ARTICLE IN PRESS

Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Aragonite saturation state in a tropical coastal embayment dominated by phytoplankton blooms (Guanabara Bay – Brazil)

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ARTICLE INFO

Keywords:
Carbonate chemistry
Coastal eutrophication
Coastal acidification
Phytoplankton blooms

ABSTRACT

The dynamics of the aragonite saturation state (Ω_{arag}) were investigated in the eutrophic coastal waters of Guanabara Bay (RJ-Brazil). Large phytoplankton blooms stimulated by a high nutrient enrichment promoted the production of organic matter with strong uptake of dissolved inorganic carbon (DIC) in surface waters, lowering the concentrations of dissolved carbon dioxide (CO_{2aq}), and increasing the pH, Ω_{arag} and carbonate ion (CO_3^{2-}), especially during summer. The increase of Ω_{arag} related to biological activity was also evident comparing the negative relationship between the Ω_{arag} and the apparent utilization of oxygen (AOU), with a very close behavior between the slopes of the linear regression and the Redfield ratio. The lowest values of Ω_{arag} were found at low-buffered waters in regions that receive direct discharges from domestic effluents and polluted rivers, with episodic evidences of corrosive waters ($\Omega_{arag} < 1$). This study showed that the eutrophication controlled the variations of Ω_{arag} in Guanabara Bay.

1. Introduction

The human activities are altering the biogeochemical cycles of essential elements at unprecedented levels (Howarth et al., 2011). The burning of fossil fuels and land-use-change activities have been altering the global cycle of carbon by increasing the emissions of carbon dioxide (CO_2) to the atmosphere (IPCC, 2013). The global average atmospheric CO_2 has increased from 277 ppmv in 1750 to approximately 400 ppmv in 2015, and, together with the increase of other greenhouse gases, are driving important environmental changes (Gattuso et al., 2015; Le Quéré et al., 2016). Taking account the global CO_2 budget calculated for the period between 2006 and 2015, approximately 43% of the total anthropogenic CO_2 emissions remained in the atmosphere (4.5 ± 0.1 Gt C yr^{-1}), whereas the oceans sequestered approximately 25% (2.6 ± 0.5 Gt C yr^{-1}) (Le Quéré et al., 2016).

When the CO_2 dissolves in the water, a series of reactions and processes takes place, producing non-ionic and ionic compounds (Millero, 2007; Dickson, 2010). The dissolved CO_2 (CO_{2aq}) is the dominant carbon dioxide species when the pH is lower than 5, however, at higher pH, the CO_{2aq} ionizes to form bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) anions (Dickson, 2010). The sum of CO_{2aq}, HCO_3^- and CO_3^{2-} comprehends the dissolved inorganic carbon (DIC). The CO_{2aq} is proportional to the partial pressure of CO_2 (pCO_2) in the water. When CO_2 hydrates and/or ionizes, it releases hydrogen ions (H^+), lowering the pH. Therefore, the absorption of CO_2 by the oceans results in a decrease in pH and CO_3^{2-} concentrations. Low pH values can inhibit and/or hinder the ability of many marine organisms to form calcium carbonate ($CaCO_3$) skeletons and shells (Gattuso et al., 2015). In extreme scenarios, this can promote dissolution of $CaCO_3$ because the water becomes undersatuated with respect to $CaCO_3$ minerals (Feely et al., 2008; Zhai et al., 2015). However, studies also showed that some organisms could be resistant to ocean acidification effects. A study conducted in an Arctic coastal region showed that the taxonomic composition of zooplankton species remained unaffected by changes in pCO_2/pH (Aberle et al., 2013). In addition, the abundance of some species of zooplankton from the Bay of Bengal were found to be

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http://dx.doi.org/10.1016/j.marpolbul.2017.10.064
Received 28 September 2017; Received in revised form 17 October 2017; Accepted 22 October 2017
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Please cite this article as: Cotovicz, L.C., Marine Pollution Bulletin (2017), http://dx.doi.org/10.1016/j.marpolbul.2017.10.064

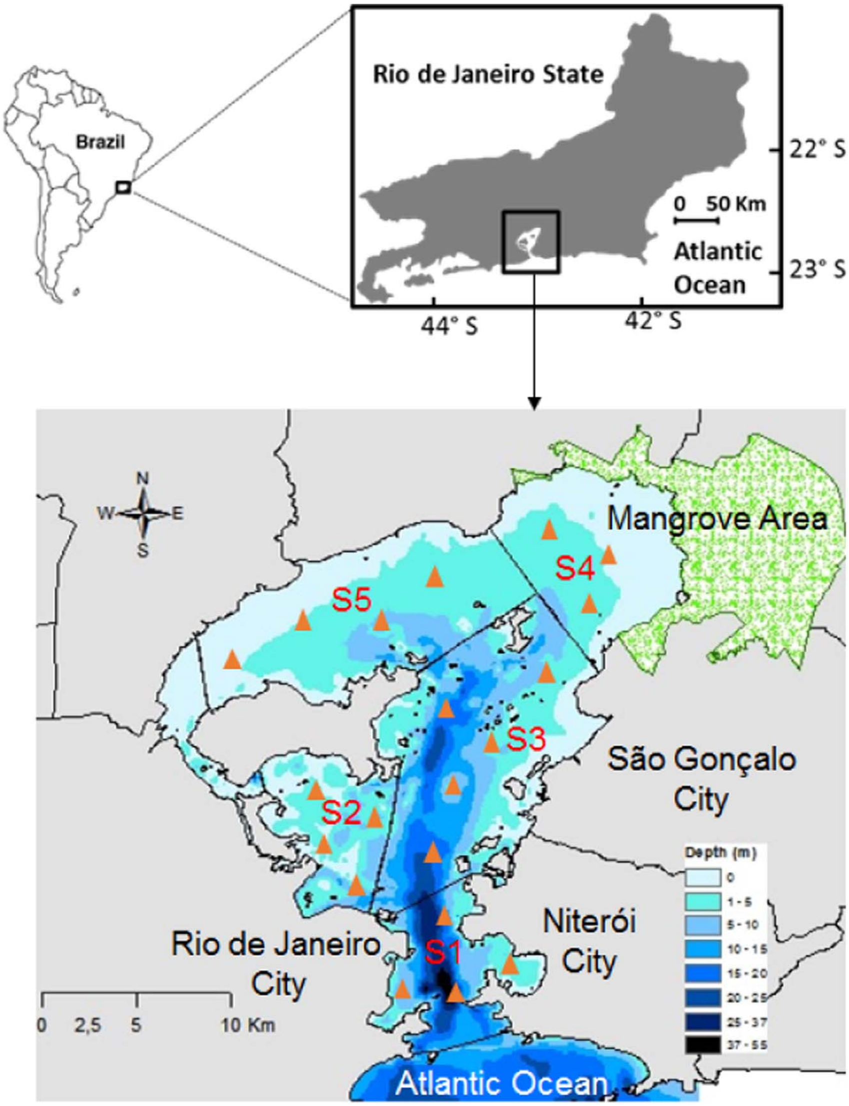

Fig. 1. Map of Guanabara Bay. The bay was divided into five sectors (S1 to S5). The red triangles represent the sampling stations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

significantly higher under elevated CO_2 levels (Biswas et al., 2012). In this way, the effects of ocean acidification seem to be specific considering different organisms and ecosystems, with winners and losers under high CO_2 conditions.

The $CaCO_3$ saturation state of seawater (Ω) with respect to a particular $CaCO_3$ mineral can be calculated to infer the tendency of precipitation or dissolution (Dickson, 2010). The aragonite is usually the principal form of $CaCO_3$ in shallow waters and is approximately 50% more soluble than calcite (Morse et al., 2007; Mucci, 1983). This mineral is essential to many phytoplanktonic and benthonic species (Gattuso et al., 2015). Due to this, the studies of saturation state of aragonite (Ω_{arag}) have received attention in the last 10 years, especially in coastal environments (Feely et al., 2010; Zhai et al., 2015; Hu et al., 2017; Xue et al., 2017). The Ω_{arag} can be defined by the formula:

$$\Omega_{ararg} = [Ca^{2+}]\,[CO_3^{2-}]/K_{sp}(arag)$$

where, $[Ca^{2+}]$ $[CO_3^{2-}]$ is the observed ion product between calcium and carbonate concentration and K_{sp}(arag) is the solubility product of aragonite in seawater. $\Omega_{arag} > 1$ indicates that the precipitation of aragonite is favored and the minerals are stable; $\Omega_{arag} < 1$ indicates that aragonite minerals are unstable in the water and can dissolve; $\Omega_{arag} = 1$ indicates equilibrium between precipitation and dissolution. The ocean acidification is commonly referred to the modifications in marine carbonate chemistry, driven by the increase of atmospheric CO_2, with the increase of CO_{2aq}, and decrease of pH, CO_3^{2}, Ω and the buffer capacity of seawater (Doney et al., 2009). This problem has recently taken attention from the scientific community due to projected threats that could affect marine species, communities and ecosystems (Doney et al., 2009; Kroeker et al., 2010; Gattuso et al., 2015).

In coastal waters, the variations of carbonate parameters are also strongly affected by the mixing processes between freshwater and seawater, upwelling and eutrophication, and the controlling mechanisms of Ω_{arag} are more complex than in the open ocean (Salisbury et al., 2008; Cai et al., 2011; Duarte et al., 2013; Zhai et al., 2015; Xue et al., 2016; Hu et al., 2017). The coastal ocean responds differently from the open ocean to CO_2 inputs, and can be more vulnerable to negative effects of ocean and coastal acidification (Zhai et al., 2015). This vulnerability was described in some coastal zones due to the influence of metabolic processes adding high CO_2 into the waters, and associated with low values of pH and $\Omega_{arag} < 1$ in sub-surface and bottom waters (Feely et al., 2008, 2010; Cai et al., 2011; Zhai et al., 2015). This occurs because the anthropogenic inputs of organic matter and nutrients associated with strong eutrophication processes have fueled massive algal blooms, which deplete the oxygen and release CO_2 when the organic matter is respired (Cai et al., 2011; Sunda and Cai, 2012; Wallace et al., 2014). Previous studies on eutrophication in coastal waters have been focused on the investigation of the nutrient, chlorophyll *a* (Chl *a*) and oxygen levels (hypoxia and anoxia) in the waters (Nixon, 1995; Bricker

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