TEMPORAL VARIATIONS AND SOURCES OF N-ALKANOLS AND STEROLS IN SEDIMENTS CORE FROM ADMIRALTY BAY, ANTARCTIC PENINSULA

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Abstract: Sterols, n-alkanols and phytol were analyzed in three sediment cores collected in different regions of Admiralty Bay (Barrel Point, Refúgio II and Ferraz). The concentrations of total sterols ranged from 0.91 to 13.99 $\mu\text{g.g}^{-1}$, total n-alkanol from 0.20 to 2.14 $\mu\text{g.g}^{-1}$ and phytol from 0.13 to 2.38 $\mu\text{g.g}^{-1}$. Cholesterol was the most abundant sterol in the three cores, while the short-chain n-alkanols were the predominant n-alkanols. Phytol showed relatively low concentrations in all cores. These results indicate marine sources as responsible for the more dominant input of sedimentary organic matter with lower contributions from terrestrial sources. The vertical distribution of the organic markers analyzed was similar, with higher concentrations found at the top layers of all cores and the lower concentrations in the deepest layers, with some variations occurring along the profile. These changes may be the result of natural events and temperature oscillation over the last century which may have altered the dynamics of the supply of organic matter of the sediments of Admiralty Bay.

Keywords: organic matter, sterols, n-alkanols, Antarctic Peninsula

Introduction

Sterols and n-alkanols are organic markers present in the polar fraction of lipid extracts in marine sediments, being directly associated with primary production (Hudson *et al.*, 2001). They are also essential to marine organisms, acting as key components of cell membranes and to the regulation of specific metabolic processes (Laureillard *et al.*, 1997). These markers are used to distinguish terrestrial and marine sources of sedimentary organic matter through, generally, the number of carbon atoms present in the aliphatic chain, and identify organisms that act as sources of these compounds (Volkman, 1986; Faux *et al.*, 2011).

The distribution of these compounds in sediment cores may be useful for the understanding of the temporal and local environmental changes based on natural and anthropogenic events in the recent past. The aim of this work was to identify variations in the input and the sources

of sedimentary organic matter deposited in sediments from Admiralty Bay, through the determination of organic markers, such as sterols and n-alkanols.

Materials and Methods

Study area

The study area was defined as Admiralty Bay (62° 02' S and 58° 21' W), the largest *fjord* in the South Shetland Islands, located on King George Island (Figure 1), with total area of 120 km². It is formed by a >500 m deep main channel, that divides the bay in three main inlets (Martel, Mackellar and Ezcurra), and in each there is a research station. The presence of high diversity of marine organisms, plants and animals, such as, fungi, mosses, birds and mammals, represents the sources of different classes of biomarkers.

Figure 1. Map of the study region with three sampling stations at Admiralty Bay (03). The arrows indicate the current circulation direction within the bay (Rakusa-Suszczewski, 1980).

Sampling

The sampling was carried out during the austral summer of 2006/2007 and 2009/2010, in three inlets around Admiralty Bay (Ferraz - FER, Barrel Point - BAR and Refúgio II - REF, Figure 1). The cores were obtained from a box core sampler, and sub-sampled into sections of 1 cm (except REF, where sections were 2 cm).

Analytical procedure

The analytical method used to analyze the sterols and n-alkanols in sediments was adapted from UNEP (1992) with modification. Around 20 g of sediment were extracted using a Soxhlet system during 8h with 80 mL of n-hexane: dichloromethane (DCM) (1:1) (both J.T. Baker), and with 100 μL of a solution containing surrogates eicosene, hexadecene (50 $\text{ng}\cdot\mu\text{L}^{-1}$) and 5 α -androstanol (20 $\text{ng}\cdot\mu\text{L}^{-1}$). This extract was reduced to c. 2 mL by rotoevaporation and submitted to a *clean up* in column chromatography using 3.2 g of silica (silica gel 60, 0.063-0.200 mm, Merck) and 1.8 g of alumina (aluminum oxide 90 active, 0.063-0.200 mm, Merck) (5% deactivated). The samples were eluted with 10 mL of n-hexane to fraction 1 (aliphatic hydrocarbons – not analyzed), 15 mL of n-hexane/DCM

30% to fraction 2 (PAHs + alkenones – not analyzed) and 5 mL of ethanol/DCM 1:9, following 20 mL of ethanol to fraction 3 (sterols and n-alkanols). The fraction 3 was evaporated to dryness and derivatized to form trimethylsilyl ethers using BSTFA (bis(trimethylsilyl)trifluoroacetamide) with 1% TMCS (trimethylchlorosilane) during 90 minutes at 65 °C. The mixture of TMS-sterols and n-alkanols derivatives was determined by the injection of 2 μL into a gas chromatograph equipped with a flame ionization detector (GC-FID).

Results

Seventeen sterols were identified, with total sterols concentration ranging from 0.91 to 2.17 $\mu\text{g}\cdot\text{g}^{-1}$ (BAR), from 1.63 to 8.59 $\mu\text{g}\cdot\text{g}^{-1}$ (REF) and from 2.64 to 13.99 $\mu\text{g}\cdot\text{g}^{-1}$ (FER). The distribution of total sterols concentration according to the depth for three cores can be visualized in Figure 2.

Total sterols in BAR showed higher concentration between 7 and 11 cm, with lower concentrations in deeper layers. In REF, higher concentrations were found from 7 cm toward the surface while FER showed some variations over time, with lower concentrations observed between 7 and 16 cm (Figure 2).

Figure 2. Vertical profile of total sterols (in $\mu\text{g}\cdot\text{g}^{-1}$) in sediment cores from Admiralty Bay, Antarctic Peninsula.

Fourteen n-alkanols were identified, with total n-alkanols concentration varies from 0.20 to 0.58 $\mu\text{g.g}^{-1}$ (BAR), 0.33 to 2.14 $\mu\text{g.g}^{-1}$ (REF) and 0.22 to 1.97 $\mu\text{g.g}^{-1}$ (FER). The distribution of total n-alkanols concentration in different layers for three cores is shown in Figure 3.

Total n-alkanols en BAR was similar to the total sterols, with highest concentrations between 7 and 11 cm. In REF, the highest values of concentrations occurred between 7 and 9 cm, while FER presented three concentrations peak at 16.5, 6.5 and 0.5 cm.

Phytol, an isoprenoid alcohol derived from chlorophyll-*a* degradation (Volkman *et al.*, 2008), was found in all cores analyzed. The distribution of phytol concentration in different layers for three cores is shown in Figure 4.

Phytol concentration varied from 0.17 to 0.26 $\mu\text{g.g}^{-1}$ (BAR), 0.13 to 2.39 $\mu\text{g.g}^{-1}$ (REF) and 0.24 to 1.26 $\mu\text{g.g}^{-1}$ (FER). Relative low concentrations and close to the detection limit were presented in the BAR, while REF and FER showed highest concentrations in top core sections, represented as the recent sediments. In the others sections, a regular distribution with no significant variations was observed.

Discussion

The variation observed along vertical profiles, for both sterols as n-alkanols, may reflect variations in the input of organic matter in the environment, besides the section with higher concentration indicating higher contributions of sedimentary material, while sections with decreased values indicate a low input or organic matter reduction on sediments (Meyers, 1997). These variations may occur due to environmental changes, which have an influence on the organic matter processes related with the input, burial and preservation and/or degradation (Faux *et al.*, 2011), or as the result of natural variability. The decreased concentrations with core depth were not constant and may also be a result of diagenesis (Burns & Brinkman, 2011).

Cholesterol was the most abundant sterol. Several organisms that inhabit the region are potential sources of cholesterol, including seal, whales and phyto and zooplankton (Volkman, 2005). The detectable concentration of 17 different sterols analyzed is an evidence of the large sources diversity of organic matter contributing to the sediment composition in Admiralty Bay. The presence of

Figure 3. Vertical profile of total n-alkanols (in $\mu\text{g.g}^{-1}$) in sediment cores from Admiralty Bay, Antarctic Peninsula.

Figure 4. Vertical profile of total phytol (in $\mu\text{g.g}^{-1}$) over the cores in Admiralty Bay, Antarctic Peninsula.

saturated sterols in sediments indicates the occurrence of diagenic process due to the fact that they are not commonly found with significant abundance in organisms (Hassett & Lee, 1977).

The predominance of short-chain n-alkanols in all cores suggest the organic matter in this region is primarily associated with marine organisms, which include sources like, aquatic algae and bacteria (Xiong *et al.*, 2010), zooplankton (Burns & Brinkman, 2011) and hydrolysis of the wax esters of zooplankton which may increase the saturated and unsaturated C_{14} - C_{22} alcohols (Volkman, 2006).

In Antarctic region, phytol contribution is related to vascular plants (*D. Antarctica* e *C. quitensis*), lichens, mosses and algae (Wang *et al.*, 2007). However, the low concentrations observed in all cores in this study compared to marine sediments from temperate/tropical areas may be related with the absence of significant sources for this compound in the region. Another explanation is to low phytol concentration is related to the degradation compound in sediments, which includes aerobic and anaerobic

biodegradation, photo degradation and sulphurization in sediment-water interface.

Conclusions

Based on the results, a multiplicity of sources of marine organic matter from sediments from Admiralty Bay could be verified, mainly associated with marine origin, with little contribution from terrestrial material. Despite of the transformation processes of organic matter, the compounds showed relative preservation, representing the variations and distribution of organic matter along the vertical profiles.

This study is a first insight about polar organic markers in sediment cores of Admiralty Bay and the results, after more deeper interpretation and including other proxies (e. hydrocarbons, elemental and isotopic analyses) may contribute to a better understanding of the processes related to organic matter contribution and the changes as a result of natural events and temperature oscillation over the last century.

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