UNIVERSIDADE FEDERAL DE PERNAMBUCO
CENTRO DE TECNOLOGIA E GEOCIÊNCIAS
DEPARTAMENTO DE OCEANOGRAFIA
PROGRAMA DE PÓS-GRADUAÇÃO EM OCEANOGRAFIA

BRENNO JANUARIO DA SILVA

ANÁLISE DO SISTEMA CARBONATO E DO ESTADO TRÓFICO DOS RECIFES DA APA COSTA DOS CORAIS/ALAGOAS: uma abordagem sazonal e experimental

Recife
2022

BRENNO JANUARIO DA SILVA

ANÁLISE DO SISTEMA CARBONATO E DO ESTADO TRÓFICO DOS RECIFES DA APA COSTA DOS CORAIS/ALAGOAS: uma abordagem sazonal e experimental

Tese apresentada ao Programa de Pós-Graduação em Oceanografia da Universidade Federal de Pernambuco, como requisito parcial para a obtenção do título de Doutor em Oceanografia.

Área de concentração: Oceanografia Abiótica.

Orientador: Prof. Dr. Manuel de Jesus Flores-Montes.

Coorientador: Prof. Dr. Paulo Jorge Parreira dos Santos.

Recife

2022

Catalogação na fonte:
Bibliotecária Sandra Maria Neri Santiago, CRB-4 / 1267

S586a Silva, Brenno Januario da.

Análise do sistema carbonato e do estado trófico dos recifes da APA Costa dos Corais/Alagoas: uma abordagem sazonal e experimental / Brenno Januario da Silva. – 2022.

91 f.: il., fig., tabs.

Orientador: Prof. Dr. Manuel de Jesus Flores-Montes.

Coorientador: Prof. Dr. Paulo Jorge Parreira dos Santos.

Tese (Doutorado) – Universidade Federal de Pernambuco. CTG. Departamento de Oceanografia. Recife, 2022.

Inclui referências e apêndices.

1. Oceanografia. 2. Eutrofização. 3. Acidificação oceânica. 4. Alcalinidade total. 5. Calcificação. 6. Recifes tropicais. 7. Nutrientes. I. Flores-Montes, Manuel de Jesus (Orientador). II. Santos, Paulo Jorge Parreira dos (Coorientador). III. Título.

UFPE

551.46 CDD (22. ed.) BCTG/2022-301

BRENNO JANUARIO DA SILVA

ANÁLISE DO SISTEMA CARBONATO E DO ESTADO TRÓFICO DOS RECIFES DA APA COSTA DOS CORAIS/ALAGOAS: uma abordagem sazonal e experimental

Tese apresentada ao Programa de Pós-Graduação em Oceanografia da Universidade Federal de Pernambuco, Cento de Tecnologia e Geociências, como requisito parcial para a obtenção do título de Doutor em Oceanografia. Área de concentração: Oceanografia Abiótica.

Aprovada em: 29/07/2022.

BANCA EXAMINADORA

____
Prof. Dr. Manuel de Jesus Flores-Montes (Orientador)
Universidade Federal de Pernambuco

____
Profa. Dra. Letícia Cotrim da Cunha (Examinadora externa)
Universidade Estadual do Rio de Janeiro

____
Prof. Dr. Guilherme Ortigara Longo (Examinador externo)
Universidade Federal do Rio Grande do Norte

____
Dra. Joseane Aparecida Marques (Examinadora externa)
Ben-Gurion University of the Negev, Zuckerberg Institute for Water Research

____
Prof. Dr. Fernando Antônio do Nascimento Feitosa (Examinador interno)
Universidade Federal de Pernambuco

O constante apoio e incentivo aos estudos me trouxeram até aqui. Me tornaram uma pessoa apaixonada pela ciência. Dedico esta Tese inteiramente aos meus pais, Aurinete Maria e Nivaldo Januario (*in memoriam*).

AGRADECIMENTOS

Agradeço primeiramente à minha mãe, Aurinete Maria, e ao meu irmão, Heitor Januario, por me apoiarem de todas as formas possíveis e imagináveis durante minha jornada no doutorado. Sem eles eu jamais conseguiria concluir esta etapa.

Aos meus amigos. Aos que eu fiz durante esse processo de pós-graduação e aos que já faziam parte da minha vida há anos. Sem nossos desabafos, choros, alegrias, trocas de vivências, momentos felizes e de apoio, tudo seria ainda mais difícil. Vocês têm minha total gratidão, admiração, e torço para vivermos ainda mais histórias juntos.

À minha psicóloga, Izabele Santos. Pessoa mais do que essencial nos últimos anos do doutorado, profissional incrível.

Ao pessoal do LOQuim. Agradeço demais por todo apoio ao longo desses quase 10 anos de parceria, em especial ao meu orientador, Manuel Flores-Montes, que vem acreditando e investindo em mim desde quando eu estava na graduação. Muito obrigado por todos seus ensinamentos, conselhos, suporte e compreensão.

Ao PELD–CCAL, por todo o apoio e financiamento das coletas e análises. Ao Pontal de Maragogi e Prefeitura Municipal de Japaratinga, por todo o suporte durante os campos, nos disponibilizando as embarcações.

Ao FUNBIO e Instituto Humanize, pelo financiamento do projeto, garantindo que eu conseguisse realizar uma das etapas mais desafiadoras do doutorado, que foi o experimento *in situ*.

Ao CNPq, pela concessão do meu salário (minha bolsa) e financiamento do projeto, possibilitando assim a realização e finalização do doutorado.

Aos funcionários e professores do Departamento de Oceanografia da UFPE.

RESUMO

Os ambientes recifais são um dos ecossistemas mais produtivos e biodiversos do mundo, entretanto, estão constantemente susceptíveis aos impactos de escala global, como a acidificação oceânica (AO), e local, como a eutrofização. O monitoramento dos parâmetros abióticos dessas regiões e a aplicação de metodologias visando mitigar esses efeitos são cada vez mais essenciais. Diante disso, o presente trabalho apresentou como objetivos principais: analisar a dinâmica sazonal do sistema carbonato e estado trófico em regiões recifais da Área de Proteção Ambiental Costa dos Corais (APACC), verificando a influência dos aportes continentais superficiais e subterrâneos; avaliar as respostas do metabolismo recifal diante de um experimento *in situ* de alcalinização. Coletamos águas superficiais dos recifes e rios, e águas intersticiais da linha de costa mensalmente ao longo de um ano, e posteriormente, um experimento de reversão da AO foi realizado em um recife da APACC. Os resultados mostram que a área recifal estudada é considerada oligotrófica, com a boa a ótima qualidade de água durante o ano todo e com condições favoráveis às atividades biológicas, como por exemplo, à calcificação. A clorofila-*a* da zona recifal foi significativamente correlacionada com a salinidade e radônio em excesso, indicando, respectivamente, a influência dos rios e da *submarine groundwater discharge* (SGD) na região, principalmente durante o período chuvoso, sendo assim, importantes fontes de nutrientes para a costa. No entanto, sinais de eutrofização foram registrados tanto nos rios, como nas águas intersticiais, caracterizando potenciais ameaças para os recifes. Através do experimento, detectamos que o aumento do pH elevou a alcalinidade total em 205.27 µmol kg^{-1} e em 50% os níveis de saturação de aragonita (Ω_{ar}) da zona recifal. Isso mostrou que a alcalinização em escala local influencia positivamente no sistema carbonato, podendo mitigar os efeitos da AO, e que o frequente monitoramento dos parâmetros abióticos de regiões recifais possibilita a identificação e caracterização de estressores ambientais.

Palavras-chaves: eutrofização; acidificação oceânica; alcalinidade total; calcificação; recifes tropicais; nutrientes.

ABSTRACT

Reef environments are one of the most productive and biodiverse ecosystems in the world, with significant ecological and socioeconomic importance. However, they are constantly susceptible to global scale impacts, such as ocean acidification (OA), and local scale impacts, such as eutrophication. Monitoring the abiotic parameters of these regions and testing methodologies to mitigate these effects are extremely essential. Therefore, we analyzed the seasonal dynamics of the carbonate system and trophic state in reef regions of the Costa dos Corais Marine Protected Area (APACC), accounting for the influence of surface and underground continental runoffs, and evaluated the responses of reef metabolism in an *in situ* alkalinization experiment. Surface waters from reefs and rivers, and porewaters from the shoreline were sampled monthly for over a year, and later, an OA reversal experiment was carried out on an APACC's reef. We found that the studied reef zone is oligotrophic, with good to excellent water quality throughout the year and favorable conditions for biological activities, such as calcification. Chlorophyll-*a* from the reef zone was significantly correlated with salinity but very rich in radon, indicating the influence of rivers and submarine groundwater discharge (SGD) in the region, respectively, especially during the rainy season, being important nutrient sources for the coast. We also recorded signs of eutrophication in both rivers and porewaters which may be threatening the reefs. The alkalinization experiment showed that raising the pH increased 205.27 µmol kg^{-1} in total alkalinity values and aragonite saturation (Ω_{ar}) levels of the reef zone in 50%. This showed that alkalization on a local scale positively influences the carbonate system and can mitigate the effects of OA and that the frequent monitoring of abiotic parameters of reef regions allowed the identification and characterization of potential environmental stressors.

Keywords: eutrophication; ocean acidification; total alkalinity; calcification; tropical reefs; nutrients.

LISTA DE FIGURAS

	TESE	
Figura 1 –	Mutualismo entre coral e endossimbionte dinoflagelado..………	14
	ARTIGO 1 – SEASONAL INFLUENCE OF SURFACE AND UNDERGROUND CONTINENTAL RUNOFF OVER A REEF SYSTEM IN A TROPICAL MARINE PROTECTED AREA	
Figura 1 –	Map of the study area with the location of the sampling stations. Black squares indicate the sampling stations for surface seawater. Porewater (yellow) and river water (red) sampling stations are divided according to the region: northernmost (circles), central (squares) and southernmost (triangles) regions……………………………………….............	26
Figura 2 –	Monthly (gray bar) and historical (black bar) rainfall during the studied period……………………………………………........	30
Figura 3 –	Mean salinity (a, b) and Chl-*a* (c, d) distributions during the rainy (left) and dry season (right)…………………………………..	30
Figura 4 –	Mean TRIX distribution during the rainy (a) and dry season (b)………………………………………………………………..	31
Figura 5 –	TA mean distribution during the rainy (a) and dry season (b) and general mean of pH (c)………………………………...…….	32
Figura 6 –	General mean $^{222}Rn_{exc}$ activities in the lagoon…………………	32
Figura 7 –	PCA results showing the scores of each variable along the first two factors…………………………………………..………..	33
Figura 8 –	Salinity vs $^{222}Rn_{exc}$ in the different water masses sampled. (a) Rivers (blue) and reefs samples (red) versus salinity, (b) and together with porewater (black). Colored ellipses mean 90% of the samples’ coverage. Solid horizontal line represents the sediment $^{222}Rn_{exc}$ equilibrium activities……………………………	35
	ARTIGO 2 – REEF METABOLISM AND CARBON CHEMISTRY RESPONSES TO AN *IN SITU* ARTIFICIAL ALKALINIZATION EXPERIMENT……………………………….	

Figura 1 –	Experimental period, dividing control (pink) and alkaline (blue) days…………………………………………………………………	53
Figura 2 –	Study area location and experimental strategy..…………………	54
Figura 3 –	Mean rhodamine WT (a, b), pH (c, d) and TA (e, f) distribution during control (left side) and alkaline days (right side)…………	56
Figura 4 –	Salinity and ΔTA box plots variation along the days. Dashed line represents the ΔTA value of 0 and the colors are respective to the treatments, alkaline (blue) and control (red)………………………...	57
Figura 5 –	TA-C_T regressions according to treatment, control (circles) and alkaline days (triangles). Colored contour and isolines are the pH variation……………………………………………………..…...	57
Figura 6 –	Mean Ω_{ar} (a, b) and Revelle factor (c, d) distribution during control (left side) and alkaline days (right side)…………………..	58

LISTA DE TABELAS

ARTIGO 1 – SEASONAL INFLUENCE OF SURFACE AND UNDERGROUND CONTINENTAL RUNOFF OVER A REEF SYSTEM IN A TROPICAL MARINE PROTECTED AREA

Tabela 1 – Trophic status classification of aquatic ecosystems based on the TRIX index………………………………………………………………….. 28

Tabela 2 – Seasonal mean and standard deviation (±) of key parameters determined in this study in samples taken from rivers and porewaters. Different superscript letters mean significant seasonal differences (*P* < 0.05)………………………………........ 34

ARTIGO 2 – REEF METABOLISM AND CARBON CHEMISTRY RESPONSES TO AN *IN SITU* ARTIFICIAL ALKALINIZATION EXPERIMENT

Tabela 1 – Predicted low tide height (m) and time (hours:minutes) during the experiment period…………………………………………………….. 52

SUMÁRIO

1	**INTRODUÇÃO……………………………………………………………**	**12**
1.1	ASPECTOS GERAIS…………………..…..……………………………	13
1.1.1	**Impactos globais………………………………………………………**	**16**
1.1.2	**Impactos locais...……………………………………………………**	**18**
1.2	OBJETIVO GERAL……………….……..………………..…………….	22
1.3	OBJETIVOS ESPECÍFICOS………..…………..…..…………………	22
1.4	HIPÓTESES……………..…...……………………………………...	22
2	**ARTIGO 1 – SEASONAL INFLUENCE OF SURFACE AND UNDERGROUND CONTINENTAL RUNOFF OVER A REEF SYSTEM IN A TROPICAL MARINE PROTECTED AREA…………..**	**23**
3	**ARTIGO 2 – REEF METABOLISM AND CARBON CHEMISTRY RESPONSES TO AN *IN SITU* ARTIFICIAL ALKALINIZATION EXPERIMENT…………………………….……………………....**	**50**
4	**CONSIDERAÇÕES FINAIS……………………………………………...**	**68**
	REFERÊNCIAS…………………………………………………………	**70**
	APÊNDICE A – MATERIAL SUPLEMENTAR ARTIGO 1.................	**87**
	APÊNDICE B – MATERIAL SUPLEMENTAR ARTIGO 2.................	**90**

1 INTRODUÇÃO

Este documento de Tese de Doutorado está organizado em formato de artigos científicos, abordando discussões sobre a dinâmica dos parâmetros do sistema carbonato e estado trófico em zonas recifais de uma Área de Proteção Ambiental (APA), em escala sazonal e diante de um experimento *in situ* de alcalinização. Até o presente momento, este é o primeiro trabalho na região nordeste do Brasil que traz dados sobre a influência de aportes continentais subterrâneos em recifes, assim como é o segundo no mundo a avaliar experimentalmente uma forma de mitigar os impactos da acidificação oceânica (AO) por remediação química.

Esta Tese apresenta-se em 4 capítulos: Este primeiro capítulo aborda aspectos gerais sobre os ambientes recifais, destacando a susceptibilidade desse ecossistema aos impactos antrópicos de escala local e global, assim como traz os objetivos e hipóteses da pesquisa. O segundo capítulo representa o artigo intitulado "*Seasonal influence of surface and underground continental runoff over a reef system in a tropical marine protected area*", publicado na *Journal of Marine Systems* (DOI: 10.1016/j.jmarsys.2021.103660), que traz os dados sobre a avaliação sazonal da área de estudo. O terceiro capítulo é sobre o artigo intitulado "*Reef metabolism and carbon chemistry responses to an in situ artificial alkalinization experiment*" que aborda o experimento *in situ* e será submetido em revistas científicas de alcance internacional. Por fim, o quarto capítulo são as considerações finais.

O presente trabalho foi realizado com o apoio do Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq - #140874/2018-6), e do Fundo Brasileiro para a Biodiversidade (FUNBIO) e Instituto Humanize, pelo edital "Bolsa Funbio – Conservando o Futuro (2019)". Também foi desenvolvido em parceria com o Programa Ecológico de Longa Duração Costa dos Corais Alagoas (PELD-CCAL), financiado pelo CNPq (#441657/2016-8), assim como pela Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES - #23038.000452/2017-16) e Fundação de Amparo à Pesquisa do Estado de Alagoas (FAPEAL - #60030.1564/2016).

1.1 ASPECTOS GERAIS

Mundialmente, centenas de milhões de pessoas obtêm recursos financeiros, direta e indiretamente, e são protegidas da dinâmica costeira através de um dos principais ecossistemas marinhos, o ambiente recifal (PENDLETON et al., 2016; ROELVINK et al., 2021). Os recifes são representados por formações rochosas, de diferentes origens e tipos, que abrigam cerca de ¼ de toda a biodiversidade marinha, apresentando, portanto, uma extrema importância ecológica, elevada produtividade, além de uma diversa conectividade com outros ecossistemas, como por exemplo, estuários e manguezais (BURKE et al., 2011; SPEERS et al., 2016; WINKINSON, 2008).

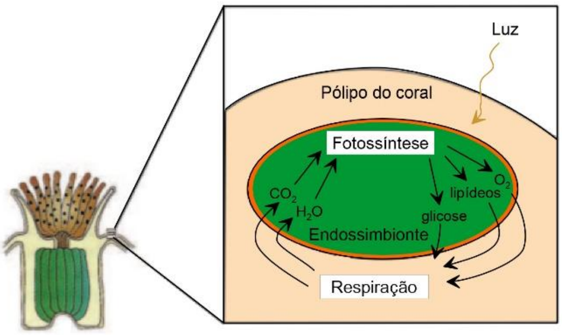
Os recifes apresentam duas principais origens, a arenítica e biogênica. Os recifes de arenito (*beachrocks*) são estruturas rochosas formadas a partir da litificação de sedimentos praiais, como areia, através da cimentação principalmente por carbonato de cálcio ($CaCO_3$) e/ou sílica (BAPTISTA, 2010; GUERRA et al., 2005). Já os recifes biogênicos são oriundos do agrupamento de esqueletos dos organismos que secretam $CaCO_3$, como os corais hermatípicos, algas calcárias, moluscos, crustáceos, dentre outros, e que crescem sobre um substrato consolidado, muitas vezes acima de um recife de arenito, formando uma base de calcário, coberta por uma fina camada viva. Esses recifes estão distribuídos em várias profundidades e distâncias da costa, e podem se apresentar em três diferentes tipos, de acordo com inúmeros fatores seculares de escala regional e global, em recifes de franja, barreira e atol (SHEPPARD et al., 2018).

No geral, os recifes estão concentrados principalmente nas bordas orientais dos continentes e em regiões tropicais, que se estendem de 30ºN a 30ºS (SHEPPARD et al., 2018; SPALDING et al., 2001). Isso se deve ao fato de que essas áreas são influenciadas por correntes oceânicas mais quentes e apresentam águas claras, oligotróficas, com salinidade marinha e substratos adequados, características essenciais para a bioconstrução e *bloom* de biodiversidade desse ecossistema (COUCE et al., 2012). Além disso, fatores seculares, como a separação dos continentes (atividade tectônica) durante a Era Mesozóica, oscilação do nível do mar e da temperatura superficial dos oceanos, também restringiram o desenvolvimento dos recifes às regiões tropicais rasas (DUBINSKY; STAMBLER, 2010; GOWER et al., 2012).

Alguns autores indicam que a quantidade de espécies encontradas por área nos recifes é maior do que em qualquer outro ecossistema, seja marinho ou terrestre (SHEPPARD et al., 2018; SPALDING et al., 2001), registrando inúmeros organismos autotróficos, base da teia trófica, como fitoplâncton, macroalgas e endossimbiontes; invertebrados, como cnidários, crustáceos e moluscos; e vertebrados, como peixes e tartarugas. Nesses ambientes é possível encontrar as mais variadas formas de reprodução, alimentação, crescimento, predação, locomoção e relações ecológicas.

Dentre as relações ecológicas mais importantes nos recifes está o mutualismo, como por exemplo, na relação entre os corais e um grupo específico de microalgas. No tecido transparente do pólipo do coral estão "hospedados" os chamados endossimbiontes, que são em sua grande maioria dinoflagelados da família Symbiodiniaceae, que representam 75% do peso do pólipo (PINET, 2009). Os corais garantem abrigo para os endossimbiontes dinoflagelados, protegendo-os da predação e disponibilizando nutrientes oriundos de seus processos metabólicos. Enquanto essas microalgas fornecem cor, oxigênio e alimento para o coral a partir da atividade fotossintética (Figura 1), caracterizando assim um sistema de reciclagem de nutrientes entre esses organismos.

Figura 1 – Mutualismo entre coral e endossimbionte dinoflagelado.



Fonte: Pinet (2009).

Os corais são considerados um dos principais grupos de organismos calcificantes recifais, sendo responsáveis por aproximadamente 15% da produção global de $CaCO_3$ (ZILBERBERG et al., 2016). Durante a calcificação e de acordo com os níveis de saturação de aragonita (Ω_{ar}) do ambiente, os corais podem realizar a deposição ou formação de $CaCO_3$ de forma direta, através da captação de cálcio (Ca^{2+}) e carbonato (CO_3^{2-}) da água do mar (equação 1) e, principalmente de forma indireta, pelos íons bicarbonato (HCO_3^-) (equação 2). Esse processo ocorre em uma região específica entre o esqueleto de calcário e a calicoderme do pólipo (tecido adjacente ao esqueleto), chamada de "sítio de calcificação" (TAMBUTTÉ et al., 2011), onde apresenta uma intensa atividade enzimática e fluxos difusivos de Ca^{2+}, que possibilitam a realização da calcificação.

$$Ca^{2+} + CO_3^{2-} \rightarrow \downarrow CaCO_3 \quad (1)$$

$$Ca^{2+} + 2HCO_3^- \rightarrow \downarrow CaCO_3 + H^+ + HCO_3^- \rightarrow \downarrow CaCO_3 + CO_2 + H_2O \quad (2)$$

Os endossimbiontes dinoflagelados também são fundamentais para o processo de calcificação dos corais, auxiliando através: do consumo de CO_2 pela fotossíntese, contribuindo para um pH alcalino e maiores níveis de Ω_{ar} no interior do tecido do coral, principalmente em regiões com alta luminosidade; metabolização de fosfatos ou compostos que dificultam a calcificação; neutralização dos H^+ diante da liberação de hidroxila (OH^-) oriunda da fotossíntese, também garantindo um pH alcalino intracelular; incremento energético (COHEN et al., 2016; ZILBERBERG et al., 2016). O mutualismo entre essas microalgas e os corais é um dos principais fatores que historicamente garantiram o desenvolvimento dos grandes recifes de corais, tendo a diversidade da Symbiodiniaceae uma relação direta com a radiação adaptativa das espécies de corais (LAJEUNESSE et al., 2018; SIMPSON et al., 2011).

A comunidade primária e de invertebrados, bentônicos ou planctônicos, são as principais bases para a sustentação e manutenção de toda a grande biodiversidade recifal, regulando a distribuição das espécies de níveis tróficos superiores (BELLWOOD et al., 2004). Essas dinâmicas são afetadas por uma série de fatores ambientais, como sazonalidade, hidrodinâmica e clima, e nas últimas décadas vêm sendo impactadas principalmente pelas atividades antrópicas (HOEGH-GULDBERG et al., 2019; HUGHES et al., 2010).

Embora os recifes representem menos do que 1% do fundo oceânico, são considerados um dos ecossistemas mais lucrativos devido à sua biodiversidade (GROOT et al., 2012). Anualmente, geram mais de 30 bilhões de dólares através da pesca, turismo, recreação e proteção da costa (HILMI et al., 2019; SPALDING et al., 2017; WOODHEAD et al., 2018), sendo o continente asiático a região que mais lucra (PENDLETON et al., 2016). No entanto, trata-se de um ecossistema extremamente sensível a estressores ambientais, e a exploração não sustentável, somada a uma série de atividades antrópicas, direta e indiretamente, vêm causando significativos impactos sobre esse ambiente em escala global, como a acidificação oceânica (AO) e aquecimento dos oceanos, e local, como a eutrofização (GUAN et al., 2020).

1.1.1 Impactos globais

Atividades antrópicas, como a queima de combustíveis fósseis (carvão mineral, gás natural e petróleo) e o intenso desflorestamento, são os responsáveis pelas grandes emissões e acúmulo de um dos principais gases do efeito estufa na atmosfera, o gás carbônico (CO_2) (DONEY; SCHIMEL, 2007). Entre o século XVIII (revolução industrial) e início do XXI, o $CO_{2(atm)}$ apresentou um aumento de aproximadamente 40%, sendo o menor período de tempo, em pelo menos 800 mil anos, em que acréscimos dessa proporção tenham acontecido (IPCC, 2021). Atualmente, a concentração desse gás está em torno de 418 ppm (NOAA, 2022) e estimativas indicam que tende a alcançar valores próximos a 800 ppm até o final deste século (ORR et al., 2005).

Os oceanos possuem inúmeras características físicas e químicas que permitem grandes trocas de gases e energia com a atmosfera, sendo considerados os maiores reservatórios ou sumidouros de carbono do mundo (MILLERO, 2005). Devido a isso, e ao fato de o CO_2 ser o maior contribuinte para o aquecimento global (IPCC, 2021), a temperatura superficial dos oceanos (SST) e as concentrações de CO_2 na água do mar vêm aumentando significativamente ao longo dos anos (CANE et al., 1997), causando grandes alterações em diversos ecossistemas marinhos, dentre eles, o recifal.

Uma das principais consequências do aumento da SST sobre os recifes é a interrupção da relação entre coral e endossimbionte dinoflagelado (Figura 1). Em situações de estresse, principalmente térmico, as microalgas, durante a fotossíntese, aumentam a produção de espécies reativas de oxigênio, como água oxigenada (H_2O_2), gerando danos ao tecido do coral, que por sua vez as “expulsam” de seus pólipos, expondo assim o esqueleto calcário e caracterizando o fenômeno de branqueamento (ARMOZA-ZVULONI; SHAKED, 2014; GLYNN, 1993; GRAHAN; SANDERS, 2015; HUGHES et al., 2018; SULLY et al., 2019).

Uma vez branqueado, as atividades metabólicas desse animal são significativamente reduzidas, diminuindo o potencial reprodutivo, bioconstrução e complexidade estrutural dos recifes, podendo resultar na bioerosão e morte de colônias (BRUNO et al., 2007; DUARTE et al., 2020; FERREIRA et al., 2012; PEREIRA et al., 2022). A perda de habitat a partir do branqueamento altera as dinâmicas tróficas do ambiente recifal como um todo, assim como deixa em situação de alerta os países que dependem economicamente desse ecossistema, como Austrália, Brasil, México e países do sudeste asiático (PENDLETON et al., 2016).

As grandes emissões de CO_2 na atmosfera também resultam no processo de AO que afeta negativamente a saúde dos ambientes recifais em escala global (YATES & HALLEY, 2006; HOEGH-GULDBERG et al., 2007; KLEYPAS et al., 2011; ALBRIGHT et al., 2016). Aproximadamente 25% do CO_2 emitido pelas atividades antrópicas é absorvido pela superfície oceânica global por difusão (SABINE et al., 2004; TAKAHASHI et al., 2009), e isso vem alterando o equilíbrio do sistema carbonato marinho, que por sua vez, trata-se da dinâmica das espécies químicas inorgânicas do carbono, conforme a equação 3:

$$CO_{2(atm)} \leftrightarrow CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \quad (3)$$

O aumento na concentração do $CO_{2(atm)}$ resulta nos maiores valores desse gás em sua forma aquosa, que ao reagir com a molécula da água, forma mais ácido carbônico (H_2CO_3), facilmente dissociado em HCO_3^- e H^+. A maior disponibilidade de H^+ no ambiente é a principal responsável pela redução do pH ($-\log_{10}[H^+]$), caracterizando assim a AO. A grande problemática desse processo é que o CO_3^{2-} dissolvido na água do mar, tende a reagir com o excesso de H^+ produzido, para manter o equilíbrio da reação (efeito tampão), se tornando assim menos biodisponível (IPCC, 2021).

A estrutura dos recifes biogênicos é constituída basicamente de $CaCO_3$ oriundo das atividades metabólicas dos organismos calcificantes. No entanto, sob as condições de AO, esses organismos apresentam suas taxas de calcificação significativamente reduzidas devido a menor disponibilidade de CO_3^{2-} ou menores valores de Ω_{ar} do ambiente, o que pode implicar em dissolução, branqueamento e morte dos corais, perda de habitat e de biodiversidade recifal (GATTUSO et al., 1998; FEARY et al., 2007; KLEYPAS et al., 2011; MARANGONI et al., 2017).

O aumento da concentração de CO_2 na atmosfera já causou uma queda de 0.1 no pH do oceano global desde o século XVIII, e de acordo com o cenário SSP3-7.0 do IPCC, antes do final do século XXI as concentrações desse gás serão elevadas o suficiente para reduzir cerca de 0.4 na escala de pH e aumentar em até 4ºC a SST

(ORR et al., 2005; IPCC, 2021; EYRE et al., 2018). Isso resultará em oceanos subsaturados em CO_3^{2-}, podendo causar uma extinção em massa dos corais, consequentemente afetando a população humana, em aspectos sociais, culturais e econômicos (PENDLETON et al., 2016). Além disso, esses impactos globais atuam em sinergia com impactos locais, deixando ainda mais o ecossistema recifal em vulnerabilidade (DUTRA et al., 2021).

1.1.2 Impactos locais

O exponencial e desordenado crescimento demográfico em regiões litorâneas é um dos principais impactos de escala local sobre os recifes. Atualmente, indústrias de monocultura e centros urbanos localizados próximos à costa (≤ 30 km), estão gerando em proporções cada vez maiores resíduos sólidos e líquidos, devido às pressões do desenvolvimento turístico, imobiliário e agrícola (LANDRIGAN et al., 2020). Entretanto, os sistemas de planejamento e tratamento desses materiais e efluentes não estão acompanhando essa demanda, resultando nos descartes inadequados em corpos hídricos, como os rios, estuários, águas subterrâneas ou diretamente nas praias, consequentemente atingindo a zona recifal (ALVES et al., 2013; CABRAL; FONSECA, 2019).

Fertilizantes utilizados na agricultura, e efluentes industriais e domésticos não tratados, como esgoto bruto, apresentam elevadas concentrações de matéria orgânica e nutrientes, principalmente os nitrogenados e fosfatados, e quando são lançados nos corpos hídricos podem causar o processo chamado de eutrofização (BEUSEN et al., 2016; CHEN et al., 2021; CLARK et al., 2017; ZHANG et al., 2017). A eutrofização é definida como o constante *input* de nutrientes em um ambiente aquático/marinho ou aumento do estado trófico local, que resulta em 5 principais efeitos:

- O significativo crescimento da biomassa fitoplanctônica, muitas vezes de microalgas tóxicas, alterando a estrutura da comunidade;
- Aumento da turbidez devido a intensa produtividade primária;
- Redução da atividade fotossintética ao longo da coluna d’água;
- Consumo do oxigênio dissolvido (OD) pela degradação do excesso de matéria orgânica, podendo ocasionar hipoxia ou anoxia;

- Morte em massa dos organismos aeróbicos locais.

Ambientes recifais afetados pela eutrofização podem apresentar uma significativa redução da cobertura coralínea ao longo do tempo devido ao branqueamento e consequente morte dos corais (GUAN et al., 2020), e da proliferação de organismos bentônicos não-bioconstrutores, principalmente da comunidade primária, como as macroalgas (DECARLO et al., 2020; WOLFF et al., 2018). Por alterar a distribuição de organismos base da teia trófica, a eutrofização causa significativa mudança em todos os níveis tróficos superiores, reduzindo a biodiversidade e favorecendo a dominância de grupos específicos (DUPREY et al., 2016).

Outro problema decorrente da eutrofização é a acidificação costeira (COTOVICZ et al., 2022; WALLACE et al., 2014). Esse processo é caracterizado pela redução do pH local devido ao aumento dos níveis de $CO_{2(aq)}$, e consequente liberação de H^+ (Equação 1), oriundo da decomposição do excesso de matéria orgânica adicionada/produzida no ambiente afetado pela eutrofização, portanto, uma fonte adicional ao CO_2 antropogênico (CAI et al., 2011; GLEDHILL et al., 2015). Diante disso, há uma alteração na dinâmica do sistema carbonato, causando impactos na biota calcificante dos ecossistemas costeiros, como rios, estuários e recifes.

Estudos demostram que algumas espécies de moluscos e peixes estuarinos, em fases iniciais da vida, são afetadas pela redução do pH e de $[CO_3^{2-}]$, apresentando suas taxas de reprodução, crescimento e sobrevivência consideravelmente reduzidas (BARTON et al., 2015; FITZER et al., 2018). Isso já vem sendo um problema mundial, em aspectos ecológicos e socioeconômicos, principalmente para os pescadores e indústrias de aquicultura e piscicultura, que utilizam desses organismos como renda, produzindo e vendendo, como por exemplo, ostras cada vez menores (BARTON et al., 2015).

Ao atingirem o ambiente recifal, essas águas acidificadas atuam em sinergia com a AO e aquecimento dos oceanos, colocando ainda mais em risco a saúde dos corais, através do branqueamento e redução do potencial de bioconstrução desses organismos. Isso pode ser intensificado de acordo com a sazonalidade, principalmente durante períodos chuvosos, onde o fluxo de águas continentais, superficiais e subterrâneas, para o oceano costeiro é significativamente elevado, consequentemente, há um aumento no transporte de nutrientes e matéria orgânica para o ecossistema recifal (GASPAR et al., 2018; SILVA et al., 2009; SILVA et al., 2022; TAILLARDAT et al., 2020).

Os recifes costeiros podem ainda sofrer com vários outros tipos de impactos locais, como por exemplo, turismo desordenado, pisoteio, acidentes com embarcações, erosão, sedimentação, sobrepesca, espécies invasoras, poluição por resíduos sólidos e contaminantes orgânicos. Por isso, são necessárias cada vez mais estratégias que visem auxiliar na preservação, conservação e resiliência desse ecossistema.

Estudos descritivos e de modelagem vêm apresentando métodos capazes de auxiliar na conservação recifal, reduzindo os impactos e agindo em sinergia com os interesses e necessidades das comunidades locais (ALLEMAND; OSBORN, 2019; FENG et al., 2016; 2017; HILMI et al., 2019; HOEGH-GULDBERG et al., 2019; LEBREC et al., 2019; PENDLETON et al., 2019). Por exemplo, em relação aos efeitos da acidificação, existem técnicas de mitigação, que atuam visando reduzir os níveis de CO_2 da água do mar, e as chamadas técnicas de adaptação recifal, que contribuem com a aclimatação dos organismos diante das mudanças climáticas e dos impactos locais (ALBRIGHT; COOLEY, 2019).

É importante destacar que a principal e mais eficiente forma de mitigação dos impactos da acidificação e das mudanças climáticas como um todo, é a redução das emissões de CO_2 na atmosfera através de políticas, acordos e metas internacionais. Além disso, existe a técnica de remediação química, que se trata da neutralização do excesso de H^+ ao adicionar no ambiente soluções básicas de tamponamento ou minerais ricos em $CaCO_3$/sílica, que não somente reduzem as concentrações de CO_2 da água do mar, mas também aumentam a alcalinidade total (AT) e as concentrações de CO_3^{2-} (ALBRIGHT et al., 2016; ALBRIGHT; COOLEY, 2019). No entanto, embora promissora, essa técnica apresenta pontos negativos ainda não totalmente explorados, tanto em ambiente laboratorial, como principalmente *in situ*, como por exemplo, a contaminação por níquel associados aos minerais de olivina e a necessidade de uma significativa infraestrutura para resultados de grande escala (ANTHONY et al., 2017; GONZÁLES; ILYINA, 2016).

Já em relação a adaptação recifal, uma das principais técnicas que possuem como objetivo contribuir com a preservação e conservação desse ecossistema é a criação de Áreas de Proteção Ambiental (APAs) ou Unidades de Conservação (UCs) marinho-costeiras (ALLEMAND; OSBORN, 2019; ALBRIGHT; COOLEY, 2019). Essa estratégia se baseia no planejamento espacial de uma determinada área, isolando microrregiões de elevado potencial ecológico e socioeconômico, utilizando, no mínimo, 4 critérios essenciais:

- Identificação e proteção de refúgios naturais: Esses refúgios tratam-se de regiões que apresentam uma certa diversidade e espécies com elevada resiliência, capazes de sobreviver às altas amplitudes dos parâmetros abióticos, em escala sazonal ou diurna, e de repovoar áreas sob impactos;
- Conectividade com outros ecossistemas: Garantir que não haja barreiras físicas que comprometam a conectividade dos recifes com outros ecossistemas, como por exemplo, estuários e manguezais;
- Priorização de regiões ameaçadas: Estabelecer normas que impeçam e limitem potenciais impactos, controlando e restringindo a visitação turística, atividade de pesca, lançamento de efluentes e resíduos sólidos nos corpos hídricos locais, quantidade e tipo de embarcações, sob o risco de multa;
- Participação de comunidades locais: Uma gestão compartilhada e participativa é de extrema importância em áreas que se utilizam dos ambientes recifais como principal fonte de renda.

O monitoramento ambiental, não somente das comunidades biológicas, mas da dinâmica dos parâmetros abióticos, como dos nutrientes dissolvidos e do sistema carbonato, é uma ferramenta de extrema importância para a aplicação e manutenção das APAs. O conhecimento e descrição sobre como essas variáveis se comportam em diferentes escalas são a base para a interpretação dos dados bióticos, identificação e quantificação dos possíveis impactos, e assim determinação das ações de mitigação.

Diante do exposto, a presente Tese visou gerar informações inéditas para a maior APA marinho-costeira do Brasil, a APA Costa dos Corais (APACC), ao analisar a sazonalidade dos nutrientes inorgânicos dissolvidos e do sistema carbonato em regiões recifais de significativa importância ecológica e socioeconômica. Além disso, aplicar um experimento de alcalinização ou reversão *in situ* dos efeitos da AO, aumentando o banco de dados sobre essa técnica.

1.2 OBJETIVO GERAL

- Analisar a dinâmica sazonal do sistema carbonato e estado trófico em regiões recifais da APACC/Alagoas, e realizar um experimento *in situ* para observar a capacidade de reversão local dos efeitos da acidificação

1.3 OBJETIVOS ESPECÍFICOS

- Avaliar a influência sazonal dos aportes continentais, superficiais e subterrâneos, sobre os recifes de Maragogi a Japaratinga no estado de Alagoas;
- Determinar as concentrações de nutrientes inorgânicos dissolvidos e Chl-*a*, assim como estimar o estado trófico dos recifes;
- Analisar os principais parâmetros do sistema carbonato nos recifes estudados;
- Avaliar as respostas do metabolismo recifal e dos parâmetros do sistema carbonato dos recifes de Japaratinga diante de um experimento *in situ* de alcalinização.

1.4 HIPÓTESES

As hipóteses testadas foram que os parâmetros abióticos dos recifes de Maragogi e Japaratinga são significativamente modulados pela sazonalidade, principalmente devido ao aumento dos aportes continentais durante o período chuvoso, e que há um aumento no potencial de calcificação recifal e da Ω_{ar} em condições de valores de pH pré-industriais.

2 ARTIGO 1 – SEASONAL INFLUENCE OF SURFACE AND UNDERGROUND CONTINENTAL RUNOFF OVER A REEF SYSTEM IN A TROPICAL MARINE PROTECTED AREA

1 INTRODUCTION

Coral reefs are among the most ecological and economically valuable ecosystems worldwide (HILMI et al., 2019; PENDLETON et al., 2016), supporting approximately a quarter of the global marine biodiversity (BURKE et al., 2011) that uses them as a site for sheltering, feeding, reproduction and spawning. Moreover, these ecosystems provide numerous services for people, directly and indirectly, including coastline protection from waves and storms, fishing activities and tourism, yielding globally billions of dollars every year (ALBRIGHT; COLEY, 2019; LAM et al., 2019).

Coral reefs have been strongly affected by anthropogenic activities and have declined by more than 50% since the 1980s (ALBRIGHT; COLEY, 2019; ANDERSSON et al., 2019; HOEGH-GULDBERG et al., 2019; PENDLETON et al., 2016). Global processes, such as ocean warming and acidification are responsible for reducing reef construction capacity and for killing thousands of calcifying organisms (ALBRIGHT et al., 2018; ALLEMAND; OSBORN, 2019; MARANGONI et al., 2017). In addition, at local scale, continental runoff are also a significant threat, which have the potential to severely reduce reef biodiversity (WEAR; THURBER, 2015).

Continental runoff, such as rivers and submarine groundwater discharge (SGD), are essential sources of solutes to the coast due to their typically high concentrations of nutrients, organic matter (OM) and trace elements (CYRONAK et al., 2013a; PAYTAN et al., 2006). SGD is defined as any and all water advection through sediments to the coastal ocean, regardless of fluid composition or driving forces (BURNETT et al., 2003), and is classified into two major kinds: Terrestrial groundwater and seawater recirculated through permeable beds, both regulated by several continental, marine and meteorological processes, and by biogeochemical reactions (BECK et al., 2015; IBÁNHEZ; ROCHA, 2014; IBÁNHEZ; ROCHA, 2017; LIU et al., 2017; MOORE, 1999; NIENCHESKI et al., 2007; WANG et al., 2015).

The significance of SGD as a solute transport vector to reef zones has been increasingly recognized by the scientific community during the last two decades. SGD is commonly traced in the coast using radioisotopes (JIANG et al., 2021; TANIGUCHI et al., 2019). Radon (^{222}Rn) and radium isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra) are natural tracers of SGD due to their constant emanation from minerals and sediments, which result in much higher radioisotope activities on groundwaters and porewaters compared to surface waters (BURNETT et al., 2003; 2006). ^{222}Rn is a product of ^{226}Ra decay and is widely used in SGD studies, mainly due to its easy and cost-effective determination, high solubility, and unreactive nature (JIANG et al., 2021; TANIGUCHI et al., 2019).

The monitoring of SGD and rivers' influence over reefs is extremely important especially in regions with high urbanization and intense land use (CARREÓN-PALAU et al., 2017; WU et al., 2013; YOUNG et al., 2015). The direct release of domestic/industrial sewage and wastewater into rivers, exacerbated in regions with low rates of water treatment, together with the indiscriminate use of fertilizers on land, which infiltrate in the soil reaching coastal aquifers, increase significantly solute transport to the coast associated to continental runoff, causing several environmental issues (BARROSO et al., 2018; GUENTHER et al., 2014).

High loads of inorganic nutrients and OM can cause deleterious effects on coastal reefs, such as the decrease in oxygen concentration, eutrophication, coastal acidification, coral bleaching, decrease of the calcification capacity and community scale changes (CAI et al., 2011; DECARLO et al., 2020; WALLACE et al., 2014; WOLFF et al., 2018). The extent of these effects can be further intensified with seasonality due to continental runoff enhancement during the tropical rainy season (MICHAEL et al., 2005; SUGIMOTO et al., 2016; TAMBORSKI et al., 2017).

In this study, we aimed to evaluate qualitatively the effects of seasonality over a tropical South Atlantic reef located in a marine protected area (MPA) and to identify the influence of continental water sources (rivers and SGD) on the reef's environmental status. We used radon (^{222}Rn) as a natural SGD tracer, and analyzed the pressure of continental sources over dissolved inorganic nutrients, chlorophyll-a (Chl-*a*) and the carbonate system within the studied reef.

2 MATERIAL AND METHODS

2.1 Site description

With an area of more than 400 km^2, the Costa dos Corais is the Brazil's largest coastal MPA. It was created to protect high density mangrove forests (PAIVA, 2017) and the biodiversity associated with its coastal reefs, in addition to supporting sustainable development through the creation of tourism, fishing, transitional and non-taken zones (PMACC, 2013).

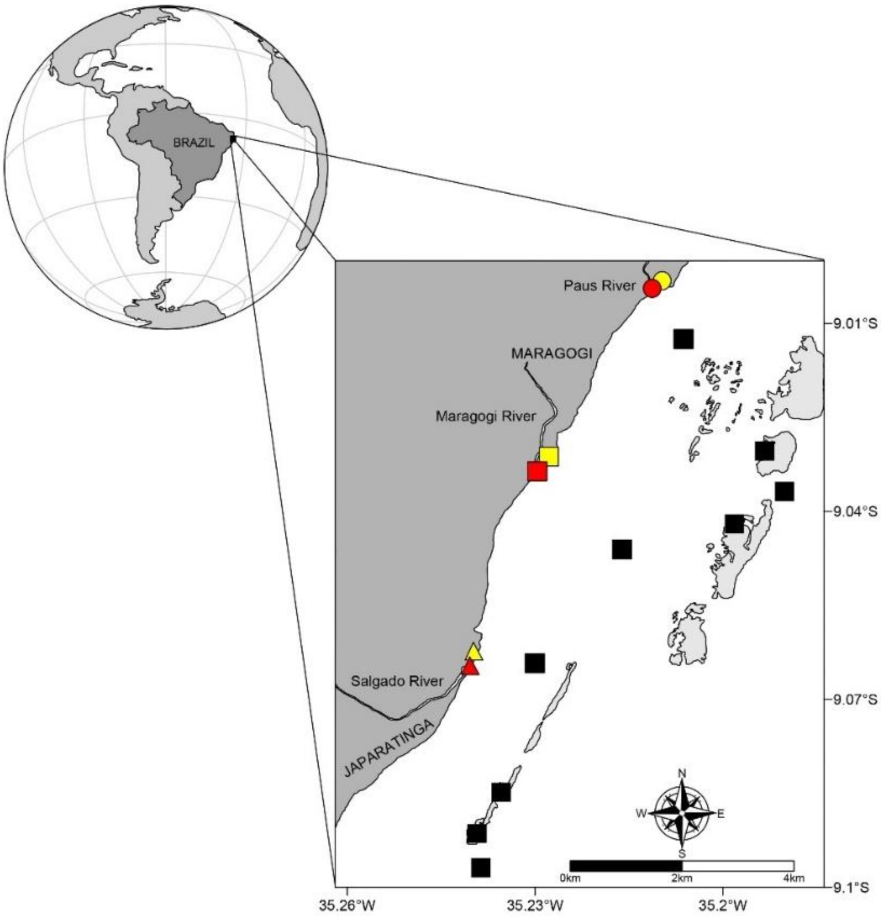
The study area is a reef lagoon of ~23 km^2, located in the northern Alagoas state between the Maragogi and Japaratinga municipalities (9°0'46.10"S, 35°12'23.10"W to 9°5'48.76"S, 35°14'19.21"W; Figure 1). It is subject to a semi-diurnal mesotidal regime, with an average depth of 4-5 m, reaching maximum depths of up to 10 m in the tidal channels within the reefs. This region is characterized by an inner and middle continental shelf covered by sand with high calcium carbonate ($CaCO_3$) content (VALLE, 2018) due to the presence of corals such as *Millepora* sp., *Mussismilia* sp., and crustose coralline algae. The reefs are mainly composed by sandstone, predominantly covered by epilithic algae with coral aggregates, and are inhabited by a wide diversity of vertebrate and invertebrate species (FERREIRA; MAIDA, 2006; SILVEIRA et al., 2014).

The climate is considered semi-humid tropical, with a rainy season between April and September, and a dry season from October to March. This coastal area receives about 60 thousand visitors each year (LINS, 2017), and has a correspondingly high development pressure and rising rates of human occupation (KASPARY, 2012); the population density is approximately 90 hab km^{-2} (IBGE, 2010). Sewage treatment is limited to a mean of 25.05% of the total domestic effluents in Maragogi and Japaratinga, reflecting the lack of planning and basic sanitation systems (IBGE, 2010; MASCARENHAS et al., 2005a, b).

The reef lagoon receives the discharge of three coastal rivers: Paus River, Maragogi River and Salgado River (Figure 1). These are important sources of solutes to the reef lagoon, especially during the rainy season. The Salgado River has the largest drainage basin area (245.3 km^2) and average runoff rate (396×10^3 m^3 d^{-1}) of the three (SEMARHN, 2005).

The coastal aquifers located within the Maragogi and Japaratinga municipalities mainly originate from mangrove and riverine-lagoon deposits, composed mainly of fine and coarse sand, muddy sediments, and organic materials (MASCARENHAS et al., 2005a, b). Groundwater is used by the local community and is accessed through more than 50 public and private wells, not all of which have been licensed (MASCARENHAS et al., 2005a, b).

Figure 1 – Map of the study area with the location of the sampling stations. Black squares indicate the sampling stations for surface seawater. Porewater (yellow) and river water (red) sampling stations are divided according to the region: northernmost (circles), central (squares) and southernmost (triangles) regions.



Source: The author (2022).

2.2 Sampling strategy and chemical analyses

Monthly sampling campaigns were carried out between July 2018 and June 2019 in the study area. Samples were always collected centered at the low tide period to obtain the highest continental influence in the lagoon. Porewater samples (n = 34) were taken with a piezometer buried at 1.5 m depth into the sand, collected with a manual water pump in three accessible locations at the shoreline (Figure 1). Water samples were stored for total alkalinity (TA), pH, nutrients, salinity, ^{222}Rn and Radium (^{226}Ra) analyses. Additionally, sediments samples (0.36 of porosity) were taken at these same sites, weighed (~130 g), stored in 250 mL air-tight bottles and filled with ^{222}Rn-free water for measurements of sediment-porewater secular ^{222}Rn equilibrium activities (CORBETT et al., 1998).

Sampling stations for surface water (0.5 m depth) were distributed from the coastal rivers to the reefs (Figure 1). During low tide, samples were taken with a 2 L Niskin bottle and stored for subsequent TA, pH, nutrients, salinity, ^{222}Rn and ^{226}Ra analyses. Salinity, temperature, and depth measurements were obtained *in situ* with an RBR® C.T.D.

^{222}Rn-in-water (n = 181) was analyzed in 250 mL water samples by using a RAD7 radon monitor coupled with a RADH2O accessory (Durridge Company®), following the air-water exchange method in a closed system (BURNETT; DULAIOVA, 2003). ^{226}Ra activities were determined based on the ingrowth of ^{222}Rn in aged samples, reanalyzing them after two months (i.e. after reaching secular equilibrium between ^{222}Rn and ^{226}Ra). The detection limit of our procedure was estimated at 36 Bq m^{-3} through the analyses of regular blanks measured in ^{222}Rn-free water (n = 24). ^{222}Rn in excess, i.e. that not supported by internal ^{226}Ra decay (1), and the radon inventory (2) were calculated as:

$$^{222}Rn_{exc} = Rn_{xy} - {}^{226}Ra_{xy} \quad (1)$$

$$RnI = Rn_{exc} \times (z_{xy} + z_{\mu}) \quad (2)$$

where $^{222}Rn_{exc}$ is the radon in excess (Bq m^{-3}), Rn_{xy} is the measured radon activity (Bq m^{-3}) and $^{226}Ra_{xy}$ is the samples' radium activity (Bq m^{-3}). RnI is the radon inventory (Bq m^{-2}), z_{xy} is the local depth at low tide (m) and z_{μ} represent the mean tidal height (m).

Water aliquots of 300 mL were used for the determination of carbonate system parameters and poisoned with 20 µL of mercury chloride ($HgCl_2$) 0.5 N immediately after sampling to prevent biological activity. TA (n = 181) was measured by a potentiometric titration method (DICKSON et al., 2007) with hydrochloric acid (HCl) 0.1 N, using the Apollo SciTech® automatic titrator in open cell with an analytical error of 1.03 µmol kg^{-1}. pH (total scale; n = 181) was analyzed by a spectrophotometric methodology (DICKSON et al., 2007), using the indicator dye *m*-purple ($C_{21}H_{18}O_5S$) ~2 mmol L^{-1}, with an analytical error of 0.008. Certified Reference Materials (CRM, Batch 144), from Scripps Institution of Oceanography, San Diego (USA), were used for the calibration and validation of the carbonate chemistry analyzes. The aragonite saturation state (Ω_{ar}) was then calculated using the CO2SYS v2.1 code from temperature, salinity, TA and pH values, where values over 1 represent a saturated status (FEELY et al., 2004; ZEEBE, 2012).

All samples for dissolved inorganic nutrients (n = 181) and Chl-*a* (n = 117) determinations were analyzed following spectrophotometric methods. Dissolved inorganic phosphorus (DIP) and dissolved silicate (DSi) were measured according to Grasshoff et al. (1983). Nitrate (NO_3^-) and nitrite (NO_2^-) were analyzed following García-Robledo et al. (2014), and ammonium (NH_3 + NH_4^+) was analyzed according to Bower and Holm-Hansen (1980). Dissolved inorganic nitrogen (DIN) values were obtained from the sum of NO_3^-, NO_2^- and NH_3 + NH_4^+ concentrations. Chl-*a* was analyzed according to the UNESCO (1966) method.

Dissolved oxygen was determined by the modified Winkler method (STRICKLAND; PARSONS, 1972). The trophic state was then estimated using the TRIX index (VOLLENWEIDER et al., 1998), calculated from dissolved oxygen saturation (DO%; UNESCO, 1973), DIP, DIN and Chl-*a* values, and samples were classified according to Table 1.

Table 1 – Trophic state classification of aquatic ecosystems based on the TRIX index.

TRIX	Trophic state
0 ≤ 4	Oligotrophic
> 4 ≤ 5	Mesotrophic
> 5 ≤ 6	Eutrophic
> 6	Hypereutrophic

Source: Vollenweider et al. (1998).

2.3 Publicly available data

The monthly rainfall rate in Maragogi during the sampling period was obtained from the Alagoas State Secretariat for the Environment and Water Resources (SEMARHN) dataset and the historical data (1993 to 2019) from the Pernambuco Water and Climate Agency (APAC). For the classification of surface water quality of the local rivers we used the weekly reports of the Environmental Institute of Alagoas (IMA). These reports define water quality for recreational use as “good” when ≥ 80% of the samples taken in one of the previous five weeks do not exceed 800 of the most probable number (MPN) of *Escherichia coli* per 100 mL, and as “bad” when these reasons are not complied or when the samples present in the last week an MPN greater than 2000.

2.4 Data analysis

Since our data set did not present normality and homoscedasticity, even after different transformations, non-parametric tests were used. PERMANOVA was used to test for significant differences in the dataset ($^{222}Rn_{exc}$, salinity, DIN, DIP, DSi, TA and pH) between seasons (rainy and dry) and sources (reefs, rivers and porewaters). Seasonal variations of each measured parameter were tested by using Kruskal-Wallis variance analysis, with significance level set at $P < 0.05$. Principal Components Analysis (PCA) was created with normalized units and a varimax rotation method. Correlations among parameters were explored with the Spearman test, also with a significance level set at $P < 0.05$.

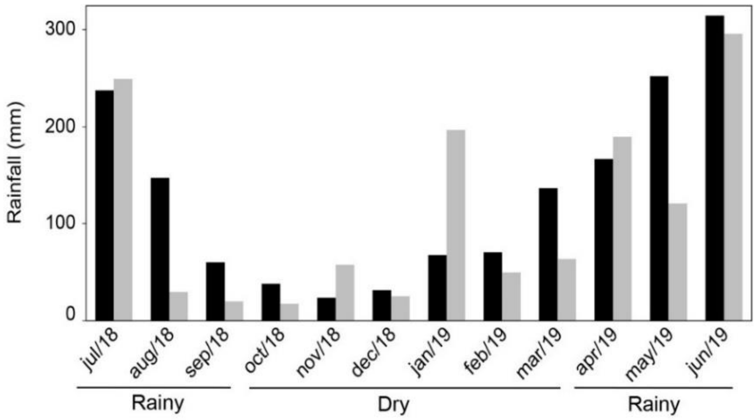
3 RESULTS

3.1 Reef lagoon

3.1.1 Hydrological data and trophic status

Rainfall during the studied period was seasonally different ($P < 0.05$), registering a mean of 139.75 ± 112.84 mm per month during the rainy season and 68.48 ± 65.45 mm per month during the dry season (Figure 2). August 2018 and February, March 2019 recorded values significantly lower than the monthly historical means ($P < 0.05$). January 2019, on the other hand, registered higher rainfall than the mean historical records ($P < 0.05$).

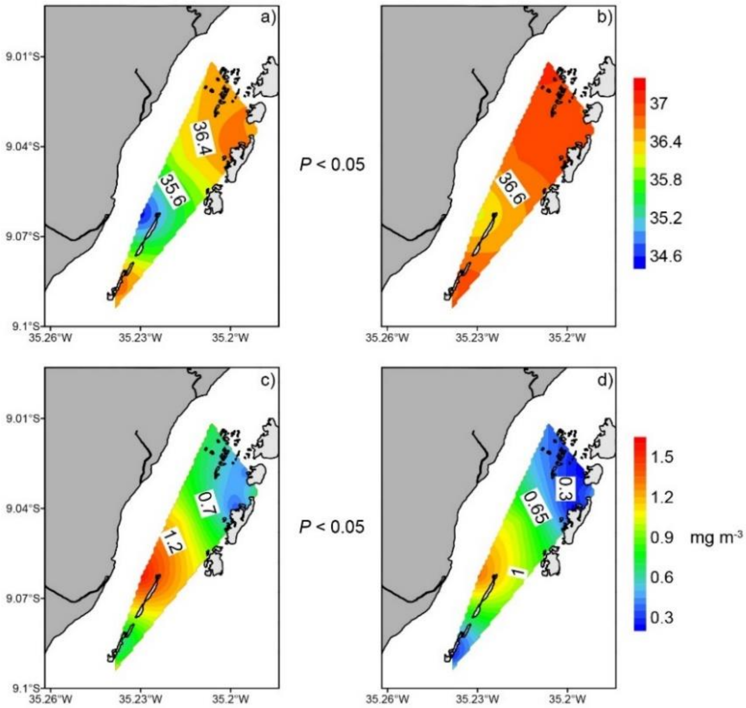
Figure 2 – Monthly (gray bar) and historical (black bar) rainfall during the studied period.



Source: The author (2022).

Salinity values decreased towards the coast and presented seasonal differences ($P < 0.05$, Figure 3a, b), registering a negative correlation with rainfall during the rainy season ($rs = 0.63$, $P < 0.05$). Chl-*a* inversely followed the salinity variation ($P < 0.05$, Figure 3c, d), similarly to other transitional water ecosystems (e.g., IBÁNHEZ et al., 2019; SILVA et al., 2019), with mean values of 1.03 ± 0.97 mg m^{-3} and 0.53 ± 0.5 mg m^{-3} in the rainy and dry season, respectively.

Figure 3 – Mean salinity (a, b) and Chl-*a* (c, d) distributions during the rainy (left) and dry season (right).

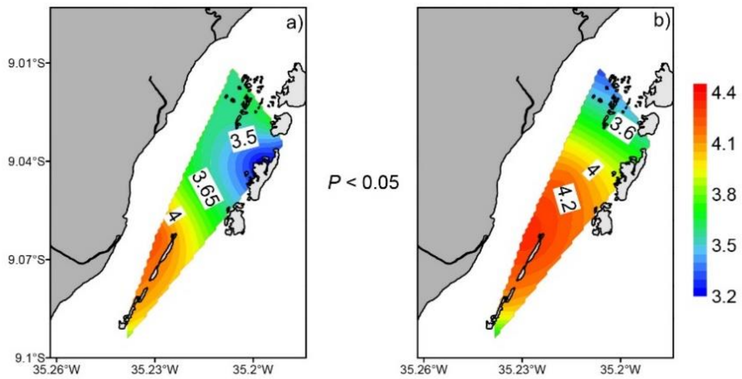


Source: The author (2022).

DSi was the most abundant nutrient, with a general mean of 11.41 ± 15.58 µmol L^{-1} and followed the Chl-*a* distribution during the rainy season (*rs* > 0.5, *P* < 0.05), positively correlated with rainfall (*rs* > 0.4, *P* < 0.05) and negatively with salinity (*rs* > 0.3, *P* < 0.05). DIP and DIN showed maximum values of 0.94 µmol L^{-1} and 5.94 µmol L^{-1} during the rainy season.

Regarding the trophic status of the reef lagoon, the calculated TRIX index showed seasonal differences (*P* < 0.05, Figure 4a, b), increasing values shoreward with values generally below or equal to 4. Nevertheless, in June 2019, November 2018 and especially July 2018 values over 5 were registered next to the Salgado River mouth (Apêndice A, Figure 1).

Figure 4 – Mean TRIX distribution during the rainy (a) and dry season (b).

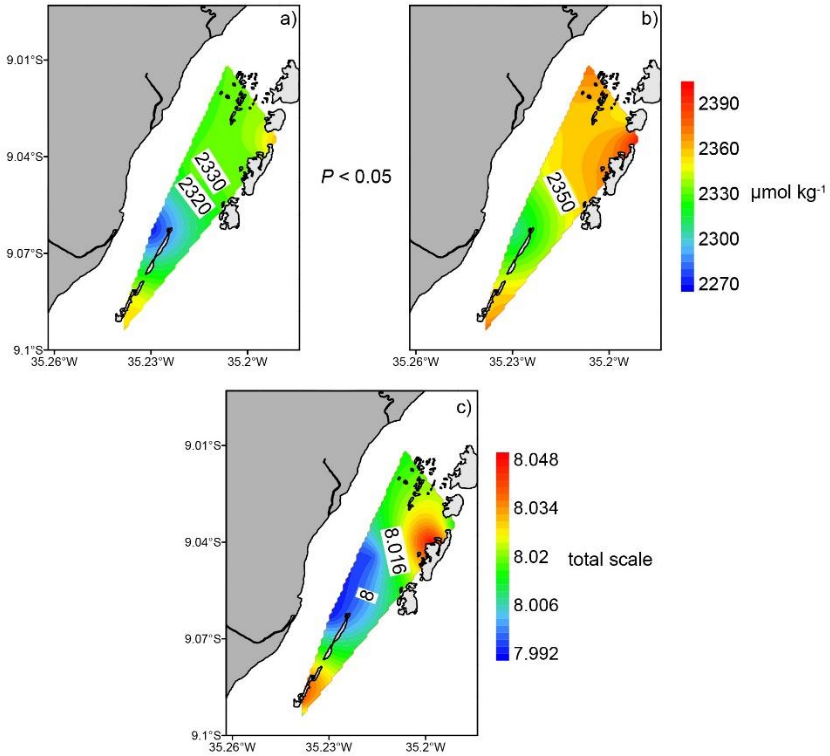


Source: The author (2022).

3.1.2 Carbonate system

Carbonate system parameters, TA and pH, presented significant positive correlation with salinity (*rs* > 0.5, *P* < 0.05), following its spatial and seasonal variations. TA registered a mean of 2305 ± 117 µmol kg^{-1} in the rainy season (Figure 5a) and of 2354 ± 82 µmol kg^{-1} (Figure 5b) in dry season, with the values increasing seaward. pH presented a general mean of 8.017 ± 0.041 (Figure 5c).

Figure 5 – TA mean distribution during the rainy (a) and dry season (b) and general mean of pH (c).

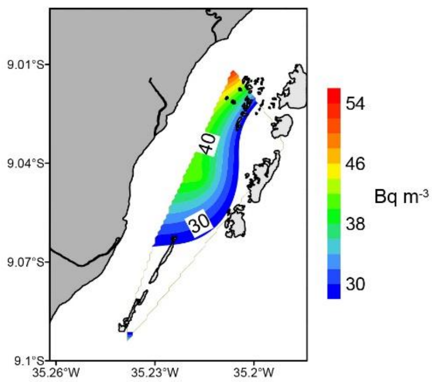


Source: The author (2022).

3.1.3 *Radon in water*

The $^{222}Rn_{exc}$ activities presented a general mean of 26.78 ± 42.25 Bq m^{-3} (Figure 6), with a maximum of 197 Bq m^{-3} registered shoreward during the rainy season. The values presented significant positive correlations with rainfall (*rs* = 0.33, *P* < 0.05) and Chl-*a* (*rs* = 0.30, *P* < 0.05) during the rainy season.

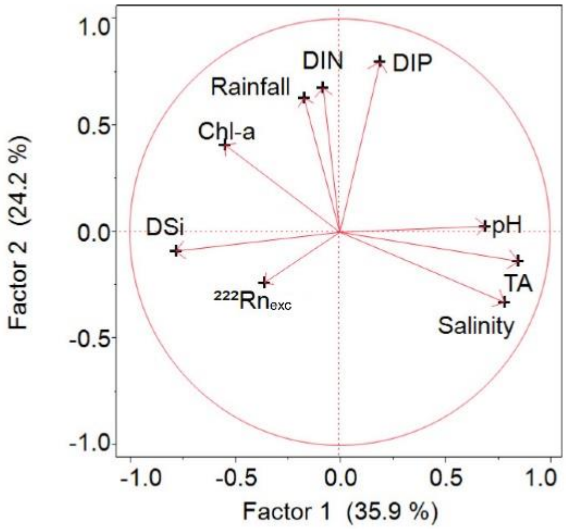
Figure 6 – General mean $^{222}Rn_{exc}$ activities in the lagoon.



Source: The author (2022).

The first two factors of the PCA employed with measured variables that presented significant correlations ($P < 0.05$) and $rs > 0.7$, explained 60.1% of the total variance (Figure 7). PCA factor 1 explained 35.9% of variation with salinity as the most significant variable, positively correlated with pH and TA, and negatively correlated with DSi. PCA factor 2 explained 24.2% with rainfall as the most significant variable, positively correlated with $^{222}Rn_{exc}$ and Chl-*a*. These results suggest that the carbonate system is mainly controlled by mixing processes, while nutrients and Chl-*a* are primarily linked to continental runoff and precipitation levels.

Figure 7 – PCA results showing the scores of each variable along the first two factors.



Source: The author (2022).

3.2 Shoreline porewaters and riverine waters

The seasonal mean values of the chemicals determined in the sampled rivers and porewaters are summarized in Table 2. $^{222}Rn_{exc}$, salinity, DIP, TA and pH varied significantly between seasons in the sampled rivers ($P < 0.05$). The Salgado River was the most different in comparison with the others ($P < 0.05$), registering the highest $^{222}Rn_{exc}$ activities and DIN concentrations, and the lowest salinity, TA and pH values.

Porewater chemical parameters presented significantly higher values compared to the sampled rivers ($P < 0.05$), except for pH, DIP and DSi. The maximum values were found especially at the central porewater station, which recorded general averages of 1742.81 ± 1339.14 Bq m^{-3}, 4183 ± 771.36 µmol kg^{-1} and of 7.48 ± 6.36 µmol L^{-1} for $^{222}Rn_{exc}$, TA and DIN respectively. PERMANOVA analysis showed that considering the set of abiotic parameters, porewaters, rivers and reefs were significantly different from each other during all the studied period (*P* < 0.05, Apêndice A, Table 1), and only reefs and rivers were affected by seasonality (*P* < 0.05, Apêndice A, Table 2).

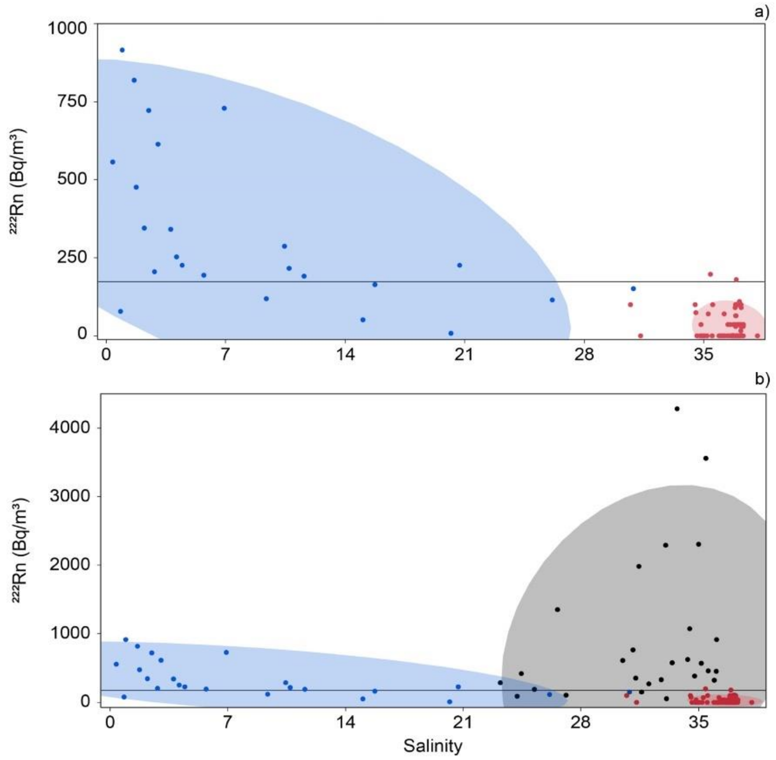
Table 2 – Seasonal mean and standard deviation (±) of key parameters determined in this study in samples taken from rivers and porewaters. Different superscript letters mean significant seasonal differences (*P* < 0.05).

	Rivers		Porewaters	
	Dry (n = 16)	Rainy (n = 14)	Dry (n = 17)	Rainy (n = 17)
$^{222}Rn_{exc}$ (Bq m^{-3})	242.50 ± 174.34^{a}	479.22 ± 312.49^{b}	874.11 ± 956.50^{a}	765.71 ± 1143.85^{a}
Salinity	11.65 ± 8.98^{a}	3.38 ± 3.50^{b}	32.93 ± 3.11^{a}	30.40 ± 4.94^{a}
TA (µmol kg^{-1})	1181.02 ± 591.60^{a}	614.4 ± 319.47^{b}	3167.08 ± 749.52^{a}	3782.41 ± 1038.41^{a}
pH	6.792 ± 0.35^{a}	6.329 ± 0.29^{b}	7.348 ± 0.150^{a}	7.338 ± 0.102^{a}
DIN (µmol L^{-1})	2.79 ± 2.75^{a}	2.89 ± 1.94^{a}	3.74 ± 3.01^{a}	5.24 ± 6.23^{a}
DIP (µmol L^{-1})	0.40 ± 0.28^{a}	0.78 ± 0.61^{b}	0.62 ± 0.78^{a}	1.30 ± 1.38^{a}
DSi (µmol L^{-1})	135.85 ± 96.23^{a}	153.03 ± 61^{a}	78.61 ± 45.38^{a}	114.52 ± 56.69^{a}

Source: The author (2022).

The high salinity registered in most of the reef samples and their low $^{222}Rn_{exc}$ activities (Figure 8a) contrasted with those measured in the rivers and porewaters (Figure 8b). In addition, sediment porewater equilibrium ^{222}Rn activities were significantly lower (*P* < 0.05) than those measured in the porewaters and rivers' samples (Figure 8), and above all the reefs', showing a mean of 174 ± 185 Bq m^{-3}.

Figure 8 – Salinity vs $^{222}Rn_{exc}$ in the different water masses sampled. (a) Rivers (blue) and reefs samples (red) versus salinity, (b) and together with porewater (black). Colored ellipses mean 90% of the samples' coverage. Solid horizontal line represents the sediment $^{222}Rn_{exc}$ equilibrium activities.



Source: The author (2022).

4 DISCUSSION

Rainfall and continental runoff in tropical coastal zones can significantly influence regional biogeochemical cycles (RUBIO-CISNEROS et al., 2018). Rainy seasons are characterized by high land-ocean nutrients and OM fluxes, with high volumes of freshwater recharging surface and underground water transport pathways which, in turn, increase their discharge to adjoining reef systems (GASPAR et al., 2018; SILVA et al., 2009; TAILLARDAT et al., 2020).

We observed lower shoreward salinity values, probably attributable to the contribution of the Salgado River (which has the highest runoff in comparison with the other rivers of the study site) during the wet season (CORDEIRO et al., 2018; JALES et al., 2012; SEMARH, 2005). This riverine input of continental water and solutes can influence the local primary productivity by regulating the abundance and distribution of the phytoplankton community (PASSOS et al. 2016), as suggested by the Chl-*a* distribution measured in the studied reef lagoon (Figure 3 c, d).

The strong significant correlations found between Chl-*a*, DSi, rainfall and salinity in the reef lagoon suggest that primary producers are dominated mainly by diatoms and fed by the continental delivery of DSi (MELO et al., 2013; SILVA et al., 2009). This group of microalgae is abundant in tropical coastal areas and uptake silica ($Si(OH)_4$) for their cell's walls construction, supported by continental runoff which is a significant source of this nutrient, especially during the rainy season (CORDEIRO et al., 2018; FERREIRA et al., 2015).

Trophic status in the reef lagoon varied mainly from mesotrophic to oligotrophic (Figure 4), shoreward to seaward respectively, with Chl-*a* and nutrients concentrations similar to other tropical reefs considered non-impacted (BARROSO et al., 2018; JALES et al., 2012; PINHEIRO et al., 2016). Nevertheless, attention must be given to the area influenced by the Salgado River, which punctually during the rainy season presented eutrophic conditions, such as those registered in July 2018 (Apêndice A, Figure 1).

In addition to the high DIN concentrations registered, the Salgado River presents poor water quality almost throughout the year (Apêndice A, Figure 2), indicating its contamination with domestic effluents (MARQUES et al., 2019; RUBIO-CISNEROS et al., 2018; WHO, 2003). An average amount of 290 m^3 d^{-1} of raw sewage and effluents from the local water treatment plants are released into the sampled rivers (SNIRH, 2015). Although this inflow of anthropogenic discharges represents less than 1% of the total riverine water transport (SEMARH, 2005), they seem enough to cause significant impacts on the reef area near the river mouth, especially during the rainy and touristic seasons, by significantly increasing riverine nutrient transport (LINS, 2017).

This is an increasing problem representing a threat to the reef lagoon by enhancing inorganic nutrient concentrations and stressing the reefs' health, promoting the proliferation of coral diseases, increasing their susceptibility to bleaching and rising the local trophic status (CARREÓN-PALAU et al., 2017; GUENTHER et al., 2015; MARRETO et al., 2017; SHTEREVA et al., 2015). Maragogi and Japaratinga municipalities present almost 50% of their land surface occupied by industrial agriculture, which is also associated to the input of nutrients into coastal waters due to the indiscriminate use of fertilizers (IBGE, 2010; KASPARY, 2012; LINS, 2017).

TA and pH values registered in the reef lagoon indicate good conditions for the survival of calcifying organisms (Figure 5), similar to other tropical reefs (CYRONAK et al., 2018; ENOCHS et al., 2019; TAKESHITA et al., 2018). Shoreward, these parameters are strongly influenced by the rainfall regime and riverine transport through saltwater and freshwater mixing processes, highlighted close to the Salgado River. Besides, the calcifying and primary producer organisms on the reefs can also influence the TA and/or pH values through net community calcification (NCC) and production (NCP), which daily regulates calcium carbonate ($CaCO_3$) and CO_2 consumption (MUEHLLEHNER et al., 2016; PINHEIRO et al., 2016; TAKESHITA et al., 2018).

In addition to the rivers, SGD can also be a significant transport pathway of terrestrial solutes to the coast (ARANDACIREROL et al., 2006; LEOTE et al., 2008; LUO et al., 2014; SZYMCZYCHA et al., 2012; WU et al., 2013). In our study area, sampled porewaters presented mostly marine salinity and the highest recorded $^{222}Rn_{exc}$ values (Table 2, Figure 8), especially in the central station, which were well above those supported by the local sediments and rivers, indicating that neither can explain these activities. Therefore, this suggests an external source of $^{222}Rn_{exc}$ to the porewaters, i.e. terrestrial groundwaters (HEISS; MICHAEL, 2014; PETERMANN et al., 2018).

As commonly found elsewhere, local terrestrial groundwaters are enriched in ^{222}Rn compared to surface waters (> 10^4 Bq m^{-3} in the studied area; IBÁNHEZ unpublished data; PAIVA; NIENCHESKI, 2018). Nevertheless, periodic salt accumulation in intertidal permeable sediments due to evaporation (GENG et al. 2016) together with a relatively low continental groundwater contribution to the overall SGD (ROBINSON et al. 2007) can mask the continental salinity signal in the porewaters, which could explain the lack of a clear correlation between salinity and $^{222}Rn_{exc}$ in these samples.

Within the reef lagoon, $^{222}Rn_{exc}$ values in the nearshore samples showed a general enrichment (Figure 6). Assuming that the lagoon is vertically well-mixed, $^{222}Rn_{exc}$ inventories in the nearshore exceeded 10^3 Bq m^{-2}. Diffusive transport of $^{222}Rn_{exc}$ originated from the sediment, calculated after Martens et al. (1980) and using the diffusion coefficient of ^{222}Rn in water presented by Schubert and Paschke (2015), would never exceed 12 Bq m^{-2} d^{-1} at our site. Therefore, these higher $^{222}Rn_{exc}$ inventories shoreward are likely originated from the advection of ^{222}Rn-rich porewaters, primarily driven by positive inland hydraulic gradients and tidal pumping (SANTOS et al. 2012).

The positive correlations of $^{222}Rn_{exc}$ with Chl-*a* and rainfall in the reef lagoon suggest that SGD is a potential source of nutrients to the lagoon (Figure 7), which enhances the local biomass and productivity, particularly during the rainy season (LEE et al., 2010; LUO et al., 2014; SU et al., 2012). DSi was the nutrient with the highest values in the sampled porewaters, followed by DIN. The dominant form of DIN was $NH_3 + NH_4^+$, indicative of reducing conditions within the sediment (1.5 m depth), which can be originated from fertilizer and wastewater leakage, NO_3^- reduction, OM remineralization, and the lack of oxygen would limit the nitrification process, thus accumulating $NH_3 + NH_4^+$ in the porewaters (CALVO-MARTIN et al. 2021; IBÁNHEZ et al., 2017; SLOMP; CAPPELEN, 2004;). Furthermore, under reducing conditions, phosphate is generally mobilized (GRIFFIOEN, 2006; SLOMP; CAPPELEN, 2004).

The N:P mean ratio in the sampled porewaters was 13.83 ± 19.08, however, the central porewater station registered the highest DIN concentrations and a N:P ratio of 27.68 ± 24.45 during the rainy season. Other studies showed that N:P ratio in groundwater and porewater is commonly higher than the Redfield ratios, and this is generally associated with highly urbanized watersheds and aquifers impacted by fertilizers (KIM et al., 2008; LAPOINTE et al., 1997; LIU et al., 2018; PAVLIDOU et al., 2014). The high N:P ratios of SGD can increase the water trophic status of the reef lagoon and cause significant changes in the phytoplankton community composition there, e.g., favoring micro and nanoplankton, and harmful microalgae proliferation (RENGARAJAN; SARMA, 2015; SU et al., 2012).

Besides nutrients, the reef carbonate system can also be influenced by SGD. Studies indicate that this source of solutes can act as positive feedback to acidification (CYRONAK et al., 2014; WANG et al., 2014; 2018) and/or increase the buffer capacity of surface waters (CYRONAK et al., 2013a, b). The local dominance of these antagonistic effects depends on different processes such as sediment carbonate dissolution rates, organic carbon concentration, rainfall, porewater residence times, temperature, net community production (NCP) and benthic calcification (LIU et al., 2014).

TA concentrations recorded in the porewaters were ~1000 µmol kg^{-1} higher than in surface waters, especially in the central site, similar to other systems (CYRONAK et al., 2013a; 2014; LIU et al., 2014). These values can be explained by bicarbonate (HCO_3^-) release during OM remineralization (SANTOS et al., 2012) and mainly by carbonate (CO_3^{2-}) dissolution from coastal carbonate rocks and sediments, which are dominant in the study area.

Concurrently, the low pH values registered in the sampled porewaters characterize an environment with high respiration and consequently high pCO_2 concentrations (WANG et al., 2018), which can decrease the Ω_{ar} of the lagoon after discharge, as suggested by the negative correlation of $^{222}Rn_{exc}$ and Ω_{ar} (rs = -0.28, P < 0.05) in the rainy season. This represents an important transport of CO_2 to the reef system that overcomes the TA input associated with SGD, acting as a positive feedback to acidification (CYRONAK et al., 2014; WANG et al., 2014; 2018). Nevertheless, this potential harmful impact of SGD on the carbonate system of the reef lagoon seemed very limited as Ω_{ar} within the lagoon remained at high levels throughout the period of study (Apêndice A, Figure 3). Further studies aiming to evaluate the diurnal variations of these parameters integrated with SGD transport estimations are needed to verify this assumption.

5 CONCLUSIONS

The studied reef lagoon presents conditions that in general favor biological activities, such as calcification and photosynthesis, with oligotrophic to mesotrophic conditions throughout the year. The spatial and seasonal amplitude of surface salinity and its correlations with most of the analyzed parameters showed that the contribution of the continental runoff studied here, mainly the rivers, is a determining factor for the transport and distribution of solutes within the lagoon, especially during the rainy season.

The rivers show an important contribution to the carbon biogeochemistry and primary production of the site, especially nearshore and during the rainy season, when their discharges are higher. However, signs of anthropogenic pressures, such as the high dissolved inorganic nutrients concentrations due to the release of untreated effluents were mainly identified in the vicinity of the Salgado River, and this is a threat to the health of the adjacent reefs by increasing the local trophic status.

The $^{222}Rn_{exc}$ activities in the reef lagoon suggest that SGD has a measurable impact over the lagoon water's composition near the shoreline. $^{222}Rn_{exc}$ correlations with rainfall and Chl-*a* suggest that SGD is a source of nutrients that can punctually drive primary production nearshore during the rainy season. Porewaters also showed an important spatial variability of the N:P ratio that can potentially affect the community structure of primary producers in surface waters and the reef metabolism.

The distance from the shore, low riverine discharges, and oceanographic factors, such as tidal dilution, coastal currents and water residence may maintain good conditions for the reefs throughout the year. However, current threats on a global and local scale, such as global warming, ocean acidification, growing urbanization and the flexibilization of environmental public policies, could increase the adverse impacts of continental runoff over the reef.

REFERENCES

ALBRIGHT, R.; COOLEY, S. A review of interventions proposed to abate impacts of ocean acidification on coral reefs. **Regional Studies in Marine Science**, v. 29, p. 100612, 2019.

ALBRIGHT, R.; TAKESHITA, Y.; KOWEEK, D. A.; NINOKAWA, A. et al. Carbon dioxide addition to coral reef waters suppresses net community calcification. **Nature**, v. 555, n. 7697, p. 516-519, 2018.

ALLEMAND, D.; OSBORN, D. Ocean acidification impacts on coral reefs: From sciences to solutions. **Regional Studies in Marine Science**, v. 28, p. 100558, 2019.

ANDERSSON, A. J.; VENN, A. A.; PENDLETON, L.; BRATHWAITE, A.; CAMP, E. F.; COOLEY, S.; GLEDHILL, D.; KOCH, M.; MALIKI, S.; MANFRINO, C. Ecological and socioeconomic strategies to sustain Caribbean coral reefs in a high-CO2 world. **Regional Studies in Marine Science**, v. 29, p. 100677, 2019.

ARANDACIREROL, N.; HERRERA-SILVEIRA, J. A.; COMÍN, F. A. Nutrient water quality in a tropical coastal zone with groundwater discharge, northwest Yucatan, Mexico. **Estuarine, Coastal and Shelf Science**, v. 68, n. 3-4, p. 445-454, 2006.

BARROSO, M. S.; SILVA, B. J.; FLORES-MONTES, M. J.; SANTOS, P. J. P. Anthropogenic impacts on coral reef harpacticoid copepods. **Diversity**, v. 10, n. 2, p. 32, 2018.

BECK, A. J.; KELLUM, A. A.; LUEK, J. L.; COCHRAN, M. A. Chemical flux associated with spatially and temporally variable submarine groundwater discharge, and chemical modification in the subterranean estuary at gloucester Point, VA (USA). **Estuaries and coasts**, v. 39, n. 1, p. 1-12, 2016.

BOWER, C. E.; HOLM-HANSEN, T. A salicylate–hypochlorite method for determining ammonia in seawater. **Canadian Journal of Fisheries and Aquatic Sciences**, v. 37, n. 5, p. 794-798, 1980.

BURKE, L. M.; REYTAR, K.; SPALDING, M.; PERRY, A. **Reefs at risk revisited.** World Resources Institute, 2011.

BURNETT, W. C.; BOKUNIEWICZ, H.; HUETTEL, M.; MOORE, W. S. et al. Groundwater and pore water inputs to the coastal zone. **Biogeochemistry**, v. 66, n. 1, p. 3-33, 2003.

BURNETT, W. C.; DULAIOVA, H. Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements. **Journal of environmental radioactivity**, v. 69, n. 1-2, p. 21-35, 2003.

CAI, W. J.; HU, X.; HUANG, W. J.; MURRELL, M. C. et al. Acidification of subsurface coastal waters enhanced by eutrophication. **Nature geoscience**, v. 4, n. 11, p. 766-770, 2011.

CALVO-MARTÍN, E.; ÁLVAREZ-SALGADO, X. A.; ROCHA, C.; IBÁNHEZ, J. S. P. Reactive solute transport through two contrasting subterranean estuary exit sites in the Ría de Vigo (NW Iberian Peninsula). **Frontiers in Marine Science**, v. 8, p. 94, 2021.

CARREÓN-PALAU, L.; PARRISH, C. C.; PÉREZ-ESPAÑA, H. Urban sewage lipids in the suspended particulate matter of a coral reef under river influence in the South West Gulf of Mexico. **Water research**, v. 123, p. 192-205, 2017.

CORBETT, D.; BURNETT, W.; CABLE, P. et al. A multiple approach to the determination of radon fluxes from sediments. **Journal of Radioanalytical and Nuclear Chemistry**, v. 236, n. 1-2, p. 247-253, 1998.

CORDEIRO, I. A.; FEITOSA, F. A. N.; FLORES-MONTES, M. J.; OTSUKA, A. Y. et al. Environmental conditions of the Suape estuarine-port complex area (Pernambuco, Brazil): phytoplankton biomass and hydrological parameters. Marine Biological Association of the United Kingdom. **Journal of the Marine Biological Association of the United Kingdom**, v. 99, n. 2, p. 291-301, 2019.

CYRONAK, T.; SANTOS, I. R.; ERLER, D. V.; EYRE, B. D. Groundwater and porewater as major sources of alkalinity to a fringing coral reef lagoon (Muri Lagoon, Cook Islands). **Biogeosciences**, v. 10, n. 4, p. 2467-2480, 2013a.

CYRONAK, T.; SANTOS, I. R.; MCMAHON, A.; EYRE, B. D. Carbon cycling hysteresis in permeable carbonate sands over a diel cycle: Implications for ocean acidification. **Limnology and Oceanography**, v. 58, n. 1, p. 131-143, 2013b.

CYRONAK, T.; SANTOS, I. R.; ERLER, D. V.; MAHER, D. T. et al. Drivers of pCO2 variability in two contrasting coral reef lagoons: The influence of submarine groundwater discharge. **Global Biogeochemical Cycles**, v. 28, n. 4, p. 398-414, 2014.

CYRONAK, T.; ANDERSSON, A. J.; LANGDON, C.; ALBRIGHT, R. et al. Taking the metabolic pulse of the world's coral reefs. **PloS one**, v. 13, n. 1, p. e0190872, 2018.

DECARLO, T. M.; GAJDZIK, L.; ELLIS, J.; COKER, D. J.; ROBERTS, M. B.; HAMMERMAN, N. M.; PANDOLFI, J. M.; MONROE, A. A.; BERUMEN, M. L. Nutrient-supplying ocean currents modulate coral bleaching susceptibility. **Science Advances**, v. 6, n. 34, p. eabc5493, 2020.

DICKSON, A. G.; SABINE, C. L.; CHRISTIAN, J. R. **Guide to best practices for ocean CO2 measurements**. North Pacific Marine Science Organization, 2007.

DULAIOVA, H.; GONNEEA, M. E.; HENDERSON, P. B.; CHARETTE, M. A. Geochemical and physical sources of radon variation in a subterranean estuary—Implications for groundwater radon activities in submarine groundwater discharge studies. **Marine Chemistry**, v. 110, n. 1-2, p. 120-127, 2008.

ENOCHS, I. C.; MANZELLO, D. P.; JONES, P. R.; STAMATES, S. J. et al. Seasonal carbonate chemistry dynamics on southeast Florida coral reefs: localized acidification hotspots from navigational inlets. **Frontiers in Marine Science**, v. 6, p. 160, 2019.

FEELY, R. A.; SABINE, C. L.; LEE, K.; BERELSON, W. et al. Impact of anthropogenic CO2 on the CaCO3 system in the oceans. **Science**, v. 305, n. 5682, p. 362-366, 2004.

FERREIRA, B. P.; MAIDA, M. **Monitoramento dos recifes de coral do Brasil**. Brasília, DF: MMA, Secretaria de Biodiversidade e Florestas, 2006.

FERREIRA, L. C.; SILVA-CUNHA, M. G. G.; AQUINO, E. P.; BORGES, G. C. P. et al. Temporal and spatial variation of phytoplankton in a tropical reef area of Brazil. **Tropical Ecology**, v. 56, n. 3, 2015.

GASPAR, F. L.; PINHEIRO, B. R.; NORIEGA, C. E. D.; ARAUJO, M. et al. Alkalinity, inorganic carbon and CO2 flux variability during extreme rainfall years (2010-2011) in two polluted tropical estuaries NE Brazil. **Brazilian Journal of Oceanography**, v. 66, p. 115-130, 2018.

GARCÍA-ROBLEDO, E.; CORZO, A.; PAPASPYROU, S. A fast and direct spectrophotometric method for the sequential determination of nitrate and nitrite at low concentrations in small volumes. **Marine Chemistry**, v. 162, p. 30-36, 2014.

GENG, X.; BOUFADEL, M. C.; JACKSON, N. L. Evidence of salt accumulation in beach intertidal zone due to evaporation. **Scientific reports**, v. 6, n. 1, p. 1-5, 2016.

GRASSHOFF, K, et al. Methods of Seawater Analyses. **Verlag Chemie**. 317, 1993.

GRIFFIOEN, J. Extent of immobilisation of phosphate during aeration of nutrient-rich, anoxic groundwater. **Journal of Hydrology**, v. 320, n. 3-4, p. 359-369, 2006.

GUENTHER, M.; FLORES-MONTES, M. J.; GONZALES-RODRIGUEZ, E.; NEUMANN-LEITÃO, S. Eutrophication effects on phytoplankton size-fractioned biomass and production at a tropical estuary. **Marine pollution bulletin**, v. 91, n. 2, p. 537-547, 2015.

HEISS, J. W.; MICHAEL, H. A. Saltwater-freshwater mixing dynamics in a sandy beach aquifer over tidal, spring-neap, and seasonal cycles. **Water Resources Research**, v. 50, n. 8, p. 6747-6766, 2014.

HILMI, N.; OSBORN, D.; ACAR, S.; BAMBRIDGE, T. et al. Socio-economic tools to mitigate the impacts of ocean acidification on economies and communities reliant on coral reefs—a framework for prioritization. **Regional Studies in Marine Science**, v. 28, p. 100559, 2019.

HOEGH-GULDBERG, O.; PENDLETON, L.; KAUP, A. People and the changing nature of coral reefs. **Regional Studies in Marine Science**, v. 30, p. 100699, 2019.

IBÁNHEZ, J. S. P.; ROCHA, C. Effects of recirculation of seawater enriched in inorganic nitrogen on dissolved organic carbon processing in sandy seepage face sediments. **Marine Chemistry**, v. 166, p. 48-58, 2014.

IBÁNHEZ, J. S. P.; ROCHA, C. Kinetics of inorganic nitrogen turnover in a sandy seepage face on a subterranean estuary. **Applied Geochemistry**, v. 87, p. 108-121, 2017.

IBÁNHEZ, J.S.P.; ARÉVALO, E.; KELLY, T.; PAPASPYROU, S.; ROCHA, C.; NICOLAIDOU, A. Unraveling the dispersion and environmental impact of anthropogenic discharges in transitional water ecosystems. **Estuarine, Coastal and Shelf Science**, v. 216, p. 204-217, 2019.

INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA. **Pesquisa Cidades**. IBGE, 2010. https://cidades.ibge.gov.br/brasil/al/maragogi (acessado 11 maio 2020).

JALES, M. C.; FEITOSA, F. A. N.; KOENING, M. L.; BASTOS, R. B. et al. O ecossistema recifal de Serrambi (nordeste do Brasil): biomassa fitoplanctônica e parâmetros hidrológicos. **Atlântica (Rio Grande)**, v. 34, n. 2, p. 87-102, 2012.

JIANG, S.; IBÁNHEZ, J.S.P.; WU, Y.; ZHANG, J. Geochemical tracers in submarine groundwater discharge research: practice and challenges from a view of climate changes. **Environmental Reviews**, v. 29, n. 2, p. 242-259, 2021.

KASPARY, M. G. A. R. Desenvolvimento turístico e o desenvolvimento local no município de Maragogi, Alagoas. **Dissertation**/Universidade Federal de Alagoas, 159, 2012.

KIM, G.; RYU, J. W.; HWANG, D. W. Radium tracing of submarine groundwater discharge (SGD) and associated nutrient fluxes in a highly-permeable bed coastal zone, Korea. **Marine Chemistry**, v. 109, n. 3-4, p. 307-317, 2008.

LAM, V. W.; CHAVANICH, S.; DJOUNDOURIAN, S.; DUPONT, S. et al. Dealing with the effects of ocean acidification on coral reefs in the Indian Ocean and Asia. **Regional Studies in Marine Science**, v. 28, p. 100560, 2019.

LAPOINTE, B. E.; LITTLER, M. M.; LITTLER, D. S. Macroalgal overgrowth of fringing coral reefs at Discovery Bay, Jamaica: bottom-up versus top-down control. Proc. 8th Int. Coral Reef Symp. 927-932, 1997.

LEE, Y. W.; KIM, G.; LIM, W. A.; HWANG, D. W. A relationship between submarine groundwater borne nutrients traced by Ra isotopes and the intensity of dinoflagellate red-tides occurring in the southern sea of Korea. **Limnology and oceanography**, v. 55, n. 1, p. 1-10, 2010.

LEOTE, C.; IBÁNHEZ, J. S.; ROCHA, C. Submarine groundwater discharge as a nitrogen source to the Ria Formosa studied with seepage meters. **Biogeochemistry**, v. 88, n. 2, p. 185-194, 2008.

LINS, A. P. G. D. Turismo e meio ambiente: o esgotamento sanitário no município de Maragogi, Alagoas. Dissertation/Universidade Federal de Alagoas, 211, 2017.

LIU, Q.; CHARETTE, M. A.; HENDERSON, P. B.; MCCORKLE, D. C. et al. Effect of submarine groundwater discharge on the coastal ocean inorganic carbon cycle. **Limnology and Oceanography**, v. 59, n. 5, p. 1529-1554, 2014.

LIU, Q.; CHARETTE, M. A.; BREIER, C. F.; HENDERSON, P. B. Carbonate system biogeochemistry in a subterranean estuary–Waquoit Bay, USA. **Geochimica et Cosmochimica Acta**, v. 203, p. 422-439, 2017.

LIU, J.; DU, J.; WU, Y.; LIU, S. Nutrient input through submarine groundwater discharge in two major Chinese estuaries: The Pearl River Estuary and the Changjiang River Estuary. **Estuarine, Coastal and Shelf Science**, v. 203, p. 17-28, 2018.

LUO, X.; JIAO, J. J.; MOORE, W. S.; LEE, C. M. Submarine groundwater discharge estimation in an urbanized embayment in Hong Kong via short-lived radium isotopes and its implication of nutrient loadings and primary production. **Marine pollution bulletin**, v. 82, n. 1-2, p. 144-154, 2014.

MARANGONI, L. F. B.; CALDERON, E. N.; MARQUES, J. A.; DUARTE, G. A. S. et al. Effects of CO2-driven acidification of seawater on the calcification process in the calcareous hydrozoan Millepora alcicornis (Linnaeus, 1758). **Coral reefs**, v. 36, n. 4, p. 1133-1141, 2017.

MARQUES, J. A.; COSTA, P. G.; MARANGONI, L. F. B.; PEREIRA, C. M.; ABRANTES, D. P.; CALDERON, E. N.; CASTRO, C. B.; BIANCHINI, A. Environmental health in southwestern Atlantic coral reefs: Geochemical, water quality and ecological indicators. **Science of The Total Environment**, v. 651, p. 261-270, 2019.

MARRETO, R. N.; BAUMGARTEN, M. G. Z.; WALLNER-KERSANACH, M. Trophic quality of waters in the Patos Lagoon estuary: A comparison between its margins and the port channel located in Rio Grande, RS, Brazil. **Acta Limnologica Brasiliensia**, v. 29, 2017.

MASCARENHAS, J. D. C.; BELTRÃO, B. A.; SOUZA-JUNIOR, L. C. D. **Projeto cadastro de fontes de abastecimento por água subterrânea estado de Alagoas: diagnóstico do município de Maragogi**. CPRM, 2005a.

MASCARENHAS, J. D. C.; BELTRÃO, B. A.; SOUZA-JUNIOR, L. C. D. **Projeto cadastro de fontes de abastecimento por água subterrânea estado de Alagoas: diagnóstico do município de Japaratinga**. CPRM, 2005b.

MELO, M. A. F.; KOENING, M. I.; FILHO, J. S. R.; TRAVASSOS, R. K. et al. Microfitoplâncton de águas costeiras adjacentes ao Porto do Recife (PE-Brasil). **Tropical Oceanography Online**, 2013.

MICHAEL, H. A.; MULLIGAN, A. E.; HARVEY, C. F. Seasonal oscillations in water exchange between aquifers and the coastal ocean. **Nature**, v. 436, n. 7054, p. 1145-1148, 2005.

MOORE, W. S. The effect of submarine groundwater discharge on the ocean. **Annual review of marine science**, v. 2, p. 59-88, 2010.

MUEHLLEHNER, N.; LANGDON, C.; VENTI, A.; KADKO, D. Dynamics of carbonate chemistry, production, and calcification of the Florida Reef Tract (2009–2010): Evidence for seasonal dissolution. **Global Biogeochemical Cycles**, v. 30, n. 5, p. 661-688, 2016.

NIENCHESKI, L. F. H.; WINDOM, H. L.; MOORE, W. S.; JAHNKE, R. A. Submarine groundwater discharge of nutrients to the ocean along a coastal lagoon barrier, Southern Brazil. **Marine Chemistry**, v. 106, n. 3-4, p. 546-561, 2007.

PAIVA, L. M. Variabilidade estrutural da floresta de mangue do estuário do rio Tatuamunha, Porto de Pedras, Alagoas, Brasil. Dissertação de mestrado/ Universidade Federal de Pernambuco, 85, 2018.

PAIVA, M.; NIENCHESKI, F. H. Advances of submarine groundwater discharge studies in South America. **Journal of the Brazilian Chemical Society**, v. 29, p. 916-924, 2018.

PASSOS, C. V. B.; FABRÉ, N. N.; MALHADO, A. C. M.; BATISTA, V. S.; LADLE, R. J. Estuarization increases functional diversity of demersal fish assemblages in tropical coastal ecosystems. **Journal of fish biology**, v. 89, n. 1, p. 847-862, 2016.

PAVLIDOU, A.; PAPADOPOULOS, V. P.; HATZIANESTIS, I.; SIMBOURA, N. et al. Chemical inputs from a karstic submarine groundwater discharge (SGD) into an oligotrophic Mediterranean coastal area. **Science of the total environment**, v. 488, p. 1-13, 2014.

PAYTAN, A.; SHELLENBARGER, G. G.; STREET, J. H.; GONNEEA, M. E. et al. Submarine groundwater discharge: an important source of new inorganic nitrogen to coral reef ecosystems. **Limnology and Oceanography**, v. 51, n. 1, p. 343-348, 2006.

PENDLETON, L.; LANGDON, C.; EKSTROM, J. A.; COOLEY, S. R. et al. Coral Reefs and People in a High-CO2 World: Where Can Science Make a Difference to People? **PloS one**, v. 11, n. 11, p. e0164699, 2016.

PETERMANN, E.; KNOLLER, K.; ROCHA, C.; SCHOLTEN, J.; STOLLBERG, R.; WEIB, H.; SCHUBERT, M. et al. Coupling end-member mixing analysis and isotope mass balancing (222-Rn) for differentiation of fresh and recirculated submarine groundwater discharge into Knysna Estuary, South Africa. **Journal of Geophysical Research: Oceans**, v. 123, n. 2, p. 952-970, 2018.

PINHEIRO, B. R.; GASPAR, F. L.; SILVA, B. J.; FLORES-MONTES, M. J. et al. Interactions between hydrology and benthic coverage at rocas atoll. **Tropical Oceanography**, 44, 2, 142-157, 2016.

PMACC – Plano de Manejo APA Costa dos Corais. Instituto Chico Mendes de Conservação da Biodiversidade, 2013.

RENGARAJAN, R.; SARMA, V. V. S. S. Submarine groundwater discharge and nutrient addition to the coastal zone of the Godavari estuary. **Marine Chemistry**, v. 172, p. 57-69, 2015.

ROBINSON, C.; LI, L.; BARRY, D. A. Effect of tidal forcing on a subterranean estuary. **Advances in Water Resources**, v. 30, n. 4, p. 851-865, 2007.

RUBIO-CISNEROS, N. T.; HERRERA-SILVEIRA, J.; MORALES-OJEDA, S.; MORENO-BÁEZ, M. et al. Water quality of inlets' water bodies in a growing touristic barrier reef Island "Isla Holbox" at the Yucatan Peninsula. **Regional studies in marine science**, v. 22, p. 112-124, 2018.

SANTOS, I. R.; EYRE, B. D.; HUETTEL, M. The driving forces of porewater and groundwater flow in permeable coastal sediments: A review. **Estuarine, Coastal and Shelf Science**, v. 98, p. 1-15, 2012.

SCHUBERT, M.; PASCHKE, A. Radon, CO_2 and CH_4 as environmental tracers in groundwater/surface water interaction studies − comparative theoretical evaluation of the gas specific water/air phase transfer kinetics. **The European Physical Journal Special Topics**, v. 224, n. 4, p. 709-715, 2015.

SECRETARIA EXECUTIVA DE MEIO AMBIENTE, RECURSOS HÍDRICOS E NATURAIS DE ALAGOAS. Balanço de disponibilidade x demanda de recursos hídricos na região hidrográfica litoral norte. **SEMARHN**, Relatório. 1-30, 2015. http://www.semarh.al.gov.br/ (acessado 20 dezembro 2019).

SISTEMA NACIONAL DE INFORMAÇÕES SOBRE RECURSOS HÍDRICOS. Atlas esgotos: despoluição de bacias hidrográficas – Sistema Maragogi. **SNIRH**, 2015. https://portal1.snirh.gov.br/arquivos/Atlas_Esgoto/Alagoas/Sistema_Atual/Maragogi.pdf (acessado 20 agosto 2021).

SHTEREVA, G.; VELIKOVA, V.; DONCHEVA, V. Human impact on marine water nutrients enrichment. **Journal of Environmental Protection and Ecology**, v. 16, n. 1, p. 40-48, 2015.

SILVA, M. H. D.; SILVA-CUNHA, M. G. G.; PASSAVANTE, J. Z. O.; GREGO, C. K. S. et al. Estrutura sazonal e espacial do microfitoplâncton no estuário tropical do rio Formoso, PE, Brasil. **Acta botanica brasilica**, v. 23, n. 2, p. 355-368, 2009.

SILVA, L. M.; FEITOSA, F. A. N.; FLORES-MONTES, M. J.; OTSUKA, A. Y.; SALDANHA-CORRÊA, F.; NORIEGA, C. Phytoplankton Productivity and Hydrology in an Impacted Estuarine Complex in Northeastern Brazil. **Open Journal of Ecology**, v. 9, n. 10, p. 458, 2019.

SILVEIRA, C. B. L.; FERREIRA, B. P.; COXEY, M. S. Variação temporal nos recifes de corais de Maragogi, APA Costa dos Corais (2010-2013). **Tropical Oceanography**, 42, 2, 2014.

SLOMP, C. P.; VAN CAPPELLEN, P. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. Journal of Hydrology. **Journal of Hydrology**, v. 295, n. 1-4, p. 64-86, 2004.

STRICKLAND, J. D.; PARSONS, T. R. A practical handbook of seawater analysis. **Bulletin of Fisheries Research**, 167, p. 1–311, 1972.

SU, N.; BURNETT, W. C.; ELLER, K. T.; MACINTYRE, H. L. et al. Radon and radium isotopes, groundwater discharge and harmful algal blooms in Little Lagoon, Alabama. **Interdisciplinary studies on environmental chemistry**, v. 6, p. 329-337, 2012.

SUGIMOTO, R.; HONDA, H.; KOBAYASHI, S.; TAKAO, Y. et al. Seasonal changes in submarine groundwater discharge and associated nutrient transport into a tideless semi-enclosed embayment (Obama Bay, Japan). **Estuaries and Coasts**, v. 39, n. 1, p. 13-26, 2016.

SZYMCZYCHA, B.; VOGLER, S.; PEMPKOWIAK, J. Nutrient fluxes via submarine groundwater discharge to the Bay of Puck, southern Baltic Sea. **Science of the Total Environment**, v. 438, p. 86-93, 2012.

TAILLARDAT, P.; MARCHAND, C.; FRIESS, D. A.; WIDORY, D.; DAVID, F.; OHTEG, N.; NAKAMURAH, T.; VINHI, T. V.; THANH-NHOJ, N.; ZIEGLER, A. D. Respective contribution of urban wastewater and mangroves on nutrient dynamics in a tropical estuary during the monsoon season. **Marine Pollution Bulletin**, v. 160, p. 111652, 2020.

TAKESHITA, Y.; CYRONAK, T.; MARTZ, T. R.; KINDEBERG, T. et al. Coral reef carbonate chemistry variability at different functional scales. **Frontiers in Marine Science**, v. 5, p. 175, 2018.

TAMBORSKI, J. J.; COCHRAN, J. K.; BOKUNIEWICZ, H. J. Submarine groundwater discharge driven nitrogen fluxes to Long Island Sound, NY: Terrestrial vs. marine sources. **Geochimica et Cosmochimica Acta**, v. 218, p. 40-57, 2017.

TANIGUCHI, M.; DULAI, H.; BURNETT, K. M.; SANTOS, I. R.; SUGIMOTO, R.; STIEGLITZ, T.; KIM, G.; MOOSDORF, N.; BURNETT, W. Submarine Groundwater

Discharge: Updates on its Measurement Techniques, Geophysical Drivers, Magnitudes and Effects. **Frontiers in Environmental science**, v. 7, p. 141, 2019.

UNESCO. International Oceanographic Tables. Volume 2. Oxygen Solubility in Sea Water, 1973.

UNESCO. Determination of photosynthetic pigments in seawater. Rapor of SCOR/UNESCO, working group 17 with meat from 4 to 6 June 1964, **Monography on Oceanography** Methodology. 69, 1966.

VALLE, M. M. Caracterização das feições sedimentares da plataforma de Alagoas, com base em levantamento aerobatimétrico LIDAR. **Dissertação de mestrado**/ Universidade Federal de Pernambuco, 96, 2018.

VOLLENWEIDER, R. A.; GIOVANARDI, F.; MONTANARI, G.; RINALD, A. Characterization of the trophic conditions or marine coastal waters with special reference to the NW Adriatic Sea: proposal for a trophic scale, turbidity and generalized water quality index. **Environmetrics: The official journal of the International Environmetrics Society**, v. 9, n. 3, p. 329-357, 1998.

WALLACE, R. B.; BAUMANN, H.; GREAR, J. S.; ALLER, R. C. et al. Coastal ocean acidification: The other eutrophication problem. **Estuarine, Coastal and Shelf Science**, v. 148, p. 1-13, 2014.

WANG, G.; JING, W.; WANG, S.; XU, Y. et al. Coastal acidification induced by tidal-driven submarine groundwater discharge in a coastal coral reef system. **Environmental science & technology**, v. 48, n. 22, p. 13069-13075, 2014.

WANG, G.; WANG, Z.; ZHAI, W. et al. Net subterranean estuarine export fluxes of dissolved inorganic C, N, P, Si, and total alkalinity into the Jiulong River estuary, China. **Geochimica et Cosmochimica Acta**, v. 149, p. 103-114, 2015.

WANG, S. L.; CHEN, C. T. A.; HUANG, T. H.; TSENG, H. C. et al. Submarine Groundwater Discharge helps making nearshore waters heterotrophic. **Scientific Reports**, v. 8, n. 1, p. 1-10, 2018.

WEAR, S. L.; THURBER, R. V. Sewage pollution: mitigation is key for coral reef stewardship. **Annals of the New York Academy of Sciences**, v. 1355, n. 1, p. 15-30, 2015.

WORLD HEALTH ORGANIZATION. **Guidelines for Safe Recreational Water Environments: coastal and fresh waters.** Geneva: WHO, 2003.

WOLFF, N. H.; SILVA, E. T.; DEVLIN, M.; ANTHONY, K. R. et al. Contribution of individual rivers to Great Barrier Reef nitrogen exposure with implications for management prioritization. **Marine pollution bulletin**, v. 133, p. 30-43, 2018.

WU, Z.; ZHOU, H.; ZHANG, S.; LIU, Y. Using 222Rn to estimate submarine groundwater discharge (SGD) and the associated nutrient fluxes into Xiangshan Bay, East China Sea. **Marine pollution bulletin**, v. 73, n. 1, p. 183-191, 2013.

YOUNG, C.; TAMBORSKI, J.; BOKUNIEWICZ, H. Embayment scale assessment of submarine groundwater discharge nutrient loading and associated land use. **Estuarine, Coastal and Shelf Science**, v. 158, p. 20-30, 2015.

ZEEBE, R. E. History of seawater carbonate chemistry, atmospheric CO_2, and ocean acidification. **Annual review of earth and planetary sciences**, v. 40, p. 141-165, 2012.

3 ARTIGO 2 – REEF METABOLISM AND CARBON CHEMISTRY RESPONSES TO AN *IN SITU* ARTIFICIAL ALKALINIZATION EXPERIMENT

1 INTRODUCTION

Coral reefs are one of the main marine ecosystems in terms of biodiversity, productivity, connectivity with other environments and social-economical aspects (ALLEMAND; OSBORN, 2019; BURKE et al., 2011; HILMI et al., 2019; HOEGH-GULDBERG et al., 2019). However, this habitat is also extremely vulnerable to several kinds of impacts on multiple scales. According to the Intergovernmental Panel on Climate Change (IPCC) global coral reefs will be almost vanished by the end of this century, especially due to climate changes impacts, such as ocean acidification (OA) (ANDERSSON et al., 2018; HUGHES et al., 2018; IPCC, 2021; KLEYPAS et al., 2011; PENDLETON et al., 2016).

The OA is characterized mainly by the decrease of the global ocean pH and carbonate (CO_3^{2-}) concentration, caused by the reactivity between the high levels of anthropogenic $CO_{2(atm)}$ and seawater, which results in a disequilibrium of the marine carbon chemistry (FEELY et al., 2009; GRUBER et al., 1996; SABINE et al., 2004).This process had caused a decline in more than 0.1 of the mean ocean pH from the beginning of the industrial period until the present day and decreased surface calcium carbonate saturation (Ω_{ar}) by 1 unit from 1800 to 2002. These changes have caused a significant decline in the net community calcification (NCC) of coral reefs and increase in calcifying organisms' mortality (ALBRIGHT et al., 2018; ANDERSSON et al., 2011; BATES et al., 2010; DOO et al., 2019; SHAW et al., 2015).

With the aim to avoid catastrophic future scenarios, decreasing anthropogenic CO_2 concentrations on the atmosphere and ocean is considered in most of the national and international plans for ocean and marine ecosystems health, conservation, and sustainability, such as the United Nations Decade of Ocean Science for Sustainable Development 2021-2030 and the Brazilian National Plan for Adaptation to Climate Change – PNA. These plans present the generation of comprehensive knowledge and understanding of the ocean, and the establishment of a carbon chemistry monitoring network among the main ways of reducing OA impacts (PNA, 2015).

Although still very scarce, scientists have been also studying tools to reduce OA effects through adaptation and mitigation methods (ALBRIGHT et al., 2016; BURNS;

CORBETT, 2020; FENG et al., 2016; 2017; LENTON et al., 2018). Adaptation techniques use ecological mechanisms to increase reefs' resilience or to adjust to the present impacts, such as by physical reef restoration, coral gardening, and the creation of a Marine Protected Area (MPA) (ALBRIGHT; COOLEY, 2019; BILLÉ et al., 2012; ROSADO et al., 2018). While mitigation techniques act on removing CO_2 from the atmosphere or ocean, e.g., through phytoremediation, with the use of aquatic plants, and through chemical remediation, also found as artificial ocean alkalinization (AOA) or coastal ocean alkalinization (COA), by buffering the products from the reaction between CO_2 and seawater (BERGSTROM et al., 2019; GONZÁLES; ILYINA, 2016).

Modeling studies indicate that chemical remediation is a promising technique that could protect marine biota from OA impacts and be a considerable carbon dioxide removal (CDR) through alkalizing agents, e.g., olivine, calcium carbonate ($CaCO_3$) and sodium hydroxide (NaOH) (FENG et al., 2016; 2017; LENTON et al., 2018). Nevertheless, these methods and their side effects are still poorly known, especially considering experimental tests with multiple variables (ALBRIGHT; COOLEY, 2019). There is only one case study in the world, which was done in an oceanic reef flat, that used a chemical remediation method *in situ* to quantify the net calcification responses to the addition of a NaOH solution, and obtained positive results, such as an increase in NCC and Ω_{ar} levels (ALBRIGHT et al., 2016).

In this study we evaluated and compared the responses of the reefs' metabolic pulse and carbon chemistry parameters in the present natural conditions and in a pre-industrial pH scenario, through an *in situ* alkalinization experiment. This experiment was applied in a tropical South Atlantic coastal reef, located in an MPA, and our working hypothesis was that the carbonate system would be significantly different between the scenarios, so we expected to see an increase of Ω_{ar} and calcification potential in pre-industrial conditions in comparison to the present conditions.

2 MATERIAL AND METHODS

2.1 Study area

The study site is a sandstone reef flat located in Japaratinga, state of Alagoas, Brazil (9°6'55.49"S, 35°15'28.39"W) and it is part of the Costa dos Corais MPA, which is Brazil's largest coastal MPA. This reef is 1 km away from the coast and is covered by mollusks, zoanthids and, corals, such as *Zoanthus* sp. and *Palythoa sp.*, and especially by the calcareous algae *Halimeda* sp (AUED et al., 2018). Japaratinga's reefs are one of the main sources of income for the local community through fishing and touristic activities (IBGE, 2010).

2.2 Experimental strategy

The experimental strategy followed the setup developed by Albright et al. (2016), which is based on the addition of an alkaline solution mixed with seawater and a tracer dye into the study area. The experiment was carried out from May 23rd to June 5th, 2021 (except June 3rd and 4th), and daily, during daytime before the low tide (Table 1), an inflatable pool with a total volume of 7 m^3 (Apêndice B, Figure 4) was filled with seawater by using three well pumps of 5 $m^3 h^{-1}$ (Apêndice B, Figure 5), each connected to a truck battery and a current inverter, stored in a watertight box (Apêndice B, Figure 6).

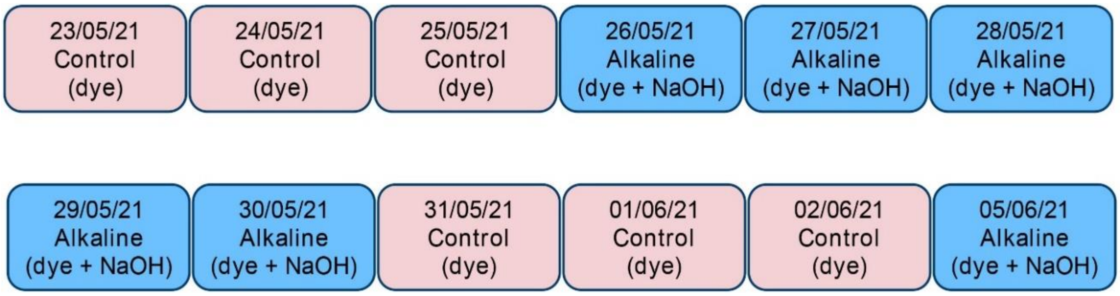
Table 1 – Predicted low tide height (m) and time (hours:minutes) during the experiment period.

Date	Low tide (m)	Time
05/23/2021	0.3	07:17
05/24/2021	0.2	08:06
05/25/2021	0.1	08:54
05/26/2021	0.0	09:30
05/27/2021	0.0	10:26
05/28/2021	0.1	11:15
05/29/2021	0.2	12:08
05/30/2021	0.3	13:02
05/31/2021	0.5	14:04
06/01/2021	0.5	15:11
06/02/2021	0.6	16:23
06/05/2021	0.6	06:54

Source: The author (2022).

The experiment was divided according to the treatment, on control days (n = 6), where only the tracer dye was added into the pool, and on alkaline days (n = 6), represented by the addition of the dye + a NaOH solution (Figure 1). The tracer dye used was the rhodamine WT (water tracer), which is a non-reactive and non-toxic compound, and every day, 10 mL of the rhodamine WT concentrated solution (20%) was diluted in 250 mL of distilled water and added to the pool (Apêndice B, Figure 4). Only during alkaline days, 700 mL of a NaOH ~ 10 M solution was introduced into the pool and mixed for about 30 minutes with the aim to increase the pH values and dissolve brucite ($Mg(OH)_2$) minerals formed by the reaction of seawater with the NaOH. These mixed solutions were daily sampled for further chemical analyses, and a tarp was used to cover the pool and avoid exchanges with the atmosphere during the process.

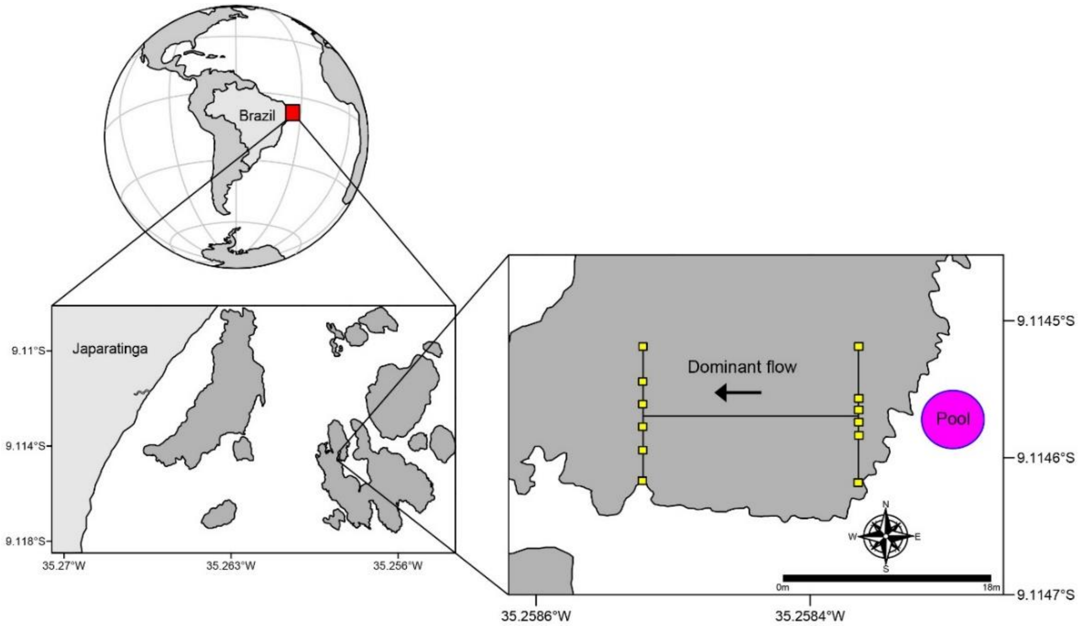
Figure 1 – Experimental period, dividing control (pink) and alkaline (blue) days.



Source: The author (2022).

2 transects of 12 m were pre-established considering the unidirectional daily flow of the seawater, one upstream of the reefs' edge and the other 18 m away, totalizing an area of 216 m^2, and each one with 6 sampling stations defined to cover the dye plume gradient (Figure 2). During the predicted time of the low tide (Table 1), the mixed solution from the control (seawater + dye) and alkaline days (seawater + dye + NaOH) was pumped onto the reef system until the dye plume reached both transects and the pool was empty (~ 30 minutes), with the sampling starting immediately after it. It was taken samples for nutrients, chlorophyll-*a* (Chl-*a*), carbonate system, dissolved oxygen (DO) and rhodamine WT analyses, and an RBR® C.T.D was used for obtaining i*n situ* temperature, salinity, and depth values.

Figure 2 – Study area location and experimental strategy.



Source: The author (2022).

2.3 Chemical analyses and metabolism estimation

For the determination of carbonate system parameters, samples were poisoned with mercury chloride ($HgCl_2$) 0.5 N after the sampling to prevent biological activity and kept in a thermostat bath at 25ºC before their analyses. TA (n = 154) was measured by a potentiometric titration method (DICKSON et al., 2007) with hydrochloric acid (HCl) 0.1 N, using the Apollo SciTech® automatic titrator in open cell with an analytical error of 1.15 µmol kg^{-1}. pH (n = 154) was analyzed by a spectrophotometric methodology (DICKSON et al., 2007), using the indicator dye *m*-purple ($C_{21}H_{18}O_5S$) ~ 2 mmol L^{-1} with an analytical error of 0.006. Certified Reference Materials (CRM, Batch 171), from Scripps Institution of Oceanography, San Diego (USA), were used for the calibration and validation of these methods. The aragonite saturation state (Ω_{ar}), Revelle Factor and total dissolved inorganic carbon (C_T) were calculated using the CO2SYS v2.1 code through temperature, salinity, TA, and pH values (FEELY et al., 2004; ZEEBE, 2012).

The balance between net organic carbon metabolism or net community production (NCP) and net inorganic carbon metabolism or NCC was determined by the regression between TA and C_T, where slopes' values close to 0 indicate the predominance of NCP, ~ 1 represents the NCP:NCC equilibrium and approached to 2 is an NCC dominance (CYRONAK et al., 2018). The net calcification potential or TA anomaly (ΔTA) was estimated by using Silva et al. (2021) dataset from the offshore stations, considering the differences in TA concentrations between the reefs and the adjacent open ocean (CYRONAK et al., 2018), where negative and positive values represent TA depletion and repletion respectively.

Rhodamine WT concentrations were determined by a colorimetric analysis. Samples were kept in a temperature-controlled water bath at 25ºC to reduce temperature errors in the fluorescence, and a standard of rhodamine WT 400 ppb was diluted to 0, 4.5, 9, 18, 36, 72, 144 ppb to create a curve for the measurement in the Ocean Optics® spectrophotometer. Values were then normalized to the mean salinity of 35.84.

All the samples for Chl-*a* (n = 20) and dissolved inorganic nutrients (n = 20) were analyzed by colorimetric methods in the Cary 100® UV-vis spectrophotometer. Chl-*a* was analyzed according to UNESCO (1966), which is based on the pigment extraction from the filter by using acetone (C_3H_6O) 90%. Nitrate (NO_3^-) and nitrite (NO_2^-) were analyzed following García-Robledo et al. (2014), and ammonium (NH_3 + NH_4^+) was by Bower and Holm-Hansen (1980). Dissolved inorganic nitrogen (DIN) values were obtained from the sum of NO_3^-, NO_2^- and NH_3 + NH_4^+ concentrations. Dissolved inorganic phosphorus (DIP) and dissolved silicate (DSi) were measured according to Grasshoff et al. (1983). DO was analyzed following Winkler's modified method (STRICKLAND; PARSONS, 1972).

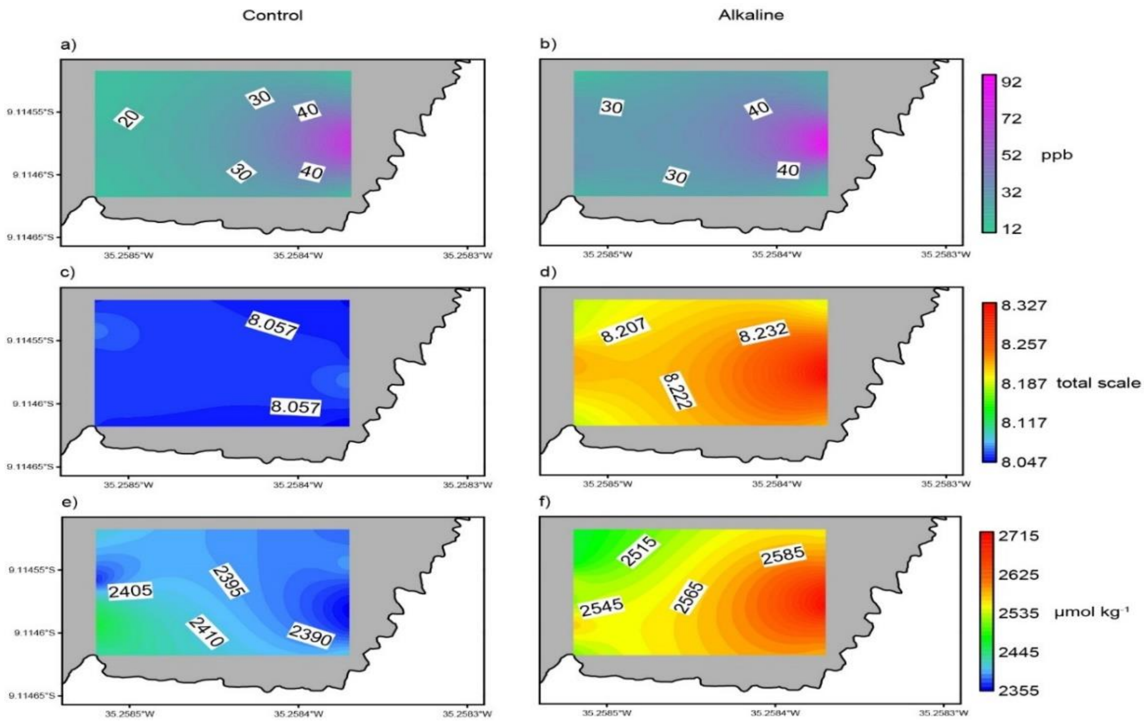
2.4 Data analysis

Non-parametric tests were applied since our dataset did not present normality and homoscedasticity. To verify differences among treatments it was used the Kruskal-Wallis variance analysis, by grouping all results from the sampling stations and comparing each analyzed parameter (TA, pH, Ω_{ar}, rhodamine WT and NCP:NCC) between control and alkaline days, with a significance level set at $P < 0.05$. Correlations among measured variables were determined with the Spearman test, also with a significance level set at $P < 0.05$. Golden Software Surfer® v.8 was used for creating the distribution maps and JMP Software® for the box plot.

3 RESULTS

The results showed that the rhodamine WT distribution was not significantly different between treatments (*P* > 0.05), with higher values upstream of the reef, decreasing downstream the transect (Figure 3a, b), and positive correlations with pH and TA only during alkaline days (*rs* > 0.28, *P* < 0.05). In these days, pH values were significantly higher (*P* < 0.05) than in controls', registering an average of 8.237 ± 0.095 (Figure 3d), while in natural conditions, presented a general mean of 8.059 ± 0.059 (Figure 3c), and positive correlations with salinity (*rs* = 0.78, *P* < 0.05) and TA (*rs* = 0.25, *P* < 0.05). For TA, there was a significant mean increase of 205.27 µmol kg^{-1} between treatments (*P* < 0.05), with the alkaline days registering the highest TA concentrations (Figure 3f).

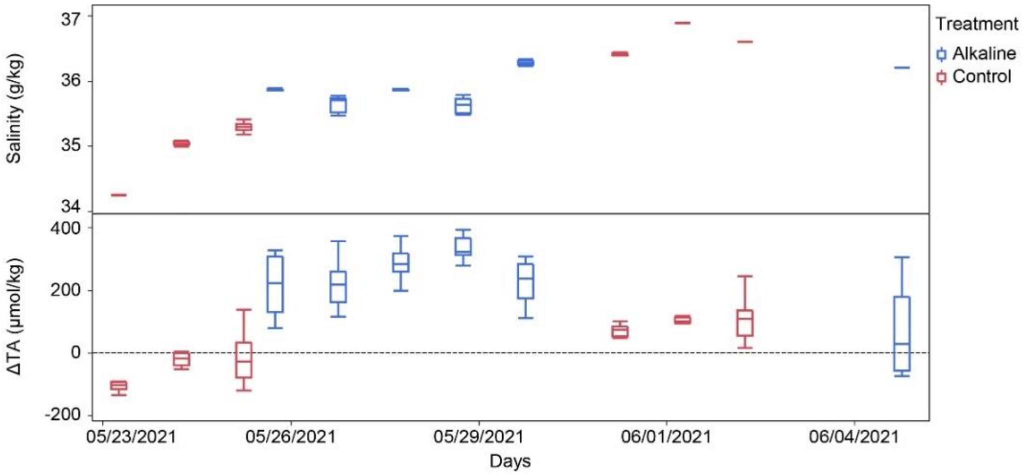
Figure 3 – Mean rhodamine WT (a, b), pH (c, d) and TA (e, f) distribution during control (left side) and alkaline days (right side).



Source: The author (2022).

The local ΔTA varied from -135.43 µmol kg^{-1} on the first control day to 454.95 µmol kg^{-1} on alkaline days (Figure 4), based on the mean TA value of the offshore region adjacent to our study area, that is 2375.02 µmol kg^{-1} (SILVA et al., 2022). ΔTA also followed the salinity values (rs = 0.68, P < 0.05), ranging values from 34.24 to 36.90 along the days (Figure 4).

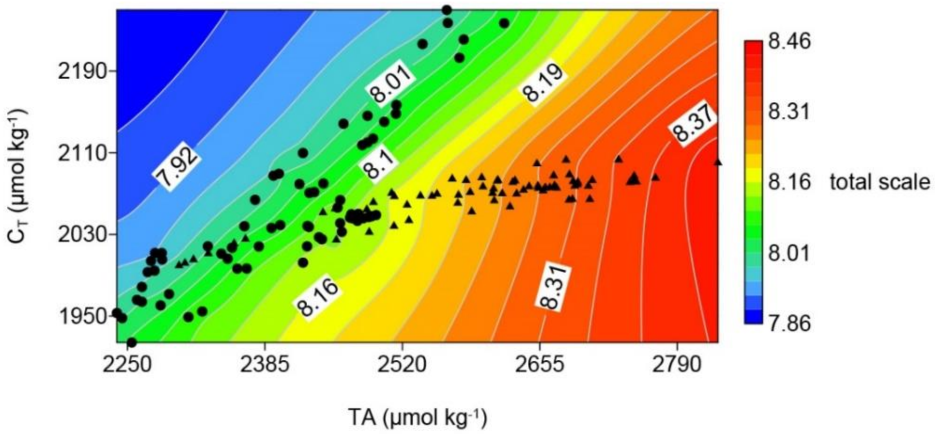
Figure 4 – Salinity and ΔTA box plots variation along the days. Box plots show the mean and standard deviation values. Dashed line represents the ΔTA value of 0 and the colors are respective to the treatments, alkaline (blue) and control (red).



Source: The author (2022).

The NCC:NCP balance presented significant changes between control and alkaline days (P < 0.05). In natural conditions, the studied reef registered TA:C_T slopes that varied from 0.39 to 1.11, with a mean of 0.87, representing an equilibrium of organic and inorganic carbon production, that followed the low pH variability throughout the days (Figure 5). While during alkaline days, the NCC metabolism was the most representative due to the slopes' values > 2, which crossed the pH isolines (Figure 5).

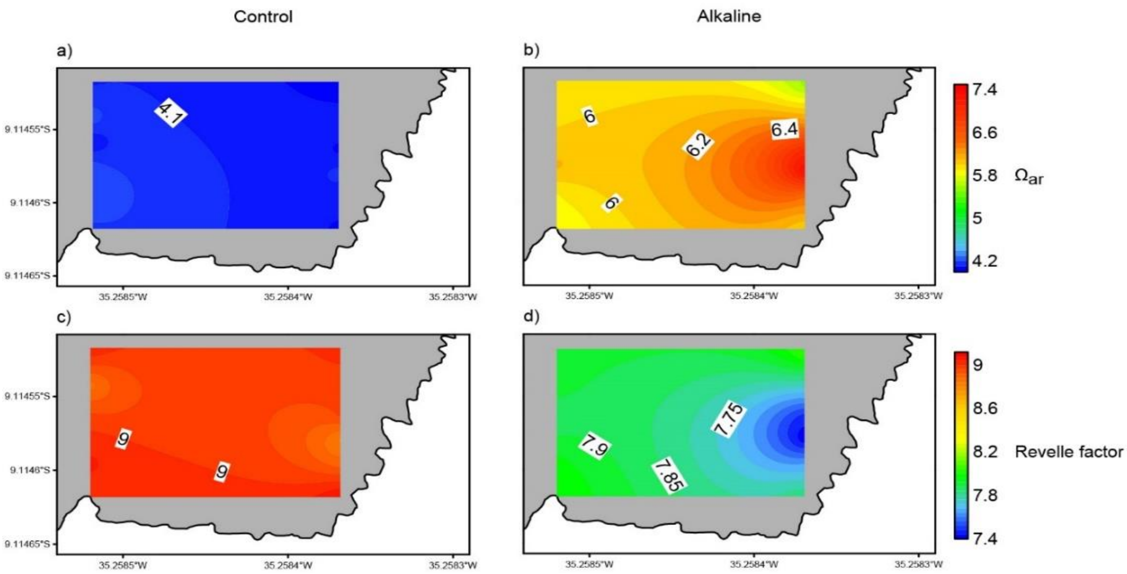
Figure 5 – TA-C_T regressions according to treatment, control (circles) and alkaline days (triangles). Colored contour and isolines are the pH variation.



Source: The author (2022).

Ω_{ar} followed pH and TA distribution and their correlations. During the control days, it was registered a general mean of 4.13 ± 0.54 (Figure 6a), significantly lower than on alkaline days ($P < 0.05$), which presented an average of 6.21 ± 1.22, with the values varying from 3.41 to 8.43 (Figure 6b). This represents an increase of more than 50% between treatments. For the Revelle factor, the values significantly decreased between control and alkaline days, registering a respectively mean of 8.97 ± 0.58 (Figure 6c) and 7.81 ± 0.56 (Figure 6d).

Figure 6 – Mean Ω_{ar} (a, b) and Revelle factor (c, d) distribution during control (left side) and alkaline days (right side).



Source: The author (2022).

4 DISCUSSION

The dynamic of TA is regulated by several physical, chemical and biological factors that can change in diel, temporal, and spatial scales, e.g., by reef metabolic rates, water residence time, and continental runoff influence (ALBRIGHT et al., 2013; PAGE et al., 2016; SHAW et al., 2015). TA concentrations registered here on the alkaline treatment were higher than those from Albright et al. (2016) experiment, and this is especially due to the latitudinal differences in meteorological and oceanographic factors, such as precipitation and the higher sea surface salinity and temperature in South Atlantic compared to South Pacific (BROULLON et al., 2019; FINE et al., 2017; LEE et al., 2006). While in natural conditions, pH and TA values were similar to other tropical reefs considered non-local impacted (BARROSO et al., 2018; PINHEIRO et al., 2016; SILVA et al., 2022), and with a trophic status that varied from oligotrophic to mesotrophic (Apêndice B, Table 3).

The use of ΔTA associated with other carbon chemistry parameters is an important indicator of reefs' susceptibilities and resistance to future climate change scenarios (COURTNEY et al., 2021; CYRONAK et al., 2018; LANGDON et al., 2010; SHAMBERGER et al., 2011). The negative values of ΔTA observed during our first three control days can be attributed to the continuous land-ocean exchanges, which, mainly during spring tides in coastal reefs, can decrease TA concentrations through freshwater input (ENOCHS et al., 2019; SILVA et al., 2022).

Moreover, the local benthic community composition also presents a significant influence on the uptake of $CaCO_3$ and TA throughout the day. Costa dos Corais' reefs is represented by a mixed coverage, with a dominance of fleshy algae and ~17% of corals and crustose coralline algae, such as *Millepora alcicornis* and *Halimeda sp* respectively (AUED et al., 2018; FERREIRA; MAIDA, 2006; SILVEIRA et al., 2014), that during the daytime, due to the high rates of NCC and CO_2 consume, can result in a TA depletion (LONGHINI et al., 2015; MURILLO et al., 2014; PAGE et al., 2016; TAKESHITA et al., 2018).

The high TA concentrations and positive ΔTA during all the alkaline days (Figure 4) evidence that the pH increment to pre-industrial levels (Figure 4) through NaOH addition was indeed responsible for a significant increase in the $CaCO_3$ production. Similar scenarios of ΔTA repletion are observed only in reefs influenced by an alkalinity input, e.g., through submarine groundwater discharge (SGD), and reefs that present a net dissolution state (CYRONAK et al., 2013a; 2013b; SHAW et al., 2015). Besides, during these days, the TA-C_T slope or NCP:NCC balance evidenced that there was a predominance of NCC (Figure 5), which represents a significant increase in the local calcification pulse, a good response for calcifying organisms' survival.

Otherwise, during control days there was an equilibrium between NCP:NCC, as also found in several tropical oceanic and coastal reefs (ALBRIGHT et al., 2013; LANTZ et al., 2013; PAGE et al., 2016; PINHEIRO et al., 2016; SILVA et al., 2022; SILVERMAN et al., 2007), and this can be a consequence of the mixed benthic community activities. This condition can maintain a constant or less pH variability (Figure 5) throughout the day due to the balance between what is produced and consumed in the photosynthesis/respiration and calcification/dissolution processes, and this can represent a resistance to the carbon chemistry's changes caused by the OA (CYRONAK et al., 2018).

Experiments in the laboratory, mesocosms, *in situ* observations, and global models describe that the reefs' metabolic activities will keep changing significantly until the end of this century (DOO et al., 2019; MARANGONI et al., 2017; PRADA et al., 2017). The calcification rates tend to decrease 11 to 34% per 1 unit of Ω_{ar} reduction and depending on the local distribution of calcifying and non-calcifying organisms, this loss is enough to cease the growth of biological reefs and prompt its dissolution (SILVERMAN et al., 2009). Nevertheless, modeling scenarios of chemical remediation, such as those in Feng et al. (2016; 2017) and Gonzáles and Ilyina (2016), indicated increases of 2.5 to 10 times in the Ω_{ar} levels of the surface global ocean, varying according to the utilized alkalinizing agent, its concentration, and the study scale.

In the first alkalinization *in situ* experiment it was also found differences in the metabolism between treatments, registering a rise of 6.9% ± 0.9% in the NCC values due to the increase of 0.4 units of Ω_{ar} during the days with NaOH use (Albright et al., 2016). Considering these estimative and the positive strong correlations between NCC and Ω_{ar} registered in several studies (ANDERSSON; GLEDHILL, 2013; JOKIEL, 2016; SHAW et al., 2015; YEAKEL et al., 2015), the mean increase of 2.8 units of Ω_{ar} registered here could rise the NCC activities in almost 50%. Nevertheless, a detailed study of the carbon chemistry diel variation in our studied reef is necessary for NCC quantitative information, since between day and nighttime can have significant differences in the metabolic activities (LONGHINI et al., 2015).

Associated with the Ω_{ar}, Revelle factor values showed that the reefs' buffering capacity was increased during alkaline days (Figure 6d) compared to natural conditions (Figure 6c), which is a good response to mitigating present climate changes conditions. Globally, the tropical zone presents the lowest values of the Revelle factor, which means that have a high equilibrium capacity for a given CO_2 perturbation due to its rising emissions into the atmosphere (EGLESTON et al., 2010; SABINE et al., 2004). However, studies around the world that use Revelle factor as an impact indicator describe that in future scenarios of OA this parameter will significantly increase on reef flats, especially those with high diel and seasonal amplitude (FABRICIUS et al., 2020; SHAW et al., 2012).

Understanding how OA will impact coral reefs on a community scale, accounting for several environmental variables including space and time is still a challenge, but extremely important for creating solutions (ALLEMAND; OSBORN, 2019; BAMBRIDGE et al., 2019; HOEGH-GULDBERG et al., 2019; WILLIAMSON et al., 2020). This is the first study on Brazilian reefs and, to our knowledge, the second in the world to use *in situ* chemical remediation as a tool for understanding how the carbon chemistry on coastal reefs would react in pre-industrial pH conditions.

As with any other technique, chemical remediation presents limitations (ALBRIGHT; COOLEY, 2019; GONZÁLEZ; ILYINA, 2016), e.g., engineering challenges, olive minerals rich in nickel, and the investment of millions of dollars for larger scales results, which is why it works better on small scales (local or regional) (ALBRIGHT et al., 2016; FENG et al., 2016; 2017). It is important to highlight that, for long time outcome, all mitigating techniques should be applied parallel to the gradual decrease of anthropogenic CO_2 into the atmosphere, and efficient effluents treatments, for coastal reefs.

Our findings suggest that the reversion of OA scenario by *in situ* alkalinization, on a local scale, could have a positive influence on the carbon chemistry dynamics of coastal reefs enhancing community calcification. The pH increment to pre-industrial values showed that there is a significant rising in the local calcification and buffering capacity due to the TA repletion and increased Ω_{ar} levels. Costa dos Corais's reefs naturally present an equilibrium of organic and inorganic carbon production and a high buffer capacity but are not safe from the OA global impacts. More studies applying chemical remediation in laboratories and especially *in situ*, considering local specifics are necessary for the improvement and understanding of mitigating techniques, and to accomplish goals from international and national plans of ocean conservation.

REFERENCES

ALBRIGHT, R.; COOLEY, S. A review of interventions proposed to abate impacts of ocean acidification on coral reefs. **Regional Studies in Marine Science**, v. 29, p. 100612, 2019.

ALBRIGHT, R.; TAKESHITA, Y.; KOWEEK, D. A.; NINOKAWA, A. et al. Carbon dioxide addition to coral reef waters suppresses net community calcification. **Nature**, v. 555, n. 7697, p. 516-519, 2018.

ALBRIGHT, R. et al. Reversal of ocean acidification enhances net coral reef calcification. **Nature**, v. 531, n. 7594, p. 362-365, 2016.

ALBRIGHT, R.; LANGDON, C.; ANTHONY, K. R. N. Dynamics of seawater carbonate chemistry, production, and calcification of a coral reef flat, central Great Barrier Reef. **Biogeosciences**, v. 10, n. 10, p. 6747-6758, 2013.

ALLEMAND, D.; OSBORN, D. Ocean acidification impacts on coral reefs: From sciences to solutions. **Regional Studies in Marine Science**, v. 28, p. 100558, 2019.

ANDERSSON, A. J.; GLEDHILL, D. Ocean acidification and coral reefs: effects on breakdown, dissolution, and net ecosystem calcification. **Annual review of marine science**, v. 5, p. 321-348, 2013.

ANDERSSON, A. J.; MACKENZIE, F. T.; GATTUSO, J-P. Effects of ocean acidification on benthic processes, organisms, and ecosystems. **Ocean acidification**, v. 8, p. 122-153, 2011.

AUED, A. W.; et al. Large-scale patterns of benthic marine communities in the Brazilian Province. **PloS one**, v. 13, n. 6, p. e0198452, 2018.

BAMBRIDGE, T.; CHLOUS, F.; D'ARCY, P.; CLAUDET, J.; PASCAL, N.; REYNAUD, S.; RODOLFO-METALPA, R.; TAMBUTTÉ, S.; THOMASSIN, A.; VIRTO, L. R. Society-based solutions to coral reef threats in french pacific territories. **Regional Studies in Marine Science**, v. 29, p. 100667, 2019.

BARROSO, M. S.; SILVA, B. J.; FLORES-MONTES, M. J.; SANTOS, P. J. P. Anthropogenic impacts on coral reef harpacticoid copepods. **Diversity**, v. 10, n. 2, p. 32, 2018.

BATES, N. R.; AMAT, A.; ANDERSSON, A. J. Feedbacks and responses of coral calcification on the Bermuda reef system to seasonal changes in biological processes and ocean acidification. **Biogeosciences**, v. 7, n. 8, p. 2509-2530, 2010.

BERGSTROM, E.; SILVA, J.; MARTINS, C.; HORTA, P. Seagrass can mitigate negative ocean acidification effects on calcifying algae. **Scientific reports**, v. 9, n. 1, p. 1-11, 2019.

BILLÉ, R.; KELLY, R.; BIASTOCH, A.; HARROULD-KOLIEB, E.; HERR, D.; JOOS, F.; KROEKER, K.; LAFFOLEY, D.; OSCHLIES, A.; GATTUSO, J. P. Taking action against ocean acidification: a review of management and policy options. **Environmental management**, v. 52, n. 4, p. 761-779, 2013.

BOWER, C. E.; HOLM-HANSEN, T. A salicylate–hypochlorite method for determining ammonia in seawater. **Canadian Journal of Fisheries and Aquatic Sciences**, v. 37, n. 5, p. 794-798, 1980.

BROULLÓN, D.; PÉREZ, F. F.; VELO, A.; HOPPEMA, M.; OLSEN, A.; TAKAHASHI, T.; KEY, R. M.; TANHUA, T.; GONZÁLEZ-DÁVILA, M.; JEANSSON, E.; KOZYR, A.; VAN-HEUVEN, S. M. A. C. A global monthly climatology of total alkalinity: a neural network approach. **Earth System Science Data**, v. 11, n. 3, p. 1109-1127, 2019.

BURKE, L. M.; REYTAR, K.; SPALDING, M.; PERRY, A. **Reefs at risk revisited.** World Resources Institute, 2011.

BURNS, W.; CORBETT, C. R. Antacids for the sea? Artificial ocean alkalinization and climate change. **One Earth**, v. 3, n. 2, p. 154-156, 2020.

COURTNEY, T. A.; CYRONAK, T.; GRIFFIN, A. J.; ANDERSSON, A. J. Implications of salinity normalization of seawater total alkalinity in coral reef metabolism studies. **Plos one**, v. 16, n. 12, p. e0261210, 2021.

CYRONAK, T.; SANTOS, I. R.; ERLER, D. V.; EYRE, B. D. Groundwater and porewater as major sources of alkalinity to a fringing coral reef lagoon (Muri Lagoon, Cook Islands). **Biogeosciences**, v. 10, n. 4, p. 2467-2480, 2013a.

CYRONAK, T.; SANTOS, I. R.; MCMAHON, A.; EYRE, B. D. Carbon cycling hysteresis in permeable carbonate sands over a diel cycle: Implications for ocean acidification. **Limnology and Oceanography**, v. 58, n. 1, p. 131-143, 2013b.

CYRONAK, T.; ANDERSSON, A. J.; LANGDON, C.; ALBRIGHT, R.; BATES, N. R.; et al. Taking the metabolic pulse of the world's coral reefs. **PloS one**, v. 13, n. 1, p. e0190872, 2018.

DICKSON, A. G.; SABINE, C. L.; CHRISTIAN, J. R. **Guide to best practices for ocean CO2 measurements**. North Pacific Marine Science Organization, 2007.

DOO, STEVE S.; EDMUNDS, PETER J.; CARPENTER, ROBERT C. Ocean acidification effects on in situ coral reef metabolism. **Scientific reports**, v. 9, n. 1, p. 1-8, 2019.

EGLESTON, E. S.; SABINE, C. L.; MOREL, F. M. Revelle revisited: Buffer factors that quantify the response of ocean chemistry to changes in DIC and alkalinity. **Global Biogeochemical Cycles**, v. 24, n. 1, 2010.

ENOCHS, I. C.; MANZELLO, D. P.; JONES, P. R.; STAMATES, S. J.; CARSEY, T. P. Seasonal carbonate chemistry dynamics on southeast Florida coral reefs: Localized acidification hotspots from navigational inlets. **Frontiers in Marine Science**, v. 6, p. 160, 2019.

FABRICIUS, K. E.; NEILL, C.; VAN OOIJEN, E.; SMITH, J. N.; TILBROOK, B. Progressive seawater acidification on the Great Barrier Reef continental shelf. **Scientific reports**, v. 10, n. 1, p. 1-15, 2020.

FEELY, R. A.; DONEY, S. C.; COOLEY, S. R. Ocean acidification: Present conditions and future changes in a high-CO_2 world. **Oceanography**, v. 22, n. 4, p. 36-47, 2009.

FEELY, R. A.; SABINE, C. L.; LEE, K.; BERELSON, W.; KLEYPAS, J.; FABRY, V. J.; MILLERO, F. J. Impact of anthropogenic CO2 on the CaCO3 system in the oceans. **Science**, v. 305, n. 5682, p. 362-366, 2004.

FENG, E. Y.; KELLER, D. P.; KOEVE, W.; OSCHLIES, A. Could artificial ocean alkalinization protect tropical coral ecosystems from ocean acidification? **Environmental Research Letters**, v. 11, n. 7, p. 074008, 2016.

FENG, E. Y.; KOEVE, W.; KELLER, D. P.; OSCHLIES, A. Model-Based Assessment of the CO2 Sequestration Potential of Coastal Ocean Alkalinization. **Earth's Future**, v. 5, n. 12, p. 1252-1266, 2017.

FERREIRA, B. P.; MAIDA, M. **Monitoramento dos recifes de coral do Brasil**. Brasília, DF: MMA, Secretaria de Biodiversidade e Florestas, 2006.

FINE, R. A.; WILLEY, D. A.; MILLERO, F. J. Global variability and changes in ocean total alkalinity from Aquarius satellite data. **Geophysical Research Letters**, v. 44, n. 1, p. 261-267, 2017.

GARCÍA-ROBLEDO, E.; CORZO, A.; PAPASPYROU, S. A fast and direct spectrophotometric method for the sequential determination of nitrate and nitrite at low concentrations in small volumes. **Marine Chemistry**, v. 162, p. 30-36, 2014.

GONZÁLES, M. F.; ILYINA, T. Impacts of artificial ocean alkalinization on the carbon cycle and climate in Earth system simulations. **Geophysical Research Letters**, v. 43, n. 12, p. 6493-6502, 2016.

GRASSHOFF, K; et al. Methods of Seawater Analyses. **Verlag Chemie**. 317, 1993.

GRUBER, N.; SARMIENTO, J. L.; STOCKER, T. F. An improved method for detecting anthropogenic CO2 in the oceans. **Global Biogeochemical Cycles**, v. 10, n. 4, p. 809-837, 1996.

HILMI, N.; OSBORN, D.; ACAR, S.; BAMBRIDGE, T.; CHLOUS, F. et al. Socio-economic tools to mitigate the impacts of ocean acidification on economies and communities reliant on coral reefs—a framework for prioritization. **Regional Studies in Marine Science**, v. 28, p. 100559, 2019.

HOEGH-GULDBERG, O.; PENDLETON, L.; KAUP, A. People and the changing nature of coral reefs. **Regional Studies in Marine Science**, v. 30, p. 100699, 2019.

HUGHES, T. P.; ANDERSON, K. D.; CONNOLLY, S. R.; HERON, S. F.; KERRY, J. T. et al. Spatial and temporal patterns of mass bleaching of corals in the Anthropocene. **Science**, v. 359, n. 6371, p. 80-83, 2018.

HUGHES, T. P.; GRAHAM, N. A.; JACKSON, J. B.; MUMBY, P. J.; STENECK, R. S. Rising to the challenge of sustaining coral reef resilience. **Trends in ecology & evolution**, v. 25, n. 11, p. 633-642, 2010.

IPCC. Summary for Policymakers. In: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Masson-Delmotte, V., P. Zhai, A. Pirani, S. L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M. I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J.B.R. Matthews, T. K. Maycock, T.

Waterfield, O. Yelekçi, R. Yu and B. Zhou (eds.)]. **Cambridge University Press**. In Press, 2021.

JALES, M. C.; FEITOSA, F. A. N.; KOENING, M. L.; BASTOS, R. B.; MACHADO, R. C. A. O ecossistema recifal de Serrambi (nordeste do Brasil): biomassa fitoplanctônica e parâmetros hidrológicos. **Atlântica (Rio Grande)**, v. 34, n. 2, p. 87-102, 2012.

JOKIEL, P. L. Predicting the impact of ocean acidification on coral reefs: evaluating the assumptions involved. **ICES Journal of Marine Science**, v. 73, n. 3, p. 550-557, 2016.

KLEYPAS, J. A.; ANTHONY, K. R.; GATTUSO, J. P. Coral reefs modify their seawater carbon chemistry–case study from a barrier reef (M oorea, F rench P olynesia). **Global change biology**, v. 17, n. 12, p. 3667-3678, 2011.

LANGDON, C.; GATTUSO, J. P.; ANDERSSON, A. Measurements of calcification and dissolution of benthic organisms and 13 communities. **Guide to best practices for ocean acidification research and data reporting, eds U. Riebesell, VJ Fabry, L. Hansson and J.-P. Gattuso (Luxembourg: Publications Office of the European Union)**, 2010.

LANTZ, C. A.; ATKINSON, M. J.; WINN, C. W.; KAHNG, S. E. Dissolved inorganic carbon and total alkalinity of a Hawaiian fringing reef: chemical techniques for monitoring the effects of ocean acidification on coral reefs. **Coral Reefs**, v. 33, n. 1, p. 105-115, 2014.

LEE, K.; TONG, L. T.; MILLERO, F. J.; SABINE, C. L.; DICKSON, A. G.; GOYET, C.; PARK, G-H.; WANNINKHOF, R.; FEELY, R. A.; KEY, R. M. Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans. **Geophysical research letters**, v. 33, n. 19, 2006.

LENTON, A.; MATEAR, R. J.; KELLER, D. P.; SCOTT, V.; VAUGHAN, N. E. Assessing carbon dioxide removal through global and regional ocean alkalinization under high and low emission pathways. **Earth System Dynamics**, v. 9, n. 2, p. 339-357, 2018.

LONGHINI, C. M.; SOUZA, M. F.; SILVA, A. M. Net ecosystem production, calcification and CO2 fluxes on a reef flat in Northeastern Brazil. **Estuarine, Coastal and Shelf Science**, v. 166, p. 13-23, 2015.

MARANGONI, L. F. B.; CALDERON, E. N.; MARQUES, J. A.; DUARTE, G. A. S.; PEREIRA, C. M.; BIANCHINI, A. Effects of CO2-driven acidification of seawater on the calcification process in the calcareous hydrozoan Millepora alcicornis (Linnaeus, 1758). **Coral reefs**, v. 36, n. 4, p. 1133-1141, 2017.

MURILLO, L. J.; JOKIEL, P. L.; ATKINSON, M. J. Alkalinity to calcium flux ratios for corals and coral reef communities: variances between isolated and community conditions. **PeerJ**, v. 2, p. e249, 2014.

PAGE, H. N.; ANDERSSON, A. J.; JOKIEL, P. L.; RODGERS, K. U. S.; LEBRATO, M.; YEAKEL, K.; DAVIDSON, C.; D'ANGELO, S.; BAHR, K. D. Differential modification of seawater carbonate chemistry by major coral reef benthic communities. **Coral Reefs**, v. 35, n. 4, p. 1311-1325, 2016.

PENDLETON, L.; LANGDON, C.; EKSTROM, J. A.; COOLEY, S. R. et al. Coral Reefs and People in a High-CO2 World: Where Can Science Make a Difference to People? **PloS one**, v. 11, n. 11, p. e0164699, 2016.

PINHEIRO, B. R.; GASPAR, F. L.; SILVA, B. J.; FLORES-MONTES, M. J. et al. Interactions between hydrology and benthic coverage at rocas atoll. **Tropical Oceanography**, 44, 2, 142-157, 2016.

PLANO NACIONAL DE ADAPTAÇÃO. PNA, https://www.gov.br/mma/pt-br/assuntos/climaozoniodesertificacao/plano-nacional-de-adaptacao. Acessed 31 July 2021, 2015.

PRADA, F.; CAROSELLI, E.; MENGOLI, S.; BRIZI, L.; FANTAZZINI, P.; CAPACCIONI, B.; PASQUINI, L.; FABRICIUS, K. E.; DUBINSKY, Z.; FALINI, G.; GOFFREDO, S. Ocean warming and acidification synergistically increase coral mortality. **Scientific Reports**, v. 7, n. 1, p. 1-10, 2017.

ROSADO, P. M.; LEITE, D. C.; DUARTE, G. A.; CHALOUB, R. M.; JOSPIN, G.; ROCHA, U. N.; SARAIVA, J. P.; DINI-ANDREOTE, F.; EISEN, J. A.; BOURNE, D. G.; PEIXOTO, R. S. Marine probiotics: increasing coral resistance to bleaching through microbiome manipulation. **The ISME journal**, v. 13, n. 4, p. 921-936, 2019.

SABINE, C. L.; FEELY, R. A.; GRUBER, N.; KEY, R. M.; LEE, K.; BULLISTER, J. L.; WANNINKHOF, R.; WONG, C. S.; WALLACE, D. W. R.; TILBROOK, B.; MILLERO F. J.; PENG, T-H.; KOZYR, A.; ONO, T.; RIOS, A. F. The oceanic sink for anthropogenic CO2. **science**, v. 305, n. 5682, p. 367-371, 2004.

SHAMBERGER, K. E. F.; FEELY, R. A.; SABINE, C. L.; ATKINSON, M. J.; DECARLO, E. H.; MACKENZIE, F. T.; DRUPP, P. S.; BUTTERFIELD, D. A. Calcification and organic production on a Hawaiian coral reef. **Marine Chemistry**, v. 127, n. 1-4, p. 64-75, 2011.

SHAW, E. C.; MCNEIL, B. I.; TILBROOK, B. Impacts of ocean acidification in naturally variable coral reef flat ecosystems. **Journal of Geophysical Research: Oceans**, v. 117, n. C3, 2012.

SHAW, E. C.; PHINN, S. R.; TILBROOK, B.; STEVEN, A. Natural in situ relationships suggest coral reef calcium carbonate production will decline with ocean acidification. **Limnology and Oceanography**, v. 60, n. 3, p. 777-788, 2015.

SILVA, B. J.; IBÁNHEZ, J. S. P.; PINHEIRO, B. R.; LADLE, R. J.; MALHADO, A. C.; PINTO, T. K.; FLORES-MONTES, M. J. Seasonal influence of surface and underground continental runoff over a reef system in a tropical marine protected area. **Journal of Marine Systems**, v. 226, p. 103660, 2022.

SILVEIRA, C. B. L.; FERREIRA, B. P.; COXEY, M. S. Variação temporal nos recifes de corais de Maragogi, APA Costa dos Corais (2010-2013). **Tropical Oceanography**, 42, 2, 2014.

SILVERMAN, J.; LAZAR, B.; EREZ, J. Effect of aragonite saturation, temperature, and nutrients on the community calcification rate of a coral reef. **Journal of Geophysical Research: Oceans**, v. 112, n. C5, 2007.

SILVERMAN, J.; LAZAR, B.; CAO, L.; CALDEIRA, K.; EREZ, J. Coral reefs may start dissolving when atmospheric CO2 doubles. **Geophysical Research Letters**, v. 36, n. 5, 2009.

STRICKLAND, J. D.; PARSONS, T. R. A practical handbook of seawater analysis. **Bulletin of Fisheries Research**, 167, p. 1–311, 1972.

TAKESHITA, Y.; CYRONAK, T.; MARTZ, T. R.; KINDEBERG, T.; ANDERSSON, A. J. Coral reef carbonate chemistry variability at different functional scales. **Frontiers in Marine Science**, v. 5, p. 175, 2018.

UNESCO. Determination of photosynthetic pigments in seawater. Rapor of SCOR/UNESCO, working group 17 with meat from 4 to 6 June 1964, Monography on Oceanography Methodology. 69, 1966.

WILLIAMSON, P.; PÖRTNER, H. O.; WIDDICOMBE, S.; GATTUSO, J. P. Ideas and perspectives: When ocean acidification experiments are not the same, repeatability is not tested. **Biogeosciences**, v. 18, n. 5, p. 1787-1792, 2020.

YEAKEL, K. L.; ANDERSSON, A. J.; BATES, N. R.; NOYES, T. J.; COLLINS, A.; GARLEY, R. Shifts in coral reef biogeochemistry and resulting acidification linked to offshore productivity. **Proceedings of the National Academy of Sciences**, v. 112, n. 47, p. 14512-14517, 2015.

ZEEBE, R. E. History of seawater carbonate chemistry, atmospheric CO2, and ocean acidification. **Annual review of earth and planetary sciences**, v. 40, p. 141-165, 2012.

4 CONSIDERAÇÕES FINAIS

Observamos ampla variação sazonal dos nutrientes inorgânicos dissolvidos e do sistema carbonato nos recifes de Maragogi à Japaratinga e que a intervenção de alcalinização alterou as respostas metabólicas recifais *in situ*. No primeiro artigo, foi possível observar uma significativa mudança nos parâmetros abióticos estudados entre o período chuvoso e de estiagem, sendo, portanto, a sazonalidade um fator importante que regula a qualidade da água da região, corroborando as hipóteses iniciais. As águas dos recifes de Maragogi à Japaratinga foram consideradas oligotróficas, com boa qualidade ao longo do ano, porém, estão susceptíveis à influência de aportes continentais, tanto superficiais (através dos rios), como subterrâneos (através da SGD), que já apresentam sinais de eutrofização. Isso pode colocar em risco a saúde dos recifes mais costeiros, principalmente em períodos de elevada precipitação, onde a influência continental é praticamente dobrada.

É importante destacar a relevância em verificar a influência da SGD sobre a região costeira. Embora a quantificação dos fluxos não tenha sido realizada no presente trabalho, os elevados valores dos nutrientes inorgânicos dissolvidos registrados nas águas intersticiais, significativamente maiores do que nos rios, e a correlação positiva entre $^{222}Rn_{exc}$ e Chl-*a* na zona recifal, são indicativos de uma grande contribuição da SGD nos ciclos biogeoquímicos e na qualidade da água dos recifes da APACC.

No segundo artigo observamos que diante de um cenário de alcalinização *in situ*, haverá um aumento no potencial de calcificação, nos valores de Ω_{ar} e na capacidade de tamponamento dos recifes de Japaratinga, influenciando positivamente na saúde dos organismos calcificantes locais. Cada vez mais se faz necessário estudos experimentais que busquem testar formas de mitigar os efeitos da AO, visando subsidiar a aplicação de técnicas que protejam os recifes, agindo em paralelo com as reduções das emissões de CO_2 na atmosfera. O estudo aqui realizado foi o segundo no mundo a aplicar uma forma de reversão ou redução dos impactos da AO, um método promissor para a proteção dos recifes costeiros em escala local.

Os recifes estão constantemente susceptíveis à ação de estressores ambientais, que geralmente atuam em sinergia, independentemente da escala. A criação e manutenção de UCs se faz necessária visando minimizar esses impactos e permitir uma maior resiliência ao ecossistema recifal. Por isso, o constante monitoramento dos parâmetros abióticos dessas regiões, possibilitando a identificação e caracterização de estressores ambientais, é uma ferramenta de extrema importância para a conservação dos recifes.

REFERÊNCIAS

ALBRIGHT, R. et al. Reversal of ocean acidification enhances net coral reef calcification. **Nature**, v. 531, n. 7594, p. 362-365, 2016.

ALBRIGHT, R.; COOLEY, S. A review of interventions proposed to abate impacts of ocean acidification on coral reefs. **Regional Studies in Marine Science**, v. 29, p. 100612, 2019.

ALBRIGHT, R.; LANGDON, C.; ANTHONY, K. R. N. Dynamics of seawater carbonate chemistry, production, and calcification of a coral reef flat, central Great Barrier Reef. **Biogeosciences**, v. 10, n. 10, p. 6747-6758, 2013.

ALBRIGHT, R.; TAKESHITA, Y.; KOWEEK, D. A.; NINOKAWA, A. et al. Carbon dioxide addition to coral reef waters suppresses net community calcification. **Nature**, v. 555, n. 7697, p. 516-519, 2018.

ALLEMAND, D.; OSBORN, D. Ocean acidification impacts on coral reefs: From sciences to solutions. **Regional Studies in Marine Science**, v. 28, p. 100558, 2019.

ALVES, G.; FLORES-MONTES, M.; GASPAR, F.; GOMES, J.; FEITOSA, F. Eutrophication and water quality in a tropical Brazilian estuary. **Journal of Coastal Research**, n. 65 (10065), p. 7-12, 2013.

ANDERSSON, A. J.; GLEDHILL, D. Ocean acidification and coral reefs: effects on breakdown, dissolution, and net ecosystem calcification. **Annual review of marine science**, v. 5, p. 321-348, 2013.

ANDERSSON, A. J.; MACKENZIE, F. T.; GATTUSO, J-P. Effects of ocean acidification on benthic processes, organisms, and ecosystems. **Ocean acidification**, v. 8, p. 122-153, 2011.

ANDERSSON, A. J.; VENN, A. A.; PENDLETON, L.; BRATHWAITE, A.; CAMP, E. F.; COOLEY, S.; GLEDHILL, D.; KOCH, M.; MALIKI, S.; MANFRINO, C. Ecological and socioeconomic strategies to sustain Caribbean coral reefs in a high-CO2 world. **Regional Studies in Marine Science**, v. 29, p. 100677, 2019.

ANTHONY, K.; et al. New interventions are needed to save coral reefs. **Nature ecology & evolution**, v. 1, n. 10, p. 1420-1422, 2017.

ARANDACIREROL, N.; HERRERA-SILVEIRA, J. A.; COMÍN, F. A. Nutrient water quality in a tropical coastal zone with groundwater discharge, northwest Yucatan, Mexico. **Estuarine, Coastal and Shelf Science**, v. 68, n. 3-4, p. 445-454, 2006.

ARMOZA-ZVULONI, R.; SHAKED, Y. Release of hydrogen peroxide and antioxidants by the coral Stylophora pistillata to its external milieu. **Biogeosciences**, v. 11, n. 17, p. 4587-4598, 2014.

AUED, A. W.; et al. Large-scale patterns of benthic marine communities in the Brazilian Province. **PloS one**, v. 13, n. 6, p. e0198452, 2018.

BAMBRIDGE, T.; CHLOUS, F.; D'ARCY, P.; CLAUDET, J.; PASCAL, N.; REYNAUD, S.; RODOLFO-METALPA, R.; TAMBUTTÉ, S.; THOMASSIN, A.; VIRTO, L. R. Society-based solutions to coral reef threats in french pacific territories. **Regional Studies in Marine Science**, v. 29, p. 100667, 2019.

BARROSO, M. S.; SILVA, B. J.; FLORES-MONTES, M. J.; SANTOS, P. J. P. Anthropogenic impacts on coral reef harpacticoid copepods. **Diversity**, v. 10, n. 2, p. 32, 2018.

BARTON, A.; et al. Impacts of coastal acidification on the Pacific Northwest shellfish industry and adaptation strategies implemented in response. **Oceanography**, v. 28, n. 2, p. 146-159, 2015.

BATES, N. R.; AMAT, A.; ANDERSSON, A. J. Feedbacks and responses of coral calcification on the Bermuda reef system to seasonal changes in biological processes and ocean acidification. **Biogeosciences**, v. 7, n. 8, p. 2509-2530, 2010.

BECK, A. J.; KELLUM, A. A.; LUEK, J. L.; COCHRAN, M. A. Chemical flux associated with spatially and temporally variable submarine groundwater discharge, and chemical modification in the subterranean estuary at gloucester Point, VA (USA). **Estuaries and coasts**, v. 39, n. 1, p. 1-12, 2016.

BELLWOOD, D. R.; HUGHES, T. P.; FOLKE, C.; NYSTRÖM, M. Confronting the coral reef crisis. **Nature**, v. 429, n. 6994, p. 827-833, 2004.

BERGSTROM, E.; SILVA, J.; MARTINS, C.; HORTA, P. Seagrass can mitigate negative ocean acidification effects on calcifying algae. **Scientific reports**, v. 9, n. 1, p. 1-11, 2019.

BEUSEN, A. H.; BOUWMAN, A. F.; VAN BEEK, L. P.; MOGOLLÓN, J. M.; MIDDELBURG, J. J. Global riverine N and P transport to ocean increased during the 20th century despite increased retention along the aquatic continuum. **Biogeosciences**, v. 13, n. 8, p. 2441-2451, 2016.

BILLÉ, R.; KELLY, R.; BIASTOCH, A.; HARROULD-KOLIEB, E.; HERR, D.; JOOS, F.; KROEKER, K.; LAFFOLEY, D.; OSCHLIES, A.; GATTUSO, J. P. Taking action against ocean acidification: a review of management and policy options. **Environmental management**, v. 52, n. 4, p. 761-779, 2013.

BOWER, C. E.; HOLM-HANSEN, T. A salicylate–hypochlorite method for determining ammonia in seawater. **Canadian Journal of Fisheries and Aquatic Sciences**, v. 37, n. 5, p. 794-798, 1980.

BROULLÓN, D.; PÉREZ, F. F.; VELO, A.; HOPPEMA, M.; OLSEN, A.; TAKAHASHI, T.; KEY, R. M.; TANHUA, T.; GONZÁLEZ-DÁVILA, M.; JEANSSON, E.; KOZYR, A.; VAN-HEUVEN, S. M. A. C. A global monthly climatology of total alkalinity: a neural network approach. **Earth System Science Data**, v. 11, n. 3, p. 1109-1127, 2019.

BRUNO, J. F. et al. Thermal stress and coral cover as drivers of coral disease outbreaks. **PLoS biology**, v. 5, n. 6, p. e124, 2007.

BURKE, L. M.; REYTAR, K.; SPALDING, M.; PERRY, A. **Reefs at risk revisited.** World Resources Institute, 2011.

BURNETT, W. C.; BOKUNIEWICZ, H.; HUETTEL, M.; MOORE, W. S. et al. Groundwater and pore water inputs to the coastal zone. **Biogeochemistry**, v. 66, n. 1, p. 3-33, 2003.

BURNETT, W. C.; DULAIOVA, H. Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements. **Journal of environmental radioactivity**, v. 69, n. 1-2, p. 21-35, 2003.

BURNS, W.; CORBETT, C. R. Antacids for the sea? Artificial ocean alkalinization and climate change. **One Earth**, v. 3, n. 2, p. 154-156, 2020.

CABRAL, A.; FONSECA, A. Coupled effects of anthropogenic nutrient sources and meteo-oceanographic events in the trophic state of a subtropical estuarine system. **Estuarine, Coastal and Shelf Science**, v. 225, p. 106228, 2019.

CAI, W. J.; HU, X.; HUANG, W. J.; MURRELL, M. C. et al. Acidification of subsurface coastal waters enhanced by eutrophication. **Nature geoscience**, v. 4, n. 11, p. 766-770, 2011.

CALVO-MARTÍN, E.; ÁLVAREZ-SALGADO, X. A.; ROCHA, C.; IBÁNHEZ, J. S. P. Reactive solute transport through two contrasting subterranean estuary exit sites in the Ría de Vigo (NW Iberian Peninsula). **Frontiers in Marine Science**, v. 8, p. 94, 2021.

CANE, M. A.; et al. Twentieth-century sea surface temperature trends. **Science**, v. 275, n. 5302, p. 957-960, 1997.

CARREÓN-PALAU, L.; PARRISH, C. C.; PÉREZ-ESPAÑA, H. Urban sewage lipids in the suspended particulate matter of a coral reef under river influence in the South West Gulf of Mexico. **Water research**, v. 123, p. 192-205, 2017.

CHEN, C. Y.; BUCKMAN, K. L.; SHAW, A.; CURTIS, A.; TAYLOR, M.; MONTESDEOCA, M.; DRISCOLL, C. The influence of nutrient loading on methylmercury availability in Long Island estuaries. **Environmental Pollution**, v. 268, p. 115510, 2021.

CLARK, C. M.; et al. Nitrogen-induced terrestrial eutrophication: cascading effects and impacts on ecosystem services. **Ecosphere**, v. 8, n. 7, p. e01877, 2017.

COHEN, I.; DUBINSKY, Z.; EREZ, J. Light enhanced calcification in hermatypic corals: new insights from light spectral responses. **Frontiers in Marine Science**, v. 2, p. 122, 2016.

CORBETT, D.; BURNETT, W.; CABLE, P. et al. A multiple approach to the determination of radon fluxes from sediments. **Journal of Radioanalytical and Nuclear Chemistry**, v. 236, n. 1-2, p. 247-253, 1998.

CORDEIRO, I. A.; FEITOSA, F. A. N.; FLORES-MONTES, M. J.; OTSUKA, A. Y. et al. Environmental conditions of the Suape estuarine-port complex area (Pernambuco, Brazil): phytoplankton biomass and hydrological parameters. Marine Biological Association of the United Kingdom. **Journal of the Marine Biological Association of the United Kingdom**, v. 99, n. 2, p. 291-301, 2019.

COTOVICZ, L. C. J.; MARINS, R. V.; ABRIL, G. Coastal ocean acidification in Brazil: a brief overview and perspective. 2022. Arq. Ciên. Mar, p. 345 – 368.

COUCE, E.; RIDGWELL, A.; HENDY, E. J. Environmental controls on the global distribution of shallow-water coral reefs. **Journal of Biogeography**, v. 39, n. 8, p. 1508-1523, 2012.

COURTNEY, T. A.; CYRONAK, T.; GRIFFIN, A. J.; ANDERSSON, A. J. Implications of salinity normalization of seawater total alkalinity in coral reef metabolism studies. **Plos one**, v. 16, n. 12, p. e0261210, 2021.

CYRONAK, T.; ANDERSSON, A. J.; LANGDON, C.; ALBRIGHT, R.; BATES, N. R.; et al. Taking the metabolic pulse of the world's coral reefs. **PloS one**, v. 13, n. 1, p. e0190872, 2018.

CYRONAK, T.; SANTOS, I. R.; ERLER, D. V.; EYRE, B. D. Groundwater and porewater as major sources of alkalinity to a fringing coral reef lagoon (Muri Lagoon, Cook Islands). **Biogeosciences**, v. 10, n. 4, p. 2467-2480, 2013a.

CYRONAK, T.; SANTOS, I. R.; ERLER, D. V.; MAHER, D. T. et al. Drivers of pCO2 variability in two contrasting coral reef lagoons: The influence of submarine groundwater discharge. **Global Biogeochemical Cycles**, v. 28, n. 4, p. 398-414, 2014.

CYRONAK, T.; SANTOS, I. R.; MCMAHON, A.; EYRE, B. D. Carbon cycling hysteresis in permeable carbonate sands over a diel cycle: Implications for ocean acidification. **Limnology and Oceanography**, v. 58, n. 1, p. 131-143, 2013b.

DECARLO, T. M.; GAJDZIK, L.; ELLIS, J.; COKER, D. J.; ROBERTS, M. B.; HAMMERMAN, N. M.; PANDOLFI, J. M.; MONROE, A. A.; BERUMEN, M. L. Nutrient-supplying ocean currents modulate coral bleaching susceptibility. **Science Advances**, v. 6, n. 34, p. eabc5493, 2020.

DICKSON, A. G.; SABINE, C. L.; CHRISTIAN, J. R. **Guide to best practices for ocean CO2 measurements**. North Pacific Marine Science Organization, 2007.

DONEY, S. C.; MAHOWALD, N.; LIMA, I.; FEELY, R. A.; MACKENZIE, F. T.; LAMARQUE, J. F.; RASCH, P. J. Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system. **Proceedings of the National Academy of Sciences**, v. 104, n. 37, p. 14580-14585, 2007.

DOO, STEVE S.; EDMUNDS, PETER J.; CARPENTER, ROBERT C. Ocean acidification effects on in situ coral reef metabolism. **Scientific reports**, v. 9, n. 1, p. 1-8, 2019.

DUARTE, G. A. S. et al. Heat waves are a major threat to turbid coral reefs in Brazil. **Frontiers in Marine Science**, p. 179, 2020.

DUBINSKY, Z.; STAMBLER, N. Coral reefs: an ecosystem in transition. **Springer Science & Business Media**, 2010.

DUPREY, N. N.; YASUHARA, M.; BAKER, D. M. Reefs of tomorrow: eutrophication reduces coral biodiversity in an urbanized seascape. **Global change biology**, v. 22, n. 11, p. 3550-3565, 2016.

DULAIOVA, H.; GONNEEA, M. E.; HENDERSON, P. B.; CHARETTE, M. A. Geochemical and physical sources of radon variation in a subterranean estuary—Implications for groundwater radon activities in submarine groundwater discharge studies. **Marine Chemistry**, v. 110, n. 1-2, p. 120-127, 2008.

DUTRA, L. X. C.; et al. Synergies between local and climate-driven impacts on coral reefs in the Tropical Pacific: A review of issues and adaptation opportunities. **Marine Pollution Bulletin**, v. 164, p. 111922, 2021.

EGLESTON, E. S.; SABINE, C. L.; MOREL, F. M. Revelle revisited: Buffer factors that quantify the response of ocean chemistry to changes in DIC and alkalinity. **Global Biogeochemical Cycles**, v. 24, n. 1, 2010.

ENOCHS, I. C.; MANZELLO, D. P.; JONES, P. R.; STAMATES, S. J. et al. Seasonal carbonate chemistry dynamics on southeast Florida coral reefs: localized acidification hotspots from navigational inlets. **Frontiers in Marine Science**, v. 6, p. 160, 2019.

EYRE, B. D.; et al. Coral reefs will transition to net dissolving before end of century. **Science**, v. 359, n. 6378, p. 908-911, 2018.

FABRICIUS, K. E.; NEILL, C.; VAN OOIJEN, E.; SMITH, J. N.; TILBROOK, B. Progressive seawater acidification on the Great Barrier Reef continental shelf. **Scientific reports**, v. 10, n. 1, p. 1-15, 2020.

FEARY, D. A.; et al. Habitat choice, recruitment and the response of coral reef fishes to coral degradation. **Oecologia**, v. 153, n. 3, p. 727-737, 2007.

FEELY, R. A.; SABINE, C. L.; LEE, K.; BERELSON, W. et al. Impact of anthropogenic CO2 on the CaCO3 system in the oceans. **Science**, v. 305, n. 5682, p. 362-366, 2004.

FENG, E. Y.; KOEVE, W.; KELLER, D. P.; OSCHLIES, A. Model-Based Assessment of the CO2 Sequestration Potential of Coastal Ocean Alkalinization. **Earth's Future**, v. 5, n. 12, p. 1252-1266, 2017.

FERREIRA, B. P.; COSTA, M. B. S. F.; COXEY, M. S.; GASPAR, A. L. B.; VELEDA, D.; ARAUJO, M. The effects of sea surface temperature anomalies on oceanic coral reef systems in the southwestern tropical Atlantic. **Coral reefs**, v. 32, n. 2, p. 441-454, 2013.

FERREIRA, B. P.; MAIDA, M. **Monitoramento dos recifes de coral do Brasil**. Brasília, DF: MMA, Secretaria de Biodiversidade e Florestas, 2006.

FERREIRA, L. C.; SILVA-CUNHA, M. G. G.; AQUINO, E. P.; BORGES, G. C. P. et al. Temporal and spatial variation of phytoplankton in a tropical reef area of Brazil. **Tropical Ecology**, v. 56, n. 3, 2015.

FINE, R. A.; WILLEY, D. A.; MILLERO, F. J. Global variability and changes in ocean total alkalinity from Aquarius satellite data. **Geophysical Research Letters**, v. 44, n. 1, p. 261-267, 2017.

FITZER, S. C.; et al. Coastal acidification impacts on shell mineral structure of bivalve mollusks. **Ecology and evolution**, v. 8, n. 17, p. 8973-8984, 2018.

GARCÍA-ROBLEDO, E.; CORZO, A.; PAPASPYROU, S. A fast and direct spectrophotometric method for the sequential determination of nitrate and nitrite at low concentrations in small volumes. **Marine Chemistry**, v. 162, p. 30-36, 2014.

GASPAR, F. L.; PINHEIRO, B. R.; NORIEGA, C. E. D.; ARAUJO, M. et al. Alkalinity, inorganic carbon and CO2 flux variability during extreme rainfall years (2010-2011) in two polluted tropical estuaries NE Brazil. **Brazilian Journal of Oceanography**, v. 66, p. 115-130, 2018.

GATTUSO, J. P.; et al. Effect of calcium carbonate saturation of seawater on coral calcification. **Global and Planetary Change**. v. 18, n.1, p. 37-46, 1998.

GENG, X.; BOUFADEL, M. C.; JACKSON, N. L. Evidence of salt accumulation in beach intertidal zone due to evaporation. **Scientific reports**, v. 6, n. 1, p. 1-5, 2016.

GLEDHILL, D. K.; et al. Ocean and coastal acidification off New England and Nova Scotia. **Oceanography**, v. 28, n. 2, p. 182-197, 2015.

GLYNN, P. W. Coral reef bleaching: ecological perspectives. **Coral reefs**, v. 12, n. 1, p. 1-17, 1993.

GONZÁLEZ, M. F.; ILYINA, T. Impacts of artificial ocean alkalinization on the carbon cycle and climate in Earth system simulations. **Geophysical Research Letters**, v. 43, n. 12, p. 6493-6502, 2016.

GOWER, D.; JOHNSON, K.; RICHARDSON, J.; ROSEN, B.; RÜBER, L.; WILLIAMS, S. Biotic evolution and environmental change in Southeast Asia. **Cambridge University Press**, v. 82, 2012.

GRAHAM, E. R.; SANDERS, R. W. Species-specific photosynthetic responses of symbiotic zoanthids to thermal stress and ocean acidification. **Marine Ecology**, v. 37, n. 2, p. 442-458, 2016.

GRASSHOFF, K; et al. Methods of Seawater Analyses. **Verlag Chemie**. 317, 1993.

GRIFFIOEN, J. Extent of immobilisation of phosphate during aeration of nutrient-rich, anoxic groundwater. **Journal of Hydrology**, v. 320, n. 3-4, p. 359-369, 2006.

GROOT, R.; et al. Global estimates of the value of ecosystems and their services in monetary units. **Ecosystem services**, v. 1, n. 1, p. 50-61, 2012.

GRUBER, N.; SARMIENTO, J. L.; STOCKER, T. F. An improved method for detecting anthropogenic CO2 in the oceans. **Global Biogeochemical Cycles**, v. 10, n. 4, p. 809-837, 1996.

GUAN, Y.; HOHN, S.; WILD, C.; MERICO, A. Vulnerability of global coral reef habitat suitability to ocean warming, acidification and eutrophication. **Global Change Biology**, v. 26, n. 10, p. 5646-5660, 2020.

GUENTHER, M.; FLORES-MONTES, M. J.; GONZALES-RODRIGUEZ, E.; NEUMANN-LEITÃO, S. Eutrophication effects on phytoplankton size-fractioned biomass and production at a tropical estuary. **Marine pollution bulletin**, v. 91, n. 2, p. 537-547, 2015.

GUERRA, N. C.; KIANG, C. H.; SIAL, A. N. Carbonate cements in contemporaneous beachrocks, Jaguaribe beach, Itamaracá island, northeastern Brazil: petrographic, geochemical and isotopic aspects. **Anais da Academia Brasileira de Ciências**, v. 77, n. 2, p. 343-352, 2005.

HEISS, J. W.; MICHAEL, H. A. Saltwater-freshwater mixing dynamics in a sandy beach aquifer over tidal, spring-neap, and seasonal cycles. **Water Resources Research**, v. 50, n. 8, p. 6747-6766, 2014.

HILMI, N.; OSBORN, D.; ACAR, S.; BAMBRIDGE, T.; CHLOUS, F. et al. Socio-economic tools to mitigate the impacts of ocean acidification on economies and communities reliant on coral reefs—a framework for prioritization. **Regional Studies in Marine Science**, v. 28, p. 100559, 2019.

HOEGH-GULDBERG, O.; et al.: Coral reefs under rapid climate change and ocean acidification. **Science**, v. 318, n. 5857, p. 1737-1742, 2007.

HOEGH-GULDBERG, O.; PENDLETON, L.; KAUP, A. People and the changing nature of coral reefs. **Regional Studies in Marine Science**, v. 30, p. 100699, 2019.

HUGHES, T. P.; ANDERSON, K. D.; CONNOLLY, S. R.; HERON, S. F.; KERRY, J. T. et al. Spatial and temporal patterns of mass bleaching of corals in the Anthropocene. **Science**, v. 359, n. 6371, p. 80-83, 2018.

IBÁNHEZ, J. S. P.; ROCHA, C. Effects of recirculation of seawater enriched in inorganic nitrogen on dissolved organic carbon processing in sandy seepage face sediments. **Marine Chemistry**, v. 166, p. 48-58, 2014.

IBÁNHEZ, J. S. P.; ROCHA, C. Kinetics of inorganic nitrogen turnover in a sandy seepage face on a subterranean estuary. **Applied Geochemistry**, v. 87, p. 108-121, 2017.

IBÁNHEZ, J.S.P.; ARÉVALO, E.; KELLY, T.; PAPASPYROU, S.; ROCHA, C.; NICOLAIDOU, A. Unraveling the dispersion and environmental impact of anthropogenic discharges in transitional water ecosystems. **Estuarine, Coastal and Shelf Science**, v. 216, p. 204-217, 2019.

INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA. Pesquisa Cidades. IBGE, 2010. https://cidades.ibge.gov.br/brasil/al/maragogi (acessado 11 maio 2020).

IPCC. Summary for Policymakers. In: Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Masson-Delmotte, V., P. Zhai, A. Pirani, S. L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M. I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J.B.R. Matthews, T. K. Maycock, T. Waterfield, O. Yelekçi, R. Yu and B. Zhou (eds.)]. **Cambridge University Press**. In Press, 2021.

JALES, M. C.; FEITOSA, F. A. N.; KOENING, M. L.; BASTOS, R. B.; MACHADO, R. C. A. O ecossistema recifal de Serrambi (nordeste do Brasil): biomassa fitoplanctônica e parâmetros hidrológicos. **Atlântica (Rio Grande)**, v. 34, n. 2, p. 87-102, 2012.

JIANG, S.; IBÁNHEZ, J.S.P.; WU, Y.; ZHANG, J. Geochemical tracers in submarine groundwater discharge research: practice and challenges from a view of climate changes. **Environmental Reviews**, v. 29, n. 2, p. 242-259, 2021.

JOKIEL, P. L. Predicting the impact of ocean acidification on coral reefs: evaluating the assumptions involved. **ICES Journal of Marine Science**, v. 73, n. 3, p. 550-557, 2016.

KASPARY, M. G. A. R. Desenvolvimento turístico e o desenvolvimento local no município de Maragogi, Alagoas. **Dissertation**/Universidade Federal de Alagoas, 159, 2012.

KIM, G.; RYU, J. W.; HWANG, D. W. Radium tracing of submarine groundwater discharge (SGD) and associated nutrient fluxes in a highly-permeable bed coastal zone, Korea. **Marine Chemistry**, v. 109, n. 3-4, p. 307-317, 2008.

KLEYPAS, J. A.; ANTHONY, K. R.; GATTUSO, J. P. Coral reefs modify their seawater carbon chemistry–case study from a barrier reef (M oorea, F rench P olynesia). **Global change biology**, v. 17, n. 12, p. 3667-3678, 2011.

LAM, V. W.; CHAVANICH, S.; DJOUNDOURIAN, S.; DUPONT, S. et al. Dealing with the effects of ocean acidification on coral reefs in the Indian Ocean and Asia. **Regional Studies in Marine Science**, v. 28, p. 100560, 2019.

LAJEUNESSE, T. C.; PARKINSON, J. E.; GABRIELSON, P. W.; JEONG, H. J.; REIMER, J. D.; VOOLSTRA, C. R.; SANTOS, S. R. Systematic revision of Symbiodiniaceae highlights the antiquity and diversity of coral endosymbionts. **Current Biology**, v. 28, n. 16, p. 2570-2580, 2018.

LANDRIGAN, P. J.; et al. Human health and ocean pollution. **Annals of global health**, v. 86, n. 1, 2020.

LANGDON, C.; GATTUSO, J. P.; ANDERSSON, A. Measurements of calcification and dissolution of benthic organisms and 13 communities. **Guide to best practices for ocean acidification research and data reporting, eds U. Riebesell, VJ Fabry, L. Hansson and J.-P. Gattuso (Luxembourg: Publications Office of the European Union)**, 2010.

LANTZ, C. A.; ATKINSON, M. J.; WINN, C. W.; KAHNG, S. E. Dissolved inorganic carbon and total alkalinity of a Hawaiian fringing reef: chemical techniques for monitoring the effects of ocean acidification on coral reefs. **Coral Reefs**, v. 33, n. 1, p. 105-115, 2014.

LAPOINTE, B. E.; LITTLER, M. M.; LITTLER, D. S. Macroalgal overgrowth of fringing coral reefs at Discovery Bay, Jamaica: bottom-up versus top-down control. **Proc. 8th Int. Coral Reef Symp**. 927-932, 1997.

LEBREC, M.; et al. Ocean acidification impacts in select Pacific Basin coral reef ecosystems. **Regional Studies in Marine Science**, v. 28, p. 100584, 2019.

LEE, K.; TONG, L. T.; MILLERO, F. J.; SABINE, C. L.; DICKSON, A. G.; GOYET, C.; PARK, G-H.; WANNINKHOF, R.; FEELY, R. A.; KEY, R. M. Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans. **Geophysical research letters**, v. 33, n. 19, 2006.

LEE, Y. W.; KIM, G.; LIM, W. A.; HWANG, D. W. A relationship between submarine groundwater borne nutrients traced by Ra isotopes and the intensity of dinoflagellate red-tides occurring in the southern sea of Korea. **Limnology and oceanography**, v. 55, n. 1, p. 1-10, 2010.

LENTON, A.; MATEAR, R. J.; KELLER, D. P.; SCOTT, V.; VAUGHAN, N. E. Assessing carbon dioxide removal through global and regional ocean alkalinization under high and low emission pathways. **Earth System Dynamics**, v. 9, n. 2, p. 339-357, 2018.

LEOTE, C.; IBÁNHEZ, J. S.; ROCHA, C. Submarine groundwater discharge as a nitrogen source to the Ria Formosa studied with seepage meters. **Biogeochemistry**, v. 88, n. 2, p. 185-194, 2008.

LINS, A. P. G. D. Turismo e meio ambiente: o esgotamento sanitário no município de Maragogi, Alagoas. Dissertation/Universidade Federal de Alagoas, 211, 2017.

LIU, J.; DU, J.; WU, Y.; LIU, S. Nutrient input through submarine groundwater discharge in two major Chinese estuaries: The Pearl River Estuary and the Changjiang River Estuary. **Estuarine, Coastal and Shelf Science**, v. 203, p. 17-28, 2018.

LIU, Q.; CHARETTE, M. A.; BREIER, C. F.; HENDERSON, P. B. Carbonate system biogeochemistry in a subterranean estuary–Waquoit Bay, USA. **Geochimica et Cosmochimica Acta**, v. 203, p. 422-439, 2017.

LIU, Q.; CHARETTE, M. A.; HENDERSON, P. B.; MCCORKLE, D. C. et al. Effect of submarine groundwater discharge on the coastal ocean inorganic carbon cycle. **Limnology and Oceanography**, v. 59, n. 5, p. 1529-1554, 2014.

LUO, X.; JIAO, J. J.; MOORE, W. S.; LEE, C. M. Submarine groundwater discharge estimation in an urbanized embayment in Hong Kong via short-lived radium isotopes and its implication of nutrient loadings and primary production. **Marine pollution bulletin**, v. 82, n. 1-2, p. 144-154, 2014.

MARANGONI, L. F. B.; CALDERON, E. N.; MARQUES, J. A.; DUARTE, G. A. S.; PEREIRA, C. M.; BIANCHINI, A. Effects of CO2-driven acidification of seawater on the calcification process in the calcareous hydrozoan Millepora alcicornis (Linnaeus, 1758). **Coral reefs**, v. 36, n. 4, p. 1133-1141, 2017.

MARQUES, J. A.; COSTA, P. G.; MARANGONI, L. F. B.; PEREIRA, C. M.; ABRANTES, D. P.; CALDERON, E. N.; CASTRO, C. B.; BIANCHINI, A. Environmental health in southwestern Atlantic coral reefs: Geochemical, water quality and ecological indicators. **Science of The Total Environment**, v. 651, p. 261-270, 2019.

MARRETO, R. N.; BAUMGARTEN, M. G. Z.; WALLNER-KERSANACH, M. Trophic quality of waters in the Patos Lagoon estuary: A comparison between its margins and the port channel located in Rio Grande, RS, Brazil. **Acta Limnologica Brasiliensia**, v. 29, 2017.

MASCARENHAS, J. D. C.; BELTRÃO, B. A.; SOUZA-JUNIOR, L. C. D. **Projeto cadastro de fontes de abastecimento por água subterrânea estado de Alagoas: diagnóstico do município de Maragogi**. CPRM, 2005a.

MASCARENHAS, J. D. C.; BELTRÃO, B. A.; SOUZA-JUNIOR, L. C. D. **Projeto cadastro de fontes de abastecimento por água subterrânea estado de Alagoas: diagnóstico do município de Japaratinga**. CPRM, 2005b.

MELO, M. A. F.; KOENING, M. I.; FILHO, J. S. R.; TRAVASSOS, R. K. et al. Microfitoplâncton de águas costeiras adjacentes ao Porto do Recife (PE-Brasil). **Tropical Oceanography Online**, 2013.

MICHAEL, H. A.; MULLIGAN, A. E.; HARVEY, C. F. Seasonal oscillations in water exchange between aquifers and the coastal ocean. **Nature**, v. 436, n. 7054, p. 1145-1148, 2005.

MILLERO, F. J. Chemical oceanography. **CRC press**, v. 30, 2005.

MOORE, W. S. The effect of submarine groundwater discharge on the ocean. **Annual review of marine science**, v. 2, p. 59-88, 2010.

MUEHLLEHNER, N.; LANGDON, C.; VENTI, A.; KADKO, D. Dynamics of carbonate chemistry, production, and calcification of the Florida Reef Tract (2009–2010): Evidence for seasonal dissolution. **Global Biogeochemical Cycles**, v. 30, n. 5, p. 661-688, 2016.

MURILLO, L. J.; JOKIEL, P. L.; ATKINSON, M. J. Alkalinity to calcium flux ratios for corals and coral reef communities: variances between isolated and community conditions. **PeerJ**, v. 2, p. e249, 2014.

NIENCHESKI, L. F. H.; WINDOM, H. L.; MOORE, W. S.; JAHNKE, R. A. Submarine groundwater discharge of nutrients to the ocean along a coastal lagoon barrier, Southern Brazil. **Marine Chemistry**, v. 106, n. 3-4, p. 546-561, 2007.

ORR, J. C.; et al. Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. **Nature**, 2005.v. 437, n.7059, p. 681-686.

PAGE, H. N.; ANDERSSON, A. J.; JOKIEL, P. L.; RODGERS, K. U. S.; LEBRATO, M.; YEAKEL, K.; DAVIDSON, C.; D'ANGELO, S.; BAHR, K. D. Differential modification of seawater carbonate chemistry by major coral reef benthic communities. **Coral Reefs**, v. 35, n. 4, p. 1311-1325, 2016.

PAIVA, L. M. Variabilidade estrutural da floresta de mangue do estuário do rio Tatuamunha, Porto de Pedras, Alagoas, Brasil. **Dissertação de mestrado**/ Universidade Federal de Pernambuco, 85, 2018.

PAIVA, M.; NIENCHESKI, F. H. Advances of submarine groundwater discharge studies in South America. **Journal of the Brazilian Chemical Society**, v. 29, p. 916-924, 2018.

PASSOS, C. V. B.; FABRÉ, N. N.; MALHADO, A. C. M.; BATISTA, V. S.; LADLE, R. J. Estuarization increases functional diversity of demersal fish assemblages in tropical coastal ecosystems. **Journal of fish biology**, v. 89, n. 1, p. 847-862, 2016.

PAVLIDOU, A.; PAPADOPOULOS, V. P.; HATZIANESTIS, I.; SIMBOURA, N. et al. Chemical inputs from a karstic submarine groundwater discharge (SGD) into an oligotrophic Mediterranean coastal area. **Science of the total environment**, v. 488, p. 1-13, 2014.

PAYTAN, A.; SHELLENBARGER, G. G.; STREET, J. H.; GONNEEA, M. E. et al. Submarine groundwater discharge: an important source of new inorganic nitrogen to coral reef ecosystems. **Limnology and Oceanography**, v. 51, n. 1, p. 343-348, 2006.

PENDLETON, L.; LANGDON, C.; EKSTROM, J. A.; COOLEY, S. R. et al. Coral Reefs and People in a High-CO2 World: Where Can Science Make a Difference to People? **PloS one**, v. 11, n. 11, p. e0164699, 2016.

PEREIRA, P. H.; et al. Unprecedented coral mortality on Southwestern Atlantic (SWA) coral reefs following major thermal stress. **Frontiers in Marine Science**, v. 9, p. 338, 2022.

PETERMANN, E.; KNOLLER, K.; ROCHA, C.; SCHOLTEN, J.; STOLLBERG, R.; WEIB, H.; SCHUBERT, M. et al. Coupling end-member mixing analysis and isotope mass balancing (222-Rn) for differentiation of fresh and recirculated submarine groundwater discharge into Knysna Estuary, South Africa. **Journal of Geophysical Research: Oceans**, v. 123, n. 2, p. 952-970, 2018.

PINET, P. R. Invitation to oceanography. **Jones & Bartlett Learning**, 2006.

PINHEIRO, B. R.; GASPAR, F. L.; SILVA, B. J.; FLORES-MONTES, M. J. et al. Interactions between hydrology and benthic coverage at rocas atoll. **Tropical Oceanography**, 44, 2, 142-157, 2016.

PLANO NACIONAL DE ADAPTAÇÃO. PNA, https://www.gov.br/mma/pt-br/assuntos/climaozoniodesertificacao/plano-nacional-de-adaptacao. Acessed 31 July 2021, 2015.

PMACC – Plano de Manejo APA Costa dos Corais. Instituto Chico Mendes de Conservação da Biodiversidade, 2013.

PRADA, F.; CAROSELLI, E.; MENGOLI, S.; BRIZI, L.; FANTAZZINI, P.; CAPACCIONI, B.; PASQUINI, L.; FABRICIUS, K. E.; DUBINSKY, Z.; FALINI, G.; GOFFREDO, S. Ocean warming and acidification synergistically increase coral mortality. **Scientific Reports**, v. 7, n. 1, p. 1-10, 2017.

RENGARAJAN, R.; SARMA, V. V. S. S. Submarine groundwater discharge and nutrient addition to the coastal zone of the Godavari estuary. **Marine Chemistry**, v. 172, p. 57-69, 2015.

ROBINSON, C.; LI, L.; BARRY, D. A. Effect of tidal forcing on a subterranean estuary. **Advances in Water Resources**, v. 30, n. 4, p. 851-865, 2007.

ROELVINK, F. E.; STORLAZZI, C. D.; VAN DONGEREN, A. R.; PEARSON, S. G. Coral reef restorations can be optimized to reduce coastal flooding hazards. **Frontiers in Marine Science**, v. 8, p. 440, 2021.

ROSADO, P. M.; LEITE, D. C.; DUARTE, G. A.; CHALOUB, R. M.; JOSPIN, G.; ROCHA, U. N.; SARAIVA, J. P.; DINI-ANDREOTE, F.; EISEN, J. A.; BOURNE, D.

G.; PEIXOTO, R. S. Marine probiotics: increasing coral resistance to bleaching through microbiome manipulation. **The ISME journal**, v. 13, n. 4, p. 921-936, 2019.

RUBIO-CISNEROS, N. T.; HERRERA-SILVEIRA, J.; MORALES-OJEDA, S.; MORENO-BÁEZ, M. et al. Water quality of inlets' water bodies in a growing touristic barrier reef Island "Isla Holbox" at the Yucatan Peninsula. **Regional studies in marine science**, v. 22, p. 112-124, 2018.

SABINE, C. L.; FEELY, R. A.; GRUBER, N.; KEY, R. M.; LEE, K.; BULLISTER, J. L.; WANNINKHOF, R.; WONG, C. S.; WALLACE, D. W. R.; TILBROOK, B.; MILLERO F. J.; PENG, T-H.; KOZYR, A.; ONO, T.; RIOS, A. F. The oceanic sink for anthropogenic CO2. **science**, v. 305, n. 5682, p. 367-371, 2004.

SANTOS, I. R.; EYRE, B. D.; HUETTEL, M. The driving forces of porewater and groundwater flow in permeable coastal sediments: A review. **Estuarine, Coastal and Shelf Science**, v. 98, p. 1-15, 2012.

SCHUBERT, M.; PASCHKE, A. Radon, CO_2 and CH_4 as environmental tracers in groundwater/surface water interaction studies − comparative theoretical evaluation of the gas specific water/air phase transfer kinetics. **The European Physical Journal Special Topics**, v. 224, n. 4, p. 709-715, 2015.

SECRETARIA EXECUTIVA DE MEIO AMBIENTE, RECURSOS HÍDRICOS E NATURAIS DE ALAGOAS. Balanço de disponibilidade x demanda de recursos hídricos na região hidrográfica litoral norte. SEMARHN, Relatório. 1-30, 2015. http://www.semarh.al.gov.br/ (acessado 20 dezembro 2019).

SHAMBERGER, K. E. F.; FEELY, R. A.; SABINE, C. L.; ATKINSON, M. J.; DECARLO, E. H.; MACKENZIE, F. T.; DRUPP, P. S.; BUTTERFIELD, D. A. Calcification and organic production on a Hawaiian coral reef. **Marine Chemistry**, v. 127, n. 1-4, p. 64-75, 2011.

SHAW, E. C.; MCNEIL, B. I.; TILBROOK, B. Impacts of ocean acidification in naturally variable coral reef flat ecosystems. **Journal of Geophysical Research: Oceans**, v. 117, n. C3, 2012.

SHAW, E. C.; PHINN, S. R.; TILBROOK, B.; STEVEN, A. Natural in situ relationships suggest coral reef calcium carbonate production will decline with ocean acidification. **Limnology and Oceanography**, v. 60, n. 3, p. 777-788, 2015.

SHEPPARD, C.; DAVY, S.; PILLING, G.; GRAHAM, N. **The biology of coral reefs**. Oxford University Press, 2017.

SHTEREVA, G.; VELIKOVA, V.; DONCHEVA, V. Human impact on marine water nutrients enrichment. **Journal of Environmental Protection and Ecology**, v. 16, n. 1, p. 40-48, 2015.

SILVA, B. J.; IBÁNHEZ, J. S. P.; PINHEIRO, B. R.; LADLE, R. J.; MALHADO, A. C.; PINTO, T. K.; FLORES-MONTES, M. J. Seasonal influence of surface and underground continental runoff over a reef system in a tropical marine protected area. **Journal of Marine Systems**, v. 226, p. 103660, 2022.

SILVA, L. M.; FEITOSA, F. A. N.; FLORES-MONTES, M. J.; OTSUKA, A. Y.; SALDANHA-CORRÊA, F.; NORIEGA, C. Phytoplankton Productivity and Hydrology in an Impacted Estuarine Complex in Northeastern Brazil. **Open Journal of Ecology**, v. 9, n. 10, p. 458, 2019.

SILVA, M. H. D.; SILVA-CUNHA, M. G. G.; PASSAVANTE, J. Z. O.; GREGO, C. K. S. et al. Estrutura sazonal e espacial do microfitoplâncton no estuário tropical do rio Formoso, PE, Brasil. **Acta botanica brasilica**, v. 23, n. 2, p. 355-368, 2009.

SILVEIRA, C. B. L.; FERREIRA, B. P.; COXEY, M. S. Variação temporal nos recifes de corais de Maragogi, APA Costa dos Corais (2010-2013). **Tropical Oceanography**, 42, 2, 2014.

SILVERMAN, J.; LAZAR, B.; CAO, L.; CALDEIRA, K.; EREZ, J. Coral reefs may start dissolving when atmospheric CO2 doubles. **Geophysical Research Letters**, v. 36, n. 5, 2009.

SILVERMAN, J.; LAZAR, B.; EREZ, J. Effect of aragonite saturation, temperature, and nutrients on the community calcification rate of a coral reef. **Journal of Geophysical Research: Oceans**, v. 112, n. C5, 2007.

SIMPSON, C.; KIESSLING, W.; MEWIS, H.; BARON-SZABO, R. C.; MÜLLER, J. Evolutionary diversification of reef corals: a comparison of the molecular and fossil records. **Evolution: International Journal of Organic Evolution**, v. 65, n. 11, p. 3274-3284, 2011.

SISTEMA NACIONAL DE INFORMAÇÕES SOBRE RECURSOS HÍDRICOS. Atlas esgotos: despoluição de bacias hidrográficas – Sistema Maragogi. SNIRH, 2015. https://portal1.snirh.gov.br/arquivos/Atlas_Esgoto/Alagoas/Sistema_Atual/Maragogi.pdf (acessado 20 agosto 2021).

SLOMP, C. P.; VAN CAPPELLEN, P. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. Journal of Hydrology. **Journal of Hydrology**, v. 295, n. 1-4, p. 64-86, 2004.

SPALDING, M.; BURKE, L.; WOOD, S. A.; ASHPOLE, J.; HUTCHISON, J.; ZU, E. P. Mapping the global value and distribution of coral reef tourism. **Marine Policy**, v. 82, p. 104-113, 2017.

SPALDING, M.; SPALDING, M. D.; RAVILIOUS, C.; GREEN, E. P. World atlas of coral reefs. **Univ of California Press**, 2001.

SPEERS, A. E.; BESEDIN, E. Y.; PALARDY, J. E.; MOORE, C. Impacts of climate change and ocean acidification on coral reef fisheries: an integrated ecological–economic model. **Ecological economics**, v. 128, p. 33-43, 2016.

STRICKLAND, J. D.; PARSONS, T. R. A practical handbook of seawater analysis. **Bulletin of Fisheries Research**, 167, p. 1–311, 1972.

SU, N.; BURNETT, W. C.; ELLER, K. T.; MACINTYRE, H. L. et al. Radon and radium isotopes, groundwater discharge and harmful algal blooms in Little Lagoon, Alabama. **Interdisciplinary studies on environmental chemistry**, v. 6, p. 329-337, 2012.

SUGIMOTO, R.; HONDA, H.; KOBAYASHI, S.; TAKAO, Y. et al. Seasonal changes in submarine groundwater discharge and associated nutrient transport into a tideless semi-enclosed embayment (Obama Bay, Japan). **Estuaries and Coasts**, v. 39, n. 1, p. 13-26, 2016.

SULLY, S.; BURKEPILE, D. E.; DONOVAN, M. K.; HODGSON, G.; VAN WOESIK, R. A global analysis of coral bleaching over the past two decades. **Nature communications**, v. 10, n. 1, p. 1-5, 2019.

SZYMCZYCHA, B.; VOGLER, S.; PEMPKOWIAK, J. Nutrient fluxes via submarine groundwater discharge to the Bay of Puck, southern Baltic Sea. **Science of the Total Environment**, v. 438, p. 86-93, 2012.

TAILLARDAT, P.; MARCHAND, C.; FRIESS, D. A.; WIDORY, D.; DAVID, F.; OHTEG, N.; NAKAMURAH, T.; VINHI, T. V.; THANH-NHOJ, N.; ZIEGLER, A. D. Respective contribution of urban wastewater and mangroves on nutrient dynamics in a tropical estuary during the monsoon season. **Marine Pollution Bulletin**, v. 160, p. 111652, 2020.

TAKAHASHI, T.; et al. Climatological mean and decadal change in surface ocean pCO 2, and net sea–air CO 2 flux over the global oceans. **Deep Sea Research Part II: Topical Studies in Oceanography**, v. 56, n. 8, p. 554-577, 2009.

TAKESHITA, Y.; CYRONAK, T.; MARTZ, T. R.; KINDEBERG, T.; ANDERSSON, A. J. Coral reef carbonate chemistry variability at different functional scales. **Frontiers in Marine Science**, v. 5, p. 175, 2018.

TAMBORSKI, J. J.; COCHRAN, J. K.; BOKUNIEWICZ, H. J. Submarine groundwater discharge driven nitrogen fluxes to Long Island Sound, NY: Terrestrial vs. marine sources. **Geochimica et Cosmochimica Acta**, v. 218, p. 40-57, 2017.

TAMBUTTÉ, S.; HOLCOMB, M.; FERRIER-PAGÈS, C.; REYNAUD, S.; TAMBUTTÉ, É.; ZOCCOLA, D.; ALLEMAND, D. Coral biomineralization: From the gene to the environment. **Journal of Experimental Marine Biology and Ecology**, v. 408, n. 1-2, p. 58-78, 2011.

TANIGUCHI, M.; DULAI, H.; BURNETT, K. M.; SANTOS, I. R.; SUGIMOTO, R.; STIEGLITZ, T.; KIM, G.; MOOSDORF, N.; BURNETT, W. Submarine Groundwater Discharge: Updates on its Measurement Techniques, Geophysical Drivers, Magnitudes and Effects. **Frontiers in Environmental science**, v. 7, p. 141, 2019.

UNESCO. Determination of photosynthetic pigments in seawater. Rapor of SCOR/UNESCO, working group 17 with meat from 4 to 6 June 1964, **Monography on Oceanography Methodology**, 69, 1966.

UNESCO. International Oceanographic Tables. Volume 2. Oxygen Solubility in Sea Water, 1973.

VALLE, M. M. Caracterização das feições sedimentares da plataforma de Alagoas, com base em levantamento aerobatimétrico LIDAR. **Dissertação de mestrad**o/ Universidade Federal de Pernambuco, 96, 2018.

VOLLENWEIDER, R. A.; GIOVANARDI, F.; MONTANARI, G.; RINALD, A. Characterization of the trophic conditions or marine coastal waters with special reference to the NW Adriatic Sea: proposal for a trophic scale, turbidity and generalized water quality index. **Environmetrics: The official journal of the International Environmetrics Society**, v. 9, n. 3, p. 329-357, 1998.

WALLACE, R. B.; BAUMANN, H.; GREAR, J. S.; ALLER, R. C.; GOBLER, C. J. Coastal ocean acidification: The other eutrophication problem. **Estuarine, Coastal and Shelf Science**, v. 148, p. 1-13, 2014.

WANG, G.; JING, W.; WANG, S.; XU, Y. et al. Coastal acidification induced by tidal-driven submarine groundwater discharge in a coastal coral reef system. **Environmental science & technology**, v. 48, n. 22, p. 13069-13075, 2014.

WANG, G.; WANG, Z.; ZHAI, W. et al. Net subterranean estuarine export fluxes of dissolved inorganic C, N, P, Si, and total alkalinity into the Jiulong River estuary, China. **Geochimica et Cosmochimica Acta**, v. 149, p. 103-114, 2015.

WANG, S. L.; CHEN, C. T. A.; HUANG, T. H.; TSENG, H. C. et al. Submarine Groundwater Discharge helps making nearshore waters heterotrophic. **Scientific Reports**, v. 8, n. 1, p. 1-10, 2018.

WEAR, S. L.; THURBER, R. V. Sewage pollution: mitigation is key for coral reef stewardship. **Annals of the New York Academy of Sciences**, v. 1355, n. 1, p. 15-30, 2015.

WILKINSON, C. *Status of coral reefs of the world: 2000*. Australian Institute of Marine Science, 2000.

WILLIAMSON, P.; PÖRTNER, H. O.; WIDDICOMBE, S.; GATTUSO, J. P. Ideas and perspectives: When ocean acidification experiments are not the same, repeatability is not tested. **Biogeosciences**, v. 18, n. 5, p. 1787-1792, 2020.

WOLFF, N. H.; SILVA, E. T.; DEVLIN, M.; ANTHONY, K. R. et al. Contribution of individual rivers to Great Barrier Reef nitrogen exposure with implications for management prioritization. **Marine pollution bulletin**, v. 133, p. 30-43, 2018.

WOODHEAD, A. J.; HICKS, C. C.; NORSTRÖM, A. V.; WILLIAMS, G. J.; GRAHAM, N. A. Coral reef ecosystem services in the Anthropocene. **Functional Ecology**, v. 33, n. 6, p. 1023-1034, 2019.

WORLD HEALTH ORGANIZATION. **Guidelines for Safe Recreational Water Environments: coastal and fresh waters.** Geneva: WHO, 2003.

WU, Z.; ZHOU, H.; ZHANG, S.; LIU, Y. Using 222Rn to estimate submarine groundwater discharge (SGD) and the associated nutrient fluxes into Xiangshan Bay, East China Sea. **Marine pollution bulletin**, v. 73, n. 1, p. 183-191, 2013.

YATES, K. K.; HALLEY, R. B. CO_3^{-2} concentration and pCO2 thresholds for calcification and dissolution on the Molokai reef flat, Hawaii. **Biogeosciences Discussions**, v. 3, n. 1, p. 123-154, 2006.

YEAKEL, K. L.; ANDERSSON, A. J.; BATES, N. R.; NOYES, T. J.; COLLINS, A.; GARLEY, R. Shifts in coral reef biogeochemistry and resulting acidification linked to offshore productivity. **Proceedings of the National Academy of Sciences**, v. 112, n. 47, p. 14512-14517, 2015.

YOUNG, C.; TAMBORSKI, J.; BOKUNIEWICZ, H. Embayment scale assessment of submarine groundwater discharge nutrient loading and associated land use. **Estuarine, Coastal and Shelf Science**, v. 158, p. 20-30, 2015.

ZALASIEWICZ, J.; et al. Are we now living in the Anthropocene?. **Gsa Today**, v. 18, n. 2, p. 4, 2008.

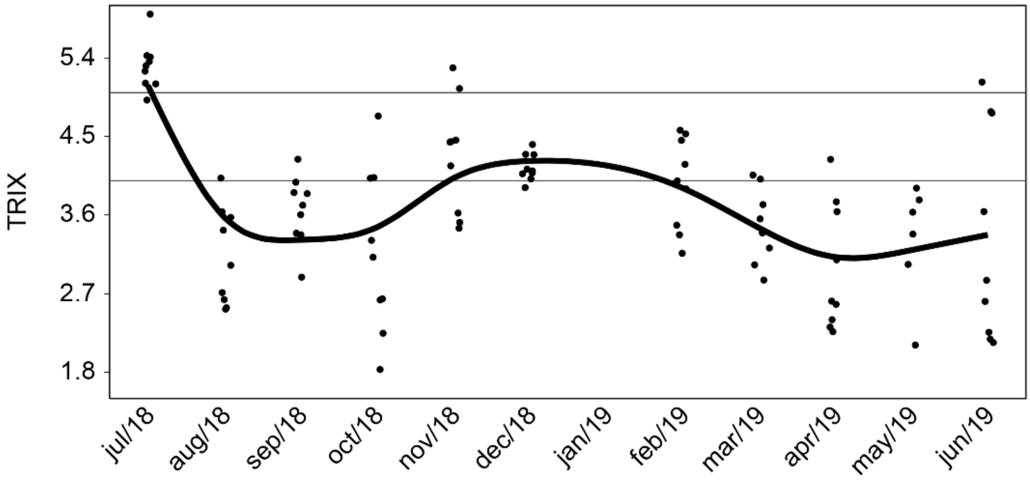
ZEEBE, R. E. History of seawater carbonate chemistry, atmospheric CO2, and ocean acidification. **Annual review of earth and planetary sciences**, v. 40, p. 141-165, 2012.

ZILBERBERG, C.; et al. Conhecendo os Recifes Brasileiros: Rede de Pesquisas Coral. **Série de livros do Museu Nacional**, p. 360, 2016.

ZHANG, W.; JIN, X.; LIU, D.; LANG, C.; SHAN, B. Temporal and spatial variation of nitrogen and phosphorus and eutrophication assessment for a typical arid river—Fuyang River in northern China. **Journal of Environmental Sciences**, v. 55, p. 41-48, 2017.

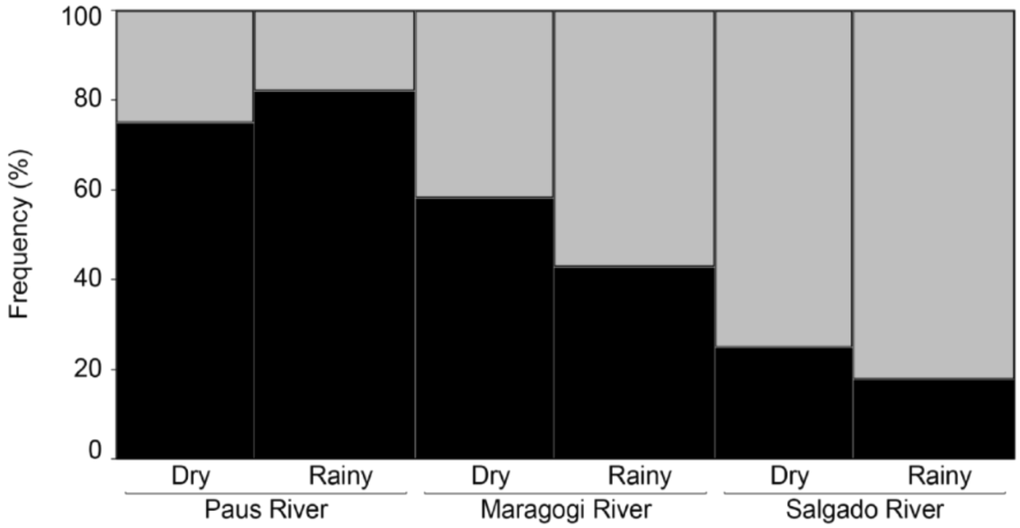
APÊNDICE A – MATERIAL SUPLEMENTAR ARTIGO 1

Figure 1 – Monthly variation of the calculated TRIX index in the studied reef lagoon.



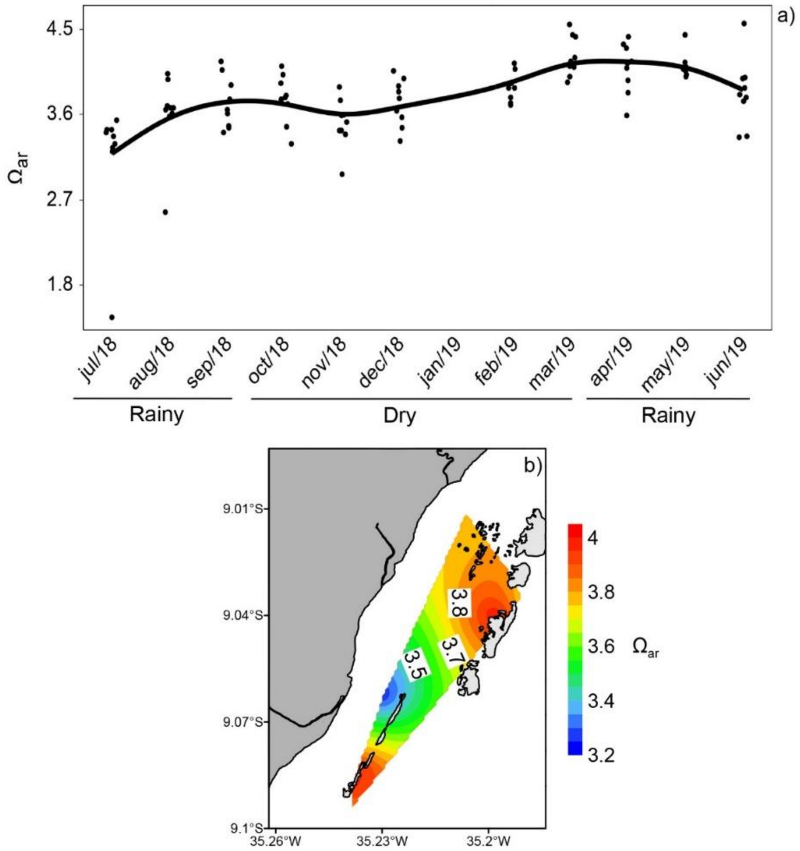
Source: The author (2022).

Figure 2 – Seasonal frequency of good (black bars) and poor (gray bars) water quality conditions in the Paus, Maragogi and Salgado rivers.



Source: The author (2022).

Figure 3 – Monthly Ω_{ar} variations in the reef lagoon (a), together with the general mean of Ω_{ar} in the lagoon (b).



Source: The author (2022).

Table 1 – Results of the PERMANOVA tests performed with the three main groups of samples collected (reefs, rivers and porewaters), organized by season (rainy and dry). Significant difference is represented by $P < 0.05$.

Rainy season	R^2	*P* value
River x Porewaters	0.5759	0.001
River x Reefs	0.7546	0.001
Porewaters x Reefs	0.4981	0.001
Dry season		
River x Porewaters	0.3657	0.001
River x Reefs	0.5851	0.001
Porewaters x Reefs	0.4831	0.001

Source: The author (2022).

Table 2 – Seasonal differences found in each group of samples with the PERMANOVA test. Significant difference is represented by $P < 0.05$.

	R^2	*P* value
Rivers		
Rainy x Dry	0.2265	0.001
Reefs		
Rainy x Dry	0.0394	0.007
Porewaters		
Rainy x Dry	0.0424	0.279

Source: The author (2022).

APÊNDICE B – MATERIAL SUPLEMENTAR ARTIGO 2

Figure 4 – Inflatable pool used during the experiment, filled with seawater mixed with rhodamine WT and NaOH.

Source: The author (2022).

Figure 5 – Well pumps used during the experiment to fill and empty the pool.

Source: The author (2022).

Figure 6 – Well pump connected to the watertight box, which presented a truck battery and a current inverter inside.

Source: The author (2022).

Table 3 – Mean and standard deviation (±) of temperature, DIN, DIP, DSi, Chl-*a*, SPM and DO during control and alkaline days, upstream and downstream the reef.

	Control		Alkaline	
	Upstream	Downstream	Upstream	Downstream
Temperature (ºC)	28.54 ± 0.24	28.53 ± 0.22	29.53 ± 1.31	29.73 ± 1.27
DIN (µmol L^{-1})	0.49 ± 0.45	1.11 ± 0.61	0.67 ± 0.47	1.14 ± 1.70
DIP (µmol L^{-1})	0.06 ± 0.11	0.05 ± 0.03	0.05 ± 0.08	0.03 ± 0.03
DSi (µmol L^{-1})	9.50 ± 10.51	11.30 ± 5.39	1.64 ± 1.98	5.45 ± 2.47
Chl-*a* (µg L^{-1})	0.63 ± 0.18	0.82 ± 0.24	0.67 ± 0.22	0.70 ± 0.34
SPM (mg L^{-1})	6.09 ± 0.36	6.93 ± 2.31	6.25 ± 0.34	6.47 ± 0.64
DO (mL L^{-1})	5.73 ± 0.75	5.91 ± 0.93	6.81 ± 1.34	7.15 ± 1.48

Source: The author (2022).