

STUDY OF THE ADSORPTION-DESORPTION PROCESS OF THE METALS: Cu, Mn, Pb and Zn IN VOLCANIC SOILS.

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ABSTRACT

The study of the processes of the adsorption – desorption of metallic trace elements or heavy metals in soils is crucial for the proposal of effective strategies for mitigation, reduction or elimination of these in natural systems.

This work presents a study of the processes of adsorption and/desorption of Cu, Mn, Pb and Zn in two Chilean soils: Alhué (VI Region, Chile) and Nueva Braunau (X Region, Chile), both of volcanic origin and agricultural use.

The soil samples studied were dried and sieved (< 2 mm or < 0.63 mm). The physicochemical characterization: pH, CE, MO, COT, N, P, CEC and texture was performed using described methods. The total fraction of each metal was obtained by microwave digestion with HNO₃ and HCl concentrated in relation 3:1. The contact time needed to reach equilibrium was determined by leaving the soil with the metal solution at different times (3, 6, 12, 24, 48 and 72 hours). The adsorption process was performed by a batch experiment, mixing different aliquots of metal solution with balancing solution (KNO₃) 0.1 molL⁻¹. Desorption was made from the 50/50 metal/balancing solution. The metals in the different soil samples and the total fraction in the soil were determined by AAS.

The distribution of the total fraction of metals in decreasing order is in Alhué soil: Mn > Pb > Cu > Zn and in Nueva Braunau soil: Mn > Pb > Zn > Cu. It was determined that the contact time at which metals reach equilibrium is 48 hours for both soils, fitting appropriately with Elovich's model.

The decreasing order of adsorption in the Alhué soil is: Cu > Zn > Pb > Mn and in the Nueva Braunau soil: Cu > Pb > Zn > Mn.

The determination of the type of adsorption was made through the application of adsorption models of Langmuir and Freundlich. Cu adjusted according to the Langmuir model on both soils. Cu and Zn conformed to Freundlich's model.

The desorption results are: Alhué soil: Pb > Mn > Zn > Cu and Nueva Braunau soil: Mn > Pb > Zn > Cu.

The negative ΔG° (Gibbs free energy change) values obtained in the present study indicate that the adsorption of metals onto soil samples is a spontaneous process and that the adsorption was an exothermic process except for Mn in both soils.

Keywords: Metallic trace elements, adsorption, desorption, Elovich model, Langmuir model, Freundlich model.

INTRODUCTION

Soils play a very important role in the environment as, among other important functions.

They control the mobility of pollutants like metallic trace elements or heavy metals mainly through sorption process directly related to the partitioning between the solid phase and soil solution [1, 2].

Soil is not only a geochemical receptor for pollutants but also acts as a natural regulator that controls the transport of chemicals and substances to the atmosphere, hydrosphere and biota. Soil contamination occurs when an element or substance is present in concentrations greater than natural ("background") as a result of human activity and has a negative effect on the environment and its components. However, there may be soils that their natural baseline is already altered, which would not allow establishing a parameter to determine how contaminated the soil could be, due to anthropic causes. Heavy metals can be geogenic in nature, that is, they come from natural processes of weathering of rocks and biogeochemical cycles, among these are volcanic eruptions and dissolution by rainwater among others; or they can be of anthropogenic origin, deriving from industrial, mining and agricultural activities. The origin of the latter can turn them into potential contaminants for water, air and soil.

Although several environmental factors influence the soil capacities for adsorbing heavy metals, colloidal soil constituents are the final agents determining soils act as sinks or sources of contamination.

Mobility of metals in soils is of special concern as although some of them can play important roles in biological processes, when concentrations are above certain thresholds mainly due to anthropogenic sources, all can pose significant risks to ecological receptors and human health [3–6] or contaminate ground water by leaching [7]. In addition, soil characteristics like: pH dissolved organic matter, ionic strength or the nature and number of different metals present also influence the extent of the adsorption capacity of soils [5, 8–12]. The mineral and organic colloidal particles of the solid phase are the most active soil components in the adsorption processes nevertheless, their high heterogeneity and variability among soils makes their exact role during heavy metal adsorption remains not clearly understood [3, 5, 13–16].

The environmental interest in heavy metals in agricultural soils is related to their cumulative nature, their persistence, their ability to inadvertently

accumulate in the soil profile up to toxic concentrations and their interaction with different soil properties that determine their accumulation, mobility and bioavailability towards other components of the ecosystem [17]. Metals accumulated on the soil surface can be slowly lost through leaching, assimilation by plants, runoff and erosion.

Bioavailability is the degree of freedom in which an element or compound of a potential source is found to be captured by an organism. The distribution of heavy metals in soil profiles as well as their availability is controlled by intrinsic properties intrinsic metal and soil characteristics [18]. Metals tend to accumulate on the soil surface and are accessible for assimilation by plants [19].

The abundance of metallic elements in the earth's crust does not exceed 0.01%, which is why they are sometimes called trace metals. It is possible to classify trace metals into two large groups: essential and non-essential. In the first, trace elements or micronutrients stand out, which are required in small quantities or quantities traced by plants and animals, because they allow completing the life cycle of organisms. However, when these trace elements exceed a certain threshold they become toxic. In this group are: Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni) and Zinc (Zn).

The second group is those that lack biological function, since their presence in minute quantities in living beings, including humans, can cause serious organic dysfunctions also turn out to be highly toxic and can accumulate in living organisms. To this category belong: Cadmium (Cd), Mercury (Hg), Silver (Ag), Arsenic (As) and Lead (Pb) [20]. As is not considered a heavy metal, but a metalloid, however, it is often included in this classification.

Plants grown in contaminated soils generally absorb more trace elements and the concentration of these in plant tissues is often directly related to their abundance in soils, and especially in soil solution; excessive concentrations of metals in the soil could impact the safety of crop production and the health of the environment, as these move through the food chain through the consumption of plants by animals and these in turn by humans [21].

The bioavailability, mobility of metals in soils, and their subsequent leaching into groundwater, depends on their characteristics physicochemical such as pH, electrical conductivity (EC), texture, organic matter (OM), total organic carbon (TOC), available phosphorus, nitrogen determination, presence of anions and cation exchange capacity [22].

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As indicated above, one of the most important characteristics of heavy metals is their persistence, which means that they can move through the different components of the trophic web and also bioaccumulate. The effect of heavy metals on the life of soil microorganisms and on major biological processes such as degradation of organic matter, nitrogen fixation, respiration is of consideration. Microorganisms are more sensitive to heavy metal stress than soil animals or plants [23].

Most of the ecological risk is associated with heavy metals that are biologically available for absorption. Heavy metals are not degraded in soils. The risk to human health and ecosystems depends on the solubility and bioavailability of the metal in the soil, therefore, the chemical immobilization of these pollutants would reduce the ecological risk [24]. The accumulation of heavy metals in agricultural soils is a risk to the life of organisms and human health; its negative effects depend on the concentration of the metal and the specific properties of the soil [25].

To evaluate the environmental impact of these polluting substances, research has been carried out for many years on this problem and its correlation with the levels found under normal conditions, which has allowed the identification of contaminated soils from the identification of contamination threshold criteria. These have made it possible to differentiate between the concentrations of these elements in a natural soil and one altered by the one altered by anthropogenic activity, its level of risk, who it affects, the level of tolerance and recovery priorities [26].

The adsorption process corresponds to a phenomenon by which a species is extracted from one phase and concentrated on the surface of another, usually a solid phase [27]. In soils, this process is attributed to the interactions between the active surface of solid particles and adsorbate (chemical species present in soil solution). The interactions that occur can be of two types, physical adsorptions or physisorption and chemical adsorptions or chemisorption. Physical adsorption results from the secondary (weak) attractive forces that occur between the particles, within which are the Van der Waals forces and the dipole-dipole interactions such as hydrogen bonds (Physisorption energy $< -25 \text{ kJmol}^{-1}$) [28]. On the other hand, chemisorption is characterized by the formation of chemical bonds. This interaction results in a chemical interaction between the adsorbate and hydrogen bonds (physisorption energy $< -25 \text{ kJmol}^{-1}$). Adsorption depends on a favorable interaction ("affinity") between a substance (adsorbate) and a surface (adsorbent). For example, when a molecule, of a gas, is adsorbed on the surface of a solid, there is a decrease in the degrees of freedom that the molecule has so that the entropy is reduced.

The adsorption phenomenon is generally described by curves called adsorption isotherms that represent the amount of compound adsorbed per gram of soil as a function of the concentration in the equilibrium of the adsorbate at a constant temperature [29]. If the adsorption process is to be favorable, the enthalpy change must be negative. For this reason, all adsorption processes are exothermic. When the isotherm is linear, it does not change the adsorption surface, whereas, when it is not favorable, that "affinity" does not adsorption. The degree of adsorption processes depends on some soil characteristics such as pH, organic matter content, type and percentage of clays, the nature of the metal and competition with other metals [30-32]. There are also other influential properties of soil in adsorption processes such as carbonate content and cation exchange capacity [33; 34].

For example, both Cu and Pb are more soluble in acidic than basic pH soils; its mobility and bioavailability in acidic soils will depend mainly on the ability of solid soil components to capture and immobilize the metal in different forms. In general, the adsorption capacity increases with increasing pH, as well as with organic matter, which tends to adsorb more metal as the pH rises [35; 36].

Desorption is a phenomenon that occurs when the exchange sites (or assets) in the soil are saturated, or there is a washing of this, which causes the metal to be bioavailable and also have freedom to move through the soil, a fact that generates a problem, since the contaminant potential can be released in large quantities towards other systems, causing expansion through the food web. When this occurs, the response or adverse effect that occurs in biological systems can cause damage to structures, functions, deaths, among others, causing a possible environmental problem.

Due to this phenomenon, the adsorption process is essential when it comes to immobilizing in the soil an element that could be toxic. There are several factors that affect the speed of the adsorption phenomenon, such as the concentration of the reactants, the temperature, the existence of catalysts and the contact surface of the reactants.

In the case of organoclays, the active sites are located on the external surface and interlaminar space, so it can be assumed that the adsorption rate depends on both external mass transport and interparticular transport.

In the first mechanism the solute molecules are transferred from the solution to the surface of the organoclay and in the second the molecules diffuse into the interlaminar

The kinetics of the adsorption process allows determining the amount of adsorbate that is recovered in a set time [37], which is why the Elovich kinetic model is used, [38]. This model was applied for many years for the interpretation of the chemisorption of a gas by a solid, being suggested as the best available procedure to describe the kinetics of chemisorption.

This model considers an exchange of species on the surface of the solid, where the active adsorbent sites are heterogeneous. This causes the Activation Energies to be different, due to second-order reaction processes. In a special way this model is applied to establish the contact time at which equilibrium is achieved in the interaction between an adsorbent and an adsorbate.

The study of the adsorption-desorption processes of heavy metals in soils is crucial in the proposal of effective strategies for mitigation, reduction, or elimination of these toxins in natural systems. [39].

The results of various investigations have concluded that the retention capacity of metal by soil components can be described by means of adsorption isotherms, and is the parameter on which the leaching of metal in the soil depends. Hence the importance of knowing the type of adsorption that occurs in the soil to predict the mobility of heavy metals [40].

In this work we studied the influence of the physicochemical characteristics of soils in the adsorption - desorption of metals Cu, Mn, Pb and Zn.

MATERIALS AND METHODS

Soil samples: The soils that will be studied in this work correspond to two soils of volcanic origin and agricultural use. The first is a soil of the VI Region and belongs to the Alhué series (Latitude: -34.0370862; Longitude: -71.0844986206835) and the second is a soil belonging to the X Region corresponds to the New Braunau series (Latitude -41.3233; Longitude -73.0808).

Sample Preparation: The collected samples were sieved to two different fractions, fraction $< 2 \text{ mm}$. for the physical-chemical characterization and fraction $< 63 \mu\text{m}$, for the determination of metals.

Material preparation: The material used for the sampling and the analysis of the samples in 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 (HNO₃) 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.

Reagents and solvents: Only analytical grade chemicals were used in the study. Aqueous solutions of the metals were prepared from Titrisol standards (Merck). All the reagents solids were Merck p.a. acid HNO₃, HCl and HF suprapur Merck

Chemical analysis: Trace elements concentrations were determined by flame atomic absorption spectrometry (AAS), using a Shimadzu atomic absorption spectrometer (model AA-6800) with an air-acetylene flame. Operational conditions were adjusted to yield optimal determination. Quantification of the metals was based upon calibration curves standard solutions for the respective metals. To verify the accuracy of the data obtained, recovery experiments were performed using standard solutions.

Physicochemical Characterization of soils [41].

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).

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 [41].

Soluble Organic Carbon (SOC): For the preparation of the digestion with potassium dichromate, the Walkley and Black [42], 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 $0.1667 \text{ mol}\cdot\text{L}^{-1}$ 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 $1.0 \text{ mol}\cdot\text{L}^{-1}$ using a platinum electrode (Hanna HI 3831 B).

Available Phosphorus: For the determination of available phosphorus in acidic soils, the Bray and Kurtz [44] 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).

Kjeldahl Nitrogen: For the determination of total nitrogen, the Kjeldahl digestion procedure [42], 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 $0.01 \text{ mol}\cdot\text{L}^{-1}$ HCl until the color changes from green to pink (Digetro VELP® Scientifica, modelo DK 6; Destilador (VELP® Scientifica model UDK 127).

Cation Exchange Capacity (CEC): For the determination of the CEC, in soil, 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 [42].

Texture, by Bouyoucos method: 50 ± 0.01 grams of soil were massed, 500 mL of distilled water and 20 mL of sodium hexametaphosphate solution (Merck p.a.) were added, the solution was stirred for 15 minutes, then the solution was quantitatively transferred to a 1 L cylinder and made up to the mark with distilled water. The specimen was covered with parafilm and shaken manually for one minute. Afterwards it was left at rest for 4 minutes; the temperature (T1) and the

hydrometer reading (L1) were measured. After two hours, the temperature (T2) and the hydrometer reading (L2) were measured again.

Analysis of trace elements in the soils

The trace elements analyzed in this study were: As, Cu, Mn, Pb and Zn.

Digestion: To perform the digestions of the total fraction of the metals in sediment, microwave oven MarsXpress 5 was used, equipped with tubes of Teflon PFA of 55 mL, protective sleeves of kevlar and an Xpress temperature sensor. This digestion allows greater control over the sample temperature and the heating rate than that of the heating plates. This digestion facilitated in closed containers ensuring that the trace analyses are accurate and precise. The total fraction was obtained by digesting 0.25 g of sediment with 10 mL of nitric acid (suprapur Merck) in a microwave oven (MarsX press) using the following conditions power 800 W; tower 100-5; time 11 min.; temperature 175 °C, maintenance 15 min.; cooling 15 min. This was based on EPA method 3015 [45], finally, the samples were kept cold (4 °C) for posterior analysis.

Chemical analysis: Trace elements concentrations were determined by flame atomic absorption spectrometry using a Shimadzu atomic absorption spectrometer (model AA-6800) with an air-acetylene flame. Operational conditions were adjusted to yield optimal determination. Quantification of the metals was based upon calibration curves standard solutions for the respective metals.

Equilibrium time or contact time determination in Alhué and Nueva Braunau soils.

1 ± 0.0001 g of each soil (<2 mm) was massed in polyethylene jars, then 10 mL of the standard $10 \text{ mg}\cdot\text{L}^{-1}$ of Cu, Mn, Pb, Zn was added separately and each jar was shaken at a speed of 100 rpm in the times: 3, 6, 12, 24, 48, 72 hours. The test was performed with duplicate for each floor and each metal. After the stirring time, it was centrifuged at 3,500 rpm for 30 minutes, the supernatant was stored and the settled material was discarded. The supernatant was filtered with $0.45 \mu\text{m}$ PVDF membranes and stored in a refrigerator until further analysis by AAS.

Adsorption curves of Cu, Mn, Pb and Zn in Alhué and Nueva Braunau soil.

A set of 11 bottles was prepared for each model under study, in each of them 1 ± 0.0001 g of soil (<2 mm) was massed, then added from a volume of 10 mL for the bottle labeled as 1 to a volume of 0 mL for flask 11 of the balancing solution, necessary to maintain the ionic strength of the solution, a volume of 0 to 10 mL of the corresponding standard metal solution of $10 \text{ mg}\cdot\text{L}^{-1}$ was subsequently added from flask 1 to flask 11, so that each resulted in a final volume of 10 mL. Once the bottles with the solutions were ready, each sample was stirred for 48 hours at 100 rpm. After the stirring time, each solution was centrifuged at 3,500 rpm for 30 minutes; the supernatant was extracted, filtered with $0.45 \mu\text{m}$ PVDF membranes and stored, until its subsequent analysis in the EAA equipment. The study was carried out in both soils with duplicate and each metal separately also with duplicate.

Desorption study of Cu, Mn, Pb and Zn

Desorption is usually measured after adsorption and is based on the sequential extraction of the metal with the balancing solution. To do this, the vials used in the adsorption study were saved. The flasks used in the adsorption study of metals containing equal volume of balancing solution and metal, samples corresponding to the bottle labeled with tube 6. The residual soil is dried at 50 °C for 1 hour and 30 minutes, transferred quantitatively to a plastic glass and chewed. Subsequently, it is transferred to a bottle and 3 mL of the $0.1 \text{ mol}\cdot\text{L}^{-1}$ KNO_3 solution is added, allowed to shake for one hour, centrifuged for 30 minutes at 3,500 rpm on the supernatant and collected in a pp vessel, the process was repeated 3 times. It is filtered with PDVF membranes of $0.45 \mu\text{m}$ pore and received in a 10 mL gauging flask, the remaining volume is completed with deionized water. Each sample is kept refrigerated until further analysis by AAS.

Data processing

Elovich model: This process allows determining the amount of adsorbate that is recovered in a set time [46]. To apply the model, the adsorbed concentration

(Cs exp.) is plotted as a function of Ln of the stirring time (Ln (t)), from which a logarithmic equation (equation 1) is applied from which the value of Cs.

$$Cs = 1 / b \text{Ln} (ab) + 1 / b \text{Ln} (t) \quad (\text{eq. 1})$$

Through this model it is possible to establish whether the experimental and theoretical data obtained have a correlation. To determine if the adjustment made by the kinetic model is good, analyze two experimental parameters: $R^2 > 0.8$ and relative error (RE) $< 10\%$,

Adsorption parameters: Soil sorption was characterized by the partition constant (kd) mL/ μg , [47, 48]. The sorption coefficient (kd), was defined by equation 2.

$$kd = Cs/Ce \quad (\text{eq. 2})$$

The linear or distribution coefficient (Kd), is related to soil organic carbon (OC) and soil organic matter (OM) by the following equations.

$$\%OC = \%OM / 1.724 \quad (\text{eq. 3})$$

$$KOM = 100 \times Kd / (\%OC) \quad (\text{eq. 4})$$

$$KOC = 100 \times Kd / (\%OC) \quad (\text{eq. 5})$$

Gibbs or free energy change: The standard Gibbs or free energy change of adsorption (ΔG) from the Freundlich isotherm can be calculated using the following relation [49, 50].

$$\Delta G = -RT \text{Ln} KOM \quad (\text{eq. 6})$$

Where, R is the gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is the Kelvin temperature (303 K).

Adsorption models

Langmuir model: This model can be applied to metals in soils, and determines the saturation of the available sites. The expression for the model is given by the following equation:

$$Q_0 = C_e / (C_s) = 1 / bX_m + C_e / X_m \quad (\text{eq. 7})$$

Where, C_s (mg g^{-1}) is the amount of pesticide adsorbed per unit mass of adsorbent, C_e (mg L^{-1}) is the equilibrium solution concentration, X_m is the adsorption capacity and b is a constant related to the energy of link between adsorbent and adsorbate.

The Langmuir parameter (R_L), calculated through the affinity constant (b), is also called: "equilibrium parameter" or "separation factor", where depending on the value of R_L , the equation is as follows:

$$R_L = \frac{1}{(1+bC)} \quad (\text{eq. 8})$$

$C = 10 \text{ mg L}^{-1}$, maximum adsorption concentration and b is the binding energy associated with adsorbent and adsorbate. Adsorption can be classified as: irreversible, if $R_L = 0$; favorable, if $0 < R_L < 1$; linear, if $R_L = 1$; unfavorable, if $R_L > 1$ sites [51].

Freundlich model: The metal concentration in the soil and soil solutions were fitted to the linearized Freundlich sorption isotherm, equation (9).

$$\ln Cs = \ln kd + 1/n \ln C_e \quad (\text{eq. 9})$$

Where C_s is the concentration of metal adsorbed in soil (mg kg^{-1}), C_e is the concentration of metal in soil solution (mg mL^{-1}); and kd are constant. The value $1/n$ is the energy distributions of the adsorption site [52].

Temkin model: The Temkin isotherm model assumes that the heat of adsorption decreases linearly in all layers of the adsorbent due to possible adsorbate/adsorbent interactions, and this adsorption is characterized by being uniform over the entire contact surface. Its application is determined by the following equation.

$$Cs = B \text{Ln} A + B \text{Ln} Ce \quad (\text{eq. 10})$$

Where C_s is the concentration adsorbed in the soil; C_e the concentration of adsorbate at equilibrium; B is Temkin's constant (kJ mol^{-1}). When Temkin's constant B is less than 8 (kJ mol^{-1}) it indicates that there is a non-weak interaction between the metal and the soil, therefore adsorption does not occur on hetero-surfaces. [53].

RESULTS AND DISCUSSION

The following table (table 1) shows the results related to the characterization of both soils.

Table 1. Characterization of physicochemical parameters of soil Alhué and Nueva Braunau.

Parameter	Alhué soil	Nueva Braunau soil
pH	5.70 \pm 0.14	4.55 \pm 0.07
CE (dS/m)	0.12 \pm 0.01	0.22 \pm 0.01
COT (%)	5.70 \pm 0.10	12.91 \pm 0.29
MO (%)	3.57 \pm 0.03	9.77 \pm 0.04
P available (mg/kg)	8.25 \pm 0.02	13.88 \pm 0.12
N kejdhall (%)	0.10 \pm 5.0 10^{-7}	0.38 \pm 2.3 10^{-6}
CIC (cmol(+)/kg)	6.31 \pm 0.43	20.10 \pm 0.10

The Alhué soil has a higher pH than the Nueva Braunau soil, which is consistent with its rainfall and drainage characteristics of region. For a neutral or weakly acidic pH, alkaline earth ions, mainly calcium and magnesium, predominate in the solution, and for acidic pH, hydrogen and Al (III) ions dominate in the solution. The availability of nutrients is higher at neutral or weakly acidic pH [54], because at low pH solubilization of metals occurs, increasing its concentration in the soil solution, thus its bioavailability [17; 50]. As for the EC, both Alhué and Nueva Braunau have their conductivities typical of non-saline soils suitable for use in agricultural activities [55]. The EC of Nueva Braunau greater soil is greater than the Alhué soil.

The relationship of MO to metals is important because the carboxylate groups (COO^-) of organic matter form stable complexes with metals; It also plays a very important role in determining soil fertility, it serves as a source of food and energy for microorganisms, participates in different edaphic chemical processes and affects the chemical properties of the soil. Among the important chemical processes involved in OM is the supply of nutrients by mineralization, in particular the release of N, P, S and micronutrients available for plants and also in cation exchange capacity.

According to what was obtained in the analysis, the Alhué soil has a low percentage of Organic Matter (OM) and CEC, which means that the formation of complexes between the OM, metal is low as well as the exchange of cations, so these parameters would not have as much influence on the retention of the metal in the soil colloids. The available P and total N are in mean values, so based on the results obtained, it can be said that it is a little fertile soil. The Nueva Braunau soil, on the other hand, has a higher percentage of OM and also in the CEC remaining in both parameters in the middle range, so unlike the Alhué soil, it would have greater formation of complexes between MO – metal and also greater exchange of cations, allowing a better adsorption of the metal by contribution of these components. On the other hand, the values of OM and CEC are related to the high content of P and the highly rich percentage of total N, which compared to what is obtained for the Alhué soil are higher. With the aforementioned it is possible to establish that the Nueva Braunau soil is more fertile than the Alhué soil. The result of this characterization agrees with what was expected regarding the topography, geographical location and plant formation of the respective soils.

Phosphorus and nitrogen in the soil are important since the former is that the first is used as an energy source in biochemical processes, on the other hand the availability of nitrogen is of great importance for plants, which absorb nitrates and ammonium that they use in the synthesis of proteins and synthesis of other organic components. The amounts of N present in the soil are controlled, in particular, by climatic conditions and vegetation, the latter also affecting, in the local conditions of topography, on the parental material, in the activities of man and in the time that these factors have acted on the soil.

CEC is a chemical property from which it is possible to infer about the type of clay present, the magnitude of the nutritional reserve and the degree of weathering of the soils. Controls the availability of nutrients for plants, also determines the role of the soil as a natural scrubber by allowing retention of contaminants incorporated into the soil; the main exchangers are clays and OM as both have colloidal properties. The higher the CEC of a soil, the more exchange sites the colloidal fraction of the soil will have, which will be available for greater adsorption and possible immobilization of metals [52].

The % of TOC, is higher in the New Braunau soil, which is consistent with the result obtained from OM, since the % of OM is higher in this soil, therefore it is expected that when analyzing the total organic carbon, this is higher in New Braunau than in Alhue soils.

Texture is the most important physical property of soil, it is stable over time, non-modifiable at the agricultural scale and essentially affects all other physical properties and many chemical and biological properties correlate with it. Among the influences that texture has on the soil and in agronomic practices, the fertility and content of organic matter is found, in the tillage of the soil, irrigation, permeability and porosity of the soil and in the adaptation of some crops [53].

The texture was determined by the Bouyoucos method and classified according to the textural triangle. The determination of texture for both soils turned out to be sandy loam, however, according to the percentages of Sand, Silt and Clay obtained for each soil, it has to be Alhue has a moderately thick texture, while New Braunau has a thick texture. This implies that metals could be retained mostly in the Alhue soil because it has a higher percentage of clay than the New Braunau soil.

Table 2. Texture of alhue and Nueva Braunau soils

Soil	Sand (%)	Loam (%)	Clay (%)	Texture (USDA)
Alhué	73.82	13.09	13.09	Sandy loam
Nueva Braunau	81.53	11.84	6.63	Sandy loam

The determination of texture for both soils turned out to be sandy loam, however, according to the percentages of Sand, Silt and Clay obtained for each soil, the Alhue soil has a moderately coarse texture, while New Braunau presents a coarse texture which implies that metals could be retained mostly in the Alhue soil because it has a higher percentage of clay than the New Braunau soil.

Concentration of heavy metals (total fraction).

In the next table is shown the concentration of the metals Cu, Mn, Pb and Zn in the Alhue and New Braunau soils.

Table 3. Concentration obtained from the total fraction of metals under study for Alhué and Nueva Braunau.

Soil	Cu (mgkg ⁻¹)	Mn (mgkg ⁻¹)	Pb (mgkg ⁻¹)	Zn (mgkg ⁻¹)
Alhué	68.03 ± 6.27	398.00 ± 8.84	72.58 ± 7.37	64.95 ± 9.85
New Braunau	91.56 ± 2.96	648.20 ± 2.79	180.20 ± 1.71	135.10 ± 2.70

Based on these data, [54, 55], it can be said that the concentrations of Cu, Mn Pb and Zn in the Alhué soil would be within the typical ranges for uncontaminated soils; for the soil New Braunau Cu, Pb and Zn would be in typical concentrations for uncontaminated soils, while Mn is above the maximum limit, being according to Kelley's references classified as a soil with light contamination (500–1000 mgkg⁻¹). The distribution of metals in Alhue soil is in the following order: Mn > Pb > Cu > Zn; while in New Braunau soil the order is: Mn > Pb > Zn > Cu, the highest concentrations were found for Mn and Pb in both soils.

Although the Mn in the New Braunau soil has a concentration that exceeds the limit for uncontaminated soil, its majority presence could be explained because the Mn is fixed on the positive surface of the cations of exchange and as it is possible to observe in Table 1 the CEC is almost three times higher in New Braunau, so there is a greater possibility of fixing the Mn.

On the other hand, pH is also an important factor in Mn retention, since decreasing the pH value increases the concentration of Mn (II) ions available to plants in the soil solution. The high Pb content in the total fraction can be explained in addition to its natural content by pesticide; while the presence of Cu and Zn in soils can come from pesticides, also from manure or slurry.

Determination of contact time.

The contact time is determined by plotting the variation of the concentration of metal adsorbed in the soil as a function of time. In la the equilibrium times for Alhue and New Braunau soil are shown with each metal under study. It is equilibrium time of each metal occurs after 48 hours of agitation. This study was necessary for the subsequent study of adsorption-desorption of the metals Cu, Mn, Pb and Zn in soils, since it establishes the equilibrium time, that is, time that is required for the adsorbate-adsorbent interaction to reach a stability with which the available sites of the adsorbent are saturated with adsorbate molecules.

Application of the Elovich Kinetic Model.

The correlation coefficients of the Elovich kinetic model allow establishing whether the adsorption kinetics of the study can be described by this model. To determine whether it is possible to apply Elovich to the study, the experimental data had to be adjusted using a logarithmic equation (eq 1). The calculation using this model allows comparing the experimental and theoretical data, obtained. To apply the model, the relationship of the of the adsorbed concentration Cs (Exp.) as a function of Ln of the stirring time, from this a logarithmic equation was obtained. In which when replacing the value of Ln of the stirring time, the value of Cs (calculated) was obtained. With the the Cs (Cal) graph was made as a function of Ln (t), obtaining a new fitted logarithmic equation. To check the effectiveness of the adjustment made to the experimental values using the Elovich equation, two parameters were analyzed: R² (correlation coefficient) and ARE that differentiates between the experimental values and those obtained from the model. These parameters will indicate a good fit and that the adsorption kinetics would be according to the Elovich model if R² > 0,8 and ARE < 10% (table 3), eq 1.

Table 4. Values of R² and %ARE calculated from the adjustment of the Elovich Model for both soils (values calculated according eq 1).

Soil	Parameter	Cu	Mn	Pb	Zn
Alhué	R ²	0.96	0.99	0.96	0.96
	% ARE	0.79	1.52	0.01	1.70
Nueva Braunau	R ²	0.96	0.96	0.96	0.96
	% ARE	0.15	0.06	0.34	0.23

According to what was obtained in Table 4, it is possible to affirm that the determination of the equilibrium time of the metals Cu, Mn, Pb and Zn in the Alhue and New Braunau soils conform to the Elovich Kinetic Model, because for all cases the correlation coefficient (R²) is greater than 0.8 and the relative error (ARE) is less than 10%, Therefore, the adsorption rate can be described through this model.

Adsorption processes

Adsorption isotherms: It is important to know the type of adsorption that occurs in the soil, because based on this; it is possible to predict the mobility of metals through the soil. Adsorption can be described by adsorption isotherms, which are obtained from the graphical representation of the adsorbed concentration (Cs) vs equilibrium concentration (Ce). Figure 1 shows the adsorption curves in both soils

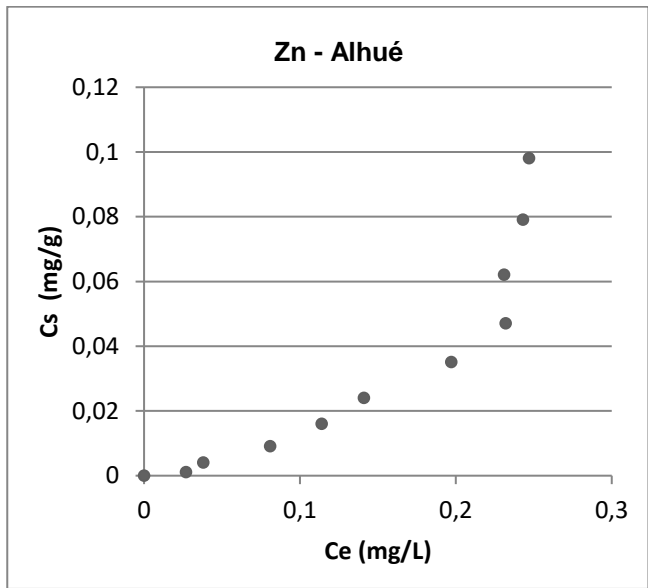
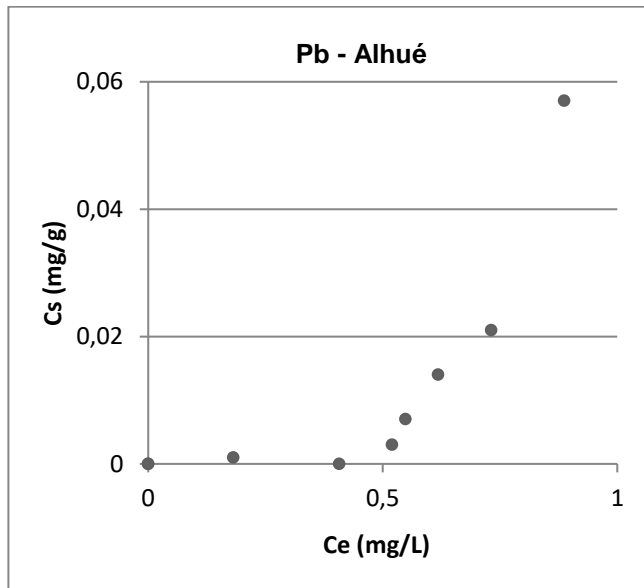
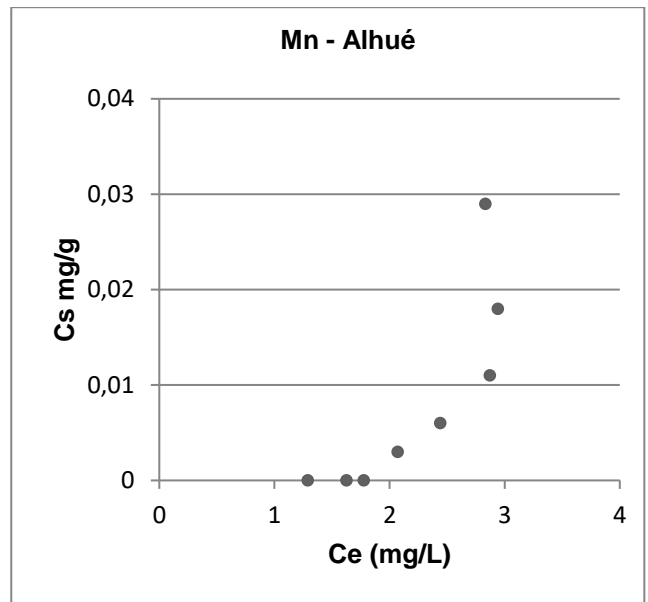
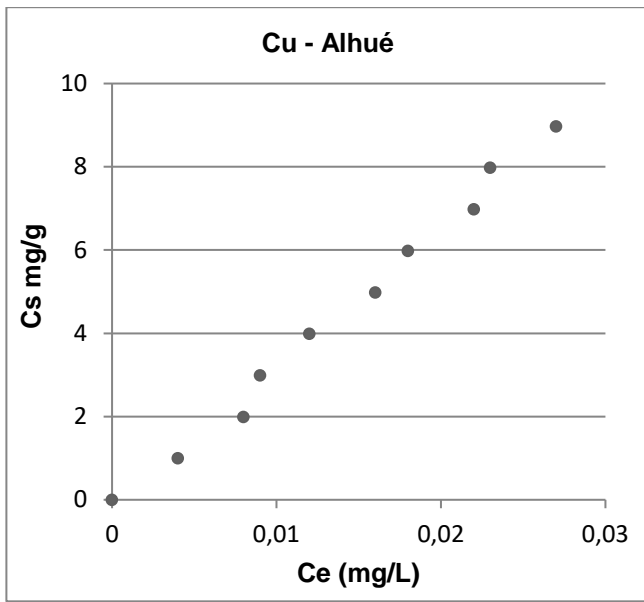
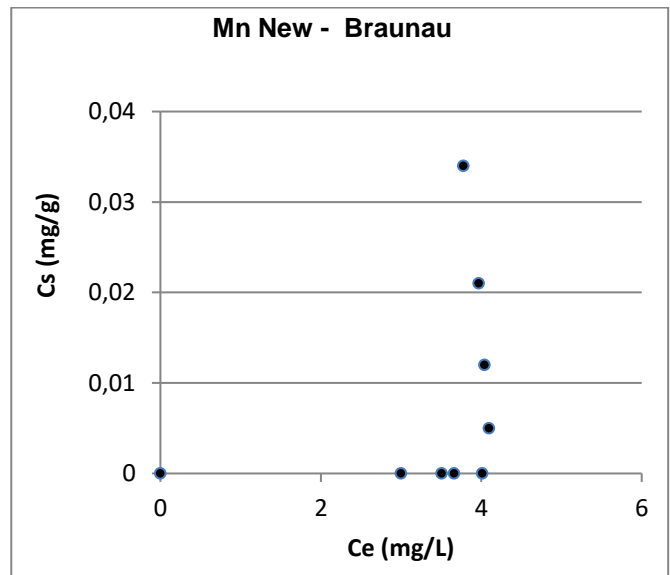
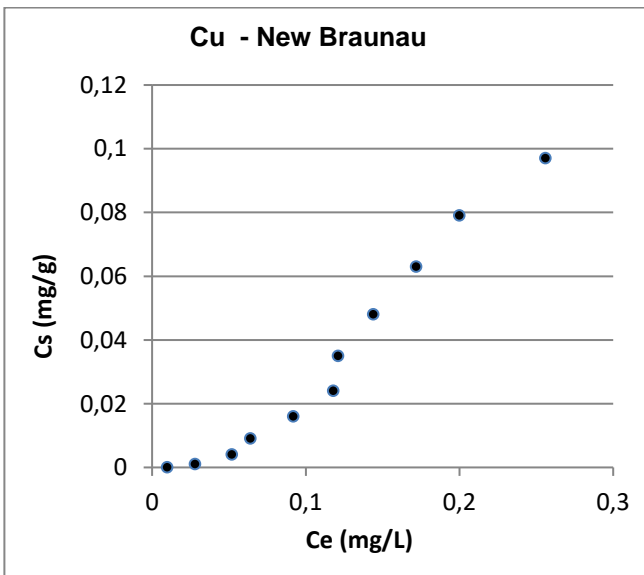


Figure 1. Sorption isotherms of Cu, Mn, Pb and Zn in Alhue Soil



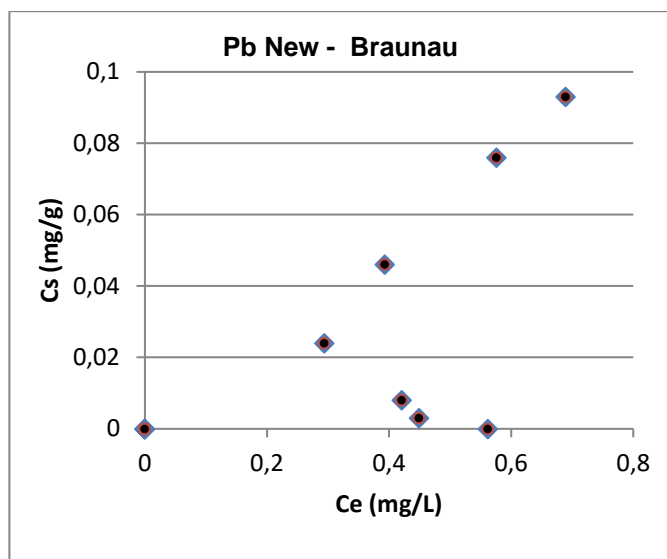


Figure 2. Sorption isotherms of Cu, Mn, Pb and Zn in New Braunau soils

By comparing the adsorption isotherms of the metals Cu, Mn, Pb and Zn for the Alhue and the New Braunau soil, with the general types of adsorption curves, it is possible to determine that: in Alhue soil, Cu, Mn, Pb and Zn present adsorption with an unfavorable trend: For the New Braunau soil, the adsorption isotherm of Cu has a favorable adsorption, Zn shows an unfavorable adsorption. Mn and Pb do not agree with any kind of general representation of isotherms [56].

Determination of Kd and Koc parameters.

Table 6. Average values of Kd and Koc of Cu, Mn, Pb and Zn calculated for the Alhue and Nueva Braunau soil. The value corresponds to the average of two measurements. Preparation 50/50 (values calculated according eqs 2, 3 and 4)

Soil	Cu		Mn		Pb		Zn	
	Kd	Koc	Kd	Koc	Kd	Koc	Kd	Koc
Alhue	1.56	75.48	0.004	0.19	0.03	1.45	0.17	8.36
Nueva Braunau	0.21	3.70	0.001	0.02	0.08	1.45	0.06	1.06

The distribution coefficient, Kd, represents the mobility of heavy metals in the soil, thus indicating the ability of the soil to retain a metals. According to the values observed in the table 6, it could be indicated that Cu is the metal sorbed the solid phase in both soils, this affinity being greater in Alhue soil.

As the constant Kd is very dependent on the characteristics of the soil, a form is used that allows normalizing the values according to the characteristics of the soil studied, that is, considering the organic carbon content thus establishing a new constant called Koc. Koc is a parameter that measures the tendency of a compound to be adsorbed by the organic fraction of the soil.

High Koc values indicate a greater affinity of metals with the organic fraction of the soil, while lower Koc values would indicate less interaction with this fraction, therefore higher migration speeds [57]. It is possible to establish that for the four metals under study: Cu, Mn, Pb and Zn, a weak Koc is found in both soils, which means that the metals could be weakly fixed to organic matter.

The order of adsorption of the metals, according to the distribution coefficient of the metals is for the Alhue soil: Cu > Zn > Pb > Mn and for the New Braunau soil, the order is: Cu > Pb > Zn > Mn, considering the contribution of organic carbon in Alhue soil is: Alhue is: Cu > Zn > Pb > Mn, while in New Braunau soil it is: Cu > Pb > Zn > Mn. Based on these results, it is possible to say that metals have the same tendency as Kd to be adsorbed in soils with the contribution of organic components, Cu in both soils being the most important metal.

Discussion of adsorption models used: Table 7 shows a summary of the relevant constants of each model: Langmuir (RL), Freundlich (KF) and Temkin (B).

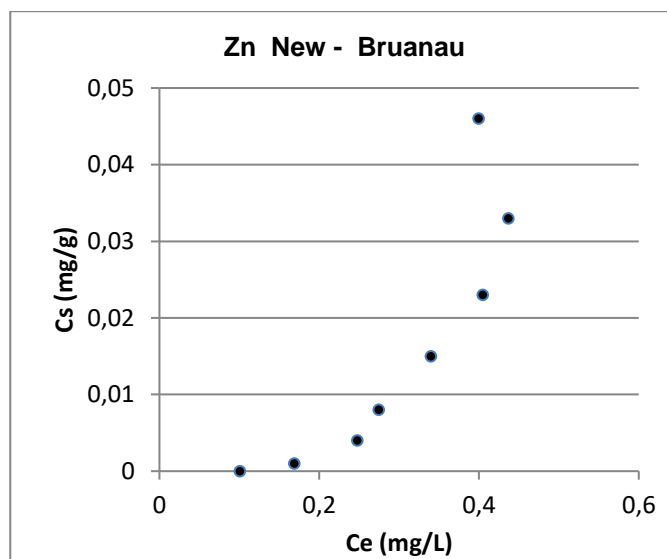


Table 7. Summary of parameters corresponding to the models applied for the four metals in both soils.

Soils	Metal	Models					
		Langmuir		Freundlich		Temkin	
		RL	R ²	K _F	R ²	B (kJmol ⁻¹)	R ²
Alhue	Cu	0.003 – 0.03	0.97	371.54	0.99	0.04	0.78
	Mn	*	0.67	*	0.92	0.03	0.61
	Pb	*	0.73	*	0.86	0.03	0.46
	Zn	*	0.79	1.20	0.97	0.03	0.67
New Braunau	Cu	0.83 – 0.98	0.89	2.63	0.98	0.3	0.67
	Mn	*	0.09	*	0.80	0.04	0.10
	Pb	*	0.03	*	0.00	0.06	0.17
	Zn	*	0.74	1.23	0.96	0.03	0.61

*: Model not applied

Langmuir's model describes adsorption isotherms that occur on homogeneous surfaces, where particles do not interact with each other. For this model, the constant RL (0 - 1) describes the maximum adsorption capacity of an adsorbent by an adsorbate. According to the RL values, Cu in both soils has a favorable adsorption, which implies that the metal is retained by the soil and could be described by the Langmuir model. With respect to metals Mn, Pb and Zn, these do not apply to the model, so other models should be considered to explain the behavior of these metals.

The Freundlich model is used for adsorption processes that occur on heterogeneous surfaces, where the existence of weak interactions between particles is considered. The KF constant can only be considered for Cu and Zn in both soils, because the Freundlich equation did not fit linearly for Mn and Pb. The value of the KF constant for Zn is relatively similar in both soils, and for Cu the value of KF in the Alhue soil is much higher than the value of the New Braunau soil, so the Cu in the Alhue soil would be strongly retained; while on the ground New Braunau could have more mobility, as could the Zn on both soils, which could be more mobile, meaning it could leach out, move through runoff, or become available to be adsorbed by plants.

Temkin's model indicates that if the value of the constant B is less than 8 kJmol⁻¹, the interactions between metal and soil are not weak, therefore the adsorption process occurs on homogeneous surfaces and for this study no metal fit the model. With respect to the metals Mn and Pb, none of them fit the studied models, which could be due to the fact that they have a different physicochemical behavior than Cu and Zn, so other models should be studied that allow for the use of metals. With respect to the metals Mn and Pb, none of them fit the studied models, which could be due to the fact that they have a different physicochemical behavior than Cu and Zn, so other models should be studied to explain their mobility.

Desorption study: Table 8 shows the values obtained for the desorption study with each metal, using KNO_3 0.1 mol/L, as an extractant solution in both soils.

Table 8. Percentage of desorption for Cu, Mn, Pb and Zn in Alhue soil and New Braunau soil. Each value corresponds to the average of two repetitions.

Soil	% Desorption			
	Cu	Mn	Pb	Zn
Alhué	*	0.92	7.55	0.44
New Braunau	*	34.68	12.54	3.20

*: No desorb, metal was not detected in solution.

The following order can be established according to the percentage of desorption: Alhue: $\text{Pb} > \text{Mn} > \text{Zn} > \text{Cu}$; New Braunau: $\text{Mn} > \text{Pb} > \text{Zn} > \text{Cu}$. Since the adsorption percentages for all metals in both soils are relatively low, except Mn in New Braunau soil, it is possible to indicate that these metals would be preferentially adsorbed in the soil, thus determining their low bioavailability to be adsorbed to be adsorbed by plants, leach through soil profiles, and/or move by runoff.

The result of the desorption study is consistent with what was studied, since, when K_d was determined, it indicated that adsorption of metals occurs in both soils, with Cu being the most retained in the Alhue and New Braunau soils; while Mn was the least adsorbed metal.

As can be seen in Table 8, Cu was not detected in the solution, which means that it was completely adsorbed by the soil, so when simulating natural rainfall conditions with KNO_3 , Cu does not solubilize. In the case of Zn, as it was seen in the adsorption study, it is retained by the soil, however, as the affinity with the solid phase of the soil was lower than for Cu, there would be the possibility of being desorbed, therefore, moving through the profiles of the soil and become bioavailable.

With respect to Mn and Pb, although it was not possible to explain the type of adsorption by the models used, but it is known that they are adsorbed by the soil, their greater desorption could be attributed to characteristics of the metal such as its ionic radius, since for both it is greater than for Cu and Zn. And since they are larger molecules, it may be more difficult for them to attach to the surface of the soil, reducing their ability to be retained. In addition, both Mn and Pb tend to be present in soils with an acidic tendency as an ion, therefore they can be desorbed more easily, since they are soluble [58,59].

Gibbs free energy change

In the next table is show the free energy change values of soil samples

Table 9. ΔG° values for metals in Alhue and New Braunau soils.

Soil	ΔG°			
	Cu	Mn	Pb	Zn
Alhué	-9971	6968	-931.6	-5338
New Braunau	-3298	9845	-931.6	-151

The negative ΔG° (Gibbs free energy change) values obtained in the present study indicate that the adsorption of metals onto soil samples is a spontaneous process and that the adsorption was an exothermic process except for Mn in both soils.

Influence of the physicochemical characteristics of soils on the adsorption – desorption of metals.

In general, with the increase in pH, the availability of metals decreases, due to the presence of poorly soluble species; as with organic matter, due to its chelating capacity. On the other hand, a higher CEC indicates a greater capacity for exchange. Based on this, it can be established that in the New Braunau soil (pH = 4.55), the availability of metals is greater with respect to the pH of the Alhue soil (5.70), if the values of OM and CEC are considered, these are higher in New Braunau (9.77% and 20.1 $\text{cmol}(+)\text{kg}^{-1}$) respectively) than in Alhue (3.57% and 6.31 $\text{cmol}(+)\text{kg}^{-1}$), so Nueva Braunau, despite being more acidic, would have a greater capacity to adsorb metals than Alhue.

It is also important to analyze the content of clays, since they have the ability to exchange cations, retaining them in the soil and consequently preventing their passage to the ground, according to this, the Alhue soil, whose main clay is halosite - 7A (13.09%), would have a higher adsorption capacity than New Braunau, allophanic (6.63%). Crystalline clays have a smaller adsorption surface and less space for intraparticle diffusion, e.g. halosite-7A, while amorphous clays have a larger adsorption surface and spaces for intraparticle diffusion, e.g., allophanic clays.

With the background obtained from the physicochemical characterization of the Alhue and New Braunau soils, it is possible to see that each of these soils has characteristics that would favor the adsorption of the metals studied, such as pH and the percentage and type of clays, however, it is necessary to consider the characteristics of each of the metals as ionic radius. Sphere of hydration, solubility, among others. For this reason, the soil-to-metal system must be known for this purpose [60, 61].

Acknowledgments. This work has been financially by Departamento de Química. Facultad de Ciencias. Universidad de Chile.

Conflict of interest. The authors declare that they have no conflict of interest.

CONCLUSIONS

- The physical and chemical characteristics determined for the Alhue and New Braunau soils indicate that the values of: pH, CE, OM, CEC and texture are within the ranges corresponding to volcanic soils.

- The concentration of the total fraction of total metals in both soils indicated the following order $\text{Mn} > \text{Pb} > \text{Cu} > \text{Zn}$.

- The study of contact time was established at 48 hours, the Elovich model adjusted correctly ($R^2 > 0.8$) and ARE ($< 10\%$).

- The values found for the distribution constant (K_d) and the constant associated with the OC content (K_{oc}) indicate that the metals are retained mainly by the solid fraction of the soil, which implies a greater difficulty of these metals to leach, and therefore a lower bioavailability.

- The descending order of the K_d and K_{oc} values of the metals is in the Alhue soil: $\text{Cu} > \text{Zn} > \text{Pb} > \text{Mn}$ and in the New Braunau soil is: $\text{Cu} > \text{Pb} > \text{Zn} > \text{Mn}$.

- The Langmuir, Freundlich and Temkin models were applied to the study of adsorption of Cu, Mn, Pb and Zn. Langmuir explained the adsorption of Cu and Freundlich Cu and Zn. Temkin's model didn't fit.

- The highest percentage of desorption was found in New Braunau soil. Cu was not desorbed in these soils.

- Among the characteristics of soils that mainly influence the adsorption/desorption processes of metals are the pH and the percentage and type of clay.

- The results obtained in this work show that Cu would not be a potential soil contaminant, since it was preferentially adsorbed, while Mn, Pb and Zn would be, although the latter two to a lesser extent, having the possibility of leaching and being mobilized through the same or another soil and also towards groundwater.

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