History of heavy metals contamination in lacustrine sediments of Admiralty bay, King George Island, Antarctic Peninsula

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A temporal reconstruction of heavy metals contamination in Admiralty bay, King George Island, was conducted through the analyses of sediment profiles. Ages of the layers were determined using \(^{210}\text{Pb}\) geochronology. Attempts had been made to examine the history of occupation and exploration of Admiralty bay based on the concentrations of the heavy metals present in the bay. Elements such as Cr, Cu and Ni, associated with paints and petroleum showed an increase in the sediment profiles of the points 1 and 5 that are in the vicinity of the focus areas. The above region has a history of fishing exploration which is nearby this research station.

[Keywords: Heavy metals; Admiralty bay, Antarctic; lacustrine sediments]

Introduction
There are few studies on the determination of the heavy metal in the matrix of ice and from the atmosphere in the Antarctica region\(^1\)\(^2\). The source of these elements is sufficiently diverse. One important matrix is to determine the local process of contamination represented in the lacustrine sediments. Heavy metal measurements in superficial sediments and soils have already been done in the region of the Admiralty Bay and in other localities of King, George\(^1\)\(^2\)\(^3\). There were no earlier attempts to determine the temporal dynamics on the contamination process of heavy metal in this regime.

Study Area
The King George Island is the largest island of the South Shetland Archipelago. It is situated in the Northwest extremity of the Antarctica Peninsula, between the coordinates of 61°54' - 62°16' S and 57°35' - 59°02' W. Local topographical variations go up to 700 meters above sea level. The island has an area of 1250 km\(^2\) and 92% of its territory being ice. The hydrology is dominated by melting water discharge. The climate can be classified as polar oceanic of the Southern Hemisphere. Its climate is determined by successive cyclonic systems, carrying warm and humid air, strong winds, great volume of precipitation\(^5\), and the snow being the main precipitation form.

Materials & Methods
The collection of sediment cores were carried out along coastal area during the austral summer of 2003/2004. The collection had been done along the coastal area of Admiralty bay. This was done in 5 different localities viz., 1) Near to the Ecology glacier, 2) Patelnia point, 3) Agat point, 4) Hannequin point and 5) Ipanema (Fig. 1). Sampling points were defined in accordance with the presence of draining basins, as well as the areas of accented glacier retraction.

An acrylic tube of 7 cm in diameter 3 mm well, was inserted in the sediment. A piston was used to draw the material by vacuum. A layer of 1 cm was

Fig. 1—Admiralty bay and sediment sampling points.
sliced for the radiometric and metal analyses. The profiles varied from 12 cm to 26 cm depths.

**Analytical methods**

**Heavy Metals in lacustrine sediments**

For the determination of the bioavailability of heavy metals; 250 mg of the sediment had been dehydrated at 150°C for 24 hours. The metals present in sediment fraction, are not embedded in crystal structure of the grain matrix in this sediment. Therefore, this fraction is expected to have been more associated with the processes of enrichment due to the contamination of the environment.

The extraction of these metals was carried out through the addition of 4 mL of HNO₃ of 0.5 M and 1 mL of HCl of 0.5 M. All reagents used were Suprapur Merk. The blanks were measured together with the samples to maintain better accuracy by avoiding the background and analytical error⁹. The samples were analyzed of ICP-OES (Ultima II model).

**²¹⁰Pb Geochronology**

The ²¹⁰Pb, a natural radionuclide of the ²³⁸U series of radioactive decay with a half-life of 22.6 years is being employed by many for the dating of recent sediments³⁻⁷ ²¹⁰Pb. In the atmosphere it is produced from the decay of the ²²²Rn. This noble gas emanates from terrestrial surface. It precipitates in the terrestrial surface by gravimetric or “washout”. Such metals are called ²¹⁰Pb unsupported, since it’s not bound in the mineral matrix of the local sediments⁵. In the specific case of the Antarctic continent, the local emanation of ²²²Rn is considered insignificant, due to covering of snow and ice. This is observed for long periods of the year on all surfaces of the islands⁶. In periglacial environment such as in Antarctica, the levels of ²¹⁰Pb in the atmosphere are the lowest in the glacial planet¹⁰.

The model defined for the interpretation of the data of ²¹⁰Pb in the sediment profiles was the model of constant flow. This is also known as CRS (Constant Rate of Supply). This model considers variations in sedimentation rates of any profile that cannot be explained by bioturbation phenomena or physical mixture of sediments¹¹. In the majority of the cases, it is clear that erosion and sedimentation rates show changes during the last, 100 years. Thus, the profile of ²¹⁰Pb may not be linear. To check the accuracy of dating process, the ¹³⁷Cs, a radionuclide produced by nuclear fission and with wide release during the nuclear tests with more intensity in 1963, was used as time-marker¹²⁻¹³.

**Results and Discussion**

The dating of the sediment profiles was utilized to determine the history of heavy metals contamination associated with the activity in the surroundings of Admiralty bay. The point 1 profile (Ecology) (Fig. 2), of metals like Cr, Ni, Cu and Co showed relatively similar behaviour, with low levels in the profile. These metals, with exception of Cr, showed a slow decrease since 1930; it reached a peak in 1960 and brought to a minimum value in the 1980’s. Between 80’s and 90’s the concentration of these metals increased. This trend drops back to low levels until the current days. Soon after, between 1980 and 1990 there is large increase in content, the same had been noted for Cr and Ni. The Zn presents a peak in 1930 and remained steady up to 1980. During 1980’s presents a peak is also present as with the other metals. The difference observed for this metal was that while all the other elements had presented stability or reduction in the concentrations, the Zn had its biggest peak in 1982, reaching 0.15 mg kg⁻¹. After this there is a fast reduction of the concentration levels.

Point 2 (Patelnia) is presented as a profile in which Zn, Co, Ni and Cr as seen with similar trend upto 1940’s where a surging peak for these elements was observed. The Co reaches to a content level of 0.15 mg kg⁻¹, the Cr, 0.06 mg kg⁻¹, the Ni, 0.07 mg kg⁻¹ and the Zn, 0.8 mg kg⁻¹. After this rise, its levels remained steady until middle of the 1990’s, where it is noticed to have downward peak and posterior reduction. After the year 2000 the increasing trend is maintained. The content of Cu was high in 1940 and soon after it has shown a reduction to the current days. In present cases, associated with the activity in the surroundings of Admiralty bay. The point 1 profile (Ecology) (Fig. 2), of metals like Cr, Ni, Cu and Co showed relatively similar behaviour, with low levels in the profile. These metals, with exception of Cr, showed a slow decrease since 1930; it reached a peak in 1960 and brought to a minimum value in the 1980’s. Between 80’s and 90’s the concentration of these metals increased. This trend drops back to low levels until the current days. Soon after, between 1980 and 1990 there is large increase in content, the same had been noted for Cr and Ni. The Zn presents a peak in 1930 and remained steady up to 1980. During 1980’s presents a peak is also present as with the other metals. The difference observed for this metal was that while all the other elements had presented stability or reduction in the concentrations, the Zn had its biggest peak in 1982, reaching 0.15 mg kg⁻¹. After this there is a fast reduction of the concentration levels.

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The profile of point 3 (Agat Point) presents a trend for the Ni, Cr, Co and Cu, without any event of oscillations in the content throughout the time. For Zn, a peak is defined in the content in the year of 1945 and soon after it has shown a reduction to the level of the previous level, but for only one small increase, observed in 1996. The Point 3, (Ipanema) had presented a profile without great alterations for the metals of Ni, Cu, Cr, Co where as Zn has put up alternate rise and falls.

Point 4 (Hannequin) demonstrates an increase for the Zn between 1940 and 1950. This level is kept until
Fig. 2—Metal profile of sediments from the sampling points of Admiralty bay.
the end of the year 1980 where a reduction is observed. Since 1980; the content level had increased to a value of 0.24 mg kg\(^{-1}\). The other metals demonstrate a small increase during the analyzed period. The fluctuations in the concentration level had been limited among the metals.

The profile of point 5 (Ipanema), near to the Commandant Ferraz Research station, has displayed the levels of Ni without alterations. For Zn, the behaviour follows a steady trend up to 1980 when it reverts to put up an increase having its peak in the year from 1990 and a reduction since 2000. The concentration is very similar to the one of the Cu and Cr, with the exception of the current trend of increase, bit it is not observed for the Cr. The Co has presented an extensive increase from years 1920, reaching its peak in the year of 1970 and a fast fall in 1980. Recently an oscillating trend may be observed.

There exist similarities in the behaviour of metals between points 1 (ecology) and 5 (Ipanema). In both, concentration is increasing in between 1930 up to 1980. During this period, the fishing stations in the region of the Admiralty bay were in operation. Moreover, activities of fishing had remained mainly in the vicinity of the sampling points 1 and 5. That would have been the cause which enabled traffic of people and materials, much more intense than the other portions of the bay. The increase in metal concentration observed between the years 1980 and 1990 can be related to the installation and maintenance of research stations. The research stations viz. Henry Arctowski (Poland) and Commandant Ferraz (Brazil), are situated near to the points 1 and 5, respectively.

The metals contamination in sediments of marine terrace and sampling soils in front of Commandant Ferraz station has been registered by Santos et al., 2005. It had been estimated that the Cr metal, in the sediments in front of the station have a value of 1.5 mg kg\(^{-1}\) was. The average value of Cr in the other points of the Admiralty bay, was 0.03 mg kg\(^{-1}\). This was the case of Co. In front of the Station, a value of 27.6 mg kg\(^{-1}\) was found and the average value of other points of the Admiralty bay was 0.1 mg kg\(^{-1}\). The values of Ni and Zn found in the region near to the Brazilian research station were 1.1 and 8.9 mg kg\(^{-1}\) respectively. The average content for the rest of Admiralty bay is 0.04 and 0.5 mg kg\(^{-1}\) respectively.

Results of the present work, demonstrate that the values of metal concentration in front of the Commandant Ferraz Station are significantly higher than those found in the other points. This confirms the difference in the behaviour in points 1 and 5 profiles, when compared to other areas of the Admiralty bay. It can be attributed to direct relation of the influence of the logistics operations on the local contamination for the concentration. The research station is currently installed fishing stations or ports and can be defined through the temporal analysis of metal concentration in the sediments.

The temporal variation in the metal concentrations observed in the sediment profiles, mainly in the Zn, Cr and Cu are the most likely impasse to the increase in human occupation in the King George Island, the most inhabited island in the region. In recent decades, there has been increase in the number of stations in view of the tourist activity. In such areas these metals can be found from the fuel utilized and in the energy generated from the research stations. Another source of these metal may be the paint used in the station and in the maintenance of theses stations. The analyses of surface sediment will demonstrates the actual variation in the metal concentrations in the different localities of the Admiralty bay. The historical record of contamination in this environment can only be accessed by geochronology of the sediments studied.

Conclusion

The reconstruction of the metal contamination in the Admiralty Bay was made possible through \(^{210}\)Pb Geochronology. An increase in the metal contamination has been observed in recent decades of metals associated with fuel utilized in the region. The probable source of these pollutants has been identified in the present study. Many other components like intercontinental atmospheric transport may be contributing to the increase in the contamination of this area.

References


2 April J M. Constraints on use of \(^{137}\)Cs as a time-marker to support CRS SIT Chronologies. Environmental Pollution, v.129, 2004

3 Dovlete C, Rusza Gy, Baciu F & Sima O. Gamma Spectrometry measurement of \(^{210}\)Pb in environmental


