Changes in the sedimentary organic carbon pool of a fertilized tropical estuary, Guanabara Bay, Brazil: an elemental, isotopic and molecular marker approach

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Abstract

Sediments from Guanabara Bay, sampled as short-cores (50–60 cm) from eight stations, were analysed for the elemental (C and N), isotopic (δ^{13}C and δ^{15}N) and molecular composition (steroids) of the organic matter. The objective of this study was to examine whether there are changes in the sources of sedimentary organic matter pool due to increasing N, P and particulate loads to the bay over the last 100 years. On average, we found a 10-fold increase in the flux of organic matter to the sediments with a maximum of 41.7 mol C m^{-2} $year^{-1}$

are well known. Less known are the effects on the cycling of organic matter in those ecosystems and the responses to the increased imbalance between natural (marine and terrestrial) and anthropogenic carbon.

The complex nature of estuaries derived from the hydrodynamics, the presence of strong physico-chemical gradients and intricate biological structure imposes difficulties in forecasting the extension of anthropogenic impacts. Multidisciplinary approaches, specific sampling strategies as well as multiple analytical tools and a variety of models have been used to tackle this problem. Investigations on the carbon cycle including, for instance, the identification of different sources and sinks, may require, in many cases, coupling information on the atomic (elemental and isotopic) and molecular composition of organic matter (Saliot et al., 1991; Summons, 1993; Saliot, 1994; Artemyev, 1996).

Guanabara Bay is an estuary located in the heart of the city of Rio de Janeiro. The alterations in the drainage basin initiated by the beginning of the 19th century led to severe environmental degradation, whose main consequences are eutrophic conditions, high sedimentation rates, elevated concentrations of toxic metals and hydrocarbons in sediments and changes in the pelagic and benthic communities (Villac et al., 1991; Hamacher, 1996; Lima, 1996; Ribeiro, 1996; Amador, 1997; Feema, 1998; Valentin et al., 1999; Carreira, 2000).

The bay is amongst the most productive marine ecosystems with an average net primary production (NPP) of 0.17 mol C m^{-2} day^{-1} (Rebello et al., 1988). The high productivity is supported by the availability of intensive sunlight and elevated temperatures throughout the year (range between 21.3 and 26.5 °C; Valentin et al., 1999), and by an estimated annual input of 3.2×10^9 mol P and 6.2×10^{10} mol N (Wagener, 1995) derived mainly from untreated sewage discharge. There is scarce information on the process of the primary production and little is known on limiting factors, although water turbidity seems to play an important role, and internal recycling of nutrients. The detailed annual input of carbon to the bay is also unknown.

Sedimentation rates in the bay changed dramatically in the course of the 20th century. Average sedimentation rates of 0.19 cm $year^{-1}$, existing prior to the middle of this century, were estimated from the average thickness of the sedimentary layer and from the stabilization of sea level in the last 3000 years (Amador, 1997). Sediment dating using ^{210}Pb gave actual sedimentation rates between 0.86 and 2.20 cm $year^{-1}$ (Lima, 1996; Moreira et al., 1997; Godoy et al., 1998a,b). The one order of magnitude change in sedimentation rate must have altered the accumulation rate and preservation of organic matter in the sediments of the bay similarly to other examples registered in the literature (Hedges and Keil, 1995; Ganesharam et al., 1999; Zimmerman and Canuel, 2000). Wagener (1995) demonstrated evidences of increasing organic carbon accumulation in sediments of Guanabara Bay due to a combined effect of N and P enrichment and fast sedimentation rates; nevertheless, no information was given on the nature of the organic material so far deposited.

In the present work, we use information on the elemental (C/N ratio), isotopic ($\delta^{13}C$ and $\delta^{15}N$) and molecular composition (sterols) of organic matter in the sediments of Guanabara Bay and nonparametric statistical tools to learn more about the qualitative and quantitative changes in the sources of organic carbon to the system. It is our goal to use our findings regarding changes in organic matter composition in this estuary to develop a general understanding of the effects of anthropogenic activities on organic matter cycling in tropical estuaries.

2. Materials and methods

2.1. Study area and sampling procedure

Guanabara Bay (see Fig. 1) is located between 22°40′–23°00′S latitude and 43°00′–43°18′W longitude and occupies an area of 346 km^2 with an average volume and depth of 2.2×10^9 km^3 and 7.7 m, respectively (Feema, 1998). The hydrographic basin extending over 4080 km^2 includes 45 rivers, 6 of which are responsible for 85% of the runoff (100 ± 59 m^3 s^{-1}). The mean half-water volume renewal time is 11.4 days, although in some parts of the bay, this time is significantly higher (Kjerfve et al., 1997 and references cited therein).

Temperature and salinity profiles show a well-mixed water condition at the entrance of the bay

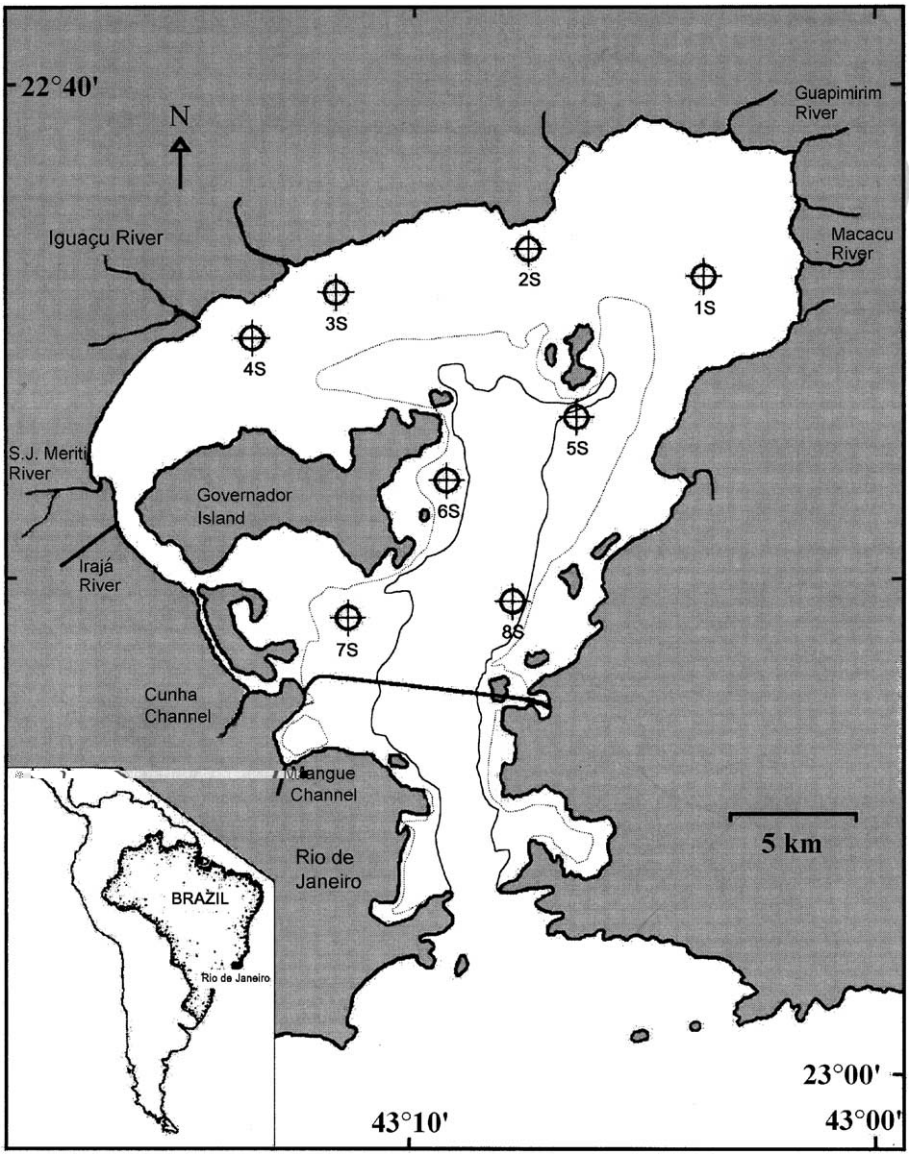

Fig. 1. Localization of Guanabara Bay and sediment sampling stations. Depth lines (dashed—5 m; solid—10 m) are based on Carta Náutica n. 1501.

extending up to 15–20 km inwards. Thereafter, the system is moderately stratified. A sandbank located at the ocean side of the bay entrance greatly influences the inner water circulation due to current channeling (Kjerfve et al., 1997).

The most prominent feature in the bay is the central channel with depths of 30–40 m and delimited by the 10-m depth isoline. Through this channel, sand is transported into the bay. The bottom topography is influenced by tidal currents that drain through the central channel, and by a strong sediment input. The enlargement subsequent to the entrance channel results in the decrease of tidal current velocities leading to the deposition of fine sands and mud.

Flocculation and deposition of clays derives also from the estuarine stratification. Continental mud is found in all this area up to the back of the bay (Quaresma, 1997). Increasing tidal velocities (up to 40 cm s^{-1} at ebby tides; JICA, 1994) along the channel that lies between Governador Island and the continent have strong influence in remobilization of sediments.

Sediments are comprised of sand, muddy sand, sandy mud and mud (Amador, 1992). Coarse sands are predominant in the central channel and in the regions near the bay mouth. Extensive mud deposits resulting from the active transport of clastic material and from the intensive primary production are found in the north area of the bay (Kjerfve et al., 1997). Here occurs the largest particulate concentrations (>22 mg l^{-1}) associated with the presence of mangroves and fluvial sources of sediments. Mangroves are very important sources of sediments in the northeast area. There are other isolated sources of high sediment inputs around in the bay margins.

A strong stratification of dissolved oxygen is observed, especially in areas where water depths are below 10 m. Surface $O_{2_{diss}}$ values can reach 300% oversaturation in the photic zone (~ 0.5 m) during light periods, while bottom (4–5 m) concentrations may be below 1 ml l^{-1}. After heavy rain or in periods of algae blooms, surface concentrations can also be very low (2 ml l^{-1}) (Rebello et al., 1988, 1990). Sediments in these areas are in general anoxic with a 2–3-cm nepheloid layer. Conditions as described favor a fast recycling of organic matter both by algae and bacterial respiration in the upper water layers and in the nepheloid sediment zone.

We selected eight sampling stations distributed as to reflect different external sources of organic matter and circulation pattern in the bay (Table 1). Sediment cores (ca. 60–70 cm length) were collected from those sites in June–July 1996 with the aid of a gravity corer fitted with internal aluminum liners. The cores were sliced (0–3 cm and at each 10–15 cm thereafter) under nitrogen atmosphere in a glove box originating 52 subsamples that were freeze-dried and ground before storage at −20 °C. Fresh sediment aliquots were used for determination of dry weight at 105 °C, grain size by sieving (fraction larger and smaller than 63 μm) and carbonate content (acid treatment). All results were corrected for carbonate content and are expressed relative to bulk sediment and on a dry-weight basis.

Table 1
Sampling locations and local water depth

Station	Latitude (S)	Longitude (W)	Depth (m)
1s	22°43.7′	43°04.3′	2.0
2s	22°43.5′	43°07.7′	2.6
3s	22°44.2′	43°11.4′	2.0
4s	22°45.5′	43°13.2′	1.8
5s	22°46.9′	43°06.7′	8.0
6s	22°48.3′	43°09.6′	6.2
7s	22°51.1′	43°11.6′	6.3
8s	22°50.7′	43°08.0′	12.9

Water samples were collected in some of the rivers of the drainage basin. Samples were taken from below surface, during low-tide stand, avoiding areas influenced by saline waters. Particulate matter was separated by filtration through 0.7-μm glass fiber filters (pre-heated at 450 °C) and treated with HCl vapors for determination of isotopic ratios of carbon and nitrogen in organic matter.

2.2. Analytical methods

2.2.1. Elemental composition

Total organic carbon (TOC) and total nitrogen (TN) were determined in 2–5 mg sediment samples, using a Carlo Erba EA 1110 analyzer. Inorganic carbon was removed prior to the analyses with hydrochloric acid. Quantification was performed by calibration curves and using cystine as standard. Reference material MESS-2 (National Research Council of Canada) was used to verify accuracy. Analytical precision was ± 1.7% for TOC and ± 2.8% for TN, while detection limits were ± 0.05 mmol g^{-1} for TOC and ± 0.007 mmol g^{-1} for TN.

2.2.2. Isotope analysis

The samples of filters and sediments were acidified to remove carbonate and dried. The carbonate-free residues were weighed in tin capsules and converted to CO_2 and N_2 for isotope analysis using a Carlo Erba elemental analyzer (EA) which is coupled to an OPTIMA stable isotope ratio mass spectrometer (Micromass, Manchester, UK). Carbon and nitrogen isotopes were determined with a single combustion using a dual furnace system composed of an oxidation

furnace at 1020 °C and a reduction furnace at 650 °C. The resulting gases are chemically dried and directly injected into the source of the mass spectrometer. The stable isotopic ratio is reported as follows:

$$\delta^N\mathrm{E} = [R_{\mathrm{sample}}/R_{\mathrm{standard}} - 1] \times 10^3 (‰)$$

where N is the heavy isotope of the element E and R is the abundance ratio of the heavy to light isotopes ($^{13}C/^{12}C$, $^{15}N/^{14}N$) of that element. The standard for carbon is the Peedee Belemnite limestone (PDB) and for nitrogen, the standard is atmospheric N_2 (air), which are assigned δ^NE values of 0.0‰. For carbon, the value is corrected for the mass overlap with the isotopes of oxygen. The reproducibility of the measurement is typically better than ±0.2‰ for these elements using the continuous flow interface on the OPTIMA. In the laboratory, the samples are commonly measured against tanks of carbon dioxide and nitrogen gases, which have been calibrated against NBS 22 and atmospheric N_2, respectively.

2.2.3. Sterols

The methods used for extraction and purification are adapted from procedures found in the literature (Readman et al., 1986, 1989; Canuel and Martens, 1993; Yunker et al., 1995). Prior to extraction, 5α-androstan-3β-ol was added to aliquots of 5–10 g of dry sediment as internal standard and equilibrated for 24 h under refrigeration. Samples were Soxhlet extracted with 200 ml of a mixture of dichloromethane and methanol (2:1) for 24 h. The bulk lipid extract was filtered through ashed (450 °C) glass wool in a separatory funnel and washed with a saturated solution of NaCl. The lower nonpolar (dichloromethane) fraction was isolated and the polar (methanol/water) fraction was re-extracted with 3 × 10-ml portions of *n*-hexane. The hexane and dichloromethane fractions were combined and rotary evaporated to about 1 ml at low (30–40 °C) temperature. The 1-ml extracts were passed through small glass columns packed with activated copper (3 M HCl for half hour) and sodium sulphate to remove sulfur and residual water, respectively. Additional sodium sulphate was added to the flask to further dry the extract overnight.

The steroids and other polar compounds were isolated by adsorption chromatography according to the procedure given by Yunker et al. (1995). A glass column (1.2 cm i.d., 25 cm height) was slurry packed with silica gel (5 g, 230–400 mesh, 5% water deactivated) and 1 cm of sodium sulphate (top). The concentrated extract (1 ml) was carefully added to the top of the column and three fractions were isolated: 12 ml of *n*-hexane (F1), 24 ml of *n*-hexane/dichloromethane (1:1, v/v) (F2) and 24 ml of 10% methanol in dichloromethane (F3—sterols and polar compounds). Only data for the F3 fraction will be considered in this paper. This fraction was vacuum evaporated, concentrated by a gentle stream of purified N_2 and stored at −20 °C until analysis by gas chromatography–mass spectrometry (GC/MS).

Quantitative analysis of 1-μl sample aliquots was performed using a Hewlett Packard 5890 gas chromatograph fitted with a splitless injector and an HP5972 mass-selective detector. An HP-5MS (low bleed 5% phenyl methyl siloxane) capillary column of 30 m × 0.25 mm i.d. (0.25 μm film thickness) was used and helium carrier gas was maintained at a constant flow rate of 1 ml min^{-1}. The column temperature was programmed from an initial 1-min hold at 60 to 250 °C at 15 °C min^{-1} and then from 250 to 300 °C at 1 °C min^{-1}, with a final hold of 5 min. The MS transfer line temperature was set to 300 °C (which gives an ion source temperature of about 165 °C). Prior to injection, the steroids were derivatized to their trimethylsilyl (TMS) ether derivative with bis(trimethylsilyl)trifluoroacetamide (BSTFA) at 80 °C for 1 h.

Authentic standards of androstanol (internal standard), cholesterol, cholestanol, campesterol, stigmasterol, ergosterol and β-sitosterol were obtained from Sigma-Aldrich, Poole, UK. All standards were greater than 98% pure. Standard solutions of all the steroids and the internal standard were analysed to confirm identity, to obtain selected ion monitoring (SIM) ions and to check linearity of response. Relative response factors were calculated for all the steroids with respect to the internal standard, androstanol. Throughout the study, standard solutions ranging from 55 to 128 ng μl^{-1} for all sterols were analysed daily to check the instrumental performance (response factors) and the chromatographic behaviour (retention times, peak shape and separation) of the standard mixture. Samples were routinely screened using SIM with molecular ions, base peak ions and/or other diagnostic ions. All data were subject to strict quality control proce-

Table 2
Elemental and isotopic composition of organic matter and sterol concentration of sediments from Guanabara Bay

Station	Legend	Mean depth (cm)	C_{org} (mmol g^{-1})	N_{total} (mmol g^{-1})	C/N ratio (molar)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	Cholesterol (μg g^{-1})	Cholestanol (μg g^{-1})	Campesterol (μg g^{-1})	Stigmasterol (μg g^{-1})	β-sitosterol (μg g^{-1})	Dinosterol (μg g^{-1})
1s	1	1.5	2.43	0.181	13.3	−23.7	7.6	1.41	2.01	0.83	1.06	2.84	20.4
	2	6.5	2.52	0.166	15.1	−24.2	6.7	0.54	0.97	0.39	0.66	1.96	14.6
	3	13.0	2.26	0.162	13.9	−24.0	7.3	0.46	0.74	0.29	0.45	1.36	12.1
	4	19.5	2.32	0.198	11.6	−22.9	7.0	0.54	0.87	0.34	0.53	1.59	14.1
	5	30.5	2.44	0.178	13.6	−22.9	6.9	0.39	0.57	0.20	0.34	1.13	12.5
	6	45.5	2.82	0.184	15.2	−24.2	6.4	0.43	0.47	0.36	0.56	1.74	11.1
	7	60.5	2.87	0.187	15.3	−23.9	4.6	0.45	0.57	0.37	0.62	1.97	15.4
2s	1	1.5	4.62	0.410	11.2	−20.7	7.8	5.28	8.93	5.00	4.43	13.4	153.3
	2	6.5	3.31	0.289	11.4	−20.1	8.0	1.81	2.98	1.42	2.03	6.46	63.8
	3	13.0	2.10	0.167	12.4	−20.4	6.1	0.45	0.88	0.33	0.60	1.44	20.5
	4	19.5	1.60	0.118	13.4	−21.6	7.3	0.19	0.22	0.09	0.14	0.34	2.89
	5	30.5	1.96	0.141	13.9	−21.8	7.5	0.12	0.15	0.05	0.09	0.20	1.25
	6	45.5	1.54	0.114	13.4	−21.0	7.4	0.10	0.11	0.03	0.06	0.13	0.41
3s	1	1.5	3.14	0.239	13.1	−22.3	5.9	4.41	7.80	2.90	2.80	4.59	38.6
	2	6.5	2.64	0.178	14.8	−22.8	7.1	0.55	1.29	0.40	0.71	1.40	10.6
	3	13.0	1.71	0.101	16.8	−22.8	5.8	0.35	0.70	0.23	0.44	1.08	8.80
	4	19.5	1.70	0.106	15.9	−23.4	7.3	0.22	0.28	0.13	0.32	0.91	4.83
	5	30.5	1.47	0.116	12.6	−22.3	6.6	0.25	0.28	0.16	0.34	0.83	4.76
	6	45.5	1.75	0.110	15.9	−22.6	6.4	0.40	0.32	0.16	0.39	0.79	6.21
4s	1	1.5	2.36	0.172	13.6	−22.5	5.9	7.80	7.54	2.33	1.88	2.07	12.48
	2	6.5	2.12	0.137	15.4	−23.7	5.9	1.33	3.72	0.46	0.83	1.36	5.10
	3	13.0	2.05	0.151	13.5	−23.4	5.0	1.41	2.38	0.24	0.54	0.85	5.99
	4	19.5	2.38	0.157	15.1	−23.9	5.4	0.67	2.43	0.25	0.52	0.78	6.14
	5	30.5	2.11	0.120	17.5	−23.3	6.4	0.34	0.98	0.12	0.31	0.54	4.07
	6	45.5	1.61	0.103	15.6	−23.3	5.2	0.21	2.39	0.09	0.32	0.70	4.99
	7	60.5	1.88	0.149	12.5	−23.1	7.4	0.19	0.43	0.09	0.28	0.57	2.82
	8	72.0	1.68	0.096	17.5	−24.3	7.0	0.32	7.71	0.11	0.36	0.72	4.06

5s	1	1.5	2.90	0.284	10.2	− 20.8	6.6	3.57	6.51	2.16	1.07	4.04	38.9
	2	6.5	2.78	0.266	10.4	− 20.0	7.0	0.79	1.98	0.53	0.34	1.77	25.4
	3	13.0	2.83	0.248	11.4	− 20.6	7.0	0.76	1.17	0.38	0.51	1.22	18.5
	4	19.5	2.34	0.200	11.7	− 21.1	7.8	0.55	0.78	0.24	0.38	0.93	14.8
	5	30.5	2.21	0.246	9.0	− 22.3	6.9	0.37	0.52	0.16	0.25	0.62	9.84
	6	45.5	1.70	0.124	13.7	− 19.3	5.7	0.23	0.31	0.08	0.18	0.47	6.37
6s	1	1.5	3.37	0.232	14.4	− 24.6	6.2	6.38	9.77	3.30	2.67	4.64	55.5
	2	6.5	2.97	0.202	14.6	− 23.0	6.7	1.44	2.78	0.75	0.75	1.56	40.1
	3	13.0	2.97	0.223	13.2	− 21.9	7.0	1.24	1.74	0.55	0.62	1.66	25.7
	4	19.5	2.62	0.200	13.0	− 21.5	7.2	0.99	1.19	0.43	0.60	1.66	15.3
	5	30.5	2.08	0.118	17.5	− 24.0	8.3	0.58	0.72	0.26	0.38	1.18	11.3
	6	45.5	1.66	0.058	28.6	− 29.5	7.4	0.24	0.32	0.10	0.20	0.55	5.72
	7	60.5	1.03	0.030	34.3	− 33.7	6.1	0.17	0.19	0.05	0.11	0.32	2.62
7s	1	1.5	3.98	0.392	10.1	− 21.2	6.0	5.02	10.9	2.61	2.57	4.74	52.6
	2	6.5	3.75	0.339	11.1	− 21.2	6.0	1.92	5.84	1.03	1.35	2.64	36.9
	3	13.0	2.88	0.231	12.4	− 21.3	7.0	1.11	2.96	0.51	0.65	1.61	25.9
	4	19.5	2.57	0.186	13.7	− 21.9	8.3	0.69	0.79	0.17	0.25	0.75	12.4
	5	30.5	2.06	0.146	14.1	− 21.9	7.8	0.37	0.49	0.14	0.19	0.48	8.54
	6	40.0	1.61	0.106	15.0	− 22.0	7.7	0.28	0.25	0.07	0.11	0.27	3.03
8s	1	1.5	2.69	0.266	10.1	− 19.9	6.6	8.43	9.36	4.24	3.10	n.d.	29.8
	2	6.5	2.93	0.270	10.8	− 21.7	8.1	2.13	3.83	1.51	1.13	2.29	22.8
	3	13.0	2.98	0.293	10.1	− 21.9	6.4	3.25	7.40	2.08	2.00	4.07	39.6
	4	19.5	2.72	0.228	11.9	− 23.0	7.4	1.40	3.72	0.97	0.86	2.04	22.5
	5	30.5	2.96	0.272	10.8	− 22.2	7.2	1.36	3.65	0.91	0.76	2.33	28.4
	6	47.0	3.14	0.234	13.3	− 22.8	7.1	1.23	3.06	0.80	0.72	1.99	29.1

Obs.: n.d. = not determined.

dures that included the analysis of spiked samples and blanks with each batch of samples analysed. Full-scan GC/MS analyses were carried out on selected samples to confirm peak identities and purity.

2.3. Statistical analyses

Factor analysis was performed as an exploratory analysis for the data set obtained (Meglen, 1992; Salau et al., 1997). We considered the data for elemental and isotopic composition of organic matter and sterols (as μg g^{-1} of dry sediment) for the 47 samples (5 samples were disregarded because they gave extreme results for some parameters that could influence in the final statistical analyses). All data were normalized (autoscaled) using mean values and standard deviations. Quartimax rotation with Kaiser normalization was selected to represent the planar projection of the three first principal component obtained by factor analysis.

3. Results and discussion

3.1. Elemental composition and flux of organic matter to the sediments

Mean total organic carbon (TOC) and total nitrogen (TN) contents (relative to the bulk sediment) are equal to 2.44 ± 0.69 mmol C g^{-1} and 0.189 ± 0.078 mmol N g^{-1}, respectively (Table 2).

TOC and TN are highly correlated ($r = 0.91$, $n = 52$, $p < 0.001$). Two processes can principally lead to this, as extensive degradation processes occurring already in the water column or an even and constant contribution from different carbon sources (Ruttenberg and Goñi, 1997). This point will be discussed below. As a result from the correlation, the overall mean C/N molar ratio (14.0 ± 4.0) is also rather constant except in the lower sections of core 6s where C/N values reached a maximum of 34.3 (Table 2).

Spatial distribution of TOC (Fig. 2) and TN concentrations in very recent layers is consistent with the most probable sources (terrestrial and/or marine) of organic matter. There are similar features in depth profiles that, however, derive from distinct process. For example, stations 1s and 4s show constant TOC and TN values with depth but in the former case, the even distribution results from the absence of major environment disturbances. In station 4s, a heavily polluted site that receives discharge of waters with more than 130 tons BOD day^{-1} (around 30% of the total estimated for the entire bay; JICA, 1994), 'dilution' caused by increasing load of inorganic particulates is most likely shaping the profile. This may result from the increase in the sedimentation rates around station 4s over the last 50 years (from 0.15 to 2.2 cm $year^{-1}$; Godoy et al., 1998a) due to deforestation and soil management. The same process may explain the results from station 8s. Stations 3s, 6s and 7s seem to be under influence of the general increasing eutrophication level in the bay over the last decades (Feema, 1998).

Station 2s appears as a site of intensive deposition of autochthonous material (as will be discussed later) and the threefold increase in TOC and TN observed for the period between 1983 and 1995 most likely results from increases in autochthonous production. Rebello et al. (1988) measured average fixation rates of more than 0.17 mol C m^{-2} day^{-1} with peak values of 0.83 mol C m^{-2} day^{-1} in this area which are supported by high nutrient concentration and good water circulation.

TOC and TN flux to the sediments were calculated accordingly to Berner (1980), assuming a mean sediment density of 2.65 g cm^{-3}, using known sedimentation rates for Guanabara Bay (Lima, 1996; Godoy et al., 1998a) and correcting for sediment porosity. The results point out a dramatic increase in the fluxes over the present century. We assume that values for the beginning of this century are good estimates of the 'background' fluxes, which were equal to 4.2 mol C m^{-2} $year^{-1}$ and 0.18 mol N m^{-2} $year^{-1}$, respectively. From that period, anthropogenic activities in Guanabara Bay especially intensified during the last three decades, leading to an increased rate of organic matter accumulation in some areas, principally due to increasing sedimentation rates. Evidence for this is found at stations 4s and 7s. At station 4s, where sedimentation increased by a factor of 10 during the last 50 years, the concentration of organic carbon is rather constant along the core but fluxes are as high as 41.7 mol C m^{-2} $year^{-1}$ (Fig. 2). At station 7s, carbon concentrations increased twofold in the same period but due to the constant sedimentation rates (0.49 cm $year^{-1}$; Godoy et al., 1998a), these fluxes

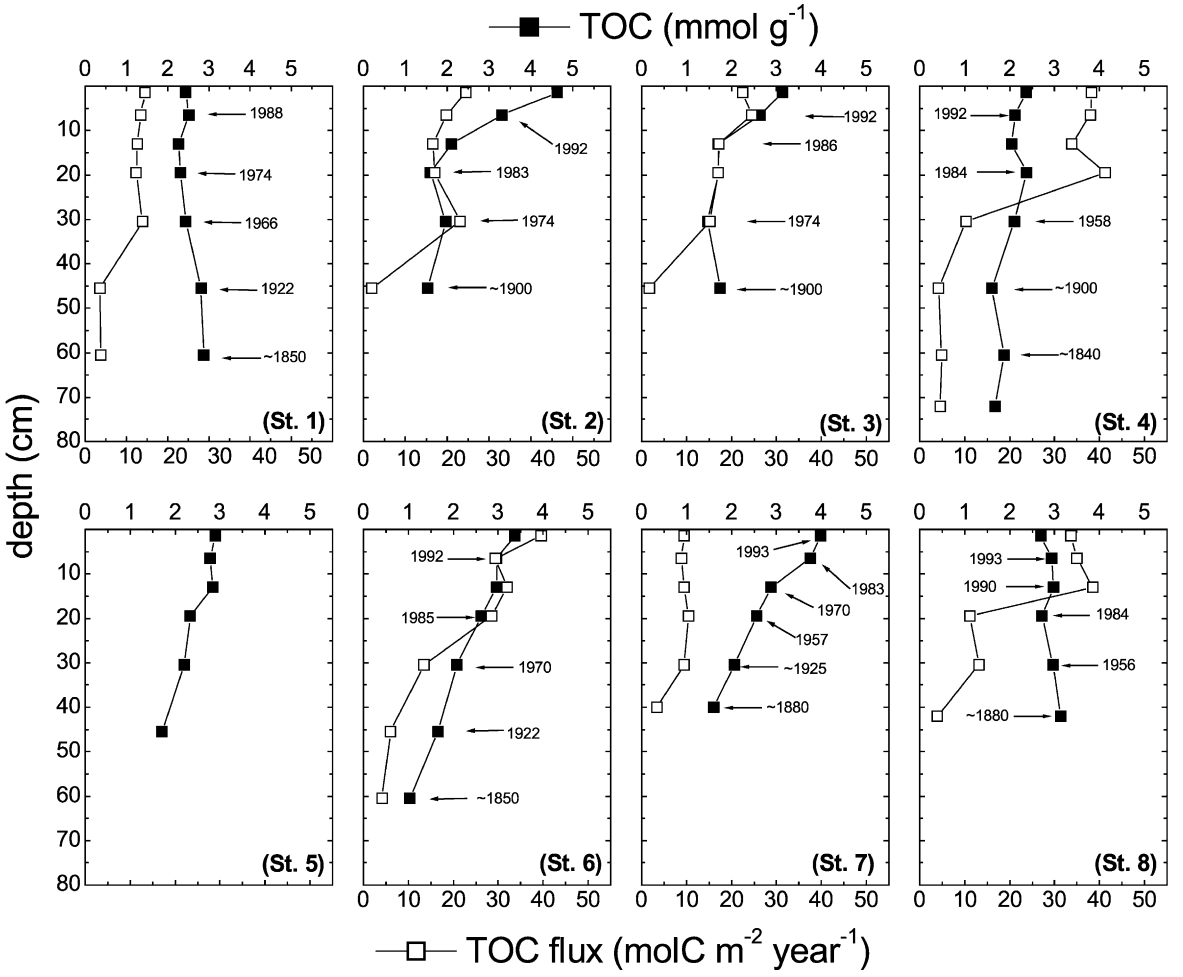

Fig. 2. Total organic carbon (TOC) concentration (full squares) and flux (open squares) to the sediments of Guanabara Bay. The mean period of sediment deposition is indicated for each sediment layer accordingly to known sedimentation rates (Lima, 1996; Godoy et al., 1998a,b), except for station 5s.

remained relatively constant over the last 80 years (8.3–12.5 mol C m^{-2} $year^{-1}$).

3.2. Isotopic composition ($\delta^{13}C$ and $\delta^{15}N$)

A wide range of $\delta^{13}C$ (Table 2) was observed that included values typical of marine plankton and those characteristic of freshwater algae and terrestrial C_3 plants (Sackett, 1986; Stein, 1991; Macko et al., 1993; Meyers, 1994, 1997). In stations 1s, 3s and 4s, $\delta^{13}C$ more negative than -22.3‰ may be related to the preferential deposition of organic matter from external sources (natural or anthropogenic). At station 2s ($\delta^{13}C = -20.8 \pm 0.7$‰) as well as at stations 5s, 7s and 8s, located near the central area of the bay (average $\delta^{13}C = -21.4 \pm 0.9$‰) where salinities are typical of seawater, organic matter is enriched in ^{13}C. Depletion in ^{13}C was observed in core samples from station 6s at depths below 30 cm (-29.5‰ and -33.7‰). In the intermediate layers of this core, $\delta^{13}C$ is in the range of -21.5‰ to -21.9‰, but in the upper layers, it becomes again depleted reaching a minimum value of -24.6‰ (0–3 cm). This may be due to contamination with petroleum residues from a nearby oil terminal as proved by means of specific PAH analyses (Lima, 1996).

As shown in Fig. 3, stations can be grouped in two sets (inner and central sites) according to the $\delta^{13}C$ and C/N values ($r = -0.68$, $n = 50$, $p < 0.001$). Organic matter from sites in the central areas of the bay (stations 2s, 5s, 7s and 8s) is low in C/N and enriched in ^{13}C as compared to the inner bay sites (stations 1s, 3s, 4s and 6s). Analysis of variance proved that the two sets of data are significantly different. Both the isotopic signature and the C/N ratio indicate the predominance of autochthonous sources of organic matter in the former group.

The sewage influence on both ratios should be negligible. This conclusion is based on previous observations (Carreira and Wagener, 1998) that show that due to the usually high temperatures, sewage material is extensively decomposed before reaching the marine environment. Contaminated rivers, channels and sewage tubing are effective bio-digesters at the local conditions. Primary producers and bacteria in the water column rapidly utilize the mineralized material leading to the deposition of organic matter predominantly of autochthonous signature.

The fate of the residual sewage material that may have resisted decomposition can be evaluated through the distribution of coprostanol, a fecal sterol (Carreira, 2000; Carreira et al., 2001). Sewage input to the bay has been steadily increasing since the 1950s particularly in the areas surrounding stations 4s, 6s, 7s, 8s and, to a lesser extent, at station 3s. The mean concentration of coprostanol in the upper sediment layer (0–3 cm) of these contaminated sites is 6.6 ± 2.7 μg g^{-1}, excluding the maximum of 40 μg g^{-1} observed at station 4s. Considering the fecal sterol distribution and the data showed in Fig. 3, it seems that only at stations 4s and 3s the $\delta^{13}C$ and C/N ratios could be somewhat influenced by sewage deposition. In the other stations (6s, 7s and 8s), the presence of autochthonous organic matter overwhelms the sewage signal in the sediment.

$\delta^{15}N$ values ranged between 4.6‰ and 8.3‰ (average 6.8‰) and did not show any obvious pat-

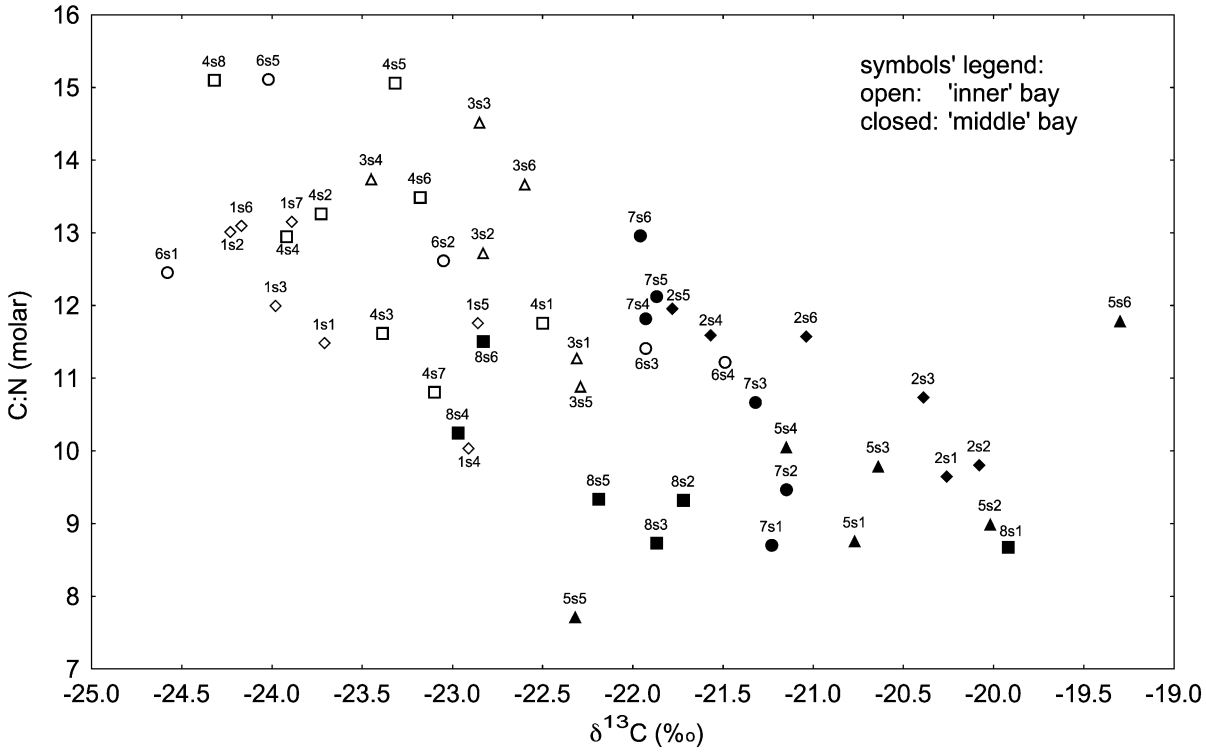

Fig. 3. Plot of C/N (molar) vs. $\delta^{13}C$ (‰). Legends are the same as in Table 2.

terns of distribution nor significant correlation between $\delta^{13}C$ ($r = -0.18$; $p = 0.19$) or C/N ratios ($r = -0.14$; $p = 0.29$). The average value of 6.8 ± 0.8 ‰ ($n = 52$, see Table 2) is comparable to those given for coastal sediments from Southeast Brazil collected from uncontaminated areas (Matsuura and Wada, 1994). $\delta^{15}N$ values reported for estuarine sediments cover a very wide range from 5.9 ‰ (Thornton and Mcmanus, 1994) to 15.0 ‰ (Middelburg and Nieuwenhuize, 1998) because of the large number of possible fractionation processes related to ammonification, nitrification, denitrification and nutrient assimilation reactions. The complexity of nitrogen cycling does not yet allow the straightforward use of $\delta^{15}N$ as an unambiguous indicator of organic matter origin. There was no correlation between $\delta^{15}N$ and C/N ratios. Therefore, in our study, contrary to $\delta^{13}C$, the time–space distribution of $\delta^{15}N$ values gave no additional information on sources contributing to the carbon pool at each observed station.

In Table 3, the results for a single survey in some of the rivers around Guanabara Bay are shown. Although these data are limited and reflect specific conditions at the time of collection (productivity of the riverine waters, dry/wet period, among others), for the least contaminated rivers (Guapimirim and Macacu rivers) $\delta^{13}C$ values more depleted than -25.75 ‰ are in the range expected for terrestrial C_3 plants and freshwater algae (Macko et al., 1993; Meyers, 1994). For most of the contaminated rivers (São João de Meriti and Irajá rivers and Cunha channel), the particulate organic matter is relatively enriched in ^{13}C compared to the raw sewage typically discharged to Rio de Janeiro coastal waters ($\delta^{13}C$ of -24.2 ‰; Carreira and Wagener, 1998). This might be explained by the presence of autochthonous sources of organic matter in these rivers but we cannot rule out the influence of estuarine material at these sampling points. In the remaining contaminated rivers (Iguaçu river and Mangue channel), the $\delta^{13}C$ values (-22.0 ± 0.5 ‰ and -23.6 ± 0.1 ‰, respectively) are typical of sewage-enriched particulate organic matter.

Similar to carbon, $\delta^{15}N$ values in the particulate material were significantly different in contaminated and uncontaminated rivers (Table 3). In the unpolluted Guapimirim and Macacu rivers, $\delta^{15}N$ values between 4.9 ‰ and 5.1 ‰ were found which are in the expected range for terrestrial organic material (Fogel and Cifuentes, 1993). $\delta^{15}N$ in the material from the other rivers were much lower, showing small variations between 0.4 ‰ and 2.0 ‰. Such values could result from atmospheric N fixation by cyanobacteria (Fogel and Cifuentes, 1993), major algae groups in Guanabara Bay (Villac, 1990; Valentin et al., 1999) and/or from raw sewage discharges (typical $\delta^{15}N$ of +2–3 ‰; Sweeney et al., 1980).

3.3. Sterols

The sterol concentration profiles (TOC normalized) shown in Figs. 4–6, excluding the fecal sterols (which were published elsewhere; Carreira, 2000; Carreira et al., 2001) are remarkably similar for almost all compounds, excluding dinosterol and β-sitosterol in station 2s, 4s and 6s. Parent compounds as, for example, cholesterol and its degradation product (cholestanol) present similar depth variation, in opposition to the expected negative correlation between their concentrations. There is a general tendency to increasing cholesterol/cholestanol ratio

Table 3
Isotopic composition ($\delta^{13}C$ and $\delta^{15}N$) for particulate matter collected in selected rivers from Guanabara bay catchment area. The water quality levels are based on the monitoring programs conducted by local environmental agency (Feema, 1998). $\delta^{13}C$ and $\delta^{15}N$ are expressed as mean values for two separate samples collected on each site

Sampling point	Water quality level	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)

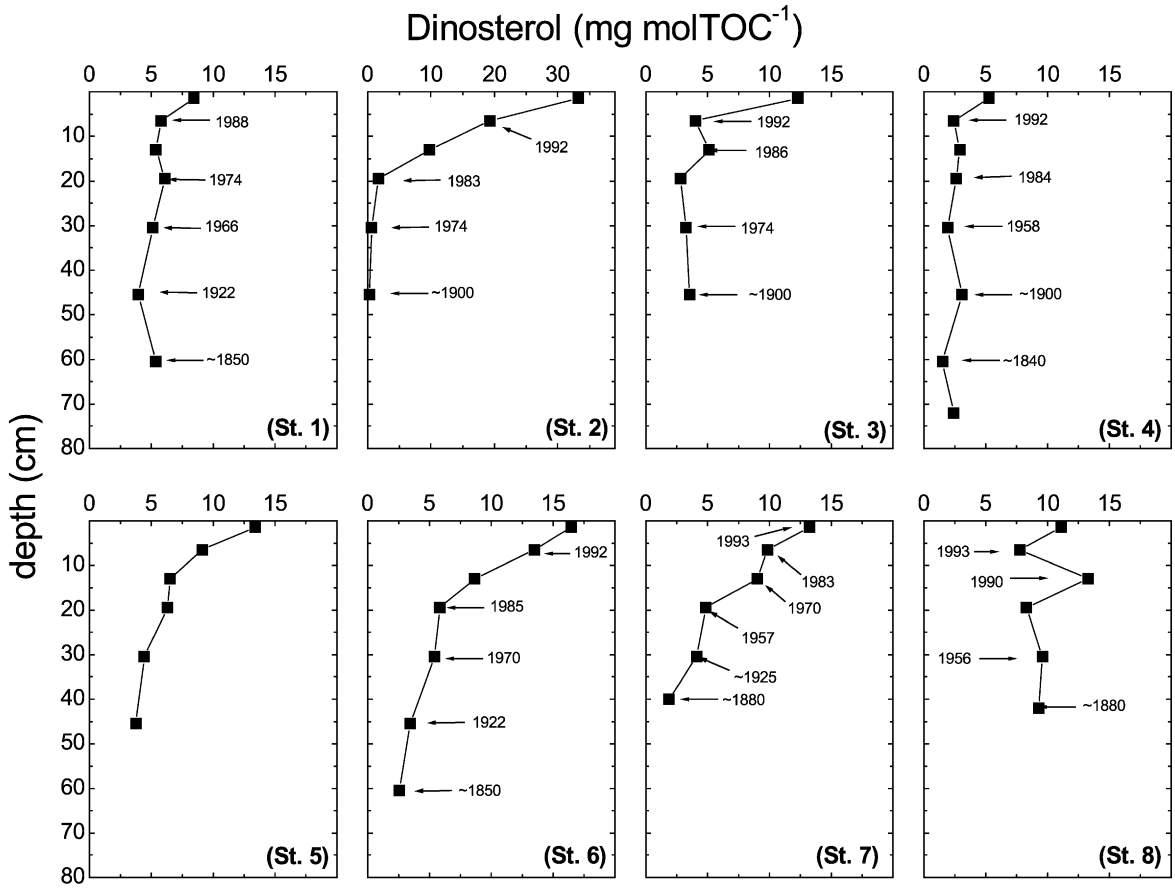

Fig. 4. Depth concentration of dinosterol normalized to TOC. The mean period of sediment deposition is indicated for each sediment layer accordingly to known sedimentation rates (Lima, 1996; Godoy et al., 1998a,b), except for station 5s.

with depth, although it rarely becomes equal or larger than 1. Ratios smaller than 1 suggest microbially mediated hydrogenation of the parent sterol (Gaskel and Eglinton, 1976; Reed, 1977). The most plausible explanation for the unusual similarity in depth profile is the occurrence of extensive microbial degradation of organic matter due to microbial activity in the water column and/or in the nepheloid layer followed then by negligible changes after burial. This topic will be further discussed later. The removal of the decay product by any given process at the same rate of production would produce the same effect and cannot be discarded, although we have for the moment no specific data to support this. A possible mechanism for this observation is similar rates for incorporation of these compounds into the bound (non-extractable) fraction (we analyzed only the sterols in the labile fraction) following the increasing degree of humification of the organic material with depth. Nonetheless, the humic fraction measured in the same samples (Carreira, 2000) decreases with depth. We have indications, however, from previous work that heterotrophic respiration rates in the water column are very high ($\sim$ 50 mmol O_2 m^{-2} day^{-1}) and of the same order of magnitude as that in sediments (Balzer et al., 1987). In addition, major sulphate reducing activity in the sediments occurs only in the top 5–7-cm layer despite sulfate and organic carbon availability (Balzer et al., 1987). We assume that the extensive degradation of organic matter during its transport to the sediments and in the early stages of burial leaves behind refractory material as the major

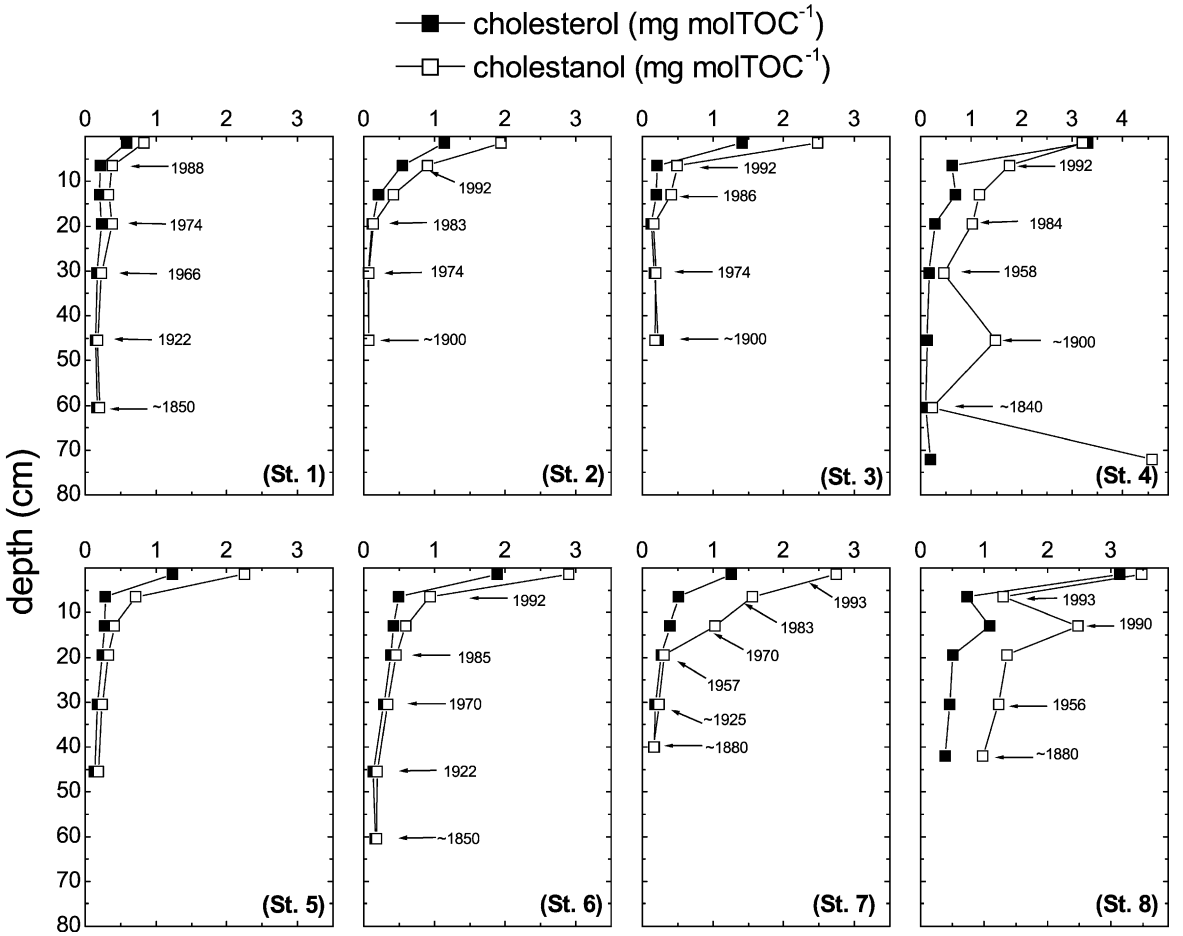

Fig. 5. Depth concentrations of cholesterol (full squares) and cholestanol (open squares) normalized to TOC. The mean period of sediment deposition is indicated for each sediment layer accordingly to known sedimentation rates (Lima, 1996; Godoy et al., 1998a,b), except for station 5s.

carbon source. The bacterial activity is then slowed down due to the decrease in the concentration of assimilable carbon.

The TOC-normalized concentration depth profiles show only a few cases of sterol enrichment relative to the bulk of organic matter over the last 20–30 years. The largest concentration gradient is observed in the layer of 0–3 cm depth, where decomposition is ongoing, but very little variation occurs at depths below 20 cm.

Dinosterol (4α,23,24-trimethyl-22-en-3β-ol) is by far the most abundant sterol found in Guanabara Bay sediments (Table 2). The concentrations are comparable to earlier data for surface sediments from the bay obtained by Chalaux (1995). Dinosterol, that derives from dinoflagellates and, in some cases, from diatoms (Robinson et al., 1984; Volkman et al., 1998), shows high enrichment (relative to TOC) in stations 2s, 5s, 6s and 7s over the last 20–30 years (Fig. 4). This may be related to the increased autochthonous production of organic matter in Guanabara Bay in response to increased nutrient availability over that period. This observation is consistent with the previously discussed $\delta^{13}C$ distribution. We did not measure brassicasterol, a specific sterol for diatoms (Volkman et al., 1998), and hence its relative importance in the sedimentary organic matter pool cannot be evaluated.

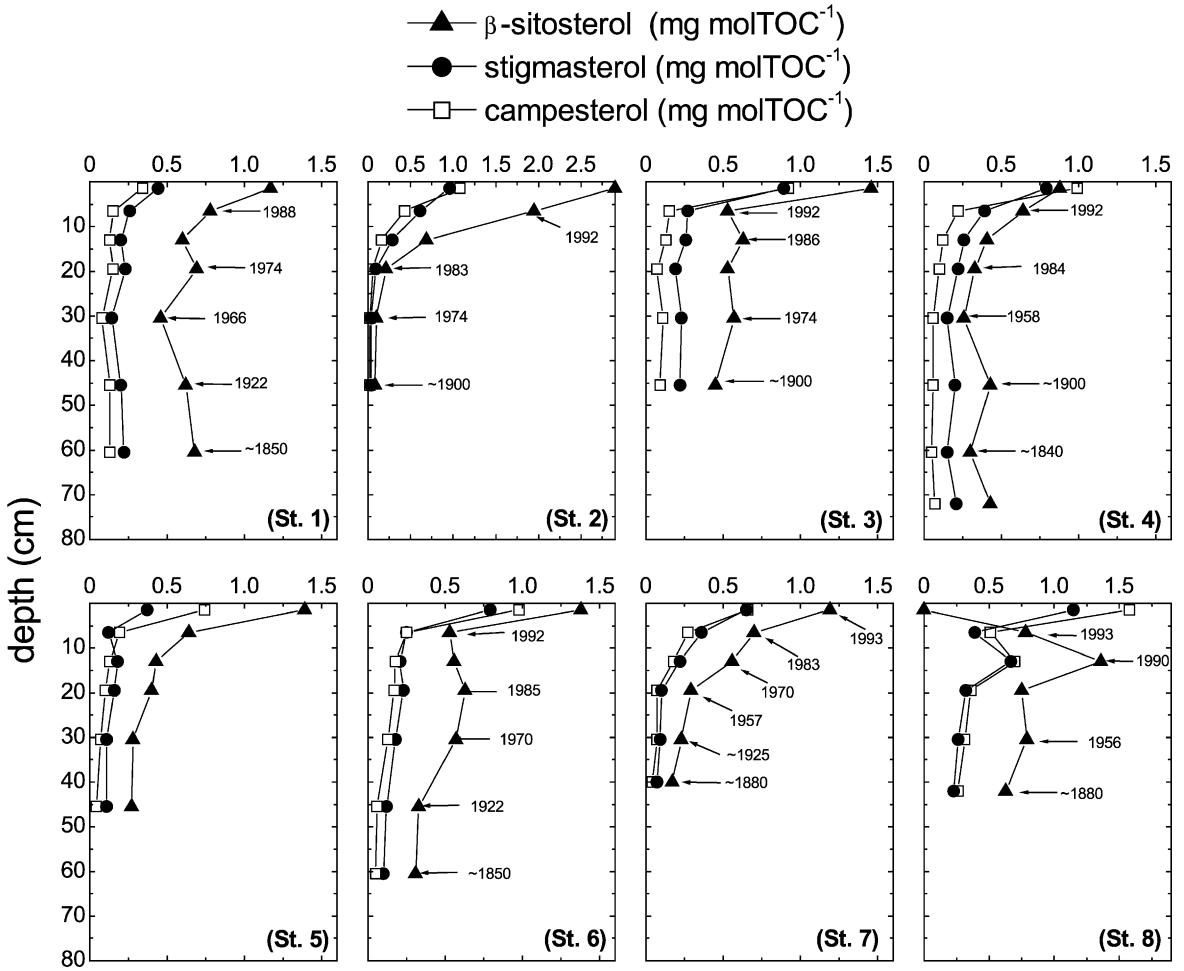

Fig. 6. Depth concentrations of β-sitosterol (full triangle), stigmasterol (full circle) and campesterol (open square) normalized to TOC. The mean period of sediment deposition is indicated for each sediment layer accordingly to known sedimentation rates (Lima, 1996; Godoy et al., 1998a,b), except for station 5s.

Other sterols that can be associated with autochthonous production of organic matter, such as cholesterol (cholest-5-en-3β-ol) and cholestanol (5α-cholestan-5β-ol) (Robinson et al., 1984; Volkman et al., 1998), however, show different depth distribution when compared to dinosterol. These sterols were only enriched in the 0–3-cm layer (Fig. 5) where cholesterol and cholestanol are degraded by microbial action at different rates than that of dinosterol (see degradation rates in Table 5).

Campesterol (24-methylcholest-5-en-3β-ol), stigmasterol (24-ethylcholesta-5,22*E*-dien-3β-ol) and β-sitosterol (24-ethylcholest-5-en-3β-ol) show major enrichments in the same sites as the autochthonous markers at stations 2s, 5s and 7s (see previous discussion) (Fig. 6). This raises questions about the specificity of these sterols as markers of vascular plants and freshwater algae inputs to the sediments of Guanabara Bay. Other authors have already addressed the problems of source specificity of those sterols (Fernandes et al., 1999; Volkman et al., 1999; Zimmerman and Canuel, 2000). Volkman (1986) and Laureillard and Saliot (1993) proposed evaluating the ratios of campesterol/stigmasterol/β-sitosterol to overcome this limitation. Ratios close to 1:1.6:6.6 indicate inputs of these compounds from terrestrial vascular

plant sources, while lower ratios suggest algae sources for these compounds. In the present study, the use of these ratios shows that β-sitosterol is probably derived from vascular plants and/or freshwater algae only in sediment layers below 20 cm depth, except for station 1s where values are compatible with terrestrial sources all over the core.

3.4. Relative proportions of terrestrial and marine organic matter

The relative abundances of riverine/terrestrial and marine organic carbon can be estimated by mass balance calculations and a two end-member model according to (Shultz and Calder, 1976):

$$\delta^{13}C_{sample} = f\delta^{13}C_{riv/terr} + (1-f)\delta^{13}C_{mar} \quad (1)$$

where f is the fraction of riverine/terrestrial organic carbon and $\delta^{13}C_{riv/terr}$ and $\delta^{13}C_{mar}$ are the isotopic signatures of riverine/terrestrial and marine organic carbon sources, respectively. In Eq. (1), we considered the $\delta^{13}C_{terr}$ of $-26.0‰$, based on the results obtained in this work for the uncontaminated rivers (see Table 3). To the $\delta^{13}C_{mar}$ end-member, we assigned a value of $-20‰$ following the data reported for Brazilian coastal systems (Matsuura and Wada, 1994).

A two end-member mixing model can only be applied to stations 1s, 2s and 5s that are subjected to minor levels of sewage input (Carreira, 2000; Carreira et al., 2001). A three end-member mixing model must be considered for the other stations. However, at the present stage, the coprostanol levels at the sources so far required are not yet known.

The calculated results (Table 4) are in agreement with our previous observations, in spite of limitations set by the presence of sewage, lack of original end-member values for marine organic matter in Guanabara Bay and the distinct $\delta^{13}C$ found for different rivers in the catchment area. In all samples from station 1s, the riverine/terrestrial inputs accounted for around 70% of total sedimentary organic matter, except for two intermediate layers. So far, there was no major temporal change in organic matter sources at this site. The opposite trend was observed at stations 2s and 5s, where more than 70% of TOC was originated from autochthonous deposition of organic matter, especially in the upper layers at station 2s (more than 80% of TOC).

Table 4
Relative proportion of marine and riverine/terrestrial organic matter in sediments with no and/or low sewage influence

Station	Mean depth (cm)	Marine (%)	Riverine/ terrestrial (%)
1s	1.5	32.7	67.3
	6.5	25.3	74.7
	13.0	28.9	71.1
	19.5	44.1	55.9
	30.5	44.9	55.1
	45.5	26.1	73.9
	60.5	30.1	69.9
2s	1.5	82.0	18.0
	6.5	84.6	15.4
	13.0	80.1	19.9
	19.5	63.3	36.7
	30.5	60.3	39.7
	45.5	70.9	29.1
5s	1.5	74.7	25.3
	6.5	85.4	14.6
	13.0	76.6	23.4
	19.5	69.3	30.7
	30.5	52.6	47.4
	45.5	95.7	4.3

Results based on a two-end member mixing model (see text for explanation).

3.5. Diagenetic alterations in the organic matter pool

We used the first order degradation model proposed by Berner (1980) and the experimental data obtained for station 1s and 7s, where sedimentation rates were constant over the last 30 and 80 years, respectively, to estimate the degradation constant (k') for the measured sterols. The results yield lower rates for station 7s where marine conditions prevail (Table 5), what is, to some extent, contrary to the general understanding that marine organic matter degrades at higher rates than the more refractory terrestrial organic materials (Henrichs, 1992; Hedges and Keil, 1995; Canuel and Martens, 1996). The deeper water column at station 7s and the unfavorable hydrodynamics to deposition may lead to sedimentation of reworked material that reside longer in the water column. The lower sedimentation rate (0.5 cm $year^{-1}$; Godoy et al., 1998a) observed in this site reinforces the possible deposition of extensively degraded material.

Table 5
Degradation constants (k') calculation considering first-order decay rates and data for stations 1s and 7s (see text for explanations)

Sterol	k' year^{-1} (1s)	k' year^{-1} (7s)
dinosterol	0.072	0.034
cholesterol	0.185	0.074
cholestanol	0.150	0.061
campesterol	0.159	0.081
stigmasterol	0.114	0.049
β-sitosterol	0.097	0.049

The model provided a good fit for the data as indicated by the high correlation coefficients (r^2>0.97) obtained for the log concentration vs. time curves. Despite these good fits, the rate constants for, for example, dinosterol, are in any case small compared to other data for recent deposits (McCaffrey, 1990; Canuel and Martens, 1996) and support our assumption of reduced bacterial decomposition of the organic material after burial.

For the sites where there are indications of an increase in carbon accumulation, we used the following procedure to derive a quantitative estimate of this process. We calculated the concentration ($C_{t_{calc}}$) that should be expected at time t after deposition and compared it to the actual $C_{t_{obs}}$ present in the sediments. $C_{t_{calc}}$ was obtained from the first order decay equation, using the sedimentation date to calculate t, assigning C_0 (initial concentration) to be the concentration of sterol in the top sediment layer and assuming that the estimated degradation rates apply to other stations. The ratio $C_{t_{calc}}/C_{t_{obs}}$ for dinosterol at station 2s, for example, is equal to 26 for the sediment layer deposited at about 22 years ago. At stations 4s, 6s and 3s the ratios varied between 2 and 3 for samples deposited up to 10–15 years ago and were smaller than 1 in older samples. At station 8s, only samples deposited 2 years ago show a ratio larger than 1 in spite of the large increase both in dinosterol concentration and carbon flux that occurred during the period between 11 and 5 years ago in the same core.

The extremely high values of the ratio cholestanol/cholesterol (on the average 1.7) for surface samples compared to the usual range of 0.1 to 0.5 given in the literature (Lajat et al., 1990; Canuel and Martens, 1993) suggests extensive microbial degradation in the water column or during the very early stages of burial. The highly anoxic character of the sediments (Balzer et al., 1987) favors microbial biohydrogenation of sterols to stanols (Mackenzie et al., 1982; Nishimura, 1982; de Leeuw and Baas, 1986). Chemical reduction in recent sediments seems to be less important (Wakeham, 1989). Nevertheless, a direct biogenic source for cholestanol (Volkman, 1986) cannot be ruled out since concentrations of this compound correlate with the high content of dinosterol (r^2>0.90, p<0.001, except at stations 4s and 8s).

The ratio of $C_{t_{calc}}/C_{t_{obs}}$ for cholestanol in station 2s, however, is close to 3 in samples where the same ratio for dinosterol is around 26. Although we are aware of the limitations of those estimates, the lower ratio for cholestanol may indicate the combined presence of the two sources. The rather constant depth profile of cholestanol/cholesterol, exceptions being stations 4s and 8s with pronounced gradients, may partly derive from low rates of degradation after burial, as discussed above.

3.6. Factor analysis

Statistical tools (factor analysis) were used to evaluate the sterol and isotopic composition data, as related to the sources of organic matter. The first three factors are responsible for more than 94% of the total variance. Factor 1 with 61.9% of the variance grouped all measured sterols and factor 3 (13.3% of variance explained) grouped C/N ratios and $\delta^{13}C$ values. Factor 2 grouped the fecal sterols that are not considered in the present work.

Factor 1 gives some resolution between upper (~ 0–16 cm) and deeper layers of sediments (0–3 cm layers of stations 4s, 2s and 8s were outliers not included in the analysis), as shown in Fig. 7A. This feature is closely related to higher concentration of sterols in recently deposited sediments, as indicated by their positive score loadings (Fig. 7B) and the concentration profiles (Figs. 4–6). Campesterol, sitosterol and β-sitosterol, commonly ascribed to riverine/terrestrial inputs (as previously discussed), loaded positively on factor 1 and are closely related to the positive loadings of dinosterol, cholesterol and cholestanol. Contributions from coprostanol, $\delta^{13}C$ and C/N ratio (Fig. 7B) to factor 1 were not significant. Therefore, factor 1, standing mainly for the sterol distribution, points out the increasing storage of carbon in the upper sediment layers, but cannot be

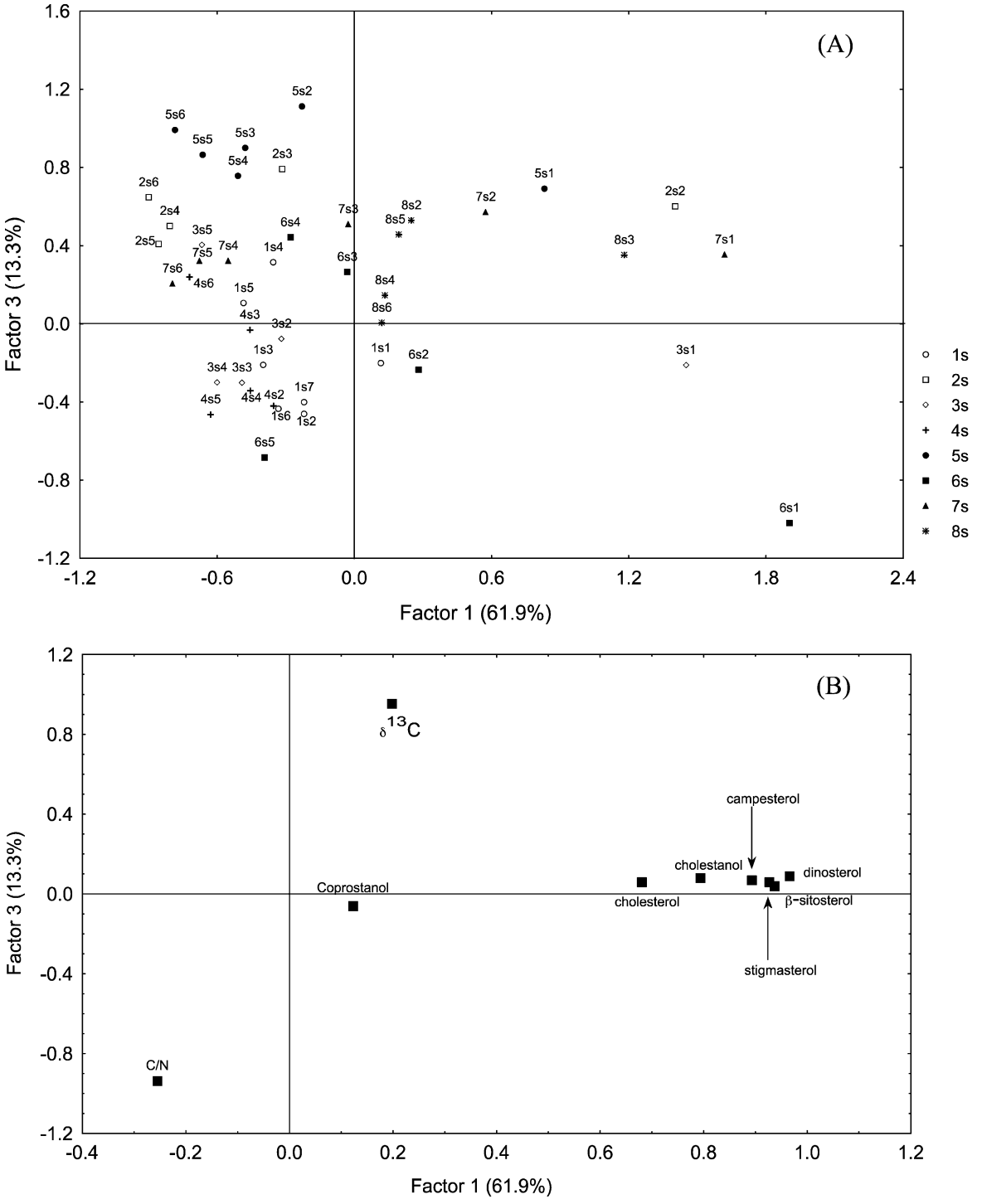

Fig. 7. Bidimensional rotated plot of factor 1 and factor 3 (Quartimax with Kaiser normalization) obtained by factor analysis for 49 sediment samples and using data for sterols, $\delta^{13}C$ and C/N ratio. (A) Sample scores; (B) variable loadings. Legend as indicated in Table 2.

used to infer about the autochthonous and/or allochthonous carbon origin. This result differs substantially from the observations reported for other estuarine systems as, for instance, in Shaw and Johns (1986), Tian et al. (1992) and Sicre et al. (1994).

Factor 3 separates samples of marine/estuarine isotopic and elemental signatures from those of typical riverine plankton/terrigenous plant signatures. Samples from sites 2s, 5s, 7s and 8s plot exclusively in the positive quadrant of factor 3 while sites 1s, 3s, 4s and 6s generally plot negatively (Fig. 7A). It is also observed that $\delta^{13}C$ and C/N ratio are inversely correlated in factor 3 (Fig. 7B) and to a lesser extent in factor 1. These results prove that there are areas in the bay preferably under influence either of autochthonous (stations 2s, 5s, 7s and 8s) or allochthonous (stations 1s, 3s, 4s and 6s) sources of organic matter.

4. Conclusions

Some insights into the sources and fate of organic matter in Guanabara Bay sediments may be inferred from the multi-parameter approach undertaken in this work. The main conclusions are summarized below.

- There are strong indications that an increase in carbon storage occurred in response to activities on land and growing eutrophic conditions in the bay. During the last 100 years, the C flux changed from a background value of 4.2 mol C m^{-2} $year^{-1}$ to a maximum of around 41.7 mol C m^{-2} $year^{-1}$.
- Increase in carbon storage is due principally to increasing sedimentation rate. Presently, high eutrophic condition and availability of sewage-derived organic material result in high primary production but also stimulate heterotrophic activity leading to intense respiration of fixed carbon already in the water column. From our data, we can conclude that increases in TOC fluxes over the period of predominantly eutrophic condition (last 30 years) would be marginal had the sedimentation rates remained constant.
- There are two distinct areas in the bay as characterized by TOC, TN and $\delta^{13}C$ data: the area including stations 1s, 3s, 4s and 6s mainly influenced by riverine/terrigenous material, and the area covered by stations 2s, 5s, 7s and 8s where organic matter preferably derives from estuarine/marine processes. Differences in those properties observed among samples may be attributed to temporal changes in sources and end-member composition, rather than preferential degradation of labile sedimentary organic matter or selective preservation of refractory constituents.
- The predominance of dinosterol in most stations supports the importance of internal sources to the bulk of sedimentary organic matter in the bay, although it is still necessary to understand the role played by other algae (ex. diatoms).
- β-sitosterol in several recently deposited sediments appears to be derived from estuarine/marine sources. However, as in the present study, multivariate analysis fitted these compounds in the same group as the other sterols derived from marine sources (cholesterol, cholestanol and dinosterol), and appropriate terrestrial markers must be identified in Guanabara Bay.

The conclusions drawn here for Guanabara Bay may apply to other tropical estuarine areas subjected to similar environmental alterations. Deforestation, soil remobilization and nutrient releases are occurring at increasing rates as population in tropical regions is driven towards coastal settlements and coastal urban areas. The subsequent increase in sedimentation rates coupled to nutrient enrichment in those regions may imply in substantial changes on global carbon budgets.

Acknowledgements

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