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Assessment of heavy metals in sediments of the Sinos river basin, southern Brazil

I. L. Schneider[1] , E. C. Teixeira[2], M. L. K. Rodrigues[2] and S. B. A. Rolim[3]

[1] Postgraduate Program in Remote Sensing – Federal University of Rio Grande do Sul (UFRGS), Brazil, ismaelquimrs@yahoo.com.br
[2] State Foundation for Environmental Protection and Postgraduate Program in Remote Sensing - Federal University of Rio Grande do Sul (UFRGS), Brazil, gerpro.pesquisa@fepam.rs.gov.br
[3] State Foundation for Environmental Protection, Brazil, metaisfepam@hotmail.com
[4] Postgraduate Program in Remote Sensing - Federal University of Rio Grande do Sul (UFRGS), Brazil, silvia.rolim@ufrgs.br

Abstract. The present study aimed to evaluate the content of Cu, Cr, Ni, and Zn and their geochemical partitioning in sediments of the Sinos river basin in southern Brazil. This basin has a high population density and a great number of industries, especially metallurgy, electroplating works, steel mills, petrochemicals, and tanneries. The total metal concentrations were determined by X-ray fluorescence, and the concentrations in the sediment phases were determined by applying the BCR-701 sequential extraction method proposed by the Community Bureau of Reference of the European Community, using ICP/OES. Heavy 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 for Cu, Cr and Zn, and in the mobile fractions for the sequentially extracted metals Cu, Cr, Zn and Ni. Cr stood out particularly in the Portão stream, showing a total concentration of 1286 mg kg^{-1}, due to the influence of tanneries in this region.

Key words: Heavy metals, Sediments, Sequential Extraction, BCR-701

Introduction

Heavy metals when dispersed in aquatic environments tend to deposit in the sediment, which besides having high retention capacity, have the potential of releasing pollutants (Passos *et al*., 2011). However, as determination of the total concentration of a metal in sediments makes no distinction between natural and anthropogenic components and the metal (Quevauviller *et al*., 1996; Relic *et al*. 2010; Passos *et al*., 2011), the quantification of potentially available or labile metals in sediments provides a better indicator of this differentiation. The procedures used to determine the levels of potentially mobile metals might involve sequential extraction techniques, where several selective reagents are used consecutively to extract metals associated with "stages operationally defined" from the sediment. These procedures aim at simulating changes in environmental conditions and thus predict the impact of a potential mobilization of metals on the surrounding environment (Bacon & Davidson, 2008).

One technique often used is the sequential extraction procedure proposed by the Community Bureau of Reference (BCR) (now Standards, Measurement and Testing Programme), which involves three steps - exchangeable metals associated with carbonates, reducible metals, and oxidizable metals (Pueyo *et al*., 2001; Quevauviller *et al*., 1996; Davidson *et al*., 1994; Davidson *et al*., 1999; Teixeira *et al*., 2003; Rodrigues & Formoso, 2006; Passos *et al*., 2011).

In the present study, we evaluated the total concentrations and the geochemical distribution of Cu, Cr, Ni and Zn in sediments of the Sinos river basin to assess the potential mobility of these metals in watercourses.

Materials and Methods

Area of Study

The Sinos river basin is located in the Northeast of the state of Rio Grande do Sul, Brazil. It occupies an area of 3,820 km² and encompasses all or part of 29 counties, of which 21 are part of the metropolitan area of Porto

Alegre (MAPA), the state's capital. The Sinos River has its source at an altitude of 600 m, its main course flows for 190 km and it finally discharges its waters at an altitude of 12 m. The basin is inhabited by approximately 1.3 million people, 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 ºC and about 1350 mm of rain per year, well distributed over the four seasons (FEPAM, 2006).

The basin can be divided into three different regions, all of which related to the corresponding section of the river: upper, middle, and lower. 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, petrochemicals and tanneries), domestic sewage, and rice farming are the main sources of concern with regard to water quality of this river basin (FEPAM, 2006).

Collection and preparation of samples

Sediment samples were collected in February and August 2010, at eight points along the main course of the Sinos River and three tributaries (the Rolante River and the mouths of the Luiz Rau and Portão streams). Samples of surface sediments were collected by using PVC, L-shaped manual collector. The material collected was stored in plastic bags, cooled to 4 ºC and sent to the laboratory, where the fraction with particle size <63 µm was separated by wet sieving. The content of interest was oven-dried at 37 ºC and was then finely homogenized in an agate mortar (Rodrigues & Formoso, 2006).

Chemical analyses

The total concentrations of metals were determined by X-ray fluorescence (XRF). The sediment samples were prepared in the form of pressed pellets and analyzed in the Laboratory of Analytical Geochemistry at the State University of Campinas.

The analyses of metal fractionation were performed by applying the sequential extraction procedure in three steps proposed by BCR (Pueyo *et al*., 2001). The procedure employed is described in Table 1. The determination of Cu, Cr, Zn and Ni concentrations in the extracts of the sequential extraction was performed in an inductively coupled plasma optical emission spectrometer (ICP-OES) of the Laboratory of Soil Science, Federal University of Rio Grande do Sul.

In this study, a fourth step corresponding to the residual fraction was considered, to evaluate the content of metal bound to the silicate matrix or to the crystalline oxides of Fe/Mn, which are not released under natural conditions. This fraction was determined by the difference between the sum of three steps sequentially extracted in relation to the total content of metals previously determined by XRF.

The accuracy of the sequential extraction procedure was verified by analysis in triplicate of the certified reference material for river sediments (BCR-701), with mean recoveries of 85-104 % for Cr, Cu, Ni and Zn. For quality control of total metals concentrations by XRF, we analyzed two reference materials (GSS-2 and GSS-5), showing mean recoveries of 88-105 % for the metals studied. The determination of metal concentrations was performed in duplicate, and the accuracy was measured by the coefficients of variation (<10 %).

Results and Discussion

Table 2 shows the total concentrations of metals and Figure 1 illustrates the percentage distribution of Cu, Cr, Zn and Ni in the four geochemical phases of sediments. The mean availability potential, measured by the ratio between the sum of concentrations in the three mobile phases and the total content, was as follows: Zn (53 %) > Cr (37 %) > Ni (36 %) > Cu (33 %).

When analyzing Table 2, we seen that from point SI 066 on there is an increase in the concentrations of Cu, Zn and Cr, and we point out the high total concentration of Cr (1286 mg kg^{-1}) at the mouth of the Portão stream. Figure 1 shows that from point SI 066 on there is also an increase in the potentially mobile phases of Cu, Cr, Ni and Zn, probably due to an increase in population density and number of industrial plants.

Table 1. Sequential extraction procedure

STEPS	REAGENTS	SEDIMENT PHASES
1	Acetic acid 0.11 M	Exchangeable - water and acid soluble species
2	0.10 M hydroxylamine hydrochloride, pH 1.5	Reducible - species associated with oxides and iron and manganese hydroxides
3	1.0 M ammonium acetate, after digestion with 8.8 M hydrogen peroxide at pH 2	Oxidizable - species bound to organic matter and sulfides
4*	Total concentration minus the sum of the previous three steps	Residual - species associated with the silicate matrix

Source: Pueyo *et al.* (2001). * Adopted herein.

Table 2. Total metal concentrations in sediment samples (mg kg^{-1}, d.w., fraction <63 µm). The codes of the points indicate the distance in kilometers from the sampling point to the mouth of the Sinos River.

Site	*Cr*	*Cu*	*Ni*	*Zn*
SI 188	120.6	69.8	39.2	132.3
Rolante river	112.4	74.2	54.1	120.9
SI 096	116.0	69.1	41.5	111.7
SI 066	137.7	75.8	48.0	149.4
Luiz Rau stream	128.2	121.0	34.9	289.2
SI 048	161.9	78.3	43.4	174.6
Portão stream	1,286	83.9	50.3	226.4
SI 036	204.4	83.7	40.3	219.3
SI 028	182.7	96.1	47.5	214.4
SI 019	177.3	100.8	43.5	316.3
SI 008	168.4	109.5	41.1	313.7

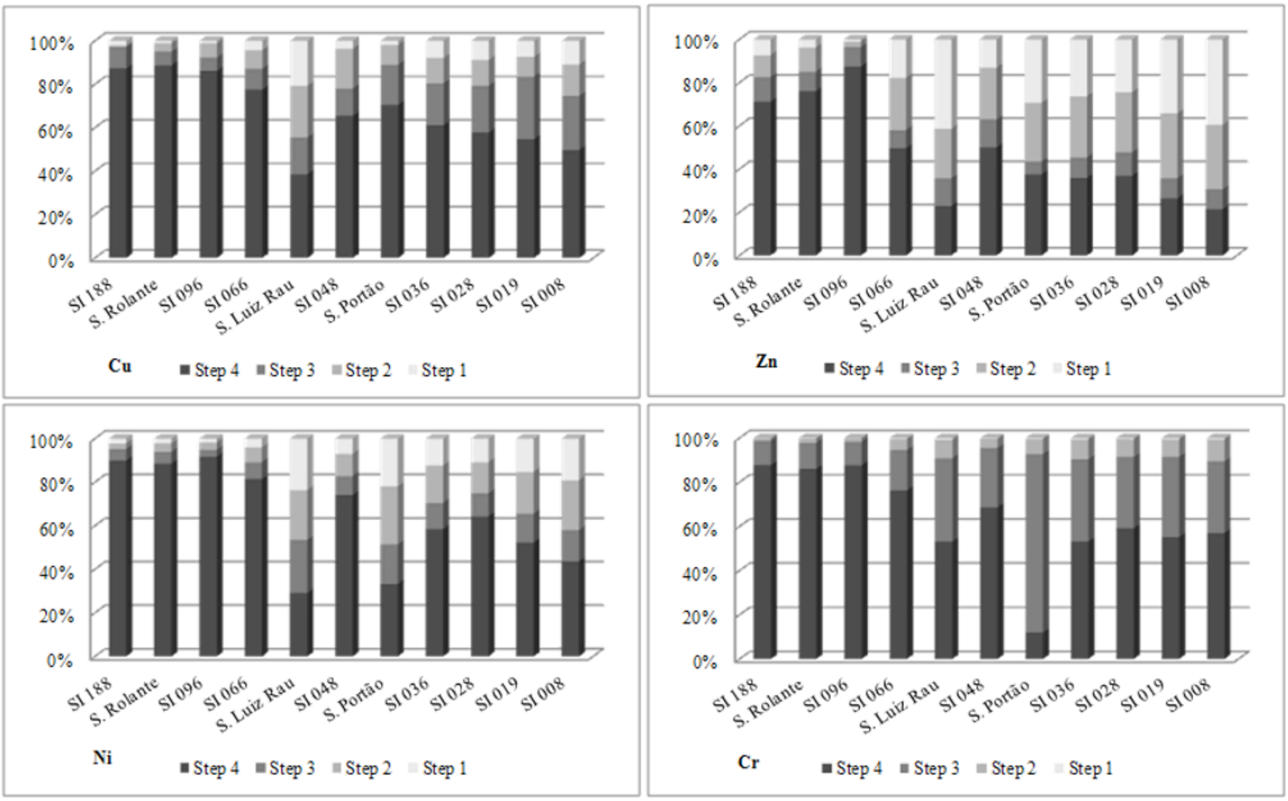

Fig. 1. Geochemical distribution of Cu, Zn, Ni and Cr in the sediments of the Sinos basin (Step 1 = exchangeable fraction and bound to carbonates; Step 2 = reducible fraction; Step 3 = oxidizable fraction; Step 4 = residual fraction).

The total concentrations of Cu are shown in Table 2. From Figure 1 on, we see that there is an increase in the potential mobility as we reach the mouth of the Sinos River, especially at the Luiz Rau stream, where it reaches 60 %. Cu was extracted mainly in the reducible and oxidizable fractions of the sequential extraction procedure, as reported by Davidson *et al*. (1994) and Vymazal *et al*. (2010).

Similarly, we found an increase in the total Zn concentrations (Table 2) and its potential mobility (Figure 1) in the lower section of the Sinos basin. Zn, frequently associated with Fe and Mn oxides (hydroxides and oxyhydroxides), was extracted mainly in the reducible phase (Vymazal *et al*., 2010). Moreover, this element also occurred in the exchangeable phase. The mobility increased from about 28 % (SI 188, the source of the Sinos River) to almost 80 % at some points (Luiz Rau stream, SI 019 and SI 008).

The total Ni concentrations (Table 2) showed no significant variations throughout the basin. However, when analyzing the mobility potential of Ni (Figure 1), we observe an increase in this metal in the exchangeable fractions from point SI 066 on. Noteworthy are the high percentages of mobility observed for the Luiz Rau and Portão streams (approx. 70 %).

For Cr, there was also an increase in total concentrations (Table 2) from the lower section of the Sinos basin. However, it is important to highlight the concentration found in the Portão stream (1286 mg kg^{-1}), which is higher than the background value of the study area, not reported in the present study. As the metals highlighted above, there is an increase in the mobile fractions (Figure 1) from point SI 066 on. Cr was extracted mainly in the oxidizable fraction, indicating its binding to organic matter (Rodrigues & Formoso, 2006; Vymazal *et al*., 2010). As for Portão stream, 1039 mg kg^{-1}, equivalent to 81 % of the total concentration of this metal, were extracted in the third step of the sequential extraction. These high Cr levels are environmental markers of effluents from tanneries, as already reported by Rodrigues & Formoso (2006), and they possibly reflect the influence of around 40 tanneries located in that region (FEPAM, 2006).

This similar behavior of increased of potentially mobile concentrations of Cu, Cr, Zn and Ni may be associated with anthropogenic contributions in the lower section of the Sinos basin. Among these contributions, there are the release of industrial and domestic effluents, urban runoff, the contribution of agricultural areas, vehicular traffic, and the burning of fossil fuels.

Conclusions

Analysis of sediments from the Sinos basin shows an increase in heavy metals concentrations nearer to the river mouth. From point SI 066 on, with its higher population density and higher number of industrial plants (mainly metal works, electroplating works, and tanneries), there is both an increase in the total concentrations (Cu, Cr and Zn) as in the sequentially extracted mobile fractions (Cu, Cr, Ni and Zn). Although Ni did not show significant variations in total concentrations throughout the basin, it shows potential mobility of up to 70 % in the Luiz Rau and Portão streams. Cu and Zn concentrations showed similar behavior, with a higher potential mobility for Cu (61 %) and Zn (77 %) in the Luiz Rau stream. Cr concentrations also increased in the lower section of the Sinos basin, especially in the Portão stream, with total concentration of 1286 mg kg^{-1} and potential mobility of 88 %. Therefore, by using sequential extraction as a tool for assessing the mobility of heavy metals in sediments, it is possible to estimate the behavior and potential availability of pollutants in the environment.

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