


Predominance of phytoplankton-derived dissolved and particulate organic carbon in a highly eutrophic tropical coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil)

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Abstract We investigate the carbon dynamics in Guanabara Bay, an eutrophic tropical coastal embayment surrounded by the megacity of Rio de Janeiro (southeast coast of Brazil). Nine sampling campaigns were conducted for dissolved, particulate and total organic carbon (DOC, POC and TOC), dissolved inorganic carbon (DIC), partial pressure of CO₂ (*p*CO₂), chlorophyll *a* (Chl *a*), pheo-pigments and ancillary parameters. Highest DOC, POC and Chl

a concentrations were found in confined-shallow regions of the bay during the summer period with strong *p*CO₂ undersaturation, and DOC reached 82 mg L⁻¹, POC 152 mg L⁻¹, and Chl *a* 800 μg L⁻¹. Spatially and temporally, POC and DOC concentrations varied positively with total pigments, and negatively with DIC. Strong linear correlations between these parameters indicate that the production of TOC translates to an equivalent uptake in DIC, with 85% of the POC and about 50% of the DOC being of phytoplanktonic origin. Despite the shallow depths of the bay, surface waters were enriched in POC and DOC relative to bottom waters in periods of high thermohaline stratification. The seasonal accumulation of phytoplankton-derived TOC in the surface waters reached about 105 g C m⁻² year⁻¹, representing between 8 and 40% of the net primary production. The calculated turnover time of organic carbon was 117 and 34 days during winter and summer, respectively. Our results indicate that eutrophication of coastal bays in the tropics can generate large stocks of planktonic biomass and detrital organic carbon which are permanently being produced and partially degraded and buried in sediments.

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Introduction

Despite the low surface area and water volume compared to the open ocean, the coastal ocean plays a highly active and disproportional role in the global carbon cycle by linking the terrestrial, oceanic, and atmospheric carbon reservoirs, and hosting a large diversity of environments (Gattuso et al. 1998; Dürr et al. 2011). In addition to the high natural regional variability, more than 45% of the global population lives along coasts and estuaries, making this area subject to intense human impacts and vulnerable to changes (Crossland et al. 2005).

Short-term controls on the carbon cycle are mainly attributed to the uptake of inorganic carbon by autotrophs and the utilization of organic carbon as an energetic resource by heterotrophs (Bianchi and Bauer 2011). In general, estuaries are considered as biogeochemical reactors that predominantly emit CO₂ to the atmosphere as a consequence of high rates of respiration of organic carbon mainly from terrestrial origin (Borges and Abril 2011). This contributes to the prevailing heterotrophic metabolism, where respiration exceeds primary production (Gattuso et al. 1998; Gazeau et al. 2005). However, these conclusions are based on studies mainly in temperate and boreal regions and in river-dominated estuaries. Recent studies conducted in tropical/subtropical marine-dominated estuaries showed that they can differ from other regions and exhibit a net autotrophic metabolism, and behave as a CO₂ sink (Maher and Eyre 2012; Kubo et al. 2017), including Guanabara Bay (Cotovicz et al. 2015).

Dissolved and particulate organic carbon (DOC and POC) in estuaries are commonly recognized as largely being derived from allochthonous sources on the watersheds or surrounding wetlands and tidal marshes (Meybeck 1993; Abril et al. 2002; Cai 2011; Bauer et al. 2013). POC distribution in estuaries generally shows a peak in the turbidity maximum zone where high concentrations of particles with a relatively poor organic content occur. Upstream and downstream of the turbidity maximum zone where light is less attenuated in the water, phytoplankton can support high rates of in situ planktonic primary production, increasing the levels of POC (Meybeck 1993; Abril et al. 2002), and sometimes the levels of DOC (Cadée 1982; Abril et al. 2002), but generally these autochthonous sources account for a small amount of the

TOC (Bianchi and Bauer 2011). However, studies also showed that the autochthonous source can be equal to or exceed the river or marine supply in estuaries in some periods of the year, or annually (Raymond and Hopkinson 2003). POC can be lost along the salinity gradient due to heterotrophic respiration, in addition to flocculation, sedimentation and photo-oxidation processes (Abril et al. 2002; Bauer et al. 2013). By contrast to POC, DOC generally exhibits a linear distribution with salinity, which suggests conservative mixing with simultaneous sources and sinks that result in small net changes in bulk concentrations (Laane 1980; Mantoura and Woodward 1983; Abril et al. 2002). In addition, the labile fraction of DOC can be mineralized in estuaries contributing to non-conservative distributions (Cadée 1982; Brockmann 1994).

Organic carbon reaching estuaries also arises from direct discharge of wastewaters from urban effluents, industries and agriculture, which bring additional inorganic and organic nutrients (Meybeck and Vörösmarty 1999; Howarth et al. 2011). Discharge of wastewaters can amplify the production of organic carbon through the stimulation of autotrophic activities in productive regions of estuaries with uptake of CO₂ (Gypens et al. 2009; Cotovicz et al. 2015), or in contrast, can reinforce the heterotrophic metabolism in light-limited regions of estuaries (Cai 2011; Borges and Abril 2011). Studies that investigated the organic and inorganic fractions in estuaries showed that the maximum POC and DOC concentrations generally coincide with maximum DIC (i.e., respiration of organic carbon and release of CO₂) (Borges and Abril 2011; Cai 2011). Here we report on a large predominance of the autochthonous source of POC and DOC in a tropical eutrophic coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil). The spatio-temporal distributions of carbon forms and pigments indicate a phytoplanktonic origin for organic carbon in the water. We analyze the reasons and main processes that may lead to such an uncommon situation in urbanized tropical estuarine systems.

Materials and methods

Study area

Guanabara Bay (Fig. 1) is a tropical marine-dominated estuary located at the southeastern coast of

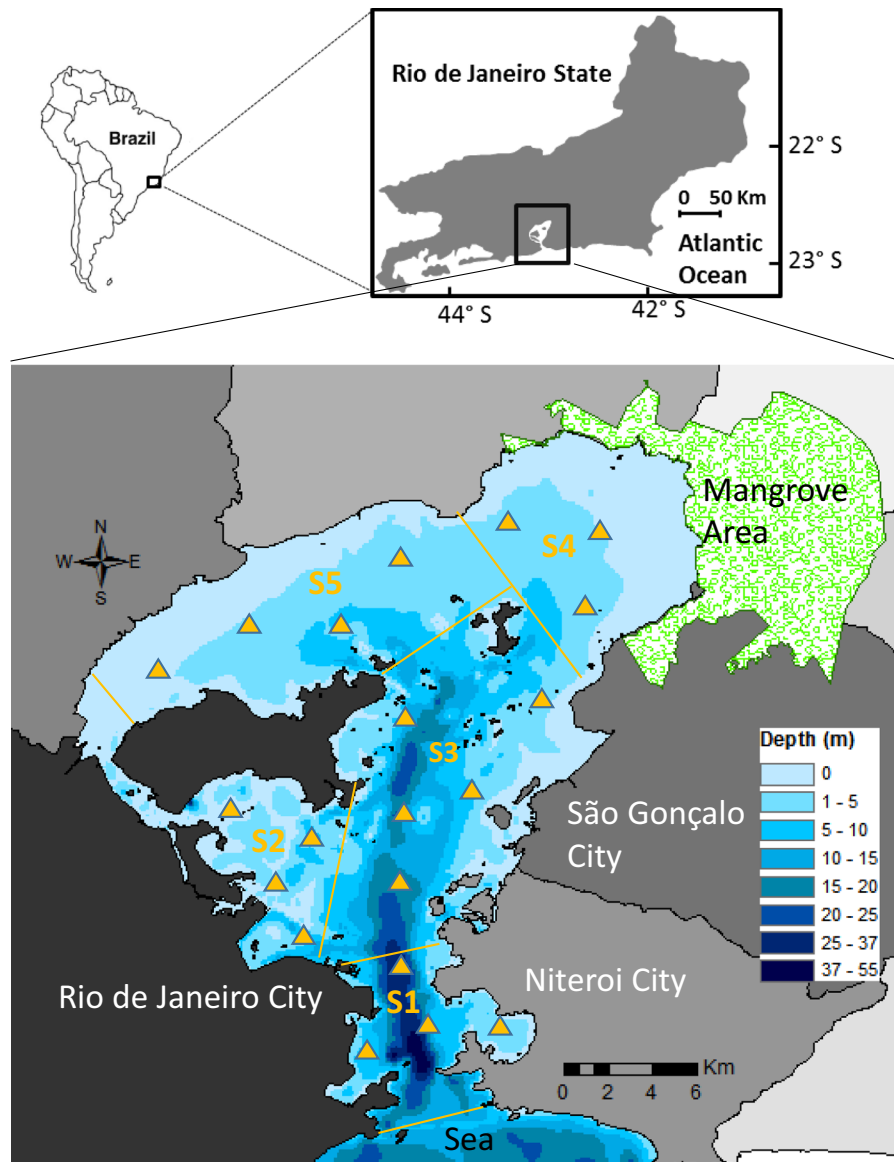


Fig. 1 Bathymetric map of Guanabara Bay. The bay was divided into five sectors (S1–S5). The orange triangles represent the sampling stations. The different grey tonalities represents

the demographic occupation around the bay, with the most dark color representing the most densely populated areas

Brazil ($22^{\circ}41'–22^{\circ}58'S$ e $43^{\circ}02'–43^{\circ}18'W$), surrounded by the Rio de Janeiro metropolitan region, with a population estimated of 11 million of inhabitants. The surface area of Guanabara Bay is 384 km^2 , with an average depth of 5.7 m, and estimated water volume of $1870 \times 10^6 \text{ m}^3$ (Kjerfve et al. 1997). The tides in the region are microtidal and semidiurnal, averaging 0.7 m and 1.3 m in amplitude during spring and neap

tide conditions, respectively. The average discharge of freshwater to the bay is $100 \pm 59 \text{ m}^3 \text{ s}^{-1}$, oscillating between $40 \text{ m}^3 \text{ s}^{-1}$ in winter, and $190 \text{ m}^3 \text{ s}^{-1}$ in summer (Kjerfve et al. 1997). The weak freshwater inputs compared to the estuarine water volume results in a large extension of saline conditions, with a relatively short water turnover time (11.4 days, on average, for renewal of 50% of the bay waters)

(Kjerfve et al. 1997). Due to its weak longitudinal estuarine mixing zone, Guanabara Bay fits in the category of an estuarine bay (Knoppers et al. 1999). The weather in Guanabara Bay is classified as tropical wet (Bidone and Lacerda, 2004), with a warm and wet summer (October to March), and a dry winter (April to November).

The human occupation in the watershed and its surrounding areas started 4 centuries ago and became more intense in 1970, when important industrial factories began to settle in the region (Bidone and Lacerda 2004). The enormous urban settlement contributes to large amounts of domestic and industrial effluents direct into Guanabara Bay. High inputs of nutrients and hydrodynamic settings with thermohaline stratification, promote high rates of primary production (Rebello et al. 1988), development of persistent phytoplankton blooms and a strong annual sink of CO₂, particularly in its mid-upper sectors (Cotovicz et al. 2015). According to Nixon (1995), the coastal marine eutrophication is defined as an increase in the supply of organic matter and nutrients to the ecosystem. Eutrophication in Guanabara Bay is characterized by the occurrence of very high Chl *a* concentrations, often reaching several hundreds of $\mu\text{g L}^{-1}$, high oxygen supersaturation, but moderate and variable dissolved nutrient concentration depending on the proximity of sewage sources and uptake by phytoplankton (Paranhos et al. 1998; Ribeiro and Kjerfve 2002; Cotovicz et al. 2015). The trophic state indexes of O'Boyle (O'Boyle et al. 2013) and Trix (Vollenweider et al., 1998) ranked the bay in the category of "eutrophic" to "hypertrophic" environment (Costa Santos 2015). In addition, previous studies showed strong increases in the rates of sedimentation (Godoy et al. 2012) and organic carbon burial (Carreira et al. 2002) in the last 50 years. Due to the large spatial variability in the hydrological and geomorphological characteristics, and the heterogeneity of human occupation of the watershed, five sectors were defined for the treatment, computations and interpretation of the data (Fig. 1), as described by Cotovicz et al. (2015, 2016).

Sampling and analytical methods

Nine sampling campaigns were conducted between April 2013 to April 2014, with a frequency varying between 30 and 45 days. Continuous measurements

for temperature, salinity, dissolved oxygen (DO), pH and $p\text{CO}_2$ were conducted for each campaign, as described in Cotovicz et al. (2015). Briefly, one submersible water pump was positioned at ~ 0.5 m depth at the side of the boat, providing continuous water flow to an acrylic chamber containing a calibrated YSI 6600 V2 multiparameter probe for the real-time measurements of temperature, salinity, pH and DO and to an equilibrator system for water $p\text{CO}_2$ measurements.

Along the continuous tracks of the boat, discrete water samples were performed for DOC, POC, Chl *a* and pheo-pigments at 16 to 19 stations distributed across the bay, except in December 2013, when only 8 stations could be sampled in sectors 3, 4 and 5 due to logistical problems (Fig. 1). Water depths at the sampling stations ranged between 2 to 30 m, averaging 5.5 m. Sub-surface water samples were collected at 0.5 m depth with a Niskin bottle and henceforth conditioned (i.e. filtrated, fixed and/or kept cooled and in the dark) for further chemical analysis in the laboratory. Vertical profiles of temperature, salinity, DO and fluorescence were performed at all discrete stations with a calibrated multiparameter probe model YSI 6600 V2. The comparison between surface and bottom waters in terms of DOC and POC concentrations was performed at some stations, during the summer period and maximum vertical stratification in sectors 3, 4 and 5.

The water was filtered through whatman GF/F glass-fibre filters (porosity 0.7 μm) followed by analysis of suspended particulate material (SPM), POC, Chl *a* and pheo-pigments, and the filtrate used for DOC. All the filters were pre-combusted (at 500° C for 6 h) and pre-weighted before utilization. After filtration, filters were dried overnight in an oven at 50 °C. SPM was determined gravimetrically. For POC analysis, the carbonate content of the filters was removed by adding some drops of HCl 2 N (Etcheber et al. 2007). The analysis of POC was carried on a LECO C-S 125 total carbon analyzer based on direct combustion in an induction furnace and infrared absorption determination of the CO₂ produced. Concerning DOC analyses, the filtrates were stored in pre-combusted and pre-decontaminated Pyrex vials, and acidified at pH 2 adding concentrated H₃PO₄. The DOC analysis were performed with a high temperature catalytic oxidation (HTCO) method (Abril et al. 2002) using a Shimadzu TOC 500 analyzer. The

reproducibility and accuracy of the DOC and POC analysis were better than 5%. Chl *a* and pheo-pigments were extracted in 90% acetone and quantified spectrophotometrically before and after acidification of the samples, with formulations and corrections proposed by Lorenzen (1967). The total pigments content was considered as the sum between Chl *a* and pheo-pigments. The DIC concentrations were calculated from the measured $p\text{CO}_2$ and total alkalinity using the dissociation constants of carbonic acid and the solubility of CO_2 as detailed in Cotovicz et al. (2015).

The climatic conditions during the sampling campaigns followed the seasonal historical pattern, excepting the months of December 2013 and January 2014, that were drier than the historical average. The months of April 2013, July 2013, August 2013, September 2013 and April 2014 were classified as winter sampling conditions, whereas the months of October 2013, December 2013, January 2014 and February 2014 comprised the summer. The online resource 1 shows all data obtained in this work. The sector-averaged values of salinity and water temperature ranged between 27.0–32.2, and 23.8–26.8 °C, respectively. In general, the upper sectors of the bay (sectors 4 and 5) presented lower salinities and higher temperatures, as expected. In these two sectors some extreme high water surface temperatures were detected, reaching up to 33.6 °C. Sector 1, near the entrance of the bay, presented the lower temperatures (24 ± 1.6 °C) and higher salinities (32.3 ± 2.0).

Statistical analysis

The Shapiro–Wilk test showed that our data did not follow a normal distribution, considering both the entire data set and the sectors separately. Consequently, non-parametric statistical tests were performed. The paired Wilcoxon test was used to assess whether bottom and surface water POC and DOC concentrations were significantly different. The seasonal differences between the sectors for the parameters considered in this study were analyzed by the Mann–Whitney test, which compares the distributions of unmatched groups. Linear regressions were calculated to analyze the correlations between variables, providing the best-fit slope and intercept and also the goodness of fit (R^2). In addition, Spearman rank correlation coefficient was calculated to assess the statistical dependence between the rankings of two

variables for the principal parameters analyzed in this study. All statistical analysis were based on $\alpha = 0.05$. The statistical tests were performed with the programs STATISTICA 7.0 and GraphPad Prism 6.

Results

The DOC and POC concentrations in Guanabara Bay showed strong spatial and temporal variations (online resource 1). Figure 2 shows the clear seasonal trend in DOC, POC, TOC, Chl *a*, $p\text{CO}_2$ and DIC concentrations. In general, DOC, POC, TOC and Chl *a* concentrations mirrored those of DIC and $p\text{CO}_2$. Considering the overall data set, the DOC and POC concentrations showed significantly higher values in summer compared to winter ($p < 0.0001$). The averaged DOC and POC concentrations in winter were, respectively, 4.4 ± 2.9 mg L⁻¹ and 3.7 ± 7.5 mg L⁻¹, whereas for summer these values were 6.5 ± 9.6 mg L⁻¹ and 7.3 ± 18.1 mg L⁻¹. Sector 1 exhibited the lower DOC and POC, higher DIC concentrations and higher salinities. The minimum and maximum DOC values in sector 1 were, respectively, 1.6 and 6.9 mg L⁻¹, whereas for POC the values ranged between 0.3 and 5.7 mg L⁻¹. The upper parts of the bay, especially sector 5, presented the highest values, with extreme high concentrations reaching up 82.6 mg L⁻¹ for DOC and 152.4 mg L⁻¹ for POC, in summer. Sector 2 also showed some high values, with maximum concentrations of 27.1 and 68.6 mg L⁻¹ for DOC and POC, respectively. Some high concentrations of DOC and POC found in sector 2 (the region most polluted by domestic effluents) were not related to phytoplankton blooms in accordance to low pigment concentrations. Temporally and spatially, DOC and POC concentrations were positively correlated (Fig. 3). Also, we found strong positive correlations between POC and TOC fractions and the total pigment concentrations (Fig. 3). For DOC, the correlation with total pigment concentration was also positive and significant (Fig. 3). To better investigate the spatio-temporal signal in the dataset (Figs. 2, 3), correlations between DOC and POC with total pigment concentrations were analyzed for each sector and season. The seasonal variation of POC with pigment concentration was still very strong if the different sectors were plotted separately. For the DOC pool, however, the seasonal

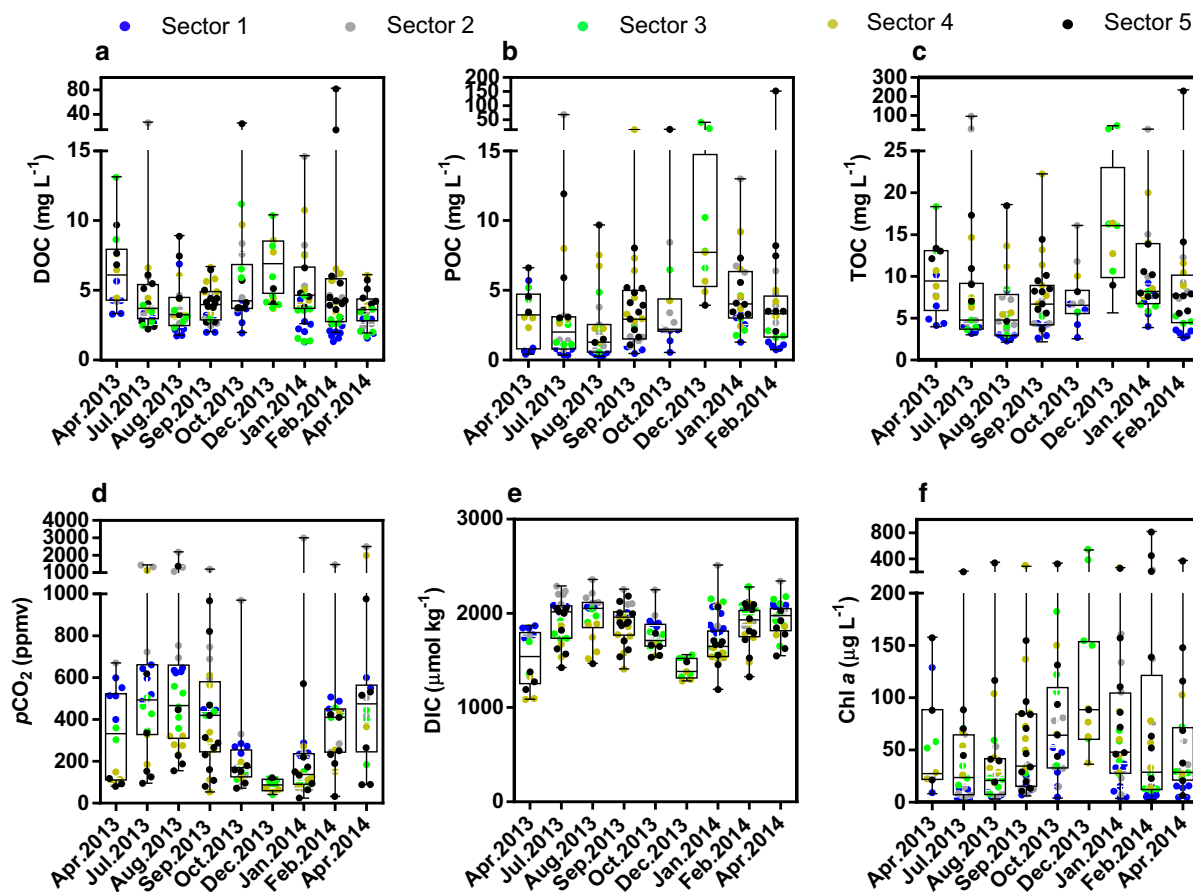


Fig. 2 Box plots (maximum, percentile 75%, median, percentile 25% and minimum) including the annual variations for the following parameters: **a** DOC; **b** POC; **c** TOC; **d** $p\text{CO}_2$; **e** DIC; **f** Chl *a* concentrations for all sampling campaigns

differences for each sector were more pronounced, and the correlations were stronger at the summer period.

DOC, POC and TOC concentrations showed negative relationships with $p\text{CO}_2$, except for few points from sector 2 that showed a positive relationship (Fig. 4). In regions that were sink of atmospheric CO_2 ($p\text{CO}_2 < 400$ ppmv, left side of Fig. 3), DOC, POC and TOC increased with decreasing $p\text{CO}_2$ and very low values of POC:Chl *a* ratios. In regions that corresponded to a source of atmospheric CO_2 ($p\text{CO}_2 > 400$ ppmv, right side of Fig. 3), POC, DOC and TOC followed positively the $p\text{CO}_2$ values and the values of POC:Chl *a* increased. The ratios of POC:Chl *a* were highest at sector 2 (maximum of 1070:1), whereas the lower values were concentrated in the intermediate and upper parts of the bay (minimum of 17:1 in sector 5). The annual average values of the POC:Chl *a* ratio were lower than 100:1 for all the

sectors, indicating a high contribution of phytoplankton to the particulate pool and low detrital contribution. Sector 2, influenced by effluents and domestic pollution, presented an annual average of 202:1. The DOC:POC ratio also showed spatial heterogeneity, although less pronounced. The values were lower at the upper parts of the bay, with a minimum of 0.5:1 in sector 5. Sector 1, dominated by the marine source, showed the highest DOC:POC values, that reached up 10:1. The seasonal variations of POC:Chl *a* and DOC:POC were less evident, with the exception of sector 1, where the DOC:POC ratios showed higher values in winter. The DOC:POC ratio was negatively correlated to the suspended particulate material concentrations. The online resource 3 provides additional data with a Spearman correlation matrix for all parameters considered in this study.

Fig. 3 Linear regressions between: **a** POC versus DOC; **b** DOC versus total pigment concentrations; **c** POC versus total pigment concentrations; **d** POC versus total pigment concentrations

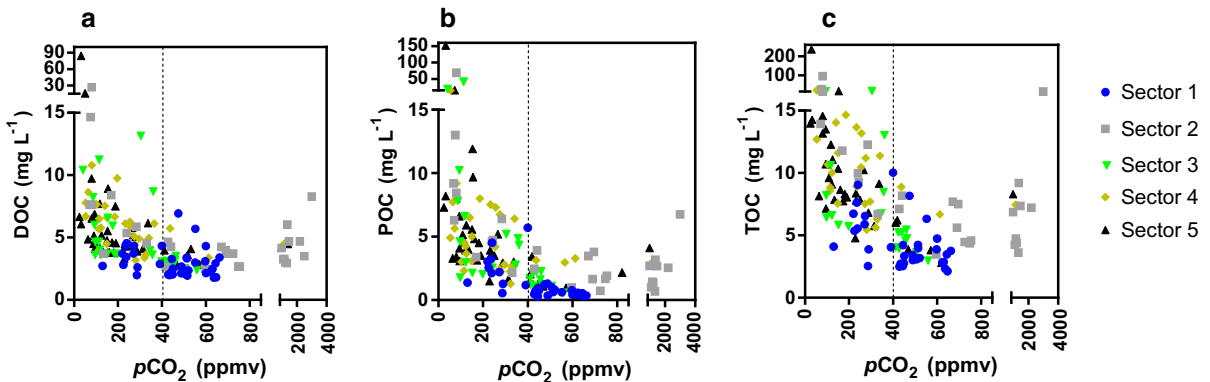
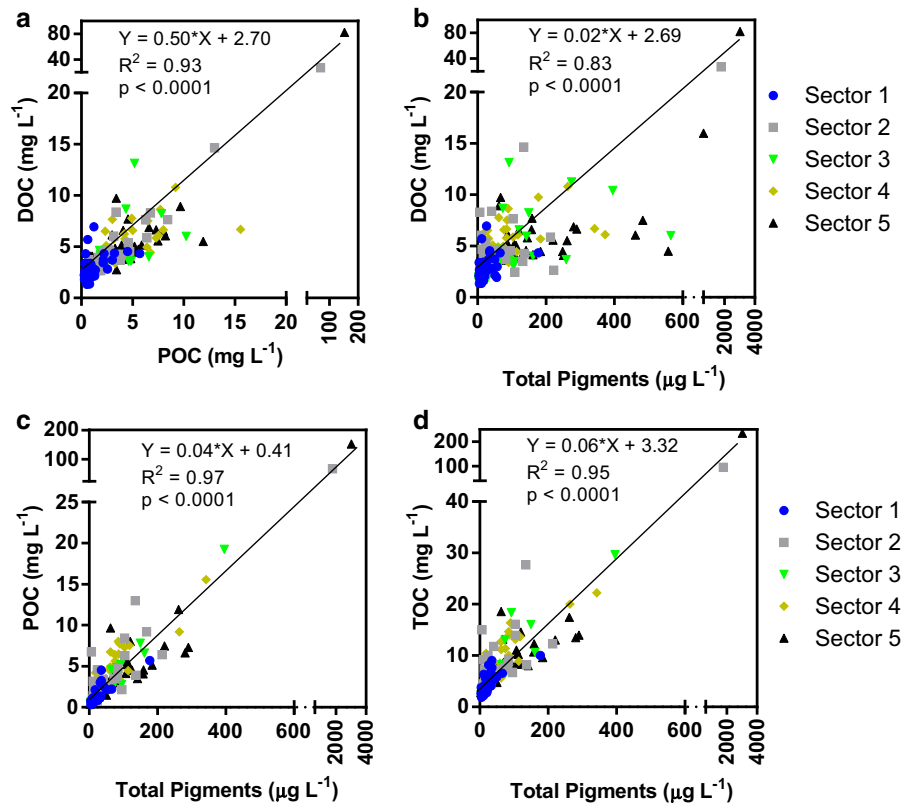


Fig. 4 Graphs showing the relationships between: **a** DOC and pCO₂; **b** POC and pCO₂; **c** TOC and pCO₂. The dashed lines at 400 ppmv represent the global average atmospheric CO₂ concentration

The differences in surface and bottom water concentrations for DOC, POC, TOC, DOC:POC ratio and POC:Chl *a* ratio were analyzed during summer, the period that experiences the strongest thermohaline stratification of the water column, particularly in the upper sectors (Kjerfve et al. 1997; Cotovicz et al. 2016). Table 1 presents the comparison between surface and bottom waters in sectors 3, 4 and 5. The

differences between surface and bottom waters for all these parameters were of high statistical significance ($p < 0.0001$), except for the POC:Chl *a* ratio. DOC, POC and TOC concentrations were about two-fold higher in surface water than in bottom water. The DOC:POC ratio was significantly lower at the surface, averaging 1.3 ± 0.6 in surface waters and 2.8 ± 1.3 in bottom waters. The POC:Chl *a* ratio did not present

Table 1 Comparison between surface and bottom waters in sectors 3, 4 and 5 for temperature, salinity, DO, Chl *a*, DOC, POC, TOC, DOC/POC ratio and POC/Chl *a* ratio (average concentrations \pm standard deviation; $n = 37$)

| | Surface water | Bottom water |
|---|----------------|----------------|
| Temperature ($^{\circ}\text{C}$)*** | 26.0 \pm 2.8 | 22.1 \pm 2.7 |
| Salinity*** | 29.3 \pm 3.8 | 33.0 \pm 2.4 |
| DO (%)*** | 128 \pm 58 | 53 \pm 23 |
| Chl <i>a</i> ($\mu\text{g L}^{-1}$)** | 62 \pm 68 | 10 \pm 12 |
| DOC (mg L^{-1})*** | 4.6 \pm 1.9 | 2.6 \pm 1.1 |
| POC (mg L^{-1})*** | 5.5 \pm 7.3 | 1.4 \pm 1.3 |
| TOC (mg L^{-1})*** | 10.5 \pm 8.7 | 4.0 \pm 2.3 |
| DOC:POC ratio*** | 1.3 \pm 0.6 | 2.8 \pm 1.3 |
| POC:Chl <i>a</i> ratio ^{ns} | 109 \pm 123 | 128 \pm 73 |

^{ns}Not significant difference between surface and bottom waters

***Significant difference between surface and bottom waters (Wilcoxon test; $p < 0.0001$)

**Significant difference between surface and bottom waters (Wilcoxon test; $p < 0.001$)

significant differences between surface and bottom waters ($p > 0.05$).

Discussion

Phytoplanktonic origin of POC in Guanabara Bay

The strong positive correlation between POC and total pigments concentrations reveals that the bay produces large amounts of organic carbon mainly in intermediate and upper sectors (Fig. 3; online resource 2), despite some lateral variations related to influence of terrestrial sources mainly from polluted rivers and sewage discharge (urban origin). If we consider the correlation between POC and Chl *a*, the coefficient is high if we remove 4 points (outliers) in the graph ($Y = 0.04 * X + 1.17$; $R^2 = 0.73$; $p < 0.0001$). These 4 points are related to phytoplankton blooms with high pheo-pigment and low Chl *a* concentrations, indicating predominance of blooms at their stage of senescence. However, Chl *a* composed about 75% of the total pigment concentrations in the bay on average, showing a large predominance of active phytoplankton during all the year. These values averaged 90% at summer, declining to 60% during winter suggesting that the proportion of active phytoplankton decreased. Thus, we choose the relationship between POC and

total pigments as a more appropriate approach to quantify the influence of phytoplankton on the POC concentrations. Considering all the data set, the y-intercept of 0.4 mg L^{-1} in the linear regression between POC and total pigment concentrations (Fig. 3) can be used to calculate the percentage of phytoplankton-derived POC, which was about 81% in winter, and 90% in summer, on average for the entire bay. Except in the highly polluted sector 2, where the correlation was weaker, the y-intercepts of the POC-pigments relationships were close to zero suggesting that detrital particulate carbon fraction is low. If we consider the y-intercepts calculated separately for each sector, except sector 2 (online resource 2), the POC-derived phytoplankton ranged between 85% in winter and 91% in summer, i.e., only about 4% of difference between the two approaches. This phytoplankton contribution to POC predominates in all the sectors at all seasons. In order to confirm this conclusion, we also applied the conceptual model of Sathyendranath et al. (2009) to infer the fraction of phytoplankton carbon in the total particulate carbon as a function of Chl *a* concentrations, which was calculated as follows:

$$C_p/C_T = 0.41 B_F^{0.18}$$

where C_p and C_T are phytoplankton carbon and total particulate carbon, respectively, and B_F is the Chl *a*. Using this formulation, the calculated phytoplankton-derived POC was about 77% in winter and increased to 88% in summer. All approaches gave very consistent results, with less than 5% of difference on average. In addition, previous works also corroborated our findings considering the source of POC, showing that the elemental (C/N of 5–8) and isotopic signatures ($\delta^{13}\text{C} = -25.3\text{‰}$ to -15.1‰) of the particulate organic matter were strongly influenced by autotrophic processes rather than allochthonous contribution (Kalas et al. 2009; Martins et al. 2016).

High contributions of phytoplankton to POC were found in other marine-dominated systems, for example, averaging 84% in a compilation of eight embayments and two semi-enclosed systems located at the coast of France (Liénaert et al. 2017), and 82% in the Venice Lagoon (Italy) (Berto et al. 2013). On the other hand, estuaries dominated by terrestrial material (river-dominated) normally present very low POC-derived phytoplankton (Abril et al. 2002; Bauer and

Bianchi 2011). For all the sampling campaigns, the average concentrations of POC in Guanabara Bay showed values well above than those normally found for mesohaline to euhaline waters in estuaries (Bianchi and Bauer 2011).

The POC:Chl *a* ratio can be used to characterize the POC in coastal waters (Banse 1977). Previous studies showed that the POC:Chl *a* ratio of living phytoplankton varies between 15 and 140 (Banse 1977; Cloern et al. 1995; Sathyendranath et al. 2009). For all the sectors of Guanabara Bay (except sector 2), the values were on average lower than 125 corroborating a large predominance of phytoplankton-derived POC. During some phytoplankton blooms, the POC:Chl *a* ratio reached 17:1, indicating exponential growing of phytoflagellates, small diatoms and/or cyanobacteria. Only sector 2 presented average values higher than 125, revealing predominance of detrital material over phytoplankton, and related to the major inputs of urban effluents (Knoppers et al. 1984; Maksymowska et al. 2000).

We also found a highly significant positive correlation between POC and the chlorophyll *c* pigment ($R^2 = 0.65$). This suggests that an important portion of the POC is composed of marine diatoms, dinoflagellates and/or brown algae, which contain chlorophyll *c* in addition to the predominant Chl *a* (Dougherty et al. 1970). Previous works in Guanabara Bay have documented occurrences of diatoms blooms near the bay mouth and the dominance of dinoflagellates at the uppers sections (Valentin et al. 1999; Kalas et al. 2009). In addition, a great deal of patchiness with a succession of intense red, brown and/or green colored waters was detected, leading to the marked short variability of $p\text{CO}_2$ and Chl *a* (Cotovicz et al. 2015), and also for DOC and POC as addressed in this study.

Phytoplanktonic origin of DOC in Guanabara Bay

The DOC and POC concentrations in Guanabara Bay were positively correlated, suggesting that these two pools had a similar source (at least for a certain part of the total concentrations). Although less pronounced than for the POC, the positive correlation between DOC and total pigment concentrations (Fig. 3) indicates an important phytoplanktonic contribution, with a *y*-intercept of 2.7 mg L^{-1} . This DOC intercept suggests the presence of two pools of DOC: a baseline of less reactive DOC (less biodegradable;

$< 2.7 \text{ mg L}^{-1}$) probably of marine and terrestrial origin, and a variable fraction apparently linked to phytoplankton ($> 2.7 \text{ mg L}^{-1}$). As pointed out for the POC fraction, this DOC baseline is probably derived from allochthonous terrestrial sources. In the northeastern part of the bay (sector 4), a mangrove forest covering an environmental protection reserve of about 43 km^2 could also contribute with organic carbon inputs to the bay (Dittmar et al. 2006). However, we found no clear enrichment of organic carbon in the sampled area closest to the mangrove. Despite the fact that we could not sample the vicinity of the mangrove, the export of organic carbon in the bay appears modest, as also observed for CO_2 and CH_4 (Cotovicz et al. 2015, 2016). Carreira et al. (2002) analyzed the isotopic signature of sedimentary organic carbon at a station located very close to this mangrove and concluded that the riverine/terrestrial inputs accounted for around 70% of total sedimentary organic matter. However, as also recently pointed out by Cordeiro et al. (2017), these less ^{13}C -enriched sediments were restricted to the area very close to the mangrove forest. Little export of mangrove material apparently occurs probably because of low tidal pumping related to the microtidal character of the bay.

Considering DOC values above the *y*-intercept of 2.7 mg L^{-1} as the phytoplanktonic DOC, the calculated phytoplankton-derived DOC was about 37% in winter, and up to 60% in summer. For each sector and season separately (online resource 2), the DOC-derived phytoplankton contribution was similar, between 30% in winter and 63% in summer. The slopes of linear regressions for each sector were, in general, higher in summer than in winter, indicating a major exudation of DOC by phytoplankton during summer. For sectors 1 and 3, during winter, the correlation coefficients were weak, indicating some contribution from allochthonous sources. In the sector 2, the most polluted area of the bay, the linear regression between DOC and total pigment concentrations was not significant consistent with a major contribution of urban sources as previous showed for POC. The baseline of non-derived phytoplanktonic material to DOC can be explained by the urban origin (sewage effluents), however, can represent also a mixing of terrestrial, marine and urban material with a more refractory characteristic.

In general, the average contribution of autochthonous sources to the DOC pool in Guanabara Bay are

higher than those generally found in estuaries (Fisher et al. 1998; Bianchi and Bauer 2011). Few reports showed a net production of DOC related to phytoplankton in other estuaries, with positive variations between the Chl *a* and associated DOC peaks (Cadée 1982, 1984; Wafar et al. 1984; Aminot et al. 1990). For example, at the Zaire River estuary, for salinities higher than 25, the DOC appear to lie above the mixing line indicating a net production (Cadée 1984).

Various factors can contribute with the release of DOC from phytoplankton, including the excretion/exudation of DOC, inefficient grazing by zooplankton, and cell lysis during senescence (Mykkestad 2000; Augusti and Duarte 2013). Over a wide range of marine and freshwater ecosystems, it has been estimated that phytoplankton releases approximately 13% of the total carbon fixed by primary production as DOC in the water (Baines and Pace 1991). If we use this latter percentage and the average net primary production of $0.17 \text{ mol C m}^{-2} \text{ day}^{-1}$ estimated by Rebello et al. (1988) in sectors 3, 4 and 5, the calculated DOC release from phytoplankton in the waters of Guanabara Bay is about $0.02 \text{ mol C m}^{-2} \text{ day}^{-1}$. This significant extracellular DOC release can explain the positive correlation between POC and DOC in Guanabara Bay, which is unusual in estuaries.

The increase of DOC in a well-mixed estuary (Morlaix Bay, western English Channel) and in the higher salinities of the Zaire River Estuary were coincident with increases in Chl *a* after a time lag, indicating that DOC was derived from decomposition of the plankton material, or cell lysis (Cadée 1984; Wafar et al. 1984). Our results in Guanabara Bay, on the other hand, did not present this time lag demonstrating that direct exudation, as important processes explaining the contribution of phytoplankton to DOC in addition to cell lysis. In the Amazon River plume it was also observed that large phytoplankton blooms exudated dissolved organic matter modifying its molecular composition (Medeiros et al. 2016).

We estimated the seasonal DOC and POC accumulations in the water for the most productive region of Guanabara Bay (sectors 3, 4 and 5) from the annual curves (Fig. 2), as in Cadée (1982). The seasonal DOC and POC accumulations were about $10 \text{ mg C L}^{-1} \text{ year}^{-1}$ and $25 \text{ mg C L}^{-1} \text{ year}^{-1}$, respectively. These values of DOC and POC accumulation per liter were by far higher than those found in other coastal systems (Cadée 1982, 1984; Wafar et al. 1984; Aminot et al.

1990). If we multiply the seasonal DOC and POC accumulation by the depth of 3 m (considered the euphotic zone), the seasonal TOC accumulation was about $105 \text{ g C m}^{-2} \text{ year}^{-1}$. This value is slightly lower than the CO_2 sink at the air water-atmosphere ($144\text{--}444 \text{ g C m}^{-2} \text{ year}^{-1}$; Cotovicz et al. 2015) and the carbon burial in the sediments ($108\text{--}492 \text{ g C m}^{-2} \text{ year}^{-1}$; Carreira et al. 2002) in this productive region. Compared to the values of net primary production (NPP) and the net community production (NCP), the seasonal TOC accumulation in the water was equal to about 8 to 41% of the NPP, and between 10 to 48% of the NCP. In the temperate Chesapeake Bay, the DOC accumulation was equivalent to 10% of NPP (Fisher et al. 1998). The sectors 1 and 2 were excluded from this analysis because the data of NPP are not available for this region.

The cycling of carbon in Guanabara Bay driven by phytoplankton

After excluding the data from sector 2 were trends are different because of the large inputs of sewage effluents (where $p\text{CO}_2$ is highest and related to the heterotrophic activities), DIC and TOC were negatively correlated, with a slope not significantly different from -1 (Fig. 5). This reveals that the production/consumption of TOC and DIC are strongly interconnected, each mole of TOC produced in the

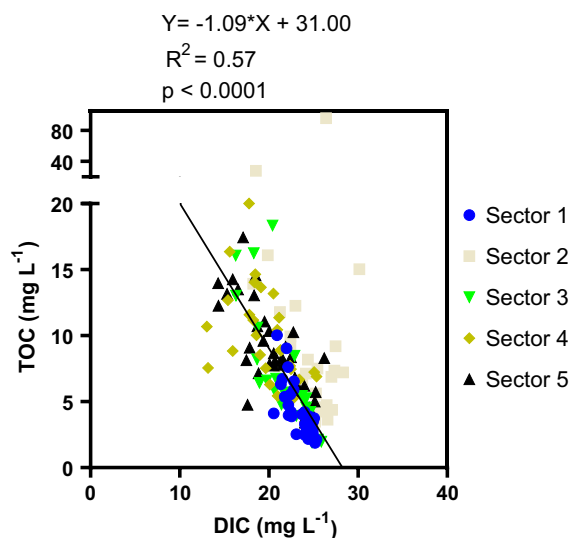


Fig. 5 Linear Regression between DIC and TOC. Note that the data from sector 2 was removed for this analysis

water being associated by an equivalent uptake of DIC. The negative relationship between the levels of $p\text{CO}_2$ and the concentrations of organic carbon also corroborates these findings (Fig. 4). Extremely high levels of primary production are able to consume approximately half of the DIC in the water, and transform it to POC, and also to DOC through exudation processes. In these high salinity waters, most of the initial DIC has a marine origin. The organic carbon produced is then in part respired and recycled to DIC by the prokaryotes, and in part buried in the sediment, however, an important amount of this TOC remains in the water. Consequently, because of eutrophication and intense phytoplanktonic production, the ecosystem has turned to a reservoir of autochthonous organic matter that is being continuously recycled. According to Moore et al. (2013), the most deficient nutrient will not become limiting if all remain replete, and this seems the case of Guanabara Bay. One recent study conducted in a boreal coastal lagoon also showed that the autochthonous organic carbon production decreased the concentration of DIC in the water and thereby contributed to atmospheric CO_2 uptake (Watanabe and Kuwae 2015). However, these authors observed a moderate tendency and not a strong relationship as in Guanabara Bay. On average throughout the year, the inorganic carbon pool accounts for approximately 69% of the total carbon in the waters of Guanabara Bay, whereas the organic carbon accounts for the remaining 31%. In the upper waters of sector 5, TOC reached 46% of the total carbon whereas in the “marine” sector 1, this percentage decreases to 15%. During the summer, the proportion of TOC increases to about 40% at surface waters as the result of the strong phytoplankton assimilation of DIC and formation of TOC. This proportion of TOC compared to the DIC is higher than what is normally found in coastal waters, where TOC normally represents less than 20% (Bauer et al. 2013).

In terms of the seasonal behavior, the summer time conditions amplified the formation of massive phytoplankton blooms and favored its spreading along large areas of the bay (Cotovicz et al. 2015), increasing the organic matter production. The role of seasonality can also be viewed with the formation of vertical thermal-haline stratification in summer due to the high incidence of photosynthetically active radiation (even at a diel scale), which was marked at intermediate and upper waters (Kjerfve et al. 1997; Cotovicz et al.

2015). The vertical stratification leads to a pattern of higher POC and DOC concentrations at surface waters compared to the bottom waters, and seem to be directly related to the high rates of primary production and exudation processes (Table 1).

A previous study showed that one important part of the POC produced at the surface waters of Guanabara Bay is transferred to the sediments and buried under anoxic conditions (Carreira et al. 2002). Using a two end-member isotopic mixing model, these authors found a predominance of 75% and 82% of phytoplanktonic source to the sedimentary organic carbon in the sectors 3 and 5 ($\delta^{13}\text{C} - 19.9\text{‰}$ to -23.7‰), a percentage very similar to what we found in POC at the same locations. A recent study showed that $\delta^{13}\text{C}$ values in surface sediments of Guanabara Bay ranged between -26.2 and -20.5‰ , with more enrichment of ^{13}C in mid-upper sectors, and less enrichment in the locations near the mangrove and under influence of riverine discharges (Cordeiro et al. 2017). An unknown fraction of this sedimentary POC can be respired and return to water column as DIC. However, just a minor portion of this DIC is re-emitted to the atmosphere due to the predominant under-saturation in $p\text{CO}_2$ in surface waters (Cotovicz et al. 2015). Overall, the averaged proportions of DOC and POC are very close in the bay, each one representing about 50% of the TOC. Especially in the upper waters dominated by phytoplankton blooms, POC can be higher than DOC. In open ocean waters, for example, the DOC fraction is normally 4 times higher than POC (Sarmiento and Gruber 2006).

Stock and turnover time of the phytoplankton-derived TOC

The turnover time for the phytoplankton-derived organic carbon was calculated for the most productive areas of the bay (sectors 3, 4 and 5) that correspond to about 74% of the total surface of Guanabara Bay. The stock of phytoplankton-derived organic carbon was estimated at about 4262 t and 10,695 t, for winter and summer, respectively, taking into account the first 3 m of water column. To calculate this stock, we did not consider the values below the y-intercepts, i.e., for all the points we removed the baseline TOC value of 3.1 mg L^{-1} that is not derived from phytoplankton. Based on the marked negative relationship between DIC and TOC (Fig. 5), we assume that the organic

carbon produced by phytoplankton quantitatively induces an equivalent air-sea CO₂ uptake. The turnover time was then calculated dividing the stock of phytoplankton-derived organic carbon by the CO₂ flux at the air–water interface. The carbon turnover times were 117 and 34 days for winter and summer, respectively. These turnover times are similar to that was found in Chesapeake Bay, where the non-conservative fraction of DOC showed a turnover time of weeks to months, whereas the POC seems to be recycled at shorter time scales from days to weeks (Fisher et al. 1998).

The faster turnover time of carbon in summer is consistent with the higher phytoplanktonic biomass (Chl *a*, Fig. 1) and primary production rates (Rebello et al. 1988). The carbon turnover time is also close to the water renewal time. The amounts of TOC produced in the bay, especially during the growth of large phytoplankton blooms, overlaps the capacity of the heterotrophic communities to remineralize all this material (nutrient depletion is frequently observed during the blooms), creating seasonal accumulation of TOC. According to Fujji et al. (2002), the decomposition rate for labile and semi-refractory POC can vary between 9–11 days and 29–88 days, respectively. In this way, the POC composition in Guanabara seems to be more labile in summer due to the enhanced rhythms of metabolic rates (photosynthesis and respiration), and more refractory in winter. Another important observation is that the generation of DOC was more important in the surface waters than in bottom waters (Table 1).

Conclusions

The control by phytoplankton of carbon dynamics was previously showed for *p*CO₂ values and fluxes (Cotovicz et al. 2015); here we show that phytoplankton also drives the organic carbon behavior. The POC and DOC pools were positively related to phytoplankton biomass. In addition, TOC maximum were associated to DIC and *p*CO₂ minimum, a very unusual pattern compared to other estuaries worldwide. In addition, the POC and DOC concentrations in Guanabara Bay were largely above the average concentrations found in other coastal zones. However, at some highly impacted regions of the bay (sector 2 and parts of sector 4 and 5), and especially during winter, the

correlations between organic carbon pools with phytoplankton pigments were weak and/or not verified due to large inputs of organic matter from sewage discharge and polluted rivers. The high rates of organic carbon burial in sediments and the low concentrations of DOC and POC at the bay entrance indicates that the most part of organic carbon is buried and/or recycled inside the bay. Eutrophication is also increasing the proportion of TOC compared to DIC, and increasing the amount of POC compared to DOC. Extreme coastal eutrophication is occurring in many developing countries, and the results found in Guanabara Bay can be one tendency in other disturbed tropical coastal waters that need to be more explored. Our findings have important implications for future developments of biogeochemical models and coastal carbon budgets in these estuarine bays.

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