

NITROGEN, PHOSPHORUS AND GRANULOMETRIC CHARACTERIZATION IN NEARSHORE SEDIMENTS OF GUANABARA BAY: TENTATIVE APPLICATION OF A SOLID PHASE DIAGENETIC MODEL

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INTRODUCTION

The processes of removal and release of phosphorus and nitrogen through the sediment/water interface are important for the functioning of aquatic ecosystems. They become even more relevant in shallow coastal waters characterized by reduced water renewal.

Sedimentary dynamics affect the concentration and remineralization of biogenic elements in sediments. The deposition of finest material provides exchange sites in clay minerals, and favours inorganic nutrients adsorption (Klump and Martens, 1981; Boatman and Murray, 1982).

The regeneration of organic matter is also related to sediment grain size. Changes in sediment surface:volume ratio affect the bacterial population development (Mann, 1982). Moreover, the modification of porosity, permeability, and proportion of mineral and organic material. can alter the magnitude of molecular diffusion and advection effects (Bernier, 1980), and vertical distribution of elements in sediment.

This work assesses the influence of qualitative variation of bottom sediment on vertical distribution of total phosphorus and nitrogen concentration, and applies a solid phase diagenetic model to estimate nutrient fluxes.

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MATERIALS AND METHODS

Site description - Guanabara Bay (Rio de Janeiro State, SE Brazil) is an estuarine complex with about 400 km². Formed by a Pleistocenic fluvial valley flooding, during Flandrian marine transgression, it is now surrounded by densely inhabited and industrialized cities.

The great continental sediment loading has been increased by anthropogenic action, through the alteration and disturbance of natural water courses, removal of plant cover and mangrove forests in drainage basins, and indiscriminated dumping.

Due to the morphology of Guanabara Bay, a great part of this solid load is retained in the water body. This is, together with artificial eutrophication, its main environmental problem.

Sampling -Five sampling stations were chosen in different sediment types along the bay (Fig. 1). Sampling was made in January 18, and March 4, 1990, during ebb-tide. All samples corresponded to subtidal sediments, except IF1, at an intertidal mudflat.

Samples were collected with a 5-cm diameter corer, sectioned in 5 cm intervals, till a 20-cm depth. Each section was placed in polythene bags, kept under ice and stored in the dark, for 1-2 hours, until analyses.

Samples were dried at 70°C during 48 h, homogenized, part being reserved for granulometric analysis. The rest was grinded and passed through a 1-mm mesh, and kept dry for chemical analysis.

Total phosphorus was measured following sediment digestion with potassium peroxodisulphate in acid medium (Nelson, 1987) followed by spectrophotometric determination as reactive phosphate (Grasshoff et al., 1983).

Wet sample oxidation was utilized for total nitrogen analysis, using sulfuric acid-hydrogen peroxic mixture (Rowland and Grimshaw, 1985), and turbidimetric reading of resulting ammonia by addition of Nessler reactant (Krug et al., 1979).

Organic matter content was measured gravimetrically, by loss on ignition at 550°C after 2 hours (Williams, 1985). Mathematical fit described in Hakanson and Jansson (1983) was applied to estimate organic carbon.

Granulometric analysis was carried out by sieve and decantation (EMBRAPA, 1987). The calculated parameters were the mean (M_z) and kurtosis (K_g) from Folk and Ward (1957), standard deviation (σ) from Inman (1952), and skewness (Warren, 1974). pH was determined in a mixture of 1 g of dry sediment and 25 ml distilled deionized water, after agitation (EMBRAPA, 1987).

RESULTS AND DISCUSSION

Physical description - Sediment collected in station IF1, the more degraded, showed a black color, giving off strong sulphidic odor. The mud flat is almost completely filled with detritus carried from a garbage deposit, which impede the sampling of a deeper core.

In station IF2, there was a thin (3 - 5 mm) superficial clear layer; the rest was gray-greenish sulphidric sand. Also in station BV, the more oceanic and less impacted site, the surface sediment (5 cm) was clear coarse sand, becoming gray with depth. In all depths, there were large amounts of mussel shell fragments.

Samples from station RB, located near a shipyard and fisheries industry, were black sulphidric sand. In station PP, sediment was a greenish silty-clay mud, without smell.

Minimum pH values were recorded at station IF1, and maxima at station BV, a fact that indicates the influence of offshore waters. Vertical changes did not exceed 1.5 units.

Textural parameters exhibited vertical variability in stations BV, RB, and PP (Tab. 1), characterized by sediments with a bimodal distribution. This could indicate that these areas are subjected to fluctuations in depositional processes, with changes in sediment type and possibly an increase in deposition rates, as reported by Amador (1980). This can be a consequence of increasing anthropogenic loading, sediment resuspension and current transport, and marine reworking of probably fluvial material (Suguio, 1973; Amador and Ponzi, 1974).

In fact, the shore near station BV is formed by highly weathered crystalline rock, with big quartz grains and a lot of clay minerals. The carrying of this material, enhanced by adjacent buildings, could be responsible for the reduction in selection from subsurface to surface sediments.

Sediment distribution in stations RB and PP changes from symmetrical to negative symmetry from surface to subsurface. In both stations the occurrence of platicurtic sediments indicates a bimodal distribution. In station RB, there is an increase in bimodality from subsurface to surface, while in station PP it is present in the deepest layer.

Nitrogen and phosphorus concentrations - Concentrations of N and P in surficial sediments ranged from 0.15 mg P . g⁻¹ in station PP to 1.62 mg P . g⁻¹ in station IF1, and from 0.56 mg N . g⁻¹ in station BV to 6.00 mg N . g⁻¹ in station IF1 (Tab. 2). In spite of the great organic matter loading, these values are unexpectedly not so high.

Similarity between stations, in terms of total phosphorus and nitrogen grade in surface layer, was tested using sequential χ^2 . For phosphorus, it was found that stations IF1 and IF2 are significantly different ($P=0.05$), and the others are similar. For nitrogen, the only different site is station IF1.

Concentrations of total phosphorus were higher than total nitrogen, as a reflection of the low superficial N:P ratio (mass) recorded in all stations (Fig. 2).

Except in station RB, C:N ratios were higher than 10, reaching values beyond 70 in station IF2. These ratios can indicate the influence of terrestrial sources of organic matter (Valiela, 1984), or the preferential release of organic nitrogen (Martens et al. 1978).

Vertical changes of total nitrogen and phosphorus - In general, phosphorus and nitrogen decrease with depth (Fig. 3), suggesting the existence of an equilibrium

between loading, remineralization and remobilization of this elements to aqueous phase, accordingly to diagenetic model (Berner, 1971, 1980).

Vertical profiles different from those expected by this model (stations RB and BV for nitrogen and organic carbon; station PP for organic carbon) may be due to changes in autochthonous and allochthonous inputs, bioturbation, resuspension and superficial sediment transport processes. These discordances can also reflect past conditions, with physico-chemical release and removal favoring organic and/or inorganic nitrogen accumulation in sediment, prevailing upon phosphorus forms.

Although all these agents can act jointly with variable relevance, granulometric distributions, indicating depositional changes, hint that physical events of change in depositional environment and bioturbation are the predominant ones.

The increase of N:P ratios with depth, at least in the first 10 cm, can be explained by the fact that organic nitrogen usually is bonded to structural components, more resistant to decomposition than phosphorus bonded compounds (Bowden, 1984). In fact, nitrogen behavior, decreasing slowly with depth, seems to control both N:P and C:N ratios in station IF2..

In spite of the high C:N ratios in most samples, there are great vertical changes, with values even lower than the average ratio in marine phytoplankton. These values are coincident with low organic carbon, suggesting that phosphorus and nitrogen are mainly in inorganic form in these layers.

Estimate of remineralized nutrient flux - Assuming a steady state deposition and burial, the diagenetic equation for first order decomposition kinetics (Berner, 1974, 1980) can be used:

$$G_z = G_m^o \exp [(-k/w) \cdot z] + G \quad (1)$$

and

$$G_m^o = G_o - G \quad (2)$$

where G_z is the element concentration in any depth z , k is a first order rate constant, w is the sediment deposition rate, G_m^o expresses the metabolizable fraction deposited, G_o the input concentration and G is the residual concentration. So, regenerated flux through sediment-water interface (J_{out}) can be estimated as:

$$J_{out} = w \cdot G_m^o = w (G_o - G) \quad (3)$$

In the same way, total depositional (J_{in}) and burial flux (J_{bur}) can be inferred by:

$$J_{in} = w \cdot G_o \quad (4)$$

and

$$J_{bur} = w \cdot G \quad (5)$$

Regenerated phosphorus or nitrogen fraction is given by:

$$\% \text{ turnover} = J_{out} / J_{in} \cdot 100 \quad (6)$$

Although J_{out} is usually defined as the flux through sediment-water interface (Klump and Martens, 1987), we believe that **potential flux** is a better term, since not all the remineralized nutrient is effectively transported to the water column, a part being retained as inorganic insoluble forms in the sediment.

To estimate nitrogen and phosphorus potential flux, curves obtained by extrapolating G_0 and G were adjusted to results. These curves were best fitted to equation (1). Results are listed in tables 3 and 4.

For flux calculations, the mean deposition rate given by Amador (1980) of $0.7875 \text{ cm} \cdot \text{y}^{-1}$ were used for the bay area where all stations are localized. This rate was corrected by average superficial sediment of $1.256 \text{ g} \cdot \text{cm}^{-3}$ (Amador 1980), equivalent to $0.988 \text{ g} \cdot \text{cm}^{-2} \cdot \text{y}^{-1}$. The change of density in function of compaction is $0.488 \text{ g} \cdot \text{cm}^{-3}$ in 4 m (Amador, 1980), assumed to be constant with depth.

The main criticism to this model concern the difficulties to measure G_0 with precision, since organic matter is continuously altered after deposition. This does not affect our data, because the surficial sediment layer is in fact a mean of the first 5 cm. However, extrapolation to the interface do not solve completely this problem, mainly in very reactive sediments.

Another problem is the temporal variation in inputs. Lasaga and Holland (1976) showed that input oscillations will only yield a non-steady state behavior in pore water concentrations if the period is less than $\frac{w^2}{D_s}$ (D_s = molecular diffusion coefficient). For our data, and diffusivities of nitrogen and phosphorus dissolved compounds ($0.4 - 6.0 \cdot 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$; Klump & Martens 1987), the period oscillation must be less than 200 - 3000 years. In spite of this, Klump and Martens (1987) confirm that steady state on dissolved pore water constituents profile is not inconsistent with non-steady state input. Actually, our results suggest a change in deposited material, but only more accurate measure of deposition rate and pore water chemistry could answer this question, which transcend our original purposes.

However, in face of the scarce data on mass transfer in this strongly polluted estuary, and of resources to make it on a suitable form, this speculation become pertinent. Furthermore, Klump and Martens (1987) applied successfully this model, comparing results obtained from direct "*in situ*" measurements to stoichiometric estimation based on annual sulfate-reduction rates, with good agreement.

Rebello *et al.* (1988) report a mean phytoplankton productivity in central Guanabara Bay of $1.06 \cdot 10^3 \text{ g C} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$, which according to the Redfield C:N:P ratio implies a demand of about $0.15 \cdot 10^3 \text{ g N} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$ and $0.03 \cdot 10^3 \text{ g P} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$. These authors argued that the high anthropogenic inputs are not enough to support these production levels, suggesting that remineralization in the water column and sediment might be important contributors. The potential role of sediment is confirmed by model application to our data (Tab. 5).

Concluding remarks - Sediments of Guanabara Bay are an important potential source of inorganic phosphorus and nitrogen to primary production, and may affect the results of announced water quality recuperation programs. There could be a great lag time between the implantation of sewage treatment plants, and reduction of primary production. Spiller and Auclair (1986) described a lapse of 7 to 14 years between the end of organic loading and water quality responses in lakes. Even having a residence time much lower than any lake, the bay circulation was seriously affected by sediment loading, especially in the more degraded western shore. Another suggested action to

improve water quality is the dredging of the main channels between Fundão and Governador Islands and the continent. Although dredging will improve water flow, it requires careful studies, since it can release, besides nutrients, heavy metals retained in this anoxic reductive environment.

The detected depositional changes are reflected in nitrogen, phosphorus and organic carbon profiles, although there is no evident correlation. Rather, these recent changes in sedimentary environment can be responsible for the "noise" in chemical constituent profiles.

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ABSTRACT

Total nitrogen, phosphorus and organic carbon were measured in sediment profiles, and correlated to granulometric distribution in different depth levels of nearshore sediments in Guanabara Bay (Brazil). This paper assesses the pool of these elements and the influence of sedimentary dynamics on it, in five different depositional environments. Textural parameters exhibit vertical changes in three stations. This is an evidence of changes in depositional processes, reflected by anomalous nutrient profiles. However, there was no correlation with granulometry, showing rather an erratic behaviour. Surficial sediment TN and TP ranged from 0.56 to 6.00 mg · g⁻¹ and 0.15 to 1.62 mg · g⁻¹, respectively. Tentative application of solid phase diagenetic model estimates fluxes of about 1.1 - 24.7 g P · m⁻² · y⁻¹ and 2.2 - 67.2 g N · m⁻² · y⁻¹. These values correspond to 4 - 82% of phosphorus and 2 - 45% of nitrogen annual average phytoplanktonic demand.

Key words: Nutrientes, granulometry, estuarine sediments, remineralization

RESUMO

Os teores de nitrogênio, fósforo total e carbono orgânico e a textura granulométrica foram analisados em diferentes níveis de profundidade de sedimentos costeiros na Baía de Guanabara (Brasil). Este trabalho teve por objetivo estimar os estoques destes elementos e avaliar a influência da dinâmica sedimentar sobre estes, em cinco diferentes ambientes deposicionais. Os parâmetros texturais exibiram variações verticais em três estações. Esta é uma evidência da ocorrência de modificações nos processos deposicionais, originando perfis anômalos de nutrientes nestes testemunhos. No entanto, este comportamento não se correlacionou com a granulometria, sendo, ao contrário, errático. A concentração de NT e PT no sedimento superficial variou de 0,56 a 6,00 mg · g⁻¹ e 0,15 a 1,62 mg · g⁻¹, respectivamente. Através da aplicação de um modelo diagenético de fase sólida foram estimados fluxos de cerca de 1,1 - 24,7 g P · m⁻² · ano⁻¹ e 2,2 - 67,2 g N · m⁻² · ano⁻¹. Estes valores correspondem a 4 - 82% da demanda média anual de fósforo pelo fitoplâncton, e 2 - 45% da de nitrogênio.

Palavras-chave: Nutrientes, granulometria, sedimentos estuarinos, remineralização.

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