Metal content and distribution in surface sediments in an industrial region

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ABSTRACT

The present study aimed to evaluate Cu, Cr, Ni, Zn, Pb, Mn, Al, and Fe contents, as well as their geochemical partitioning in Sinos River basin sediments in southern Brazil. This basin is a densely populated area with a substantial number of industries, especially metallurgy, electroplating works, steel mills, petrochemicals, and tanneries. The total metal concentrations were determined by X-ray fluorescence and the sediment phase concentrations were determined by applying the BCR-701 sequential extraction method proposed by the Community Bureau of Reference of the European Community, using ICP/OES. The contents extracted by a solution of 0.5 mol/L HCl were also considered. Metal contents were evaluated in the sediment fraction <63 μm. Results in the industrialized and densely populated region showed an increase in the total concentrations of Cu, Cr, Zn, and Pb, and in the potentially mobile fractions for Cu, Cr, Zn and Ni sequentially extracted. Cr stood out particularly in the Portão stream, showing 1,286 mg/kg as a result of the total concentration, considering the tannery region influence.

Key words: BCR-701, metals, sediment, sequential extraction.

INTRODUCTION

Metals are one of the most common pollutants in aquatic environments and may be originated from natural sources, from geological weathering or anthropogenic sources, such as industrial, agricultural, urban and domestic effluents (Hang et al. 2009, Davutluoglu et al. 2011). Metals when dispersed in aquatic environments tend to deposit in the sediments, which have high retention capacity and the potential of release these pollutants (Salomons and Stigliani 1995, Passos et al. 2011).

This release into the overlying water column may occur by changes in environmental conditions such as pH, redox potential, bioturbation and organic matter decomposition (Förstner and Kersten 1989, Davutluoglu et al. 2011). Nevertheless, the sediments act as reservoirs of metals, providing a reasonably accurate history of the pollution of the river (Sakai et al. 1986, Filgueiras et al. 2002, Hang et al. 2009, Davutluoglu et al. 2011).

However, the determination in metal total concentration in sediments is not a particularly good indicator when one looks for a distinction between natural and anthropogenic contributions

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(Quevauviller et al. 1996, Relic et al. 2010, Passos et al. 2011, Okoro et al. 2012). Thus, recent studies have used sequential extraction procedures to understand the specific chemical associations with sedimentary phases and metal sources (Rodrigues and Formoso 2006, Hang et al. 2009, Davutluoglu et al. 2011). Many of these are variants on the scheme proposed by Tessier et al. (1979). These procedures use selective reagents to consecutively extract "operationally defined phases" from the sediments, allowing for the quantification of the levels of potentially mobile metals and the establishment of associations with anthropogenic contributions (Rauret et al. 1999, Larner et al. 2008). Thus, alterations in the environmental conditions are simulated, enabling the prediction of the impact of a potential mobilization of metals on the surrounding environment (Bacon and Davidson 2008). The quantification of potentially mobile metals can also be done by simple extraction techniques (Gleyzes et al. 2002).

Currently, one technique often used is the sequential extraction procedure proposed by the Community Bureau of Reference (BCR) (now called Standards, Measurement and Testing Programme). This procedure was developed in order to solve the lack of sequential extraction procedure uniformity. Besides that, it provides a corresponding certified reference material and gives a method validation and a way of comparing the data generated (López-Sánchez et al. 1998, Rauret et al. 1999). This technique involves three steps – exchangeable metals associated with carbonates, reducible metals, and oxidizable metals (Quevauviller et al. 1996, Rauret 1998, Davidson et al. 1999, Pueyo et al. 2001, Teixeira et al. 2003, Rodrigues and Formoso 2006, Boughriet et al. 2007, Davutluoglu et al. 2011, Passos et al. 2011, Dundar et al. 2012).

Some problems have not yet been fully resolved in the use of sequential extractions, such as redistribution of analytes between the geochemical phases, lack of reagent selectivity, incomplete extraction

and precipitation of new mineral phases during the extraction. Even so, the increasing use of such schemes in the evaluation of metals in sediments has shown the usefulness of the information obtained, which many times corresponds to observable environmental effects, such as the decrease in local biodiversity (Rauret et al. 1999, Julián and Collado 2002, Bacon and Davidson 2008, Rodrigues et al. 2008).

On the other hand, to evaluate the potentially mobile metals, cold acid extraction procedures may also be used, which tries to simulate the natural removal processes of these more "reactive" elements of the sediments (Bevilacqua et al. 2009). The extraction procedure with diluted hydrochloric acid (HCl) has been frequently applied (Sutherland and Tack 2008, Bevilacqua et al. 2009, Li et al. 2009) and can be used as a first evaluation technique for monitoring the potential contamination by metals. Then, high levels identified by the extraction with HCl may be subject to further assessment, using sequential extraction procedures (Sutherland and Tack 2008).

Sinos River basin is located in an industrialized and densely populated area, where there are metallurgical industries, electroplating works, steel mills, petrochemicals and tanneries, liquid waste generators with metals. Even though sediment contamination is currently one of the most serious problems in basin environmental management, finding solutions for these problems is still poor. Robaina et al. (2002) and Oliveira et al. (2008) have studies that show an intense metal contamination in the lower Sinos River.

The aim of this study is to evaluate the geochemical distribution and potential mobility of some metals (Cu, Cr, Ni, Zn, Pb, Mn, Al, and Fe) in sediments along the Sinos River basin. These metals were selected because they indicate the industrial liquid waste markers which are located in the study area especially in the metallurgical/electroplanting and tannery sectors (Cu, Zn, Ni, Pb and Cr), as well as natural components in the area (such as Mn, Al and Fe).

STUDY AREA

Sinos River basin is located in the northeast of the state of Rio Grande do Sul, Brazil, with an extension of 3,820 km^2 crossing almost 29 counties, of which 21 are within the Porto Alegre Metropolitan Area, the capital of the state (see Fig. 1). It is bounded to the east by the Serra Geral, to the west and north by the Caí River basin, and to the south by the Gravataí River basin. Sinos River has its source at an altitude of 600 m, its main course flows is 190 km and it finally discharges at an altitude of 12 m. About 1.3 million people inhabit its basin (Comitesinos 2009), representing 13% of the total population of the state concentrated in only 3.5% of its territory. The climate is subtropical with an annual average temperature of around 20°C and about 1,600 mm of rain annually, well-distributed over the four seasons (FEPAM 2006).
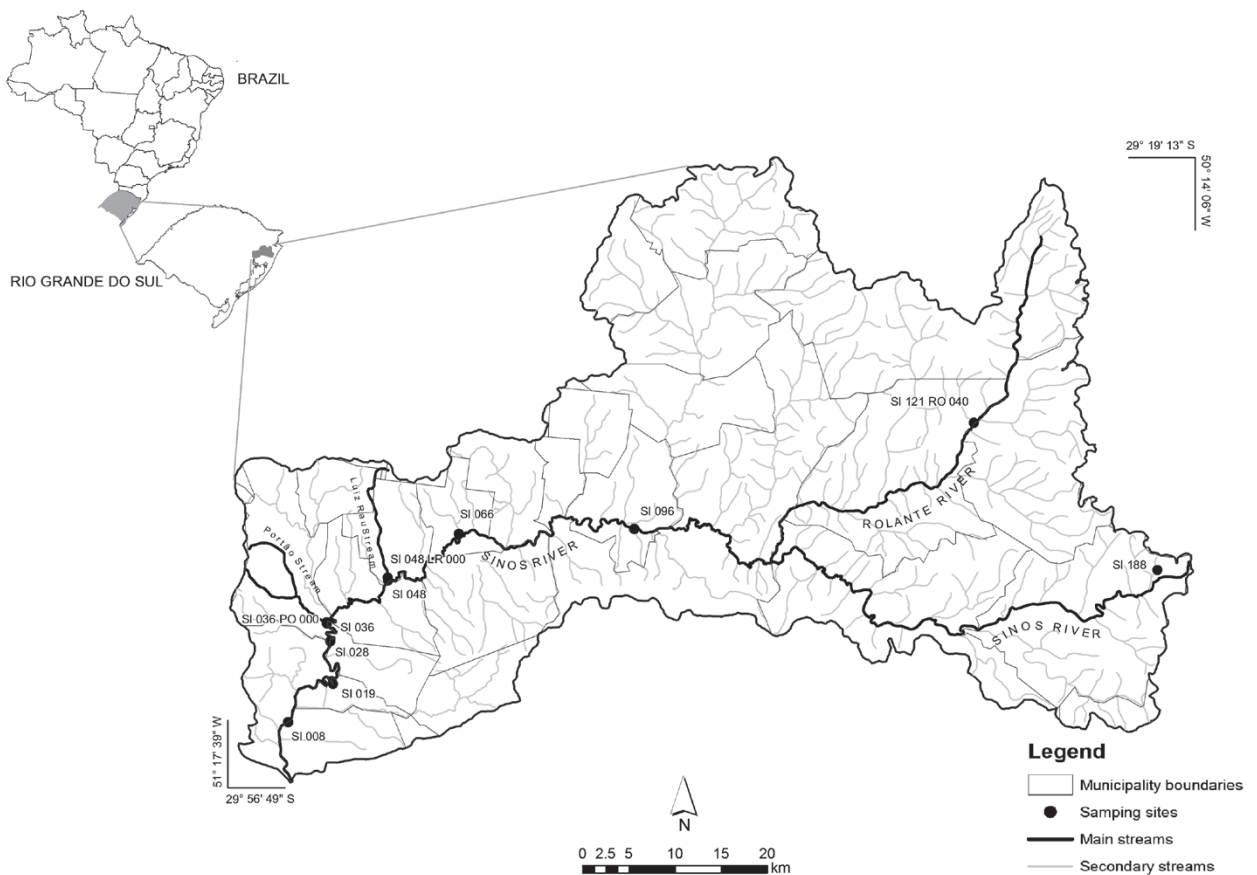

Fig. 1 - Study area with the sampling sites in the Sinos River basin.

The basin can be divided into three different regions, all of which related to the corresponding section of the river: upper, middle, and lower. In the upper part, characterized by a more rugged terrain and by agricultural activities in small farms, we selected two sampling sites (Table I). This part of the Sinos River, about 25 km long, has high declivity, with altitudes ranging between 600 m and 60 m. In the middle section of the basin, with about 125 km, the declivity of the Sinos River decreases, and we chose one sampling site (Table I). As one moves downstream, the population density and

urbanization as well as the industrial concentration increase. Presently, industrial activity (especially metallurgy, electroplating works, steel mills, petro-chemicals and tanneries), domestic sewage, and rice farming are the main sources of concern with regard to water quality of this river basin (FEPAM 2006). The lower stretch of the Sinos River has, as major tributaries, streams that drain large urban centers, such as the Luiz Rau and the Portão streams. Besides choosing sampling sites near the mouth of these streams, we also selected six additional sites along the main course of the Sinos River (Table I). The codes of the locations indicate the distance in kilometers from the sampling location to the mouth of the Sinos River.

TABLE I
Location of the sediment sampling sites.

Site	Coordinates		Stretch of river
	X	Y	
SI 188	-50.263	-29.725	Upper
Rolante river	-50.470	-29.581	Upper
SI 096	-50.850	-29.686	Middle
SI 066	-51.046	-29.691	Lower
Luiz Rau stream	-51.126	-29.734	Lower
SI 048	-51.126	-29.737	Lower
Portão stream	-51.195	-29.778	Lower
SI 036	-51.194	-29.779	Lower
SI 028	-51.191	-29.796	Lower
SI 019	-51.188	-29.838	Lower
SI 008	-51.238	-29.875	Lower

MATERIALS AND METHODS

COLLECTION AND PREPARATION OF SAMPLES

Sediment samples were collected between February and August 2010, at eight locations along the main course of the Sinos River and three tributaries (Rolante River and the mouths of Luiz Rau and Portão streams). Samples of surface sediments were collected by using a PVC, L-shaped manual collector. The material collected was stored in plastic bags, cooled to 4°C and sent to the laboratory, where the fraction with particle size <63 μm was separated by means of wet sieving. This procedure was performed on the same day

of sampling, thereby to minimize the action of microorganisms in migration processes and avoid metals redistribution. The interest content was oven-dried at 37°C and was then finely homogenized in an agate mortar.

CHEMICAL ANALYSES

Total metal concentration

To evaluate the total metal concentrations, the sediment samples were prepared as compressed pellets and analyzed in a sequential X-ray fluorescence spectrometer (PW2404, Philips), equipped with a rhodium tube. The analysis was performed at the Analytical Geochemistry Laboratory at Campinas University.

Sequential extraction

The fractional metal concentrations in the geochemical phases of the sediments was carried out according to the sequential extraction method proposed by the BCR (now Standards, Measurement and Testing Programme) (Pueyo et al. 2001, Teixeira et al. 2003, Rodrigues and Formoso 2006, Davutluoglu et al. 2011, Passos et al. 2011, Dundar et al. 2012). The procedure is explained in Table II. The quantification of metallic cations in solution was performed in an inductively coupled plasma optical emission spectrometer (ICP-OES) at the Soils Laboratory of the Federal University of Rio Grande do Sul. In this study, the fourth stage, corresponding to the metal residual fraction, was determined by the difference between the sum of the three sequentially extracted stages in relation to the total content of the metal under study, previously obtained by X-ray fluorescence.

Extraction with 0.5 mol/L HCl

The analysis of potentially mobile metals extracted with a solution of 0.5 mol/L HCl was performed as recommended by Sutherland (2002) and Sutherland and Tack (2007, 2008). The procedure involved the extraction of 0.5 g of sample with 10 mL of a

TABLE II
The BCR sequential extraction procedure.

STEPS	REAGENTS	PROCEDURE	SEDIMENT PHASES
1	Acetic acid 0.11 mol/L	1 g of sample + 40 mL of CH_3COOH stirred for 16 h at 30 rpm	Exchangeable – water soluble species and acid
2	0.10 mol/L hydroxylamine hydrochloride, pH 1.5	Residue of step 1 + 40 mL of NH_2OH. HCl stirred for 16 h at 30 rpm	Reducible – species bound to Fe and Mn oxides and hydroxides
3	1.0 mol/L ammonium acetate, after digestion with 8.8 mol/L hydrogen peroxide at pH 2	Residue of step 2 + 20 mL of H_2O_2 at 85°C almost until dry; 50 mL CH_3COONH_4 stirred for 16 h at 30 rpm	Oxidizable – species bound to organic matter and sulfides
4*	Total concentration minus the sum of the previous three steps		Residual – species bound to the silicate matrix

Source: Adapted from Davutluoglu et al. (2011). *Adopted herein.

solution of 0.5 mol/L HCl under continuous stirring at 200 rpm for 1 h at 20°C. The suspension obtained was filtered through cellulose ester filter of 0.20 mm porosity prior to quantification of Cu, Cr, Ni, Pb, and Zn, certified for the reference material BCR-701. The quantification of metallic cations in solution was performed in an ICP-OES at the Soils Laboratory of the Federal University of Rio Grande do Sul. Subsequently, the contents extracted by 0.5 mol/L HCl solution and those by sequential extraction were correlated by regressions.

GENERAL CHARACTERISTICS OF THE SEDIMENTS

Total sulfur (S) was determined by X-ray fluorescence and corresponds to indicative values. Organic matter was obtained by the loss of mass by ignition (2 h at 360°C) (Schulte and Hopkins 1996). The analysis of particle size was performed in the laboratory of the Center for Coastal Studies (CECO) of the Federal University of Rio Grande do Sul and it involved the separation of the main textural classes of sediments by sieving and sedimentation techniques. The clay minerals were also analyzed at the CECO, after preparation of slides with the oriented clay minerals. The slides were air-dried, solvated with ethylene glycol and calcinated, and were then successively analyzed by an X-ray diffractometer in the range of between 2θ 2-28 °, by using CuKα radiation.

ACCURACY OF THE CHEMICAL ANALYSIS

To assess the accuracy of the total metals concentrations, two soil reference materials were used (GSS-2 and GSS-5, China), showing mean recoveries from 88 to 105% for Cr, Cu, Ni, Pb, Zn, MnO, Al_2O_3, and Fe_2O_3. The metal concentrations determination in the reference material was performed in duplicate, with coefficients of variation <10%. The detection limits (DL) for Cr, Cu, Ni, Pb and Zn were 3, 2, 2, 3 and 2 mg/kg, respectively.

One certified sediment reference material (BCR-701) was analyzed to determine the accuracy of the sequential extraction procedure described above. The certified and analyzed values and their recoveries at each extraction step were calculated with mean recoveries from 85 to 104% for Cr, Cu, Ni, Pb, and Zn. The analyses of this certified reference material were performed in triplicate and of the sediment samples in duplicate, showing coefficients of variation <10%. The detection limits (DL) for Cr, Cu, Ni, Pb and Zn were 0.4, 0.6, 0.4, 2.0 and 2.0 mg/kg, respectively.

For the extraction procedure with a solution of 0.5 mol/L HCl, one of the samples was spiked with a known amount of each metal evaluated (Cr, Cu, Ni, Pb and Zn) and then analyzed in triplicate, with average recoveries of 91-97%. The determination of metal concentrations in the sediment samples was performed in duplicate, with coefficients of

variation <10%. The detection limits (DL) for Cr, Cu, Ni, Pb and Zn were 0.4, 0.6, 0.4, 2.0 and 2.0 mg/kg, respectively.

SEDIMENT QUALITY ASSESSMENT

The total concentrations of metal in the Sinos River basin sediments were compared with the specific literature: taking the studied background concentrations (Robaina et al. 2002), average shale (Turekian and Wedepohl 1961), and other metals levels in rivers around the globe (Irabien and Velasco 1999, Rodrigues and Formoso 2006, Boughriet et al. 2007, Li et al. 2009, Davutluoglu et al. 2011, Hang et al. 2009, Rangel et al. 2011, Dundar et al. 2012).

To assess the ecotoxicological implications of total metal concentrations in sediments, we considered sediment quality guidelines (SQGs) as: the indices established by the Canadian Council of Ministers of the Environment (CCME 1999) and the study of Long et al. (1995).

Long et al. (1995) define two sets: i) effects range low (ERL)/effects range median (ERM) and ii) the threshold effects level (TEL)/probable effects level (PEL). ERL and TEL indices refer to concentrations below which adverse effects on the wildlife in the sediment are unlikely and which would be expected only infrequently. In contrast, adverse effects are more likely to occur when metal concentrations are above ERM and PEL. The Canadian study reports the indices interim freshwater sediment quality guideline (ISQG) and probable effects level (PEL).

STATISTICAL ANALYSIS

Principal component analysis (PCA) was applied to the set of variables in the sediments in order to estimate potential emission sources. Chemical variables used in PCA were selected based on the Pearson correlation matrix, giving rise to a set of synthetic variables (principal components) based on the interrelationships of the original data. The principal components selected were those that obtained characteristic roots >1.0 after applying the Varimax rotation. The primary function of the PCA is a decrease in the number of variables while retaining the original information as much as possible, and thus variables with similar characteristics can be grouped into factors. PCA was analyzed by using Windows SPSS version 20.0.

RESULTS AND DISCUSSION

GENERAL CHARACTERISTICS OF THE SEDIMENTS

Table III shows the general characteristics of the sediments. The highest sulfur levels (S) were found at the sites near the mouth of the Sinos River (SI 019 and SI 008) and the Portão stream, while the highest organic matter (OM) were found at sites SI 188 (16.8%) and Portão stream (15.8%). The high OM content observed at the source of the Sinos River (SI 188) can be attributed to the influence of well-preserved vegetation of the river margins. At the same place a high content of sulfur was also noticed, which may be locally released during organic matter decomposition (Neue and Mamaril 1985). The OM is considered a metal geochemical carrier in some types of environments due to its capacity of absorbing and complexing metals of both terrestrial and marine origins (Salomons and Förstner 1984, Warren and Haack 2001).

Sinos River sediment grain is composed by gravel (from 0% to 75%), sand (from 16% to 98%), silt (from 1% to 62%) and clay (from 1% to 20%). The coarse sediments were found at sites SI 188 and Rolante River, in the upper part of the river basin, indicating its proximity to the bedrock. The texture of the sediments (Table III) was predominantly sand, except for site SI 028, which showed 61.7% of silt. According to Laybauer and Bidone (2001), at sites with a greater incidence of smaller particle sizes, which have an increase in the superficial area and the capacity of the cations exchange, there will be a tendency of metal accumulation in the

TABLE III

**Additional parameters used for characterizing
sediment samples from the Sinos River basin.**

Site	Particle size fraction (%)				Particle size classification	S (mg/kg)	OM (%)	Clay minerals
	gravel	sand	silt	clay				
SI 188	75.0	16.2	7.7	1.0	gravel and sand	764	16.8	smectite, illite, quartz, zeolite
Rolante river	12.8	84.6	1.9	0.8	sand	394	10.6	kaolinite, smectite, illite, k-feldspar, quartz
SI 096	0.0	48.8	34.5	16.7	mud with sand	224	8.7	kaolinite, smectite, k-feldspar, quartz
SI 066	0.0	46.0	41.6	12.4	mud with sand	511	12.1	kaolinite, smectite, k-feldspar, quartz
Luiz Rau stream	0.0	75.8	15.3	8.9	sand	267	11.1	kaolinite, smectite, illite, quartz
SI 048	0.0	71.3	19.5	9.2	sand with mud	286	10.0	kaolinite, smectite, k-feldspar, quartz
Portão stream	0.0	98.3	0.6	1.1	sand	922	15.8	barite, kaolinite smectite, quartz
SI 036	0.0	92.7	4.6	2.7	sand	637	9.8	kaolinite, smectite, illite, k-feldspar, quartz
SI 028	0.0	18.0	61.7	20.3	mud	729	11.5	kaolinite, smectite, quartz
SI 019	0.0	66.1	25.4	8.5	sand with mud	1301	12.0	kaolinite, smectite, k-feldspar, quartz
SI 008	0.0	52.2	37.4	10.3	sand with mud	1205	11.5	kaolinite, smectite, illite, quartz

sediments. Assuming the grain composition, the samples were classified into gravel and sand, sand, mud with sand, sand with mud and mud.

Concerning mineralogical analyses, quartz, kaolinite and smectite are scattered over the entire river basin (Table III), except for kaolinite at the Sinos River source (SI 188). According to Rodrigues and Formoso (2006), sediments containing smectite (expansive clays of high cation exchange capacity) can retain metals, which are subject to remobilization under changes in environmental conditions. Furthermore, illite, zeolite, K-feldspar, and barite were also identified. These minerals were probably formed by alteration of volcanic rocks of the Serra Geral Formation and sandstones of the Botucatu Formation (Oliveira et al. 2008).

STATISTICAL ANALYSIS

Table V shows the factorial weight matrix obtained from total metals concentrations in sediments from the Sinos River basin sampling. Factor analysis performed with the variables explained 43.2% for Factor 1, 22.9% for Factor 2 and 18.8% for Factor 3 of total variance. These three factors explain 84.9% of the total variance of the data.

Factor 1 explained 43.2% of the total variance of the data and had positive loadings on Cu (0.813), Pb (0.923), Zn (0.704) and Al (0.869). This factor shows these metals are from electroplating industries in which these metals are used in deposition processes and beyond aesthetic reasons, where they work in abrasion resistance and corrosion. According to Factor 1, Mn (-0.763), Fe (-0.742) and Ni (-0.636) show negative loadings and its main reason is the metallurgical and steel industries. These industries use Mn-Fe-Ni alloys in their production processes. About 70 industries are located in the Sinos River basin, and are classified into basic metallurgy and they may be responsible for the heavy metals found in Factor 1.

Factor 2 explained 22.9% of the total variance, showing loadings on Cr (0.977) and OM (0.658) that might be identified as originating from tanneries in the Sinos River basin. Other papers have reported Cr to OM association (Rodrigues and Formoso

2006, Oliveira et al. 2008, Rangel et al. 2011). This association is based on the sequential extraction, where Cr is associated to step 3 (sulfides/OM).

Factor 3 explained 18.8% of total variance, with positive loadings on Zn (0.658) and S (0.952). This leads to Zn labor in the oxidizable fraction (step 3) of the sequential extraction procedure such as sulfides, further analyzed in this paper.

TOTAL CONTENTS AND METAL FRACTIONATION

Table IV shows the results of metal concentrations in sediments (fraction <63 μm, dry weight) of the Sinos River and its tributaries and Fig. 2 shows the percentage distribution of the selected metals in the four geochemical sediment phases. The average potential availability in relation to total metal content, as measured by the sum of the three mobile phases of the BCR sequential procedure, showed some differences between the river basin subdivisions. In the upper stretch, the following metal sequence bioavailability was observed: Mn (71%) > Pb (54%) > Zn (26%) > Cr (13%) > Cu (12%) > Ni (11%) > Fe (9%) > Al (5%). For the middle stretch, the sequence was Mn (43%) > Pb (42%) > Cu (14%) > Zn (13%) > Cr (12%) > Ni (8%) > Fe (5%) > Al (4%). For the lower stretch, the sequence was Mn (76%) > Zn (65%) > Pb (51%) > Cr (46%) > Ni (45%) > Cu (41%) > Fe (17%) > Al (4%). Some differences were observed in the sequence of mobility potential in the three parts of the river basin, so that in the lower part, which shows a higher concentration of industries and habitants, there is an increase in potentially mobile fractions of Zn, Cr, Ni, Cu, and Fe.

Fe and Al showed high percentages in the residual phase (Fig. 2) in all basin samples, indicating that these elements have a low mobility in the environment where they are and that they are little affected by human activity (Li et al. 2009). The presence of the minerals kaolinite, smectite, illite, quartz (Table III) and hematite (Oliveira et al. 2008) endorse these elements in the residual stage.

Cu total concentrations (Table IV) varied from 69 to 121 mg/kg, and the maximum values were found in the Luiz Rau stream, followed by sites from the point SI 028 onwards. As for the potential mobility (Fig. 2), there is an increase onwards site SI 066, located at the beginning of the lower part of the basin. The most affected site is the Luiz Rau stream (121 mg/kg), where the potentially mobile phases reached 62% of the total content. This stream receives all discharges from one of the main urban centers and around its site there are electroplating, metallurgical and chemical industries. Cu was extracted mainly in reducible (1-24%) and oxidized (6-29%) fractions of the sequential extraction procedure, according to results from other studies that evaluated urban and industrial influences (Davidson et al. 1994, Kubová et al. 2008, Davidson et al. 2006, Rodrigues and Formoso 2006, Hang et al. 2009, Li et al. 2009, Vymazal et al. 2010, Davutluoglu et al. 2011). In addition, a high percentage in the exchangeable phase (21%) was also observed in the Luiz Rau stream, in accordance to studies by Irabien and Velasco (1999), Hang et al. (2009), and Liu et al. (2009). The increase of Cu in the oxidizable stage is related to sulfur increasing (see Table III) in the lower of the Sinos River, indicating this metal appearance as sulfides. According to Pedrozo (2003), the copper bioavailability decreases with the complexities and absorption of this element to the organic matter/sulfur and to Fe/Mn oxyhydroxides.

Zn concentrations (Table IV) ranged from 112 to 316 mg/kg, with an increase in the lower part of the Sinos River basin, in particular at the sites of the Luiz Rau stream, SI 019, and SI 008. That corresponds to the low course of the river where the sediments are deposited due to low water energy. According to Horowitz (1991) and Miller (1997), environments characterized by calm waters and thin particles tend to show high metal concentration, if compared to deposits associated to high energy regimes and thicker sediments. In this same part, there is also an increase in the potential mobility of Zn (Fig. 2), which increased from about 28% (SI
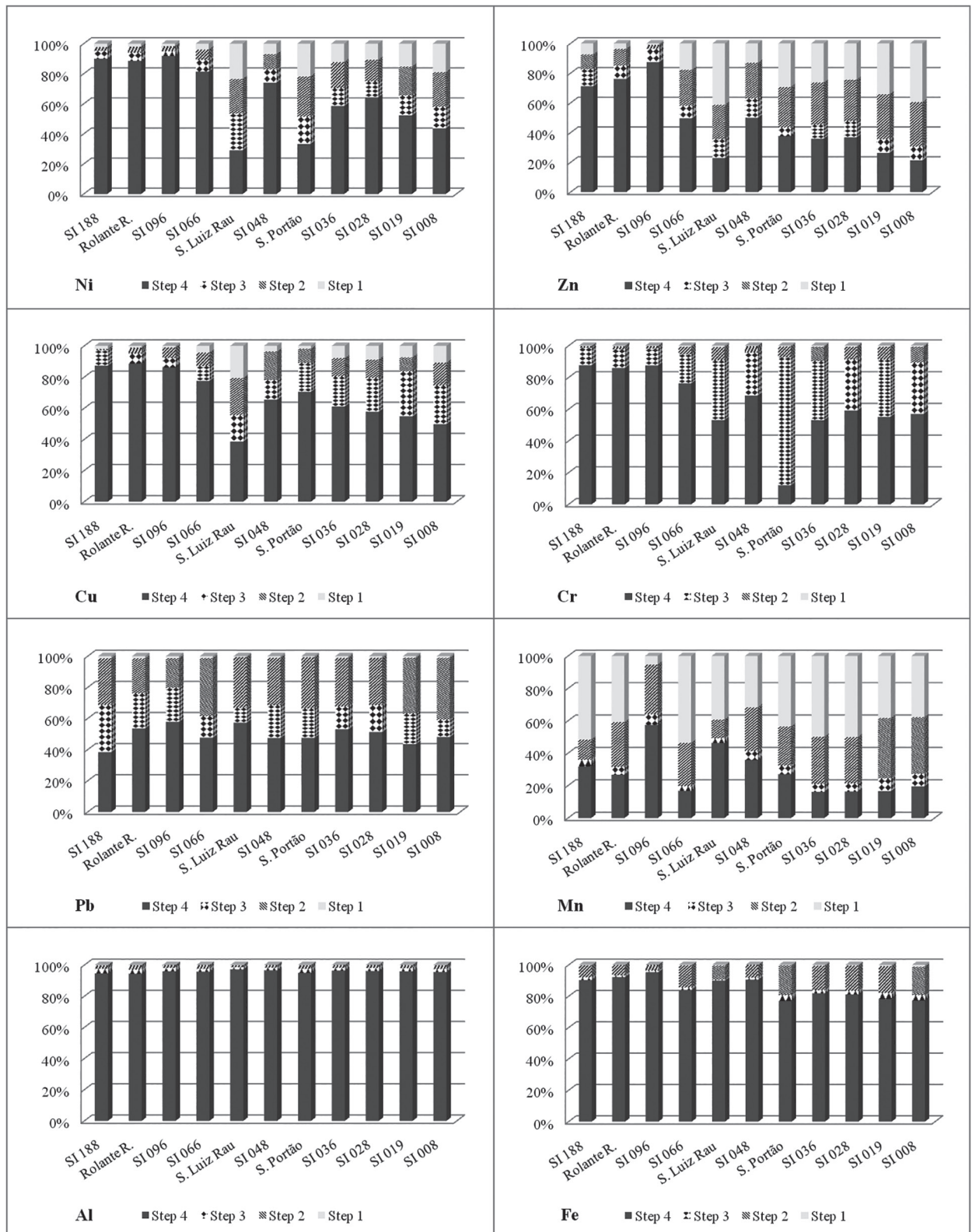
Fig. 2 - Geochemical distribution of Ni, Zn, Cu, Cr, Pb, Mn, Al and Fe in the Sinos River basin sediments (Step 1 = available fraction, i.e., exchangeable and bound to carbonates; Step 2 = reducible fraction; Step 3 = oxidizable fraction; Step 4 = residual fraction).

TABLE IV
Metals concentrations for the sequential extraction procedure BCR,
extraction with 0.5 mol/L HCl and total contents with XRF.

Site	Procedure analytical	Cu mg/kg	Zn mg/kg	Ni mg/kg	Cr mg/kg	Pb mg/kg	Al mg/g	Fe mg/g	Mn mg/g
SI 188	Step 1	1.50	9.76	0.89	0.31	<2.0	0.19	0.28	0.55
	Step 2	<0.60	13.2	0.98	1.32	8.24	2.19	6.57	0.13
	Step 3	6.87	15.2	2.06	13.2	8.32	2.78	1.45	0.04
	Step 4	60.9	94.1	35.2	106	10.6	91.2	77.6	0.34
	0.5 M HCl	-	-	-	-	-	-	-	-
	Total	69.8	132	39.2	121	27.5	96.4	85.9	1.07
Rolante River	Step 1	0.87	4.55	1.11	0.39	<2.0	0.07	0.04	0.74
	Step 2	2.87	13.5	2.15	2.10	5.68	2.54	5.67	0.50
	Step 3	4.71	10.9	2.91	13.3	5.74	2.32	0.99	0.09
	Step 4	65.8	92.0	47.9	96.6	13.6	83.2	79.4	0.48
	0.5 M HCl	16.2	13.8	2.37	1.84	7.02	-	-	-
	Total	74.2	121	54.1	112	25.4	88.1	86.1	1.81
SI 096	Step 1	0.77	1.17	0.73	0.18	<2.0	0.02	0.00	0.06
	Step 2	4.59	2.77	1.38	1.84	5.22	1.73	3.02	0.36
	Step 3	4.24	10.1	1.31	12.3	6.06	2.19	0.78	0.07
	Step 4	59.6	97.6	38.1	101.6	16.0	92.9	77.4	0.66
	0.5 M HCl	11.5	6.23	1.43	0.80	3.64	-	-	-
	Total	69.2	112	41.5	116	27.7	96.9	81.2	1.15
SI 066	Step 1	3.31	26.6	1.92	0.79	<2.0	0.07	0.19	1.02
	Step 2	6.46	36.1	3.28	6.71	11.1	2.31	9.92	0.51
	Step 3	7.29	12.5	3.73	25.2	4.16	1.90	1.10	0.05
	Step 4	58.7	74.2	39.1	105	14.2	95.2	59.0	0.32
	0.5 M HCl	29.1	48.4	3.74	5.95	11.3	-	-	-
	Total	75.8	149	48.0	138	29.9	99.4	70.2	1.90
Luiz Rau stream	Step 1	25.1	120	8.23	1.14	<2.0	0.13	0.20	0.16
	Step 2	28.8	66.6	7.98	10.6	19.4	1.60	4.75	0.05
	Step 3	20.6	36.8	8.51	48.4	5.70	1.54	0.31	0.01
	Step 4	46.6	66.3	10.2	68.1	34.0	113	47.2	0.18
	0.5 M HCl	87.2	139.1	12.0	10.5	19.1	-	-	-
	Total	121	289.2	34.9	128	59.5	116	52.4	0.40
SI 048	Step 1	2.87	22.8	3.03	0.50	<2.0	0.03	0.01	0.44
	Step 2	14.4	41.8	4.42	6.74	11.6	1.58	5.61	0.38
	Step 3	9.88	22.6	3.79	43.6	8.04	1.69	0.85	0.08
	Step 4	51.2	87.4	32.1	111	18.1	94.7	62.4	0.50
	0.5 M HCl	32.9	48.8	5.68	5.16	11.6	-	-	-
	Total	78.3	175	43.4	162	38.1	98.0	68.9	1.39
Portão stream	Step 1	1.62	66.5	11.0	5.91	<2.0	0.08	0.13	0.18
	Step 2	7.63	61.6	13.4	87.9	16.5	2.20	7.95	0.10
	Step 3	15.5	13.3	9.12	1038	9.48	2.51	1.54	0.02
	Step 4	59.1	85.0	16.8	154	23.9	90.1	32.2	0.11

TABLE IV (continuation)

Site	Procedure analytical	Cu mg/kg	Zn mg/kg	Ni mg/kg	Cr mg/kg	Pb mg/kg	Al mg/g	Fe mg/g	Mn mg/g
	0.5 M HCl	45.6	91.9	20.9	117	18.9	-	-	-
	Total	83.9	226	50.3	1286	50.3	94.9	41.8	0.41
SI 036	Step 1	6.64	57.8	4.95	1.34	<2.0	0.05	0.32	0.53
	Step 2	9.79	62.0	6.92	18.4	11.6	1.74	9.98	0.31
	Step 3	16.2	20.7	4.81	76.2	5.43	1.77	1.24	0.05
	Step 4	51.1	78.8	23.6	108	19.6	96.8	52.2	0.17
	0.5 M HCl	45.1	92.8	9.41	18.6	12.7	-	-	-
	Total	83.7	219	40.2	204	37.1	100	63.8	1.07
SI 028	Step 1	8.49	52.4	5.15	1.07	<2.0	0.05	0.29	0.57
	Step 2	11.4	59.6	6.78	14.7	10.9	1.79	10.6	0.33
	Step 3	20.8	23.3	5.06	59.0	6.20	1.98	1.57	0.06
	Step 4	55.5	79.0	30.5	108	18.4	96.2	53.3	0.19
	0.5 M HCl	53.8	88.3	10.2	15.7	12.5	-	-	-
	Total	96.1	214	47.5	183	35.9	100	65.8	1.15
SI 019	Step 1	7.51	108	6.65	1.06	<2.0	0.07	0.55	0.32
	Step 2	9.10	95.2	8.34	14.2	13.8	1.86	10.7	0.31
	Step 3	29.1	29.4	5.76	64.2	7.46	2.01	2.34	0.06
	Step 4	55.2	83.4	22.8	97.8	16.6	92.7	48.9	0.14
	0.5 M HCl	59.5	154	11.9	16.1	15.6	-	-	-
	Total	101	316	43.5	177	38.2	96.7	62.4	0.82
SI 008	Step 1	11.9	124	7.83	1.10	<2.0	0.09	0.68	0.28
	Step 2	15.8	93.7	9.40	16.8	14.7	2.31	11.0	0.26
	Step 3	27.3	29.0	5.90	54.5	4.06	1.90	2.07	0.06
	Step 4	54.4	67.0	17.9	96.0	17.7	90.4	46.7	0.14
	0.5 M HCl	73.4	156	13.0	15.8	14.6	-	-	-
	Total	109	314	41.0	168	36.8	94.7	60.4	0.73

188 at the source of the Sinos River) to almost 80% at some sites (Luiz Rau stream, SI 019, and SI 008). Zn was extracted mainly from the exchangeable (1-41%) and reducible (2-30%) phases. In Hang's et al. study (2009), which evaluates the influence of electroplating industries, Zn was also extracted preferably in the exchangeable fraction. In the reducible step of the sequential extraction, Zn associated with Fe and Mn oxides, hydroxides and oxyhydroxides, capable of removing this metal from the aqueous phase (Boughriet et al. 2007), was also extracted mainly in this step as indicated

by studies of Irabien and Velasco (1999), Rodrigues and Formoso (2006), Boughriet et al. (2007), Li et al. (2009), Liu et al. (2009), Vymazal et al. (2010), and Dundar's et al. (2012). Besides Zn and S appearance at the same statistical analysis factor, as mentioned above, proves Zn association to the sulfide oxidizable fraction form.

Pb total concentrations (Table IV) ranged from 25.4 to 59.5 mg/kg, with highest levels found in the Luiz Rau and the Portão streams. The Pb geochemical distribution was associated with the reducible (19-40%) and oxidizable (10-30%) steps,

indicating a potential average mobility of about 50%. The Pb association to these phases has been reported by several authors e.g. Davidson et al. (1994, 2006), Kubová et al. (2008), Boughriet et al. (2007), Li et al. (2009), Vymazal et al. (2010), Davutluoglu et al. (2011), and Dundar et al. (2012). Pb oxidizable fraction presence may be due to the complex-metal formation with humic substances and/or metal sulfides insoluble in the sediments (Davutluoglu et al. 2011). It has also been reported that Pb can form stable complexes with Fe–Mn oxides (Ramos et al. 1994, Liu et al. 2009). Anthropogenic Pb contributions arise from solid waste material containing batteries, electronic devices with Pb/Sn solder, and from effluents of chemical, metal plating and paint industries (Tokalioglu et al. 2003, Oliveira et al. 2008, Dundar et al. 2012).

Total Mn concentrations (Table IV) varied a lot at the studied sites (397-1,901 mg/kg), especially at the Luiz Rau and the Portão streams, which showed the lowest concentrations. Mn showed a high degree of geochemical mobility at all sites (see Fig. 2), which is not necessarily due to anthropogenic contributions, but may also be due to environmental and geochemical regional characteristics (Teixeira et al. 2003, Rodrigues and Formoso 2006). It happens because Mn tends to be present in thermodynamically less stable phases in sediments as the exchangeable ion Mn^{2+}, as easily reducible Mn oxides and as Mn trapped in carbonate minerals (Davidson et al. 1994, Robaina et al. 2002, Sakan et al. 2009). Mn was extracted mainly in the exchangeable (5-54%) and reducible (11-37%) fractions and showed a behavior similar to that in other studies (Davidson et al. 1994, Hang et al. 2009, Li et al. 2009, Liu et al. 2009, Davutluoglu et al. 2011, Dundar et al. 2012). Mn associated with the exchangeable fraction indicates that the metal is weakly adsorbed onto the sediment surface by relatively weak electrostatic interactions and that it can be easily released by ion exchange processes and dissociation of Mn bound to carbonates (Hang et al. 2009).

Total Ni concentrations (Table IV) showed no significant variations throughout the basin and varied from 35 to 54 mg/kg. With regard to the Ni geochemical distribution (see Fig. 2), there was an increase in the potentially mobile fractions of this metal from site SI 066 onwards. Noteworthy are the high rates of mobility observed for the Luiz Rau and the Portão streams (about 70%), probably in response to the wastewater from tanneries and electroplating industries. Ni was sequentially extracted in the three steps of the sequential extraction procedure: exchangeable (2-24%), reducible (2-27%) and oxidizable (3-24%).

For Cr, there was also an increase in total concentrations (Table IV) from the lower section of the Sinos River basin, varying between 112 and 1,286 mg/kg. The concentration observed in the Portão stream (1,286 mg/kg) was higher than that of the other sites studied and well above the background level of the study area (80.3 mg/kg), set up by Robaina et al. (2002). As for the geochemical distribution of Cr, we also observed an increase in the potentially mobile fractions (Fig. 2) from point SI 066 on. Cr was associated mainly with the oxidizable fraction, thus evidencing its preferential binding to organic matter (Rodrigues and Formoso 2006, Vymazal et al. 2010, Davutluoglu et al. 2011, Dundar et al. 2012). According to the data, Cr and OM appearance at the same statistical analysis factor (Table V) proves a Cr preferred association to organic fraction of the sequential extraction procedure (step 3). The preferential association of Cr to the oxidizable phase indicated that most of that metal could be retained in the sediments in the trivalent state, less toxic, and bound to organic matter (Armienta et al. 1996, Wittbrodt and Palmer 1996). From the Portão stream, we extracted 1,039 mg/kg in the oxidizable step, equivalent to 81% of the total concentration of this metal. This high association of Cr to the oxidizable fraction is evidenced by the higher OM content in relation to other sites, see Table III. These high Cr levels are

environmental markers of effluents from tanneries, as already reported by Rodrigues and Formoso (2006) and Oliveira et al. (2008), and they possibly reflect the influence of around 40 tanneries located in that region (FEPAM 2006).

In the present study, we found that the lower stretch of the Sinos River basin was the most affected area. Robaina et al. (2002) have already indicated that the sediments from the Luiz Rau stream were strongly affected by Cr (up to 1,050 mg/kg), Cu (up to 900 mg/kg), Zn (up to 3,000 mg/kg), Pb (200 mg/kg), and Ni (200 mg/kg), meaning highest pollution level according to the index adopted in that study. They also found metal levels in sediments of the main course of the Sinos River similar to those reported in this study. Oliveira et al. (2008) analyzed soil at two landfills near the Sinos River and found contamination from waste of leather industries and electroplating industries. They found concentrations of up to 1,744 mg/kg of Cr, 355 mg/kg of Zn, 94 mg/kg of Cu, and 44 mg/kg of Ni. They also pointed out the high levels of Pb (up to 70 mg/kg), reported in the study as originating from the disposal of urban solid waste that may contain batteries, electronic devices with Pb/Sn solder, material colored with lead paint, and packaging labels.

EXTRACTION WITH 0.5 MOL/L HCl

In this study, we evaluated Cu, Zn, Ni, Cr, and Pb potential mobile concentrations (Table IV) extracted by 0.5 mol/L HCl solution. As indicated by Sutherland and Tack (2008), it is possible to establish a linear regression between the concentrations extracted by 0.5 mol/L HCl and the sum of the first three steps of the sequential extraction procedure. The best linear regression was observed for Zn and is shown in Figure 3. Linear regressions found for the studied metals are shown in Table VI. All of them showed satisfactory r^2 values: Cu (r^2=0.9587), Zn (r^2=0.9961), Ni (r^2=0.9762), Cr (r^2=0.9877) and Pb (r^2=0.9049).

These regression relationships are encouraging as the HCl leach seems to be extracting the same suite of phases in the sediments as the BCR labile approach, but not to the same extent.
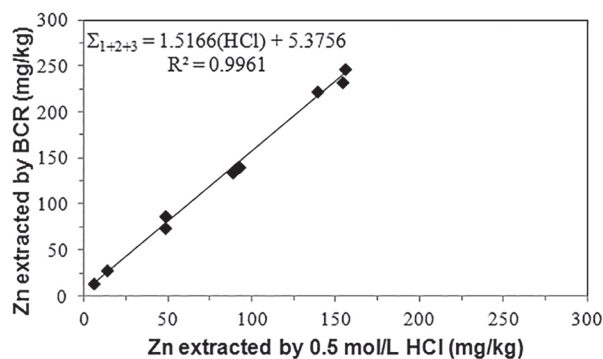

Fig. 3. Correlation between the Zn concentration extracted from sediment samples with 0.5 mol/L HCl, and the sum of three labile phases extracted by sequential extraction procedure BCR (n = 10).

Thus, through this simple, fast (1 h) and low-cost extraction procedure, it is possible to identify the samples that show higher levels of potential mobile metals in sediments, derived from anthropogenic contributions. This screening of samples allows for a more careful evaluation of only the anthropogenically impacted samples, saving time, costs, and chemical reagents. However, before adopting the dilute HCl approach for all sediments, it is imperative to conduct a preliminary investigation to establish the degree of association between anthropogenic metals leached by dilute HCl and the potential mobile fractions liberated by the BCR approach. As an example, recent data from Cook and Parker (2006) indicates that this relationship may not hold for all environments. These authors found that the 0.5 M HCl leach removed 35 times less Pb than the sum of the first three steps of the optimized BCR procedure for canal sediment contaminated by waste from a metal processing plant in France.

SEDIMENT QUALITY ASSESSMENT

Table VII shows the interval and average of the metal total concentrations for the Sinos River basin

TABLE V
Pearson correlation coefficient for metals in the sediments along the Sinos River and tributaries.

	Cr	Cu	Ni	Pb	Zn	Al	Fe	Mn	S	MO
Cr	1.000									
Cu	0.040	1.000								
Ni	0.370	0.421	1.000							
Pb	0.450	0.727[*]	0.356	1.000						
Zn	0.139	0.903[**]	0.357	0.670[*]	1.000					
Al	0.161	0.604[*]	0.687	0.710[*]	0.385	1.000				
Fe	0.655[*]	0.644[*]	0.107	0.874[**]	0.737[**]	0.431	1.000			
Mn	0.473	0.643[*]	0.505	0.777[**]	0.700[*]	0.442	0.719[*]	1.000		
S	0.280	0.346	0.059	0.054	0.638[*]	0.310	0.354	0.398	1.000	
MO	0.555	0.098	0.058	0.126	0.053	0.144	0.197	0.357	0.492	1.000

* Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

TABLE VI
Best-fit regression models correlating concentrations of metals from sediments and extracted by 0.5 mol/L HCl, as well as the sum of the three labile phases extracted by sequential extraction procedure BCR (n = 10).

Metal	Linear regression	r^2
Cu	$\Sigma_{1+2+3} = 0.8483(HCl) - 5.0143$	0.9587
Zn	$\Sigma_{1+2+3} = 1.5166(HCl) + 5.3756$	0.9961
Ni	$\Sigma_{1+2+3} = 1.5554(HCl) + 2.4542$	0.9762
Cr	$\Sigma_{1+2+3} = 0.2278(HCl) - 2.4881$	0.9378
Pb	$\Sigma_{1+2+3} = 0.9854(HCl) + 6.1679$	0.9049

sediments, having a comparison between contents that were found in rivers by different experts. It also compares the background contents under the studies (Robaina et al. 2008) and the average shale (Turekian and Wedepohl 1961). Cr, Cu and Zn average concentrations, 254, 87.5 and 206 mg/kg, respectively, show concentrations above the taken area background and the average shale. The concentration intervals for these metals were similar to those found by Irabien and Velasco (1999), Oliveira et al. (2008), Li et al. (2009) for Zn and Cu, and Rangel et al. (2011) for Zn. During these studies, contaminated sediments were evaluated as originating from urban and industrial liquid waste, featuring similarities in the taken area. About Cu and Cr total concentrations were similar to those that were found by Rodrigues and Formoso

(2006) that evaluated Cadeia-Feitoria River basin sediments. This area is damaged by tanneries.

Ni concentrations, average 44.0 mg/kg, were lower than background and shale ones. They have similar contents as those reported by Irabien and Velasco (1999), Rodrigues and Formoso (2006) and Rangel et al. (2011). Pb concentrations, average 37.0 mg/kg, were lower than background ones, except for the Luiz Rau and the Portão streams, but they were higher than average shale. Above all, Pb concentrations were similar to Irabien and Velasco (1999), Davutluoglu et al. (2011) and Hang et al. (2009). Mn concentrations, average 1,081 mg/kg, were classified as lower and higher considering background and shale levels, respectively. It must be considered that the concentrations were similar to Rodrigues and Formoso (2006) and Li et al. (2009).

Thereby, it is also important to mention that Cr, Cu, Ni, Zn and Pb concentrations higher than the background levels found in the lower Sinos River are from industries, specially electroplating and metallurgical industries, tanneries and metal industries nearby, that send off liquid waste. Another important point to be taken into consideration is the number of people living in the area, and their liquid waste. This may also be affecting the increase of metal concentrations in the lower Sinos River.

TABLE VII

Metals concentration (mg/kg) in the study area (minimum-maximum) (average) compared with values from the literature.

Location	Cr	Cu	Ni	Zn	Pb	Mn	Reference
Sinos River	112 – 1,286 254	69.2 – 121 87.5	34.9 – 54.1 44.0	112 – 316 206	25.4 – 59.5 37.0	397 – 1,901 1,081	This study
Lower part of the Sinos basin	20.0 – 1,200	20.0 – 1,175	20.0 – 325	50.0 – 5,300	20.0 – 200	*	Robaina et al. 2002
Soil at two landfills near the Sinos river	205 – 1,744	35.0 – 94.0	13.0 – 44.0	57.0 – 355	23.0 – 70.0	200 – 900	Oliveira et al. 2008
Cadeia River - Brazil	34.7 – 423	57.8 – 102	27.0 – 74.9	122 – 147	*	1,090 – 2,210	Rodrigues and Formoso 2006
Feitoria River - Brazil	169 – 1,031	93.8 – 106	71.2 – 91.1	136 – 145	*	1,080 – 2,230	Rodrigues and Formoso 2006
Estrela River - Brazil	8.44 – 100	10.0 – 74.5	26.0 – 95.9	42.5 – 351	45.8 – 121.4	164 – 811	Rangel et al. 2011
Sakarya river - Turkey	37.0	37.5	83.0	76.7	41.3	772	Dundar et al. 2012
Seyhan River - Turkey	46.3 – 122	3.68 – 57.2	82.2 – 215	34.2 – 146	11.3 – 74.7	144 – 638	Davutluoglu et al. 2011
Rivers in the Jiangsu Province - Eastern China	345 – 9,671	440 – 9,797	251 – 2,846	391 – 1,483	17.2 – 106	338 – 782	Hang et al. 2009
Brunette River - Canada	*	12.0 – 225	*	56.0 – 335	63.0 – 722	217 – 1,452	Li et al. 2009
Deûle-canal - Northern France	*	*	*	149 – 12,895	26.8 – 10,079	*	Boughriet et al. 2007
Oka River - Spain	20.0 – 180	30.0 – 150	30.0 – 130	100 – 360	30 – 110	370 – 1,600	Irabien and Velasco 1999
Background	80.3	39.4	50.5	82.4	42.0	*	Robaina et al. 2002
Average shale	90.0	45.0	68.0	95.0	20.0	850	Turekian and Wedepohl 1961

* Not available.

Moreover, in order to evaluate sediment quality, Table VIII compares the average total metal concentration with sediment quality guidelines (SQGs) from Canada (CCME 1999) and with the study of Long et al. (1995). With regard to the Canadian study, it can be seen that Cu and Cr in the three stretches of the river basin, Zn in the upper and lower stretches, and Pb in the lower stretch, showed higher average concentrations than the interim freshwater sediment quality (ISQG) value. As for the probable effects level (PEL) criterion, only Cr, in the lower stretch of the basin, showed higher average concentration. Considering the criteria of the study by Long et al. (1995), we see that the average concentrations of Cu, Ni and Cr in the three stretches, and Zn and Pb in the lower stretch, were higher than the Effect Range Low (ERL) and Threshold Effects Level (TEL) concentrations. As for PEL, only the average levels of Ni and Cr in the lower basin were higher. There were no average concentrations higher than the effect range median (ERM) criterion. Therefore, based on the SQGs approach, the Sinos River basin would be classified as an area with free to moderate toxicological risk, when considering only the total concentration of metals, except the Portão stream, that showed moderate to high pollution.

CONCLUSIONS

The higher concentrations of Cr, Cu, Zn and Pb were observed in the lower stretch of the

TABLE VIII

Comparison of average metal concentrations (mg/kg) in sediments of three stretches of the Sinos River basin with sediment quality guidelines (SQGs).

Metal	Canadian Sediment Quality Guidelines[a]		Sediment quality guidelines[b]				Average by stretch of the Sinos River basin		
	ISQG	PEL	TEL	PEL	ERL	ERM	Upper	Middle	Lower
Cu (mg/kg)	35.7	197	18.7	108.2	43	270	72.0	69.2	93.6
Zn (mg/kg)	123	315	124	271	150	410	127	112	238
Ni (mg/kg)	*	*	15.9	42.8	20.9	51.6	46.6	41.5	43.6
Cr (mg/kg)	37.3	90.0	52.3	160.4	81.0	370	116	116	306
Pb (mg/kg)	35.0	91.3	30.2	112.2	46.7	218	26.5	27.7	40.7
Al (mg/g)	*	*	*	*	*	*	92.2	96.9	100
Fe (mg/g)	*	*	*	*	*	*	86.0	81.2	60.7
Mn (mg/g)	*	*	*	*	*	*	1.44	1.15	0.98

[a]CCME (1999), [b]Long et al. (1995), * Not available.

Sinos River basin sediment. This region, that has higher population density and industrial plants (mainly metal works, electroplating industries, and tanneries), showed an increase in both the total concentrations (Cu, Cr, Zn and Pb) and in the sequentially extracted mobile fractions (Cu, Cr, Ni and Zn). Cr pointed out, particularly in the Portão stream, showed 1,286 mg/kg as the total concentration and 88% in the potentially mobile fractions, due to the influence of the local tannery. These pollutants are available in the aquatic environment due to their association with different sediment phases.

The sequential extraction indicated that the metals were associated with the exchangeable (Ni, Zn, Cu), reducible (Ni, Zn, Cu, Pb) and oxidizable phases (Ni, Cu, Cr, Pb). These results showed similar distribution with studies that evaluated sites impacted by the same anthropogenic sources. Regarding the sediment quality assessment, these regions can be classified as an area with free to moderate toxicological risk, except Portão stream, that showed moderate to high pollution.

Partial extractions are valuable tools for a preliminary survey, where critical contaminants and priority areas have to be identified. In our study, the potentially mobile metals extracted with a 0.5 mol/L HCl solution presented satisfactory correlation with the concentrations extracted by the sequential extraction scheme. Although some problems in the sequential extractions have not been fully resolved yet, the use of these procedures generate more complete information, enabling a more detailed characterization of the origin, chemical form, distribution, and metals potential availability. In this study the sequential extraction procedure demonstrated good reproducibility for the certified reference material (BCR 701) used.

Considering the factor analysis, it is possible to identify the main anthropogenic contributions in the Sinos River basin sediments. Further studies with geochemical focus are needed in order to have a better assessment of the potential retention and release of metals sediments, as well as to mineralogically feature the sediments in this area. Based on these studies, it will be possible to do an accurate assessment of the potential risk of metals contamination through their remobilization and the current condition of this study area with regards to these pollutants.

Estadual de Proteção Ambiental Henrique Luiz Roessler (FEPAM).

RESUMO

O presente estudo teve como objetivo avaliar o teor de Cu, Cr, Ni, Zn, Pb, Mn, Al e Fe e sua partição geoquímica em sedimentos da bacia hidrográfica do rio dos Sinos, Sul do Brasil. Esta bacia apresenta elevada densidade populacional e de indústrias, especialmente dos setores de metalurgia, galvanoplastia, siderurgia, petroquímica e curtumes. As concentrações totais de metais foram determinadas por fluorescência de raios-X e as concentrações nas fases dos sedimentos foram determinadas através da aplicação do esquema de extração sequencial BCR-701 proposto pelo *Community Bureau of Reference*, da Comunidade Europeia, utilizando ICP/OES. Também foram considerados os teores extraídos através de uma solução de HCl 0,5 mol/L. Os teores de metais foram avaliados na fração de sedimentos <63 μm. Os resultados na região industrializada e com alta densidade populacional mostraram um aumento nas concentrações totais, para Cu, Cr, Zn e Pb, e nas frações potencialmente móveis para Cu, Cr, Zn e Ni extraídos sequencialmente. O Cr destacou-se especialmente no arroio Portão, apresentando uma concentração total de 1.286 mg/kg, devido à influência de curtumes localizados nesta região.

Palavras-chave: BCR-701, metais, sedimentos, extração sequencial.

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