

Distribution of copper, zinc, lead and cadmium concentrations in stream sediments from the Mapocho River in Santiago, Chile

R. Segura ^{a,*}, V. Arancibia ^b, M.C. Zúñiga ^b, P. Pastén ^a

^a *Facultad de Ingeniería, Departamento de Hidráulica e Ingeniería Ambiental, Pontificia Universidad Católica de Chile, Santiago-22, Chile*

^b *Facultad de Química, Pontificia Universidad Católica de Chile, Santiago-22, Chile*

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Abstract

The Mapocho river, which crosses downtown Santiago, is one of the most important rivers in contact with a population of about six million inhabitants. Anthropogenic activities, industrialization, farming activities, transport, urbanization, animal and human excretions, domestic wastes and copper mining have affected the river, contaminating it and its sediments with heavy metals. Concentration and distribution of Cu, Zn, Pb and Cd were studied with the purpose of determining their bioavailability and their relation with the characteristics of the sediments. Freshly deposited seasonal sediments were collected from 0–8 cm depths from 6 locations (S₁ to S₆) along the 30-km long channel length, in the four seasons of year on the following dates: May 2001 (D₁, autumn); August 2001 (D₂, winter); October 2001 (D₃, spring) and January 2002 (D₄, summer). The dried samples were sifted to obtain the <63- μm sediment fraction, since it has been shown that large amounts of heavy metals are bound in the fine-grained fraction of the sediment. Cu and Zn were analyzed by atomic absorption spectrophotometry and Pb and Cd by square wave anodic stripping voltammetry. The highest concentrations of Cu (2850 $\mu\text{g g}^{-1}$) were found in the northern part of the river (S₁, average D₁–D₄), near the mountains and a copper mine, and then decreased downstream to 209 $\mu\text{g g}^{-1}$ (S₆). Total Zn showed an irregular variation, with higher values at S₁ (1290 $\mu\text{g g}^{-1}$) and high values in some winter sampling (1384 $\mu\text{g g}^{-1}$ S₄, S₅–D₂). Pb showed different trends, increasing from S₁ to S₆ (17 to 61 $\mu\text{g g}^{-1}$), with the highest values in the summer samples (83 $\mu\text{g g}^{-1}$, S₄–S₆, D₄), and total Cd increased slightly from mean values of 0.2 and 0.5 $\mu\text{g g}^{-1}$. Partition into five fractions was made using Tessier's analytical sequential extraction technique; the residue was treated with aqua regia for recovery studies, although this step is not part of the Tessier procedure. The results show that Cu, Zn and Pb in the sediments were dependent on the sampling places along the river, and variation in two years was low (D₁–D₄). The highest values of total organic matter, carbonate and conductivity were found in S₆, which has the smallest size particles, while at S₁ the sediments were predominantly sand and contain larger amounts of silica. Cu associated with carbonate decreased gradually from 58% (1771 $\mu\text{g g}^{-1}$, S₁) to 16% (32 $\mu\text{g g}^{-1}$, S₆); Cu bonded to reducible fraction was almost constant (33% to 37%), and Cu associated with oxidizable fraction increased from 7% (S₁) to 34% (S₆), but copper content was lower (214 to 68 $\mu\text{g g}^{-1}$). Zn had a similar fractionation profile. However, Pb bound to oxidizable fraction did not show significant percent variation along the river (20% to 19%), but the amount bounded was 4 to 12 $\mu\text{g g}^{-1}$. The residual fraction increased from 24% to 41% (5 to 25 $\mu\text{g g}^{-1}$, S₁ to S₆). The distribution of Cd in the sediment was almost independent of the sampling stations and was bound to carbonate, reducible and residual fraction in similar proportion. Cu and Zn at S₁ were mainly bound to carbonates and reducible phases with 91% and 73% (2779 and 965 $\mu\text{g g}^{-1}$, respectively), and with a

* Corresponding author. Tel.: +56 2 686 4723; fax: +56 2 686 4744.

E-mail address: rasegura@puc.cl (R. Segura).

change in the pH and/or the redox potential of the sediment–water system, these contaminants could easily enter the food chain. In S_6 the amount of Cu and Zn in these phases was 50% and 53% (100 to 313 $\mu\text{g g}^{-1}$, respectively).

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1. Introduction

Sediment is an integral and dynamic part of river basins, including estuaries and coastal zones. Sediment originates from the weathering of minerals and soils upstream and is susceptible to transport downstream by the river water. Sediments are usually considered as a sink for trace metals, but they can also become a source under certain conditions. Then, trace metals are able to move towards the water column or accumulate in plants and consequently contaminate the food chain. Of major concern about the presence of some metal ions in the environment are the negative health effect that they may cause in humans, animals, and plants. Heavy metal mobility, bioavailability and toxicity depend largely on the chemical state of the metals and determine the potential for environmental pollution. Metal distribution depends on the characteristics of the sediments being studied and corresponds to the place of origin, such as the amount and type of organic and inorganic matter, redox properties, pH and oxygen are among the most important chemical factors that affect the mobility of sediment-bound metals. When environmental conditions change, sediments can act as sources of metals (Gabler, 1997; Izquierdo et al., 1997; Patrick and Verloo, 1998; Wen and Allen, 1999; Bachmann et al., 2001; Zoumis et al., 2001; Morillo et al., 2002; and Martínez-Villegas et al., 2004). One of the most widely-applied procedures was proposed more than 27 years ago by Tessier et al. (1979). It partitions elements into five operationally-defined geochemical fractions including: exchangeable (F_1); carbonates (F_2 , acid-soluble); Fe and Mn oxides (F_3 , reducible); organic matter (F_4 , oxidizable); and residual (F_5). This method was modified or complemented by Thomas et al. (1994), Davidson et al. (1994), Campanella et al. (1995), Houba et al. (1996), Mester et al. (1998), Gleyzes et al (2002), and Mossop and Davidson (2003), and has been most widely used and applied not only to soils and sediments, but also to atmospheric particulate matter.

The Mapocho is a river with a nivo-pluvial regime located in the Metropolitan Region of Santiago, Chile. It has an extension of approximately 110 km from its birth in the Andes range (in the sector of mount El Plomo) to

its discharge in the Maipo river whose coordinates are: 33°27'22" S, 70°39'19" W. In its upper part its regime has a nival character, with defrosting at the beginning of spring as the source of its most significant volume. With respect to seasonal variation, the great monthly volume change goes from a maximum of 13.6 m^3/s in November to a minimum of the order of 2.3 m^3/s in April. In relation to the swells of the Mapocho river, it is possible to distinguish between those of nival origin and those of pluvial or pluvio-nival origin. The nival swells have their maximum volumes in the November–December period and they are characterized by having smaller maximum volumes than the winter swells, although they can cause destruction due to their persistence and the processes of erosion and sediment dragging associated with these phenomena.

The main objective of this study was to measure the total concentrations of Cu, Zn, Pb and Cd and apply the Tessier protocol to superficial sediments from the Mapocho river, and in that way to determine the mobilities and the ecotoxic potential of the metals. However, residual fraction was obtained with aqua regia instead of HF–HClO₄ (Sutherland and Tack, 2003) leading to good accuracy and reproducibility when sediment river reference material NCS DC 78301 was used. The protocol was applied to sediments obtained from 6 sampling stations during two years. The Mapocho is a highly contaminated river, and its course is getting gradually smaller due to urban growth, and for that reason it is more feasible for the sediments to interact with the population that lives in its neighborhood. However, no systematic study has been made on this river to assess the distribution of the heavy metals in sediments; neither have we found values for total metal in this river in the past, which would have provided the background before this fast growth.

2. Material and methods

2.1. Reagents

All reagents were analytical grade, obtained from Merck (Darmstadt, Germany). Acetic acid, hydrochloric acid and nitric acid for solution acidification were

ultrapure quality. Calibration standards of Cu, Zn, Pb and Cd were prepared by appropriate dilution of the 1000 mg L⁻¹ stock solutions (Merck). All solutions were prepared with ultrapure water from a Millipore-MilliQ system (18.0 MΩ resistance, Milford, MA, USA). Hexadistilled metallic mercury for electroanalytical measurements was purchased from Radiometer Analytical (Lyon, France). All glassware and polyethylene bottles were cleaned by soaking in 10% (v/v) HNO₃ (Merck) followed by three rinses with deionized water.

Sediment river reference material NCS DC 78301 was used for validation of the methodology for carbonates, silica, total organic matter and total concentrations of Cu, Zn, Pb and Cd.

2.2. Sediment sampling and size separation

Surface sediments (0 to ≈ 5–8 cm depth) were collected in triplicate from the Mapocho river in the four seasons of year on the following dates: May 2001 (D₁, autumn); August 2001 (D₂, winter); October 2001 (D₃, spring) and January 2002 (D₄, summer). Six sampling sites were selected from north to south along the river, at the following places: Lo Hermida (S₁), Nilhue (S₂), San Antonio (S₃), Manquehue (S₄), Mapocho (S₅) and Esperanza (S₆). The map with the sampling stations is shown in Fig. 1. Sediments were collected with plastic collectors, returned to the laboratory in polyethylene bottles, and stored at 4 °C. Prior to analysis, the sediment samples were dried at 60 °C for 48 h. Particle-

size distribution was made using several stainless steel sieves. To characterize the sediment samples in terms of particle size distribution (texture), three fractions were collected (sand 200–20 μm; silt 20–2 μm, and clay <2 μm) in pre-weighed containers, dried and weighed. All the analyses were carried out on the <63 μm fraction because this fraction minimizes the grain-size dependence of metal concentration; it has longer residence time in the river channel, and allows comparison of results (Moss and Contanzo, 1998; Datta and Subramanian, 1998). The dried samples were sifted through a 2 mm stainless steel sieve. The fraction that passed through this sieve was then sifted through a 63 μm sieve.

2.3. Physicochemical parameters

2.3.1. pH

10 g of sample were taken in 50 mL distilled water and agitated for 10 min. The solution was left undisturbed for 1 h with occasional shaking before measuring the pH. A combined glass electrode connected to a pH-meter (Orion 430, ± 0.01 pH) was used for pH measurements.

2.3.2. Conductivity

10 g of sample was taken in 50 mL distilled water and agitated for 10 min. The solution was left undisturbed for 1 h with occasional shaking before measuring the conductivity. A platinum cell connected to a conductivity meter (Hanna, ± 0.1 μS) was used for conductivity measurements.

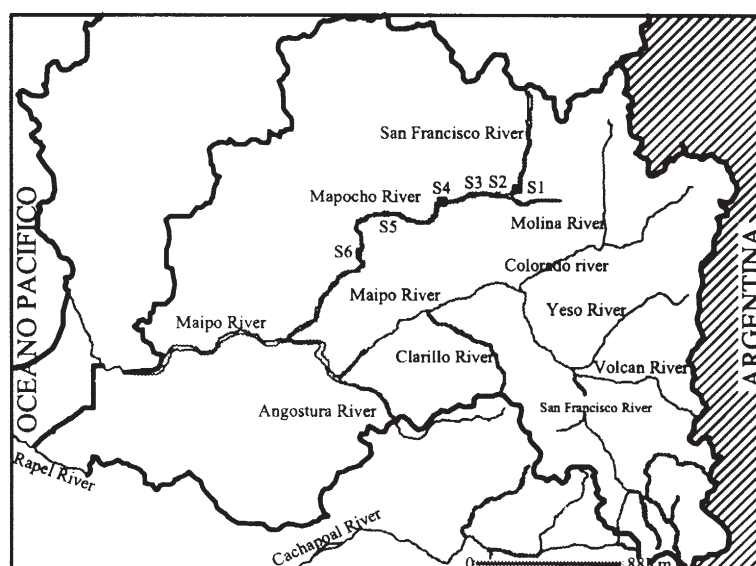


Fig. 1. Location of sediment sampling along the Mapocho river (S₁–S₆).

2.3.3. Organic matter

Organic carbon in the sediment was determined by ignition at 550 °C in a muffle furnace. The percentage of loss on ignition was considered as total organic matter (TOM).

2.3.4. Carbonate content

A 5.0-g sample of sediment was treated with 1.0 N HCl, and the unused acid was titrated with 1.0 N NaOH solution.

2.3.5. Metal extraction

The total metals were extracted from the sediment samples using digestion with aqua regia. A 1.0-g sample of sediment was treated with 15 mL HCl and 5 mL HNO₃ and kept at room temperature for 24 h. It was then heated in a sand bath on a hot plate to 50 °C for 5 h, and then refluxed at 130 °C for 3 h. Concentrated NaOH solution was added to lower the acidity. The sample was filtered, washed with deionized water, and received in 50.0 mL volumetric flasks.

2.4. Metal ion analysis

Cu and Zn concentrations were determined by flame atomic absorption spectrometry using a Perkin-Elmer atomic absorption spectrometer (Model Analyst 100) with individual hollow cathode lamps. All measurements were carried out in an air/acetylene flame, and the wavelengths used for the determination of the analytes were the following: Cu 324.3 nm and Zn 213.9 nm. Standard solutions of copper and zinc were prepared by diluting a commercial standard containing 1000 µg mL⁻¹, Merck (Darmstadt, Germany). Metal quantification was based on calibration curves which were determined several times during the period of analysis. Linear regression and detection limits (DL) were determined. Pb and Cd, were analyzed using square wave anodic stripping voltammetry (SWASV). The voltammograms were obtained with an MDE-150 polarographic stand (Radiometer Analytical, Lyon, France). The MDE-150 was controlled with TraceMaster 5 PC software. A 10 mL capacity measuring cell was equipped with a hanging mercury drop electrode (HMDE), a Ag/AgCl/3 M KCl reference electrode, an auxiliary platinum electrode, a mechanical mini stirrer, and a capillary to supply the inert gas. 10.0 mL of digested sediment sample was pipetted into the voltammetric cell and the solution was purged with argon for 5 min. Depending on the metal concentration level, electrolysis times were 60–180 s at –0.800 V with a stirring speed of 40 rad s⁻¹. After a 10-s quiescent period the potential

was scanned between –0.800 and –0.100 V using square wave modulation with 0.005 V step amplitude, 0.025 V pulse amplitude, and 0.04 s step duration. Pb and Cd were quantified using the standard addition method. All the experiments were carried out in an argon atmosphere at 25 °C.

The SWASV and AAS methods were validated using a certified reference standard for trace metals in river sediments (NCS DC78301, GBW08301 obtained from the China National Analysis Center).

2.5. Detection limits (DL)

The limit of detection was calculated from $X_{DL} = a + 3S_{x/y}$, where a is the intercept, and $S_{x/y}$ is the standard deviation of calibration curve (Miller and Miller, 1988).

2.6. Metal fractionation

2.6.1. F_1 (exchangeable fraction)

A 1.0-g sediment sample was extracted at room temperature for 1 h with 8 mL of 1.0 M MgCl₂ (pH 8.2) with continuous stirring. The extract was separated from the solid phase by centrifugation at 4000 rpm for 30 min and the supernatant was decanted into a polyethylene tube. The extract was diluted to 50 mL and stored at 4 °C. The residue was washed with 15 mL of deionized water and then centrifuged for 15 min. The supernatant was discharged without the solid residue, which was subjected to step 2 (F_2).

2.6.2. F_2 (bound to carbonates)

The residue obtained from step F_1 was leached for 6 h with continuous stirring at room temperature with 10 mL of 1.0 M sodium acetate adjusted to pH 5.0 with acetic acid. The extract was separated as in F_1 .

2.6.3. F_3 (reducible fraction)

The residue obtained from step F_2 was heated at ≈ 100 °C with 20 mL of 0.04 M hydroxylamine hydrochloride solution in 25% (v/v) acetic acid during 6 h with occasional stirring. The extract was separated as in F_1 .

2.6.4. F_4 (oxidizable fraction)

To the residue obtained from step F_3 were added 3 mL of 0.02 M HNO₃ solution and 5 mL of 30% H₂O₂ adjusted to pH 2 with HNO₃. The mixture was heated at ≈ 100 °C for 2 h with occasional stirring. A second 3 mL aliquot of 30% H₂O₂ (pH 2) was added and the sample was heated again for 3 h with stirring. After cooling, 5 mL of 3.2 M ammonium acetate in 20% (v/v)

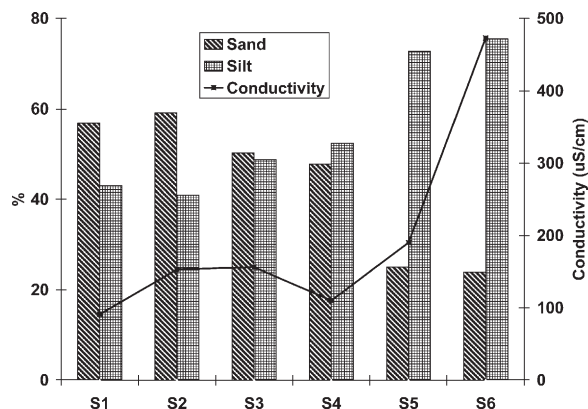


Fig. 2. Grain size distribution of sediment samples: sand (20–200 μm), silt (20–20 μm), clay (<2 μm), and conductivity results.

HNO₃ was added and the sample was diluted to 50 mL and stirring continuously for 30 min.

2.6.5. F_5^1 (residual fraction)

The residue obtained from step F₄ was digested with 10 mL of 6 M HCl and 3 mL of concentrated HNO₃, and evaporated to near dryness. The residue was then dissolved in 2 M HNO₃ solution and diluted to 50 mL with deionized water.

3. Results and discussion

3.1. Characteristics and composition of the sediments

Particle size fractionation indicated that the sediments were variable: in the S₁ station the sediments were dominated by sand (200–20 μm), while in the S₆ station the particles were of medium fine size (silt, 20–2 μm); < 2 μm clay particles were not found in these sediments.

Conductivity and resistivity can also be used as tools to classify according to grain size distribution of sediments; higher electric conductivity is representative of fine grained sediments, such as silt or clay, while sand is characterized by distinctly lower electric conductivity. Conductivity values obtained with the sediments ranged from 74.5 to 473.0 μS cm⁻¹ and the highest values were found in S₆, which contains the smallest particle size. Data for mean particle size-distribution and mean conductivity are presented in Fig. 2.

Most sediments were brown and some were brown-blue, the pH did not vary much and was slightly basic

(7.30–8.03). The change in pH along the river was not uniform. Total organic matter (TOM) in the sediments ranged from 3% in S₂–D₂ to 13% in S₆–D₄; carbonate ranged from 1% in S₁–D₂ to 10% in S₆–D₂; silica values ranged from 45% in S₄–D₁ to 95% in S₁–D₁. The highest TOM values were obtained in winter (D₂), probably due to the low temperature which causes low degradation of organic matter. Fig. 3 shows the longitudinal variation of TOM, carbonates and SiO₂ (average of 4 sampling dates) from station S₁ to S₆. It is seen that SiO₂ decreases from S₁ to S₆, and TOM and carbonate increase from S₁ to S₆. This may be due in part to the slope of the river changing from 8% to 4%, leading to the accumulation of solid residues.

3.2. Determination of aqua regia extractable concentration of Cu, Zn, Pb and Cd

Table 1 shows the accuracy of the results obtained with the aqua regia digestion method for reference material DC 78301. The SD values were between 4% and 14% for triplicate measurements. Our results are somewhat higher than the reference values. However, when the measured values were plotted versus the standard values, the following equations were obtained:

Cu: $y=0.0023x+0.0037$	$R^2: 0.9995$	DL (μg g ⁻¹): 0.100
Zn: $y=0.0034x+0.0056$	$R^2: 0.9990$	DL (μg g ⁻¹): 0.800
Pb: $y=0.9426x+2.4533$	$R^2: 0.9995$	DL (μg g ⁻¹): 0.007
Cd: $y=3.5506x+0.6665$	$R^2: 0.9999$	DL (μg g ⁻¹): 0.004

The regression coefficients were satisfactory and indicate good agreement between our data and the reference values. Pb and Cd concentrations were determined by the standard addition method. R and DL were determined for each sample. In solution DL of Pb and Cd were 0.10 and 0.08 μg L⁻¹, respectively, for reference

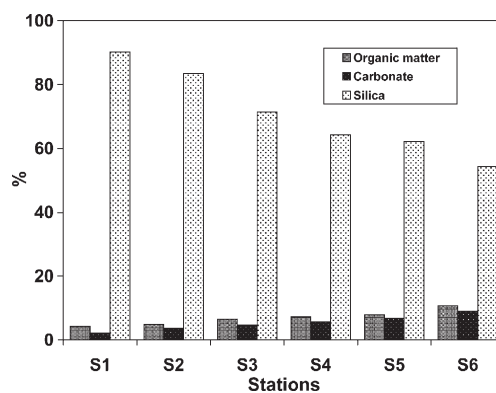


Fig. 3. Percentage of total organic matter, carbonate and silica in sediments along the Mapocho river.

¹ Digestion of the residual material with aqua regia is not a step of the Tessier method.

Table 1

Comparison of reference data supplied by the China National Analysis Center and data obtained in this work

	Cu ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)	Pb ($\mu\text{g g}^{-1}$)	Cd ($\mu\text{g g}^{-1}$)
Certified value	53±6	“251.3”	79±12	2.45±0.30
Experimental results	56.0±11.7	293.0±29.1	84.0±7.0	3.0±0.1
% recovery	106	116	106	122

material. However, the results obtained with some samples were different, obtaining values up to six times higher. Cu and Zn concentrations were determined with the normal calibration curve, obtaining DL of 2.0 and 16.0 $\mu\text{g L}^{-1}$ for Cu and Zn in solution, respectively.

The variation of Cu, Zn, Pb and Cd along the Mapocho river (S₁ to S₆ locations) for the four seasons (autumn, winter, spring, summer, D₁–D₄, respectively) is shown in Fig. 4. These results are the means of triplicate determinations. It is seen that total copper is higher at the S₁ station and then decreases until S₆, where the lowest levels are found. The mean values (S₁–S₆) were similar in the different seasons (1208; 1328; 1457 and 1365 $\mu\text{g g}^{-1}$ for D₁ to D₄, respectively). The mean values (D₁–D₄) at each sampling station were 2850±490; 1620±305; 1320±204; 1470±246; 569±400 and 209±12 $\mu\text{g g}^{-1}$ for S₁ to S₆, respectively. Total Zn shows an irregular variation, with higher values in some winter sampling (D₂). The mean values (S₁–S₆) in function of time were decreasing 1033; 1089; 768 and 455 $\mu\text{g g}^{-1}$ for D₁ to D₄, respectively. The mean values (D₁–D₄) at each station were 1290±370; 790±280; 577±309; 1020±490; 740±358 and 607±240 $\mu\text{g g}^{-1}$ for S₁ to S₆, respectively. Total Pb shows different trends, with the highest values in the summer sampling (D₄) at stations S₄, S₅ and S₆ (83 $\mu\text{g g}^{-1}$). The mean values (S₁–S₆) in function of time were increasing 25; 27; 42 and 54 $\mu\text{g g}^{-1}$ for D₁ to D₄, respectively. The mean values (D₁–D₄) at each station were 17±4; 21±6; 30±10; 43±29; 50±25 and 61±19 $\mu\text{g g}^{-1}$ for S₁ to S₆, respectively. The mean values of Cd in S₁ to S₆ locations were similar in the different seasons (0.3; 0.3; 0.4 and 0.4 $\mu\text{g g}^{-1}$ for D₁ to D₄, respectively). Cd increases slightly from S₁ to S₆, with mean values (D₁–D₄) of 0.2±0.0; 0.2±0.1; 0.3±0.0; 0.4±0.1; 0.4±0.1 and 0.5±0.0 $\mu\text{g g}^{-1}$. Moss and Contanzo (1998) reported metal concentration values in sediments to establish baseline or reference values for heavy metals in the sediments of Queensland water. They considered allowed limits for Cu, Zn, Pb and Cd of 34; 160; 15 and 0.9 $\mu\text{g g}^{-1}$, respectively (< 63 μm fraction was analyzed). We have not found past values obtained for this river to compare the results as functions of time or as background values.

There are results of metal concentrations from other rivers in the country, but these rivers have very different drainage areas compared with the Mapocho river. In the analyzed sediments, Cu far exceeded the Moss and Contanzo

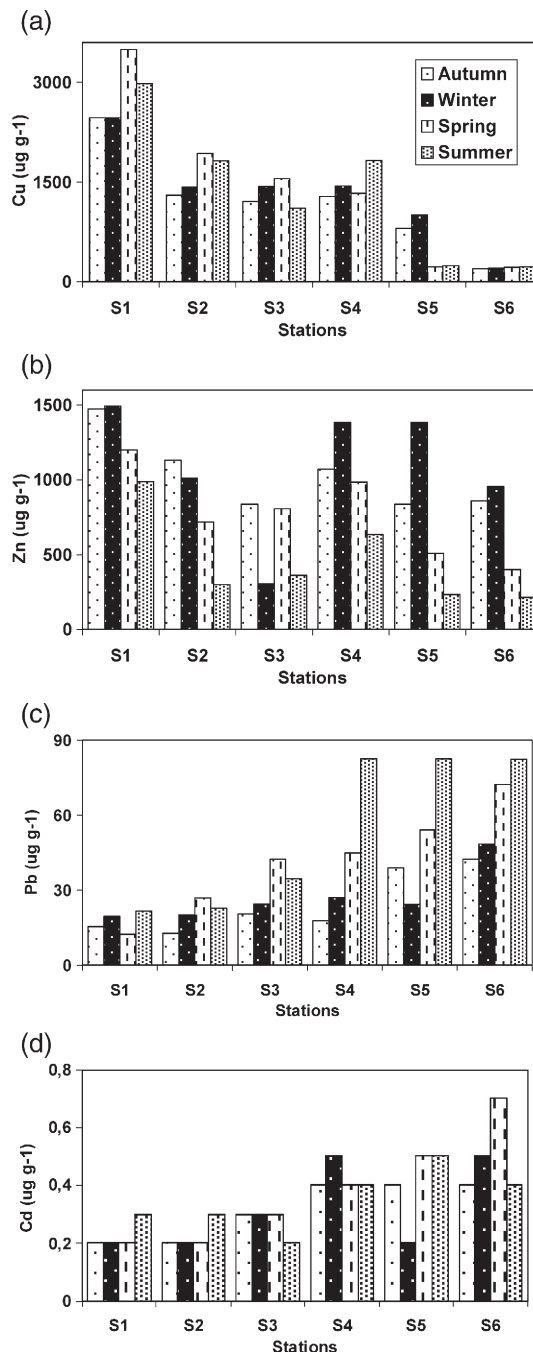


Fig. 4. Cu, Zn, Pb and Cd concentrations in sediments along the Mapocho river (S₁ to S₆ stations) obtained in the four seasons of the year. May 2001 (D₁, autumn); August 2001 (D₂, winter); October 2001 (D₃, spring) and January 2002 (D₄, summer).

(1998) values in all the samples. Cu is an essential element to biota and humans, but it is toxic in excess. Because of potential health effects, its presence in this downtown

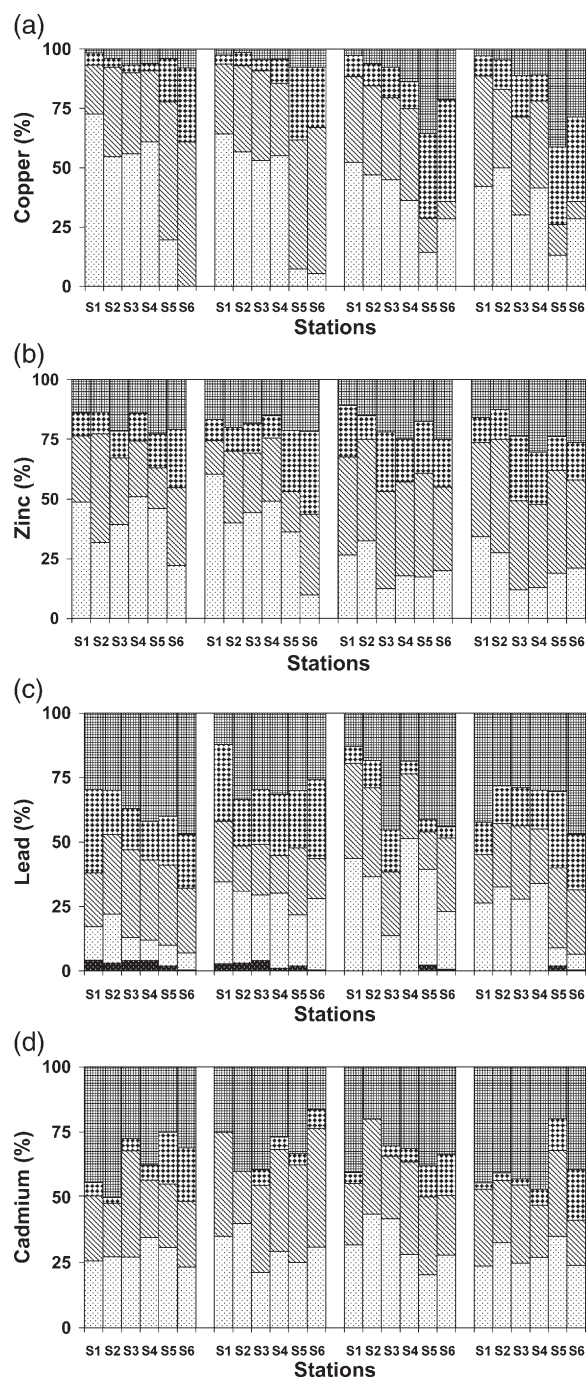







Fig. 5. Fractionation profiles of Cu, Zn, Pb and Cd in sediments along the Mapocho river (S₁ to S₆ stations) obtained in the four seasons of the year (D₁ to D₄) using the Tessier sequential extraction scheme: F₁ (exchangeable): ; F₂ (carbonates) ; F₃ (reducible) ; F₄ (oxidizable) ; F₅ (residual): .

river is of concern. Zn was also in excess at all the stations. We did not find a relation between Cu and Zn concentrations; Cu decreases from S₁ to S₆, while Zn has an irregular variation, which indicates that there are several different sources of Zn contamination. On the other hand, Pb concentration was high where Cu was low. Near the S₄ to S₆ stations there are bus terminals where the driver repair the engines and batteries and sometimes wash their vehicles in the river. However, contamination of the environment with lead may have occurred well before the introduction of leaded gasoline (Bacon and Hewitt, 2005; Brännvall et al., 1999). Pb was lower than the allowed limit only at two sampling sites, and Cd was always lower than the permissible limits considered by Moss and Contanzo (1998). However, Pb and Cd in the sediments along the Mapocho river were significantly positively correlated, with $R=0.989$.

The distribution of these metals in the sediments is not uniform over the whole section of the river. The change in concentration is due to the release of these metals from different polluting sources. The S₁ location is near a copper mine which uses an important volume of water in the different stages after extraction of the ore. The wastes go directly into the course of the river, and the metals can come in contact with the superficial sediments, contaminating them. The location S₆ is in contact with higher population than S₁.

3.3. Sequential extraction of Cu, Zn, Pb and Cd from sediments

Fractionation of Cu, Zn, Pb and Cd in the sediment samples using the procedure of Tessier et al. (1979) is shown in Fig. 5 (residual fraction was obtained with aqua regia). The sum of the metal extracted in each sequential extraction scheme was compared with the aqua regia digestion procedure for recovery studies (Table 2). Fig. 6 shows average values obtained considering four sampling dates between May 2001 and January 2002 (D₁–D₄).

The fractionation profiles of Cu, Zn and Pb in the sediments were dependent on the sampling places along the river. The mobility and bioavailability of the metals varied significantly with the sediment's properties: particle size, organic matter, carbonates, pH, redox potential and water flow.

The fractionation profile of copper shows that a major portion is bound to carbonate at site S₁ (F₂, 58%, 1771 $\mu\text{g g}^{-1}$), decreasing quite gradually to 16% (32 $\mu\text{g g}^{-1}$) at S₆. On the other hand, Cu associated with oxidizable fraction (F₄) increased from 7% at S₁ to 34% at S₆, along with the organic content which was 4, 5, 7, 7,

Table 2

Comparison of metal concentrations ($\mu\text{g g}^{-1}$) extracted according to the Tessier sequential extraction protocol and total concentrations

Cu ($\mu\text{g g}^{-1}$)												
	Autumn 2001			Winter 2001			Spring 2001			Summer 2002		
	ΣSE	D.D	% rec	ΣSE	D.D	% rec	ΣSE	D.D	% rec	ΣSE	D.D	% rec
S ₁	2466	2466	100	2513	2468	102	3749	3495	107	3486	2980	117
S ₂	1498	1298	115	1382	1420	98	1886	1929	98	1731	1820	95
S ₃	1178	1203	98	1320	1429	92	1405	1550	91	1257	1104	114
S ₄	1324	1281	103	1384	1439	96	1547	1327	117	1659	1823	91
S ₅	848	805	105	818	1010	81	222	221	101	209	240	87
S ₆	195	208	94	184	203	91	216	218	99	204	220	93
Zn ($\mu\text{g g}^{-1}$)												
	ΣSE	D.D	% rec	ΣSE	D.D	% rec	ΣSE	D.D	% rec	ΣSE	D.D	% rec
S ₁	1471	1482	99	1482	1491	99	1188	1198	99	1148	988	116
S ₂	1130	1129	100	1012	1012	100	718	736	98	320	300	107
S ₃	876	835	105	321	306	105	806	781	103	400	362	111
S ₄	876	1071	82	1306	1384	94	982	918	107	599	634	95
S ₅	851	835	102	1252	1384	91	508	512	99	211	234	90
S ₆	864	859	101	885	965	92	398	439	91	214	213	101
Pb ($\mu\text{g g}^{-1}$)												
	ΣSE	D.D	% rec	ΣSE	D.D	% rec	ΣSE	D.D	% rec	ΣSE	D.D	% rec
S ₁	17	16	110	22	19	113	14	12	113	23	22	107
S ₂	10	13	78	21	20	105	23	27	86	18	23	79
S ₃	22	20	108	26	25	106	36	42	85	24	25	98
S ₄	21	18	118	27	27	100	45	45	100	32	39	83
S ₅	44	39	113	24	24	99	44	54	82	78	83	95
S ₆	36	42	85	45	48	93	75	72	104	92	82	112
Cd ($\mu\text{g g}^{-1}$)												
	ΣSE	D.D	% rec	ΣSE	D.D	% rec	ΣSE	D.D	% rec	ΣSE	D.D	% rec
S ₁	0.2	0.2	100	0.2	0.2	100	0.2	0.2	100	0.3	0.3	100
S ₂	0.2	0.2	100	0.2	0.2	100	0.2	0.2	100	0.2	0.3	678
S ₃	0.3	0.3	100	0.3	0.3	100	0.2	0.3	67	0.2	0.2	100
S ₄	0.4	0.4	100	0.4	0.5	80	0.5	0.4	125	0.4	0.4	100
S ₅	0.5	0.4	125	0.2	0.2	100	0.6	0.5	120	0.4	0.5	80
S ₆	0.5	0.4	125	0.6	0.5	120	0.8	0.7	114	0.4	0.4	100

8 and 11% at stations S₁ to S₆, respectively. However, the amount of Cu was much greater at S₁ than at S₆ (214 to 68 $\mu\text{g g}^{-1}$ respectively). Cu bonded to the reducible phase was constant (33%, 36%, 37%, 34%, 34% and 34% in S₁ to S₆, respectively), probably because of the higher amount of this metal released with other contaminants from the local mines. Cu in residual fraction was only 3% (86 $\mu\text{g g}^{-1}$) in S₁ and 16% (33 $\mu\text{g g}^{-1}$) in S₆ sediments.

Zn had a similar fractionation profile. Zn bound to carbonate decreases from 42% (555 $\mu\text{g g}^{-1}$) to 18% (106 $\mu\text{g g}^{-1}$) in S₁ to S₆ sediments; associated with reducible fraction it was almost constant (31%, 41%, 33%, 31%, 30% and 35%); Zn associated with oxidizable fraction increased from 13% to 24% (S₁ to S₆) but the content Zn was 172 to 142 $\mu\text{g g}^{-1}$, respectively and the residual fraction increased from 14% to 23% but the

content Zn was 185 to 136 $\mu\text{g g}^{-1}$ in S₁ to S₆ locations, respectively.

Pb was the only metal extracted in the first step. F₁ concentrations found are between 0.2 to 1.0 $\mu\text{g g}^{-1}$. Pb in S₁ was almost uniformly distributed in carbonates (29%, 6 $\mu\text{g g}^{-1}$), reducible fraction (25%, 5 $\mu\text{g g}^{-1}$), oxidizable fraction (20%, 4 $\mu\text{g g}^{-1}$) and residual fraction (24%, 5 $\mu\text{g g}^{-1}$). On the other hand Pb in S₆ was distributed in carbonates (16%, 10 $\mu\text{g g}^{-1}$), reducible fraction (24%, 15 $\mu\text{g g}^{-1}$), oxidizable fraction (19%, 12 $\mu\text{g g}^{-1}$) and residual fraction (41%, 25 $\mu\text{g g}^{-1}$).

The distribution of Cd in sediments was almost independent of the sampling stations. Cd (S₁ to S₆) bonded to carbonate and reducible phase was almost constant 29%; 36%; 29%; 30%; 28% and 26%; and 29%; 25%; 32%; 29%; 31% and 28%, respectively. On the other hand, Cd in oxidizable phase was lower (3%; 1%; 4%;

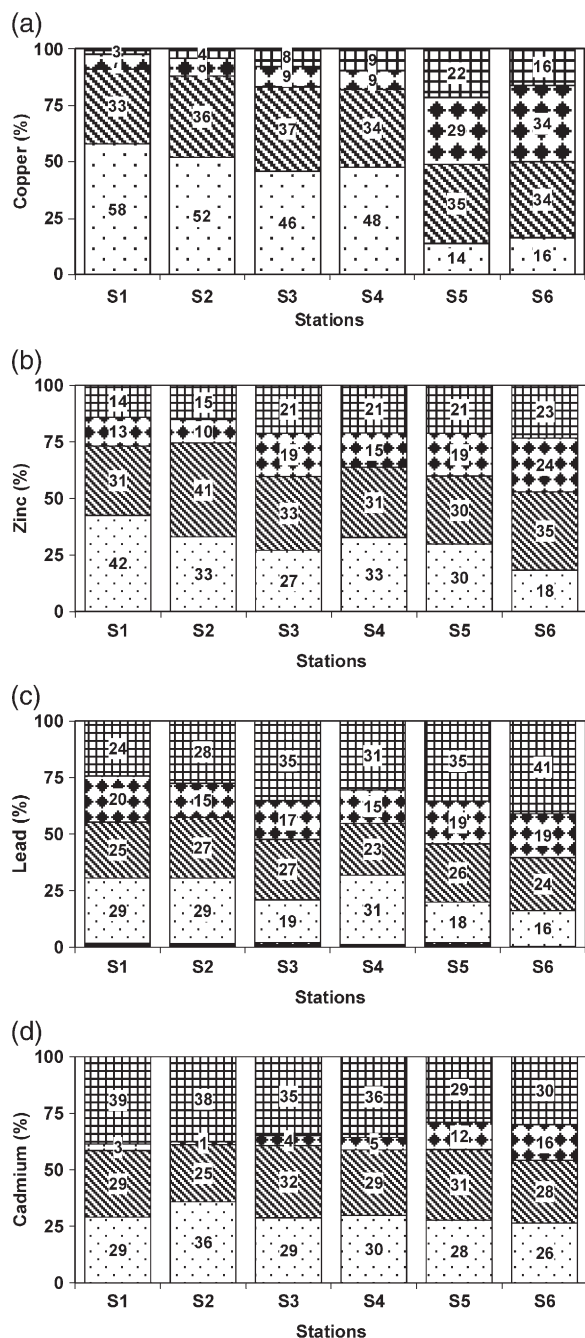


Fig. 6. Average (D₁ to D₄) fractionation profiles of Cu, Zn, Pb and Cd in sediments (S₁ to S₆ stations) along the Mapocho river: F₁ (exchangeable): ■; F₂ (carbonates): ▨; F₃ (reducible): ▩; F₄ (oxidizable): ▤; F₅ (residual): ▧.

5%; 12% and 16% along the river) and residual was higher (39%; 38%; 35%; 36%; 29% and 30% for S₁ to S₆, respectively). Cd aqua regia extraction in the total sediments was 0.2 to 0.5 $\mu\text{g g}^{-1}$ in S₁ to S₆.

Cu and Zn in S₁ sediments (which contain the largest amount of these metals) were mainly associated with carbonates (F₂), with an average of 58% (1771 $\mu\text{g g}^{-1}$) and 42% (555 $\mu\text{g g}^{-1}$), respectively. Cu and Zn associated with carbonates (in S₆ sediments) was 16% (32 $\mu\text{g g}^{-1}$) and 18% (106 $\mu\text{g g}^{-1}$), respectively. These metals were not extracted with the pH 8.2 sodium acetate solution used to obtain the exchangeable fraction F₁, but were easily extracted with the pH 5 acetate–acetic acid buffer used to obtain F₂. This indicates that when the pH of the sediment–water system is decreased, these contaminants become highly available for the biota, and this could set them free in the water. The reagents used to obtain the extractable fraction F₁ are different for various researchers (Gleyzes et al., 2002). Tessier uses MgCl₂ at pH 7.0, but this medium may solubilize the carbonates, and the metal concentration in fraction F₂ would decrease, increasing the concentration of metal ions in the F₁ exchangeable fraction. Considering F₁ and F₂ fractions copper release was 91% (2779 $\mu\text{g g}^{-1}$) and Zn release was 73% (965 $\mu\text{g g}^{-1}$) in S₁ sediments; and 50% (100 $\mu\text{g g}^{-1}$) and 53% (313 $\mu\text{g g}^{-1}$) in S₆ sediments for Cu and Zn, respectively.

On the other hand, in this study the residual fraction was obtained with aqua regia instead of HF–HClO₄ to avoid the use of HClO₄ due to its explosive character. The reference material was analyzed with prior reaction with aqua regia, giving accurate and reproducible results. This modification was made by Sutherland and Tack (2003) for the residual phase, getting good results with certified reference soils SRM 2710 and SRM 2711. However, Sutherland optimized a 4-step BCR sequential extraction procedure. They compared the Tessier scheme, the Geological Survey of Canada scheme and the original BCR scheme, finding substantial differences between metal concentrations, between fractions and between reference soils.

The present study provides a global view of Cu, Zn, Pb and Cd total concentration and distribution in stream sediments of the Mapocho river. Physicochemical properties (pH, conductivity, organic matter, grain size, etc.) and major components (CO₃²⁻, SO₄²⁻, Cl⁻, SiO₂, etc.) were also determined. Many results were obtained and at the end we found that they are related, and although the samples are of local interest, the methodology and interpretation of the data would be of interest to a much wider readership. On the other hand, trace elements can be determined using anodic stripping voltammetry because it is a sensitive and reproducible method mainly for individual extract analysis. The advantages of this method are those inherent to voltammetric techniques, which

allow high sensitivity analysis with an instrument of lower cost and maintenance than spectrometric techniques such as those that use a graphite oven and plasma.

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