ABSTRACT

This perspective paper aims at presenting the current knowledge on the processes of ocean acidification (OA) and coastal acidification (CA) in the Brazilian coastal ocean. We define and differentiate the processes of OA and CA: the first driven by the actual global increase of atmospheric carbon dioxide (CO₂); the second driven by a combination of ocean uptake of atmospheric CO₂ and other local/regional chemical additions or subtractions in aquatic ecosystems at the land-ocean interface. Regarding OA, we have centered our analysis on the data available for the main water masses along the Brazilian coast: South Atlantic Central Water (SACW), Tropical Water (TW), and Coastal Water (CW). The few data available for the shallow coastal waters (< 200 m depth) of the continental shelf reveal an increase in the anthropogenic component of the total dissolved inorganic carbon (DIC) pool in the SACW, with a decline in the ocean pH (over two decades; 1993-2013), and in the saturation state of calcium carbonate (CaCO₃) minerals. We could not find OA trends for TW and CW because no data was available. Overall, the colder water masses (SACW, Plata Plume) have lower buffering capacity and simulations show that will potentially experience earlier negative OA impacts than the warmer waters masses (TW, Amazon Plume). Regarding CA, we have identified some local/regional studies investigating the carbonate chemistry in nearshore/estuarine ecosystems, particularly on the quantification of sources and sinks of CO₂ and determining short-term variabilities. Apparently, spreading coastal eutrophication in Brazil can enhances or reduces the process of OA, depending on the net ecosystem metabolism in combination with other chemical alterations. However, we could not find medium-long term acidification trends due to the limited data. There is a limited capacity to produce long time-series of carbonate chemistry parameters in key ecosystems and regions along the Brazilian coast. This lack of past information hinders and impairs the...
scientific community for identifying potential patterns of acidification along the Brazilian coast. We call for an urgent action in Brazil, with emphasis on the establishment of moored buoys/stations and/or scientific programs in the long term with continuous, real-time measurements of the main carbonate chemistry parameters.

**Keywords**: ocean acidification, coastal acidification, coastal eutrophication, continental shelf, Southwestern Atlantic Ocean.

**RESUMO**

O presente artigo tem como objetivo apresentar o estado atual de conhecimento dos processos de acidificação do oceano (OA) e acidificação costeira (CA) no Brasil. Definimos e diferenciamos tais processos: o primeiro ocasionado pelo aumento global da concentração de CO\textsubscript{2} na atmosfera; o segundo ocasionado pela combinação do sequestro de CO\textsubscript{2} pelo oceano e outras adições ou subtrações locais/regionais de compostos químicos em ecossistemas aquáticos costeiros. Considerando a OA, a análise foi centrada nas principais massas de água presentes ao longo da costa do Brasil: Água Central do Atlântico Sul (SACW), Água Tropical (TW) e Água Costeira (CW). Os poucos dados disponíveis para águas rasas costeiras (< 200 m profundidade) revelam um aumento da contribuição antropogênea nas concentrações de carbono inorgânico dissolvido (DIC) na SACW, com declínio no pH (ao longo de duas décadas – 1993-2013), e na saturação dos minerais de carbonato de cálcio (CaCO\textsubscript{3}). Não encontramos tendências para TW e CW devido à falta de dados disponíveis. As massas de água mais frias (SACW, Pluma do Rio da Plata) têm menor capacidade de tamponamento, e simulaciones mostram que irão sentir os efeitos da acidificação antes que as massas de água mais quentes (TW, Pluma do Rio Amazonas). Considerado a CA, identificamos alguns estudos locais/regionais sobre a química do sistema carbonato em ecossistemas costeiros/estuarinos centrados na quantificação de fontes e sumidouros de CO\textsubscript{2} e determinações de variação temporal de curta escala. Aparentemente, o processo de eutrofização costeira, amplamente verificado na costa do Brasil (particularmente em regiões densamente povoadas), pode amplificar ou atenuar o processo de acidificação, dependendo do metabolismo dos ecossistemas, em combinação com outras alterações químicas. Entretanto, não encontramos tendências de acidificação de médio e longo prazo devido à falta de estudos. Existe uma restrita capacidade em produzir longas séries temporais de parâmetros do sistema carbonato em ecossistemas-chave ao longo da costa do Brasil. Dessa forma, chamamos a atenção para uma urgente ação no Brasil, com ênfase no estabelecimento de estações oceanográficas (boias oceanográficas, fundeios) e/ou programas científicos no longo prazo que contemplem medições contínuas e de alta frequência dos principais parâmetros do sistema carbonato marinho.

**Palavras-chave**: acidificação dos oceanos, acidificação costeira, eutrofização, plataforma continental, Oceano Atlântico Sudoeste.

**INTRODUCTION**

The current CO\textsubscript{2} concentration in the atmosphere is unprecedented over the past 3 million years (Willeit et al., 2019). The current rate of change of atmospheric CO\textsubscript{2} is also
unprecedented in at least the past 800,000 years (IPCC, 2021). The atmospheric CO₂ peaked in May-2021 at a monthly average of 419 ppm (UCSD-SIO 2021), which is the highest level since accurate measurements began 63 years ago; furthermore, the CO₂ levels have reached a 50% increase compared to the preindustrial average. This dramatic increase is driven by anthropogenic emissions, mainly from combustion of fossil fuels and land use changes. For the last decade (2010-2019), the anthropogenic CO₂ emissions from fossil fuel combustion and land use change were, respectively, 9.6 ± 0.5 GtC yr⁻¹ and 1.8 ± 0.7 GtC yr⁻¹ (Friendlingstein et al., 2020). The ocean has absorbed about 23% of this excess of CO₂ at 2.6 ± 0.6 GtC yr⁻¹ (Friendlingstein et al., 2020).

Considering the past two and a half centuries, the oceanic uptake of anthropogenic CO₂ is about 623 Pg CO₂ (Frindligestein et al., 2020). This additional uptake of CO₂ increases its flux across the ocean-atmosphere interface, and leads to changes in the marine carbonate system (Millero, 2007). Such changes include the increase in seawater pCO₂ and reduction in seawater pH and saturation state of CaCO₃ minerals, such as calcite and aragonite (Caldeira & Wickett, 2003; Feely et al., 2004). The changes in the ocean carbonate system linked to the oceanic uptake of anthropogenic CO₂ are commonly termed as “ocean acidification” (OA) (Caldeira & Wickett, 2003; Doney et al., 2009). These changes are not restricted to open-ocean waters, being also documented in estuarine and coastal waters (Doney et al., 2020). According to the last IPCC report, the ocean pH will decrease from a pre-industrial level around 8.1 to a level of 7.9 at end of this century based on the intermediate greenhouse gas emissions scenario (SSP2-4.5; IPCC 2021). The OA has likely problematic consequences for the marine life, with expected and already described impacts spanning from single cells to entire ecosystems and particularly critical for organisms producing CaCO₃ (Gattuso et al., 2015). Most studies have investigated the effects of OA on isolated organisms; however, the effects on communities and ecosystems are still poorly understood (Gattuso et al., 2015; Doney et al., 2020). In addition, the OA will likely affect primary productivity, mariculture, fisheries, and other important ecosystems services (Doney et al., 2020).

In addition to this alteration on the marine carbonate chemistry driven by global rise of atmospheric CO₂, there are local/regional modifications of the carbonate chemistry driven by other coastal chemical additions and subtractions that can be triggered by natural or anthropogenic processes, known as “coastal acidification (CA)” (Feely et al., 2020). These chemical changes include (but not limited to) organic matter respiration, freshwater inputs, advection of water masses (lateral and vertical transport), atmospheric pollution, and anthropogenic loading of nutrients and organic matter. Particularly, in densely populated coastal regions, the excessive anthropogenic inputs of organic matter and nutrients associated with eutrophication have fueled massive algal blooms, which deplete the oxygen and release CO₂ when the organic matter is respired (Cai et al., 2011; Wallace et al., 2014). Recent studies have been reported that coastal eutrophication is one of the most contributors to the process of CA (Cai et al., 2011; Wallace et al., 2014). The local/regional effects of acidification in some regions may exceed those expected from the atmospheric inputs (Xue et al., 2017; Cotovicz et al., 2018). However, in some regions the process of eutrophication can counter-acts the acidification by stimulating the growth of primary producers with uptake of dissolved CO₂, and rising the pH (Cotovicz et al., 2015, 2021). In this way, the land-based pollution, coastal development and eutrophication can modify the carbonate chemistry in opposite directions.
Brazil is a country with a long coastline (9,000 km), extending from equatorial (5° N) to warm-temperate latitudes (33° S) (Figure 1). The land-ocean aquatic continuum in Brazil hosts a large diversity of environments, comprising varied coastal typologies (lagoons, coastal embayment’s, river deltas, mangrove forests, salt marshes, seagrass meadows, rodolith beds, coral reefs, coastal upwelling, among others; Knoppers et al., 2009). Overall, the Northeast and the Southeast shelf waters are oligotrophic due to little freshwater input and influenced by the South Equatorial Current (SEC). The North and South shelves are the most productive regions, receiving continental inputs mainly from the Amazon and Plata Rivers, respectively. In addition, there is a considerable contribution of nutrients from anthropogenic sources affecting many estuarine and continental shelf waters, particularly in densely populated areas. The present perspective paper aims to i) report the present-day state of knowledge about the process of OA in the main water masses along the Brazilian coast; ii) report the present-day state of knowledge about the process of CA in ecosystems along the land-ocean aquatic continuum in Brazil; iii) present a brief overview about vulnerabilities, impacts, challenges and perspectives in this context of OA and CA. Here we considered the coastal zone as the estuarine, nearshore, and continental shelf waters until to the 200 m depth (Crossland et al., 2005). We have identified an alarming lack of understanding regarding the process of acidification along the Brazilian coast, mostly due to the low availability of long time series regarding the main carbonate chemistry parameters.

Figure 1 – Composite map of the South Atlantic Ocean, showing the main surface currents of the South Atlantic Subtropical Gyre with emphasis in the western region (Brazilian Coast). NBC = North Brazil Current; BC: Brazil Current; MC: Malvine Current; ACC: Antarctic Circumpolar Current; SAC: South Atlantic Current; SSEC: Southern branch of the South Equatorial Current. The color bar represents the average sea surface temperature from WOCE Global Hydrographic Climatology (WOCE, 2006), which was created using Ocean Data View software. The white dots represent the isobaths of 200 m (considered here as the limit of the coastal zone).
Differentiating the processes of ocean acidification (OA) and coastal acidification (CA)

To understand the processes of OA and CA, it is important to present briefly the marine carbonate system. When CO₂ dissolves in the seawater (through the solubility equilibrium of CO₂ between air and seawater), a series of reactions takes place, producing non-ionic and ionic compounds (Millero, 2007). The CO₂ hydrates producing carbonic acid (H₂CO₃). However, this reaction is very slow compared to the ionization of H₂CO₃. For this, at equilibrium, the H₂CO₃ represents only about 1/1000 of the concentration of dissolved CO₂ (CO₂aq). The two unionized species (H₂CO₃ + CO₂aq) are referred as CO₂*. The CO₂* is the dominant specie when the pH is < 5. At higher pH typical of seawater (~8.10), the CO₂* ionizes to form bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻). The sum of CO₂, HCO₃⁻, and CO₃²⁻ comprehends the dissolved inorganic carbon (DIC). The seawater pCO₂ is proportional to the amount of CO₂*. When CO₂ hydrates and/or ionizes, it releases hydrogen ions (H⁺) in seawater, lowering the pH. For that reason, more CO₂ in the atmosphere means more CO₂ in the seawater, with a decline in the values of pH and CO₃²⁻ (Millero, 2007). Furthermore, lower CO₃²⁻ concentrations means lower saturation state of calcite (Ω_Ca) and aragonite (Ω_Ar), which are the two primary biogenic carbonate-containing mineral that occur in seawater. The Ω_Ca and Ω_Ar infer the tendency of precipitation or dissolution of calcite and aragonite, respectively. The saturation state Ω(X) is defined by:

Ω(X) = [Ca²⁺][CO₃²⁻]/Ksp (X)

Where X refers to a particular CaCO₃ mineral (calcite or aragonite), Ca²⁺ is the concentration of calcium, CO₃²⁻ the concentration of carbonate, and Ksp is the solubility product of CaCO₃ (calcite or aragonite) in seawater at particular salinity, temperature, and pressure. In summary, the OA refers to all these changes in seawater carbonate system linked to increase of atmospheric CO₂, which includes the increase of DIC (mostly in the forms of HCO₃⁻ and CO₂*), and decrease of pH, CO₃²⁻, Ω_Ca and Ω_Ar.

The “coastal acidification” (CA) is a term normally used to describe the changes in seawater carbonate chemistry due to acidification occurring along coastlines (Feely et al., 2020). The CA was defined by Feely et al. (2020) as “a combination of ocean uptake of atmospheric CO₂ and other coastal chemical additions and subtractions that can be driven by natural or anthropogenic processes” (Feely et al., 2020). The first important observation from this definition is that the process of OA is explicit in the definition of CA. The second important observation is that the acidification in coastal zones is very complex because it combines many processes that have the potential to modify and/or increase the susceptibility of coastal ecosystems to OA (Feely et al., 2020; Cai et al., 2011). Such chemical alterations were observed in several coastal regions worldwide, particularly the freshwater influx, advection of allochthonous water masses, anthropogenic and natural loading of organic matter and nutrients. The anthropogenic loads of organic matter and nutrients have been described as important drivers of seawater acidification, leading to enhanced levels of organic matter respiration and desoxygenation (Cai et al., 2011; Wallace et al., 2014; Cotovicz et al., 2018). However, in tropical coasts colonized predominantly by mangrove forests the major contribution to organic matter discharges have been seen from this source (Cavalcante et al., 2021).
The OA process in open ocean waters is driven mainly by external loading of CO₂ (atmospheric inputs), whereas CA process is driven by a combination of external (global-driven) and internal processes (local/regional-driven). The OA was referenced in literature as “the other problem of CO₂” (in addition to the global warming; Doney et al., 2009), whereas CA was considered “the other problem of eutrophication” (in addition to the deoxygenation; Wallace et al., 2014). However, we must keep in mind that the increase of nutrient runoff can enhances the coastal primary production in several ecosystems, overpassing the rates of microbial respiration, thus increasing the pH (Cotovicz et al., 2018; Carstensen & Duarte, 2019). This means that the historical land-derived nutrient enrichment (eutrophication) can also counter-acts the process of acidification in estuarine and nearshore waters (Cotovicz et al., 2015; Tseng et al., 2011; Cotovicz et al., 2018). The ecosystem response to increased nutrient runoff seems to be largely site-specific. Furthermore, as highlighted above, other processes can influence the coastal chemical additions and subtractions and thus contributing to enhance or counter-act the process of CA (Feely et al., 2020).

There is a marked increase in studies investigating the OA process in the world (Figure 2a). The studies have started around the end of 90’ years, and augmented intensely from 2010. A total number of 5,186 peer-review articles were found with the search term “ocean acidification” in the Scopus database. The number of published papers peaked in 2017 (562 manuscripts), and then maintained an almost constant number of publications, always above 500 manuscripts per year. To refine our search to comprise studies conducted along the Brazilian coast, we included the term “Brazil” in this bibliometric survey (ocean acidification “AND” Brazil). As a result, the number of peer-review articles decreased to 29 documents (Figure 2b). Because OA is a problem with “no nationality”, we also combined the terms “ocean acidification” AND “South Atlantic”; however, the search returned even less articles (24) (Figure 2c). This number is far below compared to the combination of “North Atlantic” AND “ocean acidification”, which returned 110 published papers. Therefore, the process of OA studies in South Atlantic, and in Brazil, seems to be overlooked.

Considering the search term “coastal acidification” in the Scopus database, we found 69 published papers (Figure 3a). The number of published papers peaked in 2020 (18 articles), which means that the use of this term has increased in the last years. If we include “Brazil” in this bibliometric survey (coastal acidification “AND” Brazil), the number of peer-review articles decreased to only 2 articles (Figure 3b). However, several studies use the traditional term “OA” collectively to describe both ocean and coastal acidification (Feely et al., 2020). Indeed, if we combine the terms “ocean acidification” AND
“coastal”, the number of published papers increases to 1,004 with a marked tendency of intensification in the last years (Figure 3c). Including Brazil in this search (“ocean acidification” AND “coastal” AND “Brazil) (Figure 3d), the number of published papers decreases to 12 and well below compared to United States (95 articles; “ocean acidification” AND “coastal” AND “United States”). In brief, we can observe a lack of information on the processes of ocean and coastal acidification in Brazilian Seas.

Figure 3 – Evolution in the number of peer-review published articles on “Coastal Acidification” (CA) in the Scopus database. a) globally (only search term “coastal acidification”), and; b) in Brazil (“coastal acidification” AND “Brazil”); c) globally (“ocean acidification” AND “coastal”); d) in Brazil (“ocean acidification” AND “coastal” AND “Brazil”)

Ocean acidification in the main water masses along the Brazilian coast

The Brazilian coastal zone receives influence from the South Atlantic Subtropical Gyre (Figure 1). This gyre encompasses a system of wind-driven surface currents (Marcello; Wainer & Rodrigues, 2018; Stramma & England, 1999). The warm Brazil Current (BC) moves along the Brazilian coast southward until it meets an extension of the cold Antarctic Circumpolar Current (ACC) off Argentine coast, the Malvinas Current (MC), forming the Brazil-Malvinas confluence. From this confluence moving eastward, the meander originates the South Atlantic Current (SAC). Part of the SAC turns northwestward off South Affric coast, forming the southern branch of the South Equatorial Current (SEC). The SEC moves westward in direction to the Brazilian coast, where it bifurcates southward at around 15° (meeting the BC and closing the gyre) and northward, forming the North Brazilian Current (NBC). Regarding the water masses bordering the Southwestern Atlantic, there are three principal water masses: i) the warm and salty Tropical Water (TW) existing at the upper layer, which is carried by the BC and NBC (Rossi-Wongtschowski & Madureira, 2006); ii) the South Atlantic Central Water (SACW), which flows southward in intermediate depths, and is transported by the currents of the South Atlantic Subtropical Gyre (Rossi-
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Wongtschowski & Madureira, 2006); iii) additionally, there is the Coastal Water (CW) formed by the mixing of shelf waters and continental drainage (Castro & Miranda, 1998). Some authors define the CW as Subtropical Shelf Water (SSW) (Piola et al., 2000), which have strong influence of Plata plume in the South-Southeastern coast, and influence of the Amazon Plume on the North coast. The TW has temperatures higher than 20 °C (until ~29°C) and salinities above 36.4. TW and CW have similar temperatures; however, CW have lower salinities as result of continental runoff (Castro & Miranda, 1998). The SACW has temperatures below 20 °C and salinities slight below than those of TW (Castro & Miranda, 1998; Silveira et al., 2000). At higher depths, there is presence of the Antarctic Intermediate Water (AAIW), North Atlantic Deep Water (NADW), and Antarctic Bottom Water (ABW), which are out of the scope of this paper.

The Atlantic Ocean holds the largest stock of anthropogenic CO$_2$ representing ~38% of the total anthropogenic carbon inventory (Sabine et al., 2004). The studies investigating the OA process in the South Atlantic Ocean have been increased, particularly in the last 10 years (Wanninkhof et al., 2010; Ríos et al., 2010, 2012, 2015; Salt et al., 2015; Carvalho-Borges et al., 2018; Kitidis et al., 2017). However, the Southwestern Atlantic is particularly overlooked (Ríos et al., 2010, 2012; Carvalho-Borges et al., 2018). Ríos et al. (2010, 2012) showed that, on average, the western basin of the South Atlantic Ocean accumulates more anthropogenic carbon than the eastern basin. Regarding the main waters masses occurring along the Brazilian coast, the SACW experienced a high rate of increase in the inorganic carbon pool driven by the uptake of anthropogenic CO$_2$ from the atmosphere (Ríos et al., 2015; Salt et al., 2015). The estimates of anthropogenic carbon increase in the SACW varies between 75 to 95 μmol kg$^{-1}$ depending on the considered studies (Salt et al., 2015; Carvalho-Borges et al., 2018). The presence of anthropogenic carbon has led to the oceanic decrease in pH in the SACW, with rates of decline between -0.0015 yr$^{-1}$ to -0.0020 yr$^{-1}$ (over two decades – 1993-2013), reflecting the low buffering capacity due to the low temperatures and TA/DIC ratio (Ríos et al., 2015; Salt et al., 2015). Overall, the highest changes are located in near-surface/upper waters (0-200 m depth) in contact with atmosphere (Ríos et al., 2015; Salt et al., 2015). The changes in ocean pH related to the increase of anthropogenic CO$_2$ in the ocean are higher than the pH changes resulting from natural processes (remineralization of organic matter and changes in ocean circulation) (Ríos et al., 2015). Overall, the intrusion of anthropogenic CO$_2$ in the SACW (located around the southeastern and southern coast of Brazil) has led to a long-term pH decline of −0.17 ± 0.07 (Carvalho-Borges et al., 2018). This estimation considers the differences in pH between the beginning of the Industrial Revolution (~1750) and the time of sampling (2014). However, the observed values of Ω$_{Ca}$ and Ω$_{Ar}$ are still supersaturated within this region (Carvalho-Borges et al., 2018). The presence of anthropogenic carbon was also verified in TW but the Ω$_{Ca}$ and Ω$_{Ar}$ have remained supersaturated (average of 2.9) (Carvalho-Borges et al., 2018). No trend of OA was stablished for TW. No data was available for CW.

There are other studies investigating the carbonate chemistry in the Southwestern Atlantic (Ito et al., 2016; Bonou et al., 2016; Lefèvre et al., 2017; Cotovicz; Chielle & Marins, 2020). The focus of these studies were to describe the main carbonate chemistry parameters, particularly the ocean-atmosphere CO$_2$ exchanges; however, no OA trends were provided.

Taking account the typical salinity, temperature, and total alkalinity (TA) concentrations of the main water masses present in the Brazilian coast, and considering the different IPCC scenarios regarding the projected increase of atmospheric CO$_2$ (IPCC, 2021),
we calculated projections in the decline of pH, $\Omega_{\text{Ca}}$ and $\Omega_{\text{Ar}}$ until to the end of this century (Figure 4). For calculation purposes, we assumed that the water masses would be in equilibrium with atmospheric CO$_2$ concentrations projected until 2100 (IPCC, 2021). The calculations were performed for TW (sampled at South-Southeast and Northeast Brazilian coast; Carvalho-Borges et al., 2018; Cotovicz; Chielle & Marins, 2020), SACW (sampled at South-Southeast Brazilian coast; Carvalho-Borges et al., 2018), and Amazon Plume (sampled at North Brazilian coast; Bonou et al., 2016). As expected, we found a consistent declining trend in the levels of pH, concentrations of CO$_3^{2-}$, and the values of $\Omega_{\text{Ar}}$, $\Omega_{\text{Ca}}$ and TA/DIC ratios, corroborating the ongoing process of global OA. However, there are some differences considering the water masses. Due to differences of water solubility driven mainly by differences in seawater temperature and salinity, the concentrations of CO$_3^{2-}$, and the values of $\Omega_{\text{Ar}}$, $\Omega_{\text{Ca}}$ and TA/DIC ratio are lower for colder water masses (SACW, Plata Plume), compared to warmer water masses (TA, Amazon Plume). Therefore, the colder water masses (SACW, Plata

Figure 4 – Future scenarios of carbonate chemistry parameters for the main water masses composing the coast of Brazil. a) pH (Total Scale), b) CO$_3^{2-}$ (µmol Kg$^{-1}$), c) TA/DIC ratio, d) $\Omega_{\text{Ca}}$, e) $\Omega_{\text{Ar}}$. The solid lines represent the average of the future IPCC scenarios for the atmospheric CO$_2$ increase (SSP1-19; SSP-126; SSP2-45; SSP3-70; SSP5-58; IPCC 2021), and dashed lines represent the standard deviation. The different water masses were considered to be saturated with atmospheric CO$_2$. Where: TW at Southeast coast (Salinity 36.6; Temp. 21.3 °C; TA 2392 µmol Kg$^{-1}$); TW at Northeast coast (Salinity 36.1; Temp. 28.2 °C; TA 2340 µmol Kg$^{-1}$); CW Amazon Plume (Salinity 34.5; Temp. 27.3 °C; TA 2280 µmol Kg$^{-1}$); CW Plata Plume (Salinity 33.1; Temp. 20.5 °C; TA 2205 µmol Kg$^{-1}$); SACW at South-Southeast coast (Salinity 35.0; Temp. 11.6 °C; TA 2377 µmol Kg$^{-1}$). Data from Bonou et al., 2016; Carvalho-Borges et al., 2018; Cotovicz et al., 2020. Carbonate chemistry parameters were calculated using CO$_2$Calc (Robbins et al., 2010)
Plume) will experience negative OA impacts early than the warmer waters masses (TW, Amazon Plume). In addition, colder water masses have lower TA/DIC ratios meaning these waters have lower buffering capacity, corroborating previous findings (Rios et al., 2015; Carvalho-Borges et al., 2018). In this way, the South-Southeast Brazilian coast is more vulnerable to the threats of OA compared to the North-Northeast coast. This analysis has limitations because we did not consider other possible influences, like the biological metabolism, which could amplify or counter-act the OA (Carvalho et al., 2021), i.e., the local/regional biological processes can increase (photosynthesis; CaCO₃ dissolution) or decrease (respiration; CaCO₃ precipitation) the pH. However, this is a valid estimation assuming the equilibrium between the CO₂ concentrations in the ocean and in the atmosphere.

**Coastal acidification in ecosystems along the land-ocean aquatic continuum in Brazil**

Brazil coastal has an estimated area of 514,000 km² (including surface of inland waters and 12 miles of Territorial Sea) that represents almost half of South America (Domínguez, 2009; Marroni & Asmus, 2013). The high heterogeneity of Brazilian coast is partially explained by the extensive geographical location, encompassing intertropical, subtropical, and warm-temperate climate zones. The variability of tidal amplitude along the coastal is also diverse, generally increasing from south (< 1 m) to north (> 6 m) (Salles; Bentes & Santos, 2000). The relative contributions of energy from the movement of tides, riverine and groundwater discharges, wind forcing, and coastal currents are likewise highly variable, creating distinct patterns of water mixing along the land-ocean continuum, and distinct patterns of vertical stratification and gravitational circulation.

The variability of coastal pH results from multidrivers and is more pronounced than the open ocean pH (Duarte et al., 2013; Feely et al., 2020). The changes at river basin scale (mainly in the fluxes of TA and CO₂), together with other alterations, have contributed to decadal variability up to 0.5 units in coastal pH (Duarte et al., 2013). The diel to seasonal changes in coastal pH are also important and typically at about 0.3 units (Duarte et al., 2013). For comparison, the open ocean pH decreased at a rate of about 0.003-0.026 decade⁻¹ in surface waters considering the past 40 years (IPCC, 2021). Furthermore, coastal pH has showed tendency of acidification and sometimes basification, depending on several factors (induced by natural and anthropogenic forcing), including air-water CO₂ exchanges, export of TA and DIC from continental sources and mixing along the land-ocean aquatic continuum, balance between primary production, respiration, CaCO₃ precipitation, and CaCO₃ dissolution (Abril et al., 2003, 2021; Borges & Gypens, 2010; Cai et al., 2011; Duarte et al., 2013; Cotovicz et al., 2015, 2018; Feely et al., 2020).

Studies have demonstrated that the human inputs of nutrients and organic matter to coastal waters (eutrophication) has led to marked changes in the carbonate chemistry of surface and subsurface coastal waters (Borges & Gypens, 2010; Cai et al., 2011). The effect of coastal eutrophication on carbon cycling can enhance or counter-act the effect of OA (Bores & Gypens, 2010; Cai et al., 2011). However, the combined impact of eutrophication and OA on acidity in the coastal ocean are largely unknown. Despite some successful efforts in the implementation of wastewater treatment plans, the anthropogenic-derived loadings of nutrients and organic matter to estuaries and other coastal systems are still increasing around
the world (Breitburg et al., 2018). Brazil hosts a coastal population of ~74 million of inhabitants (40% of Brazil’s population; Marroni and Asmus, 2013). However, around 59% of the sewage produced is not treated and dumped “in nature” in Brazil (Campestrini & Jardim, 2017). This low coverage of wastewater treatment plans has led to a context of widespread and problematic process of coastal eutrophication, and particularly relevant in regions densely populated (Cotovicz et al., 2013, 2015; Noriega et al., 2014; Fonseca; Newton & Cabral, 2021).

Oxygen concentrations in coastal waters are declining due to increased loading of nutrients and organic matter, and global warming (Breitburg et al., 2018). Despite of the limited data availability, coastal waters presenting hypoxic/anoxic conditions have been reported in Brazil (Diaz & Rosenberg, 2008; Cotovicz et al., 2021; Fonseca; Newton & Cabral, 2021). The process of acidification is linked to the process of deoxygenation because the CO₂ produced during microbial respiration increases the acidity (Cai et al., 2011; Breitburg et al., 2018). For that reason, the eutrophication could increase the vulnerability of coastal waters to OA (Cai et al., 2011). This process was documented in highly polluted sectors of Guanabara Bay (Rio de Janeiro, Brazil), an eutrophic coastal embayment surrounded by a large urban area (Cotovicz et al., 2018). Very low values of Ω₄₅ were found in low-buffered waters, in regions that receive direct discharges from domestic effluents and polluted rivers. This study documented episodic occurrence of corrosive waters (Ω₄₅ < 1) only at the vicinity of sewage outlets in Guanabara Bay. The main hypothesis is that the allochthones sources (rivers, wastewater) represented the principal inputs of waters with low Ω₄₅ to the bay that are enriched in nutrients and organic matter. Indeed, the carbonate dissolution can occur in estuaries due to the intense of organic matter mineralization (Abril et al., 2003). However, in most of the waters of Guanabara Bay, hyper-oxygenated surface waters were also reported in within phytoplankton blooms (Cotovicz et al., 2015). The high nutrient enrichment in this ecosystem has stimulated the growth of large phytoplankton blooms in shallow, warm and thermally stratified waters, with strong uptake of DIC in surface waters, lowering the concentrations of CO₂ and increasing the pH, Ω₄₅ and CO₃²⁻ (Cotovicz et al., 2015, 2018). In this manner, the nutrient enrichment can amplify both production and respiration of organic matter and can reduce or exacerbate the biological-induced acidification in coastal waters (Borges & Gypens, 2010; Nixon et al., 2015; Cotovicz et al., 2018). Indeed, the carbonate chemistry in highly productive nearshore coastal ecosystems can respond more strongly to eutrophication than to OA (Borges & Gypens, 2010).

The perturbation of marine carbonate system by eutrophication leading to acidification can occurs in many other coastal ecosystems in Brazil, particularly in densely populated and urbanized regions. Some examples can be pointed. In the Jacarepagua Lagoon Complex (Rio de Janeiro, Brazil), hypoxic zones were associated with extremely high values of pCO₂ (up to 20,417 ppmv), and low pH in a region of intense aerobic and anaerobic degradation of organic matter coming from untreated domestic effluents (Cotovicz et al., 2021). In the Recife Estuarine System (Pernambuco, Brazil), high concentrations and emissions of CO₂ concomitant with hypoxic conditions were associated to the enhanced net heterotrophy of the system driven by eutrophication (Noriega et al., 2014). It is quite clear that these two coastal areas are suffering acidification; however, the term “coastal acidification, CA” was not explicitly used. In short, eutrophication has the potential to drive pH changes (increase or decrease) with an intensity much stronger than OA does in the open ocean and shelves on decadal time scales. Unfortunately, we could not find examples in literature investigating CA in the long term in Brazil, neither time-series. Important to highlight that the occurrence of high concentrations of CO₂ and low
values of pH in coastal waters in hypoxic/anoxic waters can be associated with the occurrence of high methane (CH$_4$) concentrations, a powerful greenhouse gas (Nirmal-Rajkumar et al., 2008; Cotovicz et al., 2016, 2021). In Brazil, this was verified in highly polluted areas of coastal embayment’s and lagoons (Cotovicz et al., 2015, 2021).

The CA can be caused (or counteracted) by other chemical changes along the land-ocean aquatic continuum. For example, the riverine influx can lead to acidification. Most tropical river plumes are acidic compared to the receiving ocean, and the mixing occur in continental shelf waters (Salisbury et al., 2008). The potential alterations in the magnitude of river discharge as result of climate and land-use changes represent a threat to calcifying organisms since tropical rivers enter the ocean at low $\Omega_{Ca}$ and $\Omega_{Ar}$ because of their relatively low Ca$^{2+}$ and CO$_3^{2-}$ (Salisbury et al., 2008). Brazil hosts tropical river-dominated estuaries with low TA concentrations in the river endmember, meaning that the freshwater domain of these estuaries are poorly buffered to changes in pH (Cotovicz et al., 2020; Abril et al., 2021), and this can enhances the susceptibility to OA. On the other hand, there are coastal regions along the Brazilian coast with very dry conditions (semiarid climate) where evaporation rates frequently exceed rainfall (Cavalcante et al., 2021). Evaporation can increase concentrations of TA and DIC in water, enhancing the buffering capacity (Cotovicz et al., 2021a). The advection of allochthonous water masses (upwelling and lateral transport) is another process with potential to modify the local/regional rate and/or the susceptibility to OA. Coastal upwelling of nutrient-rich SACW occurs along the Brazilian coast (latitude 15°S-30°S; Campos et al., 2013; Aguiar et al., 2014). The SACW has experiencing declining rates of pH, and present low buffering capacity. The upwelling may bring CO$_2$-enriched waters with low pH onto the shelf (estuaries, nearshore waters) (Feely et al., 2008). The lateral transport of TA and DIC to adjacent coastal waters has showed to be important in mangrove-dominated ecosystems (Sippo et al., 2016). This means that the exportation of TA and DIC from mangroves to the coastal ocean could result in a net increase in pH. Nevertheless, these observations are limited to one subtropical site and one survey preventing a generalized link between mangrove C outwelling (export) and buffering capacity. Since Brazil represents the second country in terms mangrove area (and carbon stocks), the effect of alkalinity exports on coastal buffering capacity could be significant and where systems highly sensitive to ocean acidification (i.e., coral reefs) occur. However, all these processes are largely unnoticed and needs further and urgent investigation.

**Main vulnerabilities and impacts expected along the Brazilian Coast**

The human-driving water acidification has widespread potential biological impacts, spanning from species-specific physiologies and population dynamics to communities and whole ecosystems (Doney et al., 2020). The alterations in acid-base chemistry and associated impacts have been described in estuarine, coastal, and surface open-ocean waters. The biological impacts from OA and CA are particularly relevant for shell-forming organisms. Taking into account that Brazil has a large, megadiverse coastal zone, we will present a brief overview on the most vulnerable communities and ecosystem.

**Planktonic communities**

Results obtained in experimental and in situ studies strongly suggest that OA increases primary production biomass but decreases biodiversity (Doney et al., 2020). There
are “winners” and “losers”, meaning that planktonic species tolerant to high-CO₂ conditions will become more dominant in future communities (Bach et al., 2017). However, at very high levels of CO₂ and low levels of CO₃²⁻, Ω₉Ca and ΩAr in seawater, the dissolution of CaCO₃ can overcome the precipitation (Riebesell et al., 2000). Several planktonic calcifying organisms can be found along the Brazilian coast including mollusks, coccolithophores, and foraminifers. These organisms have skeletal mineralogy formed both by aragonite and calcite minerals. Several impacts have reported regarding OA impacts on these planktonic organisms, including levels of shell dissolution, and reduced calcification due to elevated energy demand to build CaCO₃ structures (Riebesell et al., 2000; Figuerola et al., 2021).

Benthic communities

There are important calcifying organisms that can be found at the benthic environment along the Brazilian coast of ecological and commercial interest, including calcareous benthic foraminifers, ostracods, echinoderms, cnidarians, crustaceans (Vilela et al., 2003; Clemente et al., 2014). These organisms biomineralize CaCO₃ to build the shells and skeletons. There are several predicted and already described OA impacts on these benthic organisms, including shell dissolution, limited growth, lower larvae development, limited larvae dispersal, among others (Figuerola et al., 2021).

Coral reefs

Brazilian coral reefs comprise the largest area of reefs in the Southwestern Atlantic Ocean, spreading over more than 3,000 km alongshore (Leão et al., 2016). In addition, an extensive Mesophotic Coral Ecosystem (~9500 km²) has been mapped between Brazil and the Caribbean (Great Amazon Reef System; Mahiques et al., 2019). Coral reefs are considered one of the most vulnerable ecosystems to OA impacts. There are predicted global declines in the rates of coral reef calcification under low-pH conditions (Cornwall et al., 2021). A study investigated the carbonate chemistry in an equatorial continental shelf dominated by coral reefs in Brazil (Equatorial Southwestern Atlantic; Cotovicz; Chielle & Marins, 2020). The coral-reef dominated waters presented lower values of pH₉, CO₃²⁻, and ΩAr compared to nearshore regions without the influence of coral reef waters (Cotovicz; Chielle & Marins, 2020). Overall, the values of ΩAr (3.41 to 3.69) were supersaturated. However, a recent study showed that coral reefs could reach net dissolution at ΩAr>3.5 in highly damaged ecosystems (Kline et al., 2019). Indeed, in addition to OA, there are other stressors to coral reefs, like global warming and eutrophication. The eutrophication has been described in coral reefs of Brazil (Costa; Nimmo & Attrill, 2008). Nearshore reefs receive nutrient inputs from continental runoff, river discharge, and groundwater inputs. The eutrophication, together with acidification and warming, will likely have negative impacts on coral reefs in a near future, increasing bleaching events, mortality, and contributing to decreasing CaCO₃ calcification.

Rodolith beds

The Brazilian shelf, particularly at the east and northeast portions, are almost entirely covered by carbonate sediments (Knoppers; Ekau & Figueiredo, 1999). Associated to these carbonate sediments, Brazil hosts one of the largest areas in the world with presence of Rhodoliths, forming large beds in shallow waters (> 150 m), between 2²N and 27²S (Amado Filho & Pereira Filho, 2012; Horta et al., 2016). Rhodoliths are calcifying organisms that
produce CaCO$_3$. Estimations show that calcifying organisms will have difficult to biomineralized CaCO$_3$. Indeed, undersaturated conditions can occur, which will be associated with net dissolution of CaCO$_3$. Possibly, Brazil represent one of the largest marine CaCO$_3$ deposits in the world (Amado Filho & Pereira Filho, 2012). However, the process of OA on these rhodolith beds are largely unknown, with possibility to occur large CaCO$_3$ dissolution taking into account the widespread occurrence of the ecosystems in Brazil.

**Coastal upwelling regions**

The Brazilian Continental shelf is bordered by western boundary currents, with occurrence of some areas of upwelling of local/regional importance (Knoppers; Ekau & Figueiredo, 1999). Coastal upwelling of nutrient-rich SACW occurs near Cape Santa Marta (27°S-30°S; South Brazilian Coast), and Abrolhos-Campos region (15°S-23°S; East-Northeast Brazilian Coast) (Campos et al., 2013; Aguiar et al., 2014). Seasonal SACW intrusions derived from coastal upwelling has significant impacts on food web and plankton community composition (Valentin et al., 2021). Taking account, that SACW has low buffering capacity and is experiencing high rates of OA, the upwelling regions are particularly vulnerable.

**Urbanized Estuaries and Shelf Waters**

Urbanized estuaries and shelf waters are suffering with widespread eutrophication in Brazil. The eutrophication has led to changes in carbon cycling, decreasing (Cotovicz et al., 2018, 2021) or increasing (Cotovicz et al., 2015, 2021a) the aquatic pH levels. The decrease or increase in the pH levels depend on many factors, including the coastal typology, water residence time, vertical and horizontal water stratification, ecosystems metabolism, vicinity of sewage outlets and polluted rivers, and mixing with offshore waters (Cotovicz et al., 2015, 2018, 2020, 2021, 2021a; Abril et al., 2021). Like this, the answer of coastal ecosystems in face to eutrophication are strongly site-specific, with some ecosystems developing acidification of subsurface coastal waters, whereas others are counter-acting this process exhibiting increase of pH. In addition, the combined effect of eutrophication and OA on acidity in the coastal ocean could amplify the pH decline (Cai et al., 2011). The high human population in the coastal zone of Brazil associated with the poorly coverage of wastewater treatment plans will likely to contribute to increase this environmental problem in a near future.

**Perspectives on ocean and coastal acidification in Brazil, and research needs**

Surface ocean pH has declined globally (Bates et al., 2014). This trend of OA will continue worldwide as the result of increase atmospheric CO$_2$ concentrations under all emissions scenarios projected by IPCC. It is “virtually certain (99-100% probability)” that anthropogenic-derived CO$_2$ emissions are the main driver of current global OA (IPCC, 2021). As briefly exposed in this manuscript, the water masses of the South Atlantic Ocean are exhibiting pH decline following the atmospheric CO$_2$ increase. The situation is more critical for the SACW, which has experienced the fastest rates of OA. SACW is an important water mass composing the Southwestern Atlantic Ocean, achieving many coastal ecosystems in Brazil. The impacts of OA will likely to be more critical for the South and Southeast Brazilian coast due to lower-buffered waters (lower seawater temperatures) compared to Northeast and North coasts (Figure 4). Along with OA, many processes occurring in coastal ecosystems like local/regional changes in water chemistry from
freshwater inputs and excessive nutrient run-off from continental sources have the potential to cause acidification and/or to increase the vulnerability to OA. The rates of acidification of coastal waters will likely increase as result of widespread eutrophication fueling organic matter respiration along the Brazilian Coast. However, the process of eutrophication can also counter-act the OA by increasing the primary production as the result of nutrient enrichment. The ecosystem response to these perturbations evolves several hydrological and biogeochemical aspects, and seems to be site-specific. The eutrophication has been driven by poor sanitary conditions that remains unsolved for large areas of the Brazilian coast, and without perspectives for improvements at short and medium terms. Another point to be considered regarding the vulnerability of coastal water to the process of acidification is the intensity of freshwater discharge. Brazilian coast receives discharges from large river plumes, like Amazon and Plata Rivers. The freshwater inputs from these rivers can have important influences regulating the buffering capacity in coastal regions receiving these riverine discharges. All these processes need further investigation.

There are increasing efforts of the Brazilian scientific community to develop capabilities in chemical oceanography, particularly the investigation of OA in the western South Atlantic Ocean (Kerr et al., 2016). The Brazilian Ocean Acidification Research Group (BrOA; https://broa.furg.br/) was created in December 2012, aiming “to integrate Brazilian researchers into a broad national network of interdisciplinary cooperation in Ocean Acidification studies” (Kerr et al., 2021). BROA operates in estuarine, coastal and open ocean waters. The formation of this group was also important for scientists to be involved in international programs investigating OA, participation in best practices measurements, workshops, etc. (Kerr et al., 2016; Perreti et al., 2018). Another group was officially established in December 2015, the Latin-American Ocean Acidification Network (LAOCA Network) formed by researchers from Latin-American countries, including Brazil (Vargas et al., 2020). The principal mission of the LAOCA network is “to become a regional mode of articulation, communication and strengthening of the understanding of the OA process in Latin America, and its interaction with other local processes, as well as their implications for marine ecosystems and their ecosystem services”. However, despite these efforts, the analytical facilities and capabilities in Brazil remain underdeveloped (Kerr et al., 2016; Perreti et al., 2018) compared to the dimension of the Brazilian coast and the size of the problem. Consequently, it is important to share publicly, conduct procedures of Inter-calibration /inter-comparison of laboratories at National-International levels, and develop new technologies. However, it is important to highlight that some analysis and equipment have high cost, which is an additional obstacle for low-income and developing countries, like Brazil. That is why is highly recommended the utilization of data products available by global data repositories regarding CO$_2$-system, as the Surface Ocean CO$_2$ Atlas (SOCAT; https://www.socat.info/index.php/data-access/), Carbon Dioxide Information Analysis Center (CDIAC; https://cdiac.ess-dive.lbl.gov/), Global Ocean Data Analysis Project (GLODAP; https://www.glodap.info/). The latest version of GLODAP (GLODAPv2.2021), for example, contains more than 1.3 million water samples collected on 989 cruises covering several oceanic and coastal regions worldwide (Lauvset et al., 2021). These international repositories adopt the Findable, Accessible, Interoperable, and Reusable (FAIR) principles for scientific data.

It is urgent to implement time-series acquisition of marine carbonate system parameters along the Brazilian coast (North, Northeast, Southeast and South) and
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investigate the ocean uptake of anthropogenic CO₂ and OA. To our best knowledge, only the moored buoys of the PIRATA program (Prediction and Research Moored Array in the Tropical Atlantic) have been providing continuous, long data record of carbonate system parameters (fugacity of CO₂) in the waters of the Tropical/South Atlantic Ocean (Bruto et al., 2017; Bourlès et al., 2019). Ocean and coastal time-series are consistent to investigate changes in surface carbonate chemistry and trends of acidification. CO₂ time series have provided successful observations in several oceanic location for periods from 15 to 30 years (Bates et al., 2014). Along with this, it is also imperative to implement monitoring programs in the long-term in key coastal ecosystems (estuaries, river plumes, nearshore and continental shelf areas). Only in this way, we will could establish an overview in the processes of ocean and coastal acidification. Along with in situ carbonate chemistry observations, it is necessary to implement laboratory and field experiments (mesocosm) manipulating carbonate chemistry with key species/ communities/ ecosystems on a broad of realistic scenarios (Gattuso et al., 2015; Doney et al., 2020). The research fronts include many aspects at organism-level (sensitivity, acclimation and adaptation), and propagation of effects into community and ecosystem responses (Doney et al., 2020). The manipulation of carbonate chemistry along with other stressors, like deoxygenation, ocean warming, are highly desirable. Data from observations and experiments are necessary to feed modeling systems (coastal and oceanic observatories), which can be applied for local, regional and global ocean systems to improve quality of information and future projections (Franz et al., 2021). Together, all this information can conduct directions for future research and information needs for industrial leaders, policymakers and stakeholders (marine resource management, adaptation solutions). In addition, the science community should be close to the public to present the results and research implications of OA in clear and consistent terms.

There are four main actions that can be made to limit OA and CA (Gattuso et al., 2015): mitigate (reducing the drivers), protect (building or maintaining ecosystems service), adapt (human societies), and repair (damage already occurred). However, at this time, only reducing CO₂ emissions will address the ultimate problem (Gattuso et al., 2015). In addition to the decarbonization of the economy, it is important to look for nature-based approaches for mitigating greenhouse gas emissions and eventually promote carbon storage (Gattuso et al., 2018; Taillardat; Friess & Lupascu, 2018). The coastal ocean offers opportunities to reduce the ongoing climate change (coastal ocean-based solution; Gattuso et al., 2018); for example, vegetated coastal ecosystems (blue carbon) have high carbon sequestration capacity (Nellemann et al., 2009). Brazil, with its immense and megadiverse coastal area, has one great opportunity with this nature-based solution to mitigate the anthropogenic CO₂ emission, and achieve U.N. sustainable development goals and meet the Paris agreement.

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