Environmental Advances 15 (2024) 100476

Contents lists available at ScienceDirect

Environmental Advances

journal homepage: www.sciencedirect.com/journal/environmental-advances

Towards an integrated pelagic and benthic analysis of long-term coastal eutrophication (Guanabara Bay, Brazil)

Jaqueline Sá Earp Muniz[a,c], Rodrigo Coutinho Abuchacra[b,c], Fernando Cunha Peixoto[d], Paula Ferreira Falheiro Abuchacra[e], Christian J. Sanders[f], Carla Maciel Salgado[e], José Antônio Baptista Neto[g], Leonardo Amora-Nogueira[c,e], Renato Campello Cordeiro[c], Luciane Silva Moreira[c], Luana Pinho[h], Jean Louis Valentin[i], Allana Faustino[c], Ana Fonseca-Oliveira[c], Douglas Motta Pio[c], Manuela Lima Carvalho[c], Samira Cristina de Souza Pinto[c], Wilson Machado[c], Luiz Eduardo de Oliveira Gomes[e,j,k], Humberto Marotta[c,e,*]

[a] *Chemical Engineering Graduate Program, Universidade Federal Fluminense (UFF), Rua Passo da Pátria, 156, Niterói, RJ, Brazil, 24210-240*
[b] *Department of Geography, Graduate Program in Geography, Universidade do Estado do Rio de Janeiro (UERJ-FFP), Rua Dr Francisco Portela, 1470 São Gonçalo, Rio de Janeiro, Brazil, 24435-005*
[c] *Ecosystems and Global Change Laboratory (LEMG-UFF) / International Laboratory of Global Change (LINCGlobal), Biomass and Water Management Research Center (NAB-UFF), Graduate Program in Geosciences (Environmental Geochemistry), Universidade Federal Fluminense (UFF), Av. Edmundo March, s/n°, Niterói, RJ, Brazil, 24210-310*
[d] *Instituto Militar de Engenharia (IME), Praça General Tibúrcio, 80, Praia Vermelha, Rio de Janeiro, Brazil, 22290-270*
[e] *Physical Geography Laboratory (LAGEF-UFF), Department of Geography, Graduate Program in Geography, Universidade Federal Fluminense (UFF), Av. Gal. Milton Tavares de Souza, s/n°, Niterói, RJ, Brazil, 24210-346*
[f] *National Marine Science Centre, Faculty of Science and Engineering, Southern Cross University, Coffs Harbour, NSW, 2450, Australia*
[g] *Department of Geology and Geophysics/LAGEMAR, Universidade Federal Fluminense (UFF), Av. General Milton Tavares de Souza s/n, 24210-346, Niterói, RJ, Brazil*
[h] *Department of Chemical Oceanography, Rio de Janeiro State University, Pavilhão João Lyra Filho, sala 4008 Bloco E, Rua São Francisco Xavier, 524, Maracanã – RJ, 20550-900, Brazil*
[i] *Department of Marine Biology, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil*
[j] *NGO Guardiões do Mar, Rua Alfredo Azamor, 739, Boa Vista, São Gonçalo, RJ, Brazil, 24466-000*
[k] *Silvestrum Climate Associates L.L.C., 1 Lower Crescent Ave Sausalito, CA, USA*

ARTICLE INFO

Keywords:
Coastal eutrophication
Sediment burial
Water monitoring
^{210}Pb dating
Urban bay

ABSTRACT

Coastal ecosystems are important destinations for natural and anthropogenic inputs, areas experiencing eutrophication from untreated sewage globally. However, the mechanistic link of how coastal waters and sediments can jointly respond to nutrient enrichment, especially nitrogen (N) and phosphorus (P), remains relatively unknown. Here, we assessed the interdecadal variability in N and P contents, comparing four surface water sampling sites (~40-year monthly concentrations) and three ^{210}Pb dated sediment cores (~70-years) in an urban bay that has received increasingly high untreated sewage discharges over the past century (Guanabara Bay, Brazil). Major eutrophication was found, with differences between waters and sediments along sampling sites. The water concentrations of total phosphorus (TP) and dissolved inorganic nitrogen (DIN) yielded on average ~10–45 % and ~40–190 % higher in 2005–2017 compared to 1980–2005 period in the sampling site most influenced by the denser urban than the conserved area, respectively. Furthermore, 6-year average water concentrations indicated both recent initial decreases in the most urban area, potentially associated with new sanitation facilities, and high increases in those relatively more conserved areas. Conversely, TP and TN sediment burial rates were less sensitive to recent changes as compared to the water concentrations, yielding ~11 and 31 % between 1980–2005 and 2005–2017, respectively, of which also provided baselines data for earlier periods without direct pelagic

* Corresponding authors at: Ecosystems and Global Change Laboratory (LEMG-UFF) / Graduate Program in Geosciences (Environmental Geochemistry) and Graduate Program in Geography, Universidade Federal Fluminense (UFF), Av. Edmundo March, s/n°, Niterói, RJ, Brazil, 24210-310; Department of Geography, Graduate Program in Geography, Universidade do Estado do Rio de Janeiro (UERJ-FFP), Rua Dr Francisco Portela, 1470 São Gonçalo, Rio de Janeiro, Brazil, 24435-005.

E-mail addresses: rodrigo.abuchacra@uerj.br (R.C. Abuchacra), humbertomarotta@id.uff.br (H. Marotta).

https://doi.org/10.1016/j.envadv.2023.100476
Received 3 September 2023; Received in revised form 3 December 2023; Accepted 20 December 2023
Available online 21 December 2023

measurements (i.e., 1950–1980). Thus, these findings offer new insights into substantial temporal and intra-ecosystem spatial variability of coastal eutrophication, indicating that an integrated analysis between water monitoring and sediment burial is needed to improve the diagnosis and prediction capabilities necessary for effective long-term mitigation of coastal aquatic eutrophication worldwide.

1. Introduction

Coastal waters are among the most productive in the world due to large nutrient inputs from the watershed (Bauer et al., 2013; Howarth et al., 2000; Zhou et al., 2020), especially nitrogen (N) and phosphorus (P), which are often limiting and therefore support intense organic matter cycling (Teoh et al., 2016; Wilson et al., 2017). These processes related to organic matter and nutrient cycling along the land-ocean transition zone (Cai et al., 2011) also have significant implications for global greenhouse gas emissions (Spivak et al., 2019; Weber et al., 2019; Duarte and Agustí, 1998). Indeed, high remineralization (Bauer et al., 2013) and accumulation (McLeod et al., 2011) rates of organic matter may release and uptake, respectively, large amounts of carbon and nitrogen gases in bays and estuaries, where nutrients are important limiting resources to aquatic productivity (Howarth et al., 2021; Song et al., 2017; Havens et al., 2001; Fisher et al., 1992).

Along extensive shorelines, the nutrient enrichment (i.e., eutrophication) from anthropogenic sources such as untreated urban and rural wastewaters have substantially decreased the water quality, biodiversity, and multiple socioeconomic uses (Breitburg et al., 2018; Cai et al., 2011; Vitousek et al., 1997). Growing land use change has also been associated with high nutrient inputs into coastal waters and sediments (Ross and Randhir, 2022; Savage et al., 2010). Coastal eutrophication is considered a major constraint for environmental sustainability (Vea et al., 2020), leading to toxic algal blooms (Hallegraeff et al., 2021; Bakun et al., 2010), greenhouse gas emissions (Weber et al., 2019), acidification (Savoie et al., 2022; Wallace et al., 2014), and deoxygenation (Breitburg et al., 2018). The resulting metabolic responses can be highly dynamic in pelagic and benthic environments (Nedeau et al., 2003), especially under warm tropical conditions (Cotovicz et al., 2016, 2015; Marotta et al., 2010). As a result, long-term impacts over decades on water quality have increased the organic and inorganic burial in coastal aquatic sediments (Ivarsson et al., 2019; Monteiro et al., 2012).

Accordingly, integrated analysis of radiometric dating and the chemical composition of these substance have been used around the world as a proxy to address the relation between scarcity and long-term water quality data. The ^{210}Pb-dating method in sediment cores from aquatic ecosystems are a feasible alternative to cost-effective and interdecadal water monitoring in order to detect changes to aquatic systems globally (Andersen et al., 2017; Heim and Schwarzbauer, 2013; Ruiz-Fernández and Hillaire-Marcel, 2009). However, studies on interdecadal changes in nutrients comparing water content and sediment burial remain scarce, constraining our understanding on the mechanisms and response times of long-term coastal eutrophication, which are critical for mitigation efforts (Duarte and Krause-Jensen, 2018). In addition, regional and global estimates of nutrient enrichment in coastal aquatic ecosystems may also be biased as a result of the lack information relating to intra-ecosystem spatial N and P variability (Bauer et al., 2013).

Guanabara Bay has experienced significant anthropogenic impacts, jeopardizing its diverse socioeconomic and ecological values (Potratz et al., 2019). Discharges of nutrients, organic matter, and sediments (Cordeiro et al., 2021a), coupled with trace elements (Cordeiro et al., 2021b; Baptista Filho et al., 2019; Abuchacra et al., 2015), have substantially diminished the water quality of the Bay since European occupation in the 16th century. However, the degradation of Guanabara Bay intensified in the 1930s due to industrialization and substantial urban growth in the watershed (Fistarol et al., 2015; Amador, 1997). This degradation, which persists to the present day, is still associated with inadequate sewage treatment facilities (Fries et al., 2019).

Dataset integration from water monitoring programs and sediment paleolimnological studies have been considered important for a better understanding of causes and consequences of changes in nutrient levels in aquatic ecosystems (Hobæk et al., 2012; Battarbee et al., 2005), but remain scarce globally. In one of the most urbanized coasts of South America with intense eutrophication due to massive untreated sewage discharges (Fistarol et al., 2015; Kjerfve et al., 1997), this study examines the monitoring over almost 40 years along Guanabara Bay (Brazil) of which is a rare opportunity to compare water quality with sediment burial rates in order to integrate the responses of anthropogenic eutrophication between pelagic and benthic environments, especially under dynamic warm tropical conditions.

2. Material and methods

2.1. Study design

We assessed three sediment cores dated using the ^{210}Pb method (periods ~1950–2017 in core Sed-CON (our unprecedented data) and ~1950–2005 in cores Sed-URB and Sed-INT (data from Monteiro et al., 2012) associated with four surface water sampling sites (unprecedented data measured monthly from 1980 to 2017 by the Rio de Janeiro State Environmental Agency – INEA – available at in Guanabara Bay (Fig. 1 and Table 1). The inner northeastern region of this bay comprises the relatively conserved Guapimirim Environmental Protection for fringing mangroves and surrounding waters, where Sed-CON core and Wat-CON pelagic sampling site were situated. In turn, the inner northwest region is surrounded by an intermediate urban growth and was represented by the Sed-INT core and Wat-INT pelagic monitoring site. Finally, the southwestern region is located closest to the south outlet leading to the sea. This region is surrounded by the densest and oldest urban area within the watershed, where the pelagic monitoring sites Wat-URB-1 and Wat-URB-2 are situated ~3 km to the southwest and 5.5 km to the northwest, respectively, from the Sed-URB core. The distance between water and sediment sampling sites were less than ~4 km to the other regions (i.e., most conserved and influenced by intermediate urban growth).

Accordingly, we conducted a comparative analysis of water and bottom sediment data among distinct Guanabara Bay regions surrounded by 'more conserved,' 'intermediate,' and 'urbanized' watersheds. This study contributes to the development of a pelagic-sediment approach applicable to a diverse array of aquatic ecosystems globally. The changes in N and P were evaluated based on their surface waters concentrations and annual burial in bottom sediments. This approach is more suitable than the single comparison between benthic and pelagic nutrient concentrations due to the common bias from increased compaction in deeper sediments associated with granulometric variations along the benthic vertical profiles (Szmytkiewicz and Zalewska, 2014).

2.2. Study area

Guanabara Bay (Fig. 1) in Rio de Janeiro, Brazil, is a shallow tectonic embayment with an open water area ~384 km^2 and a maximum length along the north-south and east-west axes ~30 and 28 km, respectively (Fries et al., 2019). The water depth is less than 10 m over 84 % of the area (Figueiredo Jr et al., 2014) and reaches a maximum value ~40 m in the center, where an exorheic fluvial paleochannel (Marino et al., 2013) was drowned over the last eustatic sea-level rise (Abuchacra et al., 2017). The Köppen-Geiger climate classification shows that the bay region is tropical with wet summers and dry winters (Aw). At meteorological located at an island within the bay (Galeão Rio de Janeiro International Airport) over 25- and 12-year periods, monthly means of temperature varied from ~21.9 to ~27.4 °C and accumulated rainfall from ~190 to ~710 mm in winter and summer, respectively (available at https://www.icea.decea.mil.br/).

This bay is microtidal with predominantly semidiurnal regime, showing an average tidal range of ~0.7 m (Kjerfve and Lacerda, 2001). In turn, the mean water volume is estimated ~1.87 × 10^9 m^3 and the freshwater inflow from tributaries are ~33 and 186 m^3 s^{-1} in winter and summer, respectively. Although natural and anthropogenic changes may accumulate into its bottom sediments on timescales of decades and centuries (Monteiro et al., 2012) the water renewal rate is relatively short, in average ~50 % of the total volume over 11.4 days (Kjerfve

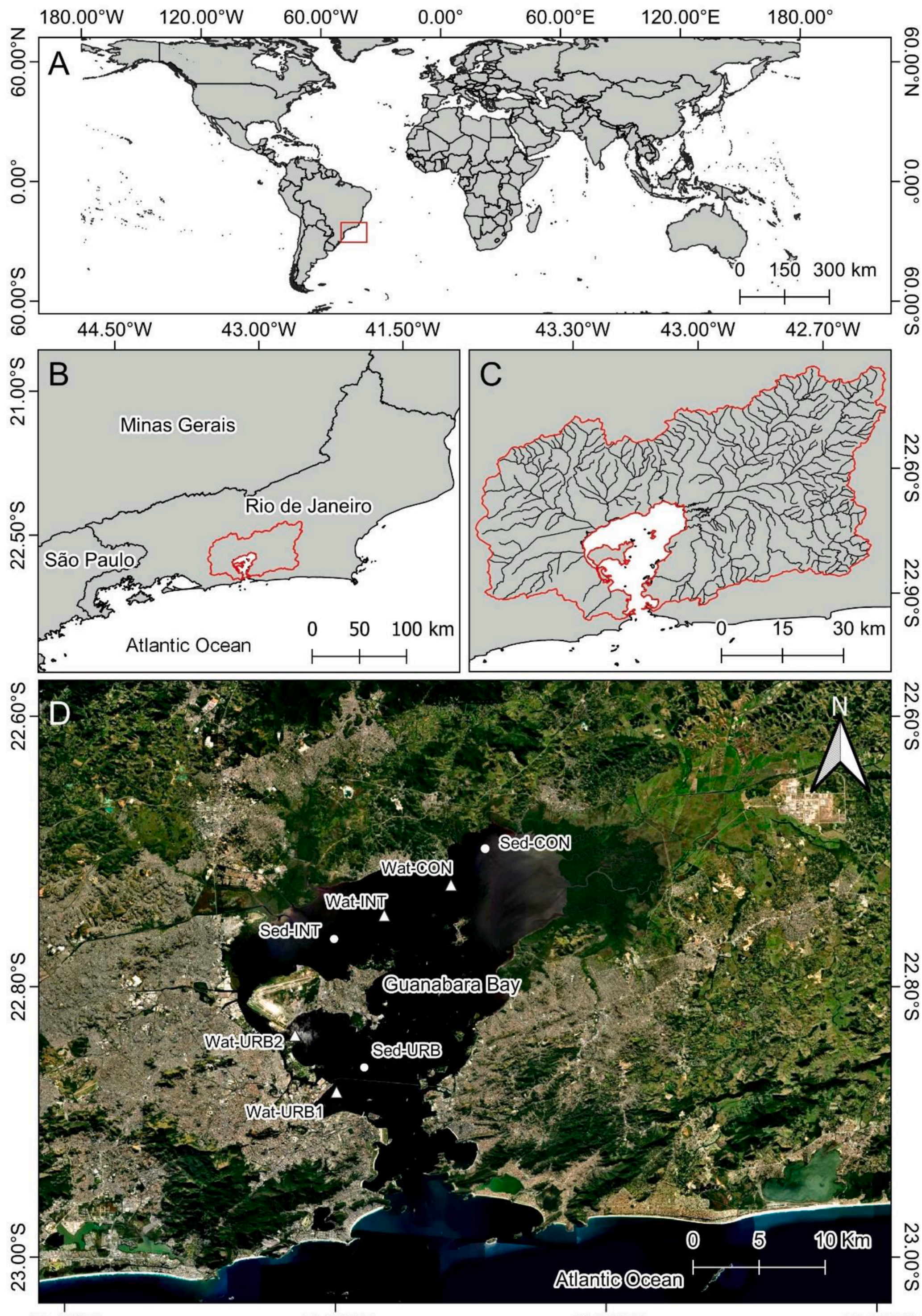

Fig. 1. Study area location (panel A) showing the Guanabara Bay (panels B, C and D). The red line shows its watershed (B) and black lines the drainage network (C). Water monitoring sites (triangles) and sediment cores (circles) are presented in panel D.

et al., 1997).

The Guanabara Bay catchment extends over more than 4070 km^2, encompassing most of the largest coastal urban region of Brazil (Rio de Janeiro metropolitan area; Fig. 1) and influenced by 55 rivers, which receive inputs from ~9 million inhabitants living in its watershed (Fries et al., 2019). Increased sediment and nutrient inputs from the catchment are attributed to deforestation and agricultural processes since the European colonization in the sixteenth century (Soares-Gomes et al., 2016), followed by untreated sewage discharges (Fig. 2), consequence of urban growth especially after the 1950s (Monteiro et al., 2012). Despite large investments in sanitation over the last century (Fistarol et al., 2015), Guanabara Bay still receives huge amounts of organic matter, N and P from untreated urban-industrial wastewaters, impacting its sediments (Fistarol et al., 2015; Kjerfve et al., 1997). Major anthropogenic changes at the western and southeastern portions, including the oldest urban settlements (Rio de Janeiro city since the 16th century), contrast with the most conserved Guapimirim Environmental Protection Area, where the largest remaining mangroves and less polluted tributaries of northeastern Guanabara Bay are situated (Fries et al., 2019).

2.3. Sample analysis

CON Sed-core samples were taken at 2 cm intervals from the 0 to 50 cm depths, and at 4 cm intervals for depths between 50 and 100 cm. Gamma-ray measurements were conducted by using a semiplanar intrinsic germanium high purity coaxial detector with 40 % efficiency, housed in a lead shield, coupled to a DSA-LX multichannel analyser (Canberra Industries). Lead-210 activity was determined by the direct measurement of 46.5 KeV gamma peak while ^{226}Ra activity was calculated averaging its daughters' peaks ^{210}Pb and ^{214}Bi (295.2 KeV) (351.9 KeV) (609.3 KeV) (Moore, 1984). Each sample was counted until the ^{210}Pb and ^{226}Ra counting errors were < 10 %. Radionuclide counts per minute were multiplied by a correction factor that integrates background gamma ray intensity and detector efficiency determined from standard (USGS Rocky Flats) calibrations. The excess ^{210}Pb activities was determined by subtracting the total ^{210}Pb concentration from the ^{226}Ra concentration (i.e., supported ^{210}Pb). Sediment Accumulation Rate (SAR) was estimated based on the Constant Rate of Supply (CRS) and used to calculate the Total Nitrogen (TN) and Total Phosphorus (TP) and Inorganic Phosphorus (IP) burial rates.

For TN, approximately 15 mg of dried and grounded sediment samples were placed in silver capsules, where we removed the calcium carbonate with HCl 1 N and then oven-dried it at 40 °C. We used a Flash Elemental Analyzer with analytical precision equal to 0.1 %. TP and IP analysis in dry and ground samples were based on Aspila et al. (1976). Only the TP samples were ignited in a muffle furnace at 550 °C (90 min). P analysis followed the extraction with HCl 1 M on an orbital shaker for 16 h, 10 min centrifugation (2000 rpm), and colorimetric reaction analysis at 880 nm in the supernatant liquid with ascorbic acid and potassium antimony and ammonium heptamolybdate (Hansen and Koroleff, 1999). The determination of TP and IP were performed in a Perkin Elmer UV/VIS spectrophotometer (Lambda 25 model). The burial rates were calculated by multiplying the SAR (cm yr^{-1}), Dry Bulk Density (g cm^{-2}), nitrogen (N), and phosphorus (P) content.

The TN, TP and ^{210}Pb chronology data from cores Sed-INT and Sed-URB were provided by Monteiro et al. (2012) and were used to calculate the TN and TP burial rates. The analysis of TP, IP and Dissolved Inorganic Nitrogen (DIN) in water from 1980 to 2017 were provided by the Rio de Janeiro State Environmental Agency following the SM 4500 A/B/E and SM 4500 A/B/F methods, respectively, as described in Baird and Bridgewater (2017). INEA does not monitor total nitrogen, so DIN data was composed by adding the ammoniacal nitrogen (N-NH_3), nitrite (NO_2), and nitrate (NO_3) concentrations.

To allow comparisons with 2 cm and 4 cm age-dated sediment layers that integrate several years, the monthly and highly variable data of nutrients in water were grouped into six periods over the past ~40 years (1980 to 1985, 1986 to 1991, 1992 to 1997, 1998 to 2003, 2004 to 2009, 2010 to 2017).

2.4. Statistical treatment

The data were log-transformed to achieve normal distribution (Berry, 1987), using D'Agostino (1986) to test the normality ($p > 0.05$) and Levene (1960) to test variance homogeneity ($p < 0.05$). Two-way ANOVA (level of significance, $p < 0.05$) was used to indicate an interaction between the first two-time periods at different Guanabara Bay sites. In the more recent period available only in Sed-CON, we used a *t*-test (at a = 0.95).

3. Results

The sampling sites show a clear increasing trend in TP, IP, and DIN concentrations in surface waters as well as in TP, IP and, TN burial rates along each sediment core, except the inorganic forms (DIN and IP) in Wat-URB-1 and Wat-URB-2 (Figs. 3–5). When we compared all periods (two-way ANOVA, $p < 0.05$; Figs. 6 and 7, and Table 2), there was a significant increase in water nutrient concentrations and burial sediment rates over time, which were both related to nutrient enrichment in the catchment. The 6-year average water temperature in each sampling site of Guanabara Bay varied by only < 1.6 °C from 1980 to 2017 (Supp. Fig. 1).

Water nutrient concentrations significantly increased from 1980 to 2005 and 2006 to 2017 in sampling sites surrounded by lower (Wat-CON) and intermediate (Wat-INT) urban uses, increasing on average between ~44 % and 16 % for TP and ~187 % and 220 % for DIN (two-way ANOVA, $p < 0.05$; Table 2; Fig. 6), respectively. The most eutrophic water sampling site was Wat-URB-2, which did not present significant differences for these concentrations from 1980 to 2005 and 2006 to 2017, presenting the highest values by periods (two-way ANOVA, $p > 0.05$; Table 2; Fig. 6).

Regarding nutrient burial rates, the least altered Sed-CON core showed no significant changes in the vertical distribution of TP and TN

Table 1
Geographical coordinates, water depth, and sampling periods for water monitoring sites – Wat-CON, Wat-INT, Wat-URB1 and Wat-URB2 – and sediment cores – Sed-CON, Sed-INT, and Sed-URB. We assigned specific code names to each sampling site: CON for conserved, INT for intermediate, and URB for urbanized. All pelagic data were sourced by the Rio de Janeiro State Environmental Agency (INEA). Benthic data from cores Sed-INT and Sed-URB were provided by Monteiro et al. (2012).

Sample source	Original code names in previous datasets	Assigned code names for sampling sites	Coordinates		Water depth (m)	Sampling periods
			Latitude	Longitude		
Pelagic (monthly water monitoring)	GN0000	Wat-CON	–22.72465°	–43.11465°	0.5	1980–2017
	GN0022	Wat-URB1	–22.87777°	–43.19916°	0.5	1980–2017
	GN0042	Wat-INT	–22.74723°	–43.16389°	0.5	1980–2017
	GN0043	Wat-URB2	–22.83583°	–43.22984°	0.5	1980–2017
Benthic (sediment core)	BG08	Sed-URB	–22.85964°	–43.17868°	8.0	2005
	BG28	Sed-INT	–22.76466°	–43.20098°	4.3	2005
	APA 1	Sed-CON	–22.69789°	–43.08940°	2.0	2017

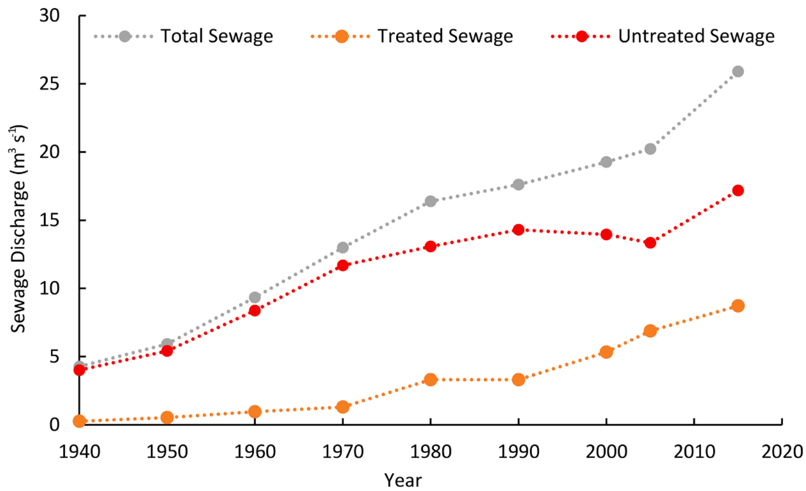

Fig. 2. Comparison between the total, treated and untreated sewage discharge in Guanabara Bay (1940-2007) from Coelho (2007) and SNIS (2015). Modified from Fries et al. (2019).

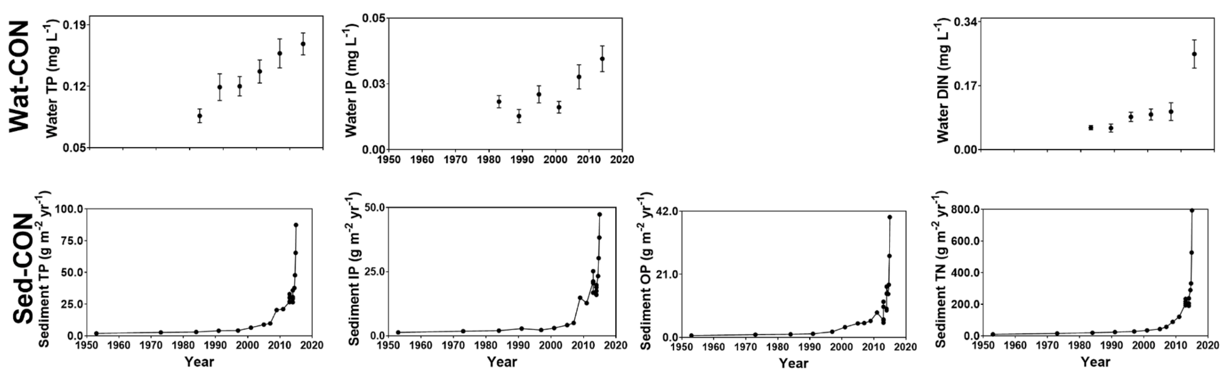

Fig. 3. Changes in nutrient sediment burial rates and water concentrations in sampling sites of the Guanabara Bay surrounded by the most conserved site: Total phosphorus (TP) and total nitrogen (TN) burial rates in Sed-CON sediment core, as well water TP, dissolved inorganic phosphorus (DIP), organic phosphorus (OP), and dissolved inorganic nitrogen (DIN) concentrations in Wat-CON. In sediment burial profiles, each filled circle represents measurements from 2-cm layers. In water concentration graphs, each filled circle represents the 6-year average and vertical bars indicate the standard error. See methods for details on study design and variables.

in burial rates in the first periods (1950–1979 and 1980–2005). However, from 2006 to 2017, mean values were higher, with values increasing ~12 % for TP and 31 % for TN (two-way ANOVA, $p < 0.05$; Fig. 7). Moreover, the intermediate eutrophic core (Sed-INT), compared to the most conserved site (Sed-CON), showed on average higher rates of ~53 % for TP and ~73 % for TN from 1950 to 1979 and ~183 % for TP and ~134 % higher rates for TN from 1980 to 2005.

In turn, the core located in the most eutrophic site (Sed-URB) shows significantly higher nutrient burial rates compared to the site influenced by intermediate urban growth (Sed-INT), with average values ~166 % higher for TP and ~127 % for TN from 1950 to 1979 and ~132 % higher for TP and ~71 % for TN from 1980 to 2005. In relation to the least altered core (Sed-CON), the most eutrophic site (Sed-URB) presented ~4-fold higher burial rates for TP and TN from 1950 to 1979 and more than ~6-fold higher values for TP and 4-fold for TN from 1980 to 2005 (two-way ANOVA, $p < 0.05$; Fig. 7).

Finally, the intermediate core (Sed-INT) showed significant changes of TP and TN burial rates between 1950–1979 and 1980–2005, which are similar to the observed significant increases in the water sampling site Wat-INT since 1980, suggesting an increased environmental degradation close to Sed-INT. The same pattern was observed at the least altered site (Sed-CON and Wat-CON; Figs. 3, 6, and 7).

4. Discussion

Overall, increases in N and P water concentrations and sediment burial in Guanabara Bay were associated with urban growth in its watershed over the past decades. The severe loss in the water quality of the urban bay here has been predicted during the past century, as a response of the insufficient sewage treatment (Fries et al., 2019; Contador and Paranhos, 1996; Paranhos et al., 1995; Amador, 1980). This confirms previous findings of nutrient-enriched waters (Fries et al., 2019) and bottom sediments in Guanabara Bay (Figueiredo Jr et al., 2014; Godoy et al., 2012; Monteiro et al., 2012) and fringing mangroves (Pérez et al., 2018; Passos et al., 2022), supporting the positive relationship between land use changes, untreated urban sewage discharges and coastal eutrophication (Ross and Randhir, 2022; Aguiar et al., 2011; Howarth et al., 2002) that have been increasingly reported worldwide (Hallegraeff et al., 2021; Breitburg et al., 2018; Diaz and Rosenberg, 2008). Nevertheless, our findings highlight significant inter-decadal and intra-ecosystem variability in nutrient enrichment, revealing novel connections between surface waters and bottom sediments in urban bays. The heightened pelagic sensitivity to eutrophication over short periods may have contributed to the observed greater variability (i.e., increased resilience in reducing nutrient stocks) compared to the sediment layer, which showed less pronounced changes over the past decades. Previous studies have documented substantial nutrient exchange

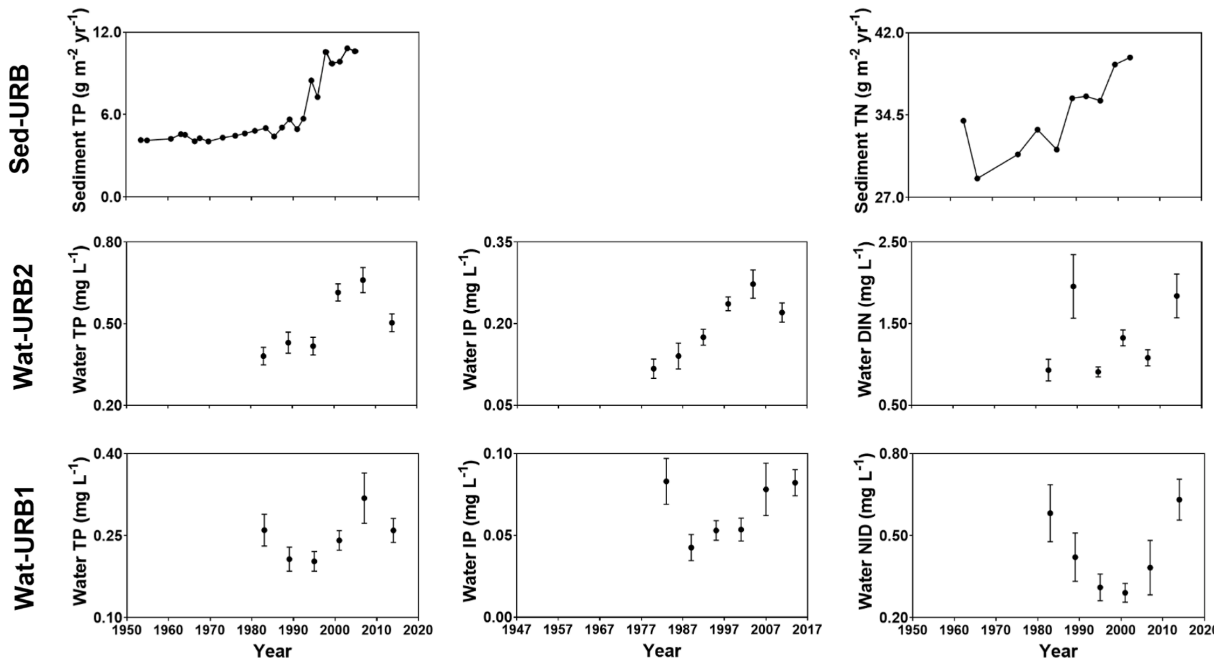

Fig. 4. Changes in nutrient sediment burial rates and water concentrations in sampling sites of the Guanabara Bay surrounded by the most urban area: TP and TN burial rates in Sed-URB sediment core, as well water TP, DIP, OP, and DIN concentrations in Wat-URB1 and Wat-URB2. Symbols, bars, and abbreviations as described in Fig. 3. See methods for details on study design and variables.

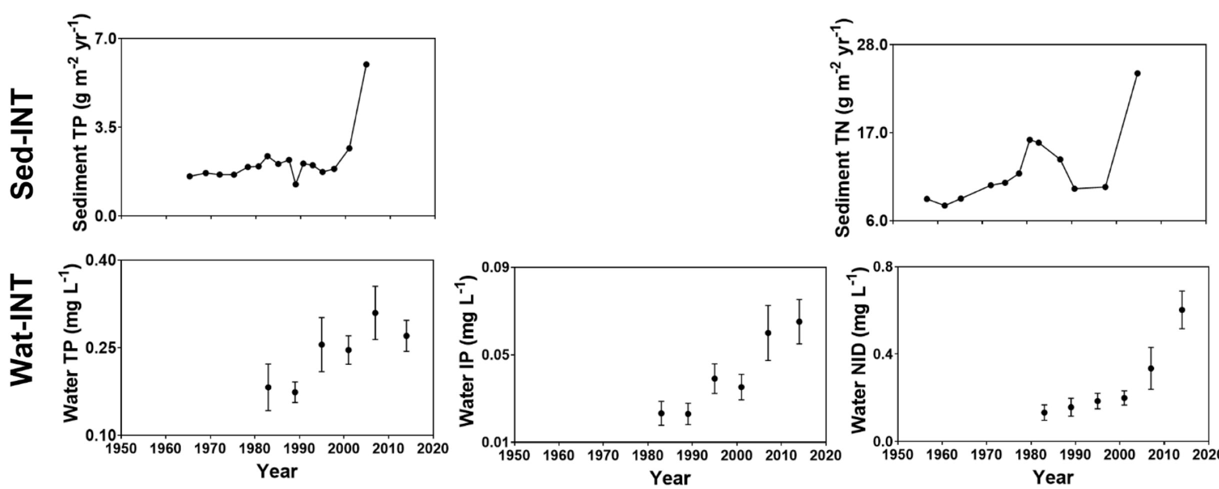

Fig. 5. Changes in nutrient sediment burial rates and water concentrations in sampling sites of the Guanabara Bay surrounded by an intermediate urban growth: TP and TN burial rates in Sed-INT sediment core, as well water TP, DIP, OP, and DIN concentrations in Wat-INT. Symbols, bars, and abbreviations as described in Fig. 3. See methods for details on study design and variables.

between coastal pelagic and benthic compartments, suggesting that internal loading from the most to least eutrophic conditions can serve as a long-term nutrient source for overlying waters, persisting even after the reduction of anthropogenic inputs (Yan et al., 2021; Testa et al., 2022).

In our 1980–2005 dataset containing all of the variables, N and P concentrations in waters and burial rates in bottom sediments were lowest at the least impacted northeastern portion (Wat-CON and Sed-CON), intermediate at that surrounded by mid-sized urban region (Wat-INT and Sed-INT), and highest at that region with the oldest and densest population growth (Wat-URB2 and Sed-URB1). Despite this expected trend from lower to higher urban sprawl in the Guanabara Bay watershed (Barroso et al., 2022; Fries et al., 2019; Fistarol et al., 2015), the water sampling site Wat-URB1 also located in the most urban area showed reduced nutrient concentrations compared to Wat-URB2 (Fig. 4). Previous evidence has indicated more severe eutrophication as a result of anthropogenic nutrient inputs with decreasing natural seawater renewal in coastal aquatic ecosystems as being a global trend (Andersen et al., 2017; Sharp et al., 2009). Accordingly, lower N and P increases in Wat-URB1 than Wat-URB2 could be attributed to the higher seawater exchange (Sampaio, 2003; Paranhos et al., 1998; Mayr et al., 1989) and subsequent capacity of nutrient exportation (Fries et al., 2019) due to its proximity to the Bays connection to the Atlantic Ocean. These changes in average N and P water concentrations and sediment burial were not related to average water temperature over the past decades, likely due to the low inter-annual variability of tropical warm conditions reported here (Supp. Fig. 1).

Regarding the human interventions to mitigate eutrophication, specific sanitation facilities in the most urban area (e.g., Penha, ETIG, and Alegria; Coelho, 2007) might account for the non-significant changes in water N and P concentrations between the periods

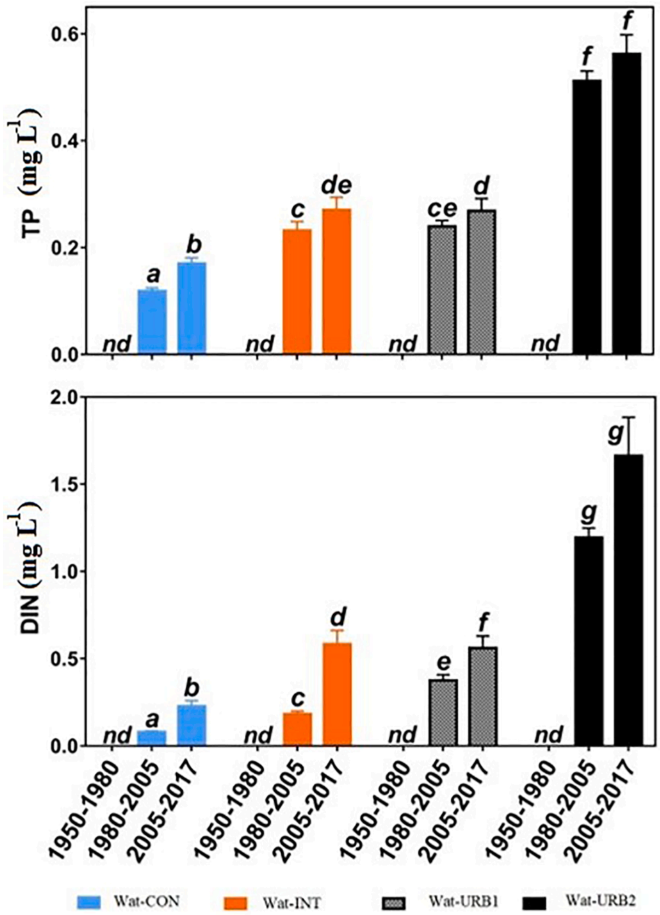

Fig. 6. Water TP and DIN in Wat-CON, Wat-INT, Wat-URB1, and Wat-URB2. The bars and error bars represent the average and standard error, respectively. Equal letters represent no statistical difference (two-way ANOVA, *post-hoc* Tukey test, $p < 0.05$). The symbol *nd* indicate no data available.

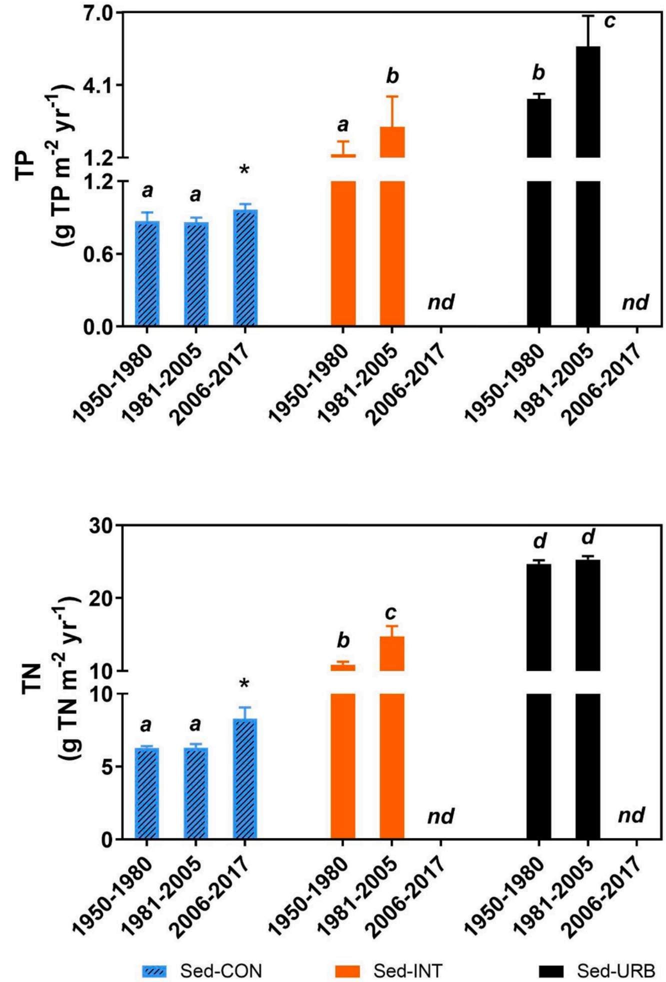

Fig. 7. TP and TN burial rates in Sed-CON, Sed-INT, and Sed-URB sediment cores. The filled bars and error bars represent the average and standard error, respectively. Equal letters represent no statistical difference (two-way ANOVA, *post-hoc* Tukey test, $p < 0.05$). Asterisks indicate differences using paired *t*-test ($p < 0.05$) from the last periods in Sed-CON, and *nd* symbol indicate no data available.

1980–2005 and 2006–2017 (Wat-URB-2) and N burial (Sed-URB) between 1950–1979 and 1980–2005 in the most impacted site. Indeed, the mitigation of eutrophication in waters (Andersen et al., 2017; Conley et al., 2009) and bottom sediments of aquatic ecosystems (Jin et al., 2020; Tu et al., 2019) have been increasingly associated with reduced anthropogenic nutrient inputs worldwide. Within the studied drainage basin, even in the most urban area where sanitation facilities could have prevented more severe, long-term eutrophication in water and bottom sediments, there were no investments in sanitation between 1979 and 1994 (Fries et al., 2019). Despite subsequent improvements in sewage treatment, they proved insufficient to offset the effect of increased urban growth (Fig. 2), showing much higher nutrient enrichment than other regions and significant increases in P burial between 1950–1979 and 1980–2005 (Figs. 3 and 4).

The growing population and industrial activity have resulted in large sewage discharges from municipalities in the Guanabara Bay watershed (Fries et al., 2019), of which only around one-third had been treated in 2015 (Fig. 2). Low-income populations have been particularly affected by water-borne diseases (Skalar et al., 2023; Coelho, 2007). This indicates that sewage inputs to the Guanabara Bay watershed have consistently increased alongside population growth since 1940 but have consistently been outpaced by the limited advances in treatment facilities, particularly between the 1970s and the early 2000s (Fig. 2).

As a result, significant water and sediment N and P increases were observed in the conserved region (Wat-CON and Sed-CON) and those influenced by intermediate urban growth (Wat-INT and Sed-INT) with less or no sanitation facilities, indicating a more severe ongoing

Table 2
Two-way ANOVA results of the effects in TP and TN in sediments cores and TP and DIN in surface waters sites for different time periods. Sum of squares (SS) ANOVA, Degrees of Freedom (DF) ANOVA, Total Variation (TV), Mean Square (MS), F test and Probability.

ANOVA	SS	DF	TV (%)	MS	F	*p* Value
TP sediment						
Periods	14.64	1	6.845	14.64	27.18	< 0.0001
Site	139.5	3	65.25	46.52	86.36	< 0.0001
Site * periods	10.28	3	4.807	3.427	6.362	0.0006
TN sediment						
Periods	52.18	1	1.905	52.18	12.92	0.0007
Site	2067	3	75.49	689.1	170.6	< 0.0001
Site * periods	37.84	3	1.382	12.61	3.123	0.0327
TP water						
Periods	0.454	3	1.317	0.151	2.892	0.0346
Site	1.02	1	33.400	1.02	19.51	< 0.0001
Site * periods	25.87	3	0.5858	8.622	164.9	< 0.0001
DIN water						
Periods	2.854	3	4.319	0.951	6.078	0.0004
Site	9.226	1	29.520	9.226	58.95	< 0.0001
Site * periods	63.06	3	1.336	21.02	134.3	< 0.0001

eutrophication in less impacted regions of the bay (Figs. 6 and 7). Another contributing to increased eutrophication in both pelagic concentrations and benthic burial at the areas with the least (Fig. 3) and intermediate (Fig. 5) impacts, were found in lower background levels as compared to the most impacted region, where urbanization and subsequent eutrophication took place earlier. This lower background increased the potential for enhanced changes with less intense nutrient inputs than along the less impacted areas. Accordingly, our results support earlier findings integrating limnological and paleolimnological evidence, which confirm the role of bottom sediments in providing baselines for environmental studies in aquatic ecosystems, critical data when direct measurements are not available (Hobæk et al., 2012; Battarbee et al., 2005). The recent N and P enrichment in surface waters and bottom sediments in the least altered areas here supports a broader view beyond the Guanabara Bay, in which a relatively later, rapid, and severe eutrophication may affect vulnerable inner coastal regions, where seawater renewal to dilute anthropogenic nutrient inputs is typically lower. Indeed, previous evidence on stronger metabolic responses with increased temperatures in waters (Lürling et al., 2017) and the bottom sediment (Spivak et al., 2019; Marotta et al., 2014; Feuchtmayr et al., 2009) also indicate that warmer conditions could make this tropical aquatic ecosystem even more sensitive to eutrophication.

Furthermore, our approach combining data from both pelagic and benthic settings within the same site indicates that even using interannual averages, waters are more sensitive to eutrophication than the bottom sediment, as nutrient decreases in pelagic environment were associated with stabilization in the benthic system (Figs. 3–5). In contrast, the sedimentary time scale was notably longer than the pelagic, complementing those periods without direct water measurements. Indeed, nutrient concentrations in water and sediments strongly depends on anthropogenic activity, but also on tributary flow and seawater renewal, resulting in great variation in distribution and transport of nutrients across bays (Fries et al., 2019). Another potential long-term source of nutrients in aquatic ecosystems, which could return to waters, is eutrophic bottom sediments returning slowly in response to the time after mitigating anthropogenic inputs (Paudel et al., 2017).

In addition to the time-scale differences (i.e., shorter in water monitoring programs and longer in sediment cores; Battarbee et al., 2005), our findings indicate that the benthic compartment is less variable, requiring more consistent mitigation measures to show effective declines in eutrophication. As found here in the most urban area, the most recent stabilization of nutrient burial is associated with decreases in 6-year average water concentrations which could be considered and used as a proxy of initial responses to partial untreated sewage treatment. These results were only identified by the integrated analysis between surface waters and bottom sediments. This represents novel mechanistic insights into how urban bays significantly respond to historically unprecedented nutrient loadings.

The challenge of mitigating nutrient pollution in bays requires a comprehensive approach, addressing a wide variety of anthropogenic sources in the watershed. This requires the integration of public and private stakeholders (Zhang et al., 2023; Chang et al., 2021; Hood et al., 2021). The substantial reduction in long-term eutrophication is increasingly critical for local, regional, and global decision-making. This includes measures associated with sustainable agriculture, urban water quality management, and the expansion or modernization of sewage treatment facilities (Sabo et al., 2022). In addition to the regulatory framework on limits for N and P inputs (Ritter, 2019), scientific research, monitoring, and increased social support through environmental education and outreach programs (O'Neil et al., 2020) are essential. Our results indicate that a comprehensive analysis of pelagic and benthic compartments should be employed to better understand the integrated dynamics of nutrient enrichment over both short- and long-term periods. Furthermore, this emphasizes the urgency of sewage treatment facilities for water quality restoration in Guanabara Bay. Such facilities should be considered an integral part of long-term governmental policies to address urban growth (Amora-Nogueira et al., 2023; Kudo and Kanda, 2020).

The novel findings presented here highlight the relatively unexplored integration between variable nutrient pelagic concentrations and burial rates. This is essential for unravelling the mechanisms governing aquatic ecosystems, underscoring the necessity of a comprehensive analysis to evaluate coastal eutrophication using data sets not only for waters, but also for bottom sediments worldwide.

5. Conclusion

This study confirms the increased nutrient enrichment in pelagic and benthic environments associated with urban growth over past decades along the watershed. The trend found in Guanabara Bay has also been reported in coastal areas worldwide, likely owing to natural factors (e.g., increased water renewal time towards inner parts) and anthropogenic influences (e.g., contrasting land uses in the catchment). Furthermore, our results also reveal that the integrated analysis between bottom sediments and waters is needed to improve our understanding of long-term coastal eutrophication. As a preferential fate for nutrient inputs from natural and anthropogenic sources in extensive watershed areas, sedimentary burial rates in bays shows fewer variable changes over longer periods than overlying water concentrations, which are in turn more dynamic over short time scales. Thus, the benthic environment may provide baseline data for past periods without monitoring programs, while direct measurements of pelagic concentrations are more accurate and sensitive to identify short-term changes. These findings highlight that while water concentrations and sediment burial rates may be comparable for general trends, they exhibit different patterns over short- and long-term periods, indicating the combined analysis of these factors are a better tool for assessing long-term coastal pollution. Therefore, an integrated framework between pelagic and benthic environments is needed to jointly assess short- and long-term nutrient dynamics in urban bays, which is urgent to support coastal management and restoration initiatives in regions facing increased anthropogenic eutrophication.

CRediT authorship contribution statement

Jaqueline Sá Earp Muniz: Conceptualization, Data curation, Writing – original draft, Validation, Visualization, Writing – review & editing. **Rodrigo Coutinho Abuchacra:** Conceptualization, Data curation, Writing – original draft, Validation, Visualization, Writing – review & editing, Investigation, Supervision, Funding acquisition, Methodology, Formal analysis. **Fernando Cunha Peixoto:** Writing – review & editing. **Paula Ferreira Falheiro Abuchacra:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft. **Christian J. Sanders:** Investigation, Supervision, Funding acquisition, Methodology, Formal analysis. **Carla Maciel Salgado:** Writing – review & editing. **José Antônio Baptista Neto:** Investigation, Supervision, Funding acquisition. **Leonardo Amora-Nogueira:** Data curation, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Renato Campello Cordeiro:** Writing – review & editing. **Luciane Silva Moreira:** Writing – review & editing. **Luana Pinho:** Writing – review & editing. **Jean Louis Valentin:** Investigation, Supervision, Funding acquisition, Writing – review & editing. **Allana Faustino:** Methodology. **Ana Fonseca-Oliveira:** Writing – review & editing. **Douglas Motta Pio:** Writing – review & editing. **Manuela Lima Carvalho:** Writing – review & editing. **Samira Cristina de Souza Pinto:** Methodology. **Wilson Machado:** Writing – review & editing. **Luiz Eduardo de Oliveira Gomes:** Writing – review & editing. **Humberto Marotta:** Conceptualization, Data curation, Writing – original draft, Validation, Visualization, Writing – review & editing, Investigation, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This study was funded by grants from the Research Support Foundation of the State of Rio de Janeiro (FAPERJ, 260100016392016 and 2033042017) and the Council for Research and Scientific Development of Brazil (CNPq, 31015220178 and 314995/2020-0) to HM (Principal Investigator). HM was awarded by CNPq Research Productivity and FAPERJ Young Scientist of Rio de Janeiro State fellowships. LAN is supported by FAPERJ scholarships for PhD and Postdoctoral studies (FAPERJ, 205.699/2022). CJS and carbon burial analyses were supported by the Australian Research Council (LE140100083). The authors are grateful for the logistical and financial support from the Long-Term Ecological Program of Guanabara Bay (PELD - CNPq 403809/2012-6, 441373/2016-0, and FAPERJ - 26/110.144/2013, 26/111.584/2014), as well as the Bays of Brazil Project (CNPq 441215/2017-3), coordinated by JLV. WM expresses gratitude to the CAPES-Print-Feedbacks Project (88887.310301/2018-00).The authors extend their gratitude for the support from the Multi-user Facility for Gas, Water, and Sediment Geochemistry at the Fluminense Federal University (GAS-UFF) and the logistical support from Carlos Oliveira. The authors would also like to thank Centro Integrado de Tradução e Escrita (CITE/UFF) for assistance with English language translation and developmental editing.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envadv.2023.100476.

References

Abuchacra, P.F.F., Aguiar, V.M.C., Abuchacra, R.C., Baptista Neto, J.A., Oliveira, A.S., 2015. Assessment of bioavailability and potential toxicity of Cu, Zn and Pb, a case study in Jurujuba Sound, Rio de Janeiro, Brazil. Mar. Pollut. Bull. 100 https://doi.org/10.1016/j.marpolbul.2015.08.012.

Abuchacra, R.C., Macario, K.C.D., Oliveira, M.I.N.de, Abuchacra, P.F.F., Fernandez, G.B., Vasconcelos, S.C.de, Oliveira, V.C.de, Ressiguier, Y.N., Figueiredo Jr, A.G., 2017. Northeast Guanabara Bay and coastal plain holocene sedimentary evolution (Brazil): a contribution. J. Sediment. Environ. 2 https://doi.org/10.12957/jse.2017.27951.

Aguiar, V.M.C., Baptista Neto, J.A., Rangel, C.M., 2011. Eutrophication and hypoxia in four streams discharging in Guanabara Bay, RJ, Brazil, a case study. Mar. Pollut. Bull. 62, 1915–1919.

Amador, E.S., 1980. Assoreamento da Baía de Guanabara. Taxas de Sedimentação. An. Acad. Bras. Cienc. 52, 723–742.

Amador, E.D.S., 1997. Baía de Guanabara e ecosistemas periféricos: homem e natureza 539.

Amora-Nogueira, L., Smoak, J.M., Abuchacra, R.C., Carvalho, C., Ribeiro, F.C.A., Martins, K.C., Fonseca-Oliveira, A.L., Carvalho, M., Machado, L.P., Souza, A.F.F., Silva, A.L.C., Enrich-Prast, A., Oliveira, V.P., Sanders, C.J., Sanders, L.M., Marotta, H., 2023. Linking centennial scale anthropogenic changes and sedimentary records as lessons for urban coastal management. Sci. Total Environ. 902 https://doi.org/10.1016/j.scitotenv.2023.165620. V.

Andersen, J.H., Carstensen, J., Conley, D.J., Dromph, K., Fleming-Lehtinen, V., Gustafsson, B.G., Josefson, A.B., Norkko, A., Villnäs, A., Murray, C., 2017. Long-term temporal and spatial trends in eutrophication status of the Baltic Sea. Biol. Rev. 92, 135–149. https://doi.org/10.1111/brv.12221.

Aspila, K.I., Agemian, H., Chau, A.S.Y., 1976. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. Analyst 101, 187–197. https://doi.org/10.1039/an9760100187.

Baird, R., Bridgewater, L., 2017. Standard Methods for the Examination of Water and Wastewater, 23rd ed. American Public Health Association, Washington DC.

Bakun, A., Field, D.B., Redondo-Rodriguez, A., Weeks, S.J., 2010. Greenhouse gas, upwelling-favorable winds, and the future of coastal ocean upwelling ecosystems. Glob. Chang. Biol. 1213–1228.

Baptista Filho, L.S., Neto, J.A.B., Martins, M.V.A., Geraldes, M.C., 2019. Sources of pollutants in the Northern/Northeast area of Guanabara Bay (SE, Brazil) since the late nineteenth century using lead isotopes and metal concentrations. J. Sediment. Environ. 4 (3), 332–349.

Barroso, G.C., Abril, G., Machado, W., Abuchacra, R.C., Peixoto, R.B., Bernardes, M., Marques, G.S., Sanders, C.J., Oliveira, G.B., Oliveira Filho, S.R., Amora-Nogueira, L., Marotta, H., 2022. Linking eutrophication to carbon dioxide and methane emissions from exposed mangrove soils along an urban gradient. Sci. Total Environ. 850 https://doi.org/10.1016/j.scitotenv.2022.157988. V.

Battarbee, R.W., John Anderson, N., Jeppesen, E., Leavitt, P.R., 2005. Combining palaeolimnological and limnological approaches in assessing lake ecosystem response to nutrient reduction. Freshw. Biol. 50, 1772–1780. https://doi.org/10.1111/j.1365-2427.2005.01427.x.

Bauer, J.E., Cai, W.-J., Raymond, P.A., Bianchi, T.S., Hopkinson, C.S., Regnier, P.A.G., 2013. The changing carbon cycle of the coastal ocean. Nature 61–70.

Berry, D.A., 1987. Logarithmic Transformations in ANOVA. Biometrics 43, 439. https://doi.org/10.2307/2531826.

Breitburg, D., Levin, L.A., Oschlies, A., Grégoire, M., Chavez, F.P., Conley, D.J., Garçon, V., Gilbert, D., Gutiérrez, D., Isensee, K., Jacinto, G.S., Limburg, K.E., Montes, I., Naqvi, S.W.A., Pitcher, G.C., Rabalais, N.N., Roman, M.R., Rose, K.A., Seibel, B.A., Telszewski, M., Yasuhara, M., Zhang, J., 2018. Declining oxygen in the global ocean and coastal waters. Science (1979), 359.

Cai, W.-J., Xinping, H., Huang, W.-J., Murrell, M.C., Lehrter, J.C., Lohrenz, S.E., Chou, W.-C., Zhai, W., Hollibaugh, J.T., Wang, Y., Zhao, P., Guo, X., Kjell, G., Minhan, D., Gwo-Ching, C., 2011. Acidification of subsurface coastal waters enhanced by eutrophication. Nat. Geosci. 4.

Chang, S.Y., Zhang, Q., Byrnes, D.K., Basu, N.B., Van Meter, K.J., 2021. Chesapeake legacies: The importance of legacy nitrogen to improving Chesapeake Bay water quality. Environ. Res. Lett. 16 (8), 085002.

Coelho, V., 2007. Baía de Guanabara: Uma História de Agressão Ambiental. Rio de Janeiro, Brazil.

Conley, D.J., Paerl, H.W., Howarth, R.W., Boesch, D.F., Seitzinger, S.P., Havens, K.E., Lancelot, C., Likens, G.E., 2009. Ecology - Controlling eutrophication: Nitrogen and phosphorus. Science 323 (1979), 1014–1015. https://doi.org/10.1126/science.1167755.

Contador, L.S., Paranhos, R., 1996. Water quality trends in Urca inlet (Guanabara Bay, Brazil) between 1986 and 1992. Arq. Biol. Technol. 39, 753–764.

Cordeiro, R.C., Santos, D.D., Santelli, R.E., Figueiredo, A.G., Moreira, L.S., Machado, W. T.V., Meniconi, M.F.G., 2021a. Bulk, isotopic, petrographic organic matter and mineral distribution as proxies of environmental process in Guanabara Bay, SE, Brazil. Geo-Marine Lett. 41, 1–18.

Cordeiro, R.C., Monteiro, F.F., Santelli, R.E., Moreira, L.S., Figueiredo, A.G., Bidone, E. D., Pereira, R.S., Anjos, L.C., Meniconi, M.F.G., 2021.. Environmental and anthropic variabilities at Guanabara Bay (Brazil): A comparative perspective of metal depositions in different time scales during the last 5,500 yrs. Chemosphere 267, 128895 v.

Cotovicz Jr, L.C., Knoppers, B.A., Brandini, N., Poirier, D., Santos, S.J.C., Abril, G., 2016. Spatio-temporal variability of methane (CH4) concentrations and diffusive fluxes from a tropical coastal embayment surrounded by a large urban area (Guanabara Bay, Rio de Janeiro, Brazil). Limnol. Oceanogr. 61, S238–S252.

Cotovicz Jr, L.C., Knoppers, B.A., Brandini1, N., Costa Santos, S.J., Abril, G., 2015. A strong CO 2 sink enhanced by eutrophication in a tropical coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil). Biogeosciences 12, 6125–6146.

D'Agostino, R.B., 1986. Goodness-of-Fit-Techniques. CRC press 68.

Diaz, R.J., Rosenberg, R., 2008. Spreading dead zones and consequences for marine ecosystems. Science 321 (1979), 926–929. https://doi.org/10.1126/science.1156401.

Duarte, C.M., Agustí, S., 1998. The CO_2 balance of unproductive aquatic ecosystems. Science 281 (1979), 234–236. https://doi.org/10.1126/science.281.5374.234.

Duarte, C.M., Krause-Jensen, D., 2018. Intervention options to accelerate ecosystem recovery from coastal eutrophication. Front. Mar. Sci. 5 (470) https://doi.org/10.3389/fmars.2018.00470.

Feuchtmayr, H., Moran, R., Hatton, K., Connor, L., Heyes, T., Moss, B., Harvey, I., Atkinson, D., 2009. Global warming and eutrophication: effects on water chemistry and autotrophic communities in experimental hypertrophic shallow lake mesocosms. J. Appl. Ecol. 46, 713–723. https://doi.org/10.1111/j.1365-2664.2009.01644.x.

Figueiredo Jr., A.G., Toledo, M.B., Cordeiro, R.C., Godoy, J.M.O., Silva, F.T, Vasconcelos, S.C., Santos, R.A., 2014. Linked variations in sediment accumulation rates and sea-level in Guanabara Bay, Brazil, over the last 6000 years. Palaeogeogr. Palaeoclimatol. Palaeoecol. 415, 83–90.

Fisher, T.R., Peele, E.R., Ammerman, J.W., Harding, L.W., 1992. Nutrient limitation of phytoplankton in Chesapeake Bay. Mar. Ecol. Prog. Ser. 82, 51–63. https://doi.org/10.3354/meps082051.

Jr., S.E.M. de P. Fistarol, G.O., Coutinho, F.H., Moreira, A.P.B., Venas, T., Cánovas, A., Coutinho, R., Moura, R.L.de, Valentin, J.L., Tenenbaum, D.R., Paranhos, R., Valle, R. deA.B.do, Vicente, A.C.P., Filho, G.M.A., Pereira, R.C., Kruger, R., Rezende, C.E., Thompson, C.C., Salomon, P.S., Thompson, F.L., 2015. Environmental and sanitary conditions of Guanabara Bay, Rio de Janeiro Front. Microbiol. 6, 1232.

Fries, A.S., Coimbra, J.P., Nemazie, D.A., Summers, R.M., Azevedo, J.P.S., Filoso, S., Newton, M., Gelli, G., de Oliveira, R.C.N., Pessoa, M.A.R., Dennison, W.C., 2019. Guanabara Bay ecosystem health report card: Science, management, and governance implications. Reg. Stud. Mar. Sci. 25 https://doi.org/10.1016/j.rsma.2018.100474.

Hallegraeff, G., Enevoldsen, H., Zingone, A., 2021. Global harmful algal bloom status reporting. Harmf. Algae 102, 101992.

Godoy, J.M., Oliveira, A.V., Almeida, A.C., Godoy, M.L.D.P., Moreira, I., Wagener, A.R., De Figueiredo Junior, A.G., 2012. Guanabara bay sedimentation rates based on ^{210}Pb dating: Reviewing the existing data and adding new data. J. Braz. Chem. Soc. 23, 1265–1273. https://doi.org/10.1590/S0103-50532012000700010.

Hansen, H.P., Koroleff, F., 1999. Determination of nutrients. Methods of Seawater Analysis. Wiley-VCH Verlag GmbH, Weinheim; New York; Chiester; Brisbane; Singapore; Toronto 159–228. 10.1002/9783527613984.ch10.

Havens, K.E., Hauxwell, J., Tyler, A.C., Thomas, S., McGlathery, K.J., Cebrian, J., Hwang, S.J., 2001. Complex interactions between autotrophs in shallow marine and freshwater ecosystems: implications for community responses to nutrient stress. Environ. Pollut. 113, 95–107.

Heim, S., Schwarzbauer, J., 2013. Pollution history revealed by sedimentary records: A review. Environ. Chem. Lett. 11, 255–270. https://doi.org/10.1007/s10311-013-0409-3.

Hobæk, A., Løvik, J.E., Rohrlack, T., Moe, S.J., Grung, M., Bennion, H., Clarke, G., Piliposyan, G.T., 2012. Eutrophication, recovery and temperature in Lake Mjøsa: Detecting trends with monitoring data and sediment records. Freshw Biol 57. https://doi.org/10.1111/j.1365-2427.2012.02832.x, 1998–2014.

Hood, R.R., Shenk, G.W., Dixon, R.L., Smith, S.M., Ball, W.P., Bash, J.O., Zhang, Y.J., 2021. The Chesapeake Bay program modeling system: Overview and recommendations for future development. Ecol. Modell. 456, 109635.

Howarth, R.W., Anderson, D.B., Cloern, J.E., Elfring, C., Hopkinson, C.S., Lapointe, B., Walker, D., 2000. Issues in ecology: Nutrient pollution of coastal rivers, bays, and seas. Issue. Ecol. 1–16.

Howarth, R.W., Chan, F., Swaney, D.P., Marino, R.M., Hayn, M., 2021. Role of external inputs of nutrients to aquatic ecosystems in determining prevalence of nitrogen vs. phosphorus limitation of net primary productivity. Biogeochemistry 154, 293–306. https://doi.org/10.1007/s10533-021-00765-z.

Howarth, R.W., Sharpley, A., Walker, D., 2002. Sources of nutrient pollution to coastal waters in the United States: Implications for achieving coastal water quality goals. Estuaries 25, 656–676.

Ivarsson, L.N., Andrén, T., Moros, M., Andersen, T.J., Lönn, M., Andrén, E., 2019. Baltic sea coastal eutrophication in a thousand year perspective. Front. Environ. Sci. 7 https://doi.org/10.3389/fenvs.2019.00088.

Jin, G., Onodera, S.ichi, Saito, M., Shimizu, Y., 2020. Sediment phosphorus cycling in a nutrient-rich embayment in relation to sediment phosphorus pool and release. Limnology (Tokyo) 21, 415–425. https://doi.org/10.1007/s10201-020-00627-x.

Kjerfve, B., Lacerda, L.D., Baía de Guanabara, G.T.N., 2001. Rio de Janeiro, Brazil. In: Seeliger, U., Kjerfve, B. (Eds.), Coastal Marine Ecosystems of Latin America. Springer-Verlag.

Kjerfve, B., Ribeiro, C.H.A., Dias, G.T.M., Filippo, A.M., Quaresma, V., da, S., 1997. Oceanographic characteristics of an impacted coastal bay: Baia de Guanahara, Rio de Janeiro, Brazil. Cont. Shelf. Res. 17, 1609–1643. https://doi.org/10.1016/S0278-4343(97)00028-9.

Kubo, A., Kanda, J., 2020. Coastal urbanization alters carbon cycling in Tokyo Bay. Sci. Rep. 10, 20413. https://doi.org/10.1038/s41598-020-77385-4.

Levene, H., 1960. Robust tests for equality of variances. Contributions to probability and statistics. Essays in honor of Harold Hotelling, pp. 279–292.

Lürling, M., Van Oosterhout, F., Faassen, E., 2017. Eutrophication and warming boost cyanobacterial biomass and microcystins. Toxins (Basel) 9 (64). https://doi.org/10.3390/toxins9020064.

Marino, I.K., Cetale Santos, M.A., Silva, C.G., 2013. Processing of high-resolution, shallow seismic profiles, Guanabara Bay - Rio de Janeiro state, Brazil. Revista Brasileira de Geofisica 31, 579–594. https://doi.org/10.22564/rbgf.v31i4.339.

Marotta, H., Duarte, C.M., Meirelles-Pereira, F., Bento, L., Esteves, F.A., Enrich-Prast, A., 2010. Long-term CO_2 variability in two shallow tropical lakes experiencing episodic eutrophication and acidification events. Ecosystems 13, 382–392. https://doi.org/10.1007/s10021-010-9325-6.

Marotta, H., Pinho, L., Gudasz, C., Bastviken, D., Tranvik, L.J., Enrich-Prast, A., 2014. Greenhouse gas production in low-latitude lake sediments responds strongly to warming. Nat. Clim. Chang. 4, 467–470. https://doi.org/10.1038/nclimate2222.

Mayr, L.M., Tenenbaum, D.R., Villac, M.C., 1989. Hydrobiological characterization of Guanabara Bay. In Coastlines of Brazil. Am. Soc. Civil Eng. 124–138.

McLeod, E., Chmura, G.L., Bouillon, S., Salm, R., Björk, M., Duarte, C.M., Lovelock, C.E., Schlesinger, W.H., Silliman, B.R., 2011. A blueprint for blue carbon: Toward an improved understanding of the role of vegetated coastal habitats in sequestering CO2. Front. Ecol. Environ. 9, 552–560. https://doi.org/10.1890/110004.

Monteiro, F.F., Cordeiro, R.C., Santelli, R.E., Machado, W., Evangelista, H., Villar, L.S., Viana, L.C.A., Bidone, E.D., 2012. Sedimentary geochemical record of historical anthropogenic activities affecting Guanabara Bay (Brazil) environmental quality. Environ. Earth Sci. 65, 1661–1669. https://doi.org/10.1007/s12665-011-1143-4.

Moore, W.S., 1984. Radium isotope measurements using germanium detectors. Nucl. Instrum. Methods Phys. Res. 3 (2–3), 407–411. https://doi.org/10.1016/0167-5087(84)90683-5.

Nedeau, E.J., Merritt, R.W., Kaufman, M.G., 2003. The effect of an industrial effluent on an urban stream benthic community: water quality vs. habitat quality. Environ. Pollut. 123, 1–13. https://doi.org/10.1016/S0269-7491(02)00363-9.

O'Neil, J.M., Newton, R.J., Bone, E.K., Birney, L.B., Green, A.E., Merrick, B., Fraioli, A., 2020. Using urban harbors for experiential, environmental literacy: Case studies of New York and Chesapeake Bay. Reg. Stud. Marine Sci. 33, 100886.

Paranhos, R., Nascimento, S.M., Mayr, L.M., 1995. On the faecal pollution in Guanabara Bay, Brazil. Fresen. Environ. Bull. 4, 352–357.

Paranhos, R., Pereira, A.P., Mayr, L.M., 1998. Diel variability of water quality in a tropical polluted bay. Environ. Monit. Assess. 50, 131–141. https://doi.org/10.1023/A:1005855914215.

Passos, T., Sanders, C.J., Barcellos, R., Penny, D., 2022. Assessment of the temporal retention of mercury and nutrient records within the mangrove sediments of a highly impacted estuary. Environ. Res. 206 https://doi.org/10.1016/j.envres.2021.112569.

Paudel, B., Weston, N., O'Connor, J., Sutter, L., Velinsky, D., 2017. Phosphorus Dynamics in the Water Column and Sediments of Barnegat Bay, New Jersey. J. Coast. Res. 78, 60–69. https://doi.org/10.2112/SI78-006.1.

Pérez, A., Machado, W., Gutiérrez, D., Borges, A.C., Patchineelam, S.R., Sanders, C.J., 2018. Carbon accumulation and storage capacity in mangrove sediments three decades after deforestation within a eutrophic bay. Mar. Pollut. Bull. 126, 275–280.

Potratz, G.L., Geraldes, M.C., Bizzi, S., Nogueira, L., Martins, M.V.A., 2019. Using lead isotopes and potentially toxic elements to trace pollutant sources in the northern region of Guanabara Bay, southeastern Brazil. Mar. Pollut. Bull. 144, 216–223.

Ritter, W.F., 2019. Progress on the Chesapeake Bay TMDL and challenges in meeting the 2025 pollution-reduction loads. In: World Environmental and Water Resources Congress 2019. Reston, VA. American Society of Civil Engineers, pp. 63–70.

Ross, E.R., Randhir, T.O., 2022. Effects of climate and land use changes on water quantity and quality of coastal watersheds of Narragansett Bay. Sci. Total Environ. 807, 151082 v.

Ruiz-Fernández, A.C., Hillaire-Marcel, C., 2009. ^{210}Pb-derived ages for the reconstruction of terrestrial contaminant history into the Mexican Pacific coast: Potential and limitations. Mar. Pollut. Bull. 59, 134–145. https://doi.org/10.1016/j.marpolbul.2009.05.006.

Sabo, R.D., Sullivan, B., Wu, C., Trentacoste, E., Zhang, Q., Shenk, G.W., Linker, L.C., 2022. Major point and nonpoint sources of nutrient pollution to surface water have declined throughout the Chesapeake Bay watershed. Environ. Res. Commun. 4 (4), 045012.

Sampaio, M., 2003. Estudo de Circulação Hidrodinâmica 3D e Trocas de Massas d'Água da Baía de Guanabara - RJ.

Savage, C., Leavitt, P.R., Elmgren, R., 2010. Effects of land use, urbanization, and climate variability on coastal eutrophication in the Baltic Sea. Limnol. Oceanogr. 55, 1033–1046. https://doi.org/10.4319/lo.2010.55.3.1033.

Savoie, A.M., Moody, A., Gilbert, M., Dillon, K.S., Howden, S.D., Shiller, A.M., Hayes, C. T., 2022. Impact of local rivers on coastal acidification. Limnol. Oceanogr. 67 (12), 2779–2795.

Sharp, J.H., Yoshiyama, K., Parker, A.E., Schwartz, M.C., Curless, S.E., Beauregard, A.Y., Ossolinski, J.E., Davis, A.R., 2009. A biogeochemical view of estuarine eutrophication: Seasonal and spatial trends and correlations in the Delaware Estuary. Estuaries Coasts 32, 1023–1043. https://doi.org/10.1007/s12237-009-9210-8.

Sklar, R., Chabrelie, A.E., Carreira, R.S., Gurian, P.L., Mitchell, J., 2023. Health risks to communities and athletes associated with swimming, wading, and sailing in water bodies of Brazil's Guanabara Bay Basin. Water 15. https://doi.org/10.3390/w15142509.

SNIS (National Sanitation Information System). 2015. Available at [http://www.snis.gov.br/diagnostico-agua-e-esgotos].

Soares-Gomes, A., da Gama, B.A.P., Baptista Neto, J.A., Freire, D.G., Cordeiro, R.C., Machado, W., Bernardes, M.C., Coutinho, R., Thompson, F.L., Pereira, R.C., 2016. An environmental overview of Guanabara Bay, Rio de Janeiro. Reg. Stud. Mar. Sci. 8, 319–330. https://doi.org/10.1016/j.rsma.2016.01.009.

Song, D., Gao, Z., Zhang, H., Xu, F., Zheng, X., Ai, J., Hu, X., Huang, G., Zhang, Haibo, 2017. GIS-based health assessment of the marine ecosystem in Laizhou Bay, China. Mar. Pollut. Bull. 125, 242–249. https://doi.org/10.1016/j.marpolbul.2017.08.027.

Spivak, A.C., Sanderman, J., Bowen, J.L., Canuel, E.A., Hopkinson, C.S., 2019. Global-change controls on soil-carbon accumulation and loss in coastal vegetated ecosystems. Nat. Geosci. 12 (9), 685–692. https://doi.org/10.1038/s41561-019-0435-2.

Szmytkiewicz, A., Zalewska, T., 2014. Sediment deposition and accumulation rates determined by sediment trap and ^{210}Pb isotope methods in the outer puck bay (Baltic Sea). Oceanologia 56. https://doi.org/10.5697/oc.56-1.085.

Teoh, H.W., Lee, S.L., Chong, V.C., Yurimoto, T., 2016. Nutrient (N, P, Si) concentration and primary production on a perturbed tropical coastal mudflat. Environ. Earth Sci. 75 https://doi.org/10.1007/s12665-016-5953-2.

Testa, J.M., Boynton, W.R., Hodgkins, C.L., Moore, A.L., Bailey, E.M., Rambo, J., 2022. Biogeochemical states, rates, and exchanges exhibit linear responses to large nutrient load reductions in a shallow, eutrophic urban estuary. Limnol. Oceanogr. 67 (4), 739–752.

Tu, L., Jarosch, K.A., Schneider, T., Grosjean, M., 2019. Phosphorus fractions in sediments and their relevance for historical lake eutrophication in the Ponte Tresa basin (Lake Lugano, Switzerland) since 1959. Sci. Total Environ. 685, 806–817. https://doi.org/10.1016/j.scitotenv.2019.06.243.

Vea, E.B., Ryberg, M., Richardson, K., Hauschild, M.Z., 2020. Framework to define environmental sustainability boundaries and a review of current approaches. Environ. Res. Lett. 15 https://doi.org/10.1088/1748-9326/abac77.

Vitousek, P.M., Mooney, H.A., Lubchenco, J., Melillo, J.M., 1997. Human domination of Earth's ecosystems. Science 277, 494–499. https://doi.org/10.1126/science.277.5325.494.

Wallace, R.B., Baumann, H., Grear, J.S., Aller, R.C., Gobler, C.J., 2014. Coastal ocean acidification: The other eutrophication problem. Estuar. Coast. Shelf. Sci. 148, 1–13. https://doi.org/10.1016/j.ecss.2014.05.027.

Weber, T., Wiseman, N.A., Kock, A., 2019. Global ocean methane emissions dominated by shallow coastal waters. Nat. Commun. 10 https://doi.org/10.1038/s41467-019-12541-7.

Wilson, J., Abboud, S., Beman, J.M., 2017. Primary production, community respiration, and net community production along oxygen and nutrient gradients: Environmental controls and biogeochemical feedbacks within and across "marine lakes. Front. Mar. Sci. 4 https://doi.org/10.3389/fmars.2017.00012.

Yan, Q., Cheng, T., Song, J., Zhou, J., Hung, C., Cai, Z., 2021. Internal nutrient loading is a potential source of eutrophication in Shenzhen Bay, China. Ecolog. Indicat. 127 https://doi.org/10.1016/j.ecolind.2021.107736.

Zhang, Q., Blomquist, J.D., Fanelli, R.M., Keisman, J.L., Moyer, D.L., Langland, M.J., 2023. Progress in reducing nutrient and sediment loads to Chesapeake Bay: Three decades of monitoring data and implications for restoring complex ecosystems. Wiley Interdiscipl. Rev.: Water 10 (5), e1671.

Zhou, Y.Y., Wang, L., Zhou, Y.Y., Mao, Z.X., 2020. Eutrophication control strategies for highly anthropogenic influenced coastal waters. Sci. Total Environ. 705 https://doi.org/10.1016/j.scitotenv.2019.135760, 135760.