FRACTIONATION OF TRACE METALS AND ARSENIC IN COASTAL SEDIMENTS FROM ADMIRALTY BAY, ANTARCTICA

<http://dx.doi.org/10.4322/apa.2014.076>

Andreza Portella Ribeiro^{1,2,*}, Keila Modesto Tramonte¹, Miriam Fernanda Batista¹,
Alessandra Pereira Majer¹, Charles Roberto De Almeida Silva¹, Guilherme Demane²,
Paulo Alves De Lima Ferreira¹, Rosalinda Carmelo Montone¹, Rubens Cesar Lopes Figueira¹

¹Instituto Oceanográfico, Universidade de São Paulo, Praça do Oceanográfico, 191, CEP 05508-900, São Paulo, SP, Brazil

²Diretoria da Saúde, Universidade Nove de Julho – UNINOVE, Rua Vergueiro, 235, CEP 01505-001, São Paulo, SP, Brazil

*e-mail: andrezpr@usp.br

Abstract: Sequential extraction, based on the method developed by the European Community Bureau of Reference, was performed to determine the mobile fractions of trace elements in sediments from Admiralty Bay, Antarctica. Except for As that is not certified, the quality of the data was found to be satisfactory for analysis as certified reference material, BCR-701, with recovery values for Cu, Ni, Pb and Zn, ranging from 90-115%. Zn and Ni were mainly found in the residual fraction, reflecting their natural contribution in the bay. As, Cu and Pb exhibited high potential mobility, above 60%, for most of the samples. Despite Pb contents being found mainly in the extractable fraction, its concentrations (ranging from 4.5 to 8.3 mg kg⁻¹) were well below the Threshold Effect Levels. In general, As and Cu mobile contents were higher than the sediment quality values, according to the Canadian Environmental Guidelines, which indicates that adverse biological effects to aquatic organisms can occur. However, since disturbances in Admiralty Bay are seldom observed, it can be inferred that As and Cu are preferably bound to the organic matter. Otherwise, this study presents the data set regarding sediments collected before the accident that happened in Ferraz Station in February of 2012. That singular event may have caused a relevant increase of available contents of the trace elements in the local aquatic system. Thus, valuable information is being provided for the future environmental monitoring, control and mitigation of arsenic and metal contamination in sediments from Antarctica.

Keywords: Antarctic sediments, arsenic, metals, sequential extraction method

Introduction

Anthropogenic trace-element contamination in aquatic systems can affect the diversity of benthic organisms (Stark *et al.*, 2003). The intake body of contaminant includes three different paths, such as pore water intake or, only, sediment intake (Simpson *et al.*, 2005).

According to Sundaray *et al.* (2011), there is no correlation between the total concentration and the elemental toxicity. Otherwise, the chemical form and mobility are the principal parameters to assess the elemental toxicity in the environment. Hence, the ability to identify the chemical forms of elements in marine and freshwater

sediments is very important to environmental monitoring studies.

Thereafter, sequential extraction techniques have been used as an alternative to evaluate the history of elemental input, diagenetic transformation within the sediments and the reactivity of trace-element species of both natural and anthropogenic sources (Passos *et al.*, 2010; Sundaray *et al.*, 2011).

Despite the importance of the Antarctic Continent to local and global environmental changes, the scientific studies regarding mobility of metals in sediments are

still scarce (Cosma *et al.*, 1994; Dalla Riva *et al.*, 2004; Ianni *et al.*, 2010). In fact, literature concerning Antarctic marine sediments focus mostly on total metal content (Negri *et al.*, 2006; Santos *et al.*, 2007), pseudo total content, using a mixture of strong acids, such as aqua regia (1 HNO₃ : 3 HCl v/v), or on extractable content by dilute acid, in most cases to HCl (Cosma *et al.*, 1994; Dalla Riva *et al.*, 2004)

The aim of this work is to contribute to the knowledge on Antarctic geochemistry regarding metals (Cu, Ni, Pb and Zn) and arsenic availability to interact to benthic organism in the aquatic systems. Thus, a sequential extraction was performed according to the procedure recommended by the Standards, Measurements and Testing programme of the European Union, SM& T, so-called BCR, (Pueyo *et al.*, 2001) in sediments from four sampling sites in Admiralty Bay, Antarctica.

Materials and Methods

Sampling

Eight short sediment cores, with depth of 10 cm, were collected in Admiralty Bay, along the Martel (sampling sites: Ferraz, Botany Point and Ullman Point) and Mackellar Inlets (sampling site: Refúgio) during the 28th Brazilian Antarctic Expedition in the 2009/2010 austral summer. To obtain undisturbed samples, the cores were sliced in 0-2, 2-6 and 6-10 cm, using a stainless steel spatula, and the sediment samples were freeze-dried, further, they were carefully homogenized in mortar and stored in polyethylene bags until chemical analysis at LaQIMar (Marine Inorganic Chemistry Laboratory), located at the Oceanographic Institute of the University of São Paulo (Brazil).

Analytical procedures

Inductively coupled plasma atomic emission spectrometer (ICP OES) was the analytical technique used to measure the levels of arsenic and metals in the sediment samples. The methodology for determining the fractionation of trace elements was the three step protocol proposed by the Standards, Measurements and Testing programme (SM & T, formerly BCR) of the European Community Bureau of Reference. BCR procedure consists of the following stages, respectively: STEP 1 (S1) – exchangeable and bound to carbonate (acid-labile fraction); STEP 2 (S2) – bound to

Fe and Mn oxides and hydroxides (reducible fraction); STEP 3 (S3) – bound to organic and matter sulphides (oxidizable fraction). The content of residual stage (STEP 4 – S4) was obtained from the difference between the total concentration of the elements, which was obtained by aqua regia digestion and the sum of stages 1, 2 and 3. Pueyo *et al.* (2001) describe the details of the BCR procedure.

Results

Except for As that is not certified, accuracy of the method was checked by analysis of six replicates of certified sediment reference material (BCR-701, European Community Bureau of Reference). For each extraction step, the experimental concentration of each metal was compared with the reference value, and the recovery calculated as the ratio (%) between measured and certified values. The quality data was found to be satisfactory with recovery values for Cu, Ni, Pb and Zn ranging from 93-113%, 109-113%, 93-111% and 90-115%, respectively.

Figures 1 and 2 show the mobile fractions (%) and the concentrations (mg kg⁻¹) for the sum of the steps (Σ S1; S2; S3). The elements presented the same behavior, i.e. their mobile fractions were in same order of magnitude, in each sampling site. Therefore, only the results for Ferraz and Refúgio are shown (Figures 1 and 2).

Ni and Zn extraction were constant (their mobile levels, for the most sediment samples, were lower than 70 and 40%, respectively). The mobile fraction of As was higher than 70% and Cu was above 60%. The highest Pb total content was 8.3 mg kg⁻¹.

Discussion

According to the Canadian Sediment Quality Guidelines (CCME, 1999), Zn total contents were well lower than the Threshold Effect Levels (TEL), indicating its lithogenic origins and limited potential bioavailabilities.

The Canadian guidelines suggest two sediment quality assessments to define three ranges of chemical concentrations, those that are rarely, occasionally, and frequently associated with adverse biological effects. TEL is the upper limit of the range of sediment chemical concentrations that is dominated by no-effect data entries and PEL (Probable Effect Level) is the range above which

Figure 1. Trace element mobile fractions, (a) in (%) and (b) in mg kg^{-1} , for Ferraz Station.

adverse biological effects are usually observed. Accordingly, for As, Cu, Pb and Zn the respectively target values, in mg kg^{-1} were established: TEL – 5.9; 35.7; 35 e 123 and PEL – 17; 197; 91.3 e 315.

Pb availability was mainly found in S2, suggesting the metal is bound to Fe-Mn oxides and can be released under anaerobic conditions. However, likewise Zn, Pb levels

in sediments do not offer a negative risk to the aquatic organism in Admiralty Bay. Indeed, As and Cu levels were between TEL and PEL targets, indicating that adverse biological effects to aquatic organisms can be observed. Otherwise, As and Cu were mainly bound to the oxidizable fraction that is not considered to be mobile and bioavailable, but may be made mobilized by decomposition processes

Figure 2. Trace element mobile fractions, in (a) in (%) and (b) in mg kg⁻¹, for Refúgio.

in acid conditions (Baig *et al.*, 2009). Disturbances are not frequent in the Antarctic environment, thus As and Cu are preferably bound to the organic matter.

Conclusions

Since there have been no relevant disturbances in the Antarctic environment until February of 2012, As and Cu mobilities to the local aquatic system could be suggested as negligible. Unfortunately, the tragic event in Ferraz Station

may have caused a significant antropoghenic input of chemical compounds into Admiralty Bay. Accordingly, the present study will provide substantial information to the future recovery works in the Antarctic landscape.

Acknowledgements

This work integrates the National Institute of Science and Technology Antarctic Environmental Research (INCT-APA) that receives scientific and financial support from

the National Council for Research and Development (CNPq process: n° 574018/2008-5) and Carlos Chagas Research Support Foundation of the State of Rio de Janeiro (FAPERJ n° E-16/170.023/2008). The authors

also acknowledge the support of the Brazilian Ministries of Science, Technology and Innovation (MCTI), of Environment (MMA) and Inter-Ministry Commission for Sea Resources (CIRM).

References

- Baig, J.A.; Kazi, T.G.; Arain, M.B.; Shah, A.Q.; Afridi, H.I.; Kandhro, G.A.; Jamali, M.K. & Khan, S. (2009). Arsenic fractionation in sediments of different origins using BCR sequential and single extraction methods. *Journal of Hazardous Materials*, 167: 745-751.
- Canadian Council of Ministers of the Environment – CCME. (1999). Protocol for derivation of Canadian sediment guidelines for protection of aquatic life. CCME-EPC-98E. Prepared by Environment Canada Guidelines Division, Technical Secretariat of CCME Task Group on water quality guidelines, Ottawa, Canada. Available from: < <http://ceqg-rcqe.ccme.ca/download/en/226/>>. Accessed in: November 02 2012.
- Cosma, B.; Soggia, F.; Abemoschi, M.L. & Frache, R. (1994). Determination of Trace Metals in Antarctic Sediments from Terra Nova Bay - Ross Sea. *International Journal of Environmental Analytical Chemistry*, 55: 121-128.
- Dalla Riva, S.; Abemoschi, M.L.; Magi, E. & Soggia, F. (2004). The utilization of the Antarctic environmental specimen bank (BCAA) in monitoring Cd and Hg in an Antarctic coastal area in Terra Nova Bay (Ross Sea-Northern Victoria Land). *Chemosphere*, 56: 59-69.
- Negri, A.; Burns, K.; Boyle, S.; Brinkman, D. & Webster, N. (2006). Contamination in sediments, bivalves and sponges of McMurdo Sound, Antarctica. *Environmental Pollution*, 143: 456-467.
- Ianni, C.; Magi, E.; Soggia, F.; Rivaro, P. & Frache, R. (2010). Trace metal speciation in coastal and off-shore sediments from Ross Sea (Antarctica). *Microchemical Journal*. 96 (2): 203-212.
- Passos, E.A.; Alves, J.C.; Santos, I.S; Alves, J.P.H.; Garcia, C.A.B & Costa, A.C.S (2010). Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. *Microchemical Journal*, 96: 50-57.
- Pueyo, M.; Rauret G.; Lück D.; Yei-Halla M.; Muntau H.; Quevauviller, Ph. & López-Sánchez, J.F. (2001). Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. *Journal of Environmental Monitoring*, 3: 243-250.
- Santos, I.R.; Fávoro, D.I.T.; Schaefer, C.E.R.G. & Silva-Filho, E.V. (2007). Sediment geochemistry in coastal maritime Antarctica (Admiralty Bay, King George Island): Evidence from rare earths and other elements. *Marine Chemistry*, 107: 464-474.
- Simpson, S.L.; Batley, G.E.; Chariton, A.A.; Stauber, J.L.; King, C.K.; Chapman, J.C.; Hyne, R.V.; Gale, S.A.; Roach, A.C. & Maher, W.A. (2005). *Handbook for Sediment Quality Assessment*. CSIRO, Bangor, NSW.
- Sundaray, S.K.; Nayak, B.B.; Lin, S. & Bhatta, D. (2011). Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments - A case study: Mahanadi basin, India. *Journal of Hazardous Materials*, 186: 1837-1846.
- Stark, J.S.; Snape, I. & Riddle, M.J. (2003). The effects of petroleum hydrocarbon and heavy metal contamination of marine sediments on recruitment of Antarctic soft-sediment assemblages: a field experimental investigation. *Journal of Experimental Marine Biology and Ecology*, 283: 21-50.