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Seasonal and spatial controls on the delivery of excess nutrients to nearshore and offshore coral reefs of Brazil

Ozeas S. Costa Jr. [a,b,*], Martin J. Attrill [a], Malcolm Nimmo [b]

[a] Marine Biology and Ecology Research Centre, School of Biological Sciences, University of Plymouth, Drake Circus, Plymouth, PL48AA, UK
[b] School of Earth, Ocean and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, PL48AA, UK

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Abstract

We examined the influence of seasonality and anthropogenic activity on the delivery of land-based nutrients to coral reefs in eastern Brazil. Seawater and porewater were sampled during dry and rainy seasons in three nearshore and offshore reefs with distinct nutrient inputs along the south coast of Bahia State, and analysed for total oxidised nitrogen (TON), soluble reactive phosphorus (SRP), reactive silica (DSi), and chlorophyll (Chl *a*). Rainfall promotes significant increase in the load of nutrients to nearshore and offshore reefs. Concentrations in urbanized reefs are on average 25% higher than non-urban reefs. 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 nearshore reefs. SRP values at the study sites are significantly higher than other coral reef areas, suggesting the occurrence of a permanent source of phosphorus along this highly terrigenous (siliciclastic) coast.

Keywords: Coastal eutrophication; Nitrogen; Phosphorus; Submarine groundwater discharge; Coral reef; Nutrients; Seasonality; Coastal urbanization

1. Introduction

Although coastal eutrophication is more common in developed countries of the Northern Hemisphere (Smith et al., 1999), the potential for nutrient contamination in Brazilian coastal waters is extremely high, especially near urban areas, as municipal sewage collection and treatment systems are frequently inadequate or even non-existent. Some of the Brazilian nearshore reefs already receive substantial supplies of nutrients from land based sources such as surface runoff, submarine groundwater discharge and untreated sewage. 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). Seasonality is an important factor affecting the degree to which groundwater nutrients influence coastal communities, and the flux of the submarine groundwater discharge has been shown to increase substantially during rainy seasons (Costa et al., 2000).

Submarine groundwater discharge (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 and Van Cappellen, 2004). A SGD occurs anywhere an aquifer is connected hydraulically to the sea through permeable

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[*] Corresponding author. Current address: St. Francis Xavier University, Earth Sciences Department, P.O. Box 5000, Antigonish, Nova Scotia, Canada B2G2W5. Tel.: +1 902 867 5151; fax: +1 902 867 2414.

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bottom sediments, with the hydraulic head being above sea level. In some areas, SGD can have greater ecological significance than surface runoff. Indeed, in areas such as the west coast of the island of Hawaii (Kay et al., 1977) and the Yucatan Peninsula (Hanshaw and Back, 1980), virtually all freshwater entering the sea is in the form of submarine discharge. 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 research carried out so far has 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 1990s 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, unpublished data). 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.

Further studies of SGD were also performed in the north coast of Bahia (Costa et al., 2000). Here, the 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. The groundwater nutrient concentration in the urbanized site was found to be many times higher than those detected in the underdeveloped area, due mainly to the widespread use of septic tanks and cesspits (Costa et al., 2000). Silicate concentrations, which along with salinity values (Montaggioni et al., 1993) and natural radioactive tracers (Oliveira et al., 2003), can be used as a marker of groundwater discharge also indicated that groundwater was likely to produce a significant input of terrestrial nutrients onto the reef. Nutrient concentration also behaved distinctly between seasons, reflecting the role of rainfall in nutrient dilution and transport. Lower levels of ammonia and higher nitrate found during the rainy season may suggest that a recharge of the permeable aquifer by oxygenated rainfall infiltration can allow an increasing oxidation of ammonia to nitrite and then to nitrate (Costa et al., 2000).

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 a 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 (Costa et al., 2002).

The objectives of this study were to establish the importance of seasonality in controlling the flux of nutrients to coastal coral reefs, and to assess the relative contribution of submarine groundwater discharge to the coastal eutrophication in the study area. We hypothesized that groundwater discharge is not uniform along the coast, in both spatial and temporal scales, and the occurrence of human settlements may greatly increase the nutrient influx to nearshore and offshore reefs.

2. Materials and methods

Three reefs were selected for sampling (Fig. 1): two nearshore (Ponta Grande 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). Seawater, porewater and sediment samples were collected and analyzed. 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. On the offshore reef, 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 flat border. In order to account for seasonal variability, sampling occurred during both dry (July–August) and rainy (February–March) seasons, over a period of 2 years. 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.

2.1. Seawater sampling and analysis

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. Sixteen true separate seawater samples were collected in four different sampling trips at each site, being eight at the surface

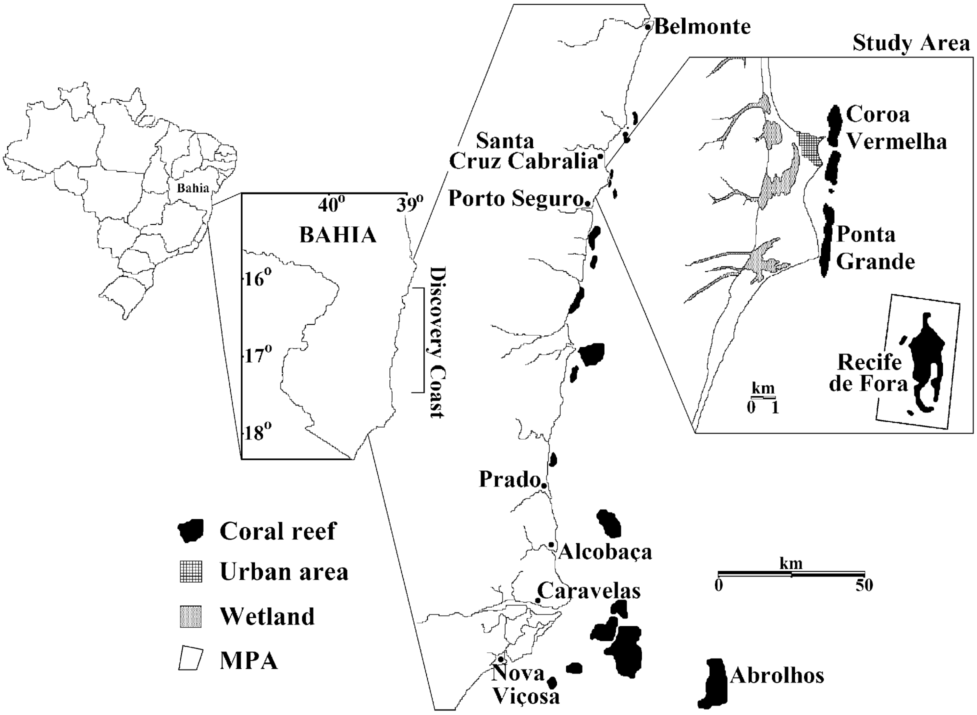

Fig. 1. Map of the Brazilian Discovery Coast, Southern Bahia, Brazil, and location of the studied reefs.

and eight at the bottom (in the nearshore reefs, only surface samples were collected on the reef flat). Triplicates from each of these samples were analyzed, and the average value (with the standard error) used in the statistical analysis. Samples were analyzed for total oxidized nitrogen (TON), which includes all dissolved inorganic nitrogen species except ammonia; soluble reactive phosphorus (SRP), which includes all orthophosphate species (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$) plus the hydrolyzed organic phosphate; reactive silica (DSi), which is the dissolved silicic acid ($Si[OH]_4$); and chlorophyll *a* (Chl *a*).

Nutrient concentrations were determined using a segmented continuous flow analyser (Skalar SAN^{plus}) incorporating a chemistry unit (SA 4000) consisting of a 4 channel module holder and two 16 channel proportioning pumps. 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. The 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. The 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. The detection limit of this method was 0.03 μmol L^{-1}.

To assess the contamination of samples due to diver re-suspension of sediments, a 2 L Nansen bottle was also used at three sampling stations (one in each reef) during the dry season. Results of this test have shown no significant variation between samples collected by diver or Nansen bottle (TON: $F=0.632$, $p=0.440$; SRP: $F=0.004$, $p=0.951$; DSi: $F=0.001$, $p=0.981$). The highest difference between the two methods was 8% but there was no clear distinction of which is more precise. Samples were filtered immediately, using a Nalgene® filtration unit connected to a hand-pump, and then frozen. 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 (−20 °C freezing) was used, and all samples were analyzed within 2 weeks of collection. A detailed description of the storage trial procedure and results can be found in Gardolinski et al. (2001). Two types of filter 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. For chlorophyll analysis, triplicates from sixteen GF/F filters, half from surface and half from bottom water samples, were analyzed. 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.

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%.

2.2. Sediment and porewater sampling and analysis

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 as water samples 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 by squeezing the sediment through a 200-μm polyester screen, supported by a jubilee clip. The squeezing was performed by a rubber piston attached to a rod and pressure was applied manually. This system was based on the “whole-core squeezer” porewater sampler developed by Bender et al. (1987). The porewater collected was then filtered and analyzed as described for seawater samples, with the exception of chlorophyll analysis which were not performed in porewater. Sediment samples were collected from each core-section, placed in zip-lock bags, identified and frozen. These samples were used for analysis of sediment texture (wet sieving method), and organic matter content (loss on ignition method).

2.3. Statistical analysis

Multifactorial ANOVA was used to analyse simultaneously the effects of season, reef sites and sample location, and their interactions, on each nutrient analyte (TON, SRP or DSi) and chlorophyll data. 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 (Miller, 1986) 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 existing with the porewater data, where in some cases there is only a single observation for each location.

3. Results

3.1. Patterns of TON distribution

TON concentrations at the nearshore reefs varied from 1.74 to 3.64 μmol L^{-1}, with the lowest values occurring during the dry season, and at Ponta Grande (Fig. 2A). In the offshore reef (Recife de Fora), TON concentrations varied from 0.41 to 0.89 μmol L^{-1}, during dry season, and from 0.52 to 1.16 μmol L^{-1} during rainy season (Fig. 2A). ANOVA results indicate that both nearshore reefs, although having similar geology, are significantly different from each other ($F=244.983$; $p<0.001$), 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 in both nearshore reefs, but did not vary significantly between seasons (Fig. 2A). On the offshore reef, peak TON values were found on the landward side of the reef during the rainy season, and on the reef flat during the dry season (Fig. 2A). Lowest values, however, always occurred at the seaward side (Fig. 2A).

Bottom samples (collected 1 m above the sediment) exhibited consistently and significantly higher TON concentrations than those collected near the surface at the same locations in all reefs and seasons (Fig. 2A), even though all sampling sites were exposed to high wave energy and strong vertical mixing. ANOVA results indicated that, although all factors presented significant results, only one interaction (season × reef) revealed a significant effect ($F=43.376$; $p<0.001$). On the offshore reef, however, the effect of season on TON

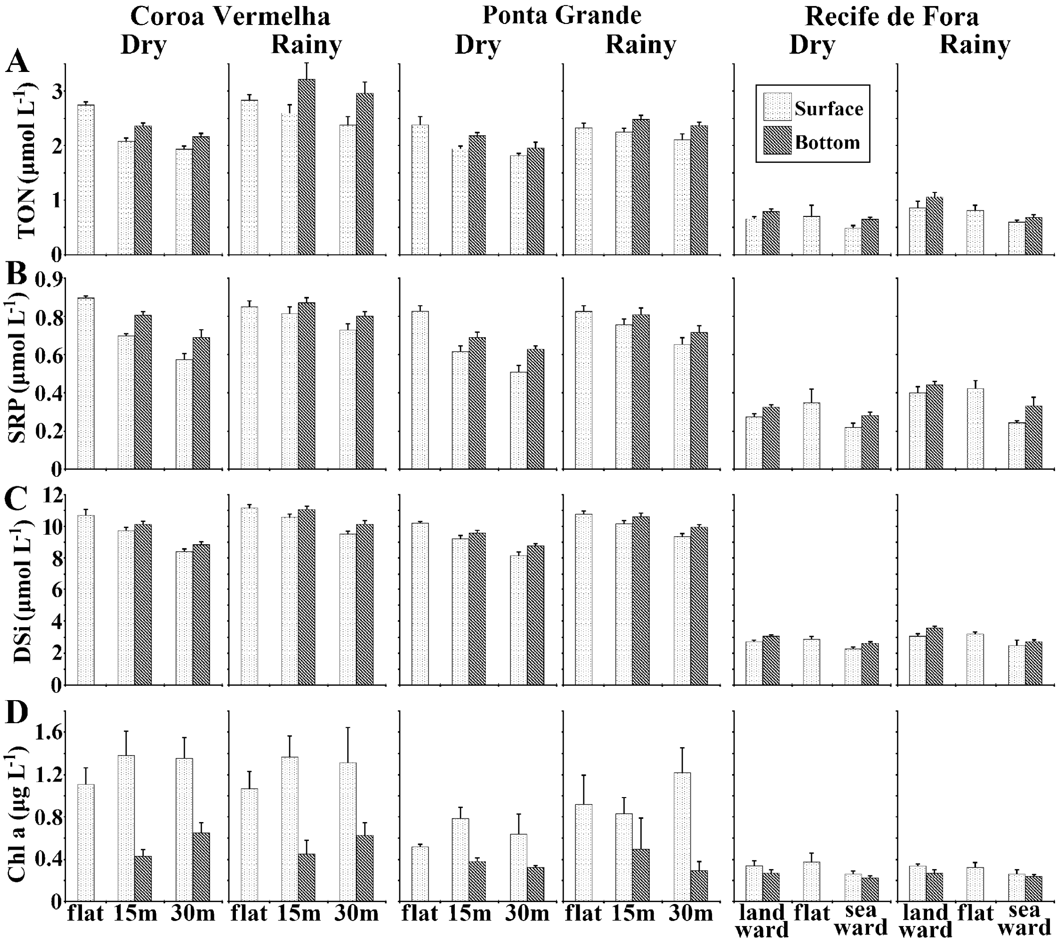

Fig. 2. Comparison of (A) TON, (B) SRP, (C) DSi, and (D) chlorophyll *a* concentrations (mean ± SE) between surface and bottom samples during dry and rainy seasons in all studied reefs ($n=8$). flat = reef flat, 15 m and 30 m = distance from the reef crest; landward and seaward sampling sites are located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

concentrations of bottom samples is highly significant ($F=36.838$; $p<0.001$), mainly because of the observed variation in landward TON concentrations between seasons (Fig. 2A).

3.2. Patterns of SRP distribution

SRP concentrations on the nearshore reefs varied from 0.46 to 0.91 µmol L^{-1} (Fig. 2B). Contrary to the trend observed for TON, the increase in SRP concentrations at Coroa Vermelha from dry to rainy season was not statistically significant ($F=2.553$; $p=0.114$). The only significant first-order interaction was that between season and sample location ($F=86.046$; $p<0.001$), and reflects the behaviour of reef flat concentrations, which did not vary significantly either between reefs or seasons (Fig. 2B). On the offshore reef, concentrations varied from 0.20 to 0.43 µmol L^{-1} during dry season, and from 0.23 to 0.46 µmol L^{-1} during rainy season (Fig. 2B), the lowest SRP values always occurring at the seaward side, in both seasons. However, unlike that observed for TON, highest SRP values always occurred on the reef flat (Fig. 2B). Furthermore, distinct seasonal responses from landward and seaward sides, in terms of SRP concentrations (Fig. 2B), resulted in a significant first-order interaction ($F=9.557$; $p<0.001$).

Samples collected near the bottom, as observed for TON, exhibited higher SRP concentration than those sampled near the surface in all reefs and seasons (Fig. 2B). Results of the multifactorial ANOVA for bottom SRP concentrations in the nearshore reefs showed a significant interaction between season × reef × location ($F=7.849$; $p=0.007$) but no first-order interaction. In the offshore reef, SRP concentrations near the bottom also showed a significant season × location interaction

($F = 7.065$; $p = 0.013$). Comparisons between surface and bottom samples revealed that the latter, although presenting consistently higher concentrations than those collected near the surface, did not vary seasonally in the same pattern as for TON concentrations (Fig. 2B).

3.3. Patterns of DSi distribution

DSi concentrations at the nearshore reefs 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 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 (Fig. 2C). On the offshore reef, DSi concentrations 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 (Fig. 2C). As observed for TON and SRP, a significant first-order interaction between season and location was found ($F = 14.408$; $p < 0.001$), and is due mainly to the fact that reef flat DSi concentrations did not experience the same increase from dry to rainy season as the other sampling sites (Fig. 2C). Differences in DSi concentrations between Coroa Vermelha and Ponta Grande were smaller than TON or SRP, although still statistically significant, with Ponta Grande presenting higher variation among seasons than Coroa Vermelha (Fig. 2C). On the offshore reef, the highest DSi values were found mostly on the reef flat, but never on the seaward side.

Concentrations near the bottom, as for TON and SRP, exhibited persistent and significantly higher concentrations than those observed in the surface samples, with higher values being recorded during the rainy season. On the offshore reef, rainy season values were higher than those from dry season, producing a significant first order interaction ($F = 51.064$; $p < 0.001$). Of all three parameters, DSi was the most stable, presenting the lowest spatial and temporal variability.

3.4. Nutrient concentrations in porewater

Porewater TON concentrations in the studied reefs (Fig. 3A) were about twice the concentration for the overlying water column. The results of the Friedman's test showed a significant statistical difference between seasons ($\chi^2 = 6.000$; $p = 0.014$), with rainy season presenting higher porewater TON concentrations than dry season (Fig. 3A). Also, concentrations at Coroa Vermelha are significantly higher than those at Ponta Grande. The significance test also revealed that 15 m porewater TON concentrations were higher than the 30 m sampling location ($\chi^2 = 4.000$; $p = 0.046$), confirming the expected pattern of decreasing porewater TON concentration with increasing distance from the reef. 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 ($\chi^2 = 4.000$; $p = 0.135$), although landward samples always presented the highest porewater TON concentrations and seaward samples the lowest values.

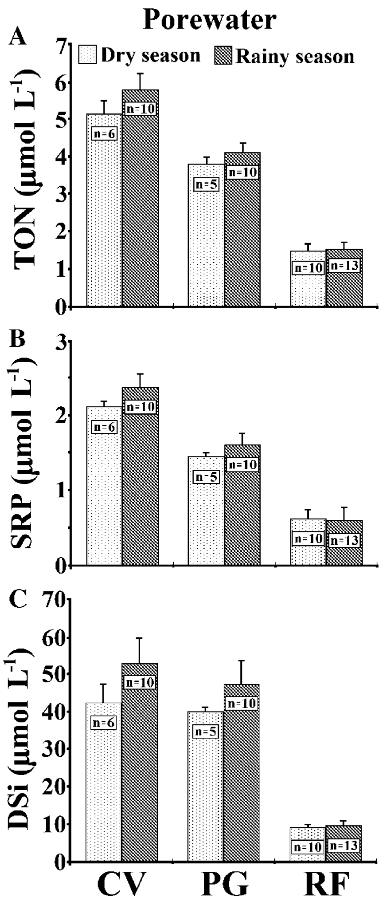

Fig. 3. Comparison of (A) TON, (B) SRP, and (C) DSi concentrations (mean ± SE) in porewater between the three studied reefs during dry and rainy seasons. CV = Coroa Vermelha, PG = Ponta Grande, RF = Recife de Fora. The sample size (n) is indicated in each column.

For SRP, no significant statistical difference was found between seasons ($\chi^2 = 2.667$; $p = 0.102$), even though concentrations during the rainy season were generally higher than dry season (Fig. 3B). There was a significant difference between the two nearshore reefs, with porewater SRP concentration at Coroa Vermelha being significantly higher than those at Ponta Grande ($\chi^2 = 6.000$; $p = 0.014$). As observed for TON, the significance test also showed that 15 m porewater SRP concentrations are higher than the 30 m sampling location ($\chi^2=4.000$; $p=0.046$). On the offshore reef, no significant statistical difference was found between seasons ($\chi^2=0.333$; $p=0.564$) or sampling location ($\chi^2=3.000$; $p=0.223$). The significance test also showed that landward samples presented the highest SRP concentrations, whilst no statistical difference was found between seaward and reef flat samples.

DSi concentrations in porewater from the nearshore reefs are more than four times the concentration in the overlying water column. On the offshore reef, porewater DSi concentrations represent about three times the concentration of the water column near the bottom. A significant statistical difference was found between seasons for the nearshore reefs ($\chi^2=6.000$; $p=0.014$), but not for the offshore reef ($\chi^2=0.333$; $p=0.564$). When comparing the two nearshore reefs, no statistical difference was observed ($\chi^2=0.667$; $p=0.414$), but they presented much higher DSi concentrations than the offshore reef (Fig. 3C). All sampling locations in the nearshore reefs (flat, 15 m and 30 m) are different from each other ($\chi^2=4.000$; $p=0.046$). On the offshore reef, landward samples presented the highest porewater DSi concentrations, and the reef flat presented the lowest values.

3.5. Chlorophyll analysis

On the nearshore reefs, mean chlorophyll *a* concentration in surface waters ranged from 0.51 to 1.38 μg L^{-1} (Fig. 2D). Although statistical tests on chlorophyll *a* data from surface samples demonstrated significant seasonal and spatial variation ($F=11.813$; $p=0.001$), post hoc tests revealed that such variation is due mainly to Ponta Grande values, in which seasonality represents a highly significant effect (Fig. 2D). Evaluation of the Coroa Vermelha's dataset alone further confirmed this, with no seasonal effect on chlorophyll *a* concentration being observed. Bottom samples showed little variation between reefs or seasons, with chlorophyll *a* concentrations ranging from 0.29 to 0.64 μg L^{-1} (Fig. 2D).

On 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}, whilst in bottom samples the concentrations were between 0.22 and 0.28 μg L^{-1}. There was a significant statistical difference between dry and rainy season in surface samples ($F=5.990$; $p=0.019$), but none was observed in bottom samples ($F=0.378$; $p=0.544$). The interaction between the effects of season and sample location is significant only for surface samples ($F=5.105$; $p=0.010$), and post hoc tests revealed that this is caused mainly by reef flat variation between seasons (Fig. 2D).

3.6. Sediment organic matter content

Organic matter (OM) content in nearshore sediments varied between 5% and 39%, during the dry season, and between 8% and 43% during the rainy season (Fig. 4). Ponta Grande had both the highest and the lowest values, presenting the most significant difference between sampling locations. On the offshore reef, sediment OM concentrations showed a distinct gradient from landward to seaward (Fig. 4). At the landward side, OM content varied around 45% in both transects and both seasons. On the reef flat, the two transects were statistically different from each other, but no seasonal variation was found. The same pattern was observed in the seaward sampling locations, with variation between transects being highly significant, but no difference between seasons observed.

4. Discussion

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

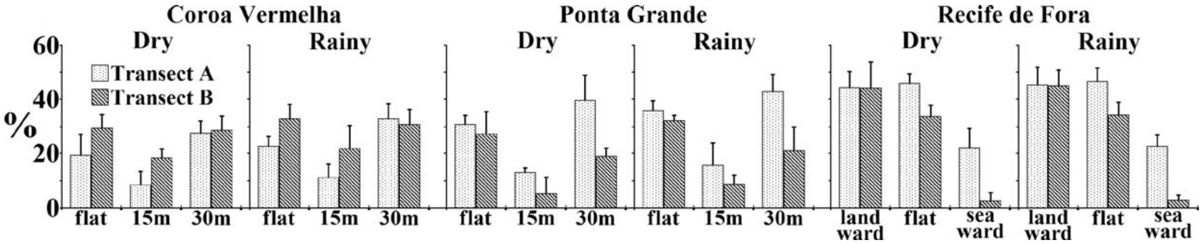

Fig. 4. Distribution of sediment organic matter at all studied reefs. Columns represent mean of replicates ($n=9$) with 95% confidence intervals. flat = reef flat, 15 m and 30 m = distance from the reef crest; landward and seaward sampling sites are located 15 m from the offshore reef.

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 buoying 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 on the offshore reef during the dry season. Additionally, there is a consistent difference within the nearshore reefs, with Coroa Vermelha showing the most elevated nutrient concentrations, probably due to untreated sewage and wastewater contributions from the nearby urban area.

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 seasonal pattern suggests that submarine groundwater discharge (SGD), rather than regeneration from the sediment, may be the cause of the elevated nutrient concentrations in the bottom layer. Calculations considering the hydraulic head and the mean sea level for the year of study yielded groundwater flow rates of 27 L m^{-2} day^{-1} (for Coroa Vermelha) and 21 L m^{-2} day^{-1} (for Ponta Grande). In addition, reef flat concentrations did not vary between seasons as 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. The use of septic tanks in the urban areas of Coroa Vermelha might well be aggravating this phenomenon through nutrient enrichment of the groundwater (as observed previously for the northern coast of Bahia—Costa et al., 2000). Our results also suggest that variation between seasons is the factor with the strongest influence on TON concentrations in the nearshore reefs and the main effect driving the differences between surface and bottom samples, primarily at Coroa Vermelha. These results support the hypothesis that SGD may be the cause of the elevated TON concentrations at the bottom layer during the rainy season, especially when considering the high wave energy at the sampling sites and the strong vertical mixing. Furthermore, the data have shown that there is also a distinction between the seasonal variation of TON concentrations from both nearshore reefs, indicating that a combination of rainfall increase and higher fluxes of SGD are playing and important role in the delivery of anthropogenic N to these coastal reef systems.

The significant second-order interaction between season and sampling location, particularly in SRP, further indicates that SGD during the dry season is localized close to the reef (15 m), whilst during the rainy season it reaches greater distances (30 m). This conclusion is corroborated by DSi concentrations, as DSi is generally higher in groundwater relatively to the surrounding seawater (Naim et al., 1997). In the study sites, high silicate levels at the discharge areas indicates that the low-salinity water reaching the nearshore reefs is 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. 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.

The data also suggest that the effect of the SGD is not restricted to the nearshore reefs, and it may be an important factor controlling the chemical and ecological differences between landward and seaward sides of the offshore reef. In fact, since the sixties (Kohout, 1960), it is accepted that the zone of diffusion (or mixing) between groundwater and seawater may go as far as 14 km seaward of the coast, thus allowing groundwater discharge to have an impact well offshore. Moore (1999) referred to this subsurface region of mixing between meteoric water and seawater in coastal aquifers as “subterranean estuaries”, suggesting that the mixing of these waters in the subsurface creates an active chemical environment. In addition to these natural chemical processes, wastewater disposal in the urban area of Coroa Vermelha adds yet another source of contaminants to the subsurface environment.

4.1. 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 1), 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

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

Sites	TON	SRP	Comments	References
Discovery Bay, Jamaica			Groundwater inputs	Lapointe, 1997
Groundwater springs	20.68 ± 5.80	0.26 ± 0.06		
Semi-enclosed grottos	13.00 ± 3.00	0.14 ± 0.06		
Back-reef	8.18 ± 2.30	0.14 ± 0.05		
Fore-reef	4.61 ± 1.58	0.13 ± 0.03		
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 and terrestrial runoff	
Tumon Bay: non-bloom water	8.04 ± 5.75	0.22 ± 0.12		
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			Florida Bay inputs	Szmant and Forrester, 1996
Long Key-inshore	1.07 ± 0.56	0.17 ± 0.08		
Long Key-offshore	0.32 ± 0.40	0.11 ± 0.09		
Biscayne National Park-inshore	0.58 ± 0.52	0.02 ± 0.02		
Biscayne National Park-offshore	0.16 ± 0.16	0.01 ± 0.01		
Key Largo-inshore	0.46 ± 0.17	0.01 ± 0.20		
Key Largo-offshore	0.22 ± 0.12	0.02 ± 0.03		
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
US 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	

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 1). 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 (Table 1). 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 and Forrester, 1996).

Most offshore reefs in the literature present extremely 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, Furnas et al., 1997). Upwelling is also a major nutrient contributor to offshore reef areas (Szmant and Forrester, 1996) with only 10% of the total nutrient demand to come from external sources. The offshore reef in the studied area, however, presented nutrient levels that are similar to nearshore reefs in Florida that receive inputs from either the Florida Bay (Szmant and Forrester, 1996) or submarine groundwater discharge (Lapointe, 1997, Table 1).

Table 2
A comparison of chlorophyll *a* concentrations (μg L^{-1}) taken from the literature and from this study

Location	Average	Comments	Reference
Chesapeake Bay, East USA	2.55	1950–1959	Harding and Perry, 1997
Chesapeake Bay, East USA	8.76	1970–1979	Harding and Perry, 1997
Chesapeake Bay, East USA	7.59	1985–1994	Harding and Perry, 1997
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, USA	0.26	Pre-bloom situation	Szmant and Forrester, 1996
Florida Keys, USA	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

If the comparison is based on SRP concentrations, the studied reefs presents the highest values of nearly all sites depicted in Table 1, the only exception being the nearshore reefs of Safaga and Quseir, in the Red Sea (Abou-Aisha et al., 1995), which receive a large phosphorus loading from phosphate factories near the coast. This high level of phosphorus in the study area 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 and Forrester, 1996). Both possibilities seem likely, although the data do 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 of a rainy season phytoplankton bloom only in Ponta Grande. The urbanized reef, instead, presented a consistent, all-seasons level of phytoplankton activity, reflecting the continuous supply of anthropogenic nutrients. The mean chlorophyll *a* concentrations reported for Ponta Grande and Coroa Vermelha reefs are also higher than those for other coral reef areas (Florida, Caribbean, and Australia, Table 2). Such concentrations are comparable with values reported for urbanized open embayments (Kaneohe Bay, Hawaii) yet well below values determined at highly eutrophic coastal embayments (Chesapeake Bay, East US Coast). 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 2).

In conclusion, rainfall promotes a significant increase in the load of nutrients to both nearshore and offshore reefs. A marked increase in nutrient concentrations of bottom samples between seasons suggests that SGD is the main contributor to such seasonal increase, particularly in areas where human activities occur. Lower nutrient concentrations in the non-urban reef reflect, in general, the lack of a continuous, permanent source of anthropogenic nutrients, in addition to active biological and chemical removal processes. Differences in nutrient concentration between nearshore and offshore reefs are more pronounced during the dry season, when the bulk of land-based nutrient contribution is confined to the nearshore reefs. Furthermore, SRP values found in the study area ranked among the highest in the world for coral reef areas, suggesting the occurrence of a significant, permanent source of phosphorus along this highly terrigenous (siliciclastic) coast. Such high values of SRP resulted in extremely low TON/SRP ratios. As a result, phytoplankton growth appears to be nitrogen-limited, particularly in the non-urban reef, as demonstrated by the occurrence of a phytoplankton bloom during the rainy season.

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Appendix A. ANOVA results for the effects of reef site, season and sample location on TON, SRP, DSi, and chlorophyll concentrations in surface samples from the nearshore reefs ($n = 8$)

Sources of variation	Nearshore-Surface							
	TON		SRP		DSi		Chl	
	F	*p*	*F*	*p*	*F*	*p*	*F*	*p*
Season	200.746	<0.001	209.305	<0.001	388.150	<0.001	8.187	0.005
Reef	244.983	<0.001	108.422	<0.001	73.333	<0.001	68.267	<0.001
Sample location	268.714	<0.001	526.730	<0.001	639.551	<0.001	6.852	0.002
Season × reef	19.873	<0.001	2.553	0.114	1.672	0.199	11.813	0.001
Season × location	46.707	<0.001	86.046	<0.001	14.408	<0.001	1.917	0.153
Reef × location	15.578	<0.001	1.521	0.224	2.730	0.071	1.116	0.332
Season × reef × location	0.198	0.821	1.617	0.205	0.098	0.907	2.353	0.101

Appendix B. ANOVA results for the effects of reef site, season and sample location on TON, SRP, DSi, and chlorophyll concentrations in bottom samples from the nearshore reefs ($n = 8$)

Sources of variation	Nearshore-Bottom							
	TON		SRP		DSi		Chl	
	F	*p*	*F*	*p*	*F*	*p*	*F*	*p*
Season	273.674	<0.001	181.260	<0.001	597.517	<0.001	1.906	0.173
Reef	145.148	<0.001	129.501	<0.001	38.563	<0.001	96.709	<0.001
Sample location	27.621	<0.001	144.216	<0.001	476.274	<0.001	4.159	0.046
Season × reef	43.376	<0.001	1.214	0.275	0.058	0.810	1.793	0.186
Season × location	0.089	0.766	0.119	0.731	3.928	0.052	8.477	0.005
Reef × location	0.513	0.477	2.163	0.147	14.672	<0.001	95.430	<0.001
Season × reef × location	1.963	0.167	7.849	0.007	0.519	0.474	2.189	0.145

Appendix C. ANOVA results for the effects of season and sample location on TON, SRP, DSi, and chlorophyll concentrations in surface samples from the offshore reef ($n = 8$)

Sources of variation	Offshore-surface							
	TON		SRP		DSi		Chl	
	F	*p*	*F*	*p*	*F*	*p*	*F*	*p*
Season	27.806	<0.001	47.187	<0.001	37.625	<0.001	5.990	0.019
Sample location	30.583	<0.001	67.779	<0.001	53.776	<0.001	70.748	<0.001
Season × location	1.992	0.149	9.557	<0.001	1.064	0.354	5.105	0.010

Appendix D. ANOVA results for the effects of season and sample location on TON, SRP, DSi, and chlorophyll concentrations in bottom samples from the offshore reef ($n = 8$)

Sources of variation	Offshore-bottom							
	TON		SRP		DSi		Chl	
	F	*p*	*F*	*P*	*F*	*P*	*F*	*p*
Season	57.811	<0.001	29.306	<0.001	94.487	<0.001	0.378	0.544
Sample location	178.223	<0.001	23.403	<0.001	405.684	<0.001	55.847	<0.001
Season × location	36.838	<0.001	7.065	0.013	51.064	<0.001	3.192	0.085

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