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Baseline concentrations of faecal sterols and assessment of sewage input into different inlets of Admiralty Bay, King George Island, Antarctica

César C. Martins [a,*], Sabrina N. Aguiar [a,b], Edna Wisnieski [c], Liziane M.M. Ceschim [c], Rubens C.L. Figueira [d], Rosalinda C. Montone [d]

[a] Centro de Estudos do Mar, Universidade Federal do Paraná, Caixa Postal 61, 83255-976 Pontal do Paraná, PR, Brazil
[b] Departamento de Geoquímica, Universidade Federal Fluminense, Morro do Valonguinho s/n, Niterói, Rio de Janeiro, RJ, Brazil
[c] Programa de Pós-Graduação em Sistemas Costeiros e Oceânicos (PGSISCO) da Universidade Federal do Paraná, Caixa Postal 61, 83255-976 Pontal do Paraná, PR, Brazil
[d] Instituto Oceanográfico, Universidade de São Paulo, Praça do Oceanográfico, 191, 05508-120 São Paulo, SP, Brazil

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ABSTRACT

The Antarctic region is one of the best preserved environments in the world. However, human activities such as the input of sewage result in the alteration of this pristine site. We report baseline values of faecal sterols in Admiralty Bay, Antarctica. Four sediment cores were collected during the 2006/2007 austral summer at the Ezcurra (THP and BAR), Mackelar (REF) and Martel (BTP) inlets. Concentrations of faecal sterols (coprostanol + epicoprostanol) were <0.16 μg g^{-1}, suggesting no sewage contamination and probable "biogenic" contributions for these compounds. Baseline values, calculated using the mean concentration of faecal sterols in core layers for THP, BAR, REF and BTP, were 0.04 ± 0.02, 0.03 ± 0.01, 0.07 ± 0.01 and 0.04 ± 0.02 μg g^{-1}, respectively. These results established as natural contributions of faecal sterols, suggesting that these markers can be useful indicators of human-derived faecal input and contributing to monitoring programs to prevent anthropogenic impacts.

The Antarctic region is considered one of the best preserved environments in the world. The ecosystem is particularly sensitive to anthropogenic changes and is highly susceptible to human impact because of its remote location and weather conditions. Local sources of contamination in the Antarctic area include scientific activities, fuel usage, garbage incineration and sewage (Aronson et al., 2011; Cai et al., 2012). Due to this real existence of sewage input to the Antarctic marine waters and its probable anthropogenic impact, the monitoring of waste discharges is important to prevent contamination of the environment (Martins et al., 2012).

Organic markers such as faecal sterols (coprostanol and epicoprostanol) have been used to detect sewage inputs in Antarctica (e.g., Green and Nichols, 1995; Martins et al., 2002; Hughes and Thompson, 2004; Montone et al., 2010) as an alternative to faecal microorganisms due to their specific source, resistance to degradation processes and chemical stability under specific temperature and salinity conditions (Colombo et al., 1989; Wakeham et al., 1997).

Faecal sterols can be associated with the faeces of marine mammals (e.g., whales and seals) (Venkatesan and Mirsadeghi, 1992; Martins et al., 2005). In Antarctica, the input of sewage to coastal waters is less than that in subtropical/tropical regions due to the limited human population along Antarctic coasts. In contrast, the abundance of marine mammals, mainly seals, is quite high because several colonies are located in Antarctic coastal areas, contributing faecal sterols that can be classified as biogenic inputs.

The determination of baseline values of these organic markers in different Antarctic regions is important to provide information about natural sources of faecal sterols and to assess anthropogenic impacts, particularly for studies near established scientific stations. The sewage input from these stations may result in changes in the environmental conditions. The aim of this study was to determine baseline concentrations of faecal sterols based on the levels of these organic markers in four short sedimentary columns sampled at the Martel, Mackelar and Ezcurra inlets, where three research stations are established. In addition to the study published by Montone et al. (2010), this study provides baseline values of faecal sterols in the main inlets of Admiralty Bay, where the majority of research activities take place.

Admiralty Bay, situated on King George Island, is 131 km wide and is one of the largest bays in the South Shetland Islands (Fig. 1). Admiralty Bay hosts a number of research stations operated by Brazil, Poland, Peru, the United States of America and Ecuador. Human occupation in the bay is represented by the presence of three main stations and refuges in the three inlets (Bıcego et al., 2009). Martel Inlet is host to the Brazilian "Ferraz Station" and two refuges; Mackelar Inlet is the location of the

* Corresponding author. Tel./fax: +55 413511 8637.
E-mail address: ccmart@ufpr.br (C.C. Martins).

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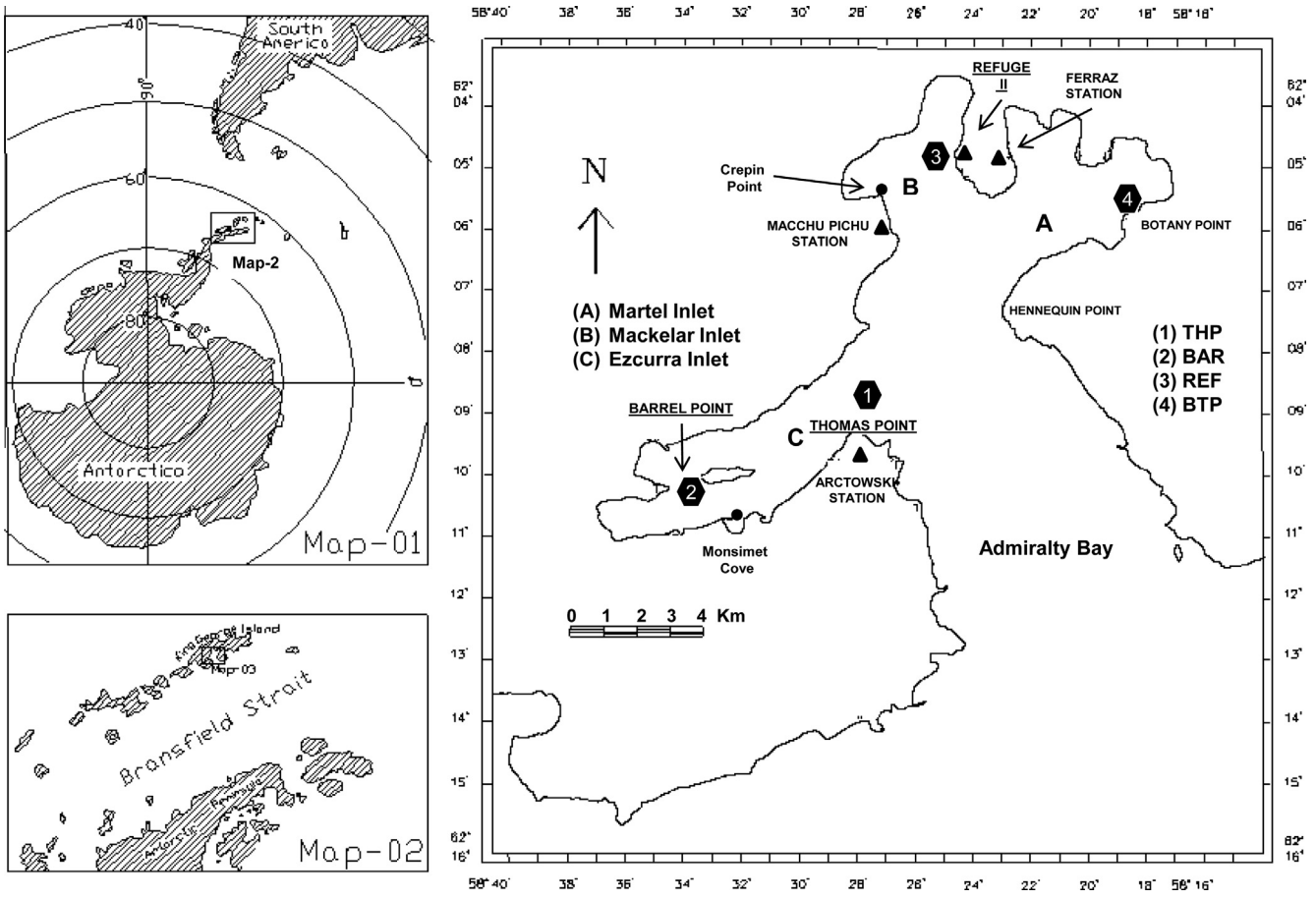

Fig. 1. Sampling stations at Admiralty Bay, King George Island, Antarctica. (1) Thomas Point (THP), (2) Barrel Point (BAR), (3) Refuge II (REF) and (4) Botany Point (BTP).

Peruvian "Machu Picchu" station, located near Crepin Point; and Ezcurra Inlet contains the Polish "Henryk Arctowski" station on the western side of Admiralty Bay (Martins et al., 2004). The area also receives several tourist and research vessels every year, which may contribute further to several types of organic contamination.

Two cores were collected in Ezcurra Inlet: one near Thomas Point (THP) and one near Barrel Point (BAR). Both cores were at a depth of 30 m. The third core was collected on the opposite border of the Peruvian station, near the Brazilian refuge (REF), at a 20 m depth, in the Mackelar Inlet. The fourth core was collected on the opposite face of the Brazilian station (BTP), at a 30 m depth, in Martel Inlet (Table 1, Fig. 1) between December 2006 and January 2007. Sediment samples were taken using a mini-box corer designed for sampling soft sediments. A set of aluminium tubes with a diameter of 25 mm was introduced into the box, and cores of approximately 20 cm were sampled and sectioned at 1 cm intervals. The samples were placed into pre-cleaned containers and stored at −20 °C. The sediments were freeze-dried and then carefully homogenised in a mortar and stored in clean glass bottles until laboratory analysis.

Faecal sterol analysis was based on a method described by Kawakami and Montone (2002). Briefly, more than 20 g of sediment from each core layer was extracted with 70 mL of ethanol using a Soxhlet system for 8 h. The surrogate 5α-cholestane was added before each extraction. The ethanol extract was reduced to approximately 2 mL by rotoevaporation. The concentrated ethanol extract was submitted to a clean-up using column chromatography with 2 g of 5% deactivated alumina and elution with 15 mL of ethanol. The extracts were evaporated to dryness and derivatised to form trimethylsilyl ethers using BSTFA (bis(trimethylsilyl)trifluoroacetamide) with 1% TMCS (trimethylchlorosilane) for 90 min at 65 °C.

The mixture of TMS sterol derivatives was analysed by the injection of 1 μL into an Agilent 6890 gas chromatograph equipped

Table 1
Sediment cores collected at Admiralty Bay, King George Island, Antarctica.

Site	Name	Latitude	Longitude	Depth (m)	Mean post-1963 sedimentation rate (cm y^{-1})
1	Thomas Point (TPH)	62°09.024′S	058°28.284′W	20	0.23 ± 0.03
2	Barrel Point (BAR)	62°10.274′S	058°35.504′W	30	0.33 ± 0.03
3	Refuge II (REF)	62°04.771′S	058°25.647′W	20	0.26 ± 0.03[a]
4	Botany Point (BTP)	62°05.841′S	058°20.320′W	30	0.28 ± 0.03

[a] Crepin Point.

Table 2
Concentrations of coprostanol, epicoprostanol and cholestanol, in μg g^{-1} dw, and coprostanol/epicoprostanol (I) and coprostanol/(coprostanol + cholestanol) (II) ratios in sediment cores (A: THP; B: BAR; C: REF; D: BTP) collected in Admiralty Bay, Antarctica.

Depth (cm)	Age	Coprostanol (μg g^{-1})	Epicoprostanol (μg g^{-1})	Cholestanol (μg g^{-1})	Coprostanol + epicoprostanol (μg g^{-1})	Ratio I	Ratio II
A							
0–1	2005	0.04	0.04	0.20	0.08	1.00	0.29
1–2	2000	0.03	0.02	0.18	0.05	1.50	0.22
2–3	1996	0.04	0.03	0.34	0.07	1.33	0.17
3–4	1992	0.02	0.01	0.26	0.03	2.00	0.10
4–5	1987	0.01	0.01	0.20	0.02	1.00	0.09
5–6	1983	0.01	0.01	0.14	0.02	1.00	0.13
7–8	1974	0.01	0.02	0.18	0.03	0.50	0.14
8–9	1970	0.02	0.01	0.19	0.03	2.00	0.14
9–10	1966	0.01	0.01	0.15	0.02	1.00	0.12
10–11	<1963	0.02	0.01	0.16	0.03	2.00	0.16
B							
0–1	2005	0.02	0.01	0.19	0.03	2.00	0.14
1–2	2002	0.01	0.02	0.29	0.03	0.50	0.09
2–4	1998	0.02	0.03	0.19	0.05	0.67	0.21
4–5	1993	0.01	0.02	0.20	0.03	0.50	0.13
5–6	1990	0.01	0.02	0.22	0.03	0.50	0.12
6–7	1987	0.01	0.01	0.15	0.02	1.00	0.12
7–8	1984	0.01	0.01	0.27	0.02	1.00	0.07
8–9	1981	0.01	0.02	0.21	0.03	0.50	0.13
10–11	1975	0.01	0.01	0.20	0.02	1.00	0.09
11–12	1972	0.01	0.02	0.09	0.03	0.50	0.25
12–13	1969	0.02	0.02	0.10	0.04	1.00	0.29
13–14	1966	0.02	0.02	0.10	0.04	1.00	0.29
14–16	<1963	0.01	0.01	0.06	0.02	1.00	0.25
C							
0–1	2005	0.04	0.04	0.39	0.08	1.00	0.17
1–2	2001	0.05	0.02	0.14	0.07	2.50	0.33
2–3	1997	0.03	0.04	0.24	0.07	0.75	0.23
3–4	1994	0.04	0.02	0.18	0.06	2.00	0.25
4–5	1990	0.04	0.04	0.30	0.08	1.00	0.21
6–7	1982	0.05	0.03	0.20	0.08	1.67	0.29
8–9	1974	0.06	<DL	0.71	0.06	nc	0.08
10–11	1967	0.05	0.02	0.33	0.07	2.50	0.18
11–12	1963	0.02	0.01	0.29	0.04	2.00	0.12
12–13	<1963	<DL	<DL	0.07	<DL	nc	nc
13–14	<1963	0.03	0.02	0.11	0.05	1.50	0.31
14–15	<1963	0.01	0.01	0.16	0.06	1.00	0.27
D							
0–1	2005	0.15	0.10	1.32	0.25	1.50	0.16
1–2	2002	0.11	0.09	0.89	0.20	1.22	0.18
2–3	1998	0.08	0.10	0.80	0.18	0.80	0.18
3–4	1995	0.04	0.04	0.49	0.08	1.00	0.14
4–5	1991	0.05	0.03	0.33	0.08	1.67	0.20
5–6	1987	0.03	0.02	0.41	0.05	1.50	0.11
6–7	1984	0.03	0.02	0.45	0.05	1.50	0.10
7–8	1980	0.04	0.02	0.33	0.06	2.00	0.15
8–9	1977	0.03	0.02	0.26	0.05	1.50	0.16
9–10	1973	0.02	0.01	0.28	0.03	2.00	0.10
10–11	1970	<DL	<DL	0.10	nc	nc	nc
11–12	1966	0.01	0.01	0.12	0.02	1.00	0.14
12–13	<1963	0.01	0.01	0.04	0.02	1.00	0.33
13–14	<1963	0.01	0.01	0.10	0.02	1.00	0.17
14–15	<1963	0.02	0.01	0.16	0.03	2.00	0.16

nc. not calculated; <DL: below detection limit (<0.01 μg g^{-1} dw).

with a flame ionisation detector (GC-FID) and a capillary fused silica column coated with 5% diphenyldimethylsiloxane (30 m, 0.32 mm ID and 0.25 μm film thickness). Hydrogen was used as the carrier gas. The oven temperature was programmed from 40 to 240 °C at 10 °C min^{-1}, then to 245 °C at 0.25 °C min^{-1} (holding for 5 min) and finally to 300 °C at 10 °C min^{-1} (holding for 5 min). Compounds were identified by matching retention times with results from standard mixtures of faecal sterols within the range of 0.25–10.0 ng μL^{-1}.

Procedural blanks were performed with each series of ten extractions, and no peaks interfered with the analyses of target compounds. The recovery of surrogates ranged from 50% to 130% (mean = 94.2 ± 16.0%). Additional details about the instrumental analysis and quality assurance results are presented in Montone et al. (2010).

For estimating the sedimentation rate, sediment samples (20 g) were counted for 90,000–120,000 s using a hyper-pure Ge detector (model GEM60190, by EGG&ORTEC) with a 1.9 keV resolution for the 1332.40 keV ^{60}Co peak. Cesium-137 activity was assayed by means of its peak at 661 keV (Figueira et al., 1998). The detailed method (calibration, detector counting efficiency and errors) was fully described in Martins et al. (2010a). International Atomic Energy Agency (IAEA) reference materials were employed to determine the detector counting efficiency in the radionuclide photopeak region. The estimated age for each section of the cores was based on the maximum activity of ^{137}Cs, corresponding to

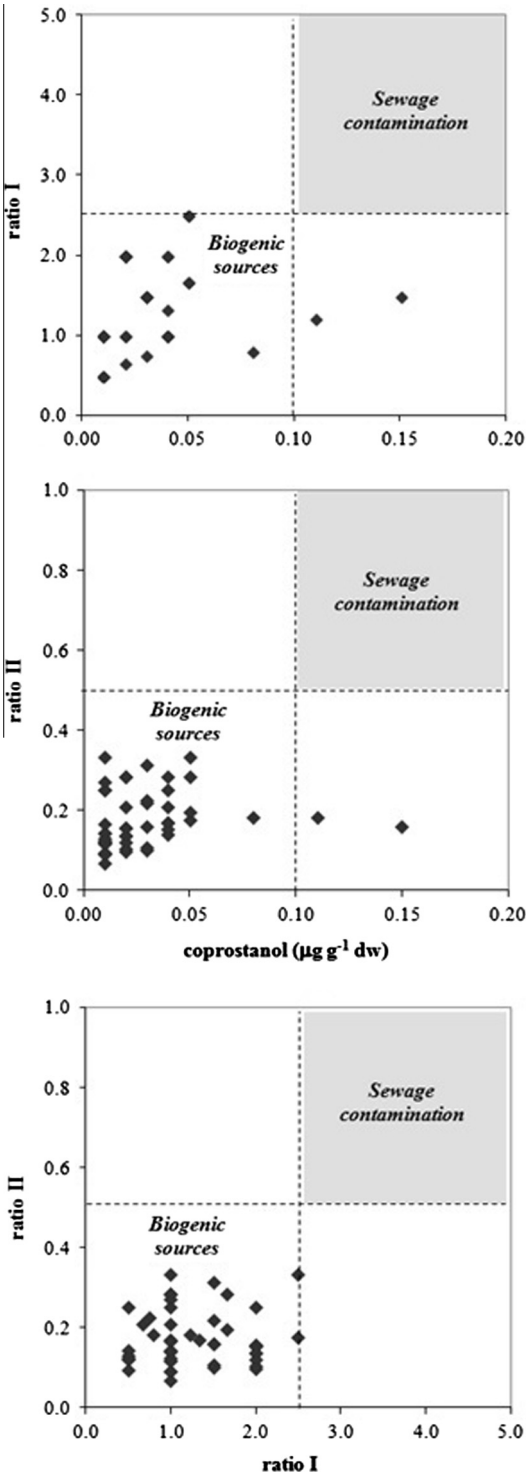

Fig. 2. Scatterplots of (a) coprostanol/epicoprostanol (ratio I), (b) coprostanol/(coprostanol + cholestanol) (ratio II) vs. coprostanol concentrations and (c) ratio I vs. ratio II, in sediments collected at Admiralty Bay, Antarctica.

1963–1965, the period of maximum fallout in the Southern Hemisphere due to atmospheric nuclear weapons testing (Abril, 2003). The sediment thickness between the depth of maximum ^{137}Cs activity and the core top was used to estimate the mean sedimentation rate for this period and these results were firstly presented by Martins et al. (2010b) and Ribeiro et al. (2011).

Based on the sedimentation rates (Table 1), the estimated dates for each section of the four examined cores were calculated using the following equation:

$$\text{estimated date} = a - (b/c) \quad (1)$$

where "estimated date" refers to the year of the section, "*a*" is the year in which the core was collected, "*b*" is the depth of the section in the core and "*c*" is the sedimentation rate of each core.

In the THP, the concentrations of coprostanol and epicoprostanol varied between 0.01 and 0.04 μg g^{-1} (mean value ± SD = 0.02 ± 0.01) and between 0.01 and 0.04 μg g^{-1} (mean value ± SD = 0.02 ± 0.01), respectively (Table 2). In the BAR, the concentrations of the faecal sterols were low, with values varying between 0.01 and 0.02 μg g^{-1} (mean value ± SD = 0.01 ± 0.01) (coprostanol) and between 0.01 and 0.03 μg g^{-1} (epicoprostanol) (mean value ± SD = 0.02 ± 0.01) (Table 2). As verified in THP and BAR, the faecal sterols were also present at low concentrations in REF. The coprostanol levels were between <DL (below the detection limit) and 0.06 μg g^{-1} (mean value ± SD = 0.04 ± 0.01), and the epicoprostanol values were between <DL and 0.04 μg g^{-1} (mean value ± SD = 0.03 ± 0.01) (Table 2). The concentrations of faecal sterols in BTP were slightly higher than those of the other sites, but only in the top 3 cm of the core (0.08–0.15 μg g^{-1} and 0.09–0.10 μg g^{-1} for coprostanol and epicoprostanol, respectively). For the middle and bottom sections of the core (>3 cm), the coprostanol levels varied between <DL and 0.05 μg g^{-1} (mean value ± SD = 0.03 ± 0.01), and the epicoprostanol varied between <DL and 0.04 μg g^{-1} (mean value ± SD = 0.02 ± 0.01), similar to the sediment cores sampled in the other inlets (Table 2).

González-Oreja and Saiz-Salinas (1998) proposed limits for coprostanol to define sewage contamination, with values below 0.50 μg g^{-1} indicating uncontaminated environments. In contrast, Writer et al. (1995) proposed that coprostanol levels above 0.10 μg g^{-1} should be associated positively with sewage input. These limits have been used to define sewage contamination in temperate and tropical/subtropical environments (Martins et al., 2008, 2011; Liebezeit and Wöstmann, 2010; Adnan et al., 2012). Despite the proximity of these sites to human activities, the probable biogenic input (although variations occurred throughout the sediment core profiles, the concentrations of coprostanol in all samples analysed were below the established limit) suggested no/low sewage input in these regions.

Coprostanol and epicoprostanol are found in sediments contaminated by sewage because they are associated primarily with human faeces (Grimalti et al., 1990). However, faeces of marine animals, such as certain species of whales, seals and sea lions, contribute large quantities of these compounds to the Antarctic environment (Venkatesan et al., 1986; Venkatesan and Santiago, 1989; Martins et al., 2002), and this contribution can be assumed to be biogenic.

To minimise the ambiguity of sources of these compounds, the use of numerical ratios involving faecal sterols is an important tool in the differentiation of the sources of faecal organic matter. Venkatesan and Santiago (1989) have proposed specific indices, such as the ratio between the concentrations of coprostanol and epicoprostanol (ratio I), to distinguish the places studied relative to the contribution of faecal sterols from human or marine mammals, specifically in the Antarctic environment. Values below 2.50 may indicate a natural contribution, whereas values above 2.50 and relatively high coprostanol concentrations (>0.10 μg g^{-1}) are strongly related to sewage input.

Sediments from the REF core did not exhibit ratio I values exceeding 2.50 (mean value ± SD = 1.59 ± 0.61), suggesting that the main source of sterols is marine mammals. The same tendency occurred in the sediment cores from Ezcurra Inlet (mean value ± SD = 1.33 ± 0.50 for THP and mean value ± SD = 0.86 ± 0.40 for BAR) and Martel Inlet (mean value ± SD = 1.41 ± 0.40 for BTP) (Table 2; Fig. 2).

The diagnostic ratio involving coprostanol and cholestanol (5α-cholestan-3β-ol) is usually considered in the assessment of sewage contamination (Grimalti et al., 1990). For instance, values for the coprostanol/(coprostanol + cholestanol) (ratio II) higher than 0.5 and relatively high coprostanol concentrations (>0.10 μg g^{-1}) indicate contamination by sewage (Leeming et al., 1998).

Sediments from the REF core showed values between 0.08 and 0.33 (mean value ± SD = 0.22 ± 0.08), and in the sediment cores from Ezcurra Inlet, the values for ratio II varied between 0.09 and 0.29 (mean value ± SD = 0.15 ± 0.06) and between 0.07 and 0.29 (mean value ± SD = 0.17 ± 0.07) for THP and BAR, respectively. In the BTP core, the values varied between 0.10 and 0.33 (mean value ± SD = 0.16 ± 0.06) (Table 2, Fig. 2).

The results of the calculation of these ratios showed that the source of sedimentary faecal sterols is mostly from biogenic contributions (Fig. 2), including the samples from the BTP top core, where the concentrations of coprostanol and epicoprostanol were slightly higher in comparison with other sites.

Based on the results obtained by ratios I and II and the coprostanol levels (<0.10 μg g^{-1}), baseline values can be determined to evaluate a hypothetical or future sewage input in these regions. The mean baseline concentrations for the sum of coprostanol and epicoprostanol are as follows: THP: 0.04 ± 0.02 μg g^{-1} (RSD = 19%); BAR: 0.03 ± 0.01 μg g^{-1} (RSD = 29%); REF: 0.07 ± 0.01 μg g^{-1} (RSD = 19%); and BTP: 0.04 ± 0.02 μg g^{-1} (RSD = 48%) (Fig. 3). The top 3 cm from the BTP core were not considered because the concentrations of faecal sterols were higher than 0.10 μg g^{-1}, and part of this value could be associated with sewage input from the Brazilian "Comandante Ferraz" station, located approximately 1.5 km from this site. In fact, these superficial sections in the BTP core cover the period after sewage input began in Martel Inlet (1998 ± 1 year).

In Martel Inlet, close to the "Comandante Ferraz" station, the values related to biogenic sources of faecal sterols (coprostanol + epicoprostanol) have been established as 0.19 μg g^{-1} (Montone et al., 2010). The present study found baseline values lower than the previous results, and these differing results can be attributed to the different environmental conditions of each inlet, essentially related to the proximity of the biogenic sources of faecal sterols, the sediment grain size and redox and hydrodynamic conditions that can reduce the accumulation and preservation of organic markers after deposition on the sea floor.

In addition, the apparent absence of faecal sterols arising from sewage input from Peruvian "Machu Picchu" and Polish "Henryk Arctowski" stations in Mackelar (REF) and Ezcurra (THP and BAR) Inlets, respectively, may be explained by the different methods for managing the sewage produced by these stations. For example, "Machu Picchu" station does not provide treatment for sewage effluent, and all wastes are removed offsite from the area of the Antarctic Treaty, whereas the Polish station primarily treats the sewage to process the effluents; the sewage is filtered, heated and bioenzyme treated. The resulting liquid is then discharged via the beach sand and gravel to the bay, whereas the solids are periodically removed from the septic tank and shipped to Poland (Tarasenko and Gilbert, 2008).

The concentrations of coprostanol in most core sections from the locations studied were <0.10 μg g^{-1}, suggesting biogenic sources of these compounds. This observation was corroborated by values found for the coprostanol/epicoprostanol ratio (<2.50) and coprostanol/(coprostanol + cholestanol) (<0.50) ratios for all sections of studied cores. The baseline values related to biogenic sources of faecal sterols (coprostanol + epicoprostanol) in the Mackelar (REF) and Ezcurra (THP and BAR) inlets were lower than the baseline values found in Martel (BTP) Inlet. Previous studies indicated the importance of defining specific baseline values for each inlet of Admiralty Bay due to the environmental particularities of the studied areas.

Despite the low concentrations of organic markers from sewage, including areas close to the stations (e.g., "Comandante Ferraz" and "Henry Arctowski" stations) that dispose of wastewater in the bay, the permanent human activities in the region require monitoring programs to determine continuing trends and to prevent the increase of anthropogenic impacts. This baseline

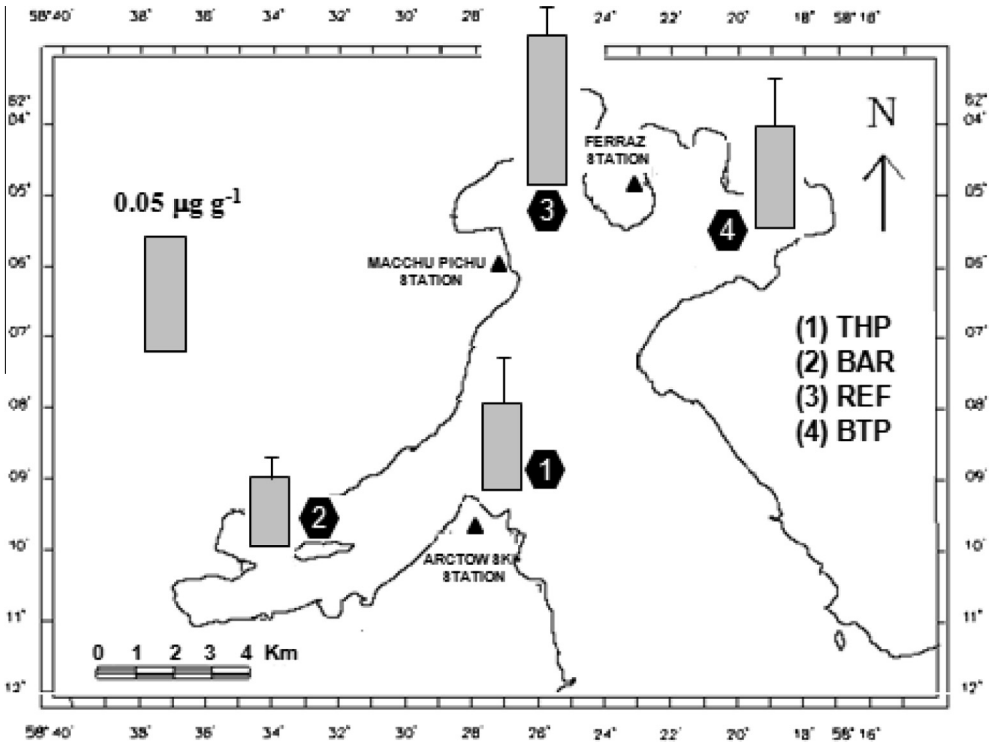

Fig. 3. Mean concentrations and standard deviations of faecal sterols, in μg tg^{-1} dw, in the sediments of Admiralty Bay.

information can be used for future evaluations of sewage inputs from stations established in the inlets studied.

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