

GEOCHEMICAL DISTRIBUTION AND MOBILITY FACTORS OF Zn AND Cu IN SEDIMENTS OF THE RECONQUISTA RIVER, ARGENTINA

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ABSTRACT

This paper describes the distributions of Cu and Zn among the geochemical phases of the surface sediments of the Reconquista River and its main tributary streams (La Choza and Durazno). The distribution patterns of both metals among the geochemical non-residual phases, obtained by a sequential extraction procedure did not suffer alteration in any of the geochemical environments of the seven sampling sites. The main mobile retention phase of Cu was organic matter-sulfide, whereas for Zn they were the oxides of Fe and Mn. The mobility factors of Cu and Zn allowed distinguishing areas of high and low anthropogenic impact. The mobility factor of Zn was close to one in the upper basin, except for La Choza Stream, presenting very high values in the main channel of the river. The mobility factor of Cu was high in the middle and low stretches of the river, while in the upper basin the content of mobile Cu was low. The decline both in mobility factors and total content of metals in the sediments near the river mouth evidenced the self-purification power of this watercourse.

Palabras clave: cobre, zinc, fraccionamiento secuencial, sedimentos fluviales

RESUMEN

Este trabajo describe la distribución del Cu y del Zn entre las fases geoquímicas de los sedimentos superficiales del cauce del Río Reconquista y sus principales arroyos tributarios (La Choza y Durazno). Los patrones de distribución de ambos metales entre las fases geoquímicas no residuales, obtenidas con un procedimiento de extracción secuencial, no sufrieron alteraciones en ninguno de los ambientes geoquímicos de los siete sitios de muestreo. La principal fase móvil de retención de Cu fue la materia orgánica-sulfuros, mientras que para el Zn fueron los óxidos de Fe y Mn. Los factores de movilidad del Cu y del Zn permiten distinguir áreas de alto y bajo impacto antropogénico. El factor de movilidad del Zn fue cercano a uno en la cuenca alta, a excepción del arroyo La Choza, presentando valores muy altos en el cauce principal del río. El factor de movilidad del Cu fue alto en las cuencas media y baja, mientras que la alta presentó contenidos bajos de Cu móvil. La disminución tanto en los factores de movilidad como en las concentraciones totales de ambos metales en la desembocadura del río, pusieron en evidencia el poder de autodepuración de este curso de agua.

INTRODUCTION

Most of the rivers and streams in urban areas of the Buenos Aires Province contain at present a high load of urban and industrial wastes (Herkovits *et al.* 1996, Castañé *et al.* 1998). The impact produced by the human activities on these watercourses results in the alteration of the natural balance of the systems. In the case of heavy-metal contamination, various studies have shown the importance of the geochemical partitioning in the sediments of streams, rivers and lakes (e.g. Allen 1993, Tack and Verloo 1995), to interpret the mechanisms that determine its association with the sediment, mobilization and bioavailability. By means of techniques of sequential chemical extractions, metals were partitioned within chemical conceptual phases, allowing the distinction between metals linked to more mobile phases (non-residual), and not very mobile metals related to the silicated minerals of sediments (residual). Several authors (e.g. Calmano *et al.* 1993) have observed that an increment in the content of heavy metals of geochemical non-residual fractions was associated to contamination processes, predominantly anthropogenic (Griffin *et al.* 1989). Lesmes (1996), who proposed a ranking of mobility factors, based on the "total metal/residual metal" ratio, applied this concept to distinguish between natural values and those originated in human activities.

The Reconquista River, receives untreated sewage and toxic effluents from the industrial belt mainly located in its middle and low basins. The river contributes a third part of the toxic contamination of De la Plata River, which provides drinkable water to the urban conglomerate of Buenos Aires City and part of the province of Buenos Aires. Previous studies have described the physical, chemical and biological conditions of this watercourse (Herkovits *et al.* 1996, Arregghini *et al.* 1997, Castañé *et al.* 1998); however, the potential ecological risk of the heavy metals associated to the river sediments has not been evaluated yet. Loez and Salibián (1990) and Castañé *et al.* (1998) have established that the average levels of dissolved heavy metals in this river surpass the established limits for the protection of the aquatic life, even in the least contaminated site (Cascallares) Cu and Zn reached very high levels. These heavy metals derive from wastes of industries such as galvanoplasty, electric materials, paints, etc., of which there are plenty in this region (Pescuma and Guaresti 1992).

The present study investigates the distribution of Cu and Zn among the geochemical phases of sediments of Reconquista River and differentiates areas of high and low potential mobility of these metals.

MATERIALS AND METHODS

Study area

The Reconquista River basin has a surface of 169,000

ha, 72,000 of which are devoted to agriculture and cattle breeding. The rest of this basin is urbanized (three million inhabitants) with over 12,000 industries located in the area. The Reconquista is a lowland river of Buenos Aires Province, that starts at the confluence of La Chozas and Durazno streams and drains into the Luján River, which in turn discharges its waters into De la Plata River. This watercourse is characterized by having a low flow during the summer ($0.6 \text{ m}^3 \text{ s}^{-1}$ to $1.0 \text{ m}^3 \text{ s}^{-1}$) which can be further reduced due to obstructions caused by the accumulation of garbage under the bridges.

Three sampling sites (Fig. 1) were located in the upper basin: La Chozas Stream (E1), Durazno Stream (E2) and Cascallares (E3=5 km). The middle basin was represented by Gorriti (E4=20 km), whereas the sampling sites of low basin were: San Martín (E5=38 km), Bancalari (E6=46 km) and Tigre (E7=55 km). The land use in the upper basin is predominantly rural and agricultural with some urban settlements in E3, while the middle basin represents the periphery of a very industrialized (food and rubber industries) and urbanized area. The low basin starts downstream of Moron Stream, which receives untreated sewage from a variety of industries (food, tannery, chemistry, and non-ferrous smelting), that confer its waters the characteristic of a raw sewer effluent. E5 and E6 also receive the impact of chemical, food, tannery and non-ferrous smelting industries, as well as of landfills and wastes of a densely populated area. E7 is located in a urban sector with few industries, near the mouth of the Reconquista River, where it flows into the Luján River, which in turn drains into the De la Plata River Estuary.

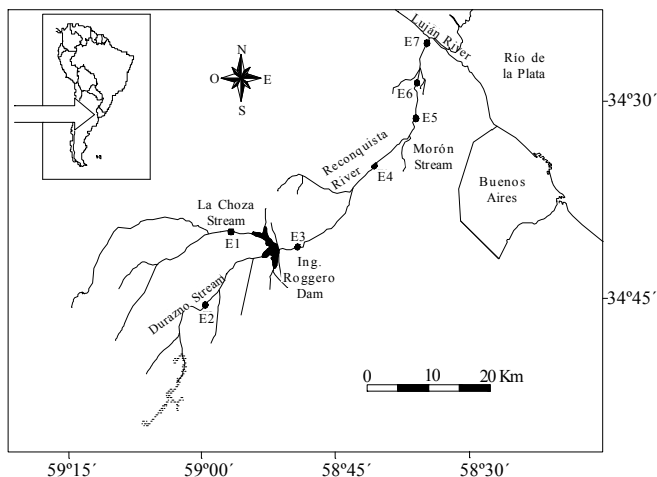


Fig. 1. Map of the investigated area and sampling locations

Sampling and chemical analysis

Sediments were collected with a grab-sampler at seven sampling stations (Fig. 1), packed in airtight plastic bags,

transported immediately to the laboratory, and frozen until analysis. Three subsamples, then pool into a composite sample, were taken in each location. Three one-gram portions (oven dry wt.) of each sample were submitted to the sequential extraction procedure of Tessier *et al.* (1979). The sequence can be summarized as follows:

Fraction 1: exchangeable, 1M MgCl₂, pH 7, for 1h.

Fraction 2: bound to carbonate, 1M sodium acetate, pH 5, for 5 h.

Fraction 3: bound to amorphous Fe and Mn oxides, 0.04 M hydroxylamine hydrochloric acid in 25 % (v/v) at 96 °C, for 6 h.

Fraction 4: bound to organic matter and sulfides, 30 % H₂O₂ and 0.02 M nitric acid at 85°C, for 5 h.

Fraction 5: residual, concentrated HNO₃, HClO₄ and HF.

The effectiveness of the sequential extraction processes was assured by comparing the sum of each fraction with the amount of all the metals extracted by HNO₃-HClO₄-HF. The error of the sequential extraction method is generally around 12 %. Cu and Zn concentrations in all the extracts were measured by inductive coupling plasma atomic emission spectrophotometry (ICPAES).

RESULTS AND DISCUSSION

Zinc

The total concentration of Zn ranged between 104 and 1,092 mg kg⁻¹ in E2 and E6, respectively (**Table I**). Zn concentrations in each chemical fraction, considered as percentages of total Zn, are shown in **Figure 2**. E2 and E3 had low percentages of non-residual Zn (21 and 26 %, respectively), indicating a low contribution of this element by human activities, but the effects of natural weathering and erosion processes on the drainage of the upper basin. On the contrary, the other sites had high levels of non-residual Zn (70-85 %), denoting a great anthropogenic accumulation of this element.

The Zn distribution among the most mobile fractions

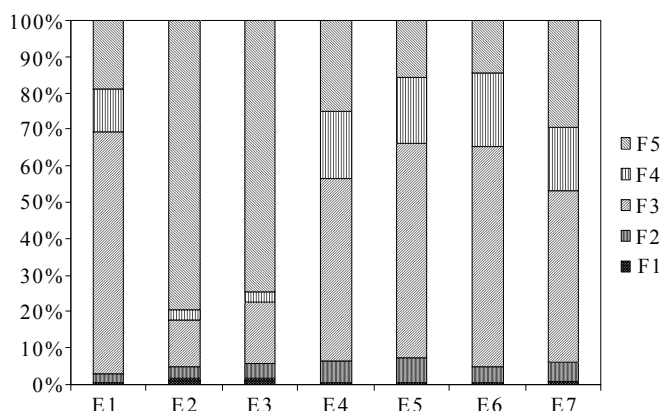


Fig. 2. Partitioning of Zn within different fractions in sediments

(F1, F2, F3, and F4) in all seven sites showed that the oxides of Fe and Mn were the most important Zn sinks (13–67 % of total Zn), followed by organic matter-sulfide (3–18 % of total Zn), carbonates (2–7 % of total Zn), and exchangeable (0.2-1.3 % of total Zn). These results would indicate that the main mechanism involved in the retention of the Zn is adsorption or coprecipitation with Fe and Mn oxides. The association between Zn and the oxides of Fe and Mn in sediments and soils has been widely recognized (Kuo *et al.* 1983, Fernandes 1997). Osaki *et al.* (1990a) studied the differential adsorption of Zn on fine particles in riverbed sediments, particulates and kaolin, observing that this metal was mostly adsorbed on fine sediments. These authors also indicate that this greater adsorption may obey to the presence of Mn and Fe oxides and/or of organic matter on these particles. Taking into account that the fraction of adsorbed metals increases at higher concentrations of adsorbent solid (Lion *et al.* 1982), a high content of Fe and Mn (2,100 µg/g and 350µg/g on average respectively) in the oxide fraction of the sediments, would facilitate a great accumulation of Zn. In addition, since Zn is the most abundant metal in these sediments (Rendina *et al.* 1997), a concentration effect (order of abundance) may also determine the high percentage of Zn adsorbed in this fraction, as previously found by Galvez-Cloutier and Dubé (1998). This does

TABLE I. RESIDUAL AND TOTAL CONTENT OF Cu AND Zn, AND THEIR MOBILITY FACTORS (*f*)

Sites	Residual Zn	Total Zn	Residual Cu	Total Cu	<i>f</i> Zn	<i>f</i> Cu
E1	86.1	459.4	26.1	37.7	5.3	1.4
E2	82.4	103.8	30.2	44.8	1.2	1.5
E3	89.2	119.8	44.4	64.5	1.3	1.4
E4	117.9	468.4	76.6	161.9	4.0	2.1
E5	158.0	994	85.3	239.6	6.3	2.8
E6	159.0	1092	99.7	255.6	6.9	2.6
E7	106.5	361	78.6	120.3	3.4	1.5

not occur in the oxidizable fraction, since Zn is unable to compete for the formation of highly stable complexes between organic matter and Cu, as observed by Nriagu and Coker (1980) in sediments of Ontario Lake.

Some authors have observed different affinities of Zn for the distinct geochemical phases of the sediments in different environments (El Ghobary and La Touche 1982, Griffin *et al.* 1989, Tingzong Guo *et al.* 1997), while others (e.g. Fernandes 1997) do not observe changes in the distribution pattern of Zn among the non-residual phases. Nevertheless, a discussion of these results is not only difficult due to the various methodologies applied to establish the relative importance of each geochemical phase in the retention of heavy metals, but also owing to the different physical and chemical conditions (e.g. Eh, pH, ionic strength) of the analyzed sediments.

The predominantly lithogenous origin of Zn, can be inferred by the high percentages of this element in the residual phase (81 % of total Zn in E2 and 76 % of total Zn in E3), in coincidence with the lower Zn content in the sediments at the upper basin, where the land use is mainly cattle raising on natural pastures. The large fraction of total Zn associated with the residual phase is unlikely to be removed due to changes in the physicochemical conditions (Griffin *et al.* 1989). The low percentages of residual Zn (18 % of total Zn) and the high concentrations of total Zn found in E1, contrasted with E2 and E3 (82 and 89 % respectively). This may be due to the effect of effluents from food industries (Pescuma and Guaresti 1992) inflowing through La Chozza Stream.

The Zn mobility factors in the seven sampling stations are shown in **Table I**. The mobility factors of Zn in E2 and E3 were close to one, indicating low contamination by this element. The other sites (E1 and the whole middle and low courses) presented very high mobility factors, denoting an important level of Zn contamination. The reducible phase (F3) of the sediments is the main contributing factor to Zn mobility. In F3 the mobilization of Zn may be coupled to the redox cycling of Mn (Osaki *et al.* 1990b), since under reducing conditions, Mn(IV) can be reduced to Mn(II) more easily than Fe (owing to differences between their redox potentials), thus inducing Zn solubilization. The decline in the Zn mobility factor and the total concentration of the metal in the sediments of E7 may obey to the dilution effect produced by the De la Plata Estuary and also to a lesser anthropic impact. The total content of Zn recorded in this site is in good agreement with the values reported by Villar *et al.* (1998) for this estuary.

Copper

The total content of Cu ranged between 37.7 and 256 mg kg⁻¹ in E1 and E6, respectively (**Table I**). The geochemical partition of Cu among sampling stations is shown in **Figure 3**. In all seven sites, the main retention

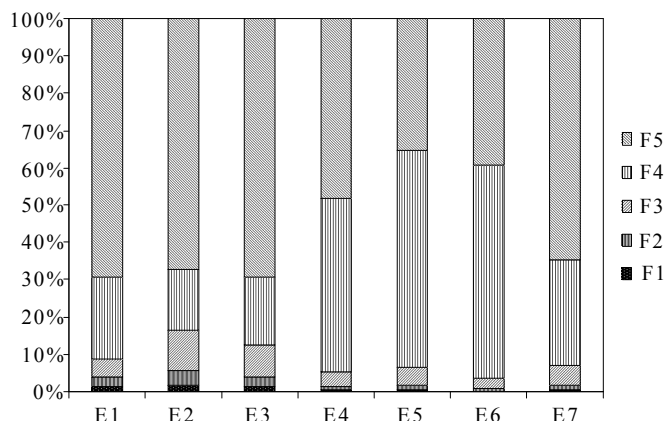


Fig. 3. Partitioning of Cu within different fractions in sediments

phase of Cu in the sediments was F4. This result is in agreement with published data (Griffin *et al.* 1989, Fernandes *et al.* 1997, Larocque and Rasmussen 1998). In its oxidizable phase, Cu can either be coupled to active sites of organic molecules (OH of carboxylic and phenolic groups of organic substances) or precipitate as sulfide. An investigation on the bed sediments of this river (Iorio *et al.* 1997) revealed that the humic compounds predominantly form complexes with Fe and Cu, having the latter one a stronger affinity for humic acids. Huang and Yang Y.L. (1995) also found a more pronounced affinity of Cu for humic acids with respect to fulvic acids, in synthetic humus-kaolin complexes. Studies on preferential absorption (Rashid 1985) indicate that among the transition metals assayed, Cu competed more strongly for the bonding sites of the humic material.

E1, E2 and E3 presented the lowest proportions of Cu in this fraction (22, 17 and 18 % of total Cu, respectively), whereas the highest percentages of this metal were found in E5 and E6 (58 and 57 %, respectively), in coincidence with the greatest contributions of organic waste of industrial origin. The significant increment of Cu in F4, starting from E4, can be related to diagenetic processes associated with a marked decline in dissolved oxygen in water column (Arreghini *et al.* 1997), and to an increase in the organic matter content of the sediment (4.8, 1.8, 2.8, 8.2, 12, 13, and 5.8 % in E1, E2, E3, E4, E5, E6, and E7, respectively), for which the sulfide content of that fraction would also increase markedly.

This deterioration on the water quality of the Reconquista River was attributed to the anthropogenic impact produced by the inflowing waters of Morón Stream (de Cabo *et al.* 2000). These authors also reported high conductivities in E5, located 1 km downstream from Morón Stream. The presence of elevated amounts of dissolved salts would transform the hydrophilic organo-metallic complexes into hydrophobic forms that would finally precipitate, thus incorporating quelated metals into

the riverbed sediments. The Cu bound to the other mobile fractions was very low, being 0.2–1.7 % in F1, 0.5–5.1 % in F2 and 2.8–11 % in F3.

Cu in the residual fraction represented 70, 68 and 70 % of total Cu in E1, E2 and E3, respectively, whereas in E4, E5 and E6 it only reached 48, 35 and 39 %, respectively. The percentage of residual Cu in E7 as similar to that of sites undergoing lesser impact (E1, E2 and E3).

The mobility factor of Cu (**Table I**) exhibited low values (close to one) in E1, E2 and E3, in coincidence with the lower content of total Cu found. Mobility factors were high (over 2) in E4, E5 and E6, but diminished in E7, probably owing to the dilution of the fluvial sediments with less polluted sediments from the estuary, and to a greater distance from the contamination sources. In all sites, the high percentages of Cu in the oxidizable phase of the sediments (F4) were responsible for the values of Cu mobility factor. In this reducing environment, the complexed metal-organic matter systems are difficult to oxidize. Bacteria cannot easily attack this humic acid fraction in anaerobic sediments; therefore, the complexes formed there are much more stable than in oxidized environments (Patrick and Pardue 1992). On the other hand, part of the Cu in F4, can precipitate as cupric sulfide under reducing conditions. In spite of being hardly soluble and also stable under reducing conditions, these compounds can be oxidized by sulfide-oxidizing bacteria to form sulfate under oxidizing conditions, thus releasing the metallic ion back into solution.

In agreement with the sequence established by Irving and Williams (1953) for the stability of complexes ($Mn < Fe = Ni < Zn < Pb < Cd < Cu$), and also with the stability of metallic sulfides, in all of the study sites the percentage of Cu in the oxidizable fraction was higher than Zn. According to these authors, the selectivity order for the amorphous oxides of Fe and Mn also denotes a higher affinity for Cu than Zn. However, in the present study, the accumulation order found in the reducible phase was the opposite one ($Zn > Cu$). This result may be attributed to a concentration effect, since the Zn content of the sediments in all seven sites was much higher than Cu. The influence of the different concentrations of heavy metals on the fraction of an adsorbed metal in multivariate systems has also been postulated by other authors for natural sediments (e.g. Galvez-Cloutier and Dubé 1998).

CONCLUSIONS

In the areas where the land use is mainly agriculture and cattle raising, the concentrations of total metals in riverbed sediments and their mobilities were low. On the contrary, in those zones where the land use is either industrial or urban, the concentrations of total metals in sediments and their mobilities increased, thus becoming ar-

reas of high risk for the aquatic life.

The lower concentrations of total metals in the sediments and the lower mobility factors found in the site closer to the river mouth are good indicators of the self-purification sites capability of the riverbed. The results of sediment fractionating indicate that in all of the study sites, the main mobile phase of Zn were the oxides of Fe and Mn. On the other hand, Cu was mainly bound to mobile phase organic matter-sulfide. The differences in the geochemical environment from the headwaters to the mouth of the Reconquista River, do not alter the distribution pattern of heavy metals among the non-residual fractions of the sediments. The values of the Zn mobility factor in middle and low stretches of the Reconquista River basin were much higher than those of Cu. This result indicates a greater contribution of anthropogenic Zn due to the influences of the large population and industrialization of this region.

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