



## Baseline

## Nutrient regeneration susceptibility under contrasting sedimentary conditions from the Rio de Janeiro coast, Brazil

Christiene R.L. Matos<sup>a</sup>, Ursula Mendoza<sup>a</sup>, Rut Diaz<sup>a</sup>, Manuel Moreira<sup>a</sup>, Andre L. Belem<sup>b</sup>, Edouard Metzger<sup>c</sup>, Ana Luiza S. Albuquerque<sup>a</sup>, Wilson Machado<sup>a,\*</sup><sup>a</sup> Programa de Geoquímica Ambiental, Departamento de Geoquímica, Universidade Federal Fluminense, Niterói, RJ 24020-150, Brazil<sup>b</sup> Departamento de Engenharia Agrícola e do Meio Ambiente, Escola de Engenharia, Universidade Federal Fluminense, São Domingos, Niterói, RJ 24210-240, Brazil<sup>c</sup> Laboratoire des Bio-Indicateurs Actuels et Fossiles, UMR6112 CNRS LPG-BIAF, Université d'Angers, 2 Boulevard Lavoisier, 49045 Angers Cedex, France

## ARTICLE INFO

## Article history:

Received 22 December 2015

Received in revised form 14 April 2016

Accepted 22 April 2016

Available online 4 May 2016

## Keywords:

Pore water

Nutrients

Eutrophication

Diagenesis

Remobilization modeling

## ABSTRACT

Dissolved silicate (DSi),  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  susceptibility to be exchanged between sediment pore waters and overlying waters was evaluated in Jurujuba Sound (JS station) and Coroa Grande Sound (CGS station), southeastern Brazil. Sedimentary elemental (C, N and P) and isotopic ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) compositions evidenced stronger anthropogenic fertilization in JS station. Net  $\text{NO}_3^-$  influxes from overlying waters occurred, which was two orders of magnitude higher under the more fertilized condition. This condition resulted in 6–13-times higher net effluxes of  $\text{NH}_4^+$ , DSi and  $\text{PO}_4^{3-}$  to overlying waters. Vertical alternation between production and consumption processes in pore waters contributed for a more limited regeneration in CGS station. This was associated with diagenetic responses to sedimentary grain size variability in deeper layers and biological disturbance in upper layers. Nearly continuous production of  $\text{NH}_4^+$ , DSi and  $\text{PO}_4^{3-}$  in pore waters implied in intensified susceptibility to remobilization under the eutrophic condition of JS station.

© 2016 Elsevier Ltd. All rights reserved.

The cycling of nutrients in coastal systems has been frequently affected by anthropogenic fertilization, implying in coastal primary production fueling (Fisher et al., 2006; Carstensen et al., 2011) and elevated nutrient accumulation within sediments (Church et al., 2006; Borges et al., 2009). Nutrient regeneration to surface water from underlying sediments has been postulated as a factor that influence the coastal primary production if these elements are not efficiently removed from pore waters by sorption and precipitation processes in the upper sediment layers (Rozan et al., 2002; Ogrinc and Faganeli, 2006). This evidences the importance of elucidating the nutrient behavior near the sediment–water interface under different degrees of anthropogenic influences (Metzger et al., 2007; Warnken et al., 2008). In addition, the modeling of nutrient production rates within pore water and exchange rates with overlying water is an interesting tool to improve our capacity to predict the nutrient regeneration responses to different environmental conditions (Glud et al., 2009; Rigaud et al., 2013). Therefore, the nutrient release potential by diffusion from pore water to overlying water for a discrete sampling time (or sequence of samplings), hereafter called

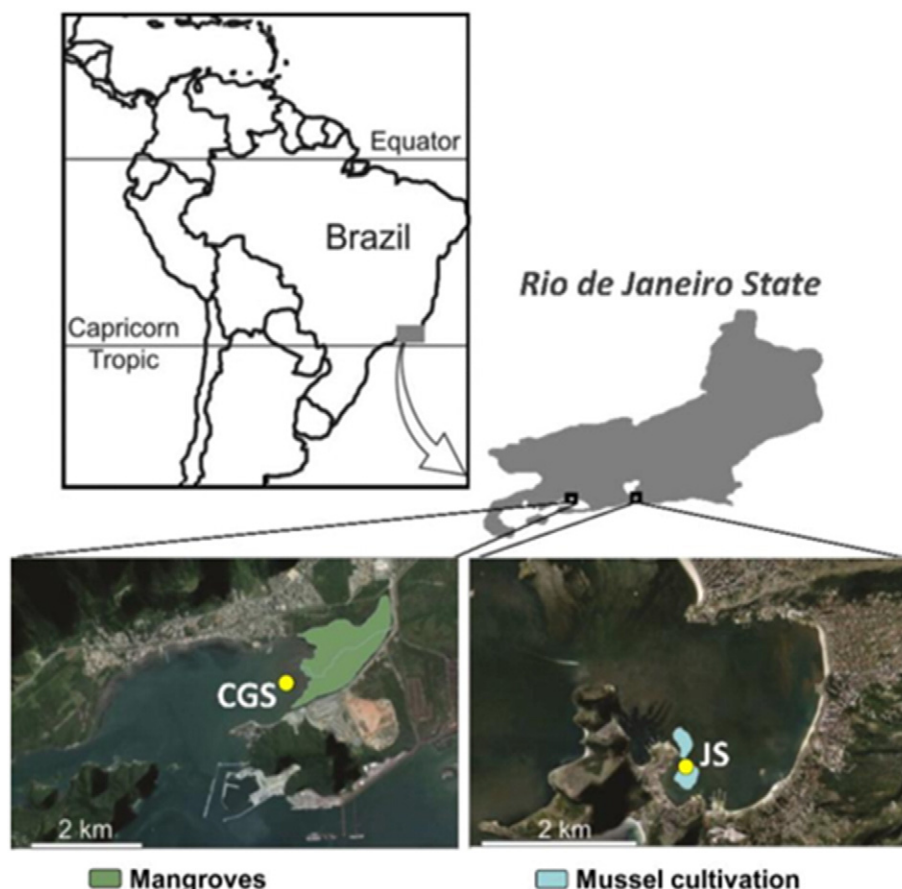
as nutrient regeneration susceptibility, can be evaluated as modeled effluxes from pore waters.

This study evaluates the nutrient (N, P and silicate) net production rates and effluxes from sediment pore waters in two areas with different degrees of anthropogenic impact, located in the Rio de Janeiro coast, southeastern Brazil. The Jurujuba Sound (JS) is located on the eastern margin of Guanabara Bay (Fig. 1) and receives urban effluents conveyed from a heavily urbanized drainage basin (Kjerfve et al., 1997; Aguiar et al., 2013). In addition, there is a mussel (*Perna perna*) cultivation area in this sampling site, which may contribute to the organic matter input to the sediments. This condition contrasts with that observed in Coroa Grande Sound (CGS), Sepetiba Bay (Fig. 1), in which lower nutrient loading occurs due to smaller urbanization of the drainage basin than that affecting Guanabara Bay. CGS sampling station is located in front of the mouth from a small river that is colonized by a mangrove forest, as it is typical in Sepetiba Bay (Fig. 1). These sites were chosen for a preliminary test of the hypothesis that the nutrient regeneration susceptibility is affected by contrasting nutrient loadings.

The accentuated water quality degradation observed in the Guanabara Bay is mainly due to emissions of sewage and industrial effluents (Kjerfve et al., 1997; Aguiar et al., 2011). This resulted in governmental initiatives to improve water quality (Kjerfve et al., 1997), although this improvement may be partly dependent on the intensity of nutrient regeneration from Guanabara Bay bottom sediments (Rebello et al., 1988). For Sepetiba Bay, enhancements of the sewage loading derived from current expansions of harboring and industrial

\* Corresponding author.

E-mail addresses: [christienematos@hotmail.com](mailto:christienematos@hotmail.com) (C.R.L. Matos), [urasmendoza@geoq.uff.br](mailto:urasmendoza@geoq.uff.br) (U. Mendoza), [ruca114@hotmail.com](mailto:ruca114@hotmail.com) (R. Diaz), [manuelmoreira@id.uff.br](mailto:manuelmoreira@id.uff.br) (M. Moreira), [andrebelem@id.uff.br](mailto:andrebelem@id.uff.br) (A.L. Belem), [edouard.metzger@univ-angers.fr](mailto:edouard.metzger@univ-angers.fr) (E. Metzger), [ana\\_albuquerque@id.uff.br](mailto:ana_albuquerque@id.uff.br) (A.L.S. Albuquerque), [wmachado@geoq.uff.br](mailto:wmachado@geoq.uff.br) (W. Machado).



**Fig. 1.** Location of sampling stations within Coroa Grande Sound (CGS) and Jurujuba Sound (JS). The cities seen on the picture are Itaguaí (CGS station) and Niterói (JS station), Rio de Janeiro State, southeastern Brazil. The main mangrove area (CGS station) and mussel cultivation area (JS station) cited in the text are highlighted.

activities in the drainage basin are expected for the next decades, in addition to historical concerns on metal pollution from industrial sources (Molisani et al., 2004; Gomes et al., 2009). This work provides a comparison of the nutrient susceptibility to undergo regeneration to overlying water under the contrasting water quality and sedimentary conditions from these bays, also allowing comparisons with future conditions of nutrient loading.

Two replicate cores were collected from each site by diving at a water column depth of ~2.5 m, using acrylic tubes (8 cm diameter, 50 cm length), between June (JS station) and July (CGS station), 2014. These cores were transported to the laboratory under refrigeration and processed within 2 h. Pore waters were sampled from one of the replicate cores with a resolution of 1-cm depth intervals for the upper 5 cm and 2-cm depth intervals for deeper layers. The overlying waters covering the sampled sediments and pore waters were retrieved using Rhyzon® collectors (7 cm length, with an average pore diameter of 0.1 µm), inserted directly into the sediment through pre-drilled holes along the acrylic tubes (Seeberg-Elverfeldt et al., 2005). The pre-drilled holes used for overlying water sampling were ~5 cm above the sediment–water interface. In order to prevent oxidation during handling, all pore water samples were processed within a N<sub>2</sub>-filled glove bag. The overlying and pore water samples were analyzed for total alkalinity (TA) and dissolved NO<sub>3</sub><sup>−</sup>, NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3−</sup>, sulfides (ΣH<sub>2</sub>S), SO<sub>4</sub><sup>2−</sup> and silica (DSi). In the glove-bag, 2 mL of each water sample were placed in 5 mL amber vials for alkalinity analyses. Another sub-sample of 1 mL was stored in a 2 mL Eppendorf tube containing 100 µL of a 5% Zn-acetate solution (Merck PA) for ΣH<sub>2</sub>S analysis. Another sub-sample of 1 mL was stored in 5 mL vials with 10 µL HCl for phosphate analysis. For sulfate and silica analyses, 1 mL sample was stored in 2 mL Eppendorf tubes. All samples were stored at 4 °C. For NO<sub>3</sub><sup>−</sup>

and NH<sub>4</sub><sup>+</sup> analyses, 4 mL sub-samples were kept frozen into 5 mL amber vials.

Sediment solid phase characterization was performed using the second replicate core, after slicing at a 1-cm resolution and storing in polyethylene bags at 4 °C until processing. Determinations of grain size, total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), and stable isotopes signatures of TOC (δ<sup>13</sup>C) and TN (δ<sup>15</sup>N) were performed. Sediment grain size was determined using a CILAS model 1064 particle size meter, after calcium carbonate and organic matter removal, and dispersion in sodium hexametaphosphate 4% (Loring and Rantala, 1992). TOC, TN, δ<sup>13</sup>C and δ<sup>15</sup>N were determined using a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer, at the Davis Stable Isotope Facility, University of California, USA. Total P contents in the sediments were determined by colorimetry, according to Grasshoff et al. (1999), following the extraction procedure from Aspila et al. (1976). Overlying water and pore water TA was measured from a 2 mL sample by potentiometric Gran titration with 0.01 mol L<sup>−1</sup> HCl immediately after removal of vials from the glove-bag. The NO<sub>3</sub><sup>−</sup>, NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3−</sup> and DSi concentrations were determined within 1 week by standard colorimetric methods (Gieskes et al., 1991). ΣH<sub>2</sub>S contents were determined by using the colorimetric method from Cline (1969), while SO<sub>4</sub><sup>2−</sup> concentrations were determined by ion chromatography.

Kinetic modeling was performed to evaluate the nutrient susceptibility to re-mobilization using the diffusion-based computer code PROFILE (Berg et al., 1998). For this evaluation, the molar concentrations of the studied chemical species in the overlying water and the molecular diffusion coefficients obtained from Li and Gregory (1974) were used. Zero-order rates of pore water concentration production or consumption ( $R_{net}$ ) were estimated, which may range from negative values

(meaning consumption) to positive values (meaning production). This approach divides the results into discrete vertical zones, assuming the absence of significant advective flux and considering that the system is, at least, in a quasi-steady-state. The PROFILE output data include estimates of effluxes or influxes across the sediment–water interface and depth-integrated  $R_{\text{net}}$  estimates per sediment area. Although steady-state assumptions may not be strictly valid for the shallow coastal environments studied (e.g., due to biological disturbances – see below), the use of this approach contributes for dimensioning nutrient re-mobilization processes (Rigaud et al., 2013; Kleeberg and Herzog, 2014). The stated hypothesis on the nutrient loading influence was tested applying the modeled nutrient effluxes data as regeneration susceptibility estimates.

Sediment grain size and geochemical properties are presented in Fig. 2. The JS core was composed of fine-grained sediments, with negligible sand contents ( $\leq 1.1\%$ ) and silt content predominance ( $\geq 80\%$ ). This pattern of grain size composition occurred in the upper 16 cm depth of the CGS core, but sand content had a higher importance below this depth (up to 44%) for this core. Mean concentrations of TOC ( $5.07$  vs.  $1.26 \text{ mmol g}^{-1}$ ), TN ( $0.53$  vs.  $0.11 \text{ mmol g}^{-1}$ ) and TP ( $56.8$  vs.  $15.7 \text{ } \mu\text{mol g}^{-1}$ ) were nearly 4–5-times higher in JS station. The more elevated nutrient concentrations observed for sediments from JS station are within the ranges observed in previous studies in eutrophic sites at a regional scale (Carreira and Wagener, 1998; Borges et al., 2009; Monteiro et al., 2011). These sediments presented upward decreases in TOC contents and C/N ratios, without clear depth variability for TN and TP. Concurrent enhancements of TOC, TN and TP concentrations were observed in the CGS station above the phase of coarser particles accumulation, which were associated with upward accumulation of more degradable organic matter, as inferred from lower C/N ratios. The recent changes in the nutrient loading to Coroa Grande Sound sediments may be attributed to anthropogenic input of sewage (Marinho et al., 2012), though at a comparatively low extent in relation to that observed in Jurujuba Sound.

The sediments from JS station had lower C/N ratios (averages =  $9.5$  vs.  $12.2$ ) and heavier signatures of  $\delta^{13}\text{C}$  (averages =  $-20.5\%$  vs.  $-23.8\%$ ), while lighter  $\delta^{15}\text{N}$  signals were also observed in CGS station (averages =  $7.4\%$  vs.  $6.5\%$ ), with the exception of the two deeper layers. This indicates higher accumulation of algal-derived TOC and TN in JS station, as implied from phytoplankton primary production stimulation in Guanabara Bay due to sewage input, besides the possible contribution from organic matter derived from direct sewage inputs (Kalas et al., 2009; Monteiro et al., 2011). These effects of anthropogenic fertilization may explain the significant positive correlation of  $\delta^{13}\text{C}$  with both  $\delta^{15}\text{N}$  ( $r = 0.64$ ;  $p < 0.01$ ) and C/N ratios ( $r = 0.82$ ;  $p < 0.001$ ) observed for JS station. Under the less-fertilized condition of CGS station,  $\delta^{13}\text{C}$  values were negatively correlated with both  $\delta^{15}\text{N}$  ( $r = -0.49$ ;  $p = 0.03$ ) and C/N data ( $r = -0.93$ ;  $p < 0.001$ ), while higher sand contents were associated with lighter  $\delta^{13}\text{C}$  values and higher C/N ratios. These results suggest higher contributions of terrestrial TOC (Meyers, 1994) during the phase of coarser particles accumulation. An influence from the closely located mangroves (Fig. 1) is expected for determining the organic matter quality in CGS station, considering the typical large capacity of mangrove systems to produce and export organic matter (Marinho et al., 2012; Sanders et al., 2010). This can contribute to explain the simultaneous subsurface increases in sand content and terrestrial organic matter isotopic signature (below 16 cm depth), probably corresponding to a period of stronger hydrodynamics.

The JS station presented variations in pore water  $\text{NO}_3^-$  concentrations ( $13.7$  to  $47 \text{ } \mu\text{mol L}^{-1}$ ), while large and nearly continuous  $\text{NH}_4^+$  enrichments (from  $430$  to  $1960 \text{ } \mu\text{mol L}^{-1}$ ) occurred with depth increase (Fig. 3). The observed  $\text{NO}_3^-$  variations may be explained by the depth variability in the intensity of N diagenetic processes, such as organic matter oxidation by  $\text{NO}_3^-$  (i.e., denitrification; Berner, 1980). However, the dissimilatory  $\text{NO}_3^-$  reduction to  $\text{NH}_4^+$  (DNRA) is a competing  $\text{NO}_3^-$  reduction process that is dominant in many tropical estuaries (Dong et al., 2011). Since high sulfide concentrations may inhibit

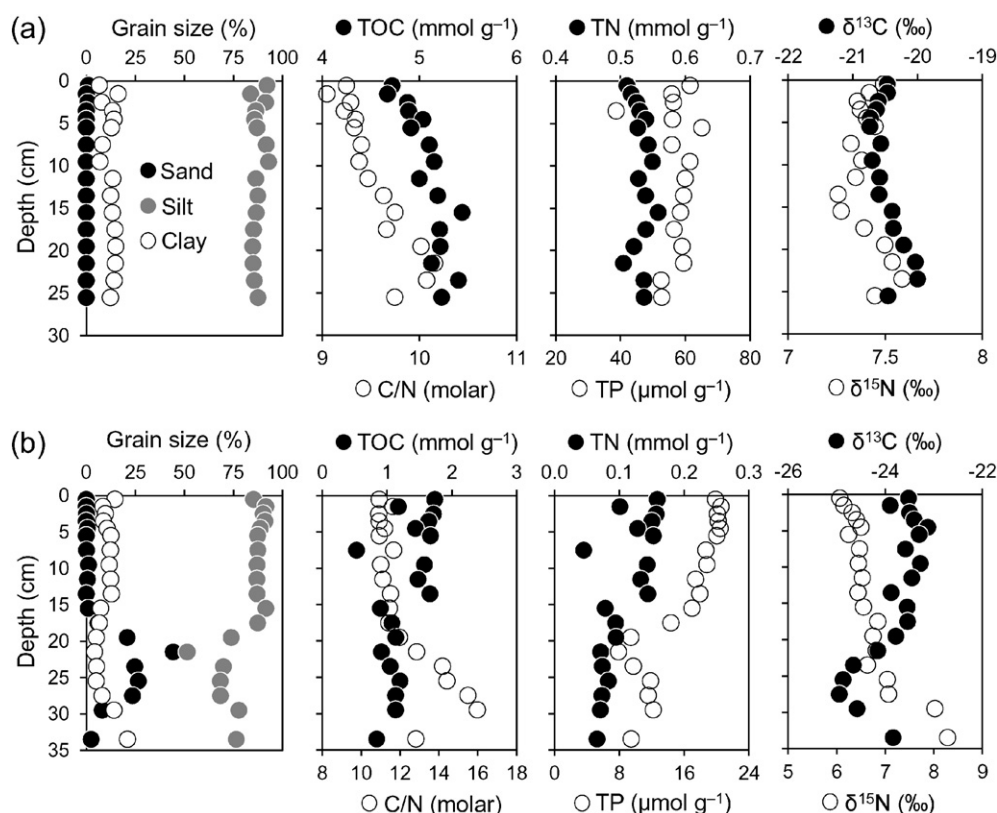


Fig. 2. Sediment grain size and geochemical properties of Jurujuba Sound core (a) and Coroa Grande Sound core (b).

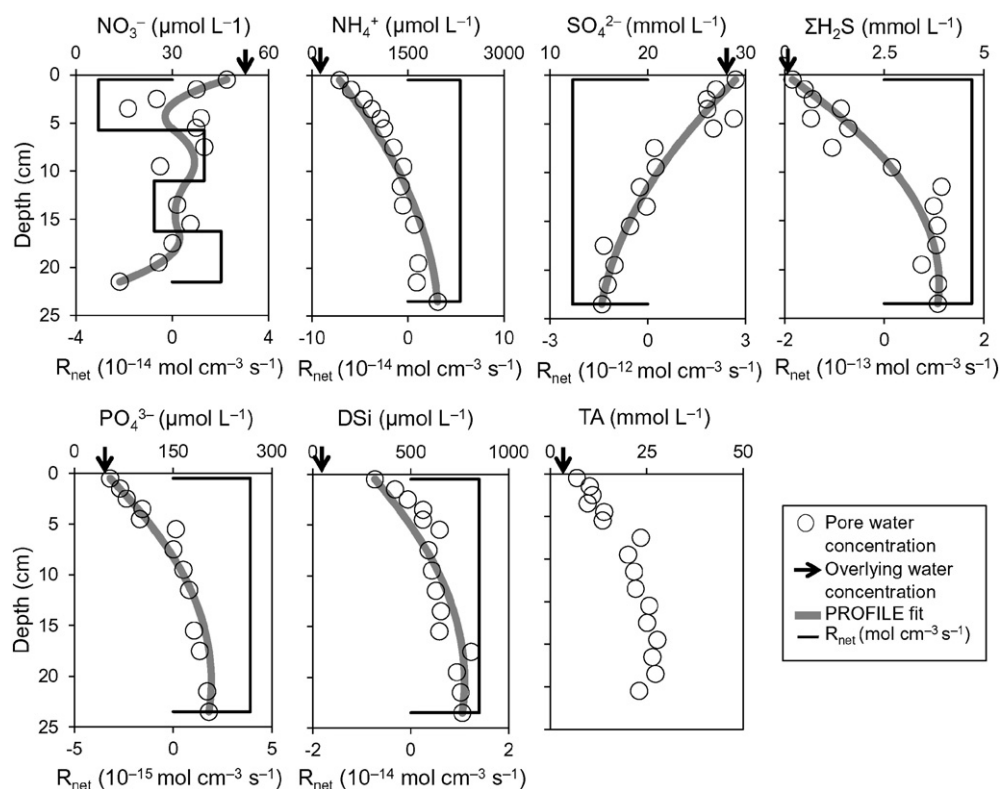


Fig. 3. Overlying and pore water concentrations of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\Sigma\text{H}_2\text{S}$ ,  $\text{PO}_4^{3-}$ , DSi and TA in Jurujuba Sound station. PROFILE fits and net reaction rates ( $R_{\text{net}}$ ) are also given.

denitrification and enhance DNRA, this latter process can be intensified with increasing  $\Sigma\text{H}_2\text{S}$  accumulation (An and Gardner, 2002). Concurrently, the  $\text{NO}_3^-$  input derived from organic matter degradation employing electron acceptors other than  $\text{NO}_3^-$  contributes for the pore water  $\text{NO}_3^-$  production (Berner, 1980). In JS station,  $\text{SO}_4^{2-}$  reduction was intensified below the upper zone of  $\text{NO}_3^-$  consumption (Fig. 3). The ratios between  $\Delta\text{TA}$  (i.e., the difference between TA from each considered layer and the uppermost layer TA; 14.4 to 22  $\text{mmol L}^{-1}$ ) and  $\Delta\text{SO}_4^{2-}$  (i.e., the difference in  $\text{SO}_4^{2-}$  contents between the uppermost layer and in each considered layer; 8.2 to 14.2  $\text{mmol L}^{-1}$ ) below this upper zone of  $\text{NO}_3^-$  consumption ranged from 1.5 to 2.2. These ratios are near the 2:1 stoichiometry that corresponds to organic matter oxidation by  $\text{SO}_4^{2-}$  reduction (Berner, 1980), evidencing the importance of this organic matter oxidation pathway. Benthic fauna activity was observed in the upper centimeters of CGS and JS sediment cores (i.e., burrowing activity occurred before core slicing and while pore water was extracted). However, the potential oxidizing effect of burrowing activity was not sufficient to avoid  $\text{SO}_4^{2-}$  consumption in JS station.

Table 1

Depth-integrated net reaction rates ( $R_{\text{net}}$ ) and net fluxes across the sediment–water interface obtained with the PROFILE code for the Jurujuba Sound (JS) and Coroa Grande Sound (CGS) stations.

	$R_{\text{net}}$ ( $\text{mol cm}^{-2} \text{s}^{-1}$ )		Flux ( $\text{mol cm}^{-2} \text{s}^{-1}$ )	
	JS	CGS	JS	CGS
$\text{NO}_3^-$	$-2.49 \times 10^{-13}$	$-2.77 \times 10^{-15}$	$1.17 \times 10^{-12}$	$6.21 \times 10^{-15}$
$\text{NH}_4^+$	$1.25 \times 10^{-12}$	$5.05 \times 10^{-13}$	$-1.42 \times 10^{-12}$	$-2.47 \times 10^{-13}$
$\text{PO}_4^{3-}$	$9.01 \times 10^{-14}$	$1.12 \times 10^{-14}$	$-7.82 \times 10^{-14}$	$-6.86 \times 10^{-15}$
DSi	$3.21 \times 10^{-13}$	$3.98 \times 10^{-14}$	$-2.78 \times 10^{-13}$	$-2.17 \times 10^{-14}$

Note:  $R_{\text{net}}$  negative values mean consumption and positive values mean production in pore waters, while negative flux values mean net efflux to overlying water and positive flux values mean influx to pore water.

Pore water TA,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\Sigma\text{H}_2\text{S}$  and DSi were highly correlated ( $r = 0.84$  to  $0.95$ ;  $p < 0.001$ ) in JS station (Fig. 3). Dissolved  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  depth variability was associated to organic matter decomposition, enhancing TA with depth and involving the sulfate-reduction pathway, while amorphous silica dissolution probably occurred concurrently, controlling DSi production (Lyons et al., 1996; Souchu et al., 1998). There is no inherent reason for a coupling between oxidation of organic matter decomposition and biogenic silica dissolution (Berelson et al., 2005). However, marine bacteria attack to dead and living diatoms and bacterial degradation of the organic matter matrix that protects diatom frustules from dissolution may occur (Bidle and Azam, 1999), which may possibly contribute for a concurrent increase in TA and DSi. The order of depth-integrated net productions of these nutrients in JS station was  $\text{NH}_4^+ > \text{DSi} > \text{PO}_4^{3-}$ , with a depth-integrated net consumption observed for  $\text{NO}_3^-$  in this station (Table 1). The same trend was observed for the estimated net exchanges across the sediment–water interface for these nutrients (Table 1). This indicates that the intensity of the nearly continuous net production of  $\text{NH}_4^+$ , DSi and  $\text{PO}_4^{3-}$  within pore waters contributed for larger effluxes, as fueled by organic matter consumption.

Fig. 4 presents pore water data from CGS station. Although  $\text{NO}_3^-$  concentrations also had variations, only consumption was implied from the PROFILE fit, and the absence of detectable  $\Sigma\text{H}_2\text{S}$  ( $< 0.5 \mu\text{mol L}^{-1}$ ) suggests a lower importance of DNRA (An and Gardner, 2002). A less intense sulfur diagenesis was also inferred (maximum  $\Delta\text{SO}_4^{2-} = 5.0 \text{ mmol L}^{-1}$ ; Fig. 4). However, the observed  $\text{SO}_4^{2-}$  production within the upper layers (Fig. 4) indicates that sulfide oxidation occurs (Aller and Rude, 1988; Diaz et al., 2012). Pore water  $\text{SO}_4^{2-}$  production was also observed within upper sediment layers from the Berre Lagoon, France, where  $\Sigma\text{H}_2\text{S}$  oxidation occurred (Rigaud et al., 2013). The absence of detectable pore water sulfide while net  $\text{SO}_4^{2-}$  consumption is observed in deeper layers from CGS station (Fig. 4) may be also due to sulfide oxidation. In addition, pore water sulfide removal in reaction with organic matter (Francois, 1987) may contribute for the absence of detectable  $\Sigma\text{H}_2\text{S}$  concentrations.



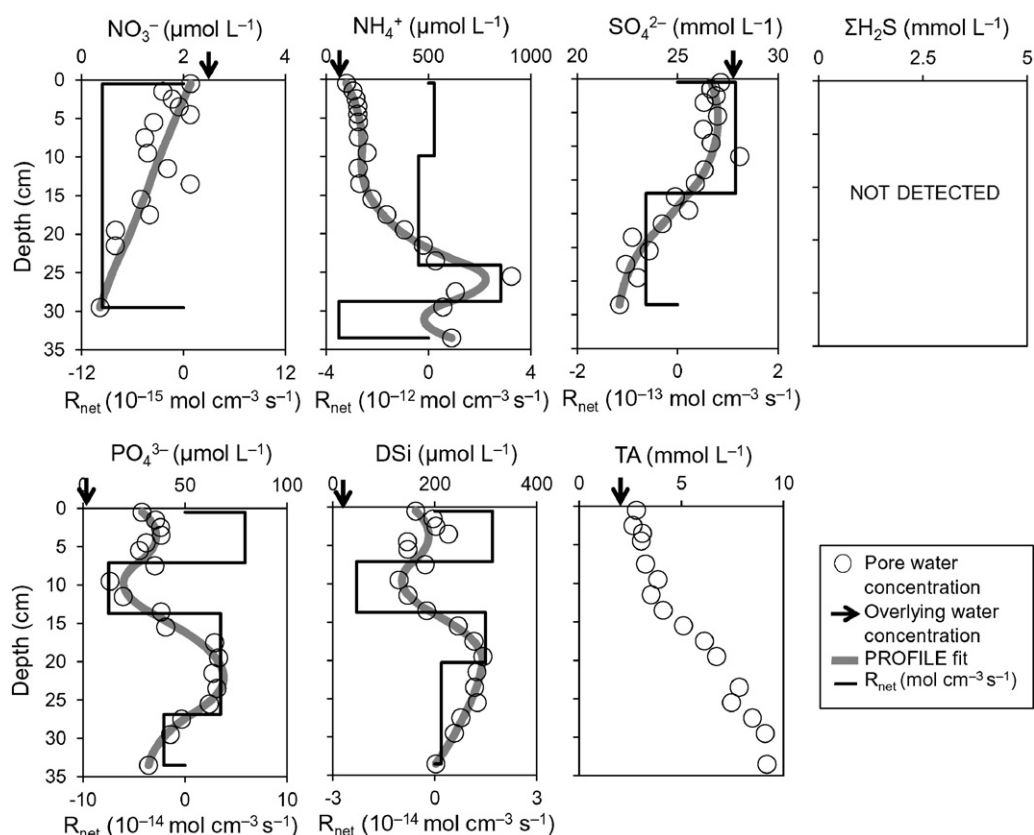


Fig. 4. Overlying and pore water concentrations of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\Sigma\text{H}_2\text{S}$ ,  $\text{PO}_4^{3-}$ , DSi and TA in Coroa Grande Sound station. PROFILE fits and net reaction rates ( $R_{\text{net}}$ ) are also given.

The  $\text{NH}_4^+$  concentrations also followed the TA trend in CGS station ( $r = 0.88$ ;  $p < 0.001$ ), whereas  $\text{PO}_4^{3-}$  and DSi presented similar depth variability, did not follow TA and showed alternations between production and consumption zones (Fig. 4). A zone of sharp elevation in the  $\text{NH}_4^+$  production occurred near the 25 cm depth, while consumption occurred below (Fig. 4). An upper zone of  $\text{SO}_4^{2-}$  production (with  $\text{PO}_4^{3-}$  and DSi variations) and a lower zone of concurrent enhancements of  $\text{SO}_4^{2-}$  reduction and production of  $\text{PO}_4^{3-}$  and DSi also occurred. This latter zone corresponds to the layers of coarse particles accumulation and organic matter quality change (Fig. 2). Coarser sediments may favor the transition between these zones, since sediment permeability can affect the organic matter diagenesis and the dynamics of nutrients in pore waters (e.g., due to advective transport facilitation; Huettel et al., 1998; Rusch et al., 2000). These results were interpreted as a pulse of nutrient production within the phase of coarser sediments accumulation, which was associated with the diagenesis of organic matter derived from mixed (marine and terrestrial) sources, as revealed by the carbon isotopic signatures (Fig. 2).

Depth-integrated net productions in CGS station were also in the order  $\text{NH}_4^+ > \text{DSi} > \text{PO}_4^{3-}$ , while  $\text{NO}_3^-$  showed net consumption (Table 1). The  $\text{NO}_3^-$  influx was two orders of magnitude lower than in the JS station, which presented 6–13-times higher net effluxes of  $\text{NH}_4^+$ , DSi and  $\text{PO}_4^{3-}$ . The C/N ratio of top sediment layers may affect the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  effluxes from pore waters, since this ratio is related with organic matter degradability (Lerat et al., 1990). Considering that the lower C/N ratio observed in JS station (Fig. 2) suggests higher degradability, this may contribute to explain the observed effluxes contrasts. The results evidenced that the alternations in diagenetic processes observed for all nutrients in CGS station and for  $\text{NO}_3^-$  in JS station can limit the upward migration, with a probable negative effect of the pore water zones of concentration depletion on the nutrient regeneration susceptibility. The occurrence of “diagenetic hotspots” with intensified microbial activity in variable depth interval has been

reported in the literature (Glud, 2008), which may contribute for the variability in consumption and production processes.

In conclusion, the pore water geochemistry revealed intensive microbial degradation of organic matter in sediments from the eutrophic JS station, with pore water  $\Delta\text{TA}:\Delta\text{SO}_4^{2-}$  ratios predominantly close to the sulfate-reduction stoichiometry. Sulfate-reduction was evidenced as a driver for the nearly continuous pore water production of nutrients with increasing depth in JS station. This trend seems to contribute for the larger nutrient regeneration susceptibilities estimated. A concurrently larger net  $\text{NO}_3^-$  influx was also inferred in this station in response to  $\text{NO}_3^-$  reduction processes (i.e., denitrification and DNRA). Pore water concentrations of  $\text{NH}_4^+$ , DSi and  $\text{PO}_4^{3-}$  from the less-fertilized CGS station were affected by vertical alternations between consumption and production processes. These alternations were associated with diagenetic responses to bioturbation in upper layers and sediment grain size variability in deeper layers. DSi production was clearly coupled with the recycling of N and P in JS station, while less-clear associations between the nutrient cycles were found under the CGS station conditions. A general intensification of the similar trends of nutrient susceptibility to be regenerated to overlying water ( $\text{NH}_4^+ > \text{DSi} > \text{PO}_4^{3-}$ ) or to undergo influx to pore water ( $\text{NO}_3^-$ ) occurred under the more-fertilized condition.

## Acknowledgments

We thank the critical comments from an anonymous reviewer. This study had financial support from the Geochemistry Network from PETROBRAS/CENPES and by the National Petroleum Agency (ANP) of Brazil (Grant 0050.004388.08.9). The authors thank the research grants from the Brazilian Research Council (CNPq) to C.R.L. Matos, A.L.S. Albuquerque and W. Machado, and from the Brazilian Ministry of Education (CAPES) to R. Diaz and M. Moreira.

## References

- 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.
- Aguiar, V.M.C., Abuchacra, P.F.F., Baptista Neto, J.A., 2013. Biogeochemistry of Jurujuba sound concerning phosphorus dynamics, Rio de Janeiro, Brazil. *J. Coast. Res. Spec. Issue* 65, 1–6.
- Aller, R.C., Rude, P.D., 1988. Complete oxidation of solid phase sulfides by manganese and bacteria in anoxic marine sediments. *Geochim. Cosmochim. Acta* 52, 751–765.
- An, S., Gardner, W.S., 2002. Dissimilatory nitrate reduction to ammonium (DNRA) as a nitrogen link, versus denitrification as a sink in a shallow estuary (Laguna Madre/Baffin Bay, Texas). *Mar. Ecol. Prog. Ser.* 237, 41–50.
- Aspila, K.L., Agemian, H., Chau, A.S.Y., 1976. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. *Analyst* 101 (287–197).
- Berelson, W.M., Prokopenko, M., Sansone, F.J., Graham, A.W., McManus, J., Bernhard, J.M., 2005. Anaerobic diagenesis of silica and carbon in continental margin sediments: discrete zones of  $\text{TCO}_2$  production. *Geochim. Cosmochim. Acta* 69, 4611–4629.
- Berg, P., Rysgaard-Petersen, N., Rysgaard, S., 1998. Interpretation of measured concentration profiles in sediment pore water. *Limnol. Oceanogr.* 43, 1500–1510.
- Berner, R.A., 1980. *Early Diagenesis*. Princeton University Press, Princeton.
- Bidle, K.D., Azam, F., 1999. Accelerated dissolution of diatom silica by marine bacterial assemblages. *Nature* 397, 508–512.
- Borges, A.C., Sanders, C.J., Santos, H.L.R., Araripe, D.R., Machado, W., Patchineelam, S.R., 2009. Eutrophication history of Guanabara Bay (SE, Brazil) recorded by phosphorus flux to sediments from a degraded mangrove area. *Mar. Pollut. Bull.* 58, 1739–1765.
- Carreira, R.S., Wagener, A.L.R., 1998. Speciation of sewage derived phosphorus in coastal sediments from Rio de Janeiro, Brazil. *Mar. Pollut. Bull.* 36, 818–827.
- Carstensen, J., Sánchez-Camacho, M., Duarte, C.M., Krause-Jensen, D., Marbà, N., 2011. Connecting the dots: responses of coastal ecosystems to changing nutrient concentrations. *Environ. Sci. Technol.* 45, 9122–9132.
- Church, T.M., Sommerfield, C.K., Velinsky, D.J., Point, D., Benoit, C., Amouroux, D., Plaa, D., Donard, O.F.X., 2006. Marsh sediments as records of sedimentation, eutrophication and metal pollution in the urban Delaware estuary. *Mar. Chem.* 102, 72–95.
- Cline, J.D., 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.* 14, 454–458.
- Diaz, R., Moreira, M., Mendoza, U., Machado, W., Böttcher, M.E., Santos, H., Bélem, A., Capilla, R., Escher, P., Albuquerque, A.L., 2012. Early diagenesis of sulfur in a tropical upwelling system, Cabo Frio, southeastern Brazil. *Geology* 40, 879–882.
- Dong, L.F., Sobey, M.N., Smith, C.J., Rusmana, I., Phillips, W., Stott, A., Osborn, A.M., Nedwell, D.B., 2011. Dissimilatory reduction of nitrate to ammonium, not denitrification or anammox, dominates benthic nitrate reduction in tropical estuaries. *Limnol. Oceanogr.* 56, 279–291.
- Fisher, T.R., Hagy III, J.D., Boynton, W.R., Williams, M.R., 2006. Cultural eutrophication in the Choptank and Patuxent estuaries of Chesapeake Bay. *Limnol. Oceanogr.* 51, 435–447.
- Francois, R., 1987. A study of sulphur enrichment in the humic fraction of marine sediments during early diagenesis. *Geochim. Cosmochim. Acta* 51, 17–27.
- Gieskes, J.M., Gamot, T., Brumsack, H., 1991. Chemical Methods for Intersitital Water Analysis, ODP Technical Note 15. A&M University, Texas.
- Glud, R.N., 2008. Oxygen dynamics of marine sediments. *Mar. Biol. Res.* 4, 243–289.
- Glud, R.N., Thamdorp, B., Stahl, H., Wenzhoefer, F., Glud, A., Nomaki, H., Oguri, K., Revsbech, N.P., Kitazato, H., 2009. Nitrogen cycling in a deep ocean margin sediment (Sagami Bay, Japan). *Limnol. Oceanogr.* 54, 723–734.
- Gomes, F.M.C., Godoy, J.M., Godoy, M.L.D.P., Carvalho, Z.L., Lopes, R.T., Sanchez-Cabeza, J.A., Lacerda, L.D., Wasserman, J.C., 2009. Metal concentrations, fluxes, inventories and chronologies in sediments from Sepetiba and Ribeira bays: a comparative study. *Mar. Pollut. Bull.* 59, 123–133.
- Grasshoff, K., Kremling, K., Ehrhardt, M., 1999. *Methods of Seawater Analysis*. third ed. Wiley, New York.
- Huetzel, M., Ziebis, W., Forster, S., Luther, G.W., 1998. Advective transport affecting metal and nutrient distributions and interfacial fluxes in permeable sediments. *Geochim. Cosmochim. Acta* 62, 613–631.
- Kalas, F.A., Carreira, R.S., Macko, S.A., Wagener, A.L.R., 2009. Molecular and isotopic characterization of the particulate organic matter from an eutrophic coastal bay in SE Brazil. *Cont. Shelf Res.* 29, 2293–2302.
- Kjerfve, B., Ribeiro, C.H.A., Dias, G.T.M., Filippa, A.M., Quaresma, V.S., 1997. Oceanographic characteristics of an impacted coastal bay: Baía de Guanabara, Rio de Janeiro, Brazil. *Cont. Shelf Res.* 17, 1609–1643.
- Kleeberg, A., Herzog, C., 2014. Sediment microstructure and resuspension behavior depend on each other. *Biogeochemistry* 119, 199–213.
- Lerat, Y., Lasserre, P., Le Corre, P., 1990. Seasonal changes in pore water concentrations of nutrients and their diffusive fluxes at the sediment–water interface. *J. Exp. Mar. Biol. Ecol.* 135, 135–160.
- Li, Y.-H., Gregory, S., 1974. Diffusion of ions in seawater and in deep-sea sediments. *Geochim. Cosmochim. Acta* 38, 703–714.
- Loring, D.H., Rantala, R.T.T., 1992. Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth-Sci. Rev.* 32, 235–283.
- Lyons, W.B., Lent, R.M., Burnett, W.C., Chin, P., Landing, W.M., Orem, W.H., McArthur, J.M., 1996. Jellyfish Lake, Palau: regeneration of C, N, Si, and P in anoxic marine lake sediments. *Limnol. Oceanogr.* 41, 1394–1403.
- Marinho, C.C., Campos, E.A., Guimarães, J.R.D., Esteves, F.A., 2012. Effect of sediment composition on methane concentration and production in the transition zone of a mangrove (Sepetiba Bay, Rio de Janeiro, Brazil). *Braz. J. Biol.* 72, 429–436.
- Metzger, E., Simonucci, C., Viollier, E., Sarazin, G., Prévot, F., Jézéquel, D., 2007. Benthic response to shellfish farming in Thau lagoon: pore water signature. *Estuar. Coast. Shelf Sci.* 72, 406–419.
- Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.* 114, 289–302.
- Molisani, M.M., Marins, R.V., Machado, W., Paraquetti, H.H.M., Bidone, E.D., Lacerda, L.D., 2004. Environmental changes in Sepetiba Bay, SE. Brazil. *Reg. Environ. Change* 4, 17–27.
- Monteiro, F.F., Cordeiro, R.C., Santelli, R.E., Machado, W., Evangelista, H., Villar, L.S., Viana, L.C.A., Bidone, E.D., 2011. Sedimentary geochemical record of historical anthropogenic activities affecting Guanabara Bay (Brazil) environmental quality. *Environ. Earth Sci.* 65, 1661–1669.
- Ogrinc, N., Faganeli, J., 2006. Phosphorus regeneration and burial in near-shore marine sediments (the Gulf of Trieste, northern Adriatic Sea). *Estuar. Coast. Shelf Sci.* 67, 579–588.
- Rebello, A.L., Ponciano, C.R., Melges, L.H., 1988. Avaliação da produtividade primária e da disponibilidade de nutrientes na Baía de Guanabara. *An. Acad. Bras. Ci.* 60, 419–430.
- Rigaud, S., Radakovitch, O., Couture, R.-M., Deflandre, B., Garnier, C., Garnier, J.-M., Cossa, D., 2013. Mobility and fluxes of trace elements and nutrients at the sediment–water interface of a lagoon under contrasting water column oxygenation conditions. *Appl. Geochem.* 31, 35–51.
- Rozan, T.F., Taillefert, M., Trouwborst, R.E., Glazer, B.T., Ma, S., Herszage, J., Valdes, L.M., Price, K.S., Luther III, G.W., 2002. Iron–sulfur–phosphorus cycling in the sediments of a shallow coastal bay: implications for sediment nutrient release and benthic macroalgal blooms. *Limnol. Oceanogr.* 47 (5), 1346–1354.
- Rusch, A., Huettel, M., Forster, S., 2000. Particulate organic matter in permeable marine sands—dynamics in time and depth. *Estuar. Coast. Shelf Sci.* 51, 399–414.
- Sanders, C.J., Smoak, J.M., Naidu, A.S., Sanders, L.M., Patchineelam, S.R., 2010. Organic carbon burial in a mangrove forest, margin and intertidal mud flat. *Estuar. Coast. Shelf Sci.* 90, 168–172.
- Seeborg-Elverfeldt, J., Schlüter, M., Feseker, T., Kölling, M., 2005. Rhizon sampling of pore waters near the sediment–water interface of aquatic systems. *Limnol. Oceanogr. Methods* 3, 361–371.
- Souchu, P., Gasc, A., Collos, Y., Vaquer, A., Tourmier, H., Bibent, B., Deslous-Paoli, J.-M., 1998. Biogeochemical aspects of bottom anoxia in a Mediterranean lagoon (Thau, France). *Mar. Ecol. Prog. Ser.* 164, 135–146.
- Warnken, K.W., Santschi, P.H., Roberts, K.A., Gill, G.A., 2008. The cycling and oxidation pathways of organic carbon in a shallow estuary along the Texas Gulf Coast. *Estuar. Coast. Shelf Sci.* 76, 69–84.