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# A simple method for evaluation of the total concentration of Cd, Cr, Cu, Pb and Zn in sediments from the São Gonçalo channel in Pelotas, RS, Brazil

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## Abstract

This study evaluated the total concentrations of Cd, Cr, Cu, Pb and Zn in sediments samples from the São Gonçalo channel, Patos-Mirim lagoon complex, RS state, Southern Brazil during 2013 autumn, winter and spring, and 2014 summer. Ultrasound-assisted extraction method was employed to extract metals from the sediment samples. The sample powder was mixed with $HNO_3$ and HF in an ultrasonic bath during 60 minutes at 25 °C. The limits of detection were 0.002; 0.026; 0.83; 0.386 and 0.44 mg kg$^{-1}$ for Cd, Cr, Cu, Pb and Zn, respectively. The accuracy of the method was confirmed by analysis of two sediment certified reference materials and its precision was determined by the values of relative standard deviation lower than 9.1%. The concentrations obtained ranged from 0.11 to 0.58 mg kg$^{-1}$ for Cd; 14.7 to 38.4 mg kg$^{-1}$ for Cr; 3.9 to 102.0 mg kg$^{-1}$ for Cu; 1.6 to 3.11 mg kg$^{-1}$ for Pb; and 29.3 to 126 mg kg$^{-1}$ for Zn. These values did not exceed the probable effect levels (PEL). Simplicity, low cost and high efficiency are some of the qualities of the method, making it adequate for routine analysis.

**Keywords:** atomic spectrometric techniques; metals; sediment; ultrasonic treatment.

## INTRODUCTION

Metals can affect the environment in different ways and become an imminent risk of intoxication to humans, depending on the chemical form and degree of toxicity of these elements. Most metals present in environmental samples as sediment and water, for example, are from different sources: lithogeny processes, anthropic activities (use of agrochemicals, industrialization, etc.) (De Azevedo & Chasin, 2003). Unfortunately, the aquatic environments are eventually the final collectors, facilitating the mobility of toxic metals for the biota (Cotta *et al.*, 2006; Jardim *et al.*, 2008).

Sediments act as a deposit and also as a source of pollution for the aquatic environment. The accumulation of contaminants as metals in sediment tends to occur through physical-chemical mechanisms such as flocculation and direct precipitation (sulphides), by adsorption on the particulate material and subsequent deposition on the depth. Thus, the contamination of the sediment is used as an important indicator of environmental pollution, helping to map and monitor anthropogenic sources of contamination or anomalies that may be caused by natural geochemistry processes (Chapman *et al.*, 2001; Hortellani *et al.*, 2005; Prica et al., 2010, Cobelo-García *et al.*, 2011; Reible, 2014).

The study area in this work, the São Gonçalo channel, is located in the Patos-Mirim lagoon complex on the coastal plain of Rio Grande do Sul, in Pelotas city (Southern Brazil). It is a natural channel 75 km long, 200 to 500 m wide and 6 m deep. It periodically undergoes changes in the direction of flow through the canal lock. The channel connects lakes Patos (estuarine portion) and Mirim (limnic portion) and is of great importance to the cities of Pelotas and Rio Grande,

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because it serves various domestic purposes, and is a source of livelihood for many families who survive by fishing. It also contributes to the irrigation of rice crops and local navigation (Burns *et al.*, 2006). The channel became the main destination of three streams that supply the city of Pelotas, besides the Piratini River. These streams cross populated urban areas occupied by residential properties, with commercial, industrial and agricultural activities that contribute with contaminants inputs to the water. In 1977, a sliding gate on dam was built on the channel in order to prevent inflow of salt water from the Patos Lagoon estuary into the Mirim lagoon. Previous studies have shown that this considerably altered the habitat and distribution of different species of fish, and interrupted connections between adjacent aquatic systems. Rice farming also has influence on the contamination of the channel, mainly when the water is used in the irrigation return to the channel and it brings residues of agrochemical products. Thus, it is important to know the levels of toxic metals in the sediments of the São Gonçalo channel to perform monitoring activities and environmental control (Burns *et al.*, 2006).

Patos Lagoon is considered one of the biggest coastal lagoon in the world (1,036,000 ha). The lagoon is connected to the ocean via a channel, extending from the city of Porto Alegre (30º30' S) to Rio Grande (32º12' S) in southern Brazil, at the Atlantic coast of South America. The Patos Lagoon estuary present high biological productivity and at the same time provide significant ecosystem services including artisanal and industrial fisheries, an industrial conglomerate and is home to an important maritime port. All marine organisms that depend on the Patos Lagoon estuary at some point in their life cycle migrate through the communication channel into the ocean (Castello, 1985; Kotzian & Marques, 2004).

The determination of metals in soils and sediments is expensive, due to their composition (high silica content). Usually, sediments are brought into solution using alkaline fusion or acid decomposition before element determinations. However, these procedures are time-consuming and require relatively high amounts of reagents. Alternatively, sample introduction as slurry for different techniques is an interesting approach that has been used (Vassileva *et al.*, 2001; Alves *et al.*, 2001; Sastre *et al.*, 2002; Vieira *et al.*, 2002; Vieira *et al.*, 2004; Collasiol *et al.*, 2004). A partial extraction of the analyte into the water phase of the slurry is obtained thereby improving the precision. Parameters as particle size, acid concentration and calibration are important factors to be considered (Bendicho *et al.*, 1991, Calle *et al.*, 2011). To increase the extraction efficiency of the analyte into the aqueous phase, one of the simplest tools that can be used is the ultrasonic bath. Thus, it is possible to work with lower acidity conditions, or more diluted solutions, a lower amount of reagents and/or samples, atmospheric pressure in a closed system, thereby preventing loss of volatile components and/or contamination. Additionally, the total time of preparation of the samples may be reduced and depending on the size of the ultrasonic bath to be used, a larger number of samples can be prepared simultaneously (Miller-Ihli, 1990; Bendicho *et al.*, 1991; Calle *et al.*, 2011; Krug, 2016). Many articles using the ultrasound-assisted extraction for the preparation of environmental samples as sediment have been published, demonstrating the importance in the development of simple and rapid methods for the determination of toxic metals in these samples (Ribeiro *et al.*, 2004; Brunori *et al.*, 2004; Elik, 2007; Arain *et al.*, 2008, Frena *et al.*, 2014).

Thus, this study aims to determine the total concentrations of Cd, Cr, Cu, Pb and Zn in sediments from estuarine and limnic portions of the São Gonçalo channel, in different seasons of 2013 and 2014. The samples were prepared using the ultrasound-assisted extraction method and the best conditions for sample preparation were optimized.

## MATERIALS AND METHODS

### *Seasonal sampling*

Sediments samples were obtained at five different sampling stations in the São Gonçalo channel (denominated P0, P1, P2, P3 and P4), in different seasons: summer, autumn, winter and spring of 2013 and summer of 2014. There were five sampling series at the 5 sampling stations to make up 25 samples, taken in triplicate, which gives a total of 125 samples. All sampling stations were properly identified with a GPS (Global Positioning System) model Garmin Etrex Vista® H, and are defined in Table 1 and identified in the image shown in Figure 1.

Surface sediment sampling was performed using a stainless steel Van Veen grab in deep and shallow waters (0 to 5 cm deep). Samples were taken from the central portion of the retained material in the sampler (without contact with the walls thereof) transferred to labeled polyethylene jars and stored under refrigeration at 4°C until transport to the laboratory. All sediments samples were dried in an oven at 60 °C; ground in an agate mortar and passed through 50 mesh polyester sieve. The samples were then stored at room temperature (25 °C) in polyethylene flasks.

### *Preliminary sediment characterization*

The sediments analyses (grain size distribution and determination of metals) were carried out using samples dried in an oven at 60 °C, with the exception of the samples analyzed for organic matter and humidity, in which wet sediments were analyzed after thawing. The humidity was determined by gravimetric method, where 20 g of sample was dried in an oven at 105 ± 5ºC for 24 h until constant weight, according to the method described by the Brazilian Agricultural Research Corporation (EMBRAPA, 1997). The quantity of organic matter was evaluated indirectly by loss of volatiles at 550 °C using a muffle furnace for a period of 4 h, according to the American Public Health Association

Figure 1. Sediment sampling stations on São Gonçalo channel in Pelotas, RS, Brazil. Source: Google Earth.

Table 1. Description of the sampling stations

| | | Latitude | Longitude |
|---|---|---|---|
| **P 0** | Pelotas stream | 31°76’14.72” | 52º28’82.49” |
| **P 1** | Near Ferry Pelotas area | 31°78’25.02” | 52°31’89.03” |
| **P 2** | Between Pelotas Port and the bridge of BR 392 | 31°79’11.84” | 52°34’86.73” |
| **P 3** | Near sliding gate | 31°82’03.16” | 52°39’27.52” |
| **P 4** | Near Paineira farm and before Piratini River | 31°90’81.14” | 52°38’12.98” |

(APHA, 2005) standard methodology. The granulometric analyses of the sediments were performed by sieving for coarse sediments, by sorting the grain sizes according to the Wentworth scale of 2 mm to 63 µm. For this, was used an agate mortar and polyester sieve.

### *Instrumentation*

Analytical measurements for Cu and Zn were carried out using a flame atomic absorption spectrometer (Perkin Elmer AAnalyst 200, Shelton, CT, USA) equipped with deuterium arc background correction and a hollow cathode lamps source: Cu (324.75 nm) and Zn (213.86 nm) were operated at 15 mA and spectral band path of 0.7 nm for both analytes. Acetylene, 99.7 % (Linde, São Paulo, Brazil), was used in the flame. Gas flow rates for flame were: 2.50 L min$^{-1}$ (fuel) and 10 L min$^{-1}$ (air). Integrated absorbance signals for Cd, Cr and Pb were measured in an atomic absorption spectrometer with a graphite furnace (Perkin Elmer PinAAncle 900z, Shelton, CT, USA) equipped with an autosampler (AS-900 model), a transverse-heated graphite tube atomizer, and Zeeman-effect background correction. Hollow cathode lamps for Cd, Cr and Pb (Perkin Elmer) were used operating at 4 mA (Cd); 25 mA (Cr) and 10 mA (Pb) and spectral band path of 0.7 nm for both analytes. Argon, 99.996 % (Linde, São Paulo, Brazil), was used as protected and purge gas. All experiments were carried out using pyrolytic graphite coated tubes with integrated platforms. The temperature program is shown in Table 2.

Samples were weighed using an analytical balance (Model 2140 from Ohaus Adventurer, Parsippany, NJ, USA) and sonicated using an ultrasonic bath (Elmasonic, Model S 40 (H), 37 kHz).

### *Reagents, solutions and certified reference materials*

In this study all chemicals and reagents used in were of analytical grade. All solutions were prepared by using deionized water obtained by a water distiller MA078 (Marconi, São Paulo, Brazil) and subsequently deionized by passing through a column CS1800 (Permution, Curitiba, PR, Brazil). Standard solutions of Cd, Cr, Cu, Pb and Zn (Merck, Darmstadt, Germany) were prepared daily by appropriate dilutions of a stock solution containing 1000 mg L$^{-1}$ of each analyte in $HNO_3$ 2% (v/v) from a standard concentrate solution. The $HNO_3$ 65% (m/m) (Synth, Diadema, SP, Brazil), HF 40% (v/v) (Vetec, SP, Brazil) and $H_3BO_3$ (Vetec, SP, Brazil) were used. The $HNO_3$ was purified by doubly subboiling distillation in a quartz system MA-075 (Marconi, São Paulo, Brazil). Palladium and Mg (Sigma-Aldrich, Sigma, St. Louis, MO, USA) were used as a chemical modifier with addition into the graphite furnace of 3 µg Mg for measurements of Cr and 3 µg Mg + 5 µg Pd for measurements of Pb and Cd. The following certified reference materials (CRM) were used to evaluate the accuracy of the method: 2704a (Buffalo River Sediment, NIST, Gaithersburg, USA) and BCR 667 (Estuarine Sediment, IRMM, Geel, Belgium).

### *Sample preparation method*

Ultrasound-assisted extraction method optimization studies were performed with sediment samples of collection point P2, using a fixed amount (100 mg) and varying the concentration of $HNO_3$, HF, temperature and time of sonication. In this step, the analytical signal was evaluated only for Cu and Zn by F AAS and the best form conditions were applied to the other analytes (Cd, Cr and Pb).

After optimization, the following method was used for sample preparation: about 100 mg of sediment were directly weighed into polypropylene flasks, followed by addition of 2 mL of $HNO_3$ 65% (v/v) and 1 mL of HF 40% (v/v). The flasks were closed and placed in an ultrasonic bath for 60 minutes at 25 °C. Afterwards, 8 mL of $H_3BO_3$ was added and then the volume was made up to 15 mL with deionized water. This addition ensures masking of fluoride ions, since the residue of the same may damage parts of the spectrometer such as the nebulizer (Krug, 2008). Blank analytical solutions were prepared simultaneously.

Figures of merit evaluated in this work were limit of detection (LOD), limit of quantification (LOQ), linearity, and accuracy calculated according to INMETRO guide (2010). Limit of detection and limit of quantification were calculated as either three or ten times the standard deviation of 10 measurements of a blank divided by the slope of the calibration curve for each analyte. Calibration curves were prepared with standard solutions of Cd, Cr, Cu, Pb and Zn in $HNO_3$ 2% (v/v).

## RESULTS AND DISCUSSION

### *Optimization of ultrasound-assisted extraction method*

Although the ultrasound-assisted extraction is promising, it is recommended that the variables that influence the extraction of the analyte sample to the aqueous phase be evaluated. The mixture of $HNO_3$ with HF was chosen taking into account the fact that $HNO_3$ is a strong acid and an important oxidizing agent for the destruction of organic matter and also the ability of HF to remove silicates, found in large quantities in sediment samples. Besides the concentration of the acids, the temperature and time of sonication were also evaluated to obtain a higher extraction efficiency of the analyte for aqueous phase (Vieira *et al.*, 2002; Vieira *et al.*, 2004).

In order to evaluate the effect of $HNO_3$ concentration in the extraction process of the metals present in the sediments, the volume of 1 mL of HF was fixed by varying the concentration of $HNO_3$ in the preparation of the sediment solutions. The samples were placed in the ultrasonic bath for 30 minutes at 30 °C. The signal of the Cu and Zn absorbances in these solutions were measured and the results obtained are shown in Figure 2A.

According to the results shown in Figure 2A, it is observed that for the Cu and Zn, the increase of the $HNO_3$ concentration did not affect the analytical signal, remaining practically stable along the evaluated concentration range. Consequently, $HNO_3$

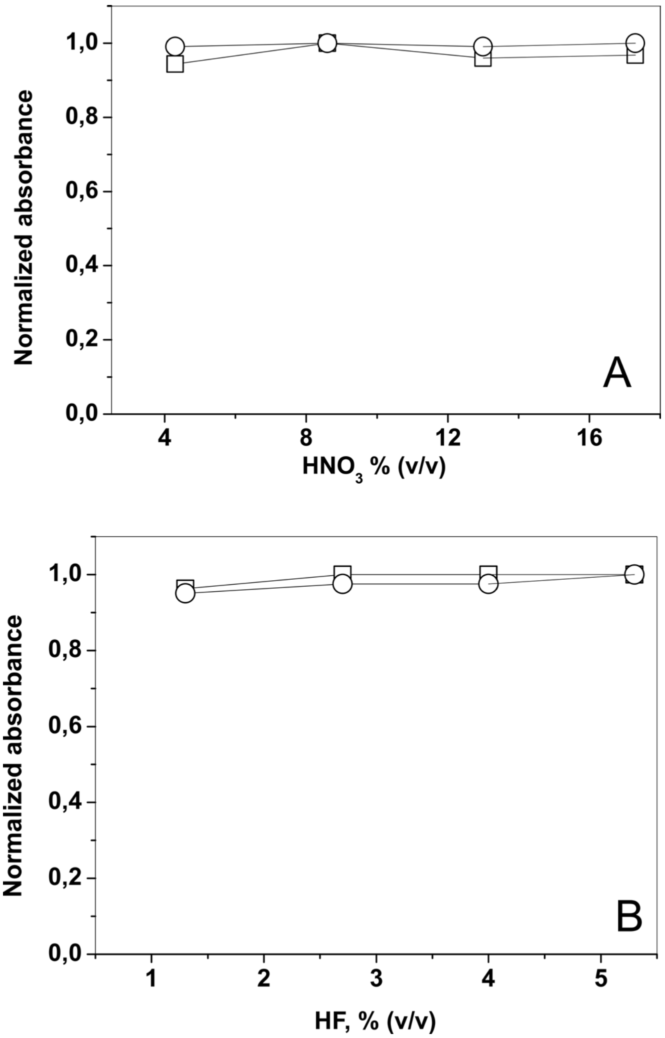

Figure 2. Effect of $HNO_3$ (A) and HF (B) concentration on absorbance signal obtained for (-□-) Cu and (-○-) Zn in sediment sample solutions.

8.6% (v/v) was used for the sediment sample preparation.

To evaluate the effect of the HF concentration, the $HNO_3$ concentration was set at 8.6% (v/v). Samples were placed in the ultrasonic bath for 30 minutes at 30 °C and the results obtained are shown in Figure 2B. As observed, there was no significant variation in the absorbance signals for both analytes evaluated when the HF concentration was increased. Thus, the concentration of HF 2.6% (v/v) was chosen for the sediment sample preparation.

Figure 3A shows the results obtained for the studies of the variation of temperature in the ultrasonic bath, in order to evaluate if there is an increase in the efficiency of the extraction process of the metals. Figure 3B shows the study of time of sonication of the sediment solutions. All solutions were prepared with $HNO_3$ 8.6% (v/v) and HF 2.6% (v/v) and sonicated during 30 minutes.

There were no significant changes on absorbance signal for Cu and Zn with the increase in the temperature of the ultrasonic bath (Figure 3A). Thus, the temperature of 25ºC was chosen for the preparation of the sediment samples. For the sonication time (Figure 3B), it was observed that there was no significant variations in the absorbance signals for Cu and Zn, even when higher sonication times were used. Similar results also were reported by Brunori *et al.* (2004) regarding temperature and time. In this way, the sonication time of 20 min was selected, in order to obtain a better extraction of the analytes for the aqueous phase.

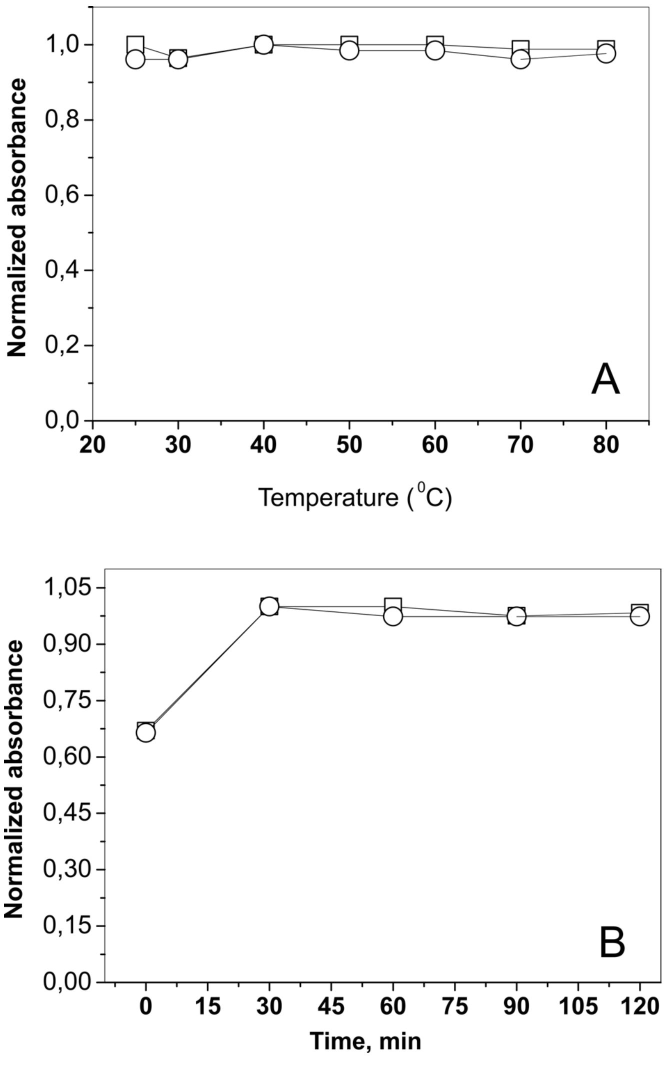

Figure 3. A: Effect of temperature of the ultrasonic bath on absorbance signal obtained in sediment solutions. B: Effect of time of sonification on absorbance signal obtained in sediment sample solutions. (-□-) Cu; (-○-) Zn.

### *Optimization of the temperature program of the graphite furnace*

After optimization of the ultrasonic assisted extraction method for Cu and Zn determinations in sediments, it was applied for the determination of Cd, Cr and Pb. As the determinations of these analytes were performed by GF AAS, the pyrolysis and atomization temperatures for Cr, Cd and Pb in a real sample of sediment were optimized. For Cd and Pb, the chemical modifier used was a mixture of $Pd(NO_3)_2$ and $Mg(NO_3)_2$, whereas for Cr only $Mg(NO_3)_2$ was used, conditions recommended by the equipment manufacturer. The pyrolysis and atomization curves for the three analytes are shown in Figure 4.

For the Cd, the pyrolysis and atomization temperatures that presented the best analytical signal and lower background values were 500 °C and 1300 °C, respectively. While for Cr, a drop of the analytical signal was observed from the pyrolysis temperature of 1400 °C and for the atomization, the signal remains practically unaltered from 2100 °C. At 750 ºC for Pb, there was also a drop in the analytical signal and this was adopted as the pyrolysis temperature. While for the atomization, the most intense analytical signal was observed between the temperatures of 1500 and 1600 °C. In this case, we decided to use the temperature of 1500 °C, since the determination of the analyte would not suffer variation up to 1600 °C, besides preserving the graphite tube. The graphite furnace temperature program used for the determination of Cd, Pb and Sn is shown in Table 2.

### *Analytical Results*

Figures of merit were obtained for the determination of the analytes Cu, Zn, Cd, Cr and Pb in sediment samples, after establishing the sample preparation method as shown in Table 3. In all curves, good correlation coefficients were obtained, with $R \geq 0.999$ and the linear range was adequate and with good linearity for all analytes. Also, good values of LOD and LOQ were obtained.

The ultrasound-assisted extraction method was applied to the analysis of 2 certified reference materials of sediment (SRM 2704a and BCR 667) in order to evaluate the accuracy. The results are show in Table 4. The application of the Student t-test at a confidence level of 95% showed good agreement between the measured and the certified values and no statistically significant difference was found, confirming the accuracy of the results for all investigated analytes. The relative standard deviation (RSD) was lower than 8.2%, which confirms the efficacy of the method for the determination of Cd, Cr, Cu, Pb and Zn in sediment samples.

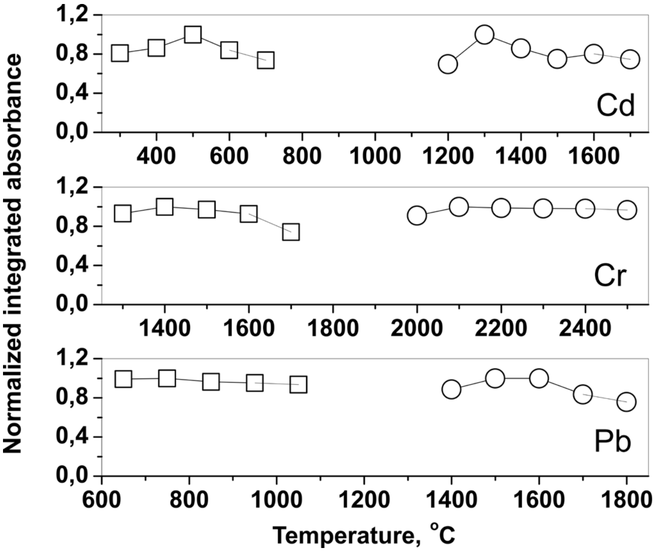

Figure 4. (-□-) Pyrolysis and (-○-) atomization curves obtained for Cd, Cr and Pb in sediment sample.

Table 2. Temperature program for Cd[a], Cr[b] and Pb[c] determinations by GF AAS

| Step | Temperature (°C) | Ramp (s) | Hold (s) | Argon flow rate (mL $min^{-1}$) |
|---|---|---|---|---|
| Drying | 110 | 10 | 30 | 250 |
| Drying | 130 | 10 | 30 | 250 |
| Pyrolysis | 500[a]; 1400[b]; 750[b]; | 10 | 20 | 250 |
| Atomization | 1300[a]; 2100[b]; 1500[b]; | 0 | 5 | - |
| Cleaning | 2300 | 1 | 3 | 250 |

Table 3. Figures of merit

|  | Slope (L $mg^{-1}$) | Linear range (mg $L^{-1}$) | LOD[a] (mg $L^{-1}$) | LOQ[a] (mg $L^{-1}$) | LOD[b] (mg $kg^{-1}$) | LOQ[b] (mg $kg^{-1}$) |
|---|---|---|---|---|---|---|
| Cu | 0.1714 | 0 - 2.5 | 0.005 | 0.02 | 0.83 | 2.7 |
| Zn | 0.3171 | 0 - 1.0 | 0.003 | 0.01 | 0.44 | 1.5 |
|  | Slope (Lμ$g^{-1}$) | Linear range **(μg $L^{-1}$)** | LOD[a] (μg $L^{-1}$) | LOQ[a] (μg $L^{-1}$) | LOD[b] (mg $kg^{-1}$) | LOQ[b] (mg $kg^{-1}$) |
| Cd | 0.0354 | 0.1 – 2.5 | 0.013 | 0.043 | 0.002 | 0.006 |
| Cr | 0.0090 | 3 – 13 | 0.175 | 0.538 | 0.026 | 0.087 |
| Pb | 0.0001 | 10 – 50 | 2.575 | 8.58 | 0.386 | 1.288 |

[a]instrumental limits; [b]method limits

### *Analysis of sediments from the* ***São Gonçalo channel***

The values obtained for humidity ranged from 42.3 to 86.6%. For organic matter, the values ranged from 1.5 to 11.0%. The highest values for humidity and organic matter were observed at P1 (collection 1, 2 and 3 in the summer, fall and winter of 2013, respectively). In 4th collection (spring of 2013) the sediment from P0 showed the higher value and in the 5th collection (summer 2014), the sample from P3, both exhibited the higher value for humidity and organic matter. Regarding the grain size distribution of sediments in the region of study, the sediments from P3 and P4 in the summer and winter of 2013; those from P4 in the fall of 2013, all stations in spring 2013 and P3 in summer of 2014 presented highest percentages of fines (fraction <63 μm).

The results obtained for the determination of analytes in sediments samples collected in different seasons of 2013 and 2014 and divided by their different sampling stations are shown in Table 5 for Cu and Zn and Table 6 for Cd, Cr and Pb, respectively. Tukey's test at the 95% confidence level was used for evaluate if the results presented or not significative variations in the concentrations of analytes for the different seasons and sampling stations.

According to the results presented in Table 5, higher concentrations values for Cu were observed at P0 (autumn and spring 2013) and P1 (summer and winter 2013). In the summer of 2014, Cu was quantified only at P0. For Zn, the higher concentrations were observed at P0 (summer, autumn and spring 2013 and summer 2014) and at P1 only in winter 2013.

For Cd, the seasons with the highest concentration were the summer and winter of 2013 and summer of 2014, in the sediments from P0 and P1stations. Concerning the Pb, the seasons which presented highest concentrations were: summer, autumn and winter of 2013 at sampling stations P0 and P1. However, the concentrations of Pb at P3 in the winter of 2014, P4 in the spring of 2013 and P3 and P4 in the summer of 2014, were below the limit of quantification of the method. For Cr, the seasons with the highest concentrations were: summer, fall and winter of 2013 at sampling stations P0 and P1.

Data obtained were analyzed and it was verified that the highest concentrations of Cd, Cr, Cu, Pb and Zn were found at collection stations P0 and P1. These stations are located close to urban areas and suffer the impact of human activities, in particular domestic disposal, disposal of electronic equipment and batteries from various regions of Pelotas city. Another factor that can influence the concentrations found is the intense agricultural activity, especially rice production that are close to the stations investigated, contributing with loads of fertilizers and agricultural residues.

Concerning the seasons in which the collections were carried out, the ones the highest concentrations of Cr, Pb and Cd were the summer, fall and winter of 2013. Autumn and winter generally are seasons with higher rain cycles, and that lead to leaching processes. In the summer, because it is a drought period, the channel flow decreases, resulting in a lower dilution capability which leads to the retention of metals in the channel sediments.

Oliveira & Mattiazzo (2001) report that the factors that control the sediment's ability to retain toxic or non-toxic metals are complex, difficult their understanding and the possibilities of predict their behavior, especially in the long term. It is known that the greater or lesser mobility of the metals is determined by the soil properties and by the organic and inorganic matter contents which may influence the reactions of precipitation, dissolution, adsorption, desorption, complexation and oxidation.

Lacerda & Marins (2006) affirm that the inclusion of metals can occur through adsorption and complexation processes, presenting a large accumulation capacity in sediments with high organic matter, which was confirmed by the results of

Table 4. Analytical results of the concentrations for Cd, Cr, Cu, Pb and Zn in CRMs using ultrasound-assisted extraction method (n=5)

| | SRM 2704a | | BCR 667 | |
|---|---|---|---|---|
| Analytes | Certified (mg kg$^{-1}$± SD) | Found (mg kg$^{-1}$± SD) | Certified (mg kg$^{-1}$± SD) | Found (mg kg$^{-1}$± SD) |
| Cd | 3.45 ± 0.22 | 3.48 ± 0.15 (4.3) | 0.67 ± 0.11 | 0.66 ± 0.04 (6.1) |
| Cr | 135 ± 5* | 135.0 ± 0.8* (0.6) | 0.178 ± 0.016* | 0.173 ± 0.006* (3.5) |
| Cu | 98.6 ± 5.0 | 94.4 ± 0.3 (0.3) | 60 ± 9 | 67 ± 3 (4.4) |
| Pb | 161 ± 17 | 148.1 ± 4.3 (2.9) | 31.9 ± 1.1 | 31.7 ± 2.6 (8.2) |
| Zn | 438 ± 12 | 430 ± 0.7 (0.1) | 0.175 ± 0.013* | 0.178 ± 0.013 (7.3) |

*g Kg$^{-1}$
SD: standard deviation
RSD: relative standard deviation, %

Table 5. Concentrations of Cu and Zn obtained by F AAS in sediment samples from the São Gonçalo channel, (n=3)

| Sampling stations | Cu (mg kg$^{-1}$± SD) | Zn (mg kg$^{-1}$± SD) |
|---|---|---|
| Summer 2013 | | |
| P0 | 14.0 ± 0.6 (4.3) $^{adik}$ | 63.7 ± 4.4 (6.9) $^{a}$ |
| P1 | 16.9 ± 1.0 (5.9) $^{bg}$ | 56.6 ± 3.3 (5.8) $^{bgho}$ |
| P2 | 13.6 ± 0.4 (2.9) $^{adil}$ | 41.5 ± 1.3 (3.1) $^{cl}$ |
| P3 | 12.7 ± 1.0 (7.8) $^{ail}$ | 40.7 ± 1.7 (4.2) $^{bcd}$ |
| P4 | 12.9 ± 0.6 (4.6) $^{adil}$ | 44.6 ± 1.4 (3.1) $^{cde}$ |
| Autumn 2013 | | |
| P0 | 22.1 ± 0.3 (1.3) $^{c}$ | 81.2 ± 2.5 (3.0) $^{f}$ |
| P1 | 15.2 ± 0.1 (0.6) $^{bd}$ | 55.9 ± 0.8 (1.4) $^{gn}$ |
| P2 | 16.6 ± 0.6 (3.6) $^{bg}$ | 62.3 ± 4.5 (7.2) $^{ah}$ |
| P3 | 14.6 ± 0.5 (3.4) $^{ab}$ | 50.7 ± 2.1 (4.1) $^{gm}$ |
| P4 | 12.7 ± 0.5 (3.9) $^{ail}$ | 41.5 ± 1.2 (2.9) $^{cd}$ |
| Winter 2013 | | |
| P0 | 69.3 ± 1.4 (2.0) $^{e}$ | 79.9 ± 0.8 (1.0) $^{f}$ |
| P1 | 102.0 ± 2.1 (2.0) $^{f}$ | 125.9 ± 1.8 (1.5) $^{i}$ |
| P2 | 18.1 ± 0.3 (1.6) $^{gj}$ | 71.8 ± 1.9 (2.6) $^{j}$ |
| P3 | 10.1 ± 0.8 (7.9) $^{h}$ | 33.1 ± 1.3 (3.9) $^{kq}$ |
| P4 | 12.1 ± 0.6 (4.9) $^{ih}$ | 39.8 ± 1.3 (3.2) $^{cd}$ |
| Spring 2013 | | |
| P0 | 19.8 ± 0.5 (2.6) $^{cj}$ | 85.7 ± 0.7 (0.8) $^{f}$ |
| P1 | 16.1 ± 0.5 (3.1) $^{bgk}$ | 53.3 ± 1.3 (2.5) $^{g}$ |
| P2 | 11.6 ± 0.5 (4.3) $^{hl}$ | 39.5 ± 1.7 (4.4) $^{cp}$ |
| P3 | 13.6 ± 0.1 (0.9) $^{adil}$ | 45.6 ± 0.7 (1.5) $^{dlm}$ |
| P4 | 12.7 ± 0.3 (2.3) $^{adil}$ | 39.4 ± 0.1 (0.2) $^{cp}$ |
| Summer 2014 | | |
| P0 | 3.9 ± 0.2 (5.1) $^{m}$ | 60.6 ± 1.7 (2.8) $^{ahn}$ |
| P1 | < LOD | 29.3 ± 0.7 (2.3) $^{k}$ |
| P2 | < LOQ | 42.3 ± 0.5 (1.2) $^{cd}$ |
| P3 | < LOQ | 31.6 ± 0.2 (0.6) $^{ko}$ |
| P4 | < LOQ | 33.7 ± 1.0 (2.9) $^{bpq}$ |

*Equals letters in the same column indicate not significant difference at $p < 0.05$
SD: standard deviation

the higher levels of metals found mainly at the collection point P1 (winter of 2013), which also presented higher values of organic matter and humidity.

In Brazil, the 2012 CONAMA Resolution 454 established legal limits for some metals and organic compounds in sediments and is based on values of Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CCME, 2001). The guidelines consist of threshold effect levels (TELs) and probable effect levels (PELs). Values below the TEL (Level 1 from CONAMA) indicate the minimal effect range within which adverse effects rarely occur; between the TEL and PEL indicate the possible effect range within which adverse effects occasionally occur and above the PEL (Level 2 from CONAMA), the probable effect range within which adverse effects frequently occur. Although such guidelines are not definitive indicators of toxicity, they have a high predictability, and the TEL/PEL-type guidelines offer scientific basis for comparability (Rezende *et al.*, 2011).

According to the values shown in Table 7, it was verified that the concentration values for Cu exceeded the TEL in sampling station P0 (autumn and spring of 2013) and P0 and P1 (winter of 2013). For Zn concentration, only at P1 (winter

Table 6. Concentrations of Cd, Cr and Pb obtained by GF AAS in sediment samples from the São Gonçalo channel, (n=3)

| Sampling stations | Cd (mg kg$^{-1}$± SD) | Cr (mg kg$^{-1}$± SD) | Pb (mg kg$^{-1}$± SD) |
|---|---|---|---|
| Summer 2013 | | | |
| P0 | 0.24 ± 0.02 (8.3) $^{af}$ | 28.5 ± 1.9 (6.6) $^{ahk}$ | 2.24 ± 0.07 (3.1) $^{acg}$ |
| P1 | 0.208 ± 0.004 (1.9) $^{adl}$ | 32.5 ± 1.5 (4.6) $^{be}$ | 2.2 ± 0.1 (4.5) $^{acg}$ |
| P2 | 0.229 ± 0.007 (3.2) $^{al}$ | 29.7 ± 1.2 (4.0) $^{abhl}$ | 1.9 ± 0.1 (5.2) $^{adg}$ |
| P3 | 0.242 ± 0.006 (2.5) $^{af}$ | 36.0 ± 1.0 (3.0) $^{ce}$ | 1.904 ± 0.006 (0.3) $^{adg}$ |
| P4 | 0.58 ± 0.01 (1.7) $^{b}$ | 30.8 ± 1.3 (4.2) $^{abe}$ | 1.77 ± 0.09 (5.1) $^{adg}$ |
| Autumn 2013 | | | |
| P0 | 0.241 ±0.009 (4.1) $^{af}$ | 31.9 ± 0.4 (1.2) $^{be}$ | 3.11 ± 0.06 (1.9) $^{beh}$ |
| P1 | 0.22 ± 0.02 (9.1) $^{al}$ | 24.7 ± 0.9 (3.6) $^{dhl}$ | 2.34 ± 0.05 (2.1) $^{ab}$ |
| P2 | 0.232 ± 0.009 (3.8) $^{al}$ | 29.8 ± 0.5 (1.7) $^{abhl}$ | 2.83 ± 0.05 (1.8) $^{bceh}$ |
| P3 | 0.165 ± 0.002 (0.9) $^{cg}$ | 38.5 ± 1.1 (2.9) $^{c}$ | 1.6 ± 0.1 (6.2) $^{ad}$ |
| P4 | 0.17 ± 0.01 (5.9) $^{cdg}$ | 28.1 ± 1.7 (6.0) $^{ahk}$ | 1.30 ± 0.04 (3.0) $^{d}$ |
| Winter 2013 | | | |
| P0 | 0.343 ± 0.003 (0.9) $^{e}$ | 33.3 ± 1.0 (3.0) $^{ef}$ | 3.2 ± 0.1 (3.1) $^{ef}$ |
| P1 | 0.28 ± 0.02 (7.1) $^{fk}$ | 32.9 ± 0.8 (2.4) $^{be}$ | 4.0 ± 0.2 (5.0) $^{f}$ |
| P2 | 0.17 ± 0.01 (5.9) $^{cdg}$ | 30.8 ± 1.8 (5.8) $^{abf}$ | 2.4 ± 0.1 (4.1) $^{abe}$ |
| P3 | 0.20 ± 0.01 (5.0) $^{ac}$ | 20.4 ± 0.8 (3.9) $^{g}$ | <LOQ |
| P4 | 0.146 ± 0.007 (4.7) $^{gj}$ | 29.4 ± 0.1 (0.3) $^{abhl}$ | 1.47 ± 0.05 (3.4) $^{dg}$ |
| Spring 2013 | | | |
| P0 | 0.51 ± 0.01 (1.9) $^{h}$ | 29.9 ± 1.5 (5.0) $^{abfhl}$ | 3.096 ± 0.003 (0.1) $^{beh}$ |
| P1 | 0.45 ± 0.02 (4.4) $^{i}$ | 22.9 ± 0.6 (2.6) $^{dg}$ | 2.4 ± 0.1 (4.1) $^{abe}$ |
| P2 | 0.17 ± 0.01 (5.8) $^{cdg}$ | 20.2 ± 1.1 (5.4) $^{g}$ | 2.1 ± 0.1 (4.7) $^{acd}$ |
| P3 | 0.110 ± 0.002 (2.2) $^{j}$ | 30.3 ± 1.2 (3.9) $^{abfh}$ | 1.6 ± 0.1 (6.2) $^{ad}$ |
| P4 | 0.296 ± 0.008 (2.5) $^{k}$ | 27.08 ± 0.09 (0.4) $^{hjl}$ | <LOQ |
| Summer 2014 | | | |
| P0 | 0.23 ± 0.02 (8.7)$^{al}$ | 27.65 ± 0.74 (2.6) $^{ahk}$ | 3.25 ± 0.07 (2.1) $^{fh}$ |
| P1 | 0.209 ± 0.005 (2.2)$^{adl}$ | 14.77 ± 0.64 (4.3) $^{i}$ | 2.15 ± 0.09 (4.2) $^{acg}$ |
| P2 | 0.196 ± 0.015 (7.5)$^{cl}$ | 24.11 ± 0.72 (2.9) $^{djl}$ | 2.07 ± 1.17 (5.6) $^{acd}$ |
| P3 | 0.25 ± 0.02 (8.0)$^{af}$ | 25.73 ± 0.99 (3.8) $^{dkj}$ | <LOQ |
| P4 | 0.39 ± 0.03 (7.7) $^{m}$ | 26.88 ± 0.65 (2.4) $^{kl}$ | <LOQ |

*Equals letters in the same column indicate not significant difference at $p < 0.05$

Table 7. Values of TEL and PEL for Cd, Cr, Cu, Pb and Zn in sediments

| Metals | Concentration (mg Kg$^{-1}$) | |
|---|---|---|
| | TEL | PEL |
| Cd | 0.7 | 4.2 |
| Cr | 52.3 | 160 |
| Cu | 18.7 | 108 |
| Pb | 30.2 | 112 |
| Zn | 124 | 271 |

2013) exceeded the TEL. However, none of the results for Cu and Zn metals exceeded the PEL. For the Cd, Pb and Cr, the concentrations obtained at all sampling stations and seasons investigated were lower than the value of TEL. These results imply a good quality of the sediment samples studied herein concerning inorganic pollutants. For all analysis, the values of RSD were lower than 9.1%.

## CONCLUSION

The ultrasound-assisted extraction method used for the determination of Cd, Cu, Pb and Zn in sediment samples is simple, fast and allowed that a larger number of samples be prepared simultaneously, thereby increasing analytical frequency. The use of ultrasonic bath increases the extraction efficiency of the analyte and is a simple instrument to handle, easily available in most laboratories with relatively low cost. It can be concluded that the São Gonçalo channel, being a natural receptor of urban wastewater in the city of Pelotas of domestic origin, rain, industrial and agricultural effluents, is presented with relevant contents of the investigated metals, but all below the minimum concentration established and, thereby the toxicity is not expected to occur.

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