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DISTRIBUTION OF STEROLS IN SEDIMENT CORES FROM MARTEL INLET, ADMIRALTY BAY, KING GEORGE ISLAND, ANTARCTICA

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Edna Wisnieski[1,*], Liziane Marcella Michelotti Ceschim[2], Sabrina Nart Aguiar[1],César de Castro Martins[1,**]

[1]Centro de Estudos do Mar, Universidade Federal do Paraná – UFPR, Pontal do Paraná, PR, Brazil
[2]Laboratório de Química Orgânica Marinha, Instituto Oceanográfico, Universidade de São Paulo – USP, São Paulo, SP, Brazil
*e-mail: *ednawisnieski@gmail.com; **ccmart@ufpr.br*

Abstract: *In the present study, sterols organic markers were applied to identify the sources of organic matter in Admiralty Bay. For this purpose, sediment samples were extracted using a Soxhlet system, clean up with column chromatography and injected into a gas chromatograph. Measurable levels of all sterols analyzed confirm the multiplicity of sources of sedimentary organic matter. In BTN and STH,the most abundant sterol was the colest-5-en-3β-ol (cholesterol) with 2.24 μg.g^{-1} and 4.12 μg.g^{-1}, respectively, while in FER, itwas the 24-metil-colest-5-en-3β-ol (campesterol) with 1.83 μg.g^{-1}. The saturated sterols have smaller concentrations in relation to parental unsaturated, which may indicate a low rate of bacterial and hydrogenation processes. A generic profile of the vertical distribution representing all 15 sterols studied was obtained by Principal Component Analysis (PCA). In three cores, the vertical distribution pattern of organic material presented the smallest values in the bottomdepth layers, reflecting the organic matter already immobilized while in the upper layers values showed a gradual increase towards the top, representing the recentdeposition of organic matter.*

Keywords: sediments, sterols, organic matter, Antarctica

Introduction

Organic markers, such as sterols, are chemical compounds with characteristics of degradation resistance and specificity according to their origin. They can be used as indicators of events and processes in the environment on a time scale (Colombo *et al.*, 1989). Particularly, sterols have been widely used as indicators of sources, bacterial reworking and diagenetic transformations of organic matter deposited in the marine sediment, such as an indicator of sewage introduction into the marine environment (Green & Nichols, 1995; Hughes & Thompson, 2004; Volkman, 2005; Yunker *et al.*, 2005).

Sterols represent a small proportion of biogenic organic matter, however, they are essential to marine organisms, because they are key components of cell membranes and for the regulation of specific metabolic processes (Laureillard *et al.*, 1997). Particulate organic matter, living organisms and sediment show the presence ofsterols, thus the determination of these organic markers helps in the understanding of sources and fate of organic matter into the marine environment, as well as fingerprints of primary production (Hudson *et al.*, 2001).

In marine organic matter the main sterols that can be found are:4α,23,24-trimetil-colesta-22E-en-3β-ol (dinosterol - photosynthetic dinoflagellates), colest-5-en-3β-ol, (cholesterol - fito and zooplankton), 24-etil-colest-5-en-3β-ol (sitosterol), 24-metil-colest-5-en-3β-ol(campesterol) (algae and bacteria) and 24-metil-colesta-5,22E-dien-3β-ol (brassicasterol - diatoms). The saturated sterols such as 5α-colestan-3β-ol (cholestanol), 24-metil-colesta-22E-en-3β-ol (campestanol) and 24-etil-colestan-3β-ol (sitostanol), are also present in different marine organisms and can be formed as result of diagenetic processes and bacterial hydrogenation of unsaturated sterols (Volkman, 2005).

Currently, the organic geochemical aspects related to the contribution and the conversion of sedimentary organic matter indicated by sterols in a given time scale in the Antarctic environment has been barely investigated. 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 research has been to study the temporal distribution of sterols as indicators of origin, input, preservation or degradation of marine organic matter in sediment cores of Martel Inlet, Admiralty Bay, Antarctica.

Material and Methods

Study area

The study area was the Martel Inlet, in Admiralty Bay, King George Island located in the South Shetland Islands, Antarctic Peninsula (62° 02' S and 58° 21' W) (Figure 1).

Admiralty Bay has an area of 131 km², reaches depths of up to 530 m and has a coastline with many bays (Santos *et al.*, 2007), the largest bay being at King George Island, one of the South Shetlands Islands. There are three large inlets in Admiralty Bay: Martel, Mackelar and Ezcurra and each of them possesses a research station. The Mackelar and Martel Inlets form the northern part of the Bay while the Ezcurra Inlet is in the west (Bromberg *et al.*, 2000). Comandante

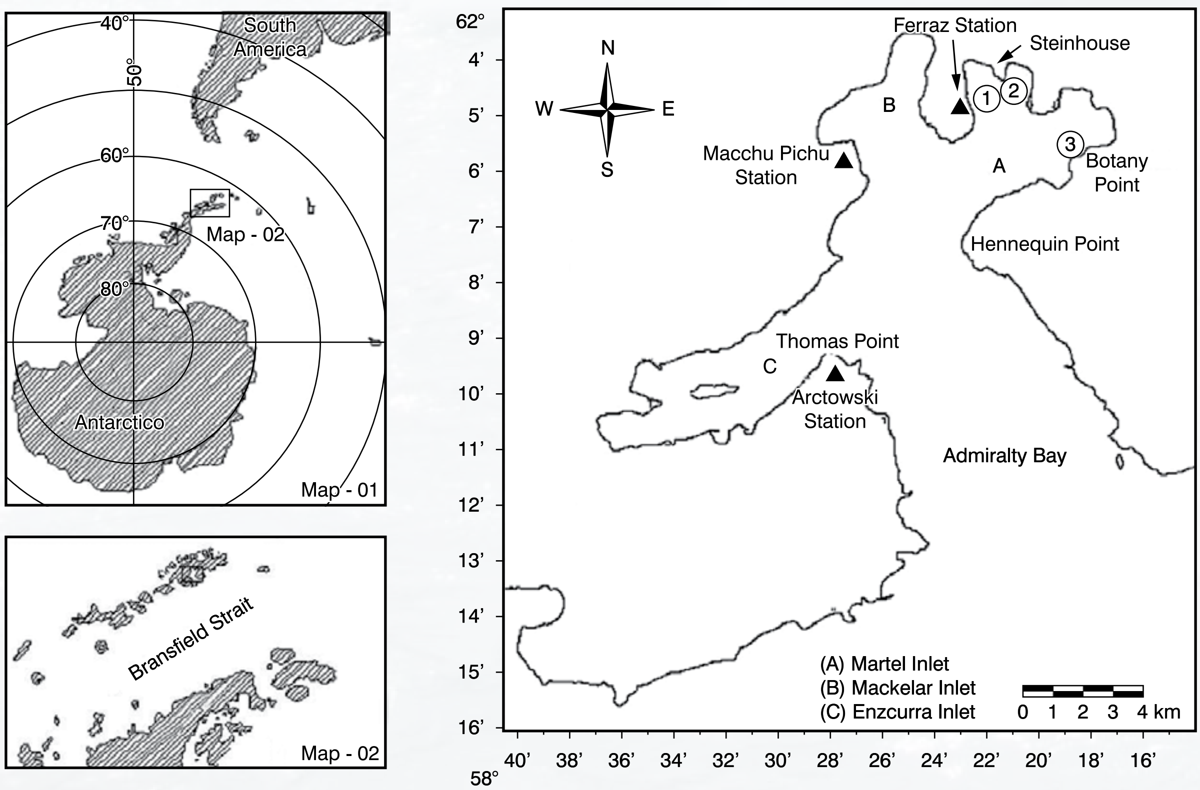

Figure 1. Sampling stations at Admiralty Bay, King George Island, Antarctica. (1): ComandanteFerraz Brazilian Antarctic Station (FER); (2): Steinhouse Glacier (STH); (3): Botany Point (BTN).

Ferraz Antarctic Station (EACF), the Brazilian station, is located in Martel Inlet.

Sampling

Sampling was carried out during the austral summer of 2007/08, in three different points in Martel Inlet named: Ferraz Station (FER), Steinhouse Glacier (STH) and Botany Point (BTN). The cores were obtained from a box core sampler, and sub-sampled into sections of 1 cm.

Analytical procedure

The analytical method used for the analysis of sterols in sediments is described in Kawakami and Montone (2002). Around 20 g of sediment from each site were extracted using a Soxhlet system for 8 hours with 70 mL of ethanol. The surrogate, 5α-cholestane was added before each extraction. The ethanol extract was reduced to c. 2 mL by rotoevaporation and submitted to a clean up with column chromatography using 2 g of 5% deactivated alumina and elution with 15 mL of ethanol. The extracts were evaporated to dryness and derivatized to form trimethylsilyl ethers using BSTFA (bis(trimethylsilyl)trifluoroacetamide) with 1% TMCS (trimethylchlorosilane) for 90 minutes at 65 °C. The mixture of TMS-sterols derivatives was determined by the injection of 2 μL into a gas chromatograph equipped with a flame ionization detector (GC-FID). Instrumental details are described by Montone *et al.* (2010).

Results and Discussion

The most abundant compound in BTN and STH was the colest-5-en-3β-ol (cholesterol) (2.24 $\mu g.g^{-1}$ and 4.12 $\mu g.g^{-1}$, respectively), producedby various organisms that inhabit the region, including seals, whales, phyto and zooplankton (Volkman, 2005).In FER, the 24-metil-colest-5-en-3β-ol (campesterol) (1.83 $\mu g.g^{-1}$), biosynthesized by Prymnesiophycean algae (*Phaeocystissp*) and cyanobacteria (Volkman, 2005) was the most abundant sterol. The detected concentrations of 15 different sterols analyzed are evidence of the variety of sources of composition of sedimentary organic matter in Martel inlet. The presence of saturated sterols in the sediment indicates the occurrence of diagenic process although they are not commonly found in significant abundance in organisms (Hassett & Lee, 1977). However, the lower concentrations of saturated sterols in relation to the unsaturated homologue may indicate low rate of bacterial and hydrogenation diagenetic processes.

A generic profile of the vertical distribution of all sterols analyzed was obtained by Principal Component Analysis (PCA), using the concentration of each compound according to different depth sections of sediment cores.

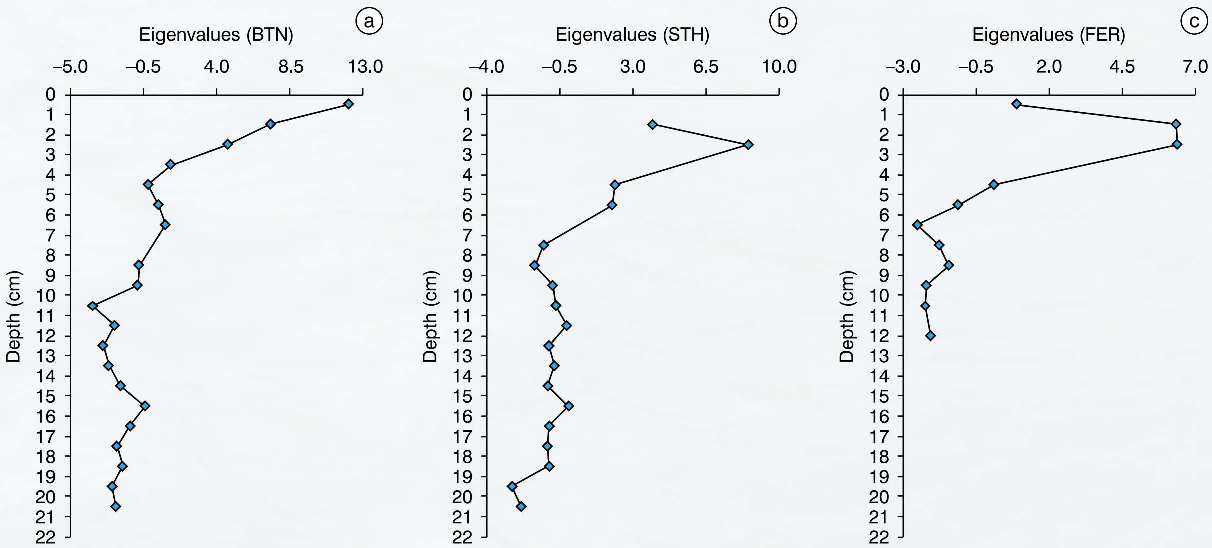

Figure 2. Vertical profilesobtained by Principal Component Analysis (PCA) to BTN, STH and FER sites.

As expected, the general profile of the three sites (Figure 2) showed highest concentrations in the upper layers. The sterol levels decreased with depth, suggesting degradation after depositional and little changes in sources of organic matter in the recent past (Hudson *et al.*, 2001).

In BTN (Figure 2a), a constant behavior can be visualized in depth sections up to 10-11 cm, indicating the immobilized organic matter (Muri & Wakeham, 2006). The lowest value at ~10 cm suggesting declines in productivity or fluxes of poor-sterol material at this point (Hudson *et al.,* 2001). A more significant peak can be seen between 15 and 16 cm and it may be associated with large inputs of organic matter to the bottom sediments of Martel Inlet as a result of natural events (period of increased melting, significant fluctuations in populations of marine organisms or changes in sediment particle size) (Hudson *et al.,* 2001). From sections 9-10 cm up to surface layers, the increased values are compatible with the recent organic matter deposition, weakly transformed in the water column and by post depositional processes.

In the cores STH (Figure 2b) and FER (Figure 2c), a similar distribution to BTN was found, except for a peak at 2 and 3 cm (STH) and from 1 to 3 cm (FER), which may have been due to the presence of fine grained particles (visual observation) in these sections resulting in high organic matter accumulation and strong accumulation of sterols due to physical adsorption(Meyers, 1994).

Conclusions

Based on the results obtained from this work, a multiplicity of sources of marine organic matter to sediments of Martel Inlet could be verified, due to all sterols analyzed having shown detectable concentrations in most of the sections of the three cores analyzed, despite of evident degradation in down-core sections.

The vertical profiles generated by PCA presented lower values in the depth layers, reflecting the organic matter already immobilized while in the upper layers values showed increased concentrations, representing the recent inputs of organic matter.

The results of this research can contribute to a better understanding of the processes related to contribution and the transformation of organic matter in Martel Inlet, serving as a basis for other environmental studies, in development in the region.

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