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Effect of acidity changes on mobility of metallic trace elemenets in maipo river sediments

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ABSTRACT

The mobility and availability of metallic trace elements in river sediments depends on their solubility and adsorption on colloidal fraction of sediment. Processes such as cation exchange, adsorption/desorption, precipitation/dissolution and complexation affects the distribution of metals between the water column and sediments, being responsible for their mobility and availability. Trace elements in sediments are retained in the matrix, the concentration of the soluble fraction is scarce, this depending both on the physical and chemical properties of the sediment and the nature of metal.

In this work we studied the effect of pH on the solubility of metallic trace elements in river sediments in order to evaluate their mobility into the water column.

Samples were collected in 3 sites of Maipo River basins: Angostura (Ang), Clarillo (Cla) and Puangue (Pu) recording sites by GPS coordinates. The sediments were characterized: pH, electric conductivity (EC), soluble organic carbon (SOC), total organic carbon (TOC), available P, carbonate and Mn, Al Fe oxides. For determination of trace elements in total fraction in sediment, samples 0.25 mg, were digested in a microwave oven and determined by AAS. To study pH effect in release of metal mass of 2.5 g sediment was stirred for 24 h with 15 mL of solutions at pH 5.0; 4.0; 3.0; 2.0, which were prepared with nitric acid. Then all the samples were centrifuged, filtered and the respective metals measured by AAS.

The content of total metals indicates that the major metals on the 3 sites were Al and Fe , Pu site presents the lowest concentrations of these two metals, Zn, Cu and Mn are higher in Pu, Mn concentration in Pu is three times higher than Cla and Ang. Mo was not detected. At pH = 2, the highest mobility was obtained according to the recoveries obtained. At pH 3, 4, 5 heavy metals are not mobilized or are obtained with very low recovery percentages. In all cases was Pu which presented the lowest recovery rates. Only Mn represents values of RAC with indicates high risk in Cla and Ang

Key words: *sediments, metallic trace elements, availability, heavy metals, AAS, acidity, RAC.*

INTRODUCTION

River systems are very important as sources of natural resources and represent considerable wealth for various activities, so knowledge of the physical and chemical characteristics of the water system: water-sediment is relevant to determine its behavior.

The movement of sediments in rivers causes them to settle on the bottom or to be in suspension, the suspended load transported by a river depends on: the relief, the extension and the geology of the drainage basin, flow, climate and vegetation. Sediments are made up of the finest particles held in suspension by current eddies and only settle when the speed of the current decreases, or when the bed becomes smoother or the current discharges into a well or lake. There is an intermediate type of movement in which the particles move downstream by bouncing or jumping, sometimes touching the bottom and sometimes advancing in suspension until they fall back to the bottom [1].

Sediment comes from natural or anthropic origin, so its composition will depend on the materials that originate it; the main thing is that this can be a parameter for the quality of the water, because it has a property of adsorbing dissolved components, immobilizing for example heavy metals, pesticides and micro plastics, among other contaminants [2].

Contaminated sediments are in direct contact with the biota, especially the benthic organisms they provide with habitat and food, leading to toxic effects and allowing the bioaccumulation of contaminant species, determining their potential transfer through food chains and eventually harm to human health [3-5]. Pollution sources include mining, industrial production, pesticide use, traffic pollution, [6-8]. Due to rapid economic development and urbanization in many countries, water pollution and degradation of aquatic ecosystems may damage the function and integrity of water resources [9].

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Among them, the mutual recharge and discharge between surface water and groundwater can affect the migration and distribution of pollutants. The subduction zone is a layer of moisture-saturated sediments that lies below the river bed and extends to the riparian zone and both sides of the river, where surface water and groundwater crossmix and interact [10].

As a transition zone connecting surface water and groundwater, water, nutrients, organic matter, and microorganisms move between ecosystem components through water exchange in the subduction zone. Physical and chemical processes and biological activities are extremely active in this region, strongly influencing important biogeochemical processes such as water exchange, solute transport, and contaminant storage in surface water-sediment-groundwater systems [11, 12, 13]. Submerged zone sediments are often a potential source of metal pollution in surrounding waters due to their capacity to accumulate metal compounds [14,15].

In recent years, sediment pollution has attracted more and more attention, and the accumulation ability of heavy metals in sediment has become a key indicator for sediment pollution prevention and control.

Heavy metals adsorbed into the sediment may be released into the water surrounding the water body through various physical, chemical, or biological mechanisms, thus causing pollution to the surrounding water [16]. Therefore, the adsorption-desorption process of heavy metals in sediment samples is indispensable to evaluate the characteristics and biological activity and availability of heavy metal contamination in the subduction zone. Miranda *et al.* [17], examined the synergistic effects of key water, sediment, and ionic properties on the sorption-desorption behavior of weakly bound heavy metals and showed that the maximum sorption of metals by sediments differed even when the environmental physico-chemical characteristics were similar.

Clay minerals have a low potential to adsorb heavy metals in the weakly-bound fraction of the sediment, and phosphorus compounds can increase this interaction [18]. In addition, Miranda et al. [19], found that particulate organic matter was the most influential nutrient in heavy metal sorption in the riverine environment [20].

Trace elements not only will affect the environmental health of an aquatic system directly, they can also do so indirectly by their ability to release pollutants into the water column, making them available to the organisms living in it [21]. Trace metals present relatively high concentrations in the surface sediments of areas disturbed by anthropic intervention and have a concentration relationship with the size of the particles and the amount of sedimentary organic matter, altering the ecological and biogeochemical balance of the ecosystem. In this sense, the determination of metals in sediments is a good indicator of the origin of contaminants in the environment and of the impacts that they can produce in aquatic biota, in addition to their possible transfer to the water column. [22].

Numerous researchers agree that more than 90% of the metallic load of a fluvial current is found in the suspended particles of the water and in the sediments [23], these studies also reveal that the metals in the sediments can be found in different fractions of the fluvial sediment, however a particular characteristic of the metals is that they are associated with the finer fraction of the sediment corresponding to a size smaller than 63 µm, this affinity of the metals for this fraction it is explained by the large contact surface and by the adsorption that occurs facilitating the transport of the contaminant towards the water column [24]. The mobility of metals depends on their solubility and their adsorption capacity in the colloidal fraction of the sediment. The interaction between different processes such as cation exchange, adsorption/desorption, precipitation/dissolution, and complex formation affect the distribution of metals between the water column and sediments, being responsible for their mobility and bioavailability [25].

In most of the speciation schemes, the existence of metals can be seen in five fractions:

- Metals in the form of exchangeable ions. These can easily be released into the water column by small environmental changes.
- Metal bound to carbonates. It is considered that the metals bound to this phase will be released when the pH of the sediments decreases, when the metals precipitated in the form of carbonates dissolve.
- Metal associated with iron and manganese oxides. The metals present in this phase will pass into the water in those areas where the sediment is under reducing conditions. These oxides are substances with high adsorption power and are thermodynamically unstable under anoxic conditions (low redox potential values).
- Metal bound to organic matter. These metals represent the fraction that would be released when going to oxidizing conditions. A typical case is the deposition of anoxic sediments on surfaces in contact with the atmosphere.
- Residual or lithogenic phase. They are metals bound to minerals, forming part of their crystalline structures. The release of metals from this phase, in a reasonable period of time, is certainly unlikely.

The sediment factors that affect the mobility of the metal are: pH, redox potential, content and type of clays, organic matter, Fe, Mn and Al oxides, and the presence of cations and anions in solution [24].

Acidity or pH affects the chemical speciation and mobility of many heavy metals. This factor also plays an important role in the interactions of metals with parameters such as water hardness (mainly Ca and Mg carbonates) and with organic compounds. The redox potential of a given environment influences metal speciation. For example, the microbial transformation of sulfate to sulfite occurs, which causes the precipitation of heavy metals.

High potentials are associated with oxidizing phenomena while low potentials are associated with reducing phenomena, which affects the state of some constituent elements of the sediments.

The content and type of clay can also influence the mobility of heavy metals. Since clays have predominantly negative charges that can be compensated by adsorbed cations, which in turn can be displaced by others existing in the ecosystem [25].

Both soluble and particulate organic matter alters the distribution of heavy metals, decreasing dissolved levels and increasing the concentration of metals in colloidal form and in suspension, as well as in sediments due to the formation of organometallic complexes.

The hydrated oxides of Fe, Mn and Al adsorb heavy metals in a specific way and determine their mobility. They also act in non-specific adsorption through cation exchange since, depending on the pH; they can have a negative charge on their surface. Oxides can also co-precipitate metal ions.The ions present in the water have a great influence on the toxicity of heavy metals, due to the formation of insoluble compounds such as carbonates or the adsorption of metals on calcium carbonate. Or is complexed for example, with chloride.

Figure 1. Sampling sites.

The pH also affects the electrical charge of the components of the colloidal fraction of the sediment – a fraction < 2□ made up of clays, oxides and organic matter that have a pH-dependent charge, which becomes more negative at alkaline pH and more positive at acidic pH. Therefore, in sediments with variable charge, the retention of metal cations increases as the pH is higher and decreases when they become more acidic. With the exception of Mo, Se, As, the mobility of heavy metals decreases with increasing pH due to their precipitation as insoluble hydroxides, carbonates, and organic and inorganic complexes.

The formation of metal complexes is also affected by pH. Elliot et al. 1986 [26], found that under acidic conditions some organic ligands complex with hydrogen ion and not with Fe (III) ion, making it more available. Changes in pH can also strongly influence the adsorption or desorption of cations by organic substances and therefore their bioavailability.

The goal of this work was to study the effect of the pH change on the concentration of metals such as: Al, Cu, Fe, Mn, Mo, Zn from Maipo River sediments and study these solubility, availability and risk assessment code (RAC).

MATERIALS AND METHODS

Description of the area

The Maipo River basin extends between the parallels 32°55'-34°15' south latitude and meridians 69°55'-71°33' west longitude, covering practically 100% of the Metropolitan region and a part of the V Region. The Maipo River is 250 km long and has an average annual flow of 92.3 m3/s draining an area of 15.304 km2.

The Maipo River basin has a high concentration of inhabitants and concentrates various industries. This has led to various problems such as pollution and flooding. In addition, it is necessary to highlight that the Maipo River meets around 70% of the current demand for drinking water and close to 90% of the irrigation demands, another intensive use is hydroelectric.

Three sites will be used for the study of heavy metals in sediments and the change in mobility with pH variations. Three sites will be used for the study of heavy metals in sediments and the change in mobility with pH variations. Angostura (Ang) 34° 2'4.10"S; 70°34'35.36"W, Clarillo (Cla) 33°42'56.61"S; 70°30'22.82"W and Puangue (Pu) 33°27'52.16" S; 71° 4'20.48"W. The sediments corresponding to the Ang, Cla, Pu sites were recorded using geographic coordinates by GPS system (Figure 1).

Sediment samples were taken using polyethylene shovels and they were deposited in 1 L bottles of the same material in order to avoid modifying the metal content [26]. For the transfer from the sampling site to the laboratory, the samples were stored in at 4°C (cold chain) for better preservation [27].

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

Table 1. Microwave conditions for sediments samples digestion.

Parameter	Maximun power (W)	Ramp (min)	Cooling (min)
Stage 1	880	4	4
Stage 2	400	4	4

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

Reagents and solvents

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

Physical chemical characterization of sediments

pH and Electrical Conductivity [28]

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 multiparaeter 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.

Soluble Organic Carbon (SOC)

For the preparation of the digestion with potassium dichromate [29], 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).

Available Phosphorus

To obtain the available phosphorus, the Olsen methodology was followed [28]. The utility of the extract ant is based on the fact that the sodium bicarbonate solution reduces the concentration of calcium, aluminum and iron (III) ions by precipitation of calcium carbonate and aluminum and iron (III) hydroxides, thus releasing phosphate ions into the solution.

2.5 g of pellet were weighed (accuracy 0.01 g) into 100 mL plastic shake flasks. In addition, a reference blank was included. 50 mL of sodium bicarbonate solution was added to each of the containers. These flasks were shaken on an orbital shaker for 30 minutes at a speed of 125 rpm. The samples were filtered with the help of fine filter paper. Next, 3 mL of the series of standards, the blank, and the sample extracts were pipetted into centrifuge tubes. 3 mL of the mixed reagent was slowly added to each tube (CO_2 evolved). The mixed reagent contains excess sulfuric acid to neutralize the sodium bicarbonate. The solutions were left to settle for approximately 1 h so that the blue color shade developed to the maximum, absorbance was measured at 880 nm.

Determination of Aluminum, Iron and Manganese oxides.

Following the method of Mehra and Jackson, 1960 [30], the sample is heated with a buffered complexing solution of sodium citrate/bicarbonate, to which solid sodium dithionite has been added as a reducing agent. 4 g of sediment was weighed and deposited in polyethylene bottles, each sample is made in duplicate and 2 blanks are included. 45 mL of citrate/bicarbonate solution was added and placed in a thermo-regulated bath at 75°C taking care that the temperature does not exceed 80°C to prevent elemental sulfur from precipitating. Added 1 g of sodium dithionite and stirred constantly for 1 minute, then occasionally for 5 minutes with a glass rod. The previous step was repeated 2 more times. 10 mL of saturated KCl solution was added (washing the rod) and heated again in the bath for 5 more minutes.

The supernatant was centrifuged at 3500 rpm for 30 min, the clear supernatant was filtered using a syringe filter and poured into a 250 mL volumetric flask. The above procedure was repeated adding the second supernatant to the 250 mL flask and topped up with deionized water. Solutions 2 10 and 100 times more diluted were prepared. For the 2nd, 5 mL of extract and 5 mL of water were taken in a centrifuge tube where it was homogenized. For 10, 2 mL of extract and 8 mL of water were taken to have a 5x extract of that extract, 5 mL and 5 mL of water were taken to obtain 10. Finally, for extract 100, 1 mL of extract diluted 1 to 1 was taken. 10 and 9 mL of water in a centrifuge tube where it was homogenized. And oxides of Mn, Fe and Al, were determined by AAS. The conversion factor was used to obtain the percent of oxides.

Determination of carbonates.

The concentrate for the analysis of anions consists of: 34 g of boric acid p.a. Merck with 23.5 mL of gluconic acid p.a. Merck, 8.6 g of lithium hydroxide monohydrate Merck p.a. and 250 mL of glycerin all of this made up to 500 mL with deionized water.

Between 20 to 30 g of the sediment was weighed with an accuracy of ± 0.01 g in a polyethylene bottle, then approximately 10 mL of milli-Q grade deionized water was gradually added to each bottle and manually stirred with the help of a spatula until reach the saturation point. Once the extract was obtained, thymol crystals were added to reduce microbial development and then the saturation extract was poured into centrifuge tubes. It was centrifuged for 30 minutes at 3500 rpm. The solid was discarded and the supernatant was used, which was filtered through 0.45 μm PVDF. Carbonate was determined by Ionic exchange high-performance liquid chromatography (IE-HPLC) [31].

To carry out the analysis in the IE-HPLC equipment, the mobile phase had to be previously prepared, which consisted of 55 mL of the concentrate for the anion analysis, with 120 mL of Merck HPLC grade acetonitrile, made up to 1L with water. milli-Q grade deionized. Once the mobile phase and the standard solutions were prepared, the equipment was programmed using the Empower Pro software, for the simultaneous quantification of the ions, taking into account the following equipment conditions:

- Conductivity of the mobile phase: 750-770 mS/cm^{-1}
- Column temperature: 35ºC
- Injection volume: 50 µL
- Mobile phase flow: 1.2 mL/min
- Column: Anion Resin IC-Pck Anion HC
- Detector: Conductivity (Waters 432)

The signals were identified by comparison with the retention times (tR), with the standard solutions.

Analysis of trace elements in the Maipo River sediments

The digestion of the samples for the determination of metals was carried out by microwave in tubes covered with Teflon PFA, 250 mg of soil with 1 mL HNO3, 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.

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 (PVDF membrane) and the solutions were stored refrigerated in centrifuge tubes until their subsequent analysis

Chemical determination of trace elements It was carried out by AAS, 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 each one with a specific wavelength and intensity: Al (309.3 nm); Cu (324.8 nm); Fe (248.3 nm); Mn (279.5 nm); Mo (313.3 nm); Zn (213. 9 nm)

Extraction of metallivc trace elements at different pHs.

The initial pH values chosen are: 2, 3, 4, 5, the sediment mass/solution volume ratio used is 0.25 g/15 mL= 0.017 g/mL. Once the samples are prepared, they are shaken for 24 hours, time considered sufficient for the system to reach equilibrium [32].

Standard solutions of Al, Cu, Fe, Mn, Mo and Zn Merck Tritisol 1000 mg/L. Different standards were prepared to obtain a calibration curve. Metals extracted were determined by AAS in the same conditions as total fraction of elements.

Risk assessment code (RAC).

The risk assessment code (RAC) uses the percentage of metals that are exchangeable. In this fraction the metals are weakly bound to the sediment and imply greater environmental risk since they are more available to the aquatic system. The values of this parameter are classified as: RAC < 1% there is no risk when; 1% ≤ RAC < 10% low risk; 10% ≤ RAC < 30% medium risk; 30% ≤ RAC < 50% high risk; 50% ≤ extremely high risk [33, 34].

Statistical Analysis.

The trace elements concetration were related to the physicochemical characteristics of the sediment using Pearson's correlations [35].

Table 2. Physicochemical characteristics of the sediments studied.

Sites	pH	EC ($mScm^{-1}$)	P ($mgkg^{-1}$)	SOC (%)	TOC (%)	Carbonate (mg/L)
Pu	7.6	0.51	10.80	0.39	2.04	50.03
Ang	6.6	1.05	2.20	2.03	7.23	75.85
Cla	6.0	0.56	0.70	2.58	9.16	9.87

RESULTS AND DISCUSSION

Physicochemical characterization of the sediments.

The following tables show the results obtained for the three selected sites in the Maipo River basin, (Table 2).

Observing Table 2 with respect to pH, it can be inferred that the Pu, Ang and Cla sites present a relatively neutral pH. The pH is related to the availability of metals, most of these tend to be more available in acid media, due to the absence of hydroxy complexes. As and Mo are the exception, since in the case of arsenic at a pH close to 6.9, soluble species of As (V) are found, mainly HAsO4 at a higher pH. In the case of molybdenum, because molybdenum IV salts are soluble at basic pH, while at acidic pH they tend to form oxyanions [36].

On the other hand, studies associated with heavy metals revealed that pH levels between 6 and 8 allow a higher percentage of metals adsorbed in the sediment, which in this case, since the pH is mostly neutral-alkaline, could mean that the metals are less available in

Table 3. Percentage of oxides (Al, Fe and Mn) for the sediments studied.

Sites	Al_2O_3	Fe_2O_3	MnO
Pu	0.09	1.02	0.25
Ang	2.09	1.64	0.05
Cla	1.13	1.47	0.04

the water system and more adsorbed in the sediments [37].

Numerous studies indicate that electrical conductivity is directly proportional to the concentrations of dissolved salts, Pu and Cla study sites present the lowest values of 0.51 and 0.56 dSm-1 respectively, and the highest value was determined for Ang. (1.05 dSm-1), a site in which it could be inferred that a moderately saline site, this could be due to the contamination of effluents from neighboring industries or urban sectors.

The SOC corresponds to the available or soluble organic carbon and the TOC correspond to the biologically resistant one, since it binds to the finest mineral fractions. The sites that present the highest percentage of TOC correspond to Cla and Ang with 7.22 and 9.16 % respectively and in the case of Ang it agrees that this same site presents the highest conductivity. It is important to highlight that organic carbon affects the distribution of metals, since these can be retained forming complexes or chelates, so with a higher percentage of carbon there could be a lower concentration of metals available, because they are retained in the sediment and vice versa. In addition, the degradation of organic carbon could cause a change in pH towards acidic value. According to the results, it can be said that Cla and Ang would be the sites that could present a greater adsorption capacity for metals, due to their high percentage of organic carbon.

Studies reveal that a high percentage of clay and organic carbon affect the adsorption capacity of all types of sediments, this is due to the large contact surface and also to the fact that clay is negatively charged; therefore it attracts molecules to neutralize the load [38].

The available phosphorus content in the sediment allows an estimation of the quality of the water courses, because it determines the degree of availability that this element presents to the water column, which makes its determination important, since being a nutrient can cause eutrophication problems in the system if it is in excess and can also contribute to the formation of poorly soluble compounds or complexes with some heavy metals. The high value of phosphorus found in Pug can be explained because it is supported by agricultural land and phosphorus is eutrophication of the system if it is in excess and can also contribute to the formation of poorly soluble compounds or complexes with some heavy metals [39].

Percentage of oxides (Al, Fe and Mn) in the sediments of the Maipo river basin.

Table 3 shows that both Al and Fe oxides are higher in Ang followed by Cla and finally Pu, however the percentage of Mn oxides is higher in Pu followed by Ang and then Cla. By increasing the content of hydrated oxides in the soil, the adsorption sites for metals increase and their mobility is directly reduced.

The importance of hydrated oxides in the retention of metals apparently depends on the oxidation-reduction conditions of the soil, since in reducing conditions there is greater dissolution of the oxides. It has been shown that Fe and Mn oxides have higher adsorption capacity for heavy metals than Al oxides and other clay minerals [30].

Figure 2. Al and Fe concentration (mg/kg) and concentration of Cu, Zn, Mn (mg/kg), in the total fraction in sediments of the Maipo river basin. Metal concentration in sediment (mg/kg), in sampling sites Pu, Ang, Cla.

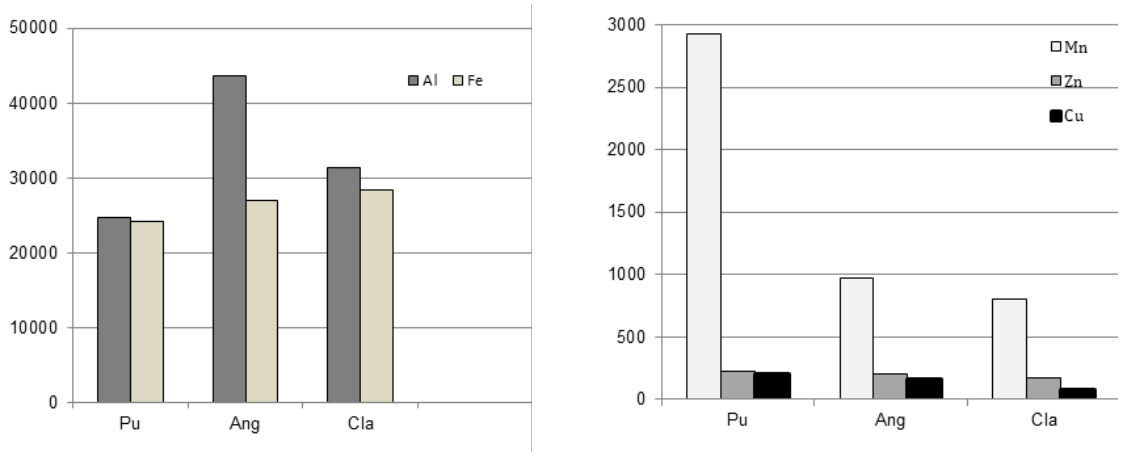


Figure 3. Concentration of trace elements: Zn, Mn, Zn, Fe and Al (mg/kg), at pH = 2, 0 in sediments of the Maipo river basin. Metal concentration in sediment (mg/kg), in sampling sites Pu, Ang, Cla.

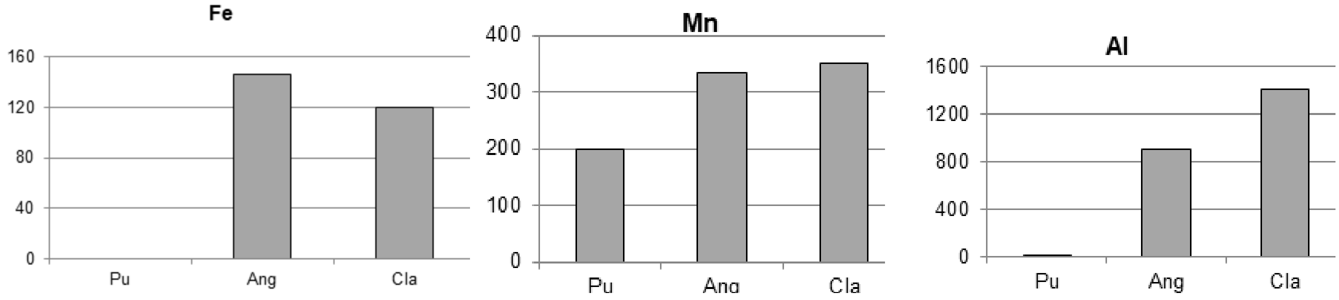
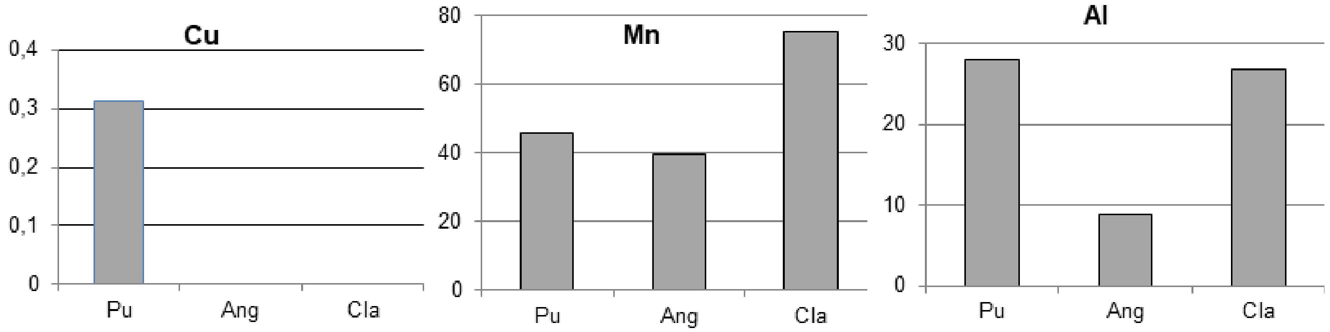


Figure 4. Concentration of trace elements: Zn, Mn, Zn, Fe and Al (mg/kg), at pH = 3, 0 in sediments of the Maipo river basin, metal concentration in sediment (mg/kg), in sampling sites Pu, Ang, Cla.



At a lower degree of crystallinity, the oxides of Fe, Mn and Al have a higher adsorption of heavy metals in the soil. The surface of the oxides is more reactive from the chemical point of view to the extent that it is less crystalline, a situation that is favored in soils from areas with a humid climate, as occurs with the soils of the south-central zone of the country

Total metal concentration in Maipo River sediments

In the next figure are shown the elements concentration of total fraction (mg/kg), in the sediments of the Maipo river basin.

From figure 2, it can be seen that aluminum and iron have the higher concentration in all the sites. This is to be expected since aluminum and iron are the 3rd and 4th most abundant elements in the earth's crust. Therefore, a large part of its concentration it is the lithogenic nature.

The second noteworthy observation is that Pu is the river with the highest content of Cu; however it is the one with the lowest content of majority metals. The Clarillo River (Cla), has less anthropogenic influence because it is a sparsely populated sector due to the Andean relief conditions and it is not yet exploited as an agricultural sector, so it can be assumed that the significant differences between the concentrations of the different sites studied could be due to human activity.

Under this premise, it is possible to indicate that the excess of Mn is of anthropogenic origin, which is explainable, as is the excess of phosphorus, because it has agricultural uses. Manganese is an essential micronutrient for plants, which is why it is found in a large amount of fertilizers and its addition in most cases is not due to the impoverishment of the soil but to the fixation of existing reserves, which is why it is necessary. In addition, Mn of easy availability, being the lack of Mn common for neutral or alkaline soils, in this study this behavior was found in Pu (pH=7.6).

It can also be seen that molybdenum is below the detection limit of the method used, being expected in sediments with low copper content, since it is common for higher concentrations of molybdenum to be associated in sites with high copper concentrations, in fact it is molybdenum one of the economically important by-products in the exploitation of copper. The rest of the metals present slight variations with respect to Cla, being probably a combination of lithogenic and anthropogenic origin [40, 41].

Figure 5. Concentration of trace elements: Zn, Mn, Zn, Fe and Al at pH = 4, 0 in sediments of the Maipo river basin, metal concentration in sediment (mg/kg), in sampling sites Pu, Ang, Cla.

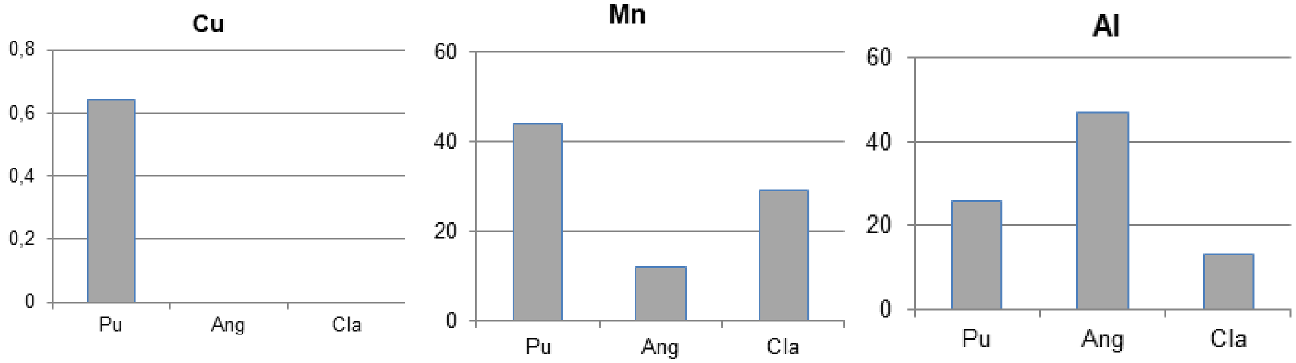
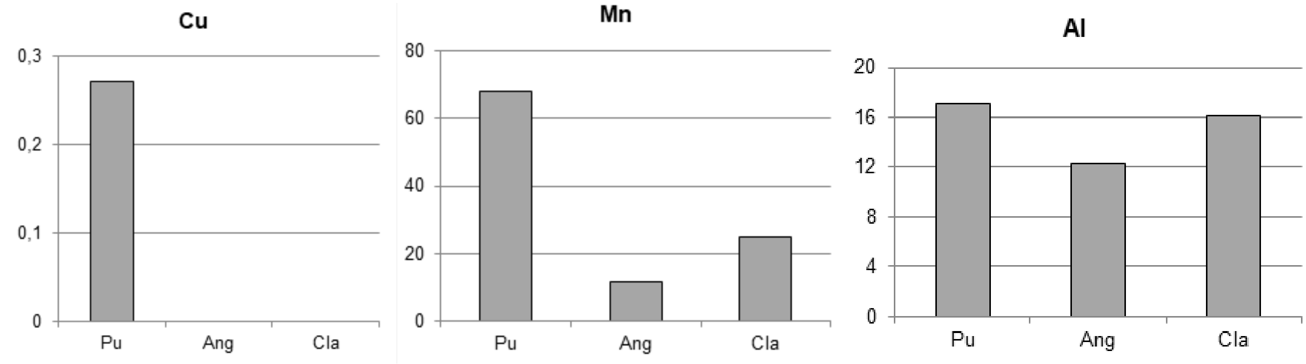


Figure 6. Concentration of trace elements: Zn, Mn, Zn, Fe and Al at pH = 5, 0 in sediments of the Maipo river basin, metal concentration in sediment (mg/kg), in sampling sites Pu, Ang, Cla.



Metal concentrations (mg/kg) in sediment in sites studied at different pHs

The next figures are shown the metals concentration at different pHs in the three sampling sites.

pH = 2

In general the order of concentration found at this pH corresponds to Al>Mn>Fe>Zn>Cu. In relation to the Pu sites, it is the site that shows the lowest concentrations of most of the metals except Mn. Concentration plots related to pH reported in the general literature indicate that at this pH most metals are in the cationic form. [36], (Figure 3).

pH = 3

In general, the order of concentration found at this pH corresponds to Al>Mn>Cu; Fe and Zn were not detected at this pH. In relation to the Pu sites, it is the site that shows the lowest concentrations of all metals, only Cu was detected (Figure 4).

pH = 4

In general the order of concentration found at this pH corresponds to Al>Mn>Fe>Cu; Zn was not detected at this pH. In relation to the Pu sites, it is the site that shows the lowest concentrations of all metals, only Cu was detected; Fe was not detected in Cla, (Figure 5).

pH = 5.0

In general, the order of concentration found at this pH corresponds to Mn>Al>Cu; Fe and Zn were not detected at this pH. In relation to the Pu sites, it is the site that shows the lowest concentrations of all metals, only Cu was detected, (Figure 6).

Each metal has its pH range in which the different species exist or can coexist, thus Al exists as a free ion pH $\leq$ 2.0, Cu at pH $\leq$ 3.0; Mn at pH$\leq$ 5.0; Fe at pH $\leq$ 2.0; Zn at pH $\leq$ 6.0 [36]. Figures 4, 5, 6 and 7 clearly show the effect of pH on the mobility of heavy metals, the most important effect being at pH 2.

It can be seen that the behavior of Cla is similar to Ang and both differ from that of Pu where it can be seen that metals remain more retained, among the conditions to consider that could support this behavior is phosphorus, which is found in a

Table 4. Percentage of oxides (Al, Fe and Mn) for the sediments studied.

Sites		Al	Cu	Fe	Mn	Zn
pH = 2.0	Pu	0.06	0.10	Not Concentration Found	6.67-low risk	Not Concentration Found
	Ang	2.03-low risk	2.36-low risk	0.54	33.44-high risk	6.25-low risk
	Cla	4.42-low risk	6.61-low risk	0.43	44.01-high risk	10.91-low risk
pH = 3.0	Pu	0.11	0.13	Not Concentration Found	1.53-low risk	Not Concentration Found
	Ang	0.02	Not Concentration Found	Not Concentration Found	3.96-low risk	Not Concentration Found
	Cla	0.08	Not Concentration Found	Not Concentration Found	9.37-low risk	Not Concentration Found
pH = 4.0	Pu	0.10	0.27	0.01	1.47-low risk	Not Concentration Found
	Ang	0.10	Not Concentration Found	0.02	0.12	Not Concentration Found
	Cla	0.04	Not Concentration Found	Not Concentration Found	0.54	Not Concentration Found
pH = 5.0	Pu	0.07	0.11	Not Concentration Found	2.26-low risk	Not Concentration Found
	Ang	0.03	Not Concentration Found	Not Concentration Found	1.18-low risk	Not Concentration Found
	Cla	0.05	Not Concentration Found	Not Concentration Found	3.13-low risk	Not Concentration Found

concentration approximately 5 times higher in Pu with respect to Ang and 15 times higher than Cla. Another parameter in which differences can be seen is the percentage of oxides, manganese being approximately 5 times higher in Pu than in Cla and Ang, both phosphorus and manganese oxides decrease the availability of zinc [30], which could explain why Zinc is not found in the entire pH range studied for Pu while it is found in Cla and Ang at pH 2.

In the case of copper, the presence of inorganic binders plays a significantly less important role than organic binders both in the chemistry and in the formation of copper complexes. A high degree of organic complexation of dissolved Cu in river waters (75 to 99% of total dissolved Cu) has been described in the literature [38]. In Pu, the organic carbon content presents the lowest values, this strong affinity with organic matter may explain the fact that Copper only appears at pH 2, while it can exist as a soluble species at pH less than 6 [36]. In the case of manganese, more information is required to determine the difference between Pu with respect to Cla and Ang, since being found mainly as manganese oxides, the redox potential is very important information when making assumptions regarding the behavior. of this, a measure that must be taken in situ and that was not determined for this work.

In the case of aluminum, the difference can be explained by the content of organic matter and phosphorus, since the capacity of aluminum to form complexes with humus has been described. In these complexes, the carbon (C) trapped in the complex is inactive and is no longer part of the active carbon in the organic fraction.

On the other hand, the hydroxyl groups combined with the complexed aluminum enter into ligand exchange reactions with $HPO4^{2-}$ and H_2PO_{4-}, strongly fixing Al. In addition, due to the strong complexation that exists between aluminum and organic matter, the reason for this can also be explained [42, 43].

Table 5. Correlations matrix (Pearson): Physicochemical characteristics of the sediments studied.

Variables	pH	EC $mScm^{-1}$	P $mgkg^{-1}$	SOC (%)	TOC (%)	Carbonate mg/L (%)	Fe_2O_3 (%)	Al_2O_3 (%)	MnO (%)	Cu	Zn	Mn	Fe	Al
pH	1	-	-	-	-	-	-	-	-	-	-	-	-	-
EC	-0.225	1	-	-	-	-	-	-	-	-	-	-	-	-
P	0.971	-0.452	1	-	-	-	-	-	-	-	-	-	-	-
SOC	-0.991	0.356	-0.994	1	-	-	-	-	-	-	-	-	-	-
OTC	-0.993	0.336	-0.992	1.000	1	-	-	-	-	-	-	-	-	-
Carbonate	0.484	0.744	0.260	-0.360	-0.380	1	-	-	-	-	-	-	-	-
Fe2O3	-0.797	0.768	-0.918	0.872	0.861	0.143	1	-	-	-	-	-	-	-
Al2O3	-0.637	0.895	-0.803	0.736	0.721	0.367	0.973	1	-	-	-	-	-	-
MnO	0.943	-0.536	0.995	-0.980	-0.975	0.166	-0.952	-0.856	1	-	-	-	-	-
Cu	0.945	0.106	0.839	-0.892	-0.901	0.744	-0.555	-0.349	0.783	1	-	-	-	-
Zn	0.976	-0.007	0.895	-0.937	-0.944	0.664	-0.645	-0.452	0.848	0.994	1	-	-	-
Mn	0.954	-0.506	0.998	-0.986	-0.982	0.201	-0.941	-0.838	0.999	0.804	0.866	1	-	-
Fe	-0.233	1.000	-0.459	0.363	0.343	0.739	0.773	0.898	-0.542	0.099	-0.014	-0.512	1	-
Al	-0.463	0.968	-0.662	0.580	0.562	0.551	0.905	0.978	-0.731	-0.148	-0.258	-0.707	0.970	1

Risc assessment code (RAC)

The RAC was determined based on the percentage of the total metal content with the metal concentration release at the acid pHs, in this work we used pH 2, 3, 4 and 5 (Table 4). Percentages of 1-10% represent low risk, 11-30% medium risk, 31-50 % high risk and > 50 % very high risk.

The following table shows the percentage ratio of the metal released versus the concentration total metal at each study site.

Table 4 shows the percentage relationship of each metal in each site with respect to the total metal concentration in the sediment, Mn was the most released metal in the three sites, and therefore more available at all pHs. Although Mn release occurred at all three sites, it should be noted that at most pHs, Mn release was higher at Ang and Cla. It should be noted that only at pH = 2.0 there is liberation of all metals, highlighting the highest values in Cla except Fe, which was higher in Ang, for all metals the least liberation occurred in Pu. Mn was the metal that shown hight risk at pH = 2.0 in Ang and Cla.In the other pHs, Mn shown low risk and Cu, al and Zn low risk only at pH = 2.0

Pearson correlations

In this study, a Pearson correlation was made (Table 5), which considers the total concentration parameters for the five metals together with the physicochemical factors of: pH, EC, % total C, available P, carbonates and % oxides for the 3 sites of the Maipo river basin.

In Table 5, the correlation factors calculated and highlighted in bold indicate that as an example, there is a perfect direct relationship between Mn and manganese oxides, that is, they increase in the same proportion in the sediments (r=0.999), which indicates that manganese is found at all 3 sites as manganese oxide. Another factor that shows a direct relationship is between the available P concentration and Mn (r=0.998). Since as mentioned above, both are closely related because they are both important nutrients. It should be noted that the correlation matrix also shows an inverse relationship between pH and OTC and SOC because OM degradation occur at pH acid. Extremely low solubility of Fe oxides at normal sediment pH, the iron released precipitates rapidly as an oxide or hydroxide. Only a small part of the oxidized iron will be incorporated into secondary clay minerals and/or is complexed by organic matter.

CONCLUSIONS

From the physical and chemical characterization of the sediments, it can be deduced that the Pu sediment presents some different characteristics in relation to the sediments of the Ang and Cla sites, with Pu being the site with the highest pH (7.6), the largest quantity of available phosphorus (10.8 mg/kg) and the lowest percentage of total carbon (2.04%). The lowest percentage of aluminum and iron oxides was Pu (0.09%, 1.02%) but with a much higher percentage of manganese oxides (0.25%). From the total metal content, it can be seen that the majority metals in the 3 sites were Al and Fe, which are also the most abundant metals in the earth's crust, so high concentrations of these are to be expected, Pu presents the lowest concentrations of these 2 metals. While Zn, Cu and Mn are higher, the concentration of Mn being three times that of Ang and Cla.

Regarding the mobility of metals according to slight changes in pH, it can be observed that indeed the effect of pH is important, but it begins to be decisive at pH 2. At pH 3, 4 and 5, metals are not significantly mobilized, except for Mn which presents hight risk.

The release of metals from the sediment at different pHs will be conditioned both by the characteristics of the metal and by the total concentration of the metal initially present in the sediment

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