.23	0.06	24.91	0.10	1.61	0.61
5	0.31	0.04	1.07	0.02	6.55	0.79	16.88	0.04	86.83	0.08	1.26	0.46
6	0.35	0.05	2.87	0.05	147.78	0.37	17.43	0.36	26.15	0.17	0.88	1.22

CF values that indicated moderate degree of contamination for Al, As, Cd, Cr, Fe, Mn, Pb, Ni and Zn and *CF* values than indicated high degree of contamination for Cu, Hg and Mo.

3.3.4 Pollution load index, *PLI*

The definitions of *PLI* classes are as follows: *PLI* < 1 means that soils are in perfect condition; *PLI* = 1 means that soils are at a baseline level of quality; and *PLI* >1 means that there is progressive site deterioration [76, 77].

Table 9. *PLI* values of the tailings studied. Contamination degree calculated in according eq. 4.

	Sites					
PLI index	1	2	3	4	5	6
	1.05	1.06	1.68	2.05	1.83	2.95

All the sites shown a progressive deterioration, highlighting the sites 4, 5 and 6.

3.3.5 Potential ecological risk

Table 10. *Ei and RI* values of the tailings studied. These index were calculated in according eq. 5 and 6.

Sites	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	RI
1	5	32.1	0.04	63.9	203.2	0.25	3.75	0.36	308.6
2	3	20.1	0.04	86.2	306	0.35	4.30	0.36	420.4
3	8	32.1	0.12	62.1	323.2	0.35	3.55	0.37	429.8
4	5	41.1	0.22	86.8	489.2	0.50	8.50	0.61	631.9
5	4	32.1	0.04	32.8	675.2	0.40	6.30	0.46	751.3
6	5	86.1	0.10	738.9	697.2	0.85	4.40	1.22	1533.8

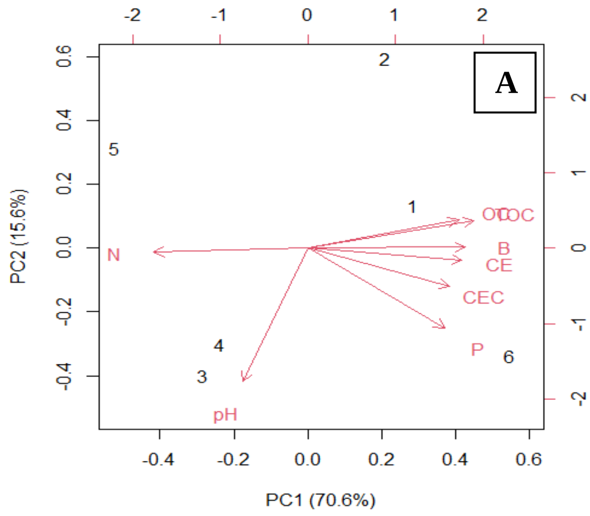
Table 11. Ei and Ri category of the tailings studied.

E_i	Category	Metals	RI	Sites
$E_i \leq 40$	Low ecological risk	As. Cr, Ni, Pb and Zn in all the sites; Cd in sites 1, 2,3,4,5;	$RI \leq 150$	
$40 < E_i \leq 80$	Moderate ecological risk	Cu in site 1, 3 and 5	$150 < RI \leq 300$	
$80 < E_i \leq 160$	Considerable ecological risk	Cd site 6, Cu site 2 and 4	$300 < RI \leq 600$	1, 2, 3
$160 < E_i \leq 320$	High ecological risk	Hg sites 1 and 2.	$600 < RI$	4, 5
$320 < E_i$	Very high ecological risk	Cu site 6; Hg site 3, 4, 5 and 6.		6

3.4 Statistical analysis

The statistical analysis of the results PCA, Cluster and Pearson Correlation will be analyzed considering the physicochemical properties of tailings and the concentration of metals

3.4.1 Principal component Analysis (PCA).



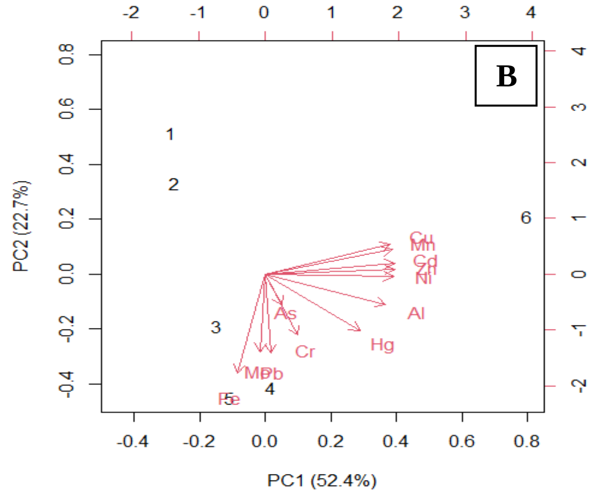


Figure 2. PCA of tailings physical chemicals characteristics (A) and trace elements concentration (B)

PCA analysis related with physicochemical characteristics of tailings (A), indicates sites 3 and 4 related to pH, while site 1 and 6 related to CO and OCD, B, EC and P. PCA analysis related with trace elements concentration (B), indicates sites 4 and 5 are important for Mo, Fe and Pb; site 6 is related with Cu, Mn, Cd and Ni.

3.4.2. Pearson`s correlations

Table 12. Pearson`s correlations related with physical chemical characteristics of tailings samples.

	pH	EC	OC	TOC	P	N	B	CEC
pH	1	-0.32	-0.42	-0.51	0.13	0.38	-0.38	-0.04
CE	-0.32	1	0.63	**0.86**	**0.87**	-0.68	**0.99**	0.56
OC	-0.42	0.63	1	**0.93**	0.49	**-0.82**	0.71	**0.81**
TOC	-0.51	**0.86**	**0.93**	1	0.66	**-0.83**	**0.91**	0.73
P	0.13	**0.87**	0.49	0.66	1	-0.66	**0.81**	0.7
N	0.38	-0.68	**-0.82**	**-0.83**	-0.66	1	-0.68	**-0.91**
B	-0.38	**0.99**	0.71	**0.91**	**0.81**	-0.68	1	0.56
CEC	-0.04	0.56	**0.81**	0.73	0.7	**-0.91**	0.56	1

Pearson`s correlations analyses show mainly positive correlations: EC-TOC; EC-P; EC-B; OC-TOC OC-CEC; OCD-B; P-B; B-TOC; B-P; CEC-OC, while negative correlations were found for: OC-N; OCD-N; N-CEC.

Table 13. Pearson`s correlations related with trace elements concentration of tailings

	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	Zn
Al	1	0.4	0.89	0.36	0.81	0.13	0.76	0.85	0.19	**0.89**	0.06	0.87
As	0.4	1	0.16	0.48	0.03	0.41	-0.1	0.11	-0.03	0.01	-0.2	0.05
Cd	**0.89**	0.16	1	0.23	**0.97**	-0.32	0.64	**0.98**	-0.15	**0.95**	-0.02	**0.99**
Cr	0.36	0.48	0.23	1	0.05	0.44	0.15	0.09	-0.17	0.27	0.59	0.25
Cu	**0.81**	0.03	**0.97**	0.05	1	-0.44	0.56	1	-0.21	**0.94**	-0.19	**0.96**
Fe	0.13	0.41	-0.32	0.44	-0.44	1	0.24	-0.39	0.68	-0.19	0.43	-0.29
Hg	0.76	-0.1	0.64	0.15	0.56	0.24	1	0.58	0.6	0.73	0.47	0.7
Mn	**0.85**	0.11	**0.98**	0.09	1	-0.39	0.58	1	-0.17	**0.94**	-0.18	**0.96**
Mo	0.19	-0.03	-0.15	-0.17	-0.21	0.68	0.6	-0.17	1	-0.04	0.33	-0.1
Ni	**0.89**	0.01	**0.95**	0.27	**0.94**	-0.19	0.73	**0.94**	-0.04	1	0.1	**0.98**
Pb	0.06	-0.2	-0.02	0.59	-0.19	0.43	0.47	-0.18	0.33	0.1	1	0.09
Zn	**0.87**	0.05	**0.99**	0.25	**0.96**	-0.29	0.7	**0.96**	-0.1	**0.98**	0.09	1

Pearson`s correlations analyses show mainly positive correlations between : Al-Ni; Cd-Al; Cd-Cu; Cd-Mn; Cd-Ni; Cd-Zn; Mn-Al; Mn-Ni; Mn-Zn; Ni-Cd; Zn-Cu; Zn-Ni.

Positive correlation between metals analyzed at different sites showed either an association/interaction between the metals or similar sources of input [78]. Strong correlation between two heavy metals may be an occurrence of strong dependence of both metals on the same causal factor [79].

CONCLUSIONS

- The average individual metal content in the studied tailings samples is ordered, from high to low, as follows: Al >Fe > Cu > Mn > Zn > Mo > Pb > Cr > Cd > Hg>Ni >As. Pearson's correlation coefficient analysis, and PCA, identified the relationship between heavy metals in tailings samples and their probable origins.

- From the evaluation of the soil pollution indices, EF, CF, Igeo, PLI, and Ei, it can be seen that the studied tailings samples show highest polluted for the concentrations of Cu, Hg and Mo and the sites more polluted were sites 4, 5 and 6.

- The results found show that the tailing under study has an important ecological risk. Studies of other tailings will be necessary, since finally these trace elements present in these tailings may affect the health of people.

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CONFLICT OF INTEREST

The authors Author declare that there is no conflict of interest regarding the publishing of this article

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