

## Combined use of aerogammaspectrometry and geochemistry to access sediment sources in a shallow coral site at Armação dos Búzios, Brazil

Danielly Godiva<sup>a</sup>, Heitor Evangelista<sup>a,\*</sup>, Milton Kampel<sup>b</sup>, Marcus Vinicius Licinio<sup>a</sup>, Casimiro Munita<sup>c</sup>

<sup>a</sup>LARAMG – Laboratório de Radioecologia e Mudanças Globais-DBB/IBRAG/Uerj, Pav. HLC. Subsolo, Rua São Francisco Xavier, 524 Maracanã, 20550-013 Rio de Janeiro, RJ, Brazil

<sup>b</sup>Instituto Nacional de Pesquisas Espaciais, Divisão de Sensoriamento Remoto, Av. dos Astronautas 1758, 12227-010 São José dos Campos, SP, Brazil

<sup>c</sup>Instituto de Pesquisas Energéticas e Nucleares – IPEN-CNEN/SP, Av Prof. Lineu Prestes 2242, Cidade Universitária USP, São Paulo, SP, Brazil

### ARTICLE INFO

#### Article history:

Received 4 August 2009

Accepted 9 February 2010

Available online 4 March 2010

#### Keywords:

radioisotopes

siderastrea stellata

sedimentation

Armação dos Búzios

aerogammaspectrometry

### ABSTRACT

Coral and reef environments in shallow waters are negatively affected by human activities in several coastal areas worldwide. It has been demonstrated that sediment influx and macronutrient discharges induce decline of coral population structure and diversity. Therefore, efforts to quantify sediment flux, sources and the biological response to sedimentation were conducted by several marine researchers. Herein, we investigated the case study of Armação dos Búzios/Brazil/Western South Atlantic, where coral colonies (mostly *Siderastrea stellata*) are under stress due to sediment apportionment as a consequence of regional human occupation. Classification of potential sediment source regions was based on a high-resolution aerogammaspectrometry survey for <sup>232</sup>Th, <sup>238</sup>U and <sup>40</sup>K in main land near shore, used as primarily tool, in combination with sediment geochemistry. This approach allowed distinguishing three hydrographic basins (Macaé river basin, São João river basin and Una river basin) as potential sources. Hierarchical cluster analysis applied to the set of parameters identified the Macaé River as the most probable sediment contributor to the coralline site.

© 2010 Elsevier Ltd. All rights reserved.

### 1. Introduction

It is estimated that one third of global reef and coralline formations have already been threatened by at least three main anthropogenic forcings: (1) induced climate change of the modern epoch; (2) over fishing; and (3) the expansion of human occupation limits near coastal ecosystems that resulted in increased terrestrial runoff of sediments as well as nutrients and chemical pollutants (Dodge and Gilbert, 1984; Edinger et al., 1999; Esslemont, 1999; Medina-Elizalde et al., 2002; David, 2003; Gardner et al., 2003; Hughes et al., 2003; McLaughlin et al., 2003; Nugues and Roberts, 2003; Pandolfi et al., 2003; Philipp and Fabricius, 2003). These processes may result in a relatively fast change in diversity and community structure through extensive mortality and inhibition of reproduction and recruitment (Smith and Buddemeier, 1992). Experimental data of Weber et al. (2006) have supported the concern on sediment and nutrient loadings by exposing corals to different sediment types, levels of concentrations and exposure times in laboratory and field conditions.

The coralline communities are often associated to clear oligotrophic marine waters and consolidated benthic substrates (McLaughlin et al., 2003) living under controlled conditions of sea temperature, salinity and light availability (Morelock et al., 1979). Sediment influx is a natural component of the environment and the coralline reef may adapt to this condition, under specific levels (Morelock et al., 1979). Despite this assertion, suspended or deposited sediments are generally recognized as having inhibitory or negative effects on reef communities (McLaughlin et al., 2003). An important component of this sediment supply may occur due to runoff and through surface wind stress that generate waves causing resuspension of sediments and turbidity in the water column. Dissolved compounds of inorganic P, organic P and N, nitrite and nitrate are normally enriched in flood plumes and often result in higher levels of biological activity such as phytoplankton blooms (Dagg et al., 2004; Devlin and Brodie, 2005). McLaughlin et al. (2003) estimated that, at the global scale, a progressive decline in reef occurrence could occur above a runoff value of  $\sim 10^{10}$  m<sup>3</sup>/year. The condition of sediments in excess may result in a stress factor for the reef environment which in turn will demand energy expenditure of corals during the process of removing sediments from living tissue (Morelock et al., 1979). Many studies were conducted with massive coral species in this context, since they generally have a longer life and, apparently, higher resistance to natural

\* Corresponding author.

E-mail addresses: [danygodiva@yahoo.com.br](mailto:danygodiva@yahoo.com.br) (D. Godiva), [evangelista.uerj@gmail.com](mailto:evangelista.uerj@gmail.com) (H. Evangelista), [milton@dsr.inpe.br](mailto:milton@dsr.inpe.br) (M. Kampel), [marcusvau@bol.com.br](mailto:marcusvau@bol.com.br) (M.V. Licinio).

disturbances, making them important species to investigate the effects of chronic disturbances, such as those caused by the intake of pollutants and sediment loads (Nugues and Roberts, 2003). Acevedo et al. (1989) and Nugues and Roberts (2003) have reported that coral mortality is normally higher near river mouths, where most of the sediments are deposited. This also encourages the development of opportunistic species (e.g., algae) that compete for space with colonies of corals. In the study of Nugues and Roberts (2003), they have concluded that the coral species *Montastrea faveolata* and *Siderastrea siderea* suffered 50% increase in mortality with respect to increased exposure to sedimentary processes in the Caribbean Sea. By contrast, they have observed that adaptation to sedimentation also may occur and that the species *Porites asteroides* and *Colpophyllia natans*, for example, were more resistant to sedimentation, and differentiated from others by their greater ability to eliminate fine particles. Similarly, the coral *Acropora* in Australia, has developed a strategy of continuous mucus secretion to clean their surface as well as to protect from desiccation during low tide exposure (Wild et al., 2004). Philipp and Fabricius (2003) suggested that the deposition of sediments can adversely affect the photosynthetic activity of zooxanthella and viability of corals. These results show the ability of coral species to “control” the stress, reducing the interference to the health of the living tissue. In resume, sedimentation can cause coral mortality directly due to high energy expenditure for particle rejection, through mucus production, polyp movement or tissue swelling, and effect indirectly through the reduction of light for photosynthesis or by stimulating the growth of competitors with coral. Further, in several environments it is the availability of suitable substrates for larval settlement rather than turbidity levels that influence majority the coral community development (e.g., Woolfe and Larcombe, 1998; Larcombe and Woolfe, 1999; Macdonald et al., 2005). Another important parameter that affects the coral development is attributed to the sea surface turbulence induced by cyclones (Nott, 2004) and hurricanes, which promote considerable change in the height of waves (McConochie et al., 2004) leading to sediment plumes intensification (Acker et al., 2004) and erosion (McConochie et al., 2004; Nott, 2004). In the Southeast, and part of the Northeast, Brazilian coast the migration of cold front systems, originated in tropical mid-latitudes and Antarctica, have great impact in the sedimentation at the continental shelf and particularly in the shallower waters (Evangelista et al., 2007; Segal et al., 2008).

For coralline reefs located in estuarine sites, great importance is devoted to identifying potential sediment loading sources, which constitute a basic tool for future coastal area management. The present study aimed at identifying the main regional sediment contributors to a coral site located at Armação dos Búzios, Tartaruga Beach/Rio de Janeiro State/Brazil, that is characterized by the occurrence of species of high endemism. Three hydrological basins associated to the rivers Macaé, São João and Una that surround the coralline area were considered as potential sources of sediment influx. Here we have explored the terrestrial aerogammasspectrometry surveys that provide surface concentration maps of  $^{232}\text{Th}$ ,  $^{40}\text{K}$  and  $^{238}\text{U}$ , and combined to sediment geochemistry (mineralogy, naturally occurring radioisotopes and rare earth elements concentrations) constituted the “sediment fingerprints”.

## 2. Study region

Tartaruga Beach (“Turtle Beach”) is located on the Northern sector of Armação dos Búzios/State of Rio de Janeiro (Fig. 1) and is the site where large colonies of a massive coral species endemic to

Brazil, *Siderastrea stellata* Verrill 1868, are found. These colonies occur along the rocky and sandy shore on the coastline (Oigman-Pszczol et al., 2004). Armação dos Búzios and surroundings are characterized by a hydrological deficit of around 100 mm/year (CILSJ technical report, 2006).

Sediment plumes at the study site are attributed to regional rivers discharge and fine material suspended in the coastal current that characterize the Southward flow of the Brazil Current (Peterson and Stramma, 1991). Coastal geomorphology in the estuarine region, near Armação dos Búzios, is responsible for hydrodynamism reduction, close to Una River and São João River mouths. Fig. 2 shows satellite images of typical winter and summer sediment plume scenarios at the study region. Summer image correspond to LANDSAT-7 ETM<sup>+</sup> (Enhanced Thematic Mapper Plus) scenes (orbits 216/76 and 216/75; dated February 13th, 2003) and winter image corresponded to CBERS-2 CCD scenes (orbits 149/125 and 149/124; acquired on July 16th, 2004). Resolutions were 30 m for LANDSAT and 20 m for CBERS, respectively. Besides the sediment influx due to river discharge, occurring predominantly in the summer season, at least two other processes are associated to sedimentation in the study region: (1) upwelling events that occur in the spring-to-summer period; (2) resuspension promoted by cold front migrations near shore which are more intense and frequent during the winter season. An inspection in summer and winter satellite images suggests that the resuspension mechanism plays an important role in plume formation, despite the turbidity associated to the continental runoff.

This study addresses the river runoff influence of three basins belonging to the Una river (UR), São João river (SJR) and Macaé river (MR). Distances of these rivers to Tartaruga Beach are 9.5 km for UR, 18.7 km for SJR, and 44 km for MR. Approximate water discharges are 4 m<sup>3</sup>/s for UR, 17 m<sup>3</sup>/s for SJR and 45.4 m<sup>3</sup>/s for MR. Significant segments of these river's margins were impacted over recent decades. Along the course of the UR, riparian vegetation was almost entirely removed and replaced by pasture. This resulted in the elimination of river's curves and the acceleration of the sediment flow, promoting a visible change in water turbidity close to the mouth of the river. A dam was constructed on the SJR course, causing flooding along ~13 km of the river. Contrarily to UR, the dam at SJR acted as a barrier to the sediment flow to the estuarine region. MR is approximately 136 km long which drains through a humid mesothermal climate domain at its source region, a location characterized by high annual precipitation ranging from 1500 to 2000 mm with peaks in December. MR main upstream tributaries and its meander section are relatively well preserved and contrasts to the estuarine region where human occupation is intense.

The hydrological basin domains were defined from the regional geological map made available by the Foundation in Rio de Janeiro (CIDE) at the 1:1000000 scale as the catchment area of the three rivers (Macaé, São João and Una) that corresponds to the alluvium/colluvium deposit represented in Fig. 1.

According to the Brazilian geological service (CPRM), main regional geological complexes of the study area are formed by (1) Região dos Lagos Complex that is a hornblende-biotite granodioritic to tonalitic calc-alkaline orthogneiss; (2) Paraíba do Sul Complex formed by São Fidélis Unit Garnet-biotite-sillimanite quartzo feldspathic gneiss (metagrey wacke), locally bearing graphite-rich domains; wide spread in situ and injected pocket sand veins of granitic leucosome. Also containing abundant interleaved calc-silicate gneiss and quartzite lenses and cordierite-sillimanite-graphite bearing varieties (kinzigite) that have transitive contacts with garnet-biotite gneiss; (3) Cretaceous/Tertiary alkaline rocks: Syenites, nepheline syenites, foyaites, fonolites,

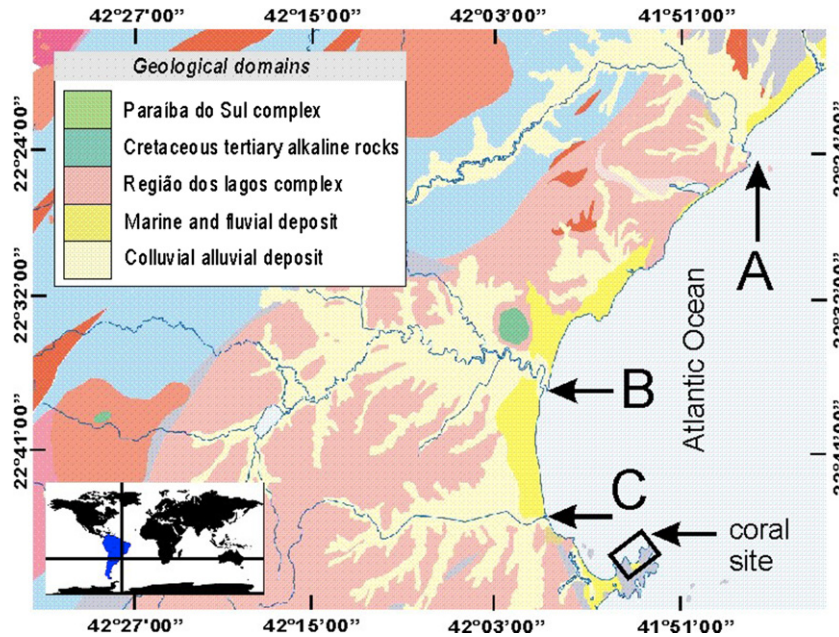


Fig. 1. Main regional geological domains and location of the studied coral site at Tartaruga Beach. Arrows indicate Macaé (A), São João (B) and Una (C) river mouths.

trachytes, tinguaites, pulaskites, umptekitites, fenites; (4) Marine and fluviomarine deposit such as the silty-clayey-sandy fluviomarine deposits rich in organic matter, encompassing recent to sub-recent shore lines and mangroves; and (5) Colluvial-alluvial deposit that constitute a fluvial and fluviomarine deposit of clay, silt and sand including talus-related gravel beds, and reworked lacustrine and mangrove sediments.

### 3. Material and methods

A high-resolution aerogammaspectrometry database, provided by the Brazilian National Department of Mineral Production (DNPM), was used to characterize main regional hydrological basins with respect to naturally occurring radionuclides from the

uranium and thorium radioactive series, as well as  $^{40}\text{K}$ . Additionally, bottom sediments of the three rivers, were sampled at their mouths, (as well as the material deposited over coral assemblages) during two field campaigns (February 2003 and June 2005). Samples were submitted to high-resolution gamma spectroscopy (owing to quantify activity concentrations of radionuclides), mineralogy (for mineral abundances) and nuclear activation to provide composition of rare earth elements, REE.

#### 3.1. Aerogammaspectrometry

The aerogammaspectrometry survey (DNPM Code 1038) provided mean surface activity concentrations of  $^{232}\text{Th}$  (ppm),  $^{238}\text{U}$  (ppm) and  $^{40}\text{K}$  (%), that were inferred from the radioisotopes  $^{208}\text{Tl}$  (2614 keV, detection range: 2410 keV–2810 keV),  $^{214}\text{Bi}$  (1765 keV, detection range: 1660 keV–1860 keV), and  $^{40}\text{K}$  (1460 keV, detection range: 1370 keV–1570 keV), respectively. The aerial profiles totaled 41,595 km in length and extended over 38,000 km<sup>2</sup>. The spacing between lines of flight was around 350 m and the gamma radiation integration intervals lasted 1 s for each measurement. Data calibration was held by CPRM (Brazilian geological service) together with the Geological Survey of Canada (GSC) and the Canadian International Development Agency (CIDA) (Mourão et al., 1997). Surface activity concentrations of  $^{232}\text{Th}$ ,  $^{238}\text{U}$  and  $^{40}\text{K}$  in the study area, obtained by the aerial survey, are shown in Fig. 3.

#### 3.2. Sediment samples

Sediment samples were collected from the bottom of the three rivers at their mouth in 15–16th February 2003 and 11–12th June 2005. During the first field campaign, samples were also taken from deposits found over the irregular surface of the coral colonies of *S. stellata*. The sediment samples were dried at 60 °C for 24 h, homogenized and sieved in fractions of 0.71 mm, 0.50 mm, 0.25 mm, 0.125 mm, and 0.075 mm. Modal grain size of sediments deposited over coral colonies was below 0.25 mm (80%). All sediments from river bottoms were, therefore, sieved at that grain fraction for further analyses.

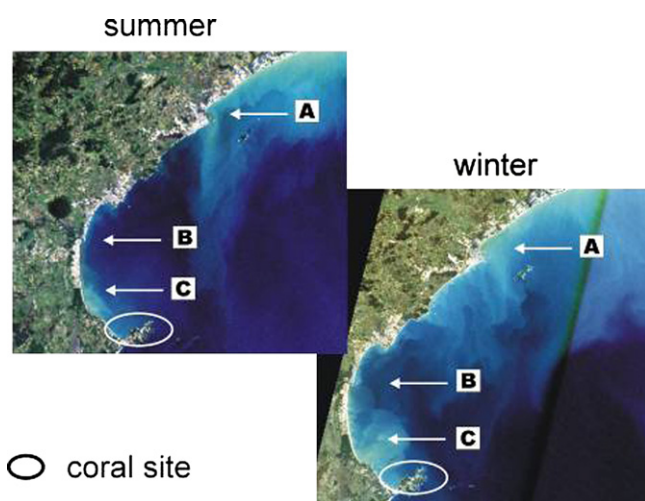
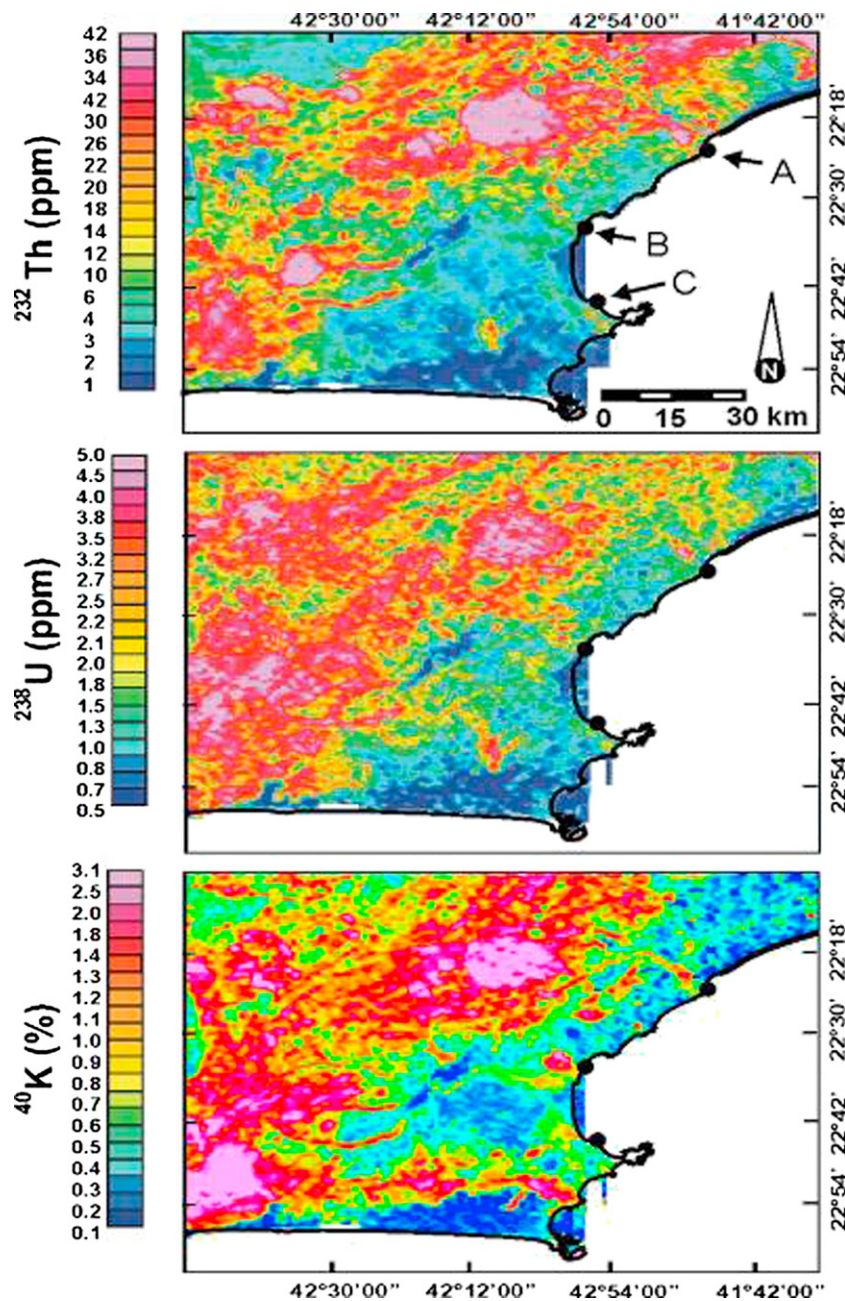


Fig. 2. LANDSAT-7 ETM<sup>+</sup> summer image for the coral site/Armação dos Buzios/Rio de Janeiro (February 13th, 2003) and CBERS-2 winter image (July 16th, 2003) showing the increase of sediment plumes. Arrows indicate location river mouth for: A: Macaé river, B: São João river and C: Una river.



**Fig. 3.** Surface concentrations of  $^{232}\text{Th}$ ,  $^{238}\text{U}$  and  $^{40}\text{K}$  for the study area (Fig. 1) obtained by aerogamaspectrometry (source: CPRM – The Brazilian geological service). Dots indicate river mouths: (A) Macaé river, (B) São João river and (C) Una river.

### 3.3. Gamma spectroscopy

Concerning the laboratory radiometric analyses, a high-resolution gamma spectrometry was employed making use of an extended energy range co-axial hyperpure germanium (HPGe) detector with relative efficiency of 20% and resolution of 2.5 keV at the  $^{137}\text{Cs}$  energy peak. Detector efficiency curves for the sediment samples were performed using a liquid solution containing a cocktail of radionuclides – NIST (serial number HV951). The solution, 10 mL, was mixed with 53 g of dried sediment of comparable density to produce the radioactive standard. The cocktail used in this study included the radionuclides  $^{133}\text{Ba}$ ,  $^{57}\text{Co}$ ,  $^{139}\text{Ce}$ ,  $^{85}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{54}\text{Mn}$ ,  $^{88}\text{Y}$ , and  $^{65}\text{Zn}$ . The radionuclides of interest to this work were  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ ,  $^{234}\text{Th}$ ,  $^{208}\text{Tl}$ ,  $^{228}\text{Ra}$  ( $^{228}\text{Ac}$ ) and  $^{212}\text{Pb}$ . The total counting

time for each sample was 24 h. Details of this method are described in Handl et al. (2008).

### 3.4. Mineralogy

The mineralogy of sediments reflects the feature of the original rock source. Therefore, this technique helps in the recognition of different sources of sediments (De Meijer and Donoghue, 1995). Samples were macerated and dried at 50 °C for 5 min. Sub-samples were prepared by adding 0.001 g of each sample to 0.399 g of potassium bromide (KBr). After homogenization, 0.3 g of this mixture was extracted for further drying and pressing (sample dryness in vacuum condition for 15 min followed by pressing under a 9 ton weight for 15 min). Pellets were then stored in an oven. The

tablets were analyzed by Fourier Transformation Infra-Red Spectrometry (FT-IR). Spectrum 3.02 software was used to archive and manipulate spectra. The percentages of major minerals present in the samples were calculated according to the standards previously obtained for aragonite, calcite, Illite, kaolinite, quartz, silica and amorphous albite.

### 3.5. Rare earth elements (REE)

The analyses of REEs were carried out by neutron activation technique. A fraction of the sediment samples was manually crushed inside an agate mortar and then sieved using 100 and 200 mesh (0.149 and 0.074 mm) sieves. Later, sub-samples of 100 mg were dried at 100 °C for 24 h and wrapped in polyethylene badges and coated with a thin aluminum hood. Both standard soil NIST-SRM 1633b and samples were irradiated during 8 h in the IEA-R1 m reactor at the Institute of Energy and Nuclear Research (IPEN-CNEN/São Paulo) under a thermal neutron flow in the order of  $1012 \text{ n cm}^{-2} \text{ s}^{-1}$ . The measurements of the gamma induced activity concentrations were performed using an HPGe detector with resolution of 1.90 keV at the energy peak of  $^{60}\text{Co}$  (1332 keV). The spectra of gamma rays were obtained and processed using Genie-2000 NAA software (Canberra®). La, Lu, Sm, U and Yb were counted 7 days after irradiation while Ce, Eu, Hf, Sc and Th were counted 25–30 days after irradiation. Detailed analytical work performed by Santos et al. (2007) showed that the coefficient of variation (CV) obtained between the NIST standard and a reference prepared sample, for the neutron activation instrumental set up, was La (CV = 4.0%), Lu (CV = 6.78%), Sm (CV = 28.8%), U (CV = 12.0%), Eu (CV = 4.9%), Yb (CV = 6.6%), Ce (CV = 3.9%), Hf (CV = 8.8%), Sc (CV = 2.8%) and Th (CV = 3.5%).

## 4. Results and discussions

### 4.1. Aerogammaspectrometry survey

From Fig. 3 one can observe that the radiometric survey for Th, U and K reflect quite well the geologic and geomorphologic features, depicting lower concentrations at the colluvial-fluviomarine deposits of clay, silt and sand including talus-related gravel beds, and reworked lacustrine and mangrove sediments; the same is valid for the Região dos Lagos Complex which consists mostly of (1) a hornblende-biotite granodioritic to tonalitic calc-alkaline orthogneiss; (2) siltic-clayey-sandy fluviomarine deposits rich in organic matter; and (3) quartz sandbars, constituting Recent dunes fields (aeolian deposits); all occurring at the SE and NE sectors of Fig. 3. Higher concentrations were found at garnet-biotite-sillimanite quartzo feldspathic gneiss (according to the geological map of Rio de Janeiro State/CPRM/DRM-RJ, released in 2000).

Maps of the aerogammaspectrometry surveys and the geological domain were overlaid in order to select the activity concentrations of  $^{232}\text{Th}$ ,  $^{238}\text{U}$  and  $^{40}\text{K}$  in the geographical domain of interest, this is, the alluvium/colluvium deposit domain of Macaé, São João and Una Rivers. Fig. 4 depicts the radionuclide distribution inside each hydrological basin.

MR and SJR presented higher activity concentrations near their respective headwaters, with a gradual reduction towards the river mouths. The relative maximum values corresponded to the upstream domain and could be associated with the proximity of granite formations, leucogranite, gneiss and magmatic areas of the Upper Proterozoic (Fundação Centro de Informações e Dados do Rio de Janeiro, 1998). Granites present typically higher concentrations of natural radionuclides when compared to other geological formations (International Atomic Energy Agency, 2003).  $^{238}\text{U}$  activity concentrations along the MR basin ranged from 3 to

57 Bq  $\text{kg}^{-1}$ . In contrast, much lower activities of  $^{238}\text{U}$  were observed in the other basins, probably due to differences of bed rock and situ rock transformation. It is expected that  $^{232}\text{Th}$ ,  $^{238}\text{U}$  and  $^{40}\text{K}$  present different environmental behavior, due to their particular solubility and because they exhibit different chemical reactivity. According to Wollenberg and Smith (1990), the ratio of radionuclides can be used to distinguish several types of rock formation. Thorium and uranium are commonly found in the Earth's crust in an average ratio ( $^{232}\text{Th}/^{238}\text{U}$ ) of 3.5 (Ivanovich and Harmon, 1992). The oxygen rich atmosphere contributes to the mobilization of thorium and uranium. Both occur with a valence state of 4+ in primary rocks and are somewhat chemically reactive. Uranium, however, can be oxidized to the state of 5+ or 6+ in an oxidizing environment and thus form complex compounds such as uranyl ( $\text{UO}_2$ ), which may subsequently be carried by water and further adsorbed in bottom sediments. Thorium can be transported in the water body and be adsorbed to the surface of clays and insoluble minerals (Ivanovich and Harmon, 1992). Potassium is considered highly chemically reactive, capable of forming a wide variety of complexes due to its smaller ionic radius, which also makes it easily allocatable to different types of crystals.

In particular, MR main upstream tributaries (São Pedro and Sana rivers) drain an homogeneous granite named Sana (location highlighted in Fig. 5). In this case, the aerogamma survey captured a radiometric anomaly corresponding to the granite formation as well as an ancient radionuclide deposit along part of the MR course suggesting that leaching processes over the granite formation have taken place over time at that location. In such case,  $^{232}\text{Th}$  distribution acted as tracer of terrigenous matter (and consequently suspended particles) into the estuarine region. A track of radionuclides along the UR presented an unclear pattern.

Most of the nine spatially distributed radionuclide ratios at the hydrological basins exhibited a log-normal behavior, according to Kolmogorov-Smirnov test, exceptions are  $^{232}\text{Th}/^{238}\text{U}$  for MR and  $^{40}\text{K}/^{232}\text{Th}$  for UR (normally distributed); their mean values and standard deviations are presented in Table 1. Mann-Whitney U test, at 95% confidence interval, indicated that radionuclide ratios of SJR and UR do not differ significantly. Additionally, Kruskal-Wallis one-way analysis of variance indicated no homogeneity among the sites as to the  $^{232}\text{Th}/^{238}\text{U}$  ratio, suggesting that radionuclides distribution in MR basin present distinct radiometric characteristic compared to SJR and UR.

In order to evaluate whether the sediments collected at the surface and in the surroundings of coral colonies at Tartaruga beach had similar radiometric characteristics when compared to the river basin compiled database, we compared the aerogammaspectrometry survey with the in situ activity concentrations obtained by the radiometric analysis (gamma spectroscopy) of the collected sediments. In this case, the mean ratio of  $^{232}\text{Th}/^{238}\text{U}$  (inferred by  $^{208}\text{Tl}/^{226}\text{Ra}$ ) was 6.7. A statistical test ( $P > 0.05$ ) carried out between  $^{232}\text{Th}/^{238}\text{U}$  ratios for the aerogamma survey and the sediment sample collected over the corals indicated that sample ratio is an expected value within the MR  $^{232}\text{Th}/^{238}\text{U}$  domain, in contrast to UR and SJR domains. Another point to consider is the behavior of the natural radionuclides during the dispersion of sediments from their discharge in the estuary up to the inner continental shelf. Segal et al. (2008) investigated the behavior of the radioisotopes  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{40}\text{K}$  in sediments collected by traps in transects perpendicular to the coastline up to 60 km in the Northeast Brazil. They have demonstrated that although a sharp decrease in the activity concentrations (a factor of  $\sim 3$  in 50 km) was observed, the  $^{40}\text{K}/^{226}\text{Ra}$ ,  $^{40}\text{K}/^{228}\text{Ra}$  and  $^{226}\text{Ra}/^{228}\text{Ra}$  ratios remained relatively constant.

The activity concentrations of gamma ray emitters from the  $^{238}\text{U}$  and  $^{232}\text{Th}$  decay series ( $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ ,  $^{234}\text{Th}$ ,  $^{208}\text{Tl}$ ,  $^{228}\text{Ra}$  ( $^{228}\text{Ac}$ ) and

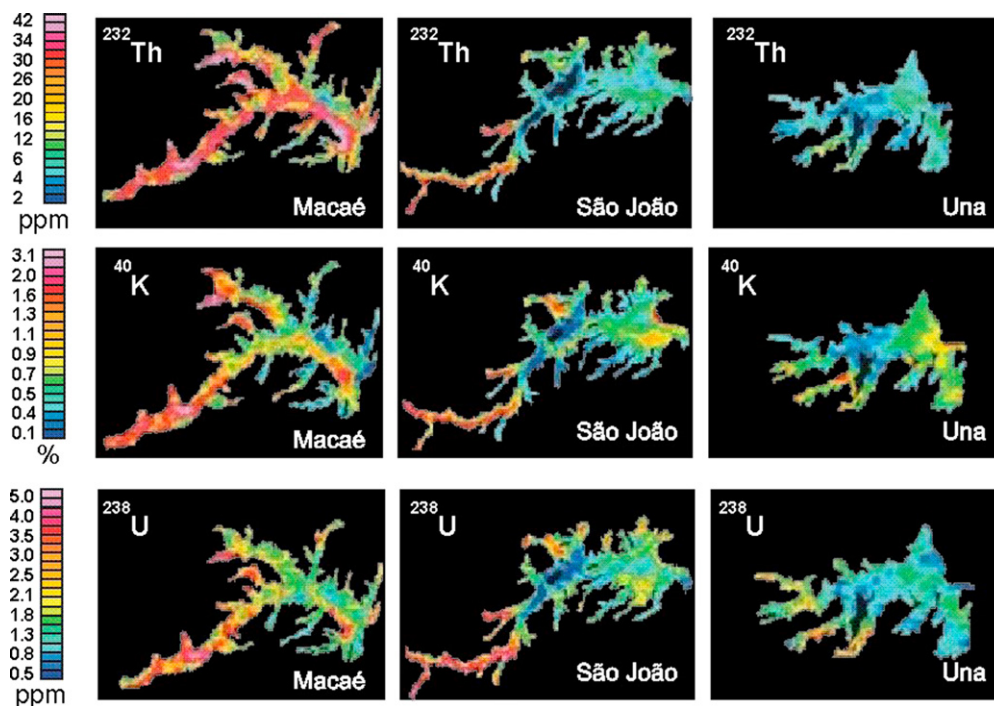


Fig. 4. Radionuclide concentration distribution at the Macaé, São João and Una river basins.

<sup>212</sup>Pb) of river bottom sediments and the material collected over coral's surface roughness clearly presents elevated radioactive content for MR when compared to SJR and UR (activity concentrations did not differ in river bottom sediments from the last two rivers, for 95% confidence level), Fig. 5. These results corroborate those obtained from aerogamaspectrometry. In general, individual radionuclide activity concentrations from MR varied from 1 to 2 orders of magnitude higher than SJR and UR.

#### 4.2. Related geochemical analyses

##### 4.2.1. Rare earth element (REE)

The presence of REEs associated to suspended particulates in estuaries and to deposited sediments may also be employed as a fingerprint of hydrological systems draining different rock types, groundwater discharge, among other sources. Particularly in estuaries, where mixing of rivers and ocean waters of very different pH and salinity takes place, can make the identification of sources somewhat complex. Elderfield et al. (1990) suggested that the catchments of rocks may play a minor role in defining the REE chemistry of river waters, while existing pools in rivers, formed by colloidal material and dissolved particulates associated to heavy REE, would play more important roles. Also, significant REE removal during the mixing of river and sea water may affect the proportion of REE in sediment grains and in the dissolved fraction. Concerning tropical and sub-tropical environments, this approach is still poorly understood. In theory, the existing highly acidic conditions, due to large amounts of dissolved organic matter and humic substances would effect significantly the REE. In this work, REEs, and additionally total U and Th, were investigated as to whether they exhibit a similar behavior to naturally occurring radionuclides, concerning the different river basins. Light lanthanoids (La, Eu, Ce, Sm), as well as U and Th, were present in higher concentrations in MR river bottom sediments comparing with Una and São João rivers (Fig. 6). The comparison of REE data for the rivers' bottom sediments and for the material over the coral colonies showed a similar pattern when compared to the set of

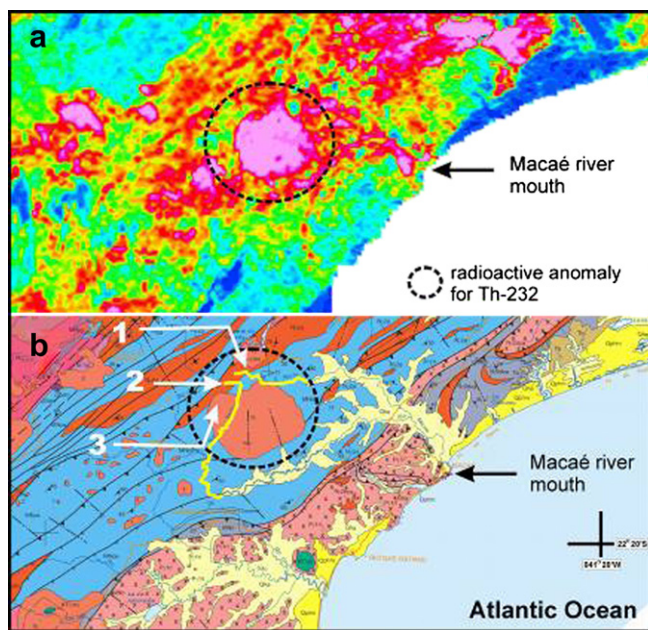


Fig. 5. <sup>232</sup>Th survey (a) and approximate corresponding geology (b) of the study site. Arrows indicate Macaé mouth and its main upstream tributaries (1: São Pedro river, 2: Sana river) and 3: Sana granite.

Table 1

Ratios of radionuclide activity concentrations for the three studied areas. (sd: standard deviation).

River Basins	<sup>232</sup> Th/ <sup>238</sup> U (mean ± sd)	<sup>40</sup> K/ <sup>232</sup> Th (mean ± sd)	<sup>40</sup> K/ <sup>238</sup> U (mean ± sd)
Macaé	8.46 ± 4.6	3.98 ± 2.49	3.77 ± 2.17
São João	3.60 ± 2.16	6.11 ± 7.37	2.94 ± 1.52
Una	4.16 ± 2.08	7.28 ± 6.52	2.79 ± 3.09

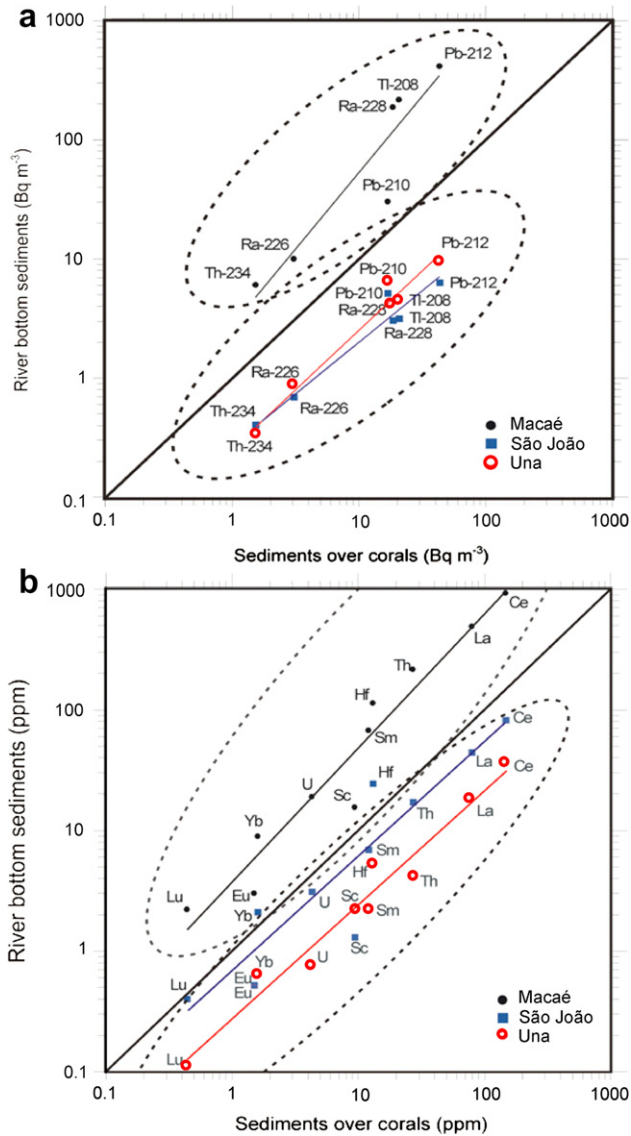


Fig. 6. (A) Regression between the activity concentrations of natural radionuclides in sediments covering coral colonies and from river bottoms of Macaé, São João and Una rivers. Ellipses in gray stress the two statistically different groups of data (95% confidence level); (B) The same for rare earth elements.

measured naturally occurring radionuclides. Therefore, the relative elevated concentrations detected by aerogamaspectrometry method for MR reflected both elevated activity concentrations of radionuclides and lanthanoids concentrations, thus distinguishing

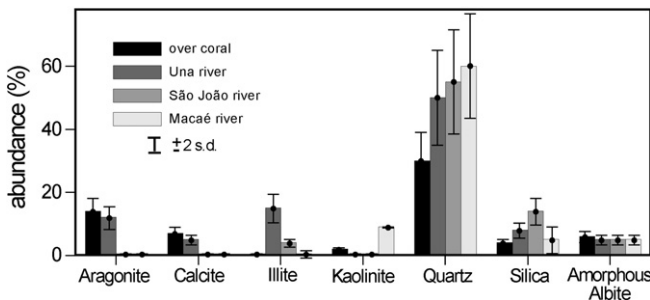


Fig. 7. Relative abundances of main minerals detected in sediments covering coral colonies and from Macaé, São João and Una rivers.

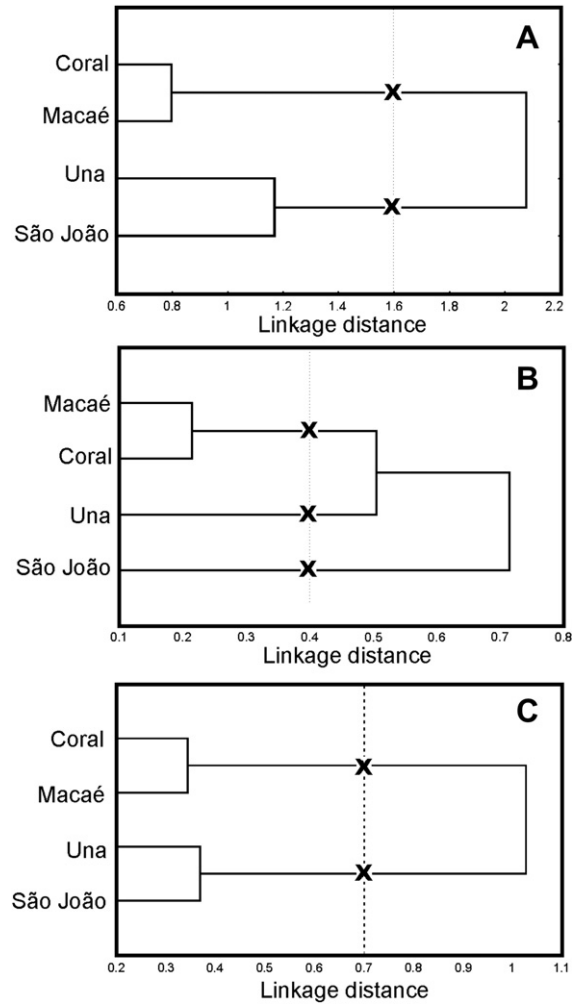


Fig. 8. Dendrograms obtained from the hierarchical cluster analysis for each parameter: gamma spectroscopy (A), rare earth elements (B), and mineralogy (C). (Ward's method for the Amalgamation rule and Euclidean distance as the linkage distance).

MR from SJR and UR. Moreover, a correlation between thorium and light REEs has been reported in fine grained sedimentary rocks (McLennan et al., 1980). The correlation between Th and heavy REEs is much less significant. In contrast, heavy lanthanoids (Lu, Yb, Hf) were more abundant in both SJR and MR while scarce in UR.

4.2.2. Mineralogy

Mineralogical analyses detected the presence of quartz, silica and amorphous albite in all sediment samples. Calcite and aragonite were identified in higher concentrations in sediments over corals and in the UR in minor percentages. Nevertheless, aragonite and calcite are components of the coralline skeleton and this material may reflect an in situ primary biogenic origin, probably attributed to sub-millimetric fragments of the coral colonies as a result tide action and the presence of small calcareous organisms associated to the coralline environment. Illite was mainly found in the SJR and UR. In contrast, kaolinite was only detected in samples over corals and in the MR. Comparative abundances of main minerals at the studied sites are presented in Fig. 7.

4.3. Clustering the parameters

Radionuclides, REEs and mineralogical data obtained from MR, SJR, UR and deposited over coral colonies were submitted to

hierarchical cluster analysis aiming at classifying sites of comparable similarities, considering the above parameterizations. We used the Ward's method as the Amalgamation rule and the Euclidean distance as the linkage distance (Digby and Kempton, 1987). The Ward method is usually regarded as efficient in geophysical studies and uses a more robust algorithm based on analysis of variance to evaluate the distances between groups of data, attempting to minimize the sum of the squared deviations from the cluster centroid that is created at each step of the method. The Euclidean distance is the most commonly employed distance. Its definition is a geometric distance computed as:  $\text{distance}(x, y) = \{\sum_{i=1}^K (x_i - y_i)^2\}^{1/2}$  for objects  $x_i$  and  $y_i$ , and  $K$  variable from raw data of comparable scale. Hierarchical cluster analysis showed similar classifications for the three above geochemical parameters. Coral and MR were classified as an independent group while SJR and UR were grouped apart (Fig. 8). This analysis fully supports the result pointed out by the aerogamaspectrometry survey, after the selection of the alluvium/colluvium deposits of the postulated source regions of sediments.

## 5. Conclusion

Sediment transport to coral reef environments is still poorly described at several ecologically relevant regions in Southern West Atlantic. This work is an effort to identify sources of sediments apportioning a shallow coral site at Armação dos Búzios/State of Rio de Janeiro/Brazil. The results presented here demonstrate the great potential of aerogamaspectrometry surveys (a common geophysical tool used worldwide) to identify coastal sources of sediments associated to estuarine systems, here also employed in combined with radiometric analyses, nuclear activation for REEs and mineralogy. In the geographical context of this work, the total aerogamaspectrometry database was selected with respect to the alluvium/colluvium geological domains that encompass three hydrological basins under investigation (Macaé, São João and Una Rivers). From the three radionuclide ratios of the aerial database ( $^{232}\text{Th}/^{238}\text{U}$ ,  $^{40}\text{K}/^{232}\text{Th}$  and  $^{40}\text{K}/^{238}\text{U}$ ),  $^{232}\text{Th}/^{238}\text{U}$  ratios were distinguishable within statistical significance and pointed out Macaé River as the main sediment contributor. This result was corroborated by the geochemical data (REEs, activity concentrations of naturally occurring radionuclides and mineralogy) of sediment samples that indicated higher similarity levels between Macaé River and the material collected on the surface of coral colonies.

## Aknowledgements

This work was funded by FAPERJ (Fundação de Apoio a Pesquisa no Estado do Rio de Janeiro), (APQ 1 E26/171.000/2002). The authors would like to acknowledge CPRM for providing U, Th and K databases and INPE (Instituto Nacional de Pesquisas Espaciais) to have provided satellite images. We also thank "Estuarine, Coastal and Shelf Science" reviewers to important suggestions on the text, which improved it much.

## References

Acevedo, R., Morelock, J., Olivieri, R.A., 1989. Modification of coral reef zonation by terrigenous sediment stress. *Palaios* 4, 92–100.

Acker, J.G., Vasilkov, A., Nadeau, D., Kuring, N., 2004. Use of SeaWiFS ocean color data to estimate neritic sediment mass transport from carbonate platforms for two hurricane-forced events. *Coral Reefs* 23, 39–47.

Consórcio Intermunicipal Lagos São João – CILSJ, 2006. Technical report. Available from: <http://www.lagossaojoao.org.br/>.

Dagg, M., Benner, R., Lohrenz, S., Lawrence, D., 2004. Transformation of dissolved and particulate materials on continental shelves influenced by large rivers: plume processes. *Continental Shelf Research* 24, 833–858.

David, C.P., 2003. Heavy metal concentrations in growth bands of corals: a record of mine tailings input through time (Marinduque Island, Philippines). *Marine Pollution Bulletin* 46, 187–196.

De Meijer, R.J., Donoghue, J.F., 1995. Radiometric fingerprinting of sediment on the Dutch, German and Danish coasts. *Quaternary International* 26, 43–47.

Devlin, M.J., Brodie, J., 2005. Terrestrial discharge into the Great Barrier Reef Lagoon: nutrient behavior in coastal waters. *Marine Pollution Bulletin* 51, 9–22.

Digby, P.G.N., Kempton, R.A., 1987. *Multivariate Analysis of Ecological Communities*, first ed. Chapman & Hall, London, UK, pp. 80–86.

Dodge, R.E., Gilbert, T.R., 1984. Chronology of lead pollution contained in banded coral skeletons. *Marine Biology* 82, 9–13.

Edinger, E.N., Limmon, G.V., Jompa, J., Windjatkomo, W., Heikoop, J.M., Risk, M.J., 1999. Normal coral growth rates on dying reefs: are coral growth rates good indicators of reef health? *Marine Pollution Bulletin* 40 (5), 404–425.

Elderfield, H., Upstill-Goddard, R., Sholkovitz, E.R., 1990. The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. *Geochimica et Cosmochimica Acta* 54 (4), 971–991.

Esslemont, G., 1999. Heavy metals in corals from Heron Island and Darwin Harbour, Australia. *Marine Pollution Bulletin* 38 (11), 1051–1054.

Evangelista, H., Godiva, D., Sifeddine, A., Leão, Z.M.A.N., Rigozo, N.R., Segal, B., Ambrizzi, T., Kampel, M., Kikuchi, R., Le Cornec, F., 2007. Evidences linking ENSO and coral growth in the Southwestern-South Atlantic. *Climate Dynamics* 1, 1–12. doi:10.1007/s00382-007-0271-8.

Fundação Centro de Informações e Dados do Rio de Janeiro, 1998. CIDE, Estado do Rio de Janeiro: Território, second ed., Fundação Centro de Informações e Dados do Rio de Janeiro, Rio de Janeiro, 80 pp.

Gardner, T.A., Cote, I.M., Gill, J.A., Grant, A., Watkinson, A.R., 2003. Long-term region-wide declines in Caribbean corals. *Science* 301, 958–960.

Handl, J., Sachse, R., Jakob, D., Michel, R., Evangelista, H., Gonçalves, A.C., Freitas, A. C., 2008. Accumulation of  $^{137}\text{Cs}$  in Brazilian soils and its transfer to plants under different climatic conditions. *Journal of Environmental Radioactivity* 99, 271–287.

Hughes, T.P., Baird, A.H., Bellwood, D.R., Card, M., Connolly, S.R., Folke, C., Grosberg, R., Hoegh-Guldberg, O., Jackson, J.B.C., Kleypas, J., Lough, J.M., Marshall, P., Nyström, M., Palumbi, S.R., Pandolfi, J.M., Rosen, B., Roughgarden, J., 2003. Climate change, human impacts and the resilience of coral reefs. *Science* 301, 929–933.

International Atomic Energy Agency, 2003. Guidelines for Radioelement Mapping Using Gamma Ray Spectrometry Data. IAEA-TECDOC-1363. IAEA, Vienna, 173 pp.

Ivanovich, M., Harmon, R.S., 1992. Uranium-series Disequilibrium: Applications to Earth. Marine and Environmental Sciences, second ed. Clarendon Press, Oxford, 901 pp.

Larcombe, P., Woolfe, K.J., 1999. Increased sediment supply to the Great Barrier Reef will not increase sediment accumulation at most coral reefs. *Coral Reefs* 18, 163–169.

Macdonald, I.A., Perry, C.T., Larcombe, P., 2005. Comment on rivers, runoff, and reefs by McLaughlin et al. [*Global Planetary Change* 39 (2003) 191–199]. *Global and Planetary Change* 45, 333–337.

McConochie, J.D., Hardy, T.A., Mason, L.B., 2004. Modelling tropical cyclone over-water wind and pressure fields. *Ocean Engineering* 31 (14–15), 1757–1782.

McLaughlin, C.J., Smith, C.A., Buddenmeier, R.W., Bartley, J.D., Maxwell, B.A., 2003. Rivers, runoff and reefs. *Global and Planetary Change* 39, 191–199.

McLennan, S.M., Nance, W.B., Taylor, S.R., 1980. Rare earth element-thorium correlations in sedimentary rocks, and the composition of the continental crust. *Geochimica et Cosmochimica Acta* 44 (11), 1833–1839.

Medina-Elizalde, M., Gold-Bouchot, G., Ceja-Moreno, V., 2002. Lead contamination in the Mexican Caribbean recorded by the coral *Montastrea annularis* (Ellis and Solander). *Marine Pollution Bulletin* 44 (5), 421–423.

Morelock, J., Boulon, K., Galler, G., 1979. Sediment Stress and Coral Reefs. Symp. Energy Industry and the Marine Environment, Guayanilla Bay, pp 46–58.

Mourão, L.M.F., Monteiro, A.C., dos Anjos, I.L.S., Escobar, L.P., Sinclair, R., 1997. Aplicação da técnica de back-calibration no Brasil para a conversão de dados aerogamaspectrométricos de CPS para a concentração de elementos. Anais do V Simpósio de Geologia do Sudeste, Rio de Janeiro, pp 331–333.

Nott, J., 2004. Palaeotespestology: the study of prehistoric tropical cyclones – a review and implications for hazard assessment. *Environmental International* 30, 433–447.

Nugues, M.M., Roberts, C.M., 2003. Partial mortality in massive reef corals as an indicator of sediment stress on coral reefs. *Marine Pollution Bulletin* 46, 314–323.

Oigman-Pszczol, S.S., Figueiredo, M.A.O., Creed, J.C., 2004. Distribuição de Comunidades Bentônicas de Substrato Rochoso do Infralitoral de Armação de Búzios, Sudeste Brasil. *Marine Ecology* 25 (3), 173–190.

Pandolfi, J.M., Bradbury, R.H., Sala, E., Hughes, T.P., Bjorndal, K.A., Cooke, R.G., McArdle, D., McClenachan, L., Newman, M.J.H., Paredes, G., Warner, R.R., Jackson, J.B.C., 2003. Global trajectories of the long-term decline of coral reef ecosystems. *Science* 301, 955–958.

Peterson, R., Stramma, L., 1991. Upper-level circulation in the South Atlantic Ocean. *Progress in Oceanography* 26 (1), 1–73.

Philipp, E., Fabricius, K., 2003. Photophysiological stress in scleractinian corals in response to short-term sedimentation. *Journal of Experimental Marine Biology and Ecology* 287, 57–78.

Santos, J.O., Munita, C.S., Meira, P.T., Oliveira, S., 2007. Estudo do Controle analítico em análises de material argiloso realizadas por ativação neutrônica. Annals of the II Congresso de Pesquisa e Inovação da Rede Norte Nordeste de Educação Tecnológica, João Pessoa – Brazil, pp 1–8.



- Segal, B., Evangelista, H., Kampel, M., Costa Gonçalves, A., Polito, P.S., Santos, E.A., 2008. Potential impacts of polar fronts on sedimentation processes at Abrolhos coral reef (South-West Atlantic Ocean/Brazil). *Continental Shelf Research* 28, 533–544.
- Smith, S.V., Buddemeier, R.W., 1992. Global change and coral reef ecosystems. *Annual Reviews of Ecology Systems* 23, 89–118.
- Weber, M., Lott, C., Fabricius, K.E., 2006. Sedimentation stress in a scleractinian coral exposed to terrestrial and marine sediments with contrasting physical, organic and geochemical properties. *Journal of Experimental Marine Biology and Ecology* 336, 18–32.
- Wild, C., Huettel, M., Kluefer, A., Kremb, S.G., Rasheed, M.Y.M., Jorgensen, B.B., 2004. Coral mucus functions as an energy carrier and particle trap in the reef ecosystem. *Nature* 428, 66–70.
- Wollenberg, H.A., Smith, A.R.A., 1990. Geochemical assessment of terrestrial  $\gamma$ -ray absorbed dose rates. *Health Physics* 58 (2), 183–189.
- Woolfe, K.J., Larcombe, P., 1998. Terrigenous sediment accumulation as a regional control upon the distribution of reef carbonates. In: Camoin, G.F., Davies, P.J. (Eds.), *Reefs and Carbonate Platforms in the Pacific and Indian Oceans*, vol. 25. International Association of Sedimentologists Special Publication, pp. 295–310.