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ADSORPTION-DESORPTION OF TRACE ELEMENTS IN SEDIMENTS OF THE MAIPO RIVER BASIN

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ABSTRACT

We studied the adsorption-desorption of Cu, Mn, Pb and Zn in Maipo river basin, one of the most perturbed rivers in Chile, and thus determined its tolerance to the addition of these metals into the sediments and the possibility of transferring the metals from the sediments to the water column. Sediments were sampled from six sites from the river basin and characterized by their pH, electrical conductivity, organic carbon, total organic carbon, water soluble phosphorus and texture. Batch sorption and kinetics experiments were conducted to obtain the retained amounts onto the sediment samples. The initial concentration of trace elements in the sediment was quantified by AAS. The metals were present in most of the sites. Sorption parameters such as Kd and Koc were determined. Metals were adsorbed in the sediment, with Mn showing the lowest affinity, Kd and Koc values and Freundlich constant (nf) support these results. Desorption less than 1% were observed for Cu, while Pb and Zn ranged from 0.6% to 6.8% and those for Mn ranged from 0% to 17.6% across sites. The tolerance of the Maipo River to metal adsorption in sediments was as follows: Pb> Cu> Zn >Mn. Desorption analysis showed that both Zn and Mn could be transferred from the sediment to the water column. The strongest correlation occurs between the pH and Kd-Pb, indicating that at higher pH values, the Pb adsorption was unfavorable, while the correlation was moderate for Cu, Mn and Zn. On the other hand, there are positive correlations between pairs of metals such as Mn-Cu, Zn-Cu, and Zn-Mn, indicating the competition of these metals for the adsorbent sites. The high concentration of Mn found in the sediment and the possibility of being transferred to the water column, due to its easy of desorption, suggest concern due to its potential risk to aquatic biota.

Keywords: Elovich model, trace elements, sediment, Sorption-desorption, Freundlich model.

1. INTRODUCTION

The pollution of aquatic and terrestrial environments by trace elements has been a matter of great concern after the industrial revolution, mainly due to its negative effects on the biota. Mining, smelting, industrial activities and traffic activities are the primary sources of trace elements pollution [1-4]. A series of physical and chemical process, such as sorption by ion exchange, complexation [5], reactions of oxidation-reduction [6] and precipitation [7] in addition desorption or bioaccumulation of heavy metals [8] can occur into bodies of water. In the case of the riverine environments, trace elements added by both natural and artificial sources are distributed between the aqueous phases and suspended as well as bed sediments during their transport. If the metal ions are tightly bound to the sediment, it is expected that metals do not present direct danger, settling to the bottom over time.

The metal concentrations in the bottom sediments can be one to three orders of magnitude greater than those in the overlying surface water [9, 10]. However, trace elements transport is reversible, and accumulated metals may be remobilized when the environmental conditions change due to natural processes or man-made influences on external parameters that influence the adsorption ability, such as the pH, hardness, organic matter, salinity and sedimentation load [11]. Trace elements in riverbed sediments could affect the water quality and therefore the biota; thus, their accumulation, toxicity, and stabilization in sediments could be used as a pollution index. Therefore, it is important to understand the interaction between sediments and pollutants in rivers. Organic matter, oxides, and clay minerals, all of which have an affinity to metals, are important adsorptive components in sediments [12, 13]. Sorption-desorption are considered a key process in the transfer of metals within rivers, playing an extremely important role in influencing the water quality to a considerable extent [14]. The sorption of trace elements onto suspended and riverbed sediments can reduce their concentrations in the water column, whereas desorption can lead to secondary metal pollution [15, 16]. Although the adsorptive properties of sediments can provide valuable information on the tolerance to heavy metal loading within a river [17, 11], the interaction mechanisms are poorly understood [18.] The Freundlich adsorption isotherm is commonly used for the description of adsorption data. The Freundlich equation is expressed as. $Cs = Kf\ Ce^{nf}$, where Cs is the amount of each metal adsorbed on the sediment (mg g^{-1} sediment), Ce is the concentration of the aqueous solution at equilibrium (mg mL^{-1}), and kf and nf are empirical constants related to the sorption phenomenon including the system characteristics (metal-sediment) .[19]

Some of the trace elements are interesting to study due to the interaction with the biota. For example, metals such as Mn, Cu, Zn and others are needed by organisms but in small quantities [20]. However, higher concentrations of these metals could drive lysosomal alterations [21], neurobiological alterations [21], and decreases in sperm motility in fish [22] and act as carcinogens [23, 24].

In Chile, metal accumulation was described in two native freshwater fish species inhabiting rivers of the country, which currently present conservation problems. For the silverside *Basilicthys microlepidotus* and the catfish *Trichomycterus areolatus*, more metal accumulation in the liver was observed than in the gills and muscle [25], and concentrations of metals in fish tissue were related to the concentrations found in the sediments of the rivers [25, 10, 27, 28], indicating the importance of the sediment for the freshwater biota. For this reason, it is important to know the tolerance of the river against an increase in the concentration of metals due to the numerous anthropic interventions of which it is subject.

The objectives of this study was to determine the Cu, Mn, Pb and Zn adsorption in sediments of the Maipo river basin and to determine the possibility of transferring these metals from sediments to the water column and to establish a relationship between the physical and chemical properties of the sediment and its tolerance to the metals retention.

2. MATERIALS AND METHODS

2.1 Study area

One of the more perturbed rivers in Chile is the Maipo River basin, located in the most densely populated area. This watershed draining an area of 15,304 km^2 over a 250 km length has water input mainly from winter precipitation. It is the main source of water in the metropolitan region, serving approximately 70% of the current demand for drinking water and approximately 90% of the irrigation demand. Additionally, water flow from the basin serves hydropower plants.

The basin is surrounded by high industrial activity, and most of the land in the basin is used for crops, vineyards, and livestock, between others. Overall, these features make the Maipo River one of the rivers most affected by human activity in Chile.

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2.2 Sampling

Sediments were sampled in the austral summer of 2014 from six sites from the Maipo River basin (Fig. 1). These sites showed differences related to their positions in the basin. Clarillo (CLA) is located in the Andes Mountains inside of the National Park Rio Clarillo, and thus the water is clean. Puangue (PU) is located in the Puangue stream, a water course that comes from the rainy waters from the coastal mountains. San Francisco de Mostazal (SFM) is located in the Angostura stream, a tributary of the Maipo River, which comes directly from the Cordillera de Los Andes. Isla de Maipo (IM) is located within an agricultural zone of the region. Finally, Peñaflor (PN) and Melipilla (MEL) are in the lower area of the river and receive treated water coming from the city of Santiago.

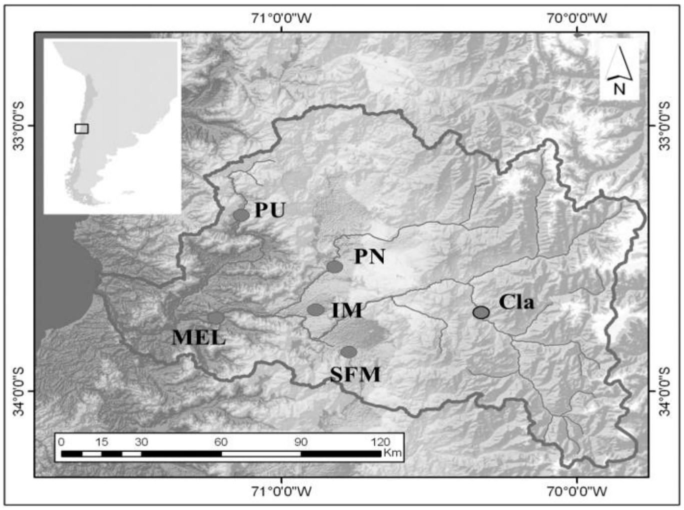

Figure 1. Sampling sites in the Maipo River basin.

2.3 Sampling procedure

Three independent sediment samples (1 kg) per sampling site were collected in a polyethylene bag from the top 10 cm of the surface using a plastic shovel, according to the sediment collection protocol [29]. Sediment samples were stored at 4 °C in the laboratory, and later, they were dried in polyethylene trays at room temperature and sieved to separate them into two fractions: a coarse fraction and fine fraction, with particle sizes of less than 2 mm for physical chemical characterization and 0.063 mm for metals determination.

2.4 Sediment analysis

The electrical conductivity (EC) and pH were determined by potentiometric methods (sediment: water; 1: 2.5). The Walkley-Black method was used to determine the organic carbon (OC) content, while the total organic carbon (TOC) was determined by a gravimetric method [30]; the water-soluble phosphorus was determined by using the Olsen method [30, 31]. The texture of the sediment was determined from the sedimentation velocity [30].

2.5 Trace elements determination

The trace elements analyzed in this study were Cu, Mn, Pb and Zn. These metals were selected due to the possibility that they could reach the river by runoff due to the human activity. The total fraction of each metal was obtained by the digestion 0.25 g of sediment with 10 mL of nitric acid (Suprapur, Merck) in a high-resolution microwave oven (MarsX press) using the following conditions: power, 800 W; tower, 100%; time, 11 min; temperature, 175 ºC, maintenance, 15 min; and cooling, 15 min. This protocol was based on EPA method 3051[32]. Trace elements concentrations were determined by flame atomic absorption spectrometry using a Shimadzu atomic absorption spectrometer (model AA-6800) with an air-acetylene flame. Operating conditions were adjusted to yield the optimal determination. The quantification of the metals was based upon calibration curves made with standard solutions prepared from 1000 mg L^{-1} Titrisol (Merck); for each metal. The following wavelength lines were used: Cu = 324.7 nm; Mn = 279.5 nm; Pb = 217.0 nm; and Zn = 213.8 nm. To ensure the accuracy of the reported data, recovery experiments were performed using a standard reference material for sediments (BCR-320R).

The experiments were performed in triplicate, and a calibration curve was obtained to determine the linear relationship between the absorbance and metal concentration in the dynamic range being used. Reagent blanks and reference material, were prepared and measured in the same way as the samples (Table 1).

Table 1. Analytical parameters estimated per each metal.

Metal	LOD (mgL^{-1})	LQD (mgL^{-1})	Certified Value (mgL^{-1})	Measurement Value (mgL^{-1})	Recovery (%)	Linearity (R^2)
Cu	0.05	0.10	1.87	1.54	82.35 ± 1.02	0.9970
Mn	0.03	0.04	25	22.3	89.20 ± 2.03	0.9990
Zn	0.13	0.25	8.9	8.1	91.01 ± 1.60	0.9991
Pb	0.19	0.23	2.37	2.42	102.11 ± 1.13	0.9960

2.6 Equilibrium time

In this study, we estimated the time at which the concentration of metal adsorbed to sediment or dissolved in the solution remains constant. To validate the subsequent adsorption isotherm a period of continuous stirring of set soil-metals is required, which must be greater than the time needed to reach equilibrium. For this purpose, 1 g of each sediment sample was weighed separately in 20 mL conical centrifuge bottles containing 10 mL of each metal solution (100 mg/L). The mixtures were shaken on a horizontal orbital shaker at 100 rpm using the following intervals: 3, 6, 12, 24, 48 and, 72 hours. Next, the suspensions were centrifuged at 3500 rpm during 15 min and the supernatant sieved with a 0.22 µm filter (PVDF) in a syringe filter (1.5 mL) before to analyzed by AAS.

2.7 Adsorption/desorption experiments

For batch experiments, 1 g of sediment from each site was taken and placed in a polyethylene bottle. A standard was prepared with 100 mg L^{-1} of each metal, and it was added to each bottle. An equilibrating solution of 0.01 M potassium nitrate (KNO_3) was added, adding uniform incremental volumes to each bottle, with 10 mL added to the first bottle and 0 mL added to the last bottle (bottles numbered 1 to 11). Samples were stirred for 48 hours according to the previously determined equilibrium time and then centrifuged for 30 minutes at 3500 rpm. The supernatant was filtered with a 0.45 µm PVDF membrane and refrigerated until analysis. The adsorbed concentration Cs (mg kg^{-1}) was calculated from the difference in the metal concentration between the aqueous phase Ce (mg L^{-1}) and the concentration added to the sediments (Ca mg L^{-1}). For desorption analysis, wet sediment was collected from the six sample sites with the highest metal concentrations, dried at room temperature for one day, and then transferred using the same containers used for adsorption. Then, 5 mL of KNO_3 0.01 M solutions was added and stirred for one hour. Afterwards, the solution was centrifuged for 15 min at 3,500 rpm to separate the solid (discarded) from the supernatant. Finally, this supernatant was filtered through a 0.45 µm PVDF membrane.

2.8 Pearson correlations

The adsorption constants (Kd) for each metal were related to the physicochemical characteristics of the sediment using Pearson correlations. Parameters showing $r > 0.7$ were considered strongly correlated, whereas r values between 0.5 and 0.7 were considered to exhibit moderate correlation [33].

3. RESULTS AND DISCUSSIONS

3.1 Features of the sediment

All of the sediment samples showed high percentages of sand and low percentages of clay and silt (Table 2). The sites IM, MEL and SFM present neutral pH values when compared with the sites CLA, PU and PN, which were more alkaline. MEL and IM present the higher total carbon contents, with values of 10.4% and 9.7%, respectively. These sites also present the highest electrical conductivities and high phosphorus concentrations. MEL also showed the highest percentage of TOC as well as water-soluble P and EC. CLA and SFM sites have the lowest EC values (0.03 and 0.09 dS m^{-1}, respectively), while the highest value was determined for MEL (1.6 dS m^{-1}), which is likely to be due to natural conditions or effluent from surrounding urban sectors and agricultural activities.

Table 2. Electrical conductivity (dS m^{-1}), pH, soluble phosphorous (mg kg^{-1}), organic carbon (% OC), total organic carbon (% TOC) and texture. Each value represents the mean taken from three samples, including standard deviation (±).

Sites	pH	EC (dScm^{-1})	P (mg kg^{-1})	(OC (%)	TOC (%)	Texture (%)		
						Silt	Clay	Sand
CLA	8.4 ± 0.2	0.30 ± 0.03	0.7 ± 0.1	0.6 ± 0.1	1.0 ± 0.6	1.0	1.2	97.8
IM	7.3 ± 0.1	0.30 ± 0.02	8.4 ± 0.4	2.9 ± 0.2	9.5 ± 0.3	1.1	5.0	94.0
SFM	7.5 ± 0.1	0.09 ± 0.03	5.4 ± 0.2	0.8 ± 0.1	5.5 ± 0.3	1.0	1.3	97.7
PN	7.9 ± 0.1	0.13 ± 0.02	6.9 ± 0.5	2.3 ± 0.1	6.6 ± 0.4	1.0	5.0	94.0
MEL	7.1 ± 0.1	1.60 ± 0.01	21.9 ± 1.7	2.1 ± 0,1	10.2 ± 0.1	1.1	11.3	87.6
PU	7.8 ± 0.1	0.20 ± 0.01	12.5 ± 0.4	1.0 ± 0.1	5.9 ± 0.3	1.0	8.3	90.7

It is known that clay and silt components adsorb more metal ions compared to sand [34]. Taking this into account, it should be noted that most river sediments in our study contained 90-95% sand and only 0-10% clay and silt. Considering the low amount of clay and silt detected in the Maipo River basin, the overall influence of sand in the adsorption of metal ions may be comparable to or even higher than that of the clay and silt fractions [11].

The pH is related to the availability of metals, as they are usually more available in acidic environments due to the absence of hydroxy-complexes, which causes precipitation and increases solubility and mobility [35]. Previous heavy metal studies have indicated that a moderately basic pH, i.e, facilitates the adsorption of metals in the sediment [36]. Thus, a predominantly neutral-alkaline pH, as observed in our study, indicates that metals would be adsorbed in the sediment and less available in the water [37]. A similar pH range has been observed in the sediment of the Tao-Che River (Taiwan) [12] and other Chilean river basins [27]. The organic carbon corresponds to the available carbon and TOC, which also contains carbon linked to the finest mineral fractions [38]. It should be noted that the organic carbon affects the distribution of metals since it may cause retention or complex chelated elements. Thus, a greater carbon percentage could lead to a lower concentration of available metals being retained in the sediment and vice versa. Other studies showed that high percentages of clay and organic carbon affect the adsorption capacity in all types of sediment [39]. In our study, data showed that the sites MEL and PU have a higher adsorption capacity for metals due to their high percentages of organic carbon. The available phosphorus in the sediment is an indicator of water quality, as it determines phosphorous availability in the water column, which may lead to eutrophication and contribute to the formation of soluble compounds or complexes with heavy metals [40]. In our data, the phosphorus availability showed a similar pattern to that presented by the EC; the sites MEL and PU have a higher concentration of phosphorus, with values of 21.9 and 12.5 mg kg^{-1}, probably related with the human population growth and the increase of industrial activities surrounding the river. The lowest value (0.7 mg kg^{-1}) was observed in the CLA site; this site is located in the mountains in a biological reserve with low impact from the cities and agricultural activity, also resulting in very low values of the TOC%, available P, and EC.

3.2 Chemical analysis of the of trace elements in sediments

The concentrations of Cu, Mn, Pb and Zn in the sediment from different sample sites are shown in the Table 3.

Table 3. Concentration of heavy metals in sediments from different sample sites. Each value is the mean of three samples ± SD. According to Ontario norms [41].

Metals **Lowest - Severe effect level** **Sites**	**Cu (μg g^{-1}) (16-110)**	**Mn (μg g^{-1}) (460-1100)**	**Pb (μg g^{-1}) (31-250)**	**Zn (μg g^{-1}) (120-820)**
CLA	251 ± 2	815 ± 6	<LOD	110 ± 1
IM	176 ± 2	748 ± 4	121 ± 3	131 ± 1
SFM	652 ± 1	43.2 ± 1	209 ± 1	133 ± 1
PN	611 ± 2	1600 ± 10	239 ± 2	182 ± 3
MEL	360 ± 1	634 ± 9	160 ± 2	159 ± 1
PU	607 ± 5	948 ± 8	160 ± 3	205 ± 1

The four metals were observed in all of the sites studied, except for Pb, which was under the detection limit at the CLA site. Manganese presents the highest concentrations in all of the sites, except in SFM. Pb and Zn showed the lowest values in all the sites. The values found for metals at all sites are within the limits corresponding to the norms of concentrations in sediments established by the norms for the protection and management of aquatic sediments of the Ontario Ministry of Environment (table 3) [41]. Except Mn in SFM site below limit and in PN site exceeded limit; Pb and Zn in CLA below limit.

Trace elements concentrations in sediment are strongly determined by the local geology or anthropogenic influences. The weathering of minerals is one of the major natural sources, while anthropogenic sources includes the use of fertilizers and herbicides, irrigation, industrial effluent and leakage from service pipes [42]. Our results show the overall pattern occurring in the sediments of the Maipo River basin, in natural conditions. Determination of soluble salts in these sediments shows sulfate concentrations 20.77 in 20.77; 14.10; 3.50; 1.58 (mgg-1) in PEL; IM; MEL; SFM respectively and carbonate 4.80; 1.83; 1.73; 1.70 (mgg-1) in PEL; MEL; SFM; IM respectively these anions can form poorly soluble or complex compounds with some metallic trace elements (unpublished results),

3.3 Adsorption kinetics of metals on sediment

The nature of interactions in the sediment matrix determines the kinetics of the primary mechanism involved during the sorption process. A corresponding time of 48 hours was set to effectively equilibrate the four metals in the sediment samples of the six sites in the Maipo River basin (Figure 2).

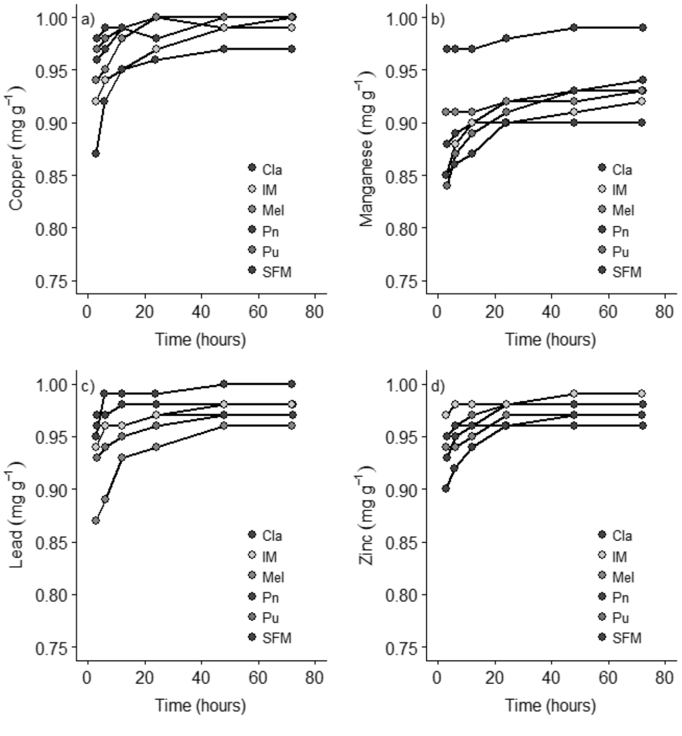

Figure 2. Curves of adsorbed metal Cu (a); Mn (b); Pb (c) and Zn (d) (mg g^{-1}) as a function of contact time (hours) onto sediment of the six sites in the Maipo River basin.

For all metals and at all sites the adsorption increases rapidly in the first hours and then it is possible to observe that the equilibrium is reached after 40 hours.

The sorption data were also analyzed with the Elovich equation [Cs = 1 / b Ln (ab) + 1 / b Ln (t)] using the experimental concentration (Cs, mg metal/kg sediment) as a function of the contact time (t). The resulting curve can be modeled according to a logarithmic regression curve, equivalent to the model parameters, with the experimental data adjusted to the equilibrium time giving a logarithmic representation. $r > 0.8$ indicates a good fit, and according to the relative error (RE) < 10%, it would be considered to agree with the Elovich model [43].

The Elovich equation shows that all of the metals studied in the Maipo River basin agree with the Elovich model, with a mean correlation of > 0.8 and RE < 10%, except for Mn in the IM site, where R is lower (0.61) and the relative error is >10%, and Zn at the SFM site, where R = 0.59 and RE is >10% (Table 4).

Table 4. Values of RE (% relative error) and R (correlation coefficient) for the metals Cu, Mn, Pb and Zn in the six sites in the Maipo River basin. Exception to the Elovich equation adjust in bold.

Site	Mn		Cu		Pb		Zn	
	RE	R	RE	R	RE	R	RE	R
CLA	0.05	0.89	0.02	0.88	0.02	0.90	0.06	0.84
IM	**0.15**	**0.61**	0.04	0.97	0.08	0.91	0.09	0.80
SFM	0.02	0.98	0.00	0.98	0.04	0.89	**0.14**	**0.59**
PN	0.01	0.94	0.06	0.88	0.03	0.88	0.03	0.92
MEL	00.0	0.87	0.06	0.88	0.03	0.83	0.02	0.87
PU	0.01	0.84	0.06	0.95	0.01	0.89	0.01	0.93

3.4 Adsorption isotherm

A adsorption isotherm shows a relationship between the amounts of metal adsorbed (Cs), per unit weight of the soil and the metal concentration in the solution at equilibrium (Ce). In the next figures is show the isotherms for Cu, Mn, Pb and Zn in the sediment of Maipo river basin.

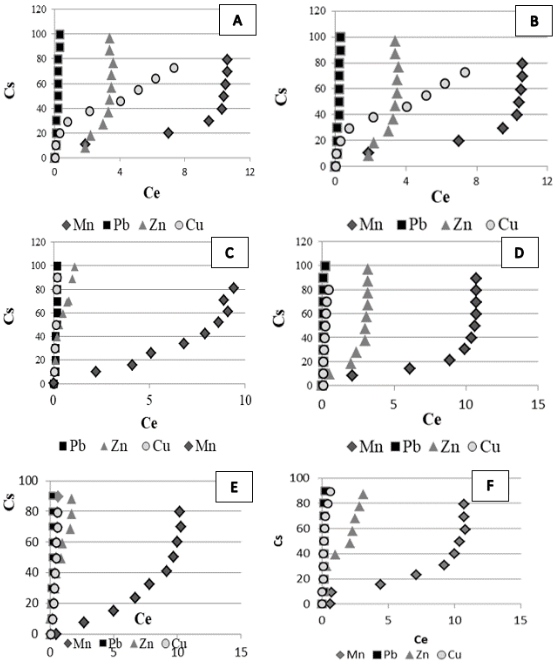

Figure 3. Adsorption isotherms of metals Cu, Mn, Pb and Zn. a) CLA (b) IM (c) MEL, d) PN (e) PU (f) SFM. Cs = adsorption concentration (mgL^{-1}); Ce = concentrations in solution (mgL^{-1}).

The analysis of the sorption over time (48 h) showed that Mn presents a similar behavior over all of the sites, indicating unfavorable adsorption. Pb shows isotherms that indicate strong adsorption in all the sites. Cu shows the same behavior in the SFM, MEL, PN and PU sites; however, the isotherms for the CLA and IM sites indicate limited adsorption, with saturation observed at the adsorbate sites. Zn show strong adsorption in CLA and PU and unfavorable adsorption on the other sites [44]. The adsorption isotherms indicate that the system or the adsorption is favorable and linear for most of the metals for all sites, except for Mn, which has unfavorable adsorption throughout all the sites. This could be one of the factors explaining the high concentration of Mn over five of the studied sites in the Maipo River basin. It is important to note that currently Mn is considered an contaminant because it is perceived as a threat to human health and to the environment. It has been classified as an essential metal; however, it can produce toxic effects when the intake is over certain levels [45].

High intakes of Mn could cause neurotoxicity in humans and because of this; many concerns have been raised by the consumption of aquatic products containing this and other heavy metals [45].

Soil sorption is characterized by the partition constant (kd) ml/μg) [46, 47]. The adsorption coefficient (kd) was defines by the next equation: $kd = Cs/Ce$. The linear or distribution coefficient (Kd) is related to soil organic carbon (OC) by the following equations; $Koc = 100\ Kd / (\%OC)$ [48, 49].

Kd values (Table 5) indicate that the concentration of adsorbed metal (Cs) is higher than the concentration of metal in the solution (Ce), with most sites presenting the pattern Pb> Cu>Zn> Mn. The Kd value is important in the adsorption process of a metal, and higher Kd values imply a greater affinity to binding sites on the adsorbent (sediment). The CLA site shows low Kd values, which could be due to the physicochemical characteristics of the site, such as a lower percentage of total carbon and pH, which are important in this process. This implies that the surface adsorption is lower compared to the other sites and other metals. According to the Kd values, Mn presents lower Koc values over all of the sites, indicating that Mn interacts less with sediments organic components. The highest Koc values were for Cu and Pb at all of the sites, except for Cu in CLA, indicating the strong interaction of this metal with the organic components of the sediments.

Table 5. Kd and Koc values, average of six repetitions over the six sites in the Maipo River basin.

Sites	Cu		Mn		Pb		Zn	
	Kd	Koc	Kd	Koc	Kd	Koc	Kd	Koc
CLA	20.6	3433	3.8	633	271	45166	18.3	3050
SFM	187	23375	5.1	638	415	56375	21.7	2713
IM	573	19578	7.2	248	363	12517	539	18586
MEL	104	22476	5.6	267	326	15523	96.9	4614
PN	472	20521	6.3	274	456	19826	447	19434
PU	275	27500	5.5	550	440	44000	71.7	7170

3.5 Freundlich model

In order to gain a better understanding of mechanisms, a Freundlich model is proposed to quantify the isotherm obtained for the four metals over the six sites in the Maipo River basin. Metals initially occupy the locations with greatest affinity, subsequently the binding force decreases logarithmically through increased occupation of the adsorption sites. The Freundlich model is frequently employed for such studies[50], the parameters nf and Kf are obtained from the curves for each metal and site; data for each metal is summarized in table 6.

Table 6. Freundlich parameters for the four metals in the six sites in the Maipo river basin.

	Cu			Mn			Pb			Zn		
Sites	nf	Kf	R^2	nf	Kf	R^2	nf	Kf	R^2	nf	Kf	R^2
CLA	3.3	1.0	0.969	1.7	45.0	0.889	1.7	85.3	0.897	1.0	1.2	0.956
IM	1.7	1.1	0.967	1.1	1.0	0.992	1.1	1.3	0.899	1.4	108	0.985
SFM	5.0	137	0.784	0.8	8.7	0.729	1.1	9.6	0.893	1.4	2344	0.892
MEL	1.4	1.4	0.961	1,3	1.8	0.904	1.3	1.0	0.959	1.1	108	0.949
PN	2.0	7.2	0.885	1.3	1.3	0.947	1.1	2.6	0.881	1.1	40.5	0.899
PU	1.7	4.5	0.908	1.4	1.5	0.723	1.7	78.7	0.656	0.3	78.7	0.949

For most sites, the adsorption of metals in sediment is well described by the Freundlich isotherm equation, with R^2 values greater than 0.959. Except, all the metals in the SFM site; Cu, Pb and Zn in the PN site; Cu, Mn and Pb in the PU site; Mn and Pb in the CLA site; and Pb in the IM site. Kf is the Freundlich adsorption (Kf^{ads}) or desorption (Kf^{des}) coefficient, and nf is the slope (Freundlich exponent or linearity factor, a constant that denotes the sorption intensity). The Freundlich model assumes that adsorption intensity (nf), greater than 1, describes a favorable adsorption in multilayers. On the contrary, if the adsorption intensity (nf) of the model is less than one, it is considered an unfavorable adsorption. In this study the adsorption of Mn in SFM and Zn in Pu sites, would be unfavorable.

3.6 Desorption of Cu, Mn, Pb, and Zn

The amounts of desorption of each metal are shown in Fig. 4. Mn presents the highest percentage of desorption. In the case of Zn, Cla, IM and SFM present a percentage of desorption greater than one percent (2 to 7%), while for the Pb and Cu metals, the percentage of desorption does not exceed 1%. Furthermore, in CLA and PU, the distribution of desorption of the four metals was Mn >Zn >Cu >Pb, and in SFM it was Mn > Zn> Pb > Cu.

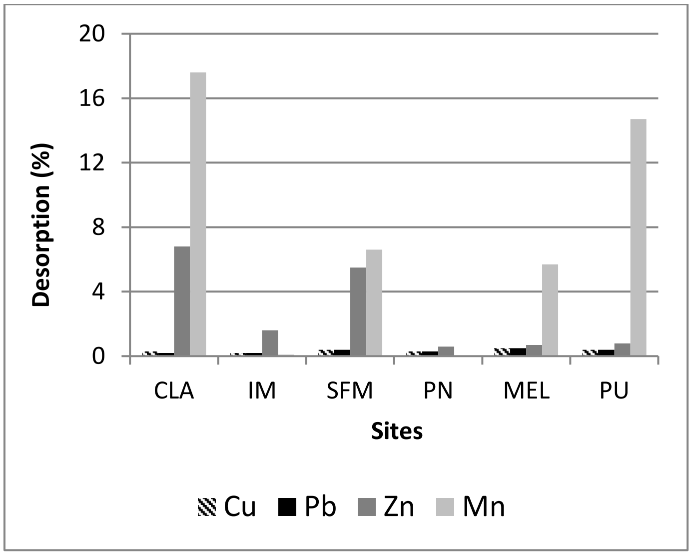

Figure 4. Concentration (%) of metals desorbed since sediments

The most desorbed metal was Mn, which confirms the fact that the adsorption process for this metal is unfavorable. This metal was desorbed in all the sites, except in IM. Another desorbed metal, although in a smaller percentage, was Zn. This indicates that both metals can be transferred to the water column. These results indicate that for these two metals, special management measures are necessary, such as continuous monitoring of the basin and especially care to avoid using these metals to avoid increasing river pollution.

3.7 Pearson correlations

Table 6. Correlation of the sediment characteristics with adsorption constant of each heavy metal.

	pH	MO	Clay	Kd-Cu	Kd-Mn	Kd-Pb	Kd-Zn
pH	1						
MO	0.58020	1					
Clay	0.57401	0.42486	1				
Kd-Cu	0.71005	0.11839	0.26292	1			
Kd-Mn	0.67769	0.05230	0.22282	0.91107	1		
Kd-Pb	0.82129	0.39281	0.81777	0.57041	0.48424	1	
Kd-Zn	0.56456	0.17711	0.12489	0.92500	0.86403	0.29467	1

The pH correlation with the metals adsorption is Pb >Cu> Mn> Zn. The strongest correlation occurs between the pH and Kd-Pb, indicating that at higher pH values, the Pb adsorption will be unfavorable, probably due to the dependence of different chemical species of Pb on the pH, while this dependence was moderate for Cu, Mn and Zn. For the content of organic matter, no significant correlation was found. The clay content only shows a correlation with the Pb, indicating that its adsorption could be associated with interactions with the clay of the sediment. Thus, these results indicate that in the MEL and PU sites, which present the highest clay contents, the Pb adsorption could be preferential. On the other hand, there are positive correlations between pairs of metals such as Mn-Cu, Zn-Cu, and Zn-Mn, indicating the competition of these metals for the adsorbent sites.

Environmental pollutants such as metals, pesticides, and other organic compounds pose serious risks to many aquatic organisms, disrupting complex fish behaviors, such as predator avoidance, reproduction, and social behaviors [51]. It is important to note that these metals are the most dangerous for the biota. For example, the fish *Sebastes schlegelii* had increased plasma cortisol, heat shock protein and immune response due to dietary lead exposure [52]. Manganese was the most concentrated metal in the Maipo River basin. Sediment studies in other basins have shown that there is a high content of Mn oxides, which indicates that a finer fraction of sediment is present [53, 28], possibly explaining the reason that this metal has the highest concentration over five sites in the Maipo River basin. To our knowledge, few studies have addressed studying the toxicity of this metal. For example, Perl and Olanow (2007) [54] showed that an excess of manganese can act as a neurotoxin in humans, and in other mammals, it has been associated with fetal toxicity and reduced postnatal growth[55, 56].

4. CONCLUSIONS

This study showed the adsorption of four metals in the Maipo River basin and indicates a different behavior of Mn, which showed higher concentrations in all sites compared to Pb, Cu and Zn, and the adsorption isotherms showed unfavorable adsorption throughout all of the sites for this metal and favorable adsorption for Pb, Cu and Zn. In the case of desorption, less than 1% of desorption was observed for all metals and sites, except for the Mn and Zn in some sites. The Kd values indicate that these metals are mostly adsorbed, and thus, it is inferred that in these six sites, these metals are not a contaminant hazard for the biota inhabiting the water-sediment system because they are unavailable, except for manganese.

According to the Pearson correlations, the pH and clay content of the sediment are important characteristics in the tolerance of the river towards possible increases in the concentrations of metals, depending on the properties of the metal, it will be necessary to increase this study incorporating other metals and continuous monitoring.

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