II – WORKSHOP OF INORGANIC MASS SPECTROMETRY – 2017

ICP-OES assessment of trace element contamination in a tropical tide dominated estuary, Caravelas, Bahia, Brazil.

José Lourenço Friedmann Angeli¹, Bianca Sung Mi Kim¹, Rubens César Lopes Figueira¹

⁽¹⁾ Instituto Oceanográfico, Universidade de São Paulo; Praça do Oceanográico, 191, São Paulo - SP, 05508-120

Keywords: ICP-OES, trace elements, sediments, Caravelas estuary

INTRODUCTION

Total sediment element contents reflect the geological origins of sediments as well as the anthropogenic inputs. Therefore, in an environmental monitoring activity, it is important to determine whether the total metal content is within the range of background values or over the concentration limits according to national legislation. However, total decomposition of the sediment sample is a major requirement, especially where normalization of trace element concentrations to those of conservative lithogenic reference elements, such as Al or Sc (Kim et al., 2017), is performed for the purpose of determining elemental enrichment factors. Total element concentrations in sediments thus, require to be being accurately determined for many purposes.

Highly sensitive spectroscopic techniques, including inductively coupled plasmaoptical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS), have great advantages for the determination of trace elements. For this purpose, sample digestion is often a necessary step before determining metal concentrations. Many studies have evaluated the trace element concentration in sediments using the USEPA 3050B (USEPA, 1996) digestion procedure, which is a very strong acid digestion that dissolve almost all elements that could become environmentally available.

Therefore, the aim of this study was to determine the total content of trace element (As, Cr, Cu, Ni, Pb and Zn) as well as conservative lithogenic elements such as Al, Fe and Sc, in order to assess the regional background levels and the anthropogenic enrichment, in sediments cores from the Caravelas estuary, a complex transitional region between the mainland and the adjacent Eastern Shelf, where the biggest and richest reef complex (Abrolhos reef) of South Atlantic Ocean is found.

MATERIAL AND METHODS

The present study is based on 3 sediment cores (T2=234 cm; T5= 144 cm and T8=122 cm) collected in 2013, from different regions, aiming to encompass the inner and outer sectors of the Caravelas estuary (Figure 1). Each core was sectioned into 2 cm layers, and samples were frozen until analysis. Sedimentation rates were established according to the 210 Pb dating model corroborated through a second radionuclide tracer such as 137 Cs and were already detailed elsewhere (Angeli et al., 2016).



Figure 1. Location of the Caravelas estuary, in relation to Brazil and the state of Bahia. Sampling sites (T2, T5 and T8) are also shown.

Elements such as Al, As, Cr, Cu, Fe, Ni, Pb, Sc and Zn were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian 710 ES) after a strong acid digestion that dissolve almost all elements that could become "environmentally available" (USEPA, 1996). Certified reference material SS-2 (EnviroMAT - contaminated soil) was subjected to the same analytical procedure in order to evaluate precision and accuracy of the method (Table 1). All results were within the recommended range of USEPA (1996), between 75% and 125%.

Element	Certified	Observed	Recovery (%)
Al	13265	13479 ± 545	102
Fe	21046	22422 ± 1323	107
As	75	$64,4 \pm 1,01$	86
Cr	34	$30,00 \pm 1,45$	88
Cu	191	$155,04 \pm 3,29$	81
Ni	54	$42,02 \pm 3,68$	78
Pb	126	$132,00 \pm 4,95$	105
Zn	467	$360,40 \pm 6,18$	77

Table 1. Recovery values for the certified reference material SS-2 (n = 5).

RESULTS AND DISCUSSION

Based on the calculated enrichment factors and the resulting profiles (Figure 2), it was concluded that the Caravelas Estuary is not significantly contaminated by trace metals such as Cr, Cu, Ni, Pb and Zn. In the case of As, high background levels, recorded at the bottom of the cores, are related to the crystalline basement of the region and the chemical weathering of rocks of the "Barreiras Group", which sediments consists mainly of (1) fine to coarse siliclastic sands, (2) gray kaolinitic clays, and (3) poorly sorted, yellow and brown coarse to conglomeratic ferruginous sandstones with a kaolinite matrix (Vilas Boas et al., 2001). However, a slight increase (1.5) in the enrichment factor in recent decades, indicates an anthropogenic influence, mainly due to expansion of the eucalyptus monoculture plantations in the region.



Figure 2. Enrichment factors of selected trace metals along the sediment cores of the Caravelas Estuary.

CONCLUSIONS

The results of this study indicate that the digestion method of USEPA 3050B combined with ICP-OES determination is an accurate method for analyzing sediments for several trace and major elements.

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