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ANTHROPOGENIC NUTRIENT POLLUTION OF CORAL REEFS IN SOUTHERN BAHIA, BRAZIL

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ABSTRACT

Spatial, temporal and anthropogenic controls on nutrient distribution were evaluated for nearshore and offshore reefs at Porto Seguro Bay, Southern Bahia. Water samples were analysed for total oxidised nitrogen (TON), soluble reactive phosphorus (SRP), reactive silica (DSi), and chlorophyll *a* (Chl). The results indicate that rainfall promotes a significant (F=19.873, p<0.001) increase in the load of nutrients to nearshore (average 12% increase) and offshore reefs (average 31% increase). Nutrient concentrations at the urbanized reef (TON=1.93-3.21μM; SRP=0.57-0.89μM; DSi=8.48-11.15μM) are on average 25% higher than at non-urban reefs and over 200% higher than the offshore reef. The urbanized reef also presented the highest rates of increase in nutrient input between dry and rainy seasons (TON=+0.36μM; SRP=+0.08μM; DSi=+0.70μM). Differences in nutrient concentration between nearshore and offshore reefs are more pronounced during dry season, when the bulk of land-based nutrient contribution is confined to the nearshore reefs. SRP values in the study area ranked among the highest in the world for coral reef areas and phytoplankton growth appears to be nitrogen-limited.

RESUMO

Este artigo discute os fatores espaço, tempo e atividade antrópica na distribuição de nutrientes em amostras dos recifes costeiros da Baía de Porto Seguro, sul do Estado da Bahia. Análises realizadas nas amostras d'água incluem a porção reativa de nitrogênio (TON), fósforo (SRP) e silicato (DSi) dissolvidos, e clorofila (Chl). Resultados indicam um aumento significante (F=19.873, p<0.001) na descarga de nutrientes durante a estação chuvosa para os recifes costeiros (média de 12%) e para o recife oceânico (média de 31%). O recife urbano (TON=1.93-3.21μM; SRP=0.57-0.89μM; DSi=8.48-11.15μM) apresentou concentrações 25% mais altas que o outro recife costeiro, e mais de 200% acima do recife oceânico. Aquele recife também apresentou as mais altas taxas de aumento na descarga de nutrientes entre as estações seca e chuvosa (TON=+0.36μM; SRP=+0.08μM; DSi=+0.70μM). A diferença nas concentrações de nutrientes entre os recifes costeiros e oceânico é maior durante a estação seca, quando a contribuição continental de nutrientes está confinada a áreas próximo à costa. As concentrações de fósforo inorgânico na área de estudo estão entre as mais altas do mundo para áreas coralinas, e o fitoplâncton parece ser limitado pela disponibilidade de nitrogênio.

Descriptors: Coastal eutrophication; Nitrogen; Phosphorus; Submarine groundwater discharge; Coral reef; Nutrients; Seasonality; Coastal urbanization.
Descritores: Eutrofização costeira; Nitrogênio; Fósforo; Descarga de água subterrânea marinha; Recife de coral; Nutrientes; Sazonalidade; Urbanização costeira.

INTRODUCTION

Flowing down from the Equator, waters from the oceanic Brazil Current induce oligotrophic and near to homogeneous conditions of the chemical constituents along the inner shelf in the Brazilian coast (KOENING; DE MACEDO, 1999). Mesotrophic or eutrophic conditions are mainly local, depending on either land-based sources (DITTMAR; LARA, 2001) or upwelling processes (CARBONEL; VALENTIN, 1999). Estuarine and coastal areas near to major urban settlements are the most eutrophic (CONTADOR; PARANHOS, 1996; AGUIAR; BRAGA, 2007), with untreated sewage discharge being one of the main sources of nutrients to coastal areas (KJERFVE et al., 1997). Land impacts upon offshore reefs are mitigated due to the efficient flushing by the Brazil Current (KNOPPERS et al., 1999). Nearshore reefs, however, are subjected to the influence of a highly siliciclastic sediment influx (LEÃO, 1996) and receive substantial supplies of nutrients from terrigenous sources such as runoff, river discharge and groundwater inputs

(COSTA et al., 2000). Widespread use of cesspits and septic tanks in urban settlements along the coast also increases the nutrient concentrations of groundwater by infiltration through highly porous sandstone and beach rocks (COSTA et al., 2000). This study evaluates the spatial, temporal and anthropogenic controls on nutrient distribution of nearshore and offshore reefs in Southern Bahia, Brazil. Seawater, porewater and sediment samples were collected along different transects during dry and rainy seasons, for two years, in three reefs with distinct nutrient inputs (two nearshore reefs, one being close to an urban settlement, and an offshore marine park). We also discuss the importance of submarine groundwater discharge (SGD) as a potential pathway for nutrient fluxes to coastal coral reefs in the study area.

SGD is a relatively common phenomenon and has been recently recognized as an important source of nutrients to coastal waters (see the review from Slomp; Van Cappellen, 2004). Estimates of freshwater groundwater flux indicate that the ratio of groundwater discharge to stream flow is 20 to 50%, and that the magnitudes of both the total dissolved nitrogen and PO_4^{3-} loads due to fresh SGD are 40 to 100% of loads carried by streams (KROEGER et al., 2007). In some areas, SGD can have greater ecological significance than surface runoff as virtually all freshwater entering the sea is in the form of submarine discharge (KAY et al., 1977; HANSHAW; BACK, 1980). Likewise, SGD can be one of the primary pathways for nutrients and contaminants to interact with overlying surface waters (RUTKOWSKI et al., 1999), and a key factor initiating phytoplankton blooms (LAPOINTE et al., 1990).

Reports of SGD in Brazil are scarce, but the research carried out so far have indicated that it is a quantitatively important component of the nutrient and water budget to coastal areas, especially near urban settlements. The first observation was made in the early 1990's, on a coastal lagoon near Rio de Janeiro City. Salinity and temperature profiles revealed an intrusion of seawater to the lagoon through the porous sediments of a sand barrier (COSTA, O.S., unpubl.). Subsequent topographic profiles also revealed that, during high tides, the lagoon level occurred at more than 1 m below the sea level, thus allowing the inflow of seawater to the choked lagoon. Windom and Niencheski (2003), studying the freshwater-seawater mixing zone in southern Brazil, also found that freshwater discharged to the ocean through permeable sediments may have a significantly different composition than that discharged at the surface. Oliveira et al. (2003, 2006) used a natural tracer (^{222}Rn) to estimate groundwater fluxes in four embayments at Ubatuba coastal area in southern Brazil. They observed significant flow of subsurface water at rates of 23 ± 22 cm day^{-1}. They also compared ^{222}Rn data to seepage measurements, finding flux rates between 1.4 and 21.6 cm day^{-1}.

Further studies of SGD were also performed in the north coast of Bahia (COSTA et al., 2000). In this study, groundwater nutrient concentration in the urbanized site was many times higher than those detected in the underdeveloped area, due mainly to the widespread use of septic tanks and cesspits. Groundwater flux was predominantly seaward due to the fact that the lagoon-level could be as high as 5.9 m above sea-level (at low tides), generating a groundwater flux of approximately 45 L m^{-2} day^{-1} towards the coastal reefs. Studies of SGD fluxes performed elsewhere revealed discharge rates ranging from 2.2 to 14.5 L m^{-2} day^{-1} (SWARZENSKI et al., 2007).

Although the direction of the groundwater flow is assumed to oscillate as the fluctuating tides create a differential head between sea level and the water table, the study of COSTA et al. (2000) has shown that this may not always be the case, and an unidirectional flow may be established. Such a permanent supply of nutrients via groundwater seepage may pose an ecological problem, leading to algal blooms and the steady deterioration of the water quality.

Seasonality is also an important factor affecting the degree to which groundwater nutrients influence coastal communities, and the flux of the SGD has been shown to increase substantially during rainy seasons. Seasonal differences in nutrient concentration presented by Costa et al. (2000) in the northern coast of the state reflect the role of rainfall in nutrient dilution and transport. Lower levels of ammonia and higher nitrate found during the rainy season indicate that a recharge of the permeable aquifer by oxygenated rainfall infiltration allow an increasing oxidation of ammonia to nitrite and then to nitrate.

MATERIAL AND METHODS

Study Area

Three reefs were selected for sampling (Fig. 1): two nearshore (Ponta Grande reef and Coroa Vermelha reef, the latter occurring close to an urbanized area) and one offshore (the Recife de Fora, a marine protected area 8 km off the coast). Two transects (six stations) were sampled at each reef. On the nearshore reefs, two stations were located on the reef flat (shallow pools), two at 15 m, and two at 30 m distance from the reef crest. Depth around the nearshore reefs is no greater than 8 m. On the offshore reef (depths vary between 6 m and 14 m), samples were collected at two stations on the reef flat (shallow pools) and two each on the landward and seaward slopes, both located 15 m distant from the reef crest.

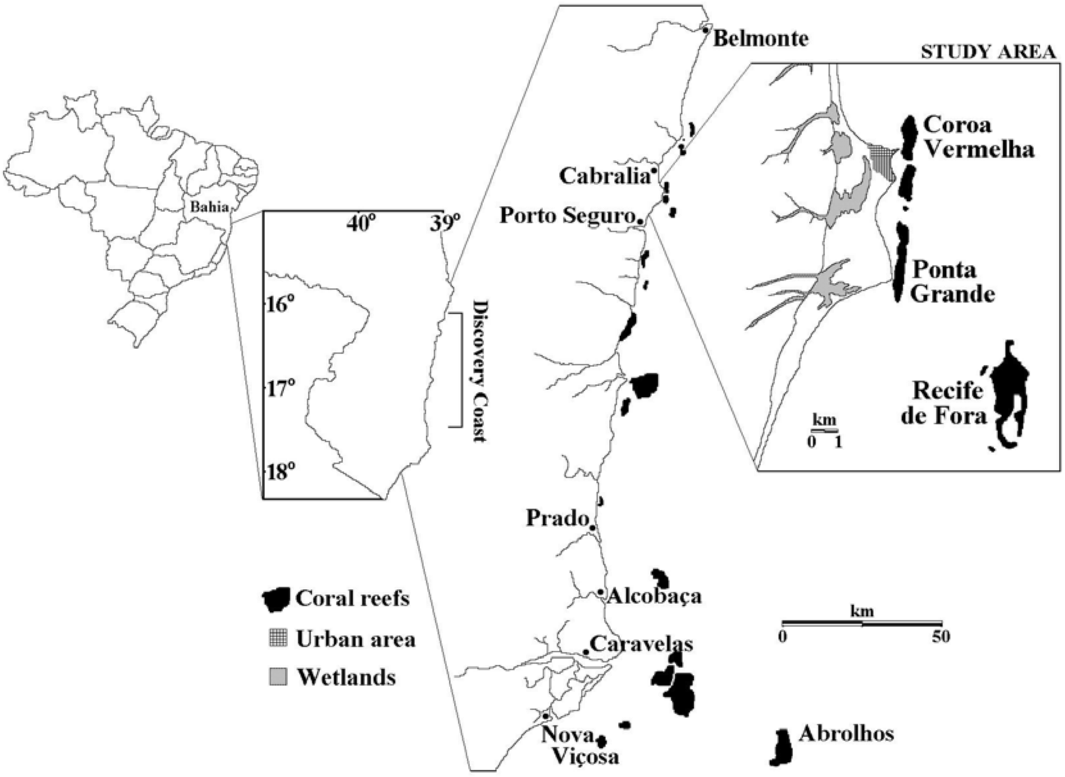

Fig. 1. Map of the Brazilian Discovery Coast, Southern Bahia, Brazil, and location of the studied reefs.

Sampling Design

In order to account for seasonal variability, sampling occurred during both dry (July-August) and rainy (February-March) seasons in 1999 and 2000. Water, porewater, and sediment sampling were performed in the last two weeks of the sampling period in both August (dry season) and March (rainy season). During the preceding 45 days of each sampling period, a benthic ecological assessment was performed on each reef, aiming to identify any spatial or temporal patterns of community structure variation within and between reefs. As phytoplankton activity can quickly deplete the dissolved nutrients from the water column, chlorophyll measurements were also performed as an additional indicator of nutrient enrichment (also on the last two weeks of each sampling period).

Seawater Sampling

Samples in the water column were collected 1 m below the surface and 1 m above the bottom in all sites where depth was higher than 3 m. In sites with depths of less than 3 m, only one sample was taken at mid-depth. Samples were collected with 5 L polyethylene bottles deployed by SCUBA diving. Samples were filtered immediately, using a Nalgene® filtration unit connected to a hand-pump, and then frozen (-20ºC). A series of measures were taken to minimize the effects of storage on analyte concentration, including: 1) the use of HDPE bottles with leak-proof screws; 2) careful cleaning and decontamination of bottles, flasks and containers that came in contact with the sample by using an overnight bath with Neutracon® (a phosphate-free, totally rinsable, surface active agent), followed by a HCl 10% acid bath; and 3) comprehensive sub-sampling procedure to detect any background contamination. A storage trial was also performed (prior to sampling) to assess the stability of TON, SRP and DSi under different storage methods and with different water matrices. A site specific protocol for sample storage (-20ºC freezing) was used, and all samples were analyzed within two weeks. A detailed description of the storage trial procedure and results can be found in Gardolinski et al. (2001). Two types of filters were used: Cellulose acetate membranes (Whatman® 0.45 μm pore size), for samples undergoing nutrient analysis, and glass fiber filters (Whatman® GF/F), for concentration of pigments for chlorophyll analysis. Procedural blanks (distilled, double deionised, UV irradiated Milli-Q water, filtered as sample) were used throughout the sampling to assure that no analyte was added during the processing of the sample. Control solutions were also used to monitor the effects of the storage period on the nutrient concentration of the water samples. At each station, a solution containing 7.14 μmol L^{-1} of N, 3.23 μmol L^{-1} of P, and 3.56 μmol L^{-1} of Si was filtered and stored as sample. Variations in the concentration of controls stayed within 6%.

Sediment and Porewater Sampling

Analysis of sediment and porewater samples aimed to identify the contribution of nutrients regenerated from the sediment. Sediment cores were collected from the same stations used for water sampling (along the reef transects described previously) using aluminum tubes (7.5 cm internal diameter). Both ends of the core were closed with PVC caps after core retrieval. Each core was divided into 10 cm-long sections. Porewater was extracted from each section using a system based on the "whole-core squeezer" porewater sampler developed by Bender et al. (1987). The porewater collected was then filtered as described for seawater samples. Sediment samples were collected from each core-section, placed in zip-lock bags, identified and frozen (-20ºC). Sediment samples were used for textural analysis (dry sieving technique – FOLK; WARD, 1957; LARSON et al., 1997) and organic matter content (loss on ignition method – HEIRI et al., 2001).

Benthic Ecological Assessment

Due to the high complexity of the reef ecosystem, and considering the time constraints of the study, only the following benthic organisms were targeted in the survey: cnidarians (including stony corals, hydrocorals, gorgonians and zoanthids) and macroalgae (including fleshy, turf and crustose coralline algae). These organisms comprised more than 3/4 of the reef cover in the study area. A detailed description of methods used and the results of statistical analysis of the distribution and ecology of macroalgae species and other benthic groups in the study area can be found in Costa et al. (2002).

Analytical Measurements

Samples were analyzed for total oxidized nitrogen (TON), soluble reactive phosphorus (SRP), and reactive silica (DSi). Nutrient concentrations were determined using a segmented continuous flow analyser (Skalar SAN^{plus}) incorporating a chemistry unit (SA 4000). For absorbance reading, a matrix photometer 6250 detector with automatic background correction was used. The automated method for determination of TON was based on the cadmium reduction method adapted for autoanalyzers (BREWER; RILEY, 1965). Detection limit was 0.07 μmol L^{-1}. The efficiency of nitrate reduction in the cadmium column was validated regularly to be over 95% by running a nitrite standard with the same concentration as the highest nitrate standard. SRP was determined by the molybdenum blue complex method (BENSON et al., 1996). Detection limit was 0.04 μmol L^{-1}. The automated method for DSi determination was based on the reduction of silicomolybdic acid with ascorbic acid, producing a blue dye, which was then measured at 810 nm (BREWER; RILEY, 1966). Detection limit was 0.03 μmol L^{-1}. For analysis of chlorophyll pigments, the visible spectrophotometry method described by ARAR (1997) was used. The detection limit for this method was 0.1 μg L^{-1} using a 2-cm glass cell. Salinity was measured using a portable Yellow Springs' salinometer model YSI® 30/10FT (range between 0-80 PSU and resolution of 0.1 PSU).

Statistical Analysis

Multifactorial ANOVA was used to analyse simultaneously the effects of season, reef sites and sample locations, and their interactions, on each nutrient analyte (TON, SRP or DSi). *Post hoc* tests (Student Newman Keuls - SNK and Tukey's pairwise comparisons) were performed to further investigate the interactions between these effects. For porewater data, values were averaged for each core in order to ascertain differences in nutrient concentrations between reefs and sampling sites. The Friedman's test was then performed to evaluate the effects of season, reef and sample location. This test is a nonparametric analogue of a two-way ANOVA and makes no assumptions about the distribution of the data. It is appropriate to the situation faced by the porewater data, where in some cases there is a single observation for each location. All multivariate analyses were completed using the PRIMER software package.

RESULTS

Nutrient Concentrations in Surface and Bottom Samples

TON concentrations at the nearshore reefs (Fig. 2A) varied from 1.74 to 2.81 μmol L^{-1}, during the dry season, and from 1.95 to 3.64 μmol L^{-1}, during the rainy season. Lowest values were always observed at Ponta Grande reef. At the offshore reef (Recife de Fora), TON concentrations varied from 0.41 to 0.89

μmol L^{-1}, during the dry season, and from 0.52 to 1.16 μmol L^{-1} during the rainy season (Fig. 2A). Bottom samples (collected 1 m above the sediment) exhibited consistently higher TON concentrations than those collected near the surface at the same locations in all seasons on both nearshore and offshore reefs (Fig. 2A).

SRP concentrations on the nearshore reefs (Fig. 2B) varied from 0.46 to 0.91 μmol L^{-1}, during the dry season, and from 0.61 to 0.91 μmol L^{-1}, during the rainy season. Values at Ponta Grande were again lower than on Coroa Vermelha at all but one sampling site (the reef flat). At the offshore reef (Fig. 2B), concentrations varied from 0.20 to 0.43 μmol L^{-1}, during the dry season, and from 0.23 to 0.46 μmol L^{-1} during the rainy season, the lowest SRP values always occurring at the seaward side, in both seasons. Samples collected near the bottom exhibited higher SRP concentration than those sampled near the surface in all reefs and seasons (Fig. 2B).

DSi concentrations at the nearshore reefs (Fig. 2C) varied from 7.96 to 11.05 μmol L^{-1}, during the dry season, and from 9.05 to 11.47 μmol L^{-1}, during the rainy season. At the offshore reef, DSi concentrations (Fig. 2C) varied from 2.13 to 3.14 μmol L^{-1}, during the dry season, and from 2.15 to 3.88 μmol L^{-1} during the rainy season. Concentrations near the bottom again exhibited persistently higher concentrations than those observed in the surface samples, with higher values being recorded during the rainy season (Fig. 2C). From all three parameters, DSi was the most stable, presenting lowest spatial and temporal variability.

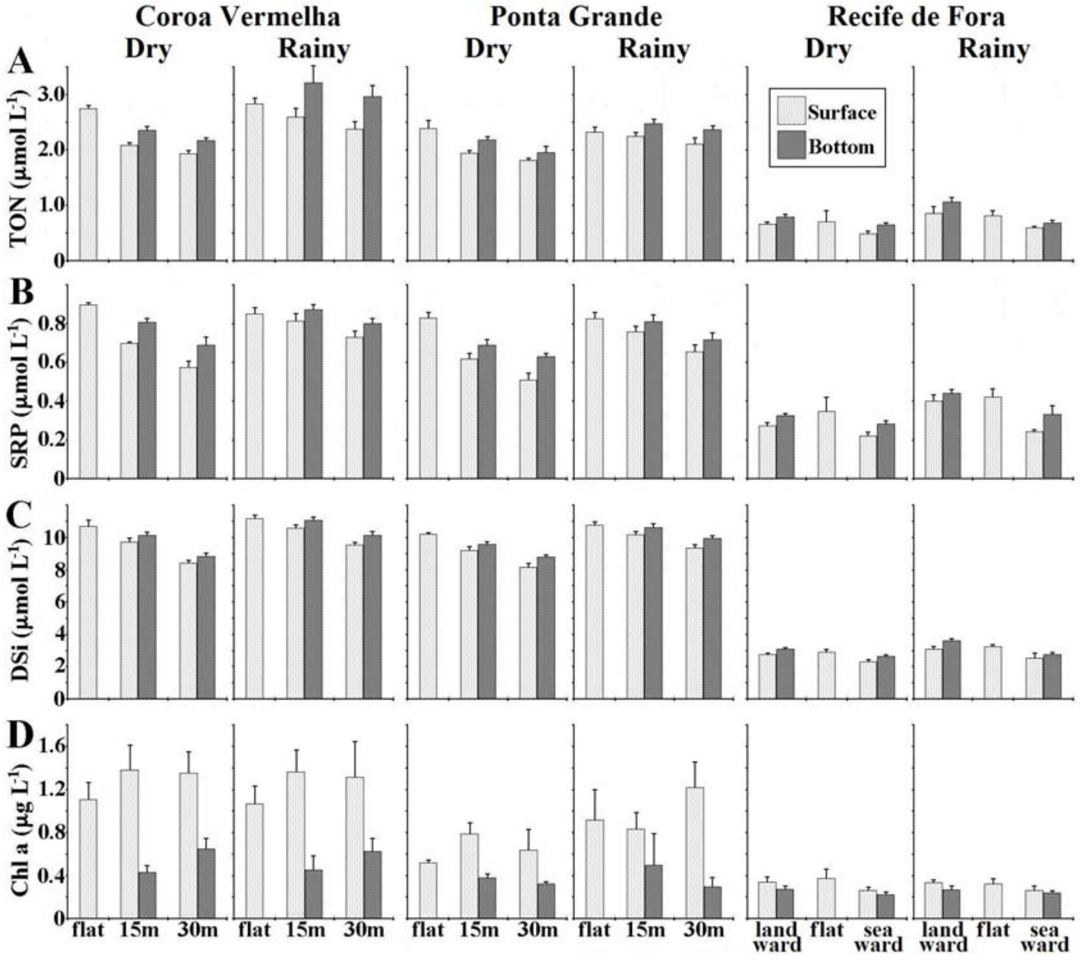

Fig. 2. Comparison of (A) TON, (B) SRP, (C) DSi, and (D) chlorophyll *a* concentrations (mean ±SE) between surface and bottom samples during dry and rainy seasons in all studied reefs (n = 8). flat = reef flat, 15m and 30 m = distance from the reef crest.

Patterns of TON Distribution

Surface TON concentrations are highly variable both within and between reefs. The nearshore reefs, although having similar geology and being exposed to the same climatic and hydrologic conditions, presented significantly different TON distribution, with Coroa Vermelha presenting results 9% higher than Ponta Grande during the dry season, and 14% higher during the rainy season. The reef flat exhibited the highest TON concentration of all sample locations, but did not vary significantly between seasons. Results of the ANOVA significance test for nearshore reefs indicates that, although all factors presented significant results, only one interaction (season x reef) revealed a significant effect. On the offshore reef, however, the season effect is highly significant, mainly because of the observed variation in landward TON concentrations. Peak values during the rainy season were found on the landward side of the reef, but the lowest values, as expected, always occurred at the seaward side, in both surface and bottom samples.

Patterns of SRP Distribution

Contrary to the trend observed for TON, there was not a significant increase in SRP concentrations at Coroa Vermelha during the rainy season, and no season x reef interaction term was evident, according to the results of ANOVA tests. The only significant first-order interaction was that between season and sample location, due mainly to the behaviour of reef flat concentrations, which did not vary significantly either between reefs or seasons. At the offshore reef, lowest SRP values always occurred at the seaward side, in both seasons. However, unlike that observed for TON, highest SRP values always occurred on the reef flat. Distinct seasonal responses from landward and seaward sides resulted in a significant first-order interaction between season and location for surface samples. The same was not observed for bottom samples ($F = 7.065$, $p = 0.013$), which, although presenting consistently higher concentrations than those collected near the surface, did not vary seasonally in the same pattern as for TON concentrations.

Patterns of DSi Distribution

As for TON and SRP, higher DSi concentrations were recorded during the rainy season. However, differences between surface and bottom samples were not as significant as those for TON concentrations. A significant first-order interaction between season and location was found ($F = 14.408$, $p = <0.001$), and is due mainly to variations in reef flat DSi concentrations between seasons. Differences in DSi concentrations between Coroa Vermelha and Ponta Grande were smaller than TON or SRP, although still statistically significant, with the latter reef presenting higher variation among seasons than Coroa Vermelha. On the offshore reef, the highest DSi values were found mostly on the reef flat, but never on the seaward side. A significant season effect was observed, with concentrations during rainy season being significantly higher than dry season.

Nutrient Concentrations in Porewater

Nutrient concentrations in porewater from the studied reefs are about twice the concentration for the overlying water column. TON concentrations (Fig. 3A) in Coroa Vermelha varied from 4.73 to 5.48 μmol L^{-1}, during the dry season, and from 5.16 to 6.22 μmol L^{-1}, during the rainy season. In Ponta Grande, concentrations ranged from 3.70 to 3.94 μmol L^{-1}, during the dry season, and from 3.81 to 4.28 μmol L^{-1}, during the rainy season. Porewater TON concentrations at the offshore reef varied between 1.26 and 1.72 μmol L^{-1}, during the dry season, and from 1.01 to 1.96 μmol L^{-1}, during the rainy season (Fig. 3A). The results of the Friedman's test for porewater TON concentrations showed a significant statistical difference between seasons ($\chi^2 = 6.000$; $p = 0.014$), with the rainy season presenting higher concentrations than the dry season. TON values at Coroa Vermelha are also significantly higher than those at Ponta Grande. The significance test also showed that concentrations in the sampling site located 15 m from the reef are higher than concentrations at 30 m. On the offshore reef, no significant difference between seasons was observed ($\chi^2 = 0.333$; $p = 0.564$). Additionally, no significant difference was found between sampling locations, although landward samples always presented the highest porewater TON concentrations and seaward samples the lowest values.

Porewater SRP concentrations (Fig. 3B) in Coroa Vermelha varied from 1.88 to 2.19 μmol L^{-1}, during the dry season, and from 1.97 to 2.57 μmol L^{-1}, during the rainy season. Values at Ponta Grande varied between 1.39 and 1.49 μmol L^{-1}, during the dry season, and 1.29 to 1.71 μmol L^{-1}, during the rainy season. Concentrations at the offshore reef varied between 0.47 and 0.82 μmol L^{-1}, during the dry season, and from 0.37 to 0.87 μmol L^{-1}, during the rainy season (Fig. 3B). Even though SRP concentrations during the rainy season were generally higher, the Friedman test found no significant statistical difference between seasons ($\chi^2 = 2.667$; $p = 0.102$). There was a significant difference between the two reefs ($\chi^2 = 6.000$; $p = 0.014$), with porewater SRP concentration at Coroa Vermelha being higher than those at Ponta Grande. As observed for TON, the significance test also showed that 15 m porewater SRP concentrations are higher than the 30 m sampling location. On the offshore reef, no significant statistical difference was found between seasons or sampling locations. The significance test also showed that landward samples presented the highest SRP concentrations, while no statistical difference was found between seaward and reef flat samples.

Porewater DSi concentrations (Fig. 3C) in Coroa Vermelha ranged from 34.01 to 46.92 µmol L^{-1}, during the dry season, and from 39.69 to 60.77 µmol L^{-1}, during the rainy season. Values at Ponta Grande varied between 37.73 and 41.40 µmol L^{-1}, during the dry season, and from 37.92 to 57.83 µmol L^{-1}, during the rainy season. Concentrations at Recife de Fora varied from 8.15 to 9.78 µmol L^{-1}, during the dry season, and from 8.06 to 11.46 µmol L^{-1}, during the rainy season (Fig. 3C). Porewater DSi concentrations are more than four times the concentration in the overlying water column. A significant statistical difference was found between seasons ($\chi^2 = 6.000$; $p = 0.014$), with DSi concentrations during rainy season being higher. No significant difference was found between the two reefs, although porewater DSi concentration at Coroa Vermelha was generally higher than those at Ponta Grande. All sampling locations (flat, 15m and 30m) are different from each other. On the offshore reef, porewater DSi concentrations represent about three times the concentration of the water column near the bottom. Results of the Friedman's test showed no significant difference between seasons ($\chi^2 = 0.333$; $p = 0.564$) or between sampling locations, with landward samples presenting the highest porewater DSi concentrations and the reef flat presenting the lowest values.

Chlorophyll *a* Concentrations

At the nearshore reefs, mean chlorophyll *a* concentration in surface waters ranged from 0.51 to 1.38 µg L^{-1} (Fig. 2D). Bottom samples showed little variation between reefs or seasons, with chlorophyll *a* concentrations ranging from 0.29 to 0.64 µg L^{-1}. At the offshore reef, chlorophyll *a* concentrations were extremely low, especially at the seaward reef (Fig. 2D). In surface waters, concentrations ranged from 0.26 to 0.38 µg L^{-1}. In bottom samples, concentrations varied between 0.22 and 0.28 µg L^{-1}. Although statistical tests on chlorophyll *a* data from surface samples have shown significant seasonal and spatial variation, *post hoc* tests revealed that such variation is due mainly to Ponta Grande values, in which seasonality represents a highly significant effect. Evaluation of the Coroa Vermelha dataset alone further confirmed this with no seasonal effect on chlorophyll *a* concentration being observed. Bottom samples showed little variation between reefs or seasons. At the offshore reef, Chlorophyll *a* concentrations were extremely low, especially at the seaward reef. There was a significant statistical difference between dry and rainy season in surface samples ($F = 5.105$, $p = 0.010$), but none was observed in bottom samples ($F = 3.192$, $p = 0.085$). The interaction between the effects of season and sample location is significant only for surface samples, and *post hoc* tests revealed that this is caused mainly by reef flat variation between seasons.

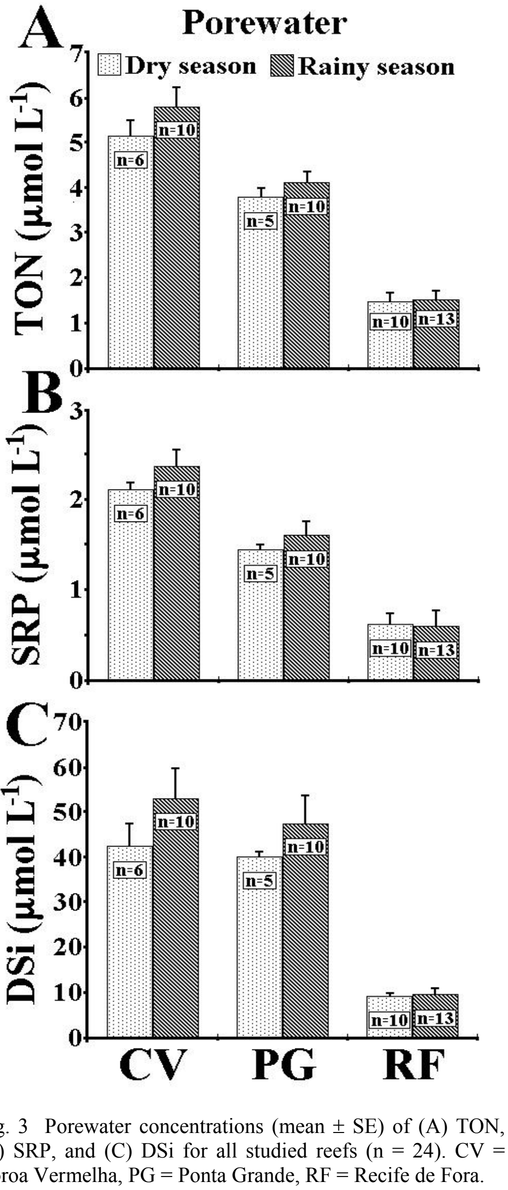

Fig. 3 Porewater concentrations (mean ± SE) of (A) TON, (B) SRP, and (C) DSi for all studied reefs (n = 24). CV = Coroa Vermelha, PG = Ponta Grande, RF = Recife de Fora.

Sediment Organic Matter Content

Organic matter (OM) content (values given in percent of dry weight) in nearshore sediments (Fig. 4A) varied between 5 and 39%, during the dry season, and between 8 and 43% during the rainy season. Ponta Grande had both the highest and the lowest values, presenting the most significant difference between sampling locations. At the offshore reef (Fig. 4B), sediment OM concentrations showed a distinct gradient from landward to seaward. At the landward side, OM content in the sediment varied around 45% in both transects and both seasons. In Ponta Grande, analysis of all OM data combined yielded no statistically significant seasonal effect (*F* = 2.226, *p* = 0.146). This may be due to the fact that OM values in Ponta Grande presented a higher degree of variability between replicates (Fig. 5).

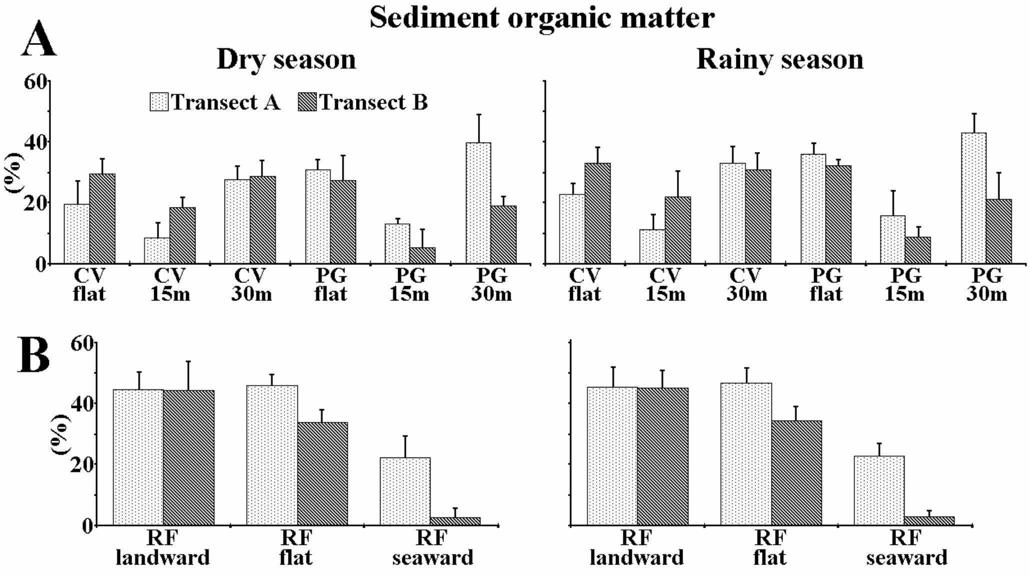

Fig. 4. Distribution of sediment organic matter at (A) nearshore and (B) offshore reefs. Columns represent mean of replicates (n = 9) with 95% confidence intervals. CV = Coroa Vermelha, PG = Ponta Grande, RF = Recife de Fora, flat = reef flat, 15 m and 30 m = distance from the reef crest.

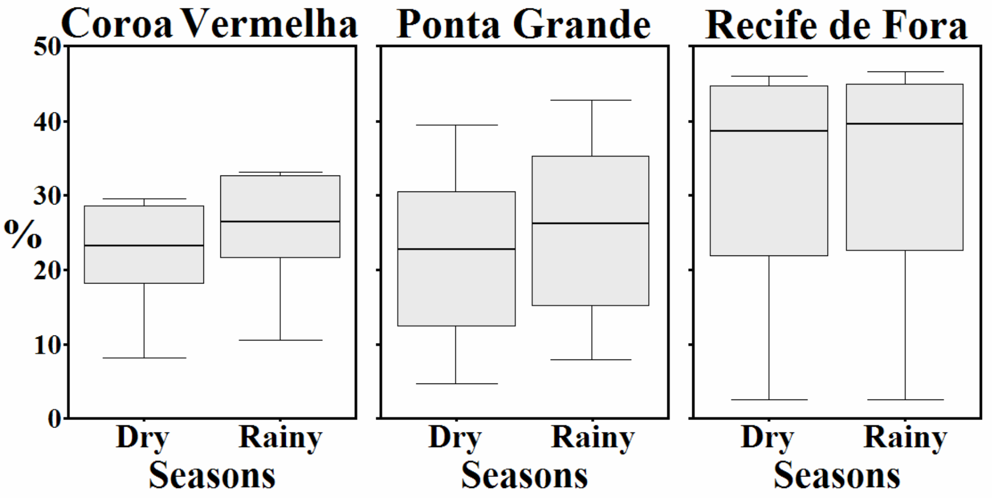

Fig. 5. Box and whisker plots for seasonal variation in sediment organic matter at all studied reefs (n = 18).

DISCUSSION

Evidence for SGD in the Study Area

As shown in Costa et al. (2000), volumes of SGD can be calculated using the hydraulic conductivity of the aquifer and the hydraulic head on flow equations based on the Darcy Law. Other studies have used similar approach (ZEKTSER, 2002; ZEKTSER; LOAICIGA, 1993; VALIELA et al., 1978). In the study area, the hydraulic head can reach 2 m at low tides, and calculations considering the mean sea level for the years of study yielded a groundwater flow rate of 27 L m^{-2} d^{-1} (for Coroa Vermelha) and 21 L m^{-2} day^{-1} (for Ponta Grande). Although these rates are not as high as the ones found in the northern coast of Bahia (COSTA et al., 2000) they are comparable to other areas with highly permeable sediments (SCHLUTER et al., 2004; CHARETTE et al., 2003; HEMOND; FIFIELD, 1982; VALIELA et al., 1978; SWARZENSKI et al., 2007). In addition, seeps along the beach face were distinguished visually. Such springs discharged in a narrow strip along the beach, mainly during low tide, with no visible difference in the flux between dry and rainy seasons. Similar springs have been observed elsewhere (STIEGLITZ, 2005; COSTA et al., 2000; CORBETT et al., 1999).

Salinity is also a good indicator of SGD. In the study area, lowest salinity values at the nearshore reefs were always found in the pools on the reef flat and in the shallow lagoon between the reef and the beach. This dilution of seawater is certainly due to SGD as there is no river or streams draining to these particular sites (the closest stream is 6 km away and the two largest rivers in the area are both located at 11 km, respectively north and south from the study sites – see Fig. 1). This pattern was observed in both dry and rainy season (Table 1). At the offshore reef, however, the shallow pools in the reef flat always presented the highest salinity values (as expected due to higher rates of evaporation), the lowest values being in the landward side of the reef. The relationship between salinity and DSi concentrations at the water-sediment interface has also been used previously as a tracer of groundwater discharge (MONTAGGIONI et al., 1993) as DSi is generally higher in groundwater relatively to the surrounding seawater (NAIM et al., 1997). In the study sites, the corresponding low salinities with high silicate levels at the discharge areas indicates that this low-salinity water is either river or groundwater derived (and not simply rainfall), which is in accordance with findings from previous studies (CUET et al., 1988; BELL, 1992).

Finally, the marked seasonal increase (from dry to rainy season) in nutrient concentrations near the bottom (for all nutrient species analyzed) is a further indicator that SGD represents an important source of nutrients to the reefs in addition to ongoing (all season) nutrient remineralization as a result of high sediment organic matter content (see Fig. 4 and the next paragraph). This difference in bottom nutrients from dry to rainy season also cannot be explained by simple seasonal stratification as the area around the reefs presents extremely high wave energy and high levels of vertical mixing.

Nutrient Supply from Sediment Regeneration

Benthic regeneration is an essential process within biogeochemical cycles of nutrients in many marine environments as well as an important source of nutrients to support coastal productivity. The quantity of organic material and nutrients in sediments will reflect the longer-term nutrient supply and productivity of an area (KLUMP; MARTENS, 1983). Remineralization rates have been found to vary significantly with season (JAHNKE et al., 2005) and this seasonal variation is probably linked to variations in organic matter inputs. In our study sites, spatial variations in the sedimentary organic matter (OM) content are more important than temporal (seasonal) patterns, particularly in Ponta Grande. This may be due to the fact that OM values in Ponta Grande presented a higher degree of variability between replicates. Nevertheless, the fact that OM accumulation near the bottom is high all through the year at both nearshore locations indicates that remineralization from the sediment is an important,

Table 1. Summary of salinity values (in PSU) for sampling sites at the nearshore reefs in both dry and rainy seasons (n = 12). CV = Coroa Vermelha, PG = Ponta Grande, flat = reef flat, 15 m and 30 m = distance from the reef crest.

		flat			**15 m**			**30 m**		
		Max	**Min**	**Mean ± SE**	**Max**	**Min**	**Mean ± SE**	**Max**	**Min**	**Mean ± SE**
Dry Season	**CV**	33.5	31.0	32.2 ± 1.7	32.7	31.7	32.3 ± 1.1	34.3	33.8	34.0 ± 0.5
	PG	33.5	32.1	32.8 ± 0.8	33.9	33.2	33.7 ± 0.4	34.8	33.8	34.1 ± 0.3
Rainy Season	**CV**	33.1	30.7	32.0 ± 1.4	32.3	31.5	32.0 ± 0.9	33.9	33.0	33.5 ± 0.6
	PG	32.8	31.9	32.4 ± 0.5	33.5	33.0	33.2 ± 0.4	34.4	33.3	33.8 ± 0.5

permanent source of nutrients to the water column at both nearshore reefs. This, however, still does not explain the seasonal increase in nutrient concentrations both in bottom samples and porewater. Changes in the water temperature have been shown to induce seasonal patterns of OM remineralization but that is not the case in the study area, where daily variations in water temperature (related to insolation and cloud cover) were far more important than seasonal patterns (COSTA, 2002).

Nitrogen Limitation of Phytoplankton Growth

Phytoplankton biomass (as estimated from Chlorophyll *a* concentrations) present a strong positive correlation with both TON and SRP concentrations (see Fig. 2D). Nevertheless, we can safely discard phosphorus as the limiting nutrient, given the fact that reactive phosphorus is present in quantities well above those for algal growth requirements, as shown by the extremely low TON:SRP ratios observed. Such TON:SRP ratios are considerably lower than the Redfield ratio (widely used to evaluate the nutrient limitation status of many marine ecosystems worldwide) and thus the study area is likely to be consistently N limited. Such finding is consistent with the majority of empirical nitrogen-based models for phytoplankton biomass and productivity that are reported in the recent literature (KELLY, 2001; NIELSEN et al., 2002; HOYER et al., 2002; SMITH, 2006).

Comparison With Other Reef Areas

TON concentrations in Coroa Vermelha and Ponta Grande are similar to those at the nearshore fringing reefs of Ghardaqa, in the Red Sea (Table 2), an arid zone with no river inflow and whose major nutrient sources are sewage outfalls. Higher TON concentrations are found only in heavy-impacted fringing reefs of the Caribbean (Jamaica), the Pacific Ocean (Guam) or in the north coast of Brazil (Guarajuba Reef), where groundwater discharge, untreated sewage from urban areas, and terrestrial run-off are causing nutrient enrichment of the coastal reefs (Table 2). Nevertheless, TON concentrations in Coroa Vermelha and Ponta Grande are considerably higher than most near-pristine Caribbean reefs. Even the Recife de Fora, whose TON concentrations varied between 0.41 and 1.16 μmol L^{-1}, presented values above those coral reef locations. In general, values of TON above 1 μmol L^{-1} are found only in waters enriched by sewage effluents (SMITH et al., 1981), groundwater springs (LAPOINTE, 1997), reef lagoons with high rates of remineralization (CROSSLAND et al., 1984) or areas close to marinas and canals (SZMANT; FORRESTER, 1996).

Most offshore reefs in the literature present considerably lower TON concentrations. The Great Barrier Reef in Australia (TON: 0.05 μmol L^{-1}) and the atolls of the Indian Ocean (TON: 0.03-0.06 μmol L^{-1}), receive nutrient supply mainly from sediment resuspension and from water column/benthic microbial regeneration (80-90% of total nutrient demand), according to Furnas et al. (1997). Upwelling is also a major nutrient contributor to offshore reef areas (SZMANT; FORRESTER, 1996) with only 10% of the total nutrient demand to come from external sources. The offshore reef in this study, however, presented nutrient levels that are similar to nearshore reefs in Florida (Table 2), which receive inputs from Florida Bay (SZMANT; FORRESTER, 1996) or submarine groundwater discharge (LAPOINTE, 1997).

If the comparison is based on SRP concentrations, the studied reefs present the highest values of nearly all sites depicted in Table 2, the only exception being the nearshore reefs of Safaga and Quseir, in the Red Sea (ABOU-AISHA et al., 1995), which receive large phosphorus loading from phosphate factories near the coast. Results from a 20-year study in Florida have shown that phosphorus is a key factor controlling the growth of reef building corals (HBOI, 2006). The high level of phosphorus in the study area also contributed to the extremely low TON:SRP ratios observed. Such low TON:SRP ratio in both nearshore and offshore reefs either suggests that there is a strong source of P to the area or that N is rapidly metabolized (as described in Szmant; Forrester, 1996). Both possibilities seem likely, although the data does not provide evidence of the latter. Either way, such TON:SRP ratios also reflect the importance of SGD as a significant pathway for nutrients and other dissolved solutes into Porto Seguro Bay, especially to the nearshore reefs where wastewater disposal practices are likely to be adding large amounts of nitrogen and phosphorus to the subsurface each year.

This can also be seen in the Chlorophyll *a* data, which clearly shows the occurrence, in the urbanized reef, of a continuously high phytoplankton activity, reflecting the constant supply of land-based nutrients. In the non-urbanized reef, however, phytoplankton blooms were only observed during the rainy season. The mean chlorophyll *a* concentrations reported for Ponta Grande and Coroa Vermelha reefs are also higher than that of other coral reef areas (Florida, Caribbean, and Australia). Such concentrations are comparable with values reported for urbanized open embayments (see Table 3). On the offshore reef, chlorophyll *a* concentrations are similar to non-bloom situations in the Florida Keys and considerably below reefs from Australia and Caribbean (Table 3).

Table 2. Typical N and P concentrations (in μmol L^{-1}) for coral reefs around the world.

Sites	TON	SRP	Comments	References
Discovery Bay, Jamaica	20.68 ± 5.80	0.26 ± 0.06	Groundwater inputs	Lapointe 1997
- Groundwater springs	13.00 ± 3.00	0.14 ± 0.06		
- Semi-enclosed grottos	8.18 ± 2.30	0.14 ± 0.05		
- Back-reef	4.61 ± 1.58	0.13 ± 0.03		
- Fore-reef				
Pago Bay, Guam - Pacific Ocean	4.16 ± 4.27	0.23 ± 0.20	Fringing reef flat	Marsh 1977
Tumon Bay, Guam: bloom water	3.57 ± 3.12	0.59 ± 0.24	Groundwater input &	
Tumon Bay: non-bloom water	8.04 ± 5.75	0.22 ± 0.12	terrestrial runoff	
Guarajuba reef, Brazil - Dry season	6.09	0.35	Near-urban area	Costa et al. 2000
Guarajuba reef - Rainy season	8.19	1.42	Groundwater inputs	
Papa Gente reef, Brazil - Dry season	0.46	0.13	Undeveloped area	
Papa Gente reef - Rainy season	1.77	0.18		
Ghardaqa, Red Sea, Egypt	1.86-3.14	0.29-0.33	Nearshore reefs	Abou-Aisha et al. 1995
Safaga, Red Sea, Egypt	0.73-1.64	0.73-0.88	Sewage inputs	
Quseir, Red Sea, Egypt	0.85-1.86	4.18-5.93		
Houtman Abrolhos Is., Australia	0.83-1.50	0.22-0.50	Sed. Remineralization	Crossland et al. 1984
Florida Keys, USA	1.07 ± 0.56	0.17 ± 0.08	Florida Bay inputs	Szmant and Forrester 1996
- Long Key - inshore	0.32 ± 0.40	0.11 ± 0.09		
- Long Key - offshore	0.58 ± 0.52	0.02 ± 0.02		
- Biscayne National Park - inshore	0.16 ± 0.16	0.01 ± 0.01		
- Biscayne National Park - offshore	0.46 ± 0.17	0.01 ± 0.20		
- Key Largo - inshore	0.22 ± 0.12	0.02 ± 0.03		
- Key Largo - offshore				
La Reunion - Indian Ocean	0.47 ± 0.07	0.11 ± 0.01	Groundwater inputs	Naim et al. 1997
- submarine beach	10.4 ± 4.1	0.16 ± 0.03		
- reef front	0.37 ± 0.04	0.11 ± 0.01		
Southeastern Florida, USA	0.43 ± 0.29	0.19 ± 0.11	Groundwater inputs	Lapointe 1997
- groundwater inputs	0.89 ± 0.27	0.19 ± 0.04		
Martinique, Caribbean	0.53-0.62	0.10-0.28	Near-urban area	Littler et al. 1993
Barbados, Caribbean	0.35-0.45	0.06		Tomascik and Sander 1985
U.S. Virgin Islands, Caribbean	0.28-0.51	0.08-0.10		Adey and Steneck 1985
Tikehau atoll, French Polynesia	0.03-0.06	0.10-0.11	Oceanic atoll	Charpy et al. 1998
Great Barrier Reef, Australia	0.05	0.08		Furnas et al. 1997
Coroa Vermelha, Brazil	1.88-3.64	0.53-0.91	Near-urban area	This study
Ponta Grande, Brazil	1.74-2.56	0.46-0.86	Groundwater inputs	
Recife de Fora, Brazil	0.41-1.16	0.20-0.46	Offshore reef	

Table 3. A comparison of chlorophyll *a* concentrations (μg L^{-1}) taken from the literature and from this study.

Location	Average	Comments	Reference
Kaneohe Bay, Hawaii	0.68	Before sewage diversion	Smith et al. 1981
Kaneohe Bay, Hawaii	0.55	After sewage diversion	Smith et al. 1981
Barbados, Caribbean	0.42	Less impacted coral reef site	Tomascik and Sander 1985
Davies reef, GBR, Australia	0.57	Offshore reef (landward)	Furnas et al. 1990
Davies reef, GBR, Australia	0.32	Offshore reef (seaward)	Furnas et al. 1990
Florida Keys, US	0.26	Pre-bloom situation	Szmant and Forrester 1996
Florida Keys, US	2.28	Post-bloom situation	Szmant and Forrester 1996
Coroa Vermelha reef, Brazil	1.22	Inshore reef, near urban area	This study
Ponta Grande reef, Brazil	0.86	Inshore reef	This study
Recife de Fora reef, Brazil	0.34	Offshore reef (landward), MPA	This study
Recife de Fora reef, Brazil	0.26	Offshore reef (seaward), MPA	This study

CONCLUSIONS

The results of both water column and porewater nutrient measurements revealed the occurrence of consistent spatial and temporal patterns. Nutrient concentrations decrease with increasing distance from the shore, reflecting terrestrial and nearshore sources of nutrients. Nutrient concentrations at the offshore reef were about threefold lower (for TON and DSi) and twofold lower (for SRP) than nearshore reefs. In general, these differences between nearshore and offshore reefs were higher during the dry season, when land-based nutrient fluxes (groundwater seepage and surface run-off) were more localized at the nearshore reefs. This pattern is consistent with observations in the field where, during the rainy season, large quantities of litter were found floating around the offshore reef (e.g. plastic bags and flasks, bottles, cans, pieces of furniture wood, etc), just after the low tide, even though the reef is located 8 km away from the coast. Such litter was not observed at the offshore reef during the dry season. In addition, there is a consistent difference within the nearshore reefs, with Coroa Vermelha showing the most elevated nutrient concentrations, due mainly to anthropogenic sources such as untreated sewage and wastewater contributions from the nearby urban area (no sewage treatment is available and the use of cesspits and septic tanks is widespread). Lower levels of nutrients in Ponta Grande reflect, in general, the lack of a continuous, permanent source, in addition to biological and chemical removal processes.

The hypothesis that rainfall promotes an increasing load of nutrients from terrigenous sources is also supported by a marked increase in nutrient concentrations near the sediment during the rainy season, notably for TON. This elevated nutrient concentration in the bottom layer during the rainy season also indicates that submarine groundwater discharge (SGD) is adding a considerable amount of nutrients to the reefs during the rainy season, over and above the ongoing supply from sediment regeneration. In addition, reef flat concentrations did not vary between seasons as it was observed for the stations at 15 m and 30 m from the reef crest, indicating that groundwater discharge percolates the porous reef structure and is likely to represent a significant supply of N for waters around the nearshore reefs, particularly in urbanized areas where wastewater disposal is adding contaminants to the subsurface environment.

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