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TEMPORAL VARIATIONS IN ALIPHATIC HYDROCARBONS IN SEDIMENT CORES FROM ADMIRALTY BAY AND DECEPTION ISLAND, ANTARCTICA

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Abstract: *The sub-Antarctic environment has been one of the most visited and densely populated areas of Antarctica, related to the presence of sealers and whalers during late-19th to early-20th century and, recently, tourists and research projects. The region has been subject to the risk of hydrocarbon contamination, since human activities in this region require the use of fossil fuels as an energy source. Temporal and spatial distribution on levels and sources of aliphatic hydrocarbons were studied in dated sediment cores from Admiralty Bay and in Deception Island. Total aliphatic hydrocarbons ranged from 3.67 to 25.5 $\mu\text{g}\cdot\text{g}^{-1}$, similar to levels found in other Antarctic areas. Temporal distributions suggested a constant input of natural sources of aliphatic hydrocarbons in older sediments (before the early-80s) and some anthropogenic contribution may be presented in recent sediments, since the early-90s. Due to the presence of biogenic contribution, other organic markers such as polycyclic aromatic hydrocarbons may be used to confirm the history of hydrocarbon input in the sediments of Admiralty Bay and Deception Island.*

Keywords: Organic Matter, Oil Contamination, South Shetland Islands

Introduction

Antarctica is one of the last remaining areas of the world minimally impacted by anthropogenic activities. However, human activities have progressively changed the region in last five decades. The scientific activities and occupation of research stations require fossil fuel, which makes the region susceptible to localized oil contamination in areas of human activity (Martins *et al.*, 2004).

Aliphatic hydrocarbons (AHs) are an important class of organic compounds related to petroleum and fossil fuels, and hence can be associated with human activities conducted in the Antarctic region. Around 90 million litres of oil are used every year to support the activities of research stations (Cripps & Shears, 1997). N-alkanes are important constituents of AHs, and are presented in petroleum and by-products. It is also the predominant constituent of biogenic hydrocarbons and has been identified in many species of marine organisms, *e.g.* algae, diatoms and coccolithophorids (Matsueda & Handa, 1986).

The present study established the distribution of AHs in sediment cores from Admiralty Bay and Deception Island, in order to evaluate the temporal and local variations in the input and sources of these compounds during the last century.

Materials and Methods

Study area

Admiralty Bay (62°02' S, 58°21' W) is the largest bay in King George Island, in the South Shetland Islands (Figure 1). The bay covers around 122 km² and the mean depth is 199 m. The bay hosts scientific stations operated by Brazil, Poland, Peru, United States of America and Ecuador.

Deception Island (62°59' S, 60°34' W) (Figure 1), located at the southwestern of Bransfield Strait, Antarctica, is a young active volcano of the Quaternary age. The volcano contains a ring-shaped volcanic caldera 8–10 km in diameter (Cooper *et al.*, 1998), which has a maximum water depth

of about 160 m in its centre and exchanges water with the Bransfield Strait. The island hosts two research stations operated by Spain and Argentina and is visited by a large number of tourists every year.

Sampling

Sediment cores were collected using a box core sampler during the austral summer of 2007/2008, at four sites: Thomas Point (THP), Refuge II (REF), Botany Point (BOT), in Admiralty Bay, and Deception Island (DCP) (Figure 1). The cores were sub-sampled into sections of 1 cm.

Analytical Procedure

The analytical procedure used is described in Martins *et al.* (2004). Briefly, 15 g of sediment were extracted in a Soxhlet apparatus for eight hours with 80 mL of a

mixture dichloromethane (DCM) and n-hexane (1:1) and the surrogates eicosene and hexadecene. This extract was reduced to c. 2 mL by rotoevaporation and purified by column chromatography using 3.2 g of silica and 1.8 g of alumina (5% deactivated), and eluted by 10 mL of n-hexane. Sample extracts were concentrated to 0.5 mL and the internal standard tetradecene was added before gas chromatographic analysis. The AHs were determined by the injection of 2 μ L extract into a gas chromatograph equipped with a flame ionization detector (GC-FID).

Results

Figure 2 presents the levels of total AHs (Σ AHs) in the sediment cores along the estimated dates for the sections.

Figure 1. Sampling stations. (THP): Thomas Point, (REF): Refuge II, (BTP): Botany Point in Admiralty Bay, and (DCP) Deception Island.

Values of Σ AHs ranged from 3.18 (DCP, 4-5cm, 1980) to 25.5 $\mu\text{g.g}^{-1}$ (THP, 3-4cm, 1995). Range and mean concentration of total n-alkanes (Σ n-alk), from n-C₁₀ to n-C₄₀, and Σ AHs, in $\mu\text{g.g}^{-1}$ are given in Table 1.

Values of Σ n-alk ranged from 0.29 (DCP, 6-7 cm, 1968) to 9.90 $\mu\text{g.g}^{-1}$ (BTP, 0-1cm, 2005).

Discussion and Conclusion

The values of Σ AHs in the present study are close or slightly higher compared to concentrations found by Martins *et al.* (2004) (0.15 to 13.3 $\mu\text{g.g}^{-1}$). Highest values were found in the section corresponding to the 90's. In general, the concentration decreased in direction of the bottom core, related to the older sediments. This trend is compatible with a survey on hydrocarbon concentrations in Admiralty Bay over 15 years (Bícego *et al.*, 2009), that found that n-alkanes concentrations generally decreased

from 1989 to 1999 and then remained nearly constant. BTP was the exception to this trend. The unresolved complex mixture (UCM), used as an indicative of biodegradation (Brassell & Eglinton, 1980) corresponded to 54.2 to 95.4 % of the Σ AHs, and tended to increase towards the bottom section.

Similar values were found previously in Antarctic marine surficial sediments: 0.06 to 9.30 $\mu\text{g.g}^{-1}$ (Cripps, 1992), 0.10 to 9.63 $\mu\text{g.g}^{-1}$ (Martins *et al.*, 2004), and 0.36 to 2.24 $\mu\text{g.g}^{-1}$ (Green & Nichols, 1995). The assessment of sedimentary n-alkanes origin in the Antarctic environment is complex because the distribution pattern of n-alkanes in the marine biota and anthropogenic sources are similar, e.g., no predominance of odd/even n-alkane carbon number. The distribution of short and long chain n-alkanes may be a useful tool for the elucidation of the origin of hydrocarbons and has been used to distinguish between hydrocarbons

Figure 2. Temporal distribution of total aliphatic hydrocarbons in the sediment cores (in $\mu\text{g.g}^{-1}$ dry weight).

Table 1. Concentrations of Σ AHs and Σ n-alk in $\mu\text{g.g}^{-1}$ for the sediment cores.

	THP ^a		REF ^b		BTP ^c		DCP ^c	
	min - max	mean $\pm$ SD	min - max	mean $\pm$ SD	min - max	mean $\pm$ SD	min - max	mean $\pm$ SD
n-alk	0.29 - 0.72	0.49 $\pm$ 0.12	0.32 - 0.68	0.43 $\pm$ 0.12	0.42 - 9.89	1.54 $\pm$ 2.67	0.29 - 1.19	0.52 $\pm$ 0.25
AHs	14.4 - 25.5	19.4 $\pm$ 3.1	10.9 - 23.3	13.8 $\pm$ 3.6	3.89 - 22.4	8.25 $\pm$ 4.77	3.67 - 9.87	6.17 $\pm$ 1.80

^an = 9; ^bn = 10; ^cn = 11; min = minimum; max = maximum; SD = standard deviation.

from oil and biogenic sources (Martins *et al.*, 2004). Only BTP presented high proportions of $n\text{-C}_{27}$ to $n\text{-C}_{31}$, suggesting some oil input.

In conclusion, this study presented ΣAHs levels similar to those previously reported for the region. Slightly higher concentrations were observed in sections corresponding to the 90's, followed by a decrease towards more recent dates. The exception was the sample BTP, which presented an increase in n -alkanes and resolved hydrocarbons towards the surface and higher proportions of $n\text{-C}_{27}$ to $n\text{-C}_{31}$. The trend observed in this study is compatible with a survey on hydrocarbons concentration in Admiralty bay undertaken over 15 years that found that n -alkane concentrations generally decreased from 1989 to 1999 and then remained nearly constant.

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