

*Full Length Research Paper*

## Determination of trace metals in sediment samples of the Santa Bárbara Channel / Pelotas / RS / Brazil

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This work deals with the determination of heavy metals (Pb, Cr, Zn and Cu) in the sediment of Santa Barbara Channel, located in Pelotas, RS. Absence of studies of the levels of heavy metals, in this channel, associated with high toxicity, bioconcentration and biomagnification capacity of these analytes makes this work necessary and explains the validity of this study. Two grams of fraction ( $< 63 \mu\text{m}$ ) of 6 sampling points, in triplicate, suffered acid digestion (4 ml of aqua regia + 1 ml of Milli-Q water and 1 ml of  $\text{HClO}_4$ ). The concentration of analytes in the extracts was performed with an atomic absorption spectrophotometer. The analytes were detected in all the sites, but at low levels of concentration, Cu ( $3.3$  to  $42.6 \text{ mg kg}^{-1}$ ), Pb ( $4.7$  to  $16.2 \text{ mg kg}^{-1}$ ), Zn ( $5.2$  to  $40.4 \text{ mg kg}^{-1}$ ) and Cr ( $2.5$  to  $21.4 \text{ mg kg}^{-1}$ ), observing a close relationship with the organic matter content and the sediments with grain size finer.

**Key words:** Trace metal pollution, Santa Bárbara channel, sediments, Urban environments.

### INTRODUCTION

Sediments have been widely used as environmental indicators, because they have great capacity to incorporate and accumulate contaminants. The pollution of sediments is closely linked to contamination of water by domestic sewage, industrial effluents, urban diffuse load and agriculture (Hortellani et al., 2008). The variations in physical and chemical parameters such as pH, salinity, content of organic chelators, including others can release pollutants incorporated into the sediment. Therefore, changes in environmental conditions and dredging can transform sediment sources of contamination (Adams et al., 1992; Caccia et al., 2003).

In addition, it has been proven that for the benthic community, and the column water, there are different pathways of exposure to contaminants such as direct by casual contact or by ingestion of sediment (Cesar et al.,

2007). Suspended sediment is the primary means of transportation of metals in water, it is important to monitor the levels of pollutants in this compartment of our water resources because metals tend to be deposited in it. The characteristics of sediments may reflect the quality of water and record the effects of anthropogenic emissions. Sediments can both accumulate metal or be a source of release for an aquatic system (Soares et al., 1999).

In general, the highest concentrations of heavy metals are found in sediments with fine-grained ( $< 63 \mu\text{m}$ ) and high concentrations of organic matter, characterizing geochemical properties important in the mobilization of inorganic pollutants in the sediment (Hortellani et al., 2008; Robaina et al., 2002). The natural behavior of metal complexes is to adsorb organic matter or even the fine-grained sediments, and in these cases can be

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assimilated by organisms, becoming part of the trophic chain (Lima et al., 2006). The toxicity of heavy metals contamination of any water resource by these elements is extremely worrying, therefore the importance of studying our rivers, channels, ponds, or our waters, in this case, the Santa Barbara Channel.

The Santa Barbara Channel is located in the City of Pelotas, Rio Grande do Sul in the south of Brazil. It is an area with average elevation of 7m over sea level and geographical position 31°45'43" south latitude and 52°21'00" west longitude. This channel is one of the points of fundamental importance in the natural process of formation and development of the City of Pelotas, in southern Brazil. The absence of awareness as well as the neglect of public policies made the channel a source of major environmental problem that directly affects the population. As the only alternative for many families, the occupation of areas on the banks of the Channel is more constant and disorderly. Any process that accompanies these irregular settlements brings even more disturbing consequences for the environment (Luzzardi et al., 2006).

Human action along this channel has been causing successive channel degradation, resulting from various forms of environmental impact, such as irregular buildings in areas of permanent preservation (APP), the issue of domestic sewage and chemicals, improper storage waste at various points on its course, and proximity to the city landfill (Siomon et al., 2006). Given the importance of the Santa Bárbara Channel to the city of Pelotas, for its location, yield function and its history, because the city was formed around it, this study aims to carry out the characterization of this channel, emphasizing the presence of heavy metals such as copper, chromium, zinc and lead, elements that are detected frequently in the environment (Poletto and Merten, 2008). No research was found, regarding contamination by heavy metals, making the study of extreme importance to obtain knowledge of its actual contamination by these metals serving, therefore the comparison for future studies.

## MATERIALS AND METHODS

### Study area

Sediment samples were collected at different points in the Channel shown in Figure 1. To determine the sampling sites, visits were made to the Channel to observe possible human actions that could be sources of contamination along its path with heavy metals and the feasibility of doing the collection at these sites. Six sampling sites were then determined, all with their geographic coordinates obtained by - GPS - Global Positioning System, model GARMIN Etrex Vista<sup>®</sup> H being: Site 1 - Under the bridge on Theodoro Müller Street (latitude 31°44'28.28" S and longitude 52°21'47.30" W); Site 2 Under the bridge, the extension of the Bento Gonçalves Avenue (latitude 31°45'23.65" S and longitude 52°21'22.20" W) Site 3 - under the bridge on Duque de Caxias Avenue neighborhood, towards the center (latitude 31° 45' 48.06" S and longitude

52°21'22.04" O) Site 4 - under the bridge Visconde da Graça Avenue (latitude 31°46'13.75" S and longitude 52°21'33.14" W); 5 - under the bridge on the road BR 392 (latitude 31°46'26.46" S and longitude 52°21'38.13" W); Site 6 - located 10 m before the inflow of Santa Barbara Channel in the São Gonçalo Channel (latitude 31°47'24.24" S and longitude 52°20'57.27" W) shown in Figure 1.

### Methodology

The Sampling was conducted in December 2009. The following water tests were made at the site: dissolved oxygen, with HOMIS oximeter model 509, conductivity, with a model CD-830 conductivity, temperature and pH, with pH meter LUTRON pH-206. Samples of surface sediment (0-5 cm) were collected using a stainless steel dredge type Van Veen, Dredge to collect sediments, recommended for geochemical analysis. Dredge simple management has good penetration even in sandy sediments. The material of the central part of the dredge was removed and stored in a polyethylene jar, previously decontaminated. After the sampling, the samples were transported in a cooler box to the laboratory and stored at  $\pm 4^{\circ}\text{C}$ . Glassware used in the treatment and storage of the samples was previously decontaminated in a solution of  $\text{HNO}_3$  10 % (v/v) for 24 h, then rinsed with distilled water and oven dried at  $105^{\circ}\text{C}$  for drying.

For freeing the analyte from the sample matrix, we used the method based on acid extraction. The sediment samples were dried at  $60^{\circ}\text{C}$  for 48 h. Then macerated with pestle and mortar and sieved to produce a size fraction of  $< 63\ \mu\text{m}$  sample. Methods which involve the use of acids like  $\text{HNO}_3$  and  $\text{HCl}$  (for extracting metals strongly absorbed by organic matter and fines), are very useful to estimate the sediment capability of transferring metals to biota. This type of extraction methodology also enables the comparison between the obtained values and guideline levels, such as TEL (Threshold Effect Level) and PEL (Probable Effect Level) from Canadian Sediment Quality Guidelines (Bordon et al., 2011). Approximately 2.0 g of each sediment sample in triplicate was weighed. Samples were mixed with 4.0 ml of aqua regia (3:1  $\text{HCl}:\text{HNO}_3$ ), 1.0 ml of high purity water (Milli-Q<sup>®</sup>) and 1.0 ml of  $\text{HClO}_4$  in beakers of 50.0 ml covered with watch glass and heated for 30.0 m at  $90^{\circ}\text{C}$  on a water bath, using the procedure of Akagi et al. (1995) and Hortellani et al. (2005). Reagents used in the extraction acid were all analytical grade Merck<sup>®</sup> brand. After cooling, the sample was then filtered through a Whatman No 41 filter paper into volumetric flasks of 50.0 ml, and the volume was made-up with Milli-Q water.

The standards were prepared from standard solutions Titrisol<sup>®</sup> brand Merck ( $1000\ \text{mgL}^{-1}$ ) to obtain the linear calibration curves: Cr ( $0.1$  to  $2.0\ \text{mgL}^{-1}$ ), Cu ( $0.5$  to  $1.5\ \text{mgL}^{-1}$ ), Zn ( $0.1$  to  $2.0\ \text{mgL}^{-1}$ ) and Pb ( $0.5$  to  $2.0\ \text{mgL}^{-1}$ ). All standards undergo the same chemical treatment of samples. The information on linear equation, detection and quantification limits,  $R^2$  values and calibration curve are shown in Table 1 and the recovery values are in Figure 4. For the chemical analysis of the proposed analytes, the technique of atomic absorption spectrometry in a flame spectrophotometer GBC Avanta Plus 932, recommended for metal analysis was used. In parallel to the analysis of the sediment, a blank sample and the certified reference material sample NMCR#4 (soil and sediment) purchased from Ultra Scientific Analytical solutions for analytical certification were determined. To prove the accuracy of the method a "T test" was applied in the results for concentrations of sediment reference.

Because of the close relationship between the concentration of organic matter in the sediment and the concentrations of heavy metals, this was evaluated indirectly for volatile loss at  $550^{\circ}\text{C}$  for 4 h in muffle furnace, according to standard methodology (APHA, 2005). The analysis of sediment particle size was determined by sieving for coarse sediments, sorting of grain sizes according to Suguio (1973). Through ten readings of blank signal sample, the

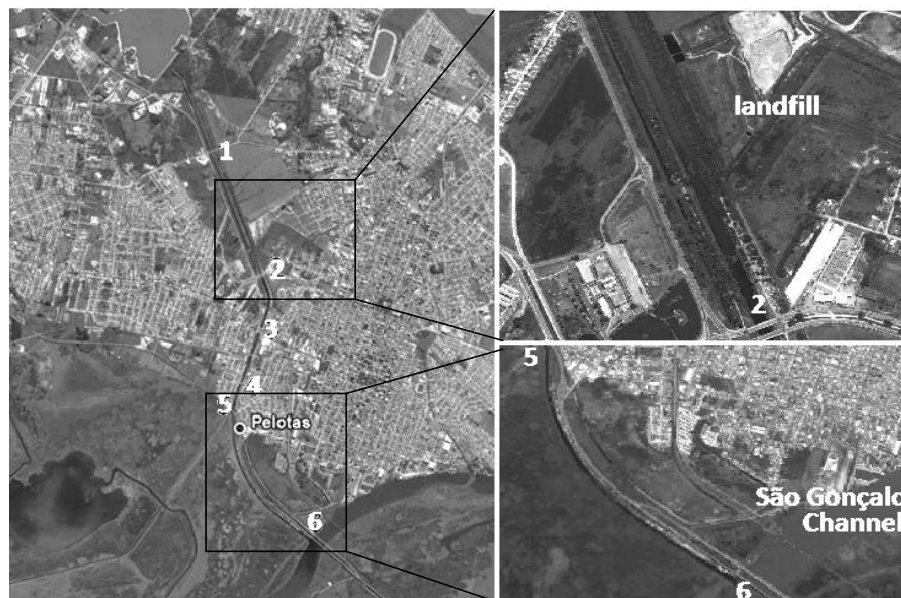


Figure 1. Location of sampling points along the Santa Barbara Channel.

Table 1. Concentrations of metals in the sediment of the Santa Barbara Channel, results, figures of merit and quality index.

Parameter	Metals concentration in sediment ( $\text{mg kg}^{-1}$ ) ( $\pm$ RSD %)			
	Cr	Zn	Cu	Pb
Site 1	3.5 $\pm$ 5.2	28.5 $\pm$ 5.9	42.6 $\pm$ 9.8	10 $\pm$ 19.0
Site 2	7.6 $\pm$ 0.8	31 $\pm$ 10.9	5.2 $\pm$ 3.3	7.5 $\pm$ 6.9
Site 3	2.5 $\pm$ 1.4	10.4 $\pm$ 1.1	3.3 $\pm$ 2.5	4.7 $\pm$ 23.5
Site 4	3.3 $\pm$ 5.1	5.2 $\pm$ 18.2	4.1 $\pm$ 1.9	6.8 $\pm$ 26.8
Site 5	7.3 $\pm$ 3.9	20.7 $\pm$ 16.4	6.6 $\pm$ 2.8	8.6 $\pm$ 9.7
Site 6	21.4 $\pm$ 4.6	40.4 $\pm$ 2.1	12.0 $\pm$ 3.0	16.2 $\pm$ 0.2
a(1)	0.043	0.2368	0.038	0.0137
b(2)	-0.003	0.0035	-0.004	0.0018
R <sup>2</sup> (3)	0.997	0.999	0.999	0.994
LOD(4)	1.2	1.1	1.5	3.5
LOQ(5)	2.5	2.3	2.8	4.5
ISQG(6)	37.3	123.0	35.7	35.0
PEL(7)	90.0	315.0	197.0	91.3

(1) slope, (2) linear coefficient, (3) linear correlation coefficient, (4) detection limit, (5) limit of quantification (6) Interim sediment quality guidelines (7), probable effect levels.

limit of detection (LOD) was calculated using the sum of the mean blank signal plus three times its standard deviation, while the limit of quantification (LOQ) was calculated by adding the sum of the mean blank signal plus ten times its standard deviation (IUPAC, 1997).

## RESULTS AND DISCUSSION

Table 1 shows the concentrations of analytes in mg per kg for the different sampling sites. At all sites, studied metals analyzed were detected, varying concentrations

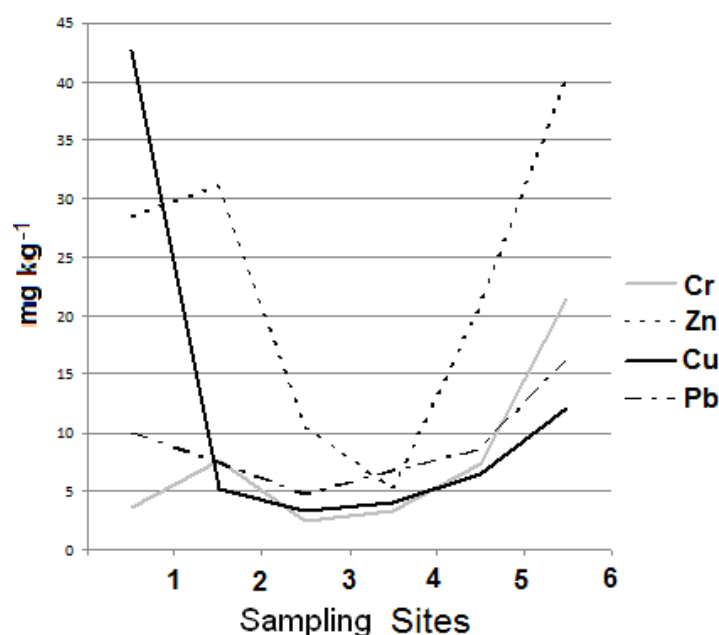
for each metal include: Cu (3.3 to 42.6  $\text{mg kg}^{-1}$ ), Pb (4.7 to 16.2  $\text{mg kg}^{-1}$ ), Zn (5.2 to 40.4  $\text{mg kg}^{-1}$ ) and Cr (2.5 to 21.4  $\text{mg kg}^{-1}$ ). The one that appeared in higher concentrations in almost all sites was Zn, this occurs because of the geology of the region (Friedrich, 2004), with the exception of site 1 where the Cu has a higher concentration and in site 4 where the Pb stood out.

Site 1 provides the best environmental conditions in relation to other parameters, though copper levels detected was greater than that of other sites. When

**Table 2.** Physical-chemical analysis *in situ*.

Parameter	Water			pH
	T (°C)	DO <sup>(1)</sup> (mg L <sup>-1</sup> )	C <sup>(2)</sup> (µs cm <sup>-1</sup> )	
Site 1	28.0	3.8	59.1	6.17
Site 2	25.0	0.9	139.4	6.38
Site 3	28.0	1.4	183.1	6.45
Site 4	23.0	1.55	180.7	6.18
Site 5	24.0	3.4	184.6	6.66
Site 6	22.0	3.2	110.6	6.25

(1)\_Dissolved Oxygen, (2) Conductance in 25°C.



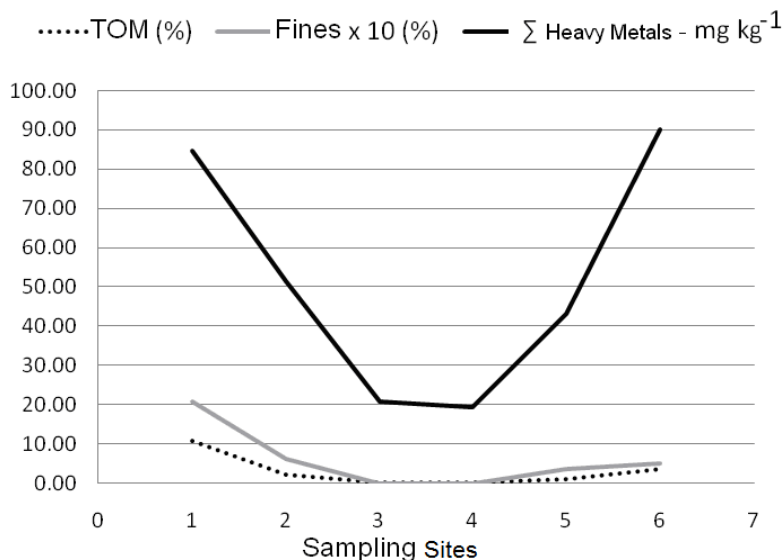
**Figure 2.** Concentrations of trace metals in parts of the Santa Barbara Channel in mg kg<sup>-1</sup>.

compared to the other sites, it has a higher concentration of dissolved oxygen and low conductivity, as shown in Table 2. The anthropogenic factors exert influences on the control of dynamics and speciation of copper in urban aquatic environments (Scheffer et al., 2007). In this sampling site were detected higher concentrations of copper, therefore recommended to study the possible sources that contribute to the input of the analyte at this point of Santa Barbara Channel.

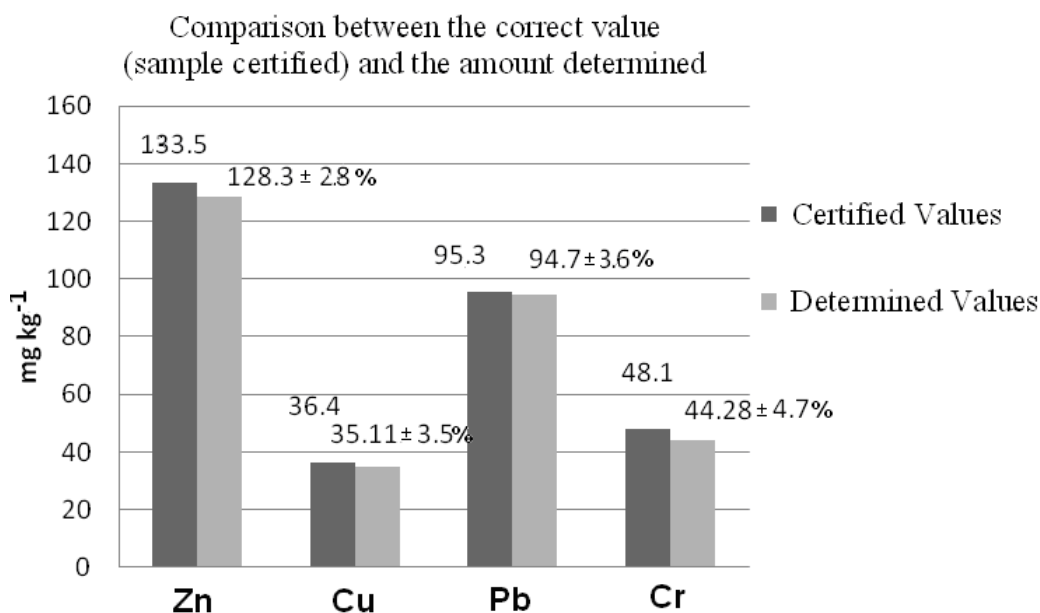
There was a significant difference between copper levels detected in site 1 compared to other sites. The concentration of 42.6 mg kg<sup>-1</sup> exceeds the Sediment Quality Index (ISQG) of 35.7 mg kg<sup>-1</sup> (CCME EPC- 98E, 1999), meaning that the environment is contaminated, indicating a possible negative impact to aquatic life, as

seen in Table 1. Site 2, located approximately 2 km from the site 1, was observed a sharp drop in dissolved oxygen accompanied by an increase in conductivity. This part of the Channel route and especially wastewater receives some drainage from the pond to stabilize the landfill located nearby, as shown in Figure 1.

Considering the sum of the analytes, as shows in Figures 1 and 2, the passage of the Channel urban area led to an enrichment of the studied metals in the sediment along the route, although the Cu concentration was presented in site 6 below the site 1. Confirming previous studies (Soares et al., 1999; Robaina et al., 2002), a close relationship was observed between the concentrations of metals, organic matter content and the percentage of fine fraction at all sites. The apparent



**Figure 3.** Comparison between the sum of trace metals studied, the content is organic matter and fines content.



**Figure 4.** Results of the analysis of certified samples.

decrease in concentrations of metals in sites 3, 4 and 5 is attributed to the hydrodynamics of the sampling sites. These are places where the flow is more intense and turbulent which hinders the deposition of particulate matter. These conditions are confirmed by increase in dissolved oxygen and by the characteristics of the sediment, like as, the particles size, very thick and very low levels of organic matter. These conditions do not

favor the deposition of metals, causing them to be dragged through the water, depositing in places with more favorable conditions, as in site 6 where the particle size is predominantly thin, with higher content of organic matter, and such behavior is illustrated in Figure 3.

The method used for metal analysis proved to be acceptable. With the application of "t test" the results found for the concentrations of metals in the sediments of

reference do not differ from the correct value within the range of confidence, a significance level of 95%, Figure 4. Through the parameters evaluated in the water, with the exception of site 1, which had a conductivity of  $59.1 \mu\text{s cm}^{-1}$ , others exceeded  $100 \mu\text{s cm}^{-1}$ , suggesting that the environment is impacted, because this concentration indicates the amount of minerals existing in the water column, indirectly representing pollutant. Levels of dissolved oxygen rates ranging from 0.9 to  $3.8 \text{ mg l}^{-1}$ , indicate a high level of organic matter, creating reducing conditions, this situation leads fermentations with the release of chemical species of unpleasant smell. Visual observation of the area, the values of physical chemical parameters confirm its impact on the aquatic life (CCME EPC- 98E, 1999), as the concentrations listed in Table 2.

## Conclusion

From the physical-chemical analysis carried out on site, it was concluded that the Santa Barbara Channel is highly impacted as confirmed by the values of conductivity and dissolved oxygen, but with regard to contamination by heavy metals, although they have been detected in all sampling sites, the levels found are low. Only the copper in site 1 showed levels above the sediment quality guidelines and lower than the probable effect levels of concentration, which may pose a risk to aquatic life.

In other points studied, all analytes were found below the sediment quality guidelines. Due to the low levels found through analysis of sediment, it is suggested that future water tests be done, because the metals may be adsorbed to suspended solids; also analyze the macrophytes and other organisms in the property, evaluating the distribution of these compounds in different environmental compartments (Mikryakova, 2002). Because Chromium VI is very harmful to the environment due to its toxicity, the authors suggest identifying the type of Cr found, through studies of speciation to identify the real contamination of this metal. It is also suggested that sampling and analysis are made at other times of the year, taking into account the climate, the rainy season and other variables that may influence the results in order to obtain more data to alert the competent bodies on contamination of this important water resource of the municipality.

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