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Distribuição da alcalinidade total, pressão parcial do CO_2 e fluxos de CO_2 na interface água-ar no ecossistema costeiro do estado de Pernambuco

RECIFE
2015

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Tese apresentada ao curso de Pós-Graduação em Oceanografia da Universidade Federal de Pernambuco, como requisito parcial para obtenção do grau de doutor em Oceanografia.
Orientador: Prof. Dr. Manuel de Jesus Flores-Montes
Co-Orientadora: Dra. Nathalie Lefèvre

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RESUMO

A plataforma continental Pernambucana é caracterizada pela oligotrofia e estabilidade térmica ao longo do ano influenciada pela corrente Norte do Brasil, que traz águas quentes e ricas em CO_2 para a plataforma continental do nordeste brasileiro. Dentre os principais rios translitorâneos de Pernambuco estão os Rios Capibaribe e Jaboatão que recebem os efluentes domésticos do Recife e região metropolitana, o que causa alterações nos ciclos naturais do carbono. Desta maneira, foram avaliadas a variabilidade da pCO_2 nos estuários do Capibaribe e de Barra de Jangadas assim como na plataforma continental interna do Estado de Pernambuco. Para análise nos estuários foram realizadas coletas durante a maré baixa, bimestralmente de Novembro de 2010 a Setembro de 2011. O estuário do Capibaribe apresentou os valores mais elevados de alcalinidade total (AT) e carbono inorgânico total (TCO_2), com diferença significativa entre os dois rios. As médias anuais de alcalinidade encontradas foram 1649 ± 390 µmol kg^{-1} no Capibaribe e 1557±315 µmol kg^{-1} em Barra de Jangadas. Em relação a pCO_2, os estuários apresentaram supersaturação de CO_2 em relação a atmosfera durante todo o ano, com médias de 3317 ± 2034 µatm no Capibaribe e 6018 ± 4589 µatm em Barra de Jangadas. Estes valores durante o período chuvoso variaram entre os estuários, com diminuição na pCO_2 no Capibaribe e aumentos de até 300% dos valores de pCO_2 em Barra de Jangadas. A fim de se obter uma melhor avaliação da distribuição espacial da pCO_2 na plataforma interna, foi construído um equipamento para a medição contínua e direta da pCO_2 na água como alternativa de baixo-custo em relação aos fabricados importados. A primeira campanha realizada aconteceu em Dezembro de 2014, partindo do porto do Recife em direção ao estuário de Barra de Jangadas. Apesar de o período seco ser o de maior produtividade primária a região apresentou-se oligotrófica, com picos de chl-*a* (8.4 mg m^3) próximo ao Capibaribe. Apenas uma pequena área apresentou subsaturação de CO_2 em relação à atmosfera, com o valor mínimo registrado de 376,6 µatm. Foi identificada uma elevada fugacidade de CO_2 (fCO_2) na área da plataforma interna, com média de 474,33 ± 66,57 µatm, resultando em um fluxo médio para a atmosfera de 8,5 ± 6,82 mmol C $m^{-2}d^{-1}$. A partir dos resultados obtidos foi proposto um modelo para predizer a fCO_2 a partir de valores de salinidade e temperatura para a plataforma interna durante o verão. Uma análise espacial e sazonal mais abrangente dos parâmetros do sistema carbonato na plataforma interna foi realizada utilizando-se dados de AT e TCO_2 em áreas com e sem influência de rios entre os anos de 2013 e 2014. As médias da pCO_2 e do pH na plataforma interna foram de 449 ± 45 µatm e 8,00 ± 0,03 respectivamente. Os parâmetros analisados foram influenciados pela distância da costa, o que resultou na elaboração de modelos para a predição de AT, TCO_2, pCO_2, pH, ΩCa e ΩAr a partir de dados de temperatura, salinidade e longitude. A região apresenta elevada alcalinidade inclusive na área influenciada por rios, onde foi encontrada a menor média de AT 2358 ± 28 µmol kg^{-1}. A região apresenta, em curto prazo, baixa vulnerabilidade ao processo de acidificação oceânica. Os valores encontrados de pCO_2 e fluxos de CO_2 na plataforma continental de Pernambuco estão acima dos estimados nas médias globais para plataformas continentais abertas baseadas em modelos matemáticos. A variabilidade na pCO_2 encontrada está ligada à própria característica da água tropical do Atlântico Sul, que cobre a rasa plataforma pernambucana com águas quentes. Onde a baixa solubilidade do CO_2 devido à alta temperatura, associada à oligotrofia e aportes de matéria orgânica fazem com que a região da plataforma seja fonte de CO_2 para atmosfera durante todo o ano.

Palavras-chave: Atlântico tropical. Acidificação oceânica. Plataforma continental. Dióxido de carbono. Modelos biogeoquímicos.

ABSTRACT

The continental shelf of Pernambuco is characterized by oligotrophy and thermal stability throughout the year, influenced by the North Brazil current that brings warm water, rich in CO_2 to the continental shelf of northeastern Brazil. The Capibaribe and Jaboatão rivers are one of the major rivers of Pernambuco. They receive a large input of domestic effluents from Recife and its metropolitan area, which causes changes in the natural carbon cycle. Here we evaluated the pCO_2 variability in these two estuaries and in the inner shelf area of Pernambuco. To evaluate the role of the estuaries, samples were collected bimonthly during low tide, on a seasonal cycle from November 2010 to September 2011. The Capibaribe estuary presented the highest values of total alkalinity (TA) and total inorganic carbon (TCO_2), with a significant difference between the two rivers. Both estuaries showed seasonal variation in TCO_2 and TA values. The annual TA averages were 1649 ± 390 µmol kg^{-1} in the Capibaribe and 1557 ± 315 µmol kg^{-1} at Barra de Jangadas. Regarding the pCO_2, the estuaries were saturated in CO_2 throughout the year, with average for the dry season of 3317 ± 2034 µatm in the Capibaribe and 6018 ± 4589 µatm in Barra de Jangadas. These values varied seasonally between estuaries, with a pCO_2 decrease during the rainy season in the Capibaribe, and an increase of up to 300% in the Barra de Jangadas estuary. In order to obtain a better evaluation of the spatial distribution of pCO_2 over the shelf waters, it was developed an equipment for the continuous and direct measurement of sea surface pCO_2 as low-cost alternative to the commercially manufactured ones. The first cruise took place in December 2014, starting from the port of Recife towards the Barra de Jangadas estuary. Even though the dry period has shown the highest primary productivity, the region presented itself as oligotrophic, with peaks of chl-a (8.4 mg m^3) under influence of the Capibaribe plume. Only a small area showed CO_2 subsaturation to the atmosphere, with the minimum value of 376.6 µatm. In general, a high CO_2 fugacity (fCO_2) was identified in the entire area of the inner shelf, with average of 474.33 ± 66.57 µatm, resulting in an mean flux to the atmosphere of 8.5 ± 6.82 mmol C m^{-2} d^{-1}. It was proposed a model to predict the fCO_2 using salinity and temperature values for inner the shelf during the summer. A more comprehensive spatial and seasonal distribution of the carbonate parameters was conducted by using values of TA TCO_2 in areas subjected and non-subjected to riverine inputs during 2013 and 2014. The area presents a relative stability to what concerns the pCO_2 and pH distribution, with overall average values of 449 ± 45 µatm and 8.00 ± 0,03 respectively. In general, the parameters analyzed were influenced by the distance from the coast, resulting in the development of prediction models for TA, TCO_2, pCO_2, pH, ΩCa and ΩAr using temperature, salinity and longitude data. The area has a low vulnerability to ocean acidification process, the TA is high even in the areas under riverine influence, where the lowest average values was registered 2358 ± 28 µmol kg^{-1}. The values of pCO_2 and CO_2 fluxes found on the continental shelf of Pernambuco are above those expected on global averages estimated by mathematical models for open continental shelf. The variability in pCO_2 found is linked to the own characteristic of the South Atlantic tropical water, which covers the shallow Pernambuco platform with warm waters. The low solubility of CO_2 due to high temperature, combined with oligotrophy and the transport of organic matter to be respired outside the estuaries, turns the continental shelf into a source of CO_2 to the atmosphere throughout the year.

Keywords: Tropical Atlantic. Ocean acidification. Continental shelf. Carbon dioxide. Biogeochemical models.

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1 INTRODUÇÃO

O oceano é um importante reservatório no ciclo de carbono, fato que reduz os efeitos do aumento de CO_2 atmosférico. Aproximadamente 26% das emissões anuais de CO_2 são absorvidas através da superfície oceânica (QUÉRÉ, LE *et al.*, 2014), capacidade que deverá diminuir ao longo dos próximos cem anos, em consequência do aumento das emissões antrópicas de CO_2 (PACHAURI *et al.*, 2014). Antes da Revolução Industrial, a absorção e liberação de CO_2 pelos oceanos estavam em relativo equilíbrio. Estima-se, através de testemunhos de geleiras na Antártica, que a concentração atmosférica de CO_2 variou, nos últimos 800 mil anos, entre 180 e 280 ppm nos períodos de glaciação e deglaciação, respectivamente (SIGMAN *et al.*, 2010). Em maio de 2013, a concentração de CO_2 na atmosfera ultrapassou as 400µatm de acordo com o monitoramento global da pCO_2 realizado pela NOAA. Em setembro de 2015, o valor reportado é de 397.4 ppm, de acordo com os dados do Scripps Institute of Oceanography, Observatório de Mauna Loa – Hawai. Este aumento de 110µatm representa um crescimento de mais de 40% em relação aos níveis pré-industriais.

De acordo com o relatório do IPCC 2014, caso não seja tomada nenhuma providência pelos países em termos de redução da emissão de gases geradores de efeito estufa (CO_2, CH_4, N_2O), até o ano 2100 espera-se um aumento na temperatura média do planeta de 4 ± 2 °C e uma elevação no nível médio dos oceanos de 0.7 ± 0.2 m. Tal cenário pode trazer consequências sobre a qualidade de vida humana, principalmente pela diminuição da qualidade e disponibilidade de água potável, desertificação, perdas de áreas agrícolas, acidificação marinha, maior frequência de eventos extremos e perdas de biodiversidade (PACHAURI *et al.*, 2014).

Aproximadamente 60% das grandes cidades distribuídas ao redor da Terra estão localizadas próximas a regiões estuarinas, atribuindo a estes ambientes uma grande importância para o planeta (Geophysics Study Committee apud MIRANDA *et al.*, 2002). Essas regiões são as principais fornecedoras de nutrientes para a região costeira, pois recebem e concentram o material originado de sua bacia de drenagem e podem vir a receber aportes significativos por ação antrópica (PEREIRA-FILHO *et al.*, 2006).

A costa do Brasil possui mais de 8000 km e concentra 50,7 milhões de pessoas, o correspondente a 26.6% da população brasileira (IBGE,2010). O crescimento

populacional que vem ocorrendo nestas áreas leva a um aumento na exportação de nutrientes para a costa, devido ao lançamento de esgoto sem tratamento em rios e estuários. Tais ambientes possuem um papel essencial no transporte e transformação do carbono de origem continental e atmosférico para o oceano (SABINE *et al.*, 2004); (CHEN, 2004). Estudos recentes demonstram que mudanças no uso e ocupação do solo em bacias hidrográficas podem alterar os balanços naturais de íons bicarbonato e gerar alcalinidade em estuários (CAI eWANG, 1998; WANG e CAI, 2004),

Porém ainda é incerta a influência que esses processos de balanço entre produção de alcalinidade e maior exportação de nutrientes para a zona costeira exercem na magnitude da captura/emissão de CO_2, alterando os balanços naturais de produção e mineralização da matéria orgânica (BORGES, 2011).

Os ecossistemas costeiros de transição são considerados fontes de CO_2 para a atmosfera, de acordo com Laruelle *et al*. (2010), que realizaram o cálculo da emissão de CO_2, baseando-se na compilação de dados de diversos trabalhos e agrupando os ambientes costeiros em grupos tipológicos. A média estimada por esses autores para estuários é da ordem de $0,27 \pm 0,23$ Pg C a^{-1}; já em plataformas continentais tropicais abertas a estimativa é de $0,083 \pm 0,097$ Pg C a^{-1}. Contudo, nos últimos anos, muita atenção foi dada à dinâmica do carbono inorgânico nos grandes rios e estuários do mundo, principalmente nas altas e médias latitudes, a despeito da grande contribuição dos pequenos rios e estuários tropicais que, juntos, cobrem uma área maior que a de estuários temperados (BORGES *et al.*, 2005). Dessa forma, os valores atuais de fluxo tidos como referência utilizam poucos dados de regiões tropicais, o que leva à estimativa de médias globais tendenciosas (CAI, 2011).

Apesar da grande área representada pelo litoral brasileiro, poucos estudos foram realizados no país para a estimativa da variabilidade do carbono inorgânico e dos fluxos de CO_2, concentrando-se sobretudo em estuários situados nas regiões Norte e Nordeste. A maioria desses trabalhos faz a utilização da alcalinidade e pH para realizar os cálculos do sistemas carbonato, o que gera incertezas em relação aos cálculos da pressão parcial do CO_2, principalmente em áreas com baixas quantidades de oxigênio dissolvido (ABRIL *et al.*, 2014).

Um dos pioneiros foi o trabalho de Souza *et al.* (2009) no estuário do rio Piauí, em Sergipe, quando os autores reportaram um fluxo de 13 mol CO_2 $m^{-2}a^{-1}$. Já em Pernambuco, Noriega *et al.* (2013) estimaram um fluxo médio entre 10,95 e 17,52 mol CO_2 $m^{-2}.a^{-1}$, para o estuário do Capibaribe, e a emissão de CO_2 para estuários do Nordeste do Brasil em -0,35 Tg C a^{-1}. De maneira geral, os estuários do Norte e Nordeste são fontes de CO_2 para a atmosfera durante todo o ano e contribuem com cerca de 1,01 Tg C a^{-1}. Os valores de pCO_2 oscilam na faixa do reportado para estuários tropicais, com exceção para aqueles encontrados em áreas de classificação climática de semiárido, que apresentaram as menores médias. Além disso, em Pernambuco, a pCO_2 em estuários apresenta boa correlação (r^2 = 0.89) com a densidade populacional das bacias hidrográficas, influenciadas pelo lançamento de esgoto sem tratamento (NORIEGA; ARAUJO, 2014; NORIEGA *et al.*, 2014). Entretanto, recentemente na região Sudeste, mais precisamente na Baía de Guanabara – RJ, utilizando as metodologias de medições diretas de pCO_2 e alcalinidade total, foi reportado que 90% da área da baía atua como sumidouro de CO_2 atmosférico influenciado pela eutrofização antropogênica, absorvendo em média -19,6 molC m^2 a^{-1} (COTOVICZ *et al.*, 2015).

Nesse contexto, faltam trabalhos em áreas de plataforma continental, bem como nos estuários das regiões Sudeste e Sul do país, a fim de suprir a lacuna relacionada ao balanço de carbono na costa brasileira. Na maioria das regiões cujos ecossistemas costeiros estão submetidos a um maior número de tensores, como aumento populacional e eutrofização dos rios, não há dados suficientes para avaliar a aplicação de modelos existentes (COOLEY *et al.*, 2009). Assim, o inventário de locais de absorção e liberação de CO_2 em áreas costeiras é visto atualmente como parte essencial para a obtenção de um melhor entendimento do ciclo global do carbono.

A implantação de metodologias analíticas seguras e simples tem se transformado em ferramenta importante nos estudos ambientais, de forma a permitir o conhecimento dos processos básicos que controlam a dinâmica costeira. Isso pode favorecer a definição de planos de gerenciamento ambiental direcionados aos problemas locais que levem à preservação e ao uso sustentável das áreas costeiras do litoral pernambucano, onde a ocupação cresce de forma acelerada. É exemplo disso o crescimento da Região Metropolitana do Recife em torno do lazer, com desenvolvimento do turismo, além do setor industrial, petroquímico, de construção naval e portuária.

2 JUSTIFICATIVA

A plataforma continental de Pernambuco é conhecida pela abundância em organismos calcificantes que, ao morrerem ou sofrerem quebra de suas estruturas, geram sedimentos calcários biodetríticos (Manso *et al.*, 2004). Porém muito pouco se sabe sobre a dinâmica do sistema carbonato nas águas dessa região. Estudos na costa pernambucana se fazem necessários para podermos compreender melhor os processos da dinâmica do CO_2 e do sistema carbonato em áreas costeiras diante das mudanças climáticas atuais.

A falta de informações para a compreensão dos fatores que conduzem e/ou influenciam os processos de trocas gasosas na interface oceano-atmosfera no litoral brasileiro, especificamente na região Nordeste do Brasil, é um fator limitante na gestão litorânea, uma vez que estas áreas estão submetidas ao crescimento populacional, poluição aquática através da matéria orgânica e desmatamento, sendo de grande importância realizar pesquisas que auxiliem neste entendimento para a conservação da biota marinha e controle climático. Dessa maneira, a implementação de técnicas modernas para os estudos ambientais é uma necessidade crescente para o gerenciamento costeiro, dada a necessidade de se obterem resultados com maior confiabilidade e de rápido acesso para a comunidade científica.

A fugacidade do CO_2 na água do mar é controlada pelas trocas na interface oceano-atmosfera, pelas variações de temperatura e salinidade da superfície do mar, pela mistura de massas de água e pela atividade biológica. As regiões onde predominam a emissão ou absorção do CO_2 nas bacias oceânicas são conhecidas. No entanto, a dinâmica do fluxo de CO_2 em áreas costeiras ainda carece de estudos que elucidem as variações causadas pelos aportes fluviais, atividade biológica e ação antrópica.

Para estimar os fluxos de CO_2 na interface oceano-atmosfera a nível mundial com maior precisão, é necessário realizar estudos de monitoramento da pCO_2 em escala regional, o que nos permitirá avaliar as mudanças e tendências de pCO_2 e melhorar os atuais modelos climáticos. Também é fundamental conhecer a influência fluvial sobre a alcalinidade e o carbono inorgânico em áreas costeiras, além de sua relação com o ciclo global do carbono e o processo de acidificação marinha e sua potencial influência sobre a fisiologia dos organismos calcários que abundam na região.

3 OBJETIVOS

3.1 Objetivo geral

Realizar um estudo sobre as características espaciais e sazonais das emissões de CO_2 e a sua relação com a alcalinidade total e biomassa fitoplanctônica, nas águas costeiras do litoral de Pernambuco, em áreas sob influência de importantes estuários da Região Metropolitana do Recife e na Área de Proteção Ambiental Costa dos Corais – Tamandaré.

3.2 Objetivos específicos

- Quantificar as concentrações de CO_2 nas águas marinhas do litoral de Pernambuco;
- Determinar as variações espacial e temporal da AT, pCO_2, pH;
- Identificar locais de absorção ou emissão de CO_2 no bioma costeiro-marinho pernambucano;
- Determinar a influência dos estuários submetidos a atividades industriais, turísticas e dos efluentes urbanos, nas concentrações de CO_2 no litoral de Pernambuco;
- Utilizar a plataforma continental externa e áreas sem influência significativa de rios como ponto controle para avaliar as condições ambientais do bioma costeiro-marinho do Estado de Pernambuco;
- Avaliar os graus de saturação da Calcita e Aragonita na região da plataforma interna de Pernambuco;
- Correlacionar os resultados das variáveis hidrológicas analisadas para determinar o grau de interação entre elas;
- Estabelecer um modelo descritivo para as áreas estudadas;

4 HIPÓTESES

A concentração de CO_2 na região costeira de Pernambuco está sob influência dos aportes continentais e da crescente interferência antrópica, levando a alterações nas características relacionadas ao sistema carbonato e na magnitude e direção dos fluxos de CO_2 na interface oceano atmosfera.

5 FUNDAMENTAÇÃO TEÓRICA

5.1 Ciclo Natural do Carbono

Na escala global, o principal reservatório de carbono é a litosfera, ocorrendo nas rochas principalmente na forma de $CaCO_3$, entretanto o tempo necessário para sua conversão no ciclo biogeoquímico é tão grande que se torna insignificante na escala humana. A matéria orgânica fóssil presente na litosfera constitui um importante reservatório de carbono que, após o período industrial, vem sendo extraído e introduzido novamente no ciclo do carbono, diminuindo a quantidade dos reservatórios a cada dia. Neste contexto, os oceanos são considerados os maiores sumidouros de CO_2 atmosférico, uma vez que absorvem grande parte das emissões humanas vindas da queima de combustíveis fósseis (IPCC, 2007).

A atmosfera apresenta pequenas concentrações de carbono, ocorrendo principalmente na forma de dióxido de carbono (CO_2), metano (CH_4), monóxido de carbono (CO), além dos CFCs, de maneira que são considerados gases traços, o que os torna bons marcadores de perturbações antrópicas.

O ciclo biogeoquímico do carbono regula a transferência do carbono entre a atmosfera, as rochas, solos, rios e oceanos. O CO_2, solúvel em água, é trocado entre a atmosfera e a hidrosfera pelo processo de difusão. Essa troca é contínua até o estabelecimento de um equilíbrio entre a pressão parcial do CO_2 da atmosfera e da água. Outra maneira de troca de carbono ocorre pela erosão das rochas, processo responsável por trocar cerca de 80% do total de CO_2 entre a parte sólida da litosfera. O CO_2 atmosférico dissolve-se na água da chuva, produzindo H_2CO_3. Essa solução ácida, nas águas superficiais ou subterrâneas, facilita a erosão das rochas. O intemperismo e a erosão provocam a liberação dos íons Ca_2^+ e HCO_3^-, que podem ser lixiviados para os oceanos (IPCC, 2007). Os organismos marinhos assimilam Ca_2^+ e HCO_3^- e os usam para construção de suas estruturas calcárias. Quando esses organismos morrem, as conchas depositam-se, acumulando-se como sedimentos ricos em carbonatos. Esse sedimento de fundo, participando do ciclo tectônico, pode migrar para uma zona cuja pressão e calor fundem parcialmente os carbonatos. A formação desse magma libera CO_2, que escapa para a atmosfera pelos vulcões (IPCC, 2007).

O ciclo biológico do carbono inicia-se pela absorção do CO_2 atmosférico pelas plantas e microalgas através da fotossíntese, sendo devolvido à atmosfera por meio da respiração de plantas, animais e microrganismos. Os animais realizam apenas a respiração, liberando o CO_2 na atmosfera. Quando morrem, caso a decomposição da

matéria orgânica seja total, há liberação de gás carbônico, gás metano e água. Caso seja parcial, há a transformação em material combustível como petróleo e carvão (IPCC, 2007). A matéria orgânica combustível, quando queimada, é devolvida para a atmosfera na forma de CO_2. Nos oceanos, além dos carbonatos inorgânicos, também existem consideráveis quantidades de carbono orgânico dissolvido e particulado.

5.2 Perturbações antrópicas

As atividades humanas sobre o ciclo do carbono alteram significativamente os balanços naturais desse elemento. Notadamente, a produção de cimento e queima de combustíveis fósseis são as atividades que mais alteram o ciclo do carbono (QUÉRÉ, LE *et al.*, 2014). Estima-se que, para a década de 2004-2013, as emissões médias por essas atividades foram de +8,9 ± 0,4 GtC a^{-1}, que somadas com +0,9 ± 0,5 Gt C a^{-1} pelas emissões por conta de mudanças no uso e ocupação do solo (desflorestamento e queimadas), totalizam +9,8 Gt C a^{-1} (QUÉRÉ, LE *et al.*, 2014). Entretanto, os sumidouros terrestres (-2,9 ± 0,8 Gt C a^{-1}) e oceânico (-2,6 ± 0,5 GtC a^{-1}) juntos não superam as emissões, o que leva a um acúmulo de CO_2 na atmosfera da ordem de 4,3 ± 0,1 Gt C a^{-1}, o correspondente a 43% a^{-1} das emissões totais de CO_2 (QUÉRÉ, LE *et al.*, 2014). Estima-se que essa taxa de aumento de dióxido de carbono atmosférico tenha passado de 1,7 Gt C a^{-1}, nos anos 1960, para os níveis atuais. Tal aumento na concentração do CO_2 atmosférico vem da capacidade limitada das reservas de absorverem o CO_2 oriundo das atividades humanas (QUÉRÉ, LE *et al.*, 2014).

5.3 Ciclo oceânico do carbono

O dióxido de carbono se encontra na água do mar, tanto na forma de gás dissolvido como na forma de carbonatos e bicarbonatos, apresentando uma especial importância no controle do mecanismo ácido-base do meio, visto que as três formas estão ligadas por uma estreita relação de equilíbrio. A importância desse fenômeno é extraordinária, já que tanto o dióxido de carbono como os carbonatos exercem uma grande influência na vida marinha, não só como fonte de carbono para a fotossíntese, mas também para a formação de estruturas esqueléticas de uma grande variedade de organismos que habitam os oceanos (MACÊDO *et al.*, 2004).

Mais de 90% do carbono oceânico é inorgânico: menos de 1% está sob a forma de CO_2, 94% está sob a forma de íons bicarbonato HCO_3^- e 5% sob a forma de íons carbonato CO_3^{2-}. Essas diferentes espécies de carbono inorgânico são ligadas entre si pelas suas equações de equilíbrio reversíveis (MILLERO, 2007).

O gás carbônico presente na atmosfera é dissolvido no oceano, e sua hidratação conduz à formação de ácido carbônico, um ácido fraco que se dissocia formando íons bicarbonato e carbonato, com liberação de íons H^+, segundo as reações abaixo (MILLERO, 2007):

$$CO_{2aq} + H_2O \rightarrow H_2CO_3$$

O H_2CO_3 e o CO_2 são espécies eletronicamente neutras. Como o H_2CO_3 ocorre apenas em pequenas quantidades, suas espécies não são dissociáveis, e o CO_2 é expresso como $[CO_2] = [H_2CO_3]+[CO_{2aq}]$. As duas equações de equilíbrio químico para o HCO_3^- e CO_3^- são expressas abaixo (MILLERO, 2007):

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \text{ com um } K_1 = \frac{[HCO_3^-]+[H^+]}{CO_2}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \text{ com um } K_2 = \frac{[CO_3^{2-}]+[H^+]}{HCO_3^-}$$

As constantes de dissociação K_1 e K_2 dependem da temperatura e salinidade da água do mar, além da pressão. O carbono inorgânico dissolvido (CID) pode ser definido como a soma das formas inorgânicas do carbono segundo a equação abaixo e pode ser expresso em µmol kg^{-1} (MILLERO, 2007).

$$CID = [HCO_3^-] + [CO_3^{2-}] + [CO_2]$$

Após a dissolução do CO_2 na água, processos de hidratação acontecem e resultam em ácido fraco (ácido carbônico), que reage com os ânions carbonatos e moléculas de água para formar o bicarbonato. A capacidade do sistema carbonato oceânico para neutralizar tais mudanças na concentração de CO_2 atmosférico é foco de vários estudos. Atualmente, esta capacidade depende dos aportes de cátions do lixiviamento das rochas e da dissolução dos carbonatos de origem química e biogênica, segundo a reação a seguir (MILLERO, 2007):

$$CO_2 + CaCO_3 + H_2O \leftrightarrow 2HCO_3 + Ca^{2-}$$

Essa capacidade de neutralizar a entrada de prótons na água do mar pode ser definida como alcalinidade. De maneira simplificada, a alcalinidade pode ser considerada a medida da quantidade de prótons que podem ser aceitos pelas bases fracas presentes na água do mar. E pode ser definido pela equação geral simplificada abaixo. Nesta equação,

a quantidade de íons carbonato é multiplicada por 2, uma vez que são necessários 2 prótons para que ele seja convertido em CO_2 (MILLERO, 2007).

$$TA \approx [HCO_3^-] + 2[CO_3^{2-}]$$

Uma definição mais completa de alcalinidade total pode ser descrita como o número de moles de íons H^+ equivalentes ao excesso de receptores de prótons (bases formadas a partir dos ácidos fracos com uma constante de dissociação $K \leq 10^{-4.5}$ a 25° C por uma força iônica nula) sobre os doadores (ácidos cuja constante de dissociação $K > 10^{-4.5}$) em uma parcela de 1kg de água do mar (MILLERO, 2007).

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] + [NH_3] + [HS^-] - [H^+]_F - [HSO_4^-] - [HF] - [H_3PO_4]$$

A concentração de CO_2 na água está ligada à pressão parcial do CO_2 (pCO_2), através da Lei de Henry:

$$[CO_2] = k_0(T,S)pCO_2$$

A constante K_0 corresponde à solubilidade do CO_2 na água do mar, que é dependente da temperatura (T) e salinidade (S), e expressa em mol kg^{-1} atm^{-1}. A pCO_2 é utilizada para os gases perfeitos, mas, como o CO_2 se comporta como um gás real, a fugacidade do CO_2 é a forma mais precisa a ser utilizada. Entretanto, a relação entre pCO_2 e fCO_2 é muito pequena e varia de 0.996 e 0.997 para temperaturas entre 0 e 30 °C a 1atm (DICKSON *et al.,* 2007). Sendo assim, a diferença entre eles pode ser negligenciada. A pressão parcial do CO_2 pode ser expressa através da seguinte equação:

$$pCO_2 = xCO_2(P_{atm} - P_{H_2O})$$

Onde Patm é a pressão atmosférica, pH_2O é a pressão de vapor da água calculado em função da salinidade e temperatura e xCO_2 é a concentração molar do CO_2.

A fugacidade do CO_2 (fCO_2) é calculada pela fórmula abaixo, descrita em Doe (1994):

$$fCO_2 = pCO_2 \exp p \frac{B+2\delta}{RT}$$

$$B=(-1636.75+12.0408T-0.0327957T^2+0.0000316528)10^{-6}$$

$$\delta=(57.7-0.118T)10^{-6}$$

A pressão é representada por p em Pa. O parâmetro δ e B é o primeiro coeficiente do virial do CO_2 definido por Weiss (1974) expressos em m^3 mol^{-1}. O valor de R representa a constante dos gases perfeitos R=8.314 JK^{-1} mol^{-1}, e T a temperatura em Kelvin.

5.4 Variabilidade da pCO_2 na água do mar

As variações da pCO_2 na água do mar estão relacionadas a diferentes processos de trocas gasosas com a atmosfera, atividade biológica, circulação de massas d'água e efeitos termodinâmicos. Dentre esses processos, se destacam a chamada bomba biológica, a contra bomba biológica e a bomba de solubilidade do CO_2.

A bomba biológica atua na transferência do carbono inorgânico da atmosfera para as regiões profundas dos oceanos, através da síntese de matéria orgânica pelos produtores primários. Ela consiste na absorção do CO_2 pelo fitoplâncton, diminuindo a pressão parcial do CO_2 na água e favorecendo a absorção de CO_2 atmosférico por diferença de pressão (TSUNOGAI *et al.*, 1999). Além do carbono inorgânico, o processo fotossintético depende da disponibilidade de luz e nutrientes na camada eufótica. Tal processo acontece com mais intensidade em subsuperfície, e no Atlântico Tropical os maiores picos de produtividade primária ocorrem próximos à zona de 1% de luminosidade (PASSAVANTE e FEITOSA, 2004). Uma vez formado o carbono orgânico, após a morte dos organismos, há o afundamento dessa biomassa e consequente decomposição, passando para a forma de carbono orgânico dissolvido e/ou particulado. Dessa maneira, após a oxidação/respiração da matéria orgânica, o CO_2 retorna para o ciclo.

Em ambientes costeiros sob influência de aportes continentais de rios e estuários, pode haver estímulo da produtividade primária, aumentando a absorção de CO_2 atmosférico (LEFÉVRE *et al.*, 2010; CHEN *et al.*, 2012). Em contrapartida, em alguns ambientes costeiros, tal efeito pode ser contrabalanceado pelo transporte direto de CO_2 e matéria orgânica a ser oxidada na região da plataforma interna, levando a um aumento da pCO_2 na água do mar nas áreas mais próximas das bocas dos rios (JIANG *et al.*, 2013).

Outro mecanismo importante é a bomba de solubilidade, que está ligada ao efeito da temperatura e salinidade da água do mar sobre a solubilidade do CO_2. De acordo com a relação termodinâmica $\frac{\partial fCO_2}{\partial SST} / fCO_2$, definida por Takahashi *et al.* (1993), a pCO_2 na água varia aproximadamente 4% $°C^{-1}$. Desta maneira, o aumento da solubilidade do CO_2

na água do mar ocorre principalmente em altas latitudes, nas zonas de formação de águas profundas, quando as águas frias e densas absorvem o CO_2 atmosférico por conta da elevada solubilidade, transportando-o para as regiões profundas dos oceanos. Transferido para as águas profundas e entrando na circulação oceânica termohalina, o CO_2 retorna para atmosfera nas zonas de ressurgência.

5.5 Metodologias aplicadas à determinação dos parâmetros do sistema carbonato na água do mar

Quando pelo menos dois dos parâmetros relacionados ao sistema carbonato são medidos em uma amostra de água do mar (pH, alcalinidade total, carbono inorgânico dissolvido, pCO_2 ou fCO_2), pode-se calcular os demais a partir da temperatura, da salinidade e das constantes de dissociação do bicarbonato e do carbonato (MILLERO, 2007).

Contudo existem algumas considerações em relação às metodologias utilizadas. O pH é o parâmetro mais difícil de ser medido com precisão. Por ser uma expressão de um potencial em escala logarítmica, pequenas variações no seu valor podem levar a grandes erros no cálculo da pCO_2. Desse modo, a metodologia mais confiável para sua determinação é a que dispensa a utilização de eletrodos, como a determinação espectrofotométrica (DICKSON *et al.*, 2007).

Dentre os métodos utilizados para medir os valores de pCO_2, o método direto com a utilização de equilibradores acoplados a um analisador de gases com detecção infravermelha é atualmente reconhecido como a melhor abordagem para o desenvolvimento de pesquisas relacionadas à dinâmica do CO_2 nos ambientes aquáticos (DICKSON *et al.*, 2007).

5.6 Desenvolvimento de um equipamento para a medição direta da pCO_2 na água do mar

Para realizar a medição direta da pCO_2 na água do mar, um pequeno volume de ar fica em contato com um grande volume de água do mar que flui continuamente pelo sistema de equilibradores (Figura 1). Os equilibradores têm a função de equilibrar a pCO_2 da água que flui pelo sistema com uma pequena parcela de ar atmosférico. Quando em equilíbrio, a concentração de CO_2 é a mesma na parcela de ar atmosférico e na água do mar que passa nos equilibradores. Como o detector infravermelho Licor 7000 só trabalha com gases, a medição é realizada na parcela de ar em equilíbrio dentro do equilibrador principal. Assim, o ar é continuamente empurrado no sistema por um fluxo em direção

ao detector infravermelho de CO_2. Antes de chegar ao detector, o ar vindo dos equilibradores passa por um condensador e uma armadilha química de perclorato de magnésio, a fim de que a leitura no sensor infravermelho não sofra interferência do vapor d'água.

Neste sentido, foi desenvolvido um equipamento para a medição da pCO_2 *underway* com o objetivo de ser uma alternativa menos onerosa para a obtenção de resultados tão bons quanto os de sistemas pré-montados importados. Tal fato representa, ainda, uma transferência de tecnologia entre Brasil e França para aplicação em meio acadêmico.

O sistema é portátil e capaz de operar em barcos relativamente pequenos (≈ 10m), assim como em cruzeiros oceanográficos. O hardware de automação é composto por uma placa relê de 16 canais que é controlada através de um módulo de aquisição de dados da National Instruments (DAQ USB 6212). Esse módulo é responsável pela aquisição dos dados analógicos provenientes dos barômetros e controla as válvulas solenoides e de pinçamento, permitindo assim a alternância entre as diferentes medidas realizadas durante o cruzeiro (xCO_2 no ar atmosférico, na água do mar e os ciclos de auto calibração com gases de referência). Todos os demais sensores (termistor do equilibrador principal, termosal, GPS e o Licor 7000) são conectados a um computador através de um hub serial RS232 para USB modelo MOXA U-PORT -8.

O software, escrito com Labview, controla a operação do sistema (e.g. abertura das válvulas e os ciclos de gases), bem como a gravação dos dados adquiridos que subsidiam os cálculos de fluxos de CO_2 na interface oceano-atmosfera (dados de GPS; pressão atmosférica; pressão de equilíbrio; temperaturas da superfície do mar, temperatura de equilíbrio, temperatura da medição; salinidade, as concentrações de CO_2 na água e no ar atmosférico). Além disso, realiza ciclos de autocalibração, através da leitura de quatro padrões de gases com concentrações conhecidas de CO_2 (Figuras 2 e 3).

A água do mar entra no sistema por bombeamento com uma vazão regulada entre 5-7 l min^{-1}. Antes de entrar nos equilibradores a água passa por um Termosalinógrafo modelo SBE 45, que registra a temperatura e salinidade da água da superfície do mar. A temperatura dentro do equilibrador principal é medida por um termistor modelo SBE 38, localizado na saída do equilibrador principal. A diferença entre a temperatura da

superfície do mar e da água dentro do sistema de equilibradores deve ser menor que 0,5 °C.

O ar circula em um circuito semifechado pelo sistema em uma tubulação de Tygon, o ar sai dos equilibradores em equilíbrio com o CO_2 da água do mar e saturado em vapor d'água. A fim de se retirar a umidade para não prejudicar as medidas no detector infravermelho, o ar passa primeiramente por uma "armadilha" fria (0 °C) para condensar a umidade, na sequência, passa por uma "armadilha" química, que consiste em um tubo com perclorato de magnésio. É necessário ficar atento à armadilha de perclorato, pois quando esta fica saturada de água pode causar a obstrução do fluxo de ar. Este é o único ponto do processo que necessita de supervisão e faz com que o sistema funcione de maneira semiautônoma.

A pressão atmosférica e a pressão de equilíbrio (dentro do equilibrador principal) são medidas por dois barômetros modelo Vaisala PTB 110. Para a amostragem do ar atmosférico, faz-se necessária a instalação de uma tubalação para captação do ar atmosférico livre de contaminação da exaustão do barco/navio. Esta tubulação é de um material especial resistente a choque, inerte e impermeável ao CO_2, modelo Dekabon Synflex.

O ar proveniente dos equilibradores passa pelo sistema por períodos de três horas, durante o qual a xCO_2 é gravada continuamente. A cada três horas o sistema realiza a auto calibração através da leitura de padrões secundários de CO_2 em quatro concentrações: o zero (gás nitrogênio), uma baixa ≈280 ppm, uma média ≈360 ppm e uma alta ≈500 ppm. Estes padrões foram calibrados em relação a padrões de CO_2 primários obtidos junto a NOAA. As leituras da xCO_2 em ar atmosférico é realizada a cada seis horas.

Figura I.1: Sistema de equilibradores. (1 - entrada de água do mar; 2 - pré-equilibrador; 3 - equilibrador principal, 4 - sonda da temperatura de equilíbrio; 5 - saída do ar em direção ao painel de medida)

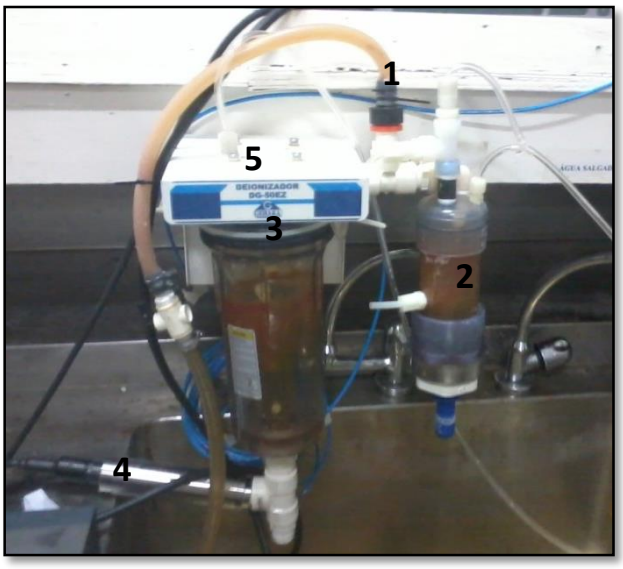


Foto: O autor

Figura I.2: Visão geral do sistema para medição contínua da pCO_2.
(1 – equilibradores; 2 - unidade condensadora; 3 – painel de medidas; 4 – Licor 7000; 5 – computador; 6 – GPS; 7 – barômetros; 8 – caixa de controle eletrônico; 9 – termosal; 10 – cilindros com gases de referência)

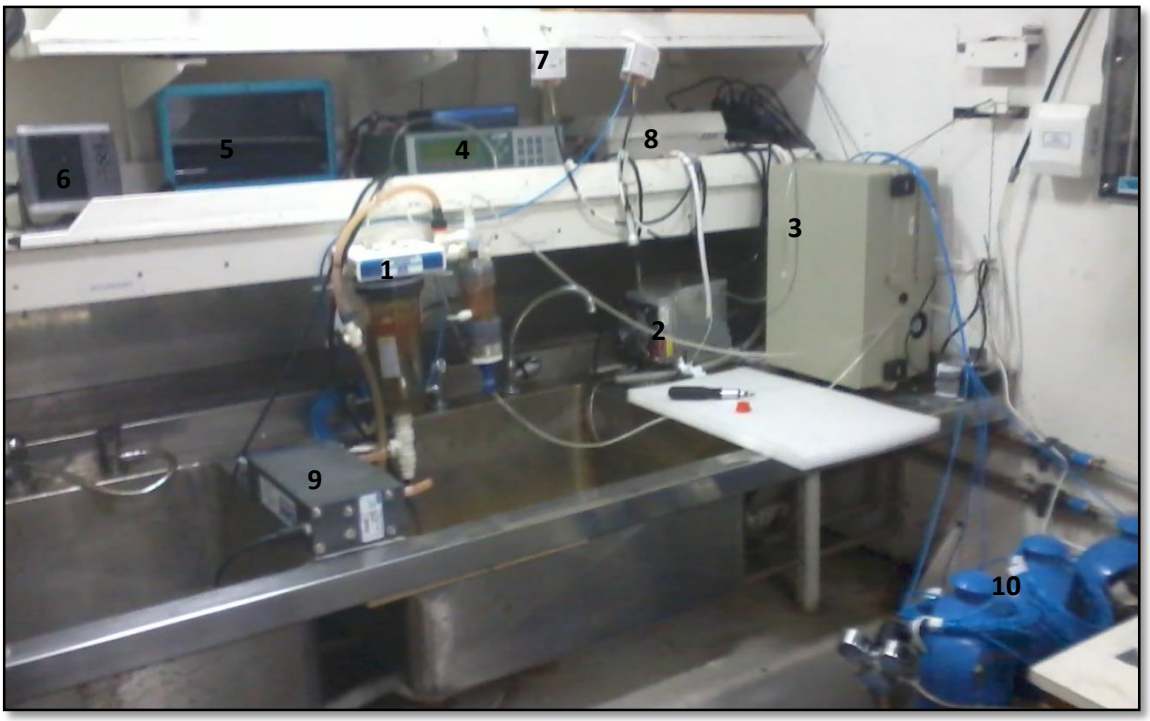


Foto: O autor

Figura I.3: Painel de medidas, parte operacional do sistema que alterna entre os fluxos dos gases - amostra, referência, ar atmosférico. (1 - condensador; 2 - armadilha química; 3 - válvulas controladoras do sistema; 4 - válvulas controladoras dos cilindros de referências; 5 - bomba para captação do ar atmosférico)

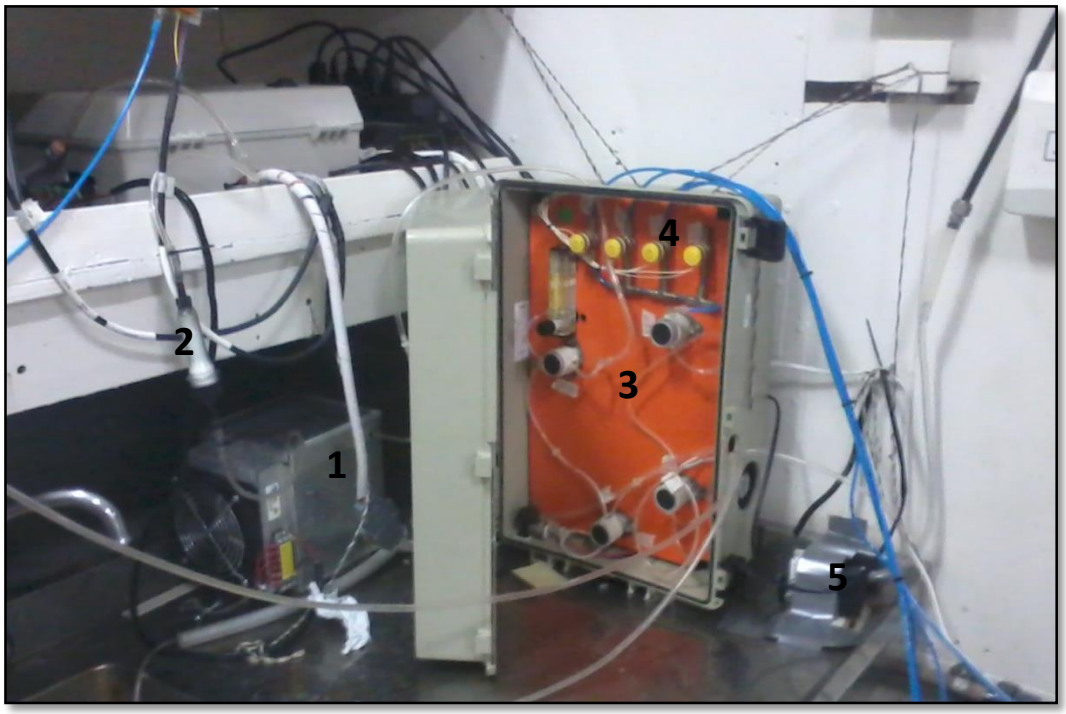


Foto: Autor

5.7 Fluxos de CO_2 na interface água-ar

Nossa compreensão sobre a absorção pelos oceanos do CO_2 atmosférico vem das diferenças observadas na pressão parcial de CO_2 (pCO_2) entre a superfície do oceano e atmosfera (TAKAHASHI *et al.*, 2002, 2014). Como a variabilidade espacial e temporal do pCO_2 nas águas superficiais é muito maior que na atmosfera, a direção e a magnitude da direção do fluxo são reguladas principalmente por mudanças no gradiente dos valores oceânicos.

Os fluxos de CO_2 para a atmosfera, entretanto, dependem do cálculo da constante de velocidade de troca k(CO_2), que apresenta grande variabilidade ligada às características ambientais locais geradoras de turbulência, como maré, profundidade, intensidade de vento, além das influências termodinâmicas (RAYMOND *et al.*, 2000; ABRIL; BORGES, 2004; BORGES *et al.*, 2004). Como ainda não existe um consenso em relação a qual constante utilizar, deve-se escolher a constante calculada de acordo com a semelhança de ambientes. Atualmente, para cálculos de fluxos oceânicos, a mais utilizada é a constante de Sweeney (SWEENEY *et al.*, 2007), enquanto para estuários

submetidos a velocidades de vento menores do que 5 m s^{-1} a mais apropriada é a de Raymond e Cole (2001).

De maneira geral, os fluxos de CO_2 entre a água e a atmosfera podem ser medidos de acordo com a equação a seguir:

$$F(CO_2) = k(CO_2) \cdot KH \cdot \Delta pCO_2$$

Onde F é o fluxo do CO_2 em (mmol $m^{-2}d^{-1}$), $k(CO_2)$ é a velocidade de troca do CO_2, KH é a solubilidade do CO_2 (WEISS, 1974) e ΔpCO_2 é a diferença de pCO_2 entre a superfície da água e a atmosfera. Valores positivos indicam fluxo resultante no sentido água-atmosfera.

6 ÁREA DE ESTUDO

A variabilidade do CO_2 no Atlântico Tropical é controlada pelas ressurgências equatorial e da costa africana, além da influência das águas doces provenientes dos rios e da precipitação. A ressurgência na costa leste da bacia do Atlântico traz à superfície águas ricas em CO_2 que sofrem advecção para oeste pela corrente sul equatorial (LEFÈVRE *et al.*, 2008; TAKAHASHI *et al.*, 2009). Essa corrente diverge em duas, próximo ao Brasil: a corrente do Brasil, que se dirige para o sul, e a corrente norte do Brasil, para o norte (PETERSON; STRAMMA, 1991).

Assim, a plataforma continental de Pernambuco encontra-se sob influência desta água quente, pobre em nutrientes e saturada em CO_2. É importante também ressaltar a estabilidade térmica do ambiente, no sentido vertical, apesar da ocorrência de águas de diferentes origens (MACÊDO *et al.*, 1998; FLORES MONTES *et al.*, 2002).

O litoral de Pernambuco tem aproximadamente 187 km de extensão e abrange 21 municípios em uma área de 4.447,80 km^2. Está situado entre as coordenadas geográficas de 7º 32’S e 8º 56’S, e 34º 11’ W (Figura I.4). Ele é subdividido em Litoral Norte, Núcleo Metropolitano e Litoral Sul. Tem como limites, ao norte, o município de Goiana, e, ao sul, o município de São José da Coroa Grande. Nesse contexto, a cidade do Recife e região metropolitana são consideradas a 6ª região mais populosa do Brasil, com cerca de

3.743.854 habitantes e densidade populacional de aproximadamente 1352,53 hab/km^2 (IBGE, 2010).

A pluviometria local se apresenta atualmente com períodos chuvosos em que as maiores precipitações ocorrem nos meses de maio, junho e julho, enquanto os meses de outubro, novembro e dezembro são os mais secos (CPRH, 2008). A pluviometria anual da região é superior a 1.000 mm, registrando-se chuvas durante todo o ano (MEDEIROS & KJERFVE, 1993). No período de menor precipitação, é registrada media mensal igual a 80,31 mm de chuva. Durante o período de maior precipitação, registra-se média mensal de 270,11 mm. Predominam na área, ao longo de todo o ano, os ventos alísios de sudeste e nordeste. A velocidade média alcança 3,2 m.s^{-1}. Os ventos são mais intensos no período chuvoso, atingindo 4,0 m.s^{-1}, enquanto no período seco atingem 2,20 m.s^{-1} (MEDEIROS & KJERFVE, 1993)

A partir da análise da morfologia e da distribuição dos diversos tipos de sedimentos da plataforma continental do nordeste por França (1976), foi proposta uma subdivisão da plataforma nordestina em três trechos por Araújo *et al.* (2004):

- **Plataforma interna:** limitada pela isóbata de 20m, com relevo suave, mostrando algumas irregularidades devido à presença de recifes, canais e ondulações. A plataforma é coberta por areia terrígena, com muito pouco cascalho e lama, e baixo teor em carbonato de cálcio. Os componentes bióticos são muito retrabalhados.
- **Plataforma média:** de 20 a 40m de profundidade, com um relevo bem mais irregular, recoberto por sedimentos grosseiros de origem biogênica, com um teor em carbonato de cálcio superior a 90%. As associações carbonáticas mostram sinal de retrabalhamento.
- **Plataforma externa:** a partir de 40m de profundidade, coberta com areias biodetríticas, cascalhos de algas e lama cinza azulada. As *Halimeda* tendem a ser mais abundantes, e o teor em carbonato de cálcio é superior a 75%. As associações carbonáticas são muito retrabalhadas.

Perfis batimétricos da plataforma continental pernambucana foram elaborados por Araújo *et al.* (2004), utilizando dados de projetos pretéritos. A plataforma continental pernambucana apresenta largura média em torno de 35km e profundidade média de 59m.

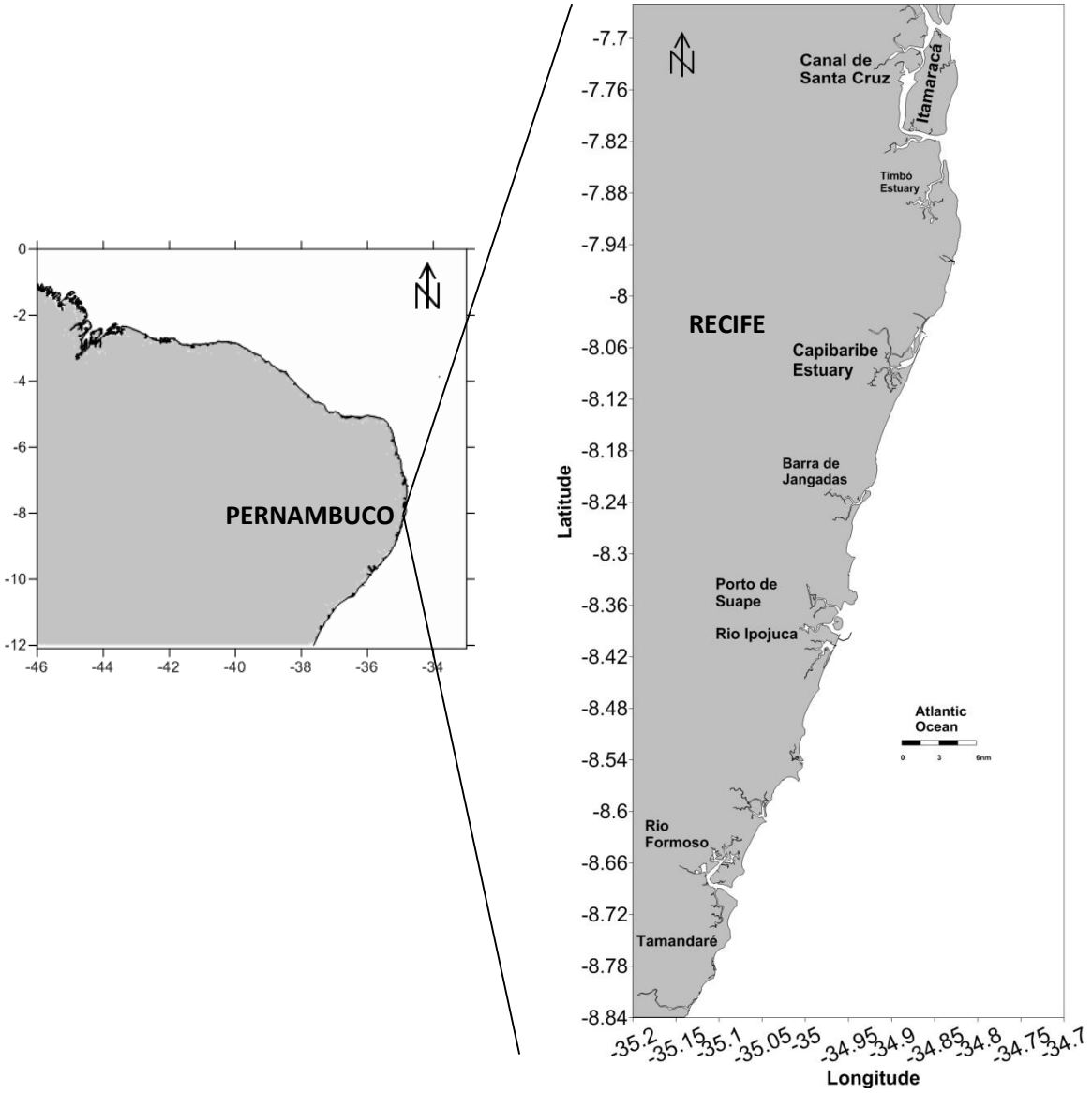
Na região em frente à ilha de Itamaracá, a largura da plataforma é de 39,18 km, com profundidade máxima de 50 m; em frente ao porto do Recife, a largura da plataforma é de 36,96 km com profundidade máxima de 65m e, em frente ao porto de Suape, a largura da plataforma é de 31,96 km, atingindo a profundidade máxima de 65m.

Uma característica deste litoral é a presença de uma diversidade de ecossistemas marinhos de grande importância ecológica e econômica, entre eles recifes de corais, distribuídos ao longo de toda a plataforma continental, dentre os quais se destacam aqueles situados dentro da APA dos Corais e os de Porto de Galinhas, no Litoral Sul. Também são encontrados bancos de macroalgas que podem apresentar uma biomassa maior que 1 kg m^{-2}. Verifica-se ainda a ocorrência de bancos de algas calcárias, de formas ramificadas do gênero *Lithothamnium* e extensas áreas de *Halimeda* vivas e mortas.

Os rios urbanos localizados no Grande Recife apresentam elevados teores de matéria orgânica, intensos processos de eutrofização e baixa qualidade ambiental das águas circulantes. Alguns trabalhos já apontam para a diminuição da qualidade ambiental dos rios localizados na Região Metropolitana do Recife nos últimos anos (TRAVASSOS *et al.*, 1993; KOENING *et al.*, 1995; FEITOSA *et al.*, 1999; GASPAR, 2006; FLORES MONTES *et al.*, 2011).

A influência do material em suspensão carreado pelos rios Capibaribe e Beberibe, que desaguam na região do porto do Recife, foi registrada até cerca de 9 milhas náuticas de distância da costa (RESURREIÇÃO *et al.*, 1996). Há uma tendência natural de diminuição do material em suspensão e da produtividade primária com o afastamento da linha de costa, não só em áreas sob a influência portuária, mas em toda a plataforma continental de Pernambuco (PASSAVANTE E FEITOSA, 2004).

Figura I.4: Mapa da costa de Pernambuco compreendida na área de estudo.



Fonte: O autor

7 MANUSCRITO 1

Aceito para publicação na Tropical Oceanography (ANEXO 1)

ALKALINITY, INORGANIC CARBON AND CO_2 FLUX VARIABILITY DURING EXTREME RAINFALL YEARS (2010-2011) IN TWO TROPICAL ESTUARIES - NE BRAZIL

ABSTRACT

The susceptibility of coastal environments to shifts in the biogeochemical cycles of carbon and nutrients driven by anthropogenic pressure and climate change is a real challenge for the scientific community. We investigated the spatial and seasonal variability of total alkalinity, total inorganic carbon, pCO_2 and CO_2 fluxes in two tropical estuaries with high population densities. The high alkalinity found in both estuaries may act as an additional buffer to the process of coastal acidification due to eutrophication.The pCO_2 in the estuary of Barra de Jangadas increased almost 300% during the extreme rainfall event; meanwhile it decreased in the Capibaribe estuary, suggesting the influence by lateral inputs of soil CO_2 to the first one. The CO_2 fluxes found for the Capibaribe ($+32.8 \pm 20.5$ molC m^{-2} y^{-1}) and Barra de Jangadas estuaries ($+68.2 \pm 58.8$ molC m^{-2} y^{-1}) are considered elevated and comparable to the proposed averages for polluted estuaries at high and mid-latitudes.

Keywords: anthropogenic pollution; ocean acidification; eutrophication; extreme event.

RESUMO

A suscetibilidade dos ambientes costeiros às mudanças nos ciclos biogeoquímicos do carbono e nutrientes impulsionados pela pressão antrópica e mudanças climáticas é um verdadeiro desafio para a comunidade científica. Foi investigada a variabilidade espacial e sazonal da alcalinidade total, carbono inorgânico total, pCO_2 e fluxos de CO_2 em dois estuários tropicais de elevada densidade populacional. A elevada alcalinidade encontrada em ambos os estuários pode atuar como um tampão adicional para o processo de acidificação costeira devido à eutrofização. O pCO_2 no estuário de Barra de Jangadas aumentou quase 300% durante o evento de chuva extrema; enquanto diminuiu no estuário do Capibaribe, sugerindo a influência de entradas laterais de CO_2 do solo para o primeiro. Os fluxos de CO_2 encontrados para os estuários do Capibaribe ($32,8 \pm 20,5$ molC m^{-2} a^{-1})

e Barra de Jangadas (68,2 ± 58,8 molC m^{-2} a^{-1}) são considerados elevados e comparáveis às médias propostas para estuários poluídos em altas e médias latitudes

Palavras-chave: poluição antrópica, acidificação marinha, eutrofização, evento extremo

INTRODUCTION

Estuaries have an essential role in the transportation and transformation of carbon from continental and atmospheric origin to the ocean (SABINE *et al.*, 2004; CHEN, 2004). Some studies show that changes in land use and land cover in river basins can alter the natural balance of bicarbonate ions and contributes to alkalinity inputs to estuaries (CAI; WANG, 1998; WANG; CAI, 2004). However, remains uncertain the effect of the allochtonous and autochtonous inputs on the balance of alkalinity and nutrients in estuaries, which may affect the magnitude of the capture/emission of CO_2 and lead to changes in the natural balances of production and mineralization of organic matter (BORGES, 2011).

Much attention has been given to the dynamics of inorganic carbon in large rivers and estuaries across the globe, especially in mid and high latitudes, despite the significant contribution of small tropical rivers and estuaries, which together cover an area larger than the temperate estuaries (BORGES, 2005). As a result of limited data from tropical regions, current estimates of global average flux values are biased (CAI, 2011). Moreover, CO_2 flux to the atmosphere depends on the calculation of the exchange rate k, which shows great variability linked to local environmental features such as tide, depth, direction and wind intensity (RAYMOND; COLE, 2001; ABRIL, BORGES, 2004; BORGES *et al.*, 2004).

The anthropogenic pressure adds several stressors to the coastal environments, such as pollution, overfishing, changes in the land use and cover, amongst others. These impacts are expected to increase in the future with continued changes in the global climate system and increases in human population levels (HOWARD *et al*,. 2013). According to Trenberth (2011), it is expected that the effect of climate change on winds and precipitation may be moderated, but will vary regionally. Consequently, these climate change effects may alter the water residence time in estuaries, which is an important factor of the alkalinity regulation in these environments (CAI, 2011) and the magnitude of the CO_2 fluxes at the air/water interface.

The Brazilian coast has over 8000 km and is home to 50.7 million people, equivalent to 26.6% of the country's population (IBGE, 2010). Population growth in these areas has led to an increase in nutrient export to the coast, due to the release of untreated sewage into rivers and estuaries (NORIEGA ; ARAUJO, 2009). According to Noriega *et al.,* (2013) the estimated average flux for the Capibaribe estuary ranges 10.95 to 17.52 molCO_2 m^{-2} y^{-1} during high tide in a regular rainfall year.Tthey also reported the average emissions of 0.35 Tg C y^{-1} for estuaries in the Brazilian Northeast.

In the present study, we analyzed the seasonal and spatial distribution of alkalinity, dissolved inorganic carbon, pCO_2 and CO_2 fluxes in two estuaries located in areas of high population density during a seasonal cycle of extreme pluviometry using measurements of total alkalinity, pH, temperature, salinity, dissolved inorganic nitrogen, total phosphorus (TP) and silicate.

METHODS

Study site description

There are three major rivers in the RMR, which are Capibaribe, Jaboatão and Pirapama, whose waters are used for public water supply and disposal of industrial effluents and domestic sewage without appropriate treatment. The land use activity in these watersheds is primarily urban and industrial, including areas of sugarcane monocultures, and some remaining areas of Atlantic Forest and mangroves (CPRH, 2011). A number of studies have identified an increase in nutrient concentrations, human eutrophication and algal blooms in this region in recent years (TRAVASSOS *et al.,* 1993; KOENING *et al.,* 1995; FEITOSA *et al.,* 1999; NORIEGA; ARAUJO, 2009; NORIEGA; ARAUJO, 2011; FLORES MONTES *et al.,* 2011).

The Capibaribe River watershed comprises a drainage area of ≈7,557 km^2 and is used by a population of approximately 1,328,361 inhabitants (CPRH, 2011). The Capibaribe estuary has a mean depth of 3m and an approximate area of ≈19 km^2 which is completely inserted within the city of Recife.

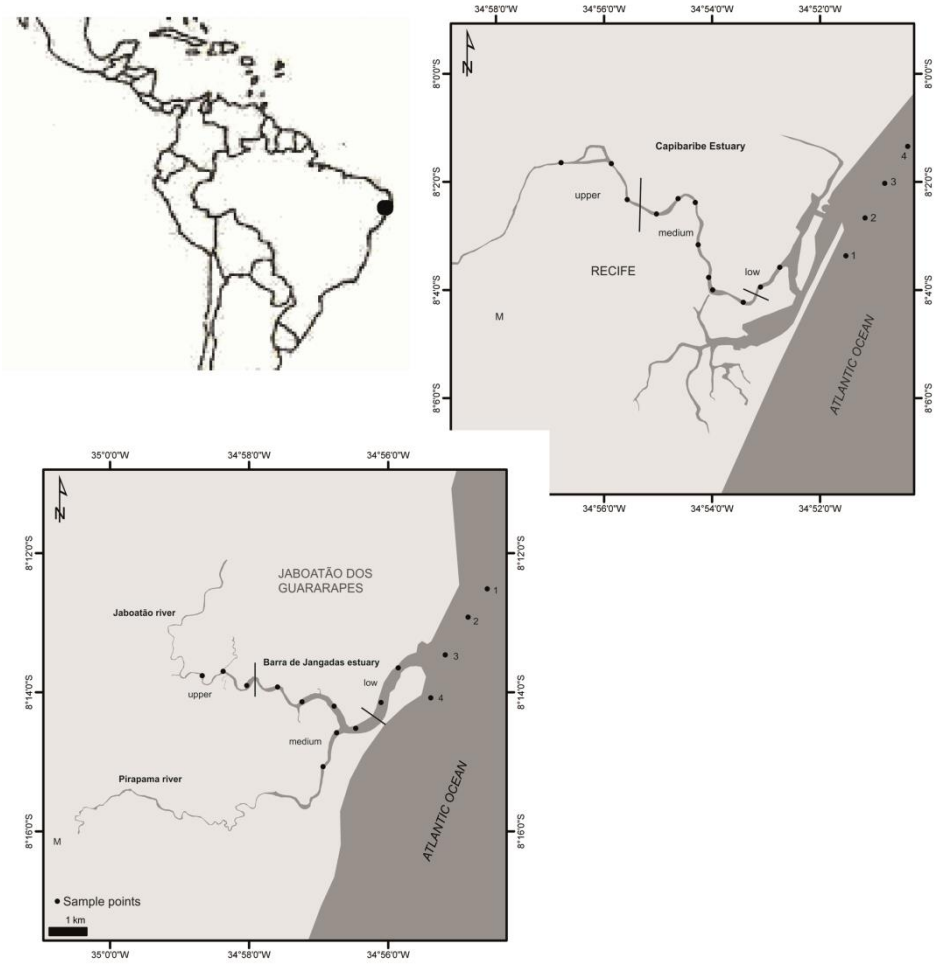
The region of the Barra de Jangadas (BJ) estuary is formed by the union of the Jaboatão and Pirapama rivers, which together drain an area of approximately 1,022 km^2 and is used by a population of approximately 1,347,053 inhabitants (CPRH, 2011). This estuary covers approximately 14 km^2 and has an average depth of 2.6 m and a variable width of approximately 150 m.

The estuaries located in the RMR are under a semidiurnal tidal regime with present mean ranges of 1.3 m during the neap tide and 1.8 m during spring tide (ARAUJO *et al.*, 1999).

Sampling

We divided the estuaries into different segments according to the longitudinal saline gradient classification proposed by McLusky (1993). Six sampling campaigns were performed bimonthly between November 2010 and September 2011 at 12 stations distributed across the Capibaribe estuary and 11 stations in the Barra de Jangadas estuary (Fig. 1). There were also four sampling stations located within each river plume.

Figure II.1: Map of the study area with the respective sampling stations. The numbers indicate the river plumes stations. The M indicates the meteorological stations at which the precipitation, evaporation and wind speed data were obtained.



Source: The author

The samples were taken from the surface layer during the low-water spring tide to assess the influence of the riverine and urban inputs to the coastal areas. The water samples were collected with Niskin oceanographic bottles and sent to the Laboratory of Chemical Oceanography and the Primary Productivity Lab, at the Federal University of Pernambuco (UFPE) where they were processed and analyzed.

Temperature and salinity were determined in situ with a CTD SBE19. pH was measured on board with a Ross combination electrode, measured on the total scale with a precision of ±0.01 units and accuracy of 0.1%.

The meteorological data of precipitation, air temperature, atmospheric pressure and wind speed were obtained from the Pernambuco Agency of Water and Climate (APAC) and the National Institute of Meteorology (INMET). River discharge data were obtained from the National Agency of Waters (ANA).

Analyses

Dissolved oxygen (DO) was determined using the modified Winkler method (STRICKLAND;PARSONS, 1972) with an accuracy of ± 1.3 μmol.L^{-1}. Oxygen saturation was calculated from temperature and salinity of the water according to Garcia and Gordon, 1992.

Samples for analysis of the biological oxygen demand (BOD) were collected according to the recommendations described in Standard Methods - APHA (1995), and incubated for five days at 20°C ($BOD_{5,20}$).

The acid neutralizing capacity (ANC) was determined in unfiltered water samples by potentiometric titration with H_2SO_4 0.016 mol L^{-1} as described in Rounds (2012) with a precision of 15 μmol Kg^{-1} and an accuracy of 2% .

The samples for determination of total phosphorus (TP) precision 0.1 μmol Kg^{-1} , and accuracy of 1%, dissolved reactive silicate $Si(OH)_4$ – precision 1 μmol Kg^{-1} and accuracy 2% , dissolved inorganic nitrogen (DIN), which is the sum of ammonia-N – (NH_4 + NH_3) precision 0.1 μmol Kg^{-1} and accuracy 2%, nitrite (NO_2^-) precision 0.1 μmol Kg^{-1} and accuracy 1%; and nitrate (NO_3^-) precision 0.5 μmol Kg^{-1} and accuracy 1% , were analyzed by the methods described in Grashoff *et al.* (1983) and are expressed in

μmol Kg^{-1}. The method for determining phytoplankton biomass (*Chl-a*) was the spectrophotometric analysis described in UNESCO (1966).

Calculations

Carbon dioxide solubility in the water was calculated according to Weiss (1974). Total inorganic carbon $TCO_2 = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}]$ and the partial pressure of CO_2 (pCO_2) were calculated with the CO_2calc software, developed by Robbins *et al.* (2010), using alkalinity, pH, temperature, salinity, TP and reactive silica data. We used the dissociation constants of carbonic acid according to Millero *et al.* (2006), and the dissociation constants of borate and sulfate according to Dickson (1990a) and Dickson (1990b), respectively.

CO_2 flux was calculated as follows:

$$F(CO_2) = k(CO_2) \,.\, K_H^{CO2} \,.\, \Delta pCO_2 \qquad \text{(Eq. 1)}$$

Where $F(CO_2)$ is the air/water flux of CO_2 (mmol m^{-2} d^{-1}), $k(CO_2)$ is the transfer velocity of CO_2, K_H^{CO2} is the solubility of CO_2 (WEISS, 1974) and ΔpCO_2 is the difference of pCO_2 between surface water and the atmosphere. Positive values indicate outgassing towards the atmosphere.

The pCO_2 in the atmosphere was calculated as follows :

$$pCO_{2atm} = xCO_{2atm} \,.\, (P_{atm} - pH_2O) \qquad \text{(Eq. 2)}$$

Where P_{atm} is the atmospheric pressure and xCO_{2atm} is the molar concentration of CO_2 in dry air in parts per million, obtained from the NOAA station located in Maxaranguape, 330 km north from Recife. Finally pH_2O is the vapor pressure of water at the sea surface.

The gas transfer velocity $k(CO_2)$ was calculated using the formula of Raymond and Cole (2001):

$$K(CO_2) = 1{,}91.\exp(0{,}35.(u)).(Sc/600)^{-0{,}5} \qquad \text{(Eq. 3)}$$

Where *u* $(m.s^{-1})$ is the mean wind speed 10 m above the sea surface during the sampling campaign day, and *Sc* is the Schmidt number in salt water for the CO_2, calculated as a function of temperature.

An empirical model developed by Cole and Cloern (1987) for estimating phytoplankton productivity in the coastal areas was used. The above authors found a mean coefficient of determination r^2=0.82 using nine data sets and a highly significant relationship ($p<0.001$) between production and *B*, Z_p, and *I* for the pooled data (n=211) given by:

$$P(\text{mmol C m}^{-2}\ d^{-1}) = B \times Zp \times I \qquad \text{(Eq. 4)}$$

where *B* represents the phytoplankton biomass (mg m^{-3} of chlorophyll-*a*),*Zp* is the photic depth in meters (measured by Secchi disk), and *I* is the surface irradiance.

The depth limit of the photic layer (Z_p), which receives 1% of the radiation that reaches the surface, was calculated using the equation Z_p=4.61/k proposed by Cole and Cloern (1987), where *k* is the coefficient of light attenuation calculated using the depth of disappearance of the Secchi disk (Z_{ds}), ($k=1{,}7/Z_{ds}$) as described by Poole & Atkins (1929).

The radiometric irradiance data used to calculate productivity were obtained from the Center for Weather Forecasting and Climate Studies / National Institute for Space Research - CPTEC/INPE, available at www.cptec.inpe.br. These data were converted to photosynthetically active radiation (PAR – cal.g. $cm^{-2}.d^{-1}$) by applying the correction factor of 0.47, as described by Vollenweider (1974). Values of PAR were converted to values of quantum E ($m^2\ d^{-1}$) using a correction factor of 0.192, as described by Colijin (1982).

Statistics

We used the t-test to compare the historical means with the 2010/2011 monthly means of precipitation and wind velocities, with a significance level $\alpha = 0.05$. We used the Kruskal-Wallis test, with a level of significance $\alpha = 0.05$ to identify whether had seasonal and/or spatial differences in the pooled data.

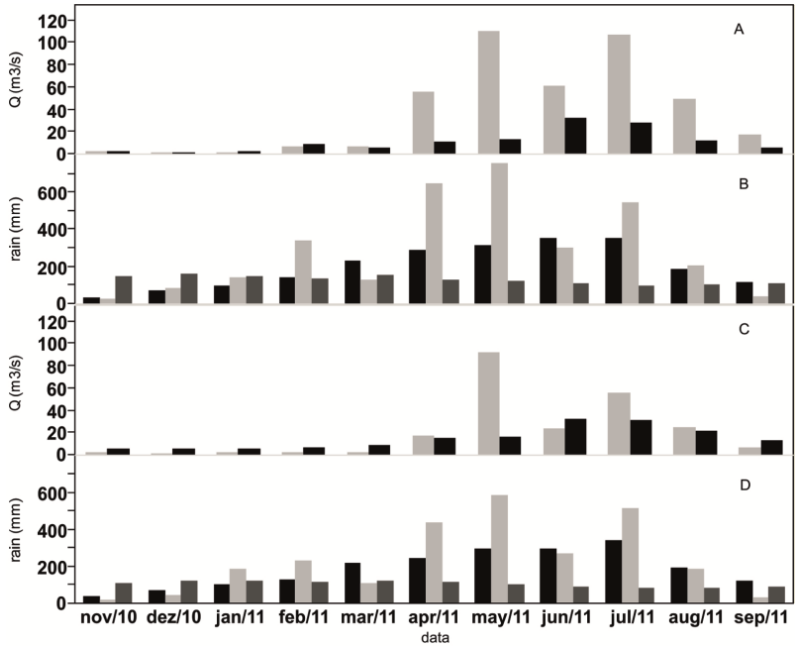
RESULTS

Climatology and river discharge

The average air temperature ranged between 23.71°C and 27.91°C . The mean wind speed for the area was 1.82 m s^{-1}, varying between 0.6 and 2.86 m s^{-1}. These values are close to the average wind speed from 1990-2010 of 2.2 m s^{-1}.

During the period from 2010 to 2011, the rainfall was above the expected values for some months of the rainy season (April to July), relative to the climatological average from 1990 to 2010 (Fig. 2 B, D). There was no significant difference in annual precipitation (p=0.3149), only in the monthly distribution of the rainfall as shown by the t test (p = 0.017). The river discharge values for the Capibaribe (37.7 m^3 s^{-1}) and Pirapama (20.7 m^3 s^{-1}) found during this study were higher than the averages calculated from data provided by the Brazilian National Agency of Waters (Fig. 2 A, C).

Figure II.2: River discharge (gray) and mean discharge (black) from 1986 to 2009 in the Capibaribe (A) and from 1990 to 2009 in Barra de Jangadas (D). Monthly precipitation in the cities of Recife (B) and Jaboatão (D),monthly precipitation (gray), Thornthwaite's potential evapotranspiration (dark gray), average precipitation from 1990 to 2010 (black).



Dissolved Oxygen

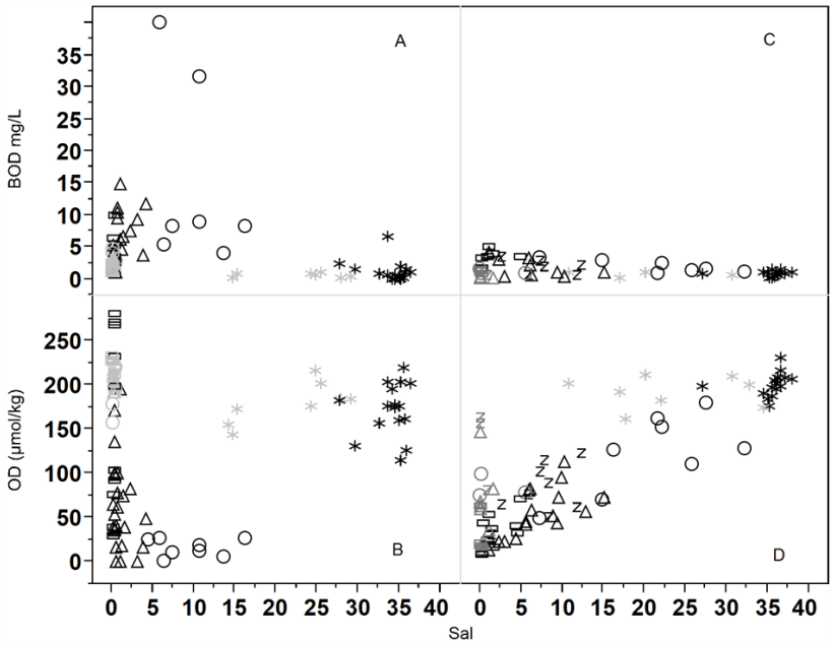
Seasonally, the maximum dissolved oxygen values registered in the Capibaribe estuary were found during the rainy season (Table 1) (p <0.0001). During the dry season, in November 2010 and September 2011, the oxygen values found in this estuary increased

during phytoplanktonic blooms. No seasonal variability was identified for this parameter at Barra de Jangadas estuary with low values throughout the study (Table 1).

The highest dissolved oxygen saturations (%DO) were found in the river plumes, with annual mean values ± sd of 98 ± 10% and 86 ± 14% for Barra de Jangadas and Capibaribe, respectively. A seasonal difference was identified only in the BJ plume, where the mean %DO decreased from 104% during the dry season to 88% (p=0.0024) during the rainy season (Table 2).

The most extreme variability of the %DO was found in the Capibaribe estuary. The spatial distribution pattern of the %DO tended to decrease toward the lower estuary, with an annual mean value ± standard deviation (sd) of 74 ± 33% in the upper estuary and 29 ± 34% in the lower estuary, where anoxic conditions were not rare. In Barra de Jangadas, the maximum %DO annual average was found at the low estuary 50 ± 20%, decreasing toward the upper estuary (14.8 ± 8.7%), and resulting in an average overall oxygen saturation below 30% throughout the study period.

Figure II.3: Overall distribution of the BOD and OD for the Capibaribe (A, B) and Barra de Jangadas (C,D) (black=dry season; gray = rainy season).*river plume; circles - lower estuary; triangles - medium estuary; rectangles -upper estuary; *z* Pirapama.



The Capibaribe estuary showed an annual average $BOD_{5,20}$ of 5.6 mg L^{-1}, three times higher than the mean found for the BJ estuary (1.82 mg L^{-1}). There was no clear variability linked to seasonal cycles. Spatially, most of the elevated values were found

within the estuaries (Table 1) and these values showed no correlation with salinity (Figure 3).

DIN, TP, Silicate and Chl-*a*

The Capibaribe estuary and its plume showed the highest average concentrations of all nutrients. The results of inorganic dissolved nutrients are presented in Table 1 for estuaries and Table 2 for the river plumes. In this estuary, dissolved inorganic nitrogen (DIN) was negatively correlated with salinity, decreasing seaward (r^2 = 0.69). No correlation between these parameters was identified in the Barra de Jangadas estuary (Figure 4). There was a significant difference in the mean values of DIN between rainy and dry seasons only within the Capibaribe estuary ($p < 0.0001$). The annual overall average DIN concentrations were 22.5 ± 7.34 µmol kg^{-1} for the Capibaribe and 12.9 ± 7.65 µmol kg^{-1} for the Barra de Jangadas estuary.

Table II.1: Seasonal mean, minimum and maximum values of the measured parameters in the Capibaribe and Barra de Jangadas estuaries.

		ESTUARY			
		Capibaribe		BJ	
		dry *n=42*	wet *n=24*	dry *n = 40*	wet *n= 19*
TA µmol Kg^{-1}	Mean	1808	1373	1616	1058
	Min - max	1307 - 2421	973 - 1859	746 - 2090	622 - 1388
pH	Mean	7.34	7.43	7.21	6.67
	Min - max	7.01 - 8.09	7.2 - 7.62	6.78 - 7.98	6.39 - 6.91
DIN µmol Kg^{-1}	Mean	20.0	26.6	12.7	13.4
	Min - max	3.8 - 37.7	15.3 - 39.3	3.3 - 39.8	8.3 - 17.5
TP µmol Kg^{-1}	Mean	8.8	4.4	4.7	2.3
	Min - max	1.5 - 22	2.9 - 8.6	0.67 - 30.7	1.29 - 3.22
$Si(OH)_4$ µmol Kg^{-1}	Mean	108.9	131.1	89.0	102.6
	Min - max	10.5 - 207.3	38.5 - 209.5	10.17 - 194.3	38.73 - 195.5
%OD	Mean	32.5	83.1	29.9	28.1
	Min - max	0 - 116	63 - 94	3.4 - 85	6.2 - 65
chl-*a* mg m^3	Mean	40.2	6.3	5.7	4.8
	Min - max	10 - 85	3.81 - 10.48	0.6 - 34.7	1.03 - 8.02
	N	14	8	16	5
DBO mg L^{-1}	Mean	7.87	2.61	2.22	0.84
	Min - max	0.7 - 39.9	0.92 - 4.55	0.42 - 5.03	0.09 - 1.5
	N	33	25	28	11

The estuarine plumes showed a clear correlation between DIN and rainfall r^2 = 0.60 and 0.78 for the Capibaribe and Barra de Jangadas plumes, respectively. Through a seasonal comparison of DIN, we found p values of 0.0011 and 0.0006 for the BJ and Capibaribe plumes respectively. The increased riverine influence during the rainy season

augmented the DIN concentrations in the plumes (Table 2) as also seen by the salinity decrease.

The total phosphorus (TP) maximum values were found during the dry season in both estuaries ($p=0.0191$) for Barra de Jangadas and ($p<0.0001$) for the Capibaribe estuary. The mean overall TP concentrations found within BJ and Capibaribe estuaries were 3.53 ± 2.11 µmol kg^{-1} and 7.18 ± 4.51 µmol kg^{-1}, respectively.

Table II.2: Seasonal mean, minimum and maximum values of the measured parameters in the Capibaribe and Barra de Jangadas estuarine plumes

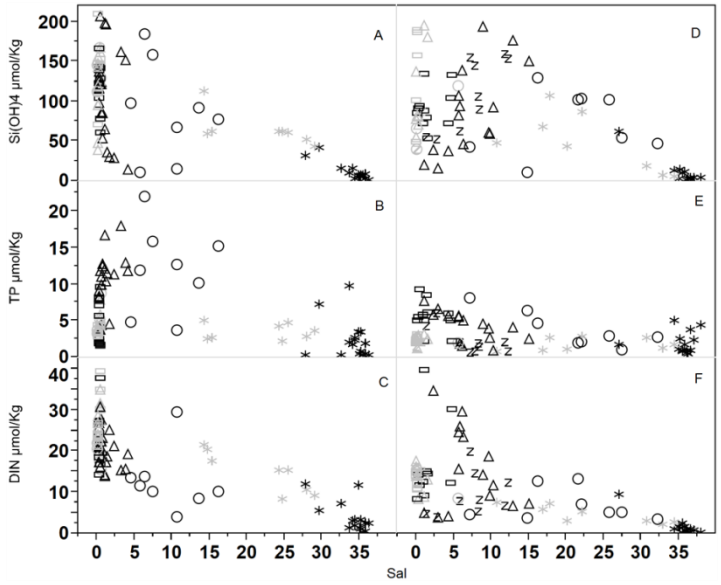
	PLUME			
	cap		BJ	
	dry *n = 16*	wet *n=8*	dry *n=15*	wet *n=8*
TA µmol Kg^{-1}	2266	2067	2262	1904
	2094 - 2499	1721 - 2433	2038 - 2383	1250 - 2266
pH	8.13	7.84	8.17	8.01
	7.97 - 8.32	7.31 - 8.17	7.96 - 8.28	7.76 - 8.21
DIN µmol Kg^{-1}	3.7	14.8	1.5	4.6
	ND - 12	8.3 - 21.6	ND - 9.59	2.1 - 7.61
TP µmol Kg^{-1}	2.4	3.5	1.9	1.8
	ND - 9.75	2.22 - 5.09	0.5 - 5.1	0.8 - 2.9
$Si(OH)_4$ µmol Kg^{-1}	11.1	64.4	9.7	48.1
	1 - 41.5	42.7 - 113.6	0.8 - 61.8	6.3 - 107
%OD	88.5	83.0	104.1	88.8
	60 - 114	63- 101	91 - 119	72 - 101
chl-*a* mg m^3	5.0	2.4	3.2	1.5
	0.24 - 19.29	1.15 - 3.93	0.21 - 9.67	0.8 - 2.49
	16	8	16	8
DBO mg L^{-1}	1.17	0.58	0.89	0.66
	0.01 - 6.6	0.12 - 1.15	0.14 - 1.5	0.12 - 1
	16	7	15	4

Seasonally, there were significant changes in the silicate concentrations (Table 1) in the Capibaribe estuary ($p=0.0289$) and in the plumes of the Capibaribe ($p=0.0001$) and BJ ($p=0.0041$). The mean ± sd concentrations increased from 5.98 ± 4.74 µmol kg^{-1} in the dry season to 48.11 ± 37.31 µmol kg^{-1} in the rainy season at BJ plume. In the Capibaribe plume the mean values ranged from 11.8 ± 11.15 µmol kg^{-1} in the dry season to 64.44 ± 21.05 µmol kg^{-1} during the rainy season ($p=0.0001$).

The productivity within the estuaries is shown in figures 5 A and 5 B. There was no correlation between rainfall and chl-*a* in the Barra de Jangadas estuary ($r^2 = 0.01$). In the Capibaribe estuary the average chl-*a* concentration was higher during the dry season,

influenced by the recurrent algal blooms, and resulted in a negative correlation between rainfall and chl-*a* r^2 = 0.50 with significant seasonal difference (p=0.0002). During the campaigns it was possible to identify an algal bloom event in November 2010 in both estuaries, when the chl-*a* values ranged the maximum of 85.11 mg m^{-3} in the Capibaribe, and 34.71 mg m^{-3} in the BJ estuary. A second bloom event was registered in September 2011, though less intense and only in the Capibaribe estuary, where the chl-*a* values ranged from a minimum of 22.94 mg m^{-3} to a maximum of 50.34 mg m^{-3}. In the river plumes (Figures 5 C, D) the productivity was very low throughout the year and showed only a significant seasonal variation in the Capibaribe plume due to the algal blooms (p= 0.0011).

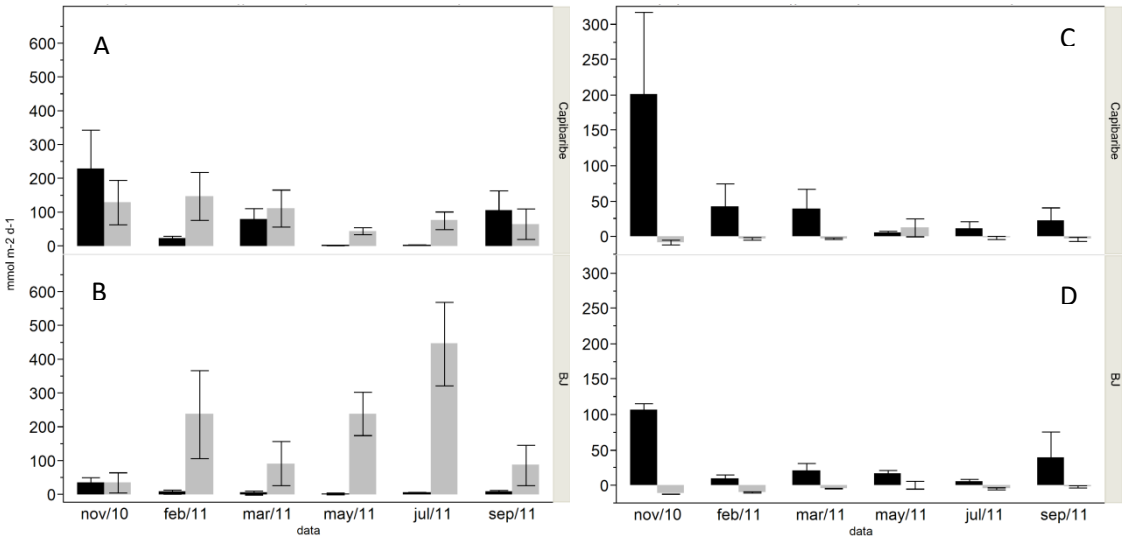
Figure II. 4: Overall distribution of the dissolved nutrients along the salinity gradient in the estuaries of Capibaribe (A,B,C) and Barra de Jangadas (D,E,F), (black = dry season; gray = rainy season). *river plume; circle - lower estuary; triangle - medium estuary; rectangle - upper estuary; z - Pirapama.



Total Alkalinity, TCO_2, pH

The spatial variability of total alkalinity (TA) and pH are shown in Figure 6. Within the estuaries the alkalinity increases towards the lower estuary as a result of greater seawater influence. A positive correlation between TA and salinity was weak in the Capibaribe estuary r^2= 0.42, but the correlation between these parameters was more evident in the BJ estuary r^2=0.62 (Figure 6 A, C).

Figure II. 5: monthly variability of the CO_2 fluxes (gray) and primary productivity (black) within the estuaries of Capibaribe (A) and Barra de Jangadas (B), and in the river plumes (C), (D). Error bars represents standard deviation.



Total alkalinity was higher in Capibaribe, with an annual average of 1649 ± 390 µmol kg^{-1}, ranging from 1557±315 µmol kg^{-1} in the upper estuary to 1860 ± 49 µmol kg^{-1} in the lower estuary. For the Barra de Jangadas estuary, the annual average alkalinity was 1430 ± 375 µmol kg^{-1} and ranged from 1138 ± 288 µmol kg^{-1} in the upper estuary to 1668 ± 361 µmol kg^{-1} in the lower estuary.

We found a significant seasonal difference in the TA values ($p<0.0001$), with the lowest average alkalinities recorded during the rainy season in both estuaries (Table 1), with annual mean ± sd of 1078 ± 244 and 1372 ± 375 µmol kg^{-1} in BJ and Capibaribe estuaries, respectively. When we compared the alkalinity among locations, we found a significant difference between estuaries ($p=0.0278$) with the lowest values found in the Barra de Jangadas. There was no significant difference in TA between river plumes, with an annual average of 2142 ± 308 µmol kg^{-1} in BJ and 2196 ± 198 µmol kg^{-1} in Capibaribe.

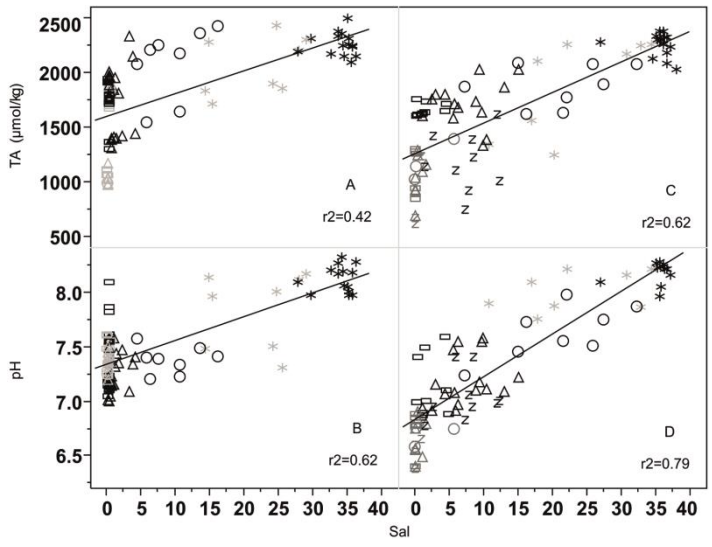
With regard to pH, both estuaries showed a positive correlation with salinity, $r^2=0.62$ and 0.79 for the Capibaribe and Barra de Jangadas, respectively (Figure 6 B, D). Average pH values within the BJ estuary were lower during the rainy months (6.70 ± 0.21) and higher in the dry season (7.21 ± 0.32). For the Capibaribe estuary, the pH values varied seasonally with mean ± sd for the rainy and dry seasons of 7.42 ± 0.11 and 7.33 ± 0.23 (Table 1).

The pH values also varied seasonally in both river plumes, with the lowest values recorded during the rainy season p=0.0372 and p=0.0301 for the Capibaribe and Barra de Jangadas plumes respectively (Table 2).

The TCO_2 was also higher in the Capibaribe than in BJ (p=0.0027), with annual averages of 1764 ± 407 µmol kg^{-1} and 1638 ± 306 µmol kg^{-1}, respectively. Variations in TCO_2 values accompanied variation in alkalinity and were lower during the rainy season in both estuaries. The maximum relative HCO_3^- contribution to TCO_2 were registered in the Capibaribe estuary with a mean ± sd of 91 ± 3.68% of the TCO_2 composed by HCO_3^- (Figure 7).

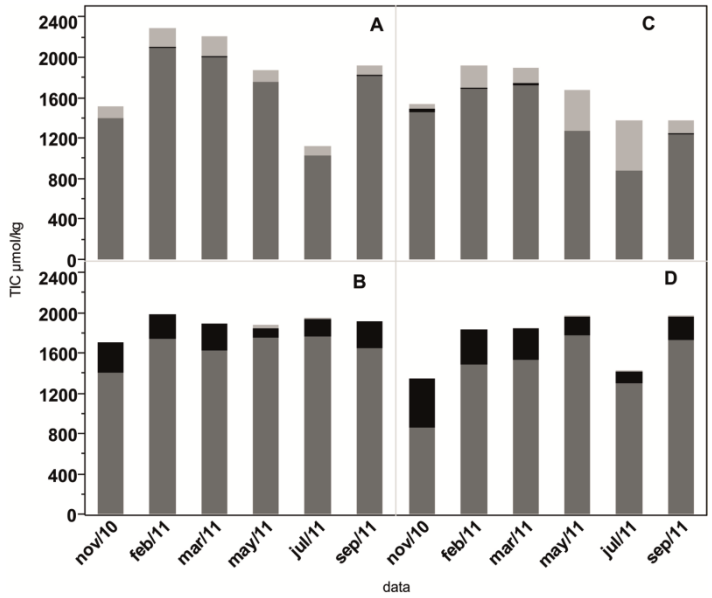
Although the TCO_2 did not show a seasonal variation in the river plumes, the relative contribution of inorganic carbon species varied, with a decrease in the percentage of CO_3^{2-} ions and a relative increase of HCO_3^- ions and $CO_{2(aq)}$ (Figure 7), accompanied by a pH decrease during the high discharge months of April and May 2011.

Figure II.6: Overall distribution along a salinity gradient of total alkalinity (TA) and pH in the estuaries of Capibaribe (A,B) and Barra de Jangadas (C,D) (black=dry season; gray=rainy season).*river plume; circle - lower estuary; triangle - medium estuary; rectangle - upper estuary; *z* Pirapama).



Source: The author

Figure II.7: Monthly variability of the mean inorganic carbon species to TCO_2 within the estuaries of Capibaribe (A), Barra de Jangadas (C), and in river plumes (B) Capibaribe, and (D) Barra de Jangadas. (dark gray - [HCO_3^-], Black – [CO_3^{2-}], light gray - [CO_2]).



Source: The Author

Water pCO_2 and CO_2 fluxes

We found a different seasonal pattern in the water pCO_2 and CO_2 fluxes (FCO_2) for each estuary. The pCO_2 and consequently the FCO_2 were higher during the rainy season in the Barra de Jangadas estuary and during the dry season in the Capibaribe estuary (Figures 5 and 8).

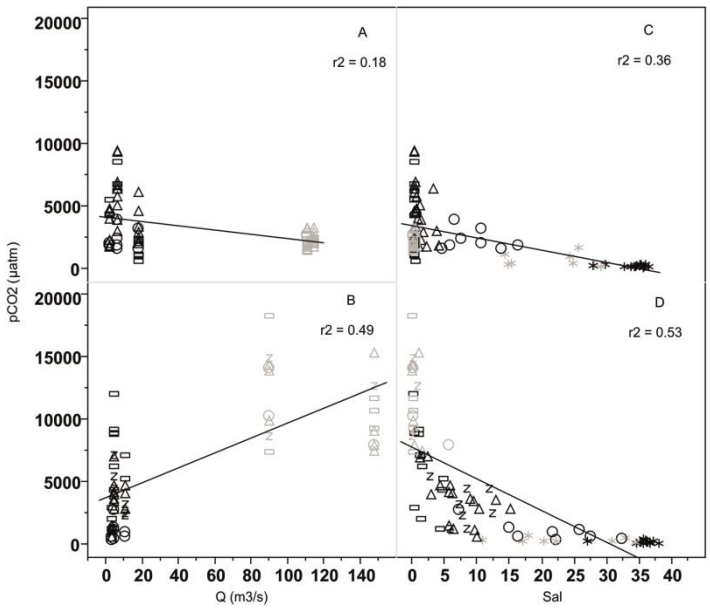
Values of TA, pH and salinity for the river plume areas were lower during the rainy season, resulting in a pCO_2 increase during the rainy months with mean values ± sd of 667 ± 537 µatm in Capibaribe and 332 ± 189 µatm in BJ (Figure 8 B). During the dry season the mean pCO_2 values found were 237 ± 86 µatm and 166 ± 112 µatm for the river plumes of Capibaribe ($p = 0.0110$) and Barra de Jangadas ($p = 0.0131$), respectively.

The maximum pCO_2 values were registered in the areas most influenced by the fluvial waters, with low salinity, pH and alkalinity. The maximum water pCO_2 values were found in the upper Barra de Jangadas estuary and decreased towards the sea $r^2= 0.53$ (Figure 9 D), but this correlation was not clear in the Capibaribe estuary $r^2=0.36$ (Figure 9 B). The annual overall mean pCO_2 in the Capibaribe estuary was 3317 ± 2034 µatm, it ranged from 3142 ± 2282 µatm in the upper estuary to 2316 ± 710 µatm in the lower

estuary. In Barra de Jangadas the annual overall pCO_2 mean was 6018 ± 4589 µatm, with average values ± sd ranging from 7852 ± 4308 µatm in the upper estuary to 3533 ± 4615 µatm in the lower estuary, where CO_2 subsaturation states were frequent during the dry season.

The monthly variability of FCO_2 in the estuaries is presented in Figure 5 A and B. In the Capibaribe estuary the values ranged from 106.6 mmolC m^{-2} d^{-1} to 61.62 mmolC m^{-2} d^{-1} between dry and rainy periods, resulting in an annual average of 90 mmolC m^{-2} d^{-1}. In the BJ estuary the average FCO_2 ranged from 117 mmolC m^{-2} d^{-1} to 348 mmolC m^{-2} d^{-1} between the dry and rainy seasons, respectively, resulting in an annual average of 186 mmolC m^{-2} d^{-1}. This annual FCO_2 average found for the BJ estuary showed a large influence of the rainy season, when the maximum values ranged from 180 mmolC m^{-2} d^{-1} in the lower estuary to 653 mmolC m^{-2} d^{-1}, in the upper estuary, with an average for the rainy season of 348 mmolC m^{-2} d^{-1}. During the dry season, the average FCO_2 (117 mmolC m^{-2} d^{-1}) was close to that found for the Capibaribe (106 mmol C m^{-2} d^{-1}).

Figure II.8: Correlation between river discharge (Q) and pCO_2 within the Capibaribe (A); and Barra de Jangadas (B) estuaries. Overall distribution of pCO_2 in the Capibaribe (C), and Barra de Jangadas (D), along a salinity gradient (black = dry season; gray = rainy season). *river plume; circle – lower estuary; triangle - medium estuary; rectangle - upper estuary; z Pirapama).



Source: The author

DISCUSSION

Nutrients and productivity

The link between nutrient dynamics and the ecosystem response under different hydrological regimes at various spatiotemporal scales is still a challenge for the scientific community (CHEN;HONG, 2012; NIXON *et al.*, 2014). There are some opposing views, with reports of nutrient enrichment exacerbating the larger scale decline in oceanic pH (CAI *et al*., 2011; DUARTE *et al*., 2013). However, Borges and Gypens (2010), found that the increase in the primary productivity due eutrophication may counter the effects of ocean acidification due increased productivity leading to CO_2 absorption.

Despite the increased nutrient concentrations in the river plumes during the wet season, the *Chl-a* and productivity values are higher during the dry season, as a consequence of the algal blooms. However, the extent and duration of the seasonal variability of primary production on the continental shelf is not clear. It is expected that the area under influence of the river plumes increases with the river discharge, which would also increase the net productivity in the coastal zone.

According to Resurreição *et al.*, (1996), who studied productivity during a seasonal cycle on a transect of the continental shelf in front of the Capibaribe, there is no significant seasonal variation in the chl-*a* concentration at a distance of approximately 4 nautical miles (nm) from the coast. However, additional studies are needed to explain how the increase in nutrient export is affecting the extent of seasonal gross primary productivity over time.

The Capibaribe river showed a greater mean discharge in comparison with the BJ estuary during the study period, 37.7 $m^3\ s^{-1}$ and 20.7 $m^3\ s^{-1}$ respectively. Through integration of the average flow and $BOD_{5,\ 20}$ values (Q_{mean} x $BOD_{5,20mean}$), we find the residual organic loading rate of 19.13 t $BOD_{5,\ 20}\ d^{-1}$ and 3.33 t $BOD_{5,\ 20}\ d^{-1}$ for Capibaribe and Barra de Jangadas, respectively. According to Noriega and Araujo (2009) the major source of nutrients to the coastal zone in the Pernambuco state is the wastewater. They estimated a phophorus input to the ocean of 37,048 t P y^{-1}, where anthropogenic sources accounted for 99.7 % of the emissions.

The elevated organic load has driven the nutrient availability in the studied areas, especially in the Capibaribe estuary. The augmented rivers' discharge increased the TP,

DIN and silicate concentrations found in the river plumes during the rainy season, due to a flushing effect in the estuaries. Such process brings more organic matter to be respired over the continental shelf.

Alkalinity and inorganic carbon

The climatic factors are important drivers of the alkalinity concentrations found in the estuaries here studied. During the extreme rainfall events in April and May 2011, we registered the lowest concentrations of HCO_3^-. So it is reasonable to assume that during a regular rainfall year such decrease in the HCO_3^- concentrations may be less intense, prevailing the high alkalinity scenario throughout the year. These findings are in accordance with the work of Cai *et al*. (2008) in the case of the Huanghe river, when the authors reported a low presence of carbonate mineral content in the watershed, but its waters show high HCO_3^- concentrations up to 2.6 mM due to dry climate, net evaporation and the silicate weathering in watershed which also releases HCO_3^- to the water.

The net balance of alkalinity in the Capibaribe and BJ estuaries probably is not an export of alkalinity to coastal waters, but an additional buffering to estuarine proton inputs from organic matter respiration.

In a tropical river in Brazil, Mortatti *et al*., (2006) found a mean TCO_2 of 2591 µmol kg^{-1} and attributed 45.5% of the HCO_3^- concentration to anthropogenic sources, 47.8% to weathering and 6.7% to the pluvial input. Araujo *et al.,* (2013) calculated the inorganic carbon species for the 2002-2010 period, in a fluvial section of the Capibaribe river, and found values of TCO_2 ranging from 596 to 2235 µmol kg^{-1}, increasing over time, and attributed the pattern to enhanced organic load associated with population growth over the period.

Several metabolic and diagenetic processes are responsible for the TCO_2 and total alkalinity consume/production in estuaries. The photosynthesis consumes, and both aerobic and anaerobic organic matter oxidation produce CO_2. These processes decrease/increase the TCO_2 in seawater, but not total alkalinity since there is an adjustment of carbonate species and pH according to the equilibrium conditions (ZEEBE AND WOLF-GLADROW, 2001; WOLF-GLADROW, *et al.,* 2007). Sulfate reduction and methane production releases HCO_3^-, but also CO_2 and lowers pH, and the final result depends on the total sediment chemistry (VAN DER WEIJDEN, 1992). The prevalence

of these anaerobic reactions in anoxic estuarine waters and sediments is a drawback to carbonate system calculations using pH and total alkalinity, since the real amount of carbonate alkalinity is unknown.

The input of high alkalinity freshwater to the Capibaribe and BJ estuaries may counterbalance the acidification, except by estuarine organic matter respiration, from natural and anthropogenic sources, which decreases pH. From the low oxygen saturation found in Barra de Jangadas estuary <30% throughout the year, and in the Capibaribe estuary during the dry season, we may assume that the anaerobic oxidation of organic matter, which favors HCO_3^- production and increases the alkalinity is an important aspect in the alkalinity regulation of these estuaries (FRANKIGNOULLE *et al*. 1996; ABRIL; FRANKIGNOULLE, 2001; ABRIL; BORGES, 2004; THOMAS *et al.*, 2009). However, further studies are necessary to understand which processes control the alkalinity and inorganic carbon variability in the Capibaribe and BJ estuaries.

pCO_2 and CO_2 fluxes

The rivers' discharge is usually correlated with pCO_2 when there is a significant contribution to the estuary from the upper river (JIANG *et al.*, 2013). The absence of correlation between these parameters in the Capibaribe and BJ estuaries (Figure 8 A, B), may be related to the land use in the watershed. The Capibaribe estuary, which is located entirely within an urban area, showed a decrease in pCO_2 during the rainy season, in accordance with previous works of Noriega *et al*. (2013). This kind of decrease was also reported by Abril *et al.*, (2000) in the Scheldt estuary. In such environments, the processes of organic matter mineralization and the microbial respiration rates are the main drivers of CO_2 variability inside the estuary (ZHAI *et al.*, 2005; BORGES;ABRIL, 2011).

The variability of $CO_{2\,(aq)}$ and pH in rivers and estuaries are under influence of the soil CO_2 runoff from wetlands and mangroves, which have a potential effect on the process of pCO_2 increase in water bodies, as reported by Abril and Borges (2004), Cai *et al.*, (2011), Sarma *et al.*, (2012) and Abril *et al.*, (2014a). The BJ estuary appears to be more susceptible to this type of input because its margins still have dense mangrove areas and extensive wetlands which are exposed during the low tide period. The weak correlation with river discharge ($r^2 = 0.49$) suggests that it has also been influenced by the high alkalinity freshwater input and the predominance of estuarine biological processes (production/remineralization of organic matter) compared with advective fluxes.

At BJ the average pCO_2 found (6081 μatm) are within the range of 400 to 10000 μatm proposed by Chen *et al.,* (2012) in a review of several studies in estuarine environments. Recently, Noriega *et al.,* (2014a) reported values of pCO_2 in 12 estuaries of Northeast Brazil ranging from 987 to 8970 μatm. Elevated pCO_2 values in estuaries are reported by Sarma *et al.,* (2012); they found values ranging from 359 to 18492 μatm in a study of 27 Indian estuaries.

Except during the extreme rainy months, the river plumes of BJ and Capibaribe estuaries acted like autotrophic areas, although their low productivity they were predominantly in a state of CO_2 undersaturation (Figure 5 C, D). However, such undersaturation may be overestimated due the utilization of pH and TA for the CO_2 system parameters calculations (ABRIL *et al.,* 2014b). During the rainy season in the Capibaribe river plume, especially in May, a CO_2 supersaturation was observed, varying from a mean flux value of - 4.01 mmolC m^{-2} d^{-1} during the dry season, to a positive mean of + 5.7 mmolC m^{-2} d^{-1} during the rainy season.

The average annual CO_2 fluxes found for the urban tropical estuaries evaluated here, of +32,8 ± 20.5 molCm^{-2} y^{-1} and+68.2 ± 58.8 molC m^{-2} y^{-1} for the Capibaribe and BJ estuaries, respectively, are higher than those reported for another tropical Brazilian estuary by Souza *et al.,* (2009) of 13 molCm^{-2} y^{-1} and are above the average for tropical estuaries proposed by Borges *et al.,* (2005) of 17 molC m^{-2} y^{-1}.

The FCO_2 average values found in the present work are comparable to those recently reported for 28 estuaries of the north and northeast regions of Brazil by Noriega *et al.,* (2014b). They proposed a mean value of 20 ± 16 molC m^{-2} y^{-1}during a regular rainfall season. The FCO_2 averages found in the present work are also comparable to those values proposed by Borges *et al.,* (2005), for polluted environments at mid and high latitudes (46 molC m^{-2} y^{-1}) and the average flux of 62 molC m^{-2} y^{-1} proposed by Frankignoulle *et al.* (1998) and 68 molC m^{-2} y^{-1} by Chen *et al*. (2012) for the inner portion of estuaries.

CONCLUSION

The net balance of alkalinity in the studied estuaries is, probably, an additional buffering to estuarine proton inputs from organic matter respiration. However, further studies are needed to investigate the causes of the alkalinity variability in the area

The extreme precipitation event exposed the susceptibility of the Barra de Jangadas estuary to the input of soil CO_2 from wetlands and mangroves increasing the average pCO_2 values nearly 300% during months of extreme rainfall. However, the low correlations of pCO_2 with rivers' discharges, which we found in both estuaries, evidenced the influence of the high alkalinity fresh water input and the predominance of biogeochemical processes of production/remineralization of organic matter, from natural and anthropogenic sources, compared with the advective fluxes of inorganic carbon. Such input of high alkalinity freshwater to the Capibaribe and Barra de Jangadas estuaries may counterbalance the acidification process in the coastal zone caused by eutrophication.

The CO_2 fluxes found for both estuaries are considered elevated and are comparable to the proposed averages for polluted estuaries at high and mid-latitudes, illustrating the effects of anthropogenic pressure on rivers and estuaries in densely populated tropical areas. These findings may aid our understanding of biogeochemical coastal processes under different global climate change scenarios of drought or increased rainfall in eutrophic, shallow and well-mixed tropical estuaries.

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8 MANUSCRITO 2

A ser submetido para publicação na Estuarine Coastal and Shelf Science (ANEXO 2)

UNDERWAY MEASUREMENTS OF CO_2 IN A TROPICAL INNER SHELF CLOSE TO TWO POLLUTED ESTUARIES IN NORTHEAST BRAZIL.

ABSTRACT

The concern about the increase of carbon dioxide (CO_2) concentration in the atmosphere and its impact in the coastal zones were receiving little attention regarding the importance of these areas on carbon biogeochemical processes, and the C fluxes between land, ocean and atmosphere. The lack of accurate inorganic carbon data on coastal oceans has been considered a big issue. In order to overcome this problem, a custom-made underway system was developed to measure the CO_2 fugacity (fCO_2) *in situ*. Here, we present the first underway fCO_2 measurements obtained over the inner continental shelf in front of the city of Recife to Jaboatão dos Guarrarapes, between the latitudes -8.01 to -8.25. Although the cruise spanned less than 1º of latitude a strong fCO_2 variability was observed in surface water. The mean flux of 3.1 molC $m^{-2}y^{-1}$ for the inner shelf of the Metropolitan Region of Recife (MRR) obtained in this study is higher than available estimates for tropical open shelf environments. The scarce CO_2 database in tropical, shallow, nearshore environments might have led to an underestimation of the global CO_2 emissions in those regions. Our data indicates that the fCO_2 is enhanced by the riverine transport of nutrients, inorganic and organic carbon. However, further studies are necessary to cover a more extensive area and identify spatial and seasonal patterns of the fCO_2 distribution over the Brazilian inner and outer continental shelf, thus contributing to the understanding of coastal processes related to the impact of ocean acidification and their ecological and economic implications for the region.

Keywords: fCO_2; Coastal zone; ocean acidification, CO_2 fluxes

RESUMO

A preocupação com o aumento da concentração de dióxido de carbono (CO_2) na atmosfera e seus impactos na zona costeira estavam recebendo pouca atenção em relação a importância dessas áreas nos processos biogeoquímicos do carbono, e dos fluxos de carbono entre terra, oceano e atmosfera. A falta de dados precisos sobre carbono

inorgânico em oceanos costeiros tem sido considerada um grande problema. De modo a ultrapassar esse problema, um sistema feito por encomenda foi desenvolvido para medir a fugacidade do CO_2 (fCO_2) continuamente *in situ*. Neste trabalho apresentamos as primeiras medições de fCO_2 contínuas obtidas ao longo da plataforma continental interna num trecho em frente à cidade de Recife até Jaboatão dos Guarrarapes, entre as latitudes -8.01 e -8,25. Embora o cruzeiro percorreu menos que 1° de latitude, uma forte variabilidade de fCO_2 foi observada em águas superficiais. O fluxo médio de 3,1 molC $m^{-2}a^{-1}$ para a plataforma interna da Região Metropolitana do Recife (RMR) obtido neste estudo é maior do que as estimativas disponíveis para ambientes de plataforma tropicais abertas. O escasso banco de dados de CO_2 em ambientes costeiros tropicais rasos pode ter levado a uma subestimação das emissões globais de CO_2 nessas regiões. Nossos dados indicam que o fCO_2 é reforçada pelo transporte fluvial de nutrientes, carbono inorgânico e orgânico. No entanto, mais estudos são necessários para cobrir uma área mais extensa e identificar padrões espaciais e temporais da distribuição fCO_2 sobre a plataforma continental interna e externa brasileira, contribuindo para a compreensão dos processos costeiros relacionados com o impacto da acidificação dos oceanos e os seus valores ecológicos e implicações econômicas para a região.

Palavras-chave: fCO_2; Zona costeira; acidificação oceânica, fluxos de CO2

INTRODUCTION

The coastal oceans are considered areas with intense biogeochemical activity, which links fluxes of energy and matter between land, the open ocean and the atmosphere (THOMAS *et al.,* 2009). Despite the great variability of the partial pressure of carbon dioxide (pCO_2) in coastal oceans, the actual global CO_2 fluxes estimates are based on literature compilations with insufficient data to cover the full spatial extent of the coastal ocean adequately and the diversity of biogeochemical carbon cycling related to contrasting physical and biogeochemical settings (Borges, 2011). Past studies in the coastal zone have not given much attention to estuaries that receive little freshwater, even though this kind of environment is considered an important geographic feature (JIANG *et al.*, 2008).

It is expected that the absorption of atmospheric CO_2 in coastal zones may be minor compared to the input of all land-derived materials, particularly within eutrophic

regions where excessive nutrient loading and organic matter production have been associated with large hypoxic events (WALLACE *et al.*, 2014). However, there is a significant variability in the coastal ocean with regions acting as a sink of CO_2 for the atmosphere (CHEN *et al.*, 2012; CHOU *et al.*, 2013; COTOVICZ *et al.*, 2015) and other regions acting as a source (BORGES;FRANKIGNOULLE, 2002; KÖRTZINGER, 2003; LEFÈVRE, 2009; CHEN *et al.*, 2012; COBO-VIVEROS *et al.*, 2013).

Open ocean waters in tropical regions are typically oversaturated in CO_2, as the northeastern Brazilian continental shelf that is normally oligotrophic, and therefore exhibit low productivity. Recent studies in the north and northeastern Brazilian estuaries have reported these environments as sources of CO_2 to the atmosphere (SOUZA *et al.*, 2009; NORIEGA *et al.*, 2014). In the southeastern Brazil an enhanced sink of CO_2 due eutrophication was reported by Cotovicz *et al.* (2015) in a semi-enclosed embayment.

Here, we present the first underway fCO_2 measurements obtained over the inner continental shelf in front of the city of Recife, the 6th most populated area of Brazil. The underway fCO_2 was measured using a custom-made system capable to run on relatively small boats. It is an accurate, affordable option to encourage new groups for CO_2 observation in the coastal oceans and thus increase the efforts to improve our understanding of the carbon dynamics in such environments.

MATERIAL AND METHODS

Description of the CO_2 system

A custom-made automated air–sea equilibration system to measure the CO_2 mole fraction (xCO_2) in the air has been developed at the Chemical Oceanography laboratory in the Federal University of Pernambuco - Brazil, in cooperation with the Institut de Recherche pour le Développement (IRD) – LOCEAN, France.

The system is portable, compact and is designed to operate on small boats (≈ 10m) and during oceanographic cruises as well. It consists of an air–seawater equilibrator described by Pierrot *et al.*, (2009), a non-dispersive infrared detector (Li7000, LiCor Inc., USA), a GPS/air inlet module and a series of valves automatically controlled by a program written in Labview 2014.

The automation hardware is composed of a 16 channel relay board controlled through a National Instruments data acquisition module (USB-6212). The module collects data of the barometers and also controls the solenoid and pinch valves. All the other sensors, GPS and infrared analyzer are connected to the computer through an 8-port serial RS232 to usb converter.

Seawater is pumped to the system from the pump of the ship at about 0.8m deep at a rate of 20 l min^{-1}. The pump has a strong flow rate due to the boats' own requirements for engine cooling water. Before entering the air-sea equilibrator system, the seawater outlet is connected to a portable thermosalinograph model SBE 45 which records the sea surface temperature (SST) and sea surface salinity (SSS). In order to reduce the water flow in the equilibrator a 1/8′ diameter pvc tubing is used so the seawater circulates in the equilibrator at a rate of 5-7 l min^{-1}.

The water temperature inside the air-sea equilibrator is monitored by a SBE 38 thermistor sensor located at the seawater outlet of the main equilibrator. The difference between the SST and the temperature in the equilibrator is usually lower than 0.5 °C.

A closed loop of air circulates in the equilibrators and is dried by passing through a cold trap at 0 °C and then through a water trap made of magnesium perchlorate to remove the remaining water vapor. This chemical trap is the only constraint of the system which makes it semi-autonomous, as it is necessary to change the chemical every day. When the chemical is saturated with water, it tends to block the circulation of air.

Two barometers Vaisala PTB 110 measure the atmospheric pressure and the pressure in the main equilibrator. An air uptake is installed at the bow of the ship and the air is continuously pumped to measure CO_2 in the atmosphere.

Analysis and calibration cycles

The gas stream from the equilibrator headspace circulates for periods of 3 hours through the system and the xCO_2 is recorded continuously. The analyzer is calibrated every 3 h with three secondary dry gas CO_2 standards of 281.05 ppm, 363.45 ppm and 498.97 ppm calibrated against NOAA primary gas standards. The zero of the infrared detector is set with nitrogen gas, free of water and CO_2. Measurements of xCO_2 in the atmosphere are performed every 6 hours, after the seawater cycle.

The program records the data of all the sensors: GPS (time and position), the infrared analyzer (xCO_2, humidity, temperature and pressure in the reading cell), barometric pressure sensors and the thermosalinograph.

Data processing

The partial pressure of CO_2 in the equilibrator is computed from the molar fraction xCO_2 in dry air using the following formula:

$$pCO_2 = xCO_2 (P_{atm} - pH_2O) \quad \text{(eq.1)}$$

Where P_{atm} is the atmospheric pressure and pH_2O is the water vapor pressure calculated as a function of SST and salinity using the formula of Weiss and Price (1980). To take into account the non-ideal behavior of the CO_2, the fugacity of CO_2 is calculated instead of the partial pressure but the difference between the two is only in the order of a few µatm. The fugacity of fCO_2 in the equilibrator is given by Doe (1994):

$$fCO_2 = pCO_2 \exp[(B + 2\delta)Patm /RT_{equ}] \quad \text{(eq.2)}$$

where $B=-1636.75+(12.0408Tequ)-(0.0327957Tequ^2)+0.0000316528Tequ^3)$, T_{equ} is the equilibrator temperature in Kelvin, $\delta=57.7-0.118Tequ$ and $R=8.31\ JK^{-1}\ mol^{-1}$.

A temperature correction is then made using the formula of Takahashi *et al*., (1993) to convert the fugacity of CO_2 given at the equilibrator temperature to the fugacity of CO_2 at the sea surface temperature according to:

$$fCO_{2sst} = fCO_{2Tequ} \exp[0.0423(SST-T_{equ})] \quad \text{(eq.3)}$$

where SST is the sea-surface temperature in Kelvin.

The equations used to calculate the atmospheric fugacity are the same as those described above with the difference that the atmospheric pressure and the SST should be used instead of the equilibrator pressure and temperature. Also, no temperature correction (eq.3) is applied.

The CO_2 flux is calculated as follows:

$$F(CO_2) = k(CO_2) \cdot K_H^{CO2} \cdot \Delta fCO_2 \quad \text{(Eq. 4)}$$

Where $F(CO_2)$ is the air/water flux of CO_2 (mmol $m^{-2}d^{-1}$), $k(CO_2)$ is the transfer velocity of CO_2, K_H^{CO2} is the solubility of CO_2 Weiss (1974) and ΔfCO_2 is the difference of fCO_2 between surface water and the atmosphere. Positive values indicate outgassing towards the atmosphere.

The gas transfer velocity $k(CO_2)$ is calculated using the formula of Raymond and Cole (2001):

$$k(CO_2) = 1{,}91 \cdot \exp(0{,}35 \cdot (u)) \cdot (Sc/600)^{-0{,}5} \quad \text{(Eq. 5)}$$

where u (ms^{-1}) is the mean wind speed 10 m above the sea surface during the sampling campaign day, and Sc is the Schmidt number in salt water for the CO_2, calculated as a function of temperature.

Sample collection and analyses

A sampling campaign was conducted in December 10 2014, in the coastal area near of the city of Recife (Figure 1). In addition, subsurface seawater samples were collected with Niskin bottle at six stations and analyzed at the laboratories of Chemical Oceanography and Primary Productivity at Federal University of Pernambuco.

Alkalinity samples were analyzed by potentiometric titration with open-cell according to the method described in Dickson *et al.*, (2007). The accuracy (±0.1 %) and precision (± 6 μmol kg sw^{-1}) of the analysis was tested against the Certified Reference Material (CRM) batch 132, for seawater analysis of alkalinity and dissolved inorganic carbon provided by A. Dickson of the Scripps Institute.

Dissolved oxygen (DO) was determined using the Winkler method with an accuracy of ± 1.3 μmol L^{-1}.

The total phosphorus (TP) and total nitrogen (TN) were analyzed by the method of simultaneous oxidation of nitrogen and phosphorus compounds by persulphate (GRASSHOFF; EHRHARDT, 1983). The precision and accuracy of the method is respectively 0.1 μmol kg sw^{-1} and 0.5% for the TP and 0.5 μmol kg sw^{-1} and 1% for the TN.

The samples for the determination of the phytoplankton biomass (*Chl-a*) were filtered in 47µm GF-C filters and analyzed later by the spectrophotometric method described in UNESCO (1966).

Study site

The continental shelf of the Pernambuco estate in northeast Brazil is about 180 km long and is located between the latitudes -7.5 to -9.0. It is characterized by a reduced width, shallow depth with a subtle slope, warm water, high salinity >36 and is almost entirely covered by biogenic carbonate sediments (MANSO *et al.*, 2004). The area experiences semi-diurnal tides, with a mean range of 1.67m, a neap tide range of 0.97m, and a spring tide range of 2.07m (ROLLNIC *et al.*, 2011).

The Metropolitan Region of Recife (MRR) is considered the 6th most populated area of Brazil with approximately 3,743,854 inhabitants and a population density of about 1,352.53 inhabitants / km^2 (IBGE, 2010).

The Capibaribe River watershed comprises a drainage area of 7,557 km^2 and is used by a population of approximately 1,328,361 inhabitants. The Capibaribe estuary has a mean depth of 3m and a surface of 19 km^2 which is completely inserted within the city of Recife (Figure 1).

The Barra de Jangadas (BJ) estuary is formed by the Jaboatão and Pirapama rivers that merge and drain an area of ≈1,022 km² and is used by a population of 1,347,053 inhabitants (CPRH, 2011). This estuary covers approximately 14 km^2 and has an average depth of 2.6 m and a variable width of about 150 m. The monthly mean discharges of these estuaries are presented in Figure 3.

The land use activity in the watersheds of the MRR is primarily urban and industrial, including areas of sugarcane monocultures, Atlantic Forest and mangroves (CPRH, 2011).

The lack of appropriate sewage treatment led to eutrophication and development of algal blooms in these watersheds, as pointed out by numerous studies (TRAVASSOS *et al.*, 1993; KOENING *et al.*, 1995; FEITOSA *et al.*, 1999; FLORES MONTES *et al.*, 2011). These studies reported an increase of nutrient supply to the coastal ocean and the effects of pollution over ecosystems and primary productivity.

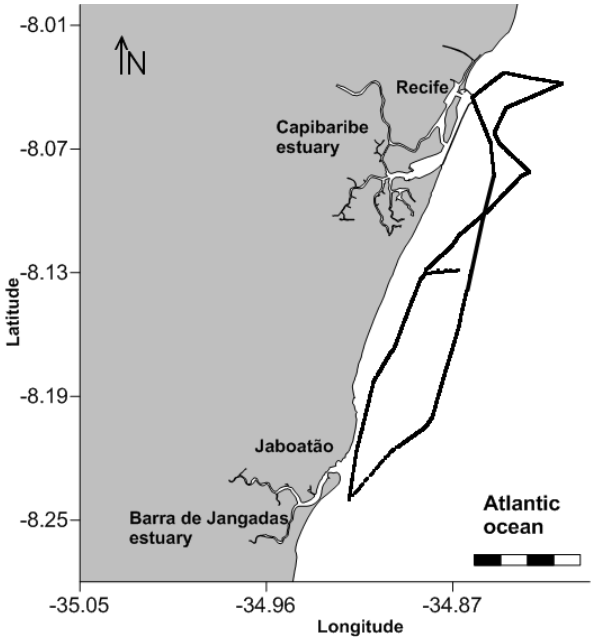
The climate of the MRR is tropical humid, or Am, according to the Köppen classification (PEEL *et al.*, 2007). The mean air temperatures are high throughout the year, ranging between 24°C and 29°C (Figure 2A). The rainy season occurs from May to July (Figure 2B) and concentrates about 50% of the total annual rainfall, which on average is greater than 2000 mm. Consequently, the months with the highest discharge are also from May to July (Figure 2D). The mean annual wind speed over the period from 1961-2014 is 2.70 ms^{-1} (Figure 2C) and the average for December 2014 was 1.9 ms^{-1}.

RESULTS

Salinity and temperature

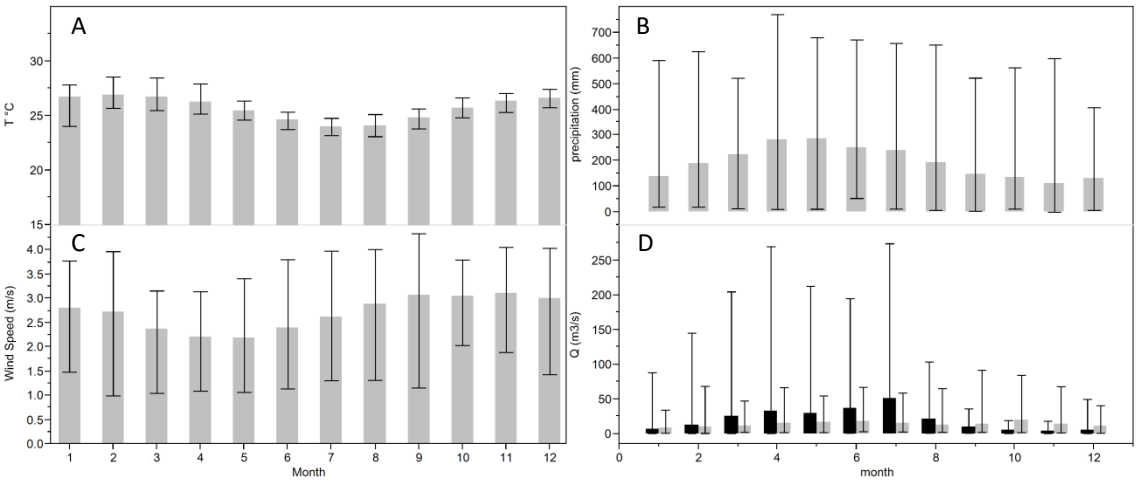
The spatial distribution of salinity is shown in Figure 3A. The areas with lower salinity (<35) correspond to the regions under the influence of riverine inputs. The lowest salinities are observed in front of the Capibaribe river mouth because of its increased discharge (2.35 m^3s^{-1}) when compared to that of the Barra de Jangadas (1.28 m^3s^{-1}) in December 2014. It is possible to identify a southward deflection of the water which exits the Capibaribe estuary due to the effect of the northeast wind which drives the current southward to the coast. In front of the Capibaribe estuary there is an artificial reef to protect the port area. This reef channels the water that exits the estuary. This explains why some water with salinity >35 can be observed so close to the river mouth.

Figure III.1: Map of the study area with the cruise track outside the port of Recife.



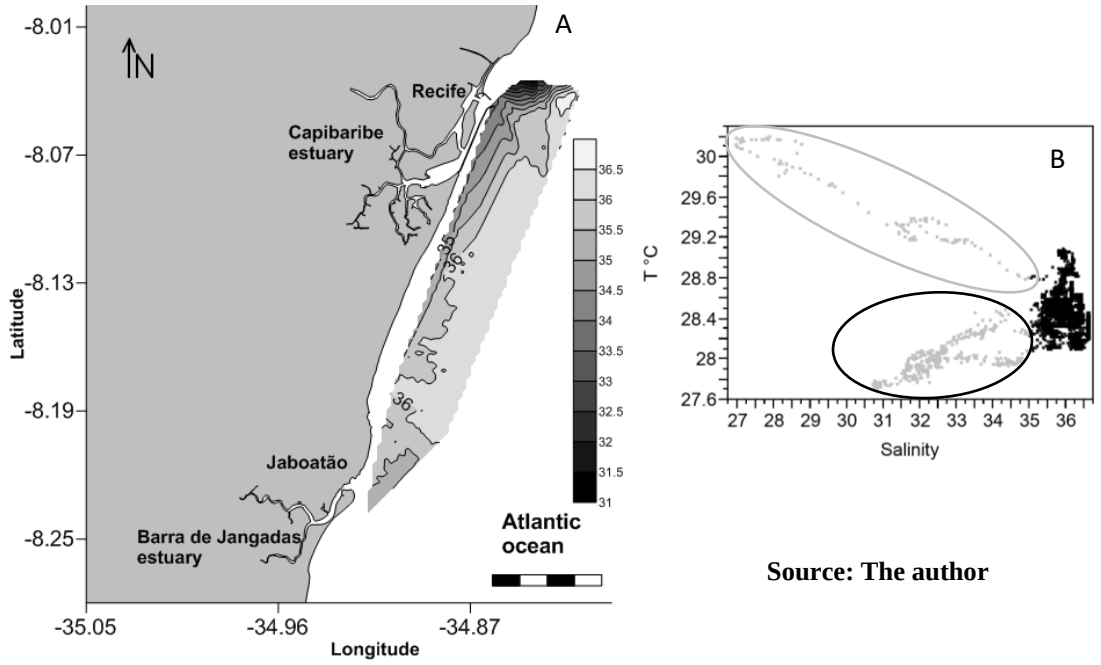
Source: The author

Figure III.2: Climatological means of (A) air temperature; (B) precipitation; (C) wind speed over the period 1961-2014 (D) river discharge over the period 1956-2014 for the Capibaribe estuary (black) and over the period 1986-2014 for the Barra de Jangadas estuary (gray). The error bars represent the range of the values.



The temperature-salinity diagram identifies the different water masses sampled during the cruise: water inside the port of Recife, the river plume and the nearshore coastal water (Figure 3B). The black ellipse represents the water mass inside the port during the flood to ebb tide at about 7 am (GMT -3), while the gray ellipse is the water mass inside the port during the ebb to flood tide at about 1 pm. These water masses inside the port were significantly different in temperature and salinity ($p<0.0001$, $\alpha=0.05$) as shown by the analysis of variance.

Figure III.3: (A) Sea surface salinity distribution in the area outside the port. (B) TS diagram with in gray the water masses inside the port and in the river plumes with salinity <35. The black ellipse is the water mass inside the port during the ebb tide and the gray ellipse is the water mass inside the port during the flood tide.



Source: The author

fCO_2 variability

The boat departed from the city of Recife and atmospheric and seawater fCO_2 were recorded underway. The atmospheric fCO_2 averaged 397.43 ± 1.6 µatm. The fCO_2 showed some spatial variability corresponding to the different continental influences. The area inside the port and close to the Capibaribe mouth showed very high fCO_2 values (Figure 4A). The highest fCO_2 were found in the port during the flood tide with values reaching up to 1400 µatm and associated with salinity <30.

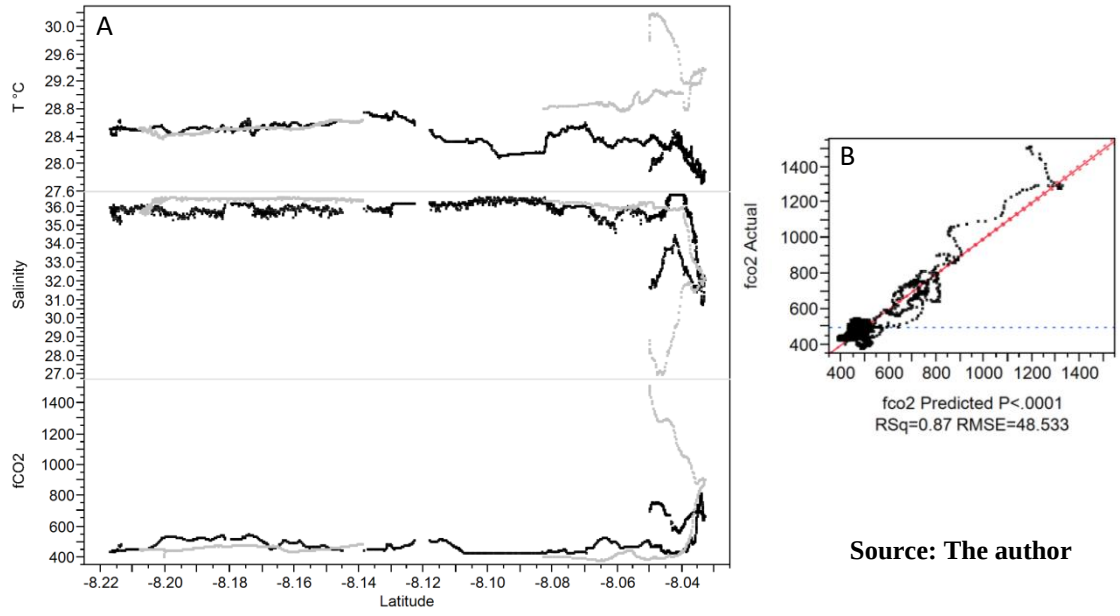
We found a good correlation between fCO_2, salinity and temperature (r^2=0.87) (Figure 4B):

$$fCO_2 = 743.93 + 90.18*T - 79.28*S \quad \text{(Eq. 6)}$$

This relationship is stronger than the one with salinity only (r^2=0.82).

The lowest fCO_2 values were found in the south part of the estuarine plume, during the way back to the port in salinities >34.5, when the minimum value of 376.6 µatm was registered (Figure 4A). In the inner shelf area, the average fCO_2 474.33 ± 66.57 (Figure 5A, C) was always above the equilibrium with the atmospheric fCO_2 of 390.41 ± 0.24 µatm. Such values resulted in a net mean flux of 8.5 ± 6.82 mmol C $m^{-2}d^{-1}$, and a median flux of 6.79 mmol C $m^{-2}d^{-1}$ (Figure 5 B).

Figure III.4: (A) latitudinal distribution of salinity, temperature and fCO_2. The black dots correspond to the data collected from the port of Recife to the Barra de Jangadas estuary, and the gray dots to the data collected in the port on the way back. (B) Observed fCO_2 as a function of calculated fCO_2 from the regression model. The 1:1 line is in red.



Source: The author

Tidal variations

The seawater fCO_2 values inside the port of Recife showed a significant difference between the tides. The highest fCO_2 values are associated with the lowest salinities. This suggests a stronger continental influence. The Table 1 summarizes the means ± sd of these parameters under different tidal stages inside the port.

Table III.1: Summary statistics of SST, SSS, fCO_2 and CO_2 fluxes inside the port of Recife in the lower portion of the Capibaribe estuary.

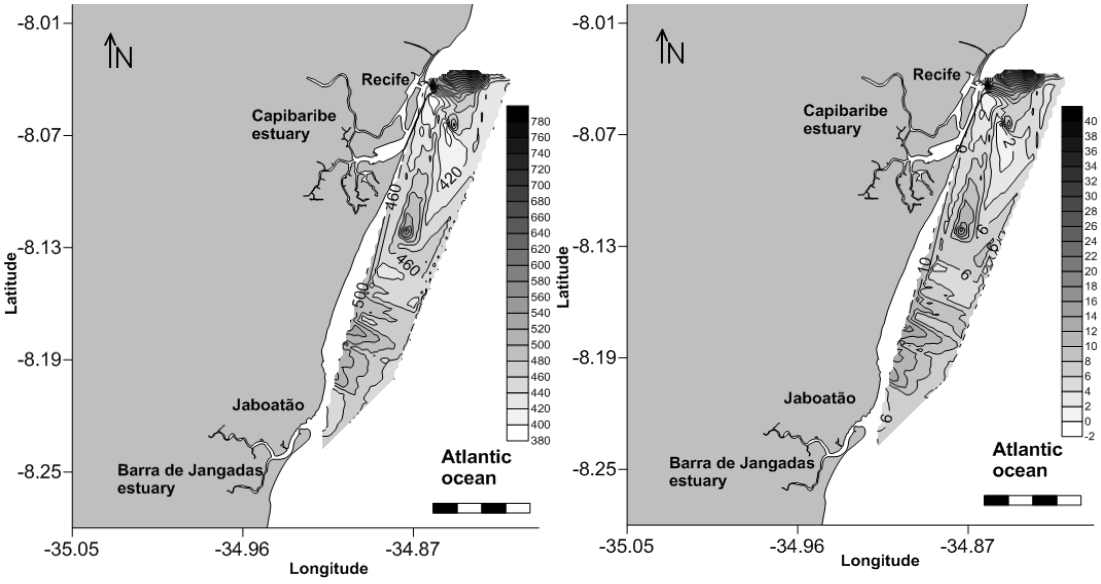
	overall	Ebb tide	Flood tide
SST (°C)	28.38 ± 0.7	28.00 ± 0.17	29.49 ± 0.43
SSS	32.19 ± 1.72	32.678 ± 1.121	30.895 ± 2.418
fCO_2 (µatm)	749.6 ± 224.4	659.1 ± 86.3	1002.1 ± 299.5
CO_2 flux (mmol $m^{-2}d^{-1}$)	28.1 ± 23.6	18.6 ± 8.9	54.7 ± 31.7

Source: The author

Chemical analysis

The spatial variability of dissolved oxygen (DO) is given in Figure 6A. The lowest OD values were found in the areas under riverine influence, in front of the Capibaribe estuary and especially in the south, close to the Barra de Jangadas estuary, where the minimum of 163 µmol Kg_{sw}^{-1} was registered. The average value of dissolved oxygen in the area was 188.8 ± 19.5 µmol Kg_{sw}^{-1} (Table 2).

Figure III.5: Spatial distribution over the inner shelf of seawater fCO_2 (A) and CO_2 fluxes (B).



Source: The author

The dissolved silica, total phosphorus and total nitrogen distributions are given in figure 6 B, C and D respectively. All these parameters showed higher concentrations in the river plumes, especially close to the Capibaribe estuary, where the highest values registered were 6.82 µmol Kg_{sw}^{-1} of dissolved silica; 1.37 µmol Kg_{sw}^{-1} of total phosphorus; 16.87 µmol Kg_{sw}^{-1} of total nitrogen. The average values of these parameters are summarized in Table 2.

With regard to the chl-*a* distribution, almost the whole area can be considered as oligotrophic (≤1.5 mg m^{-3}). However the mean value was calculated excluding two peak concentrations found in the Capibaribe estuarine plume with values of 8.77 and 3.34 mg m^{-3} (Figure 6E).

Table III.2: Average values ± standard deviation of the chemical analyses in the MRR inner shelf.

Parameter	average ± sd
DO µmol kg^{-1}	188.8 ± 19.5
$Si_2(OH)_4$ µmol kg^{-1}	4.38 ± 1.82
total P µmol kg^{-1}	0.74 ± 0.37
total N µmol kg^{-1}	11.54 ± 4.01
Chl-*a* mg m^{-3}	0.71 ± 0.57
TA µmol kg^{-1}	2350.6 ± 22.21

Source: The author

The alkalinity distribution was also controlled by the riverine inputs, with the highest values found in front of the Capibaribe estuary (Figure 6F); while the lowest values were registered in the southern area from Recife, close to the Barra de Jangadas estuary.

DISCUSSION

Salinity, dissolved oxygen and nutrients distribution

The river discharge of the Capibaribe was higher (2.35 m^3s^{-1}) than the Barra de Jangadas estuary (1.28 m^3s^{-1}). This was confirmed by the salinity distribution with salinity values around 30 close to the Capibaribe estuary. Close to the Barra de Jangadas the minimum salinity was as high as 35. Once these estuarine waters reach the shelf, the surface and bottom currents in this area, influenced by the northeast and east winds during

summer, have a tendency to transport the water and materials towards the coast, where the coast-parallel component of the current is mainly southward, with a northward direction in some areas (ROLLNIC *et al.*, 2011).

It is possible to identify this influence of the current over the distribution of salinity and the analyzed parameters in the study site (Figures 3 and 5). During the trajectory from the port of Recife to Barra de Jangadas, the boat was as close as possible to the coast, which is protected by a natural line of beachrocks about 1km seaward. The low salinity water that exits the Capibaribe can be observed in the area closer to the coast, with salinity values <35 (figure 3A). The core of the Barra de Jangadas estuarine plume was probably located south of the river mouth, driven by the predominant southward direction of the currents and, therefore, it was not sampled during this cruise.

The total phosphorus, total nitrogen and dissolved oxygen values give us an idea of the nutrient loading to the inner shelf by these estuaries, with lower oxygen, and higher concentrations of total phosphorus and nitrogen close to the Capibaribe (Figure 6). This confirms a seasonal estimate of organic load from these estuaries to the coast by Gaspar *et al.*, (in press), who through integration of the average flow and the biological oxygen demand ($BOD_{5,\ 20)}$ values (Q_{mean} x $BOD_{5,20mean}$), found a residual organic loading rate of 19.13 t $BOD_{5,\ 20}$ d^{-1} and 3.33 t $BOD_{5,\ 20}$ d^{-1} for the Capibaribe and Barra de Jangadas estuaries respectively. According to Noriega and Araújo (2009), the wastewater is the major source of nutrients to the coastal areas of the Northeast Brazil accounting for 51% of N and 45% of P among all natural and anthropogenic sources combined.

fCO_2, CO_2 flux, chl-a and alkalinity variability

From the inner port area to the river plume and the inner shelf we found a large variability of fCO_2 values leading to regions of source and sink of CO_2 to the atmosphere. The area of the port located in the lower Capibaribe estuary showed high fCO_2 and acted as a source of CO_2 to the atmosphere during the whole day.

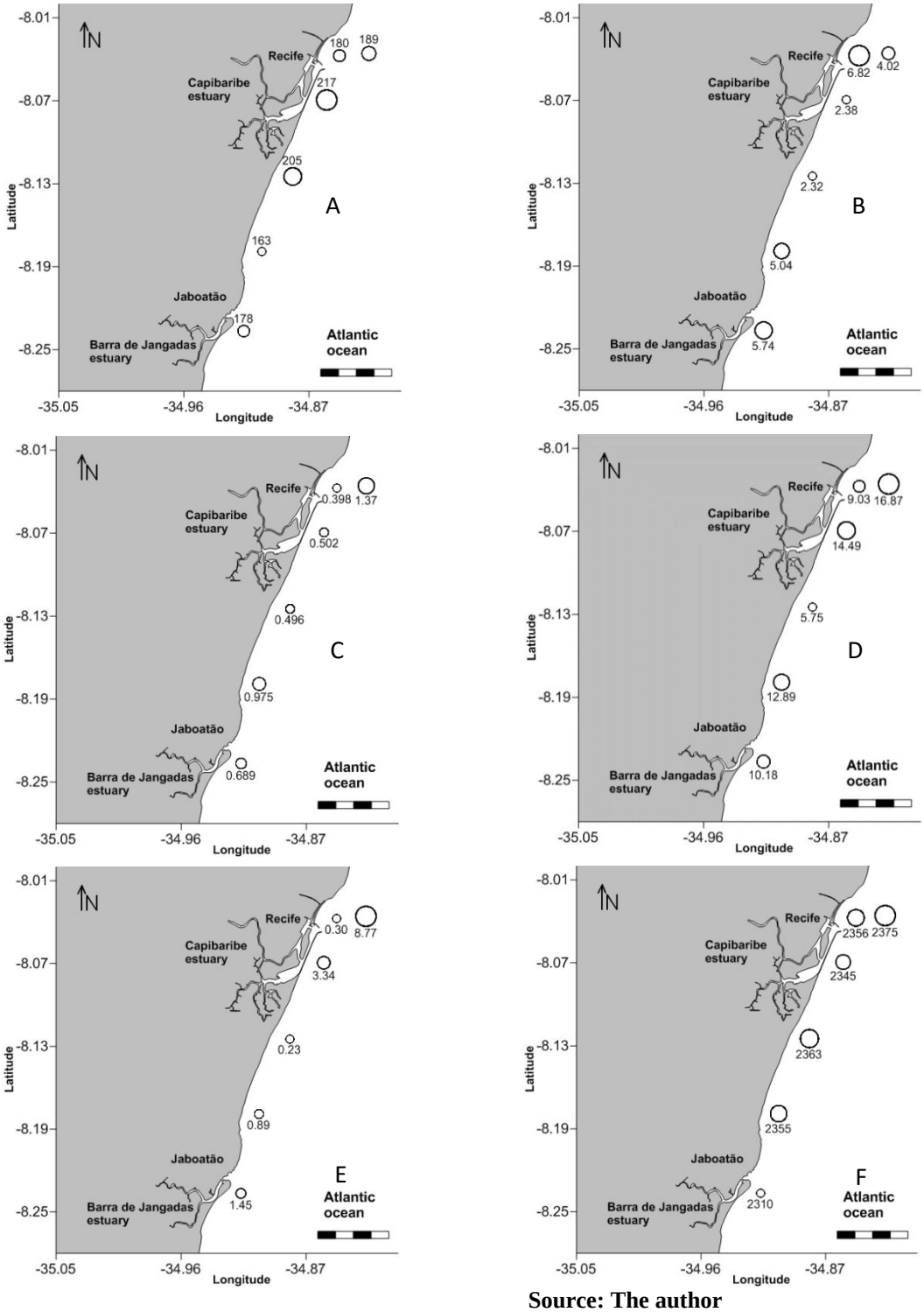
A negative correlation between salinity and fCO_2 was observed in the lower Capibaribe estuary (r^2= -0.77), such correlation indicates the typical pattern of increasing heteretrophy towards the upper estuary reported by Laruelle *et al.*, (2010) and Chen *et al.*, (2012) who compiled the pCO_2 data of several works on estuaries worldwide. Thus, during a tidal cycle the low salinity water, which arrives during ebb and low tides, reaches

the lower Capibaribe estuary and the inner shelf, enriched in CO_2. Such increase in the pCO_2 during low tides was also reported by Jiang *et al.*, (2008) when comparing different types of estuaries in the southeastern USA. In addition, the pCO_2 in water increases with increasing temperature. Moreover, it is reported a turbulence effect caused by the tidal currents and bottom stress, mainly in shallow estuaries, which may shift the CO_2 fluxes (RAYMOND; COLE, 2001; ZAPPA *et al.*, 2003, 2007)

The average fCO_2 (749.6 ± 224.4) and CO_2 flux (10.3 ± 8.6 mol C $m^{-2}y^{-1}$) are in accordance with the recent flux estimates of 9.92 ± 15.2 mol C $m^{-2}y^{-1}$ and pCO_2 of 692 ± 178 µatm for lower estuaries by Chen *et al.*, (2012). The values here reported are above the average pCO_2 value of 389 ± 112 µatm proposed by Noriega *et al.*, (2013) for the lower Capibaribe estuary, using TA and electrode pH for the calculation of the pCO_2 system parameters.

In the Capibaribe River plume, the high fCO_2 values slightly decreased seaward and were counterbalanced by an enhanced primary productivity, which decreased the fCO_2 values in small areas over the inner shelf (Figure 5A). The inner shelf was a net source of CO_2 to the atmosphere with higher fCO_2 values closer to the coast. The enhanced phytoplankton productivity was not enough to significantly counterbalance the CO_2 export from the estuary. Probably, the organic carbon transported to the inner shelf of the MRR is being respired there, increasing the fCO_2 values. In addition it is a shallow environment with depths around 12 m, and it is subjected to semidiurnal and mesotidal regime. Such characteristics helps to break the water column stratification and allows that the CO2 respired in the water column bottom to be released in the seawater surface.

Figure III.6: Spatial distribution of (A) dissolved oxygen (µmol.Kg$_{sw}$); (B) dissolved silica (C) total phosphorus (µmol.Kg$_{sw}$); (D) total nitrogen (µmol.Kg$_{sw}$); (E) chlorophyll-*a* (mg.m^3); (F) total alkalinity (µmol.Kg$_{sw}$).



Source: The author

Usually, continental shelves sustain a relatively high level of biological productivity which may decrease the CO_2 concentrations (JIANG *et al.*, 2013). The importance of the Capibaribe river to sustain the productivity over the inner shelf was previously reported by Resurreição, *et al.*, (1996) and Otsuka *et al.*, (in press). Recent studies suggest that the increased human-induced nutrient loading may have enhanced the primary productivity and consequently the CO_2 uptake in the inner shelf of the Changjiang Estuary (CHOU *et al.*, 2013) and in a semi-enclosed embayment estuary at the Guanabara Bay - Brazil (COTOVICZ *et al.*, 2015). Similarly, Gypens *et al.*, (2009) developed a model for the Scheldt estuary plume and found that the system could have changed its metabolic status from heterotrophic to autotrophic due an increased anthropogenic nutrient input, which stimulated the primary productivity.

However, such increased CO_2 uptake due to eutrophication may be counterbalanced by the heterotrophy supported by direct riverine inputs of CO_2 and organic carbon (SMITH; HOLLIBAUGH, 1993; RAYMOND *et al.*, 2000; JIANG *et al.*, 2008) and tidal exchange with intertidal marshes and mangroves (BORGES, 2003; WANG; CAI, 2004). Low latitude coastal oceans (0-30°) are considered sources of CO_2 to the atmosphere because they receive 2/3 of the organic carbon transported by rivers (BORGES *et al.*, 2005). Tropical estuaries which receive low quantities of freshwater tend to be the main site of the organic carbon respiration, because of the increased microbial activity related to higher temperature, resulting in less organic carbon export when compared to fast transit rivers (CAI, 2011b).

The high alkalinity freshwater from the Capibaribe may constitute an additional buffer to counterbalance the effects of the ocean acidification led by the organic carbon oxidation in subsurface. According to Gaspar *et al.* (in press) during summer, there is enrichment on the HCO_3^- concentrations inside the Capibaribe estuary due an increased residence time and they also pointed out a relative increase of HCO_3^- in the inner shelf close to the Capibaribe plume, compared to Barra de Jangadas.

The average flux of 3.1 molC $m^{-2}y^{-1}$ for the inner shelf of the MRR is above the global mean of 0.9 ± 1 molC $m^{-2}y^{-1}$ for tropical open shelf environments proposed by Laruelle *et al.*,(2010), which was calculated excluding nearshore environments.

CONCLUSION

The development of a CO_2 system led to the first underway fCO_2 measurements in the tropical inner shelf of Northeast Brazil from the city of Recife to Jaboatão dos Guararapes between the latitudes -8.01 to -8.25. Although the cruise spanned less than 1º of latitude a strong fCO_2 variability was observed in surface water. The Capibaribe lower estuary acts as a permanent source of CO_2 to the atmosphere and are above the previous estimative for the area which relied in electrode pH and TA for pCO_2 calculation. The highest fCO_2 values are related to lower salinities and elevated temperatures, being modulated by tidal oscillations.

The fCO_2 in the nearshore area is being enhanced by the riverine transport of inorganic and organic carbon. The primary productivity in the area is sustained by the nutrient inputs from the rivers to the oligotrophic tropical shelf. However such planktonic productivity is not enough to significantly decrease the fCO_2 in the seawater to undersaturation state in relation to the atmosphere.

The CO_2 distribution was obtained in December when the river discharge is quite low. The mean flux of 3.1 molC $m^{-2}y^{-1}$ for the inner shelf of the MRR is higher than available estimates for tropical open shelf environments. There might be an underestimation of the global CO_2 emissions due to the scarce CO_2 database in tropical, shallow, nearshore environments. However, further studies are necessary to cover a more extensive area and identify spatial and seasonal patterns of the fCO_2 distribution over the Brazilian continental shelf.

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9 MANUSCRITO 3

Artigo a ser submetido para a Regional Climate Change (ANEXO III)

CO_2 SYSTEM PARAMETERS ON RIVERINE AND MARINE DOMINATED CONTINENTAL SHELF OF PERNAMBUCO, BRAZIL.

ABSTRACT

The continental shelves of tropical environments are considered sources of CO_2 to the atmosphere, but there are still very few data for this area. This study aimed to assess the spatial and seasonal variability of the carbonate parameters over the Pernambuco state's continental shelf, by the analysis of total alkalinity (TA) and total inorganic carbon (TCO_2) in river and marine dominated sections of the Pernambuco state continental shelf. The TCO_2 spatial distribution was similar to all studied areas with an overall mean of 2057.9 ± 21.9 µmol kg^{-1}. Nevertheless, it showed a seasonal variability with the lower values occurring during the wet season for the inner shelf stations. The pCO_2 was higher in the riverine section with average of 463.8 ± 72.2 µatm, while the lowest values were registered in the shelf break with average of 412.8 ± 8.6 µatm. The pCO_2, pH and TCO_2 showed seasonal variabilities only in the riverine inner shelf section, with lower pCO_2 and TCO_2 and higher pH during the wet season, owing to the increased fluvial discharge and its influence over the proximal shelf. The thermal stability and the shallow depths of the continental shelf seems to be the main mechanism which keeps the elevated pCO_2, while the direct transport of CO_2 by the rivers are restricted to the proximal area of the river mouths. The correlation with the longitude used on the models may explain the interference of parameters not measured during the study, such as biological activity, turbulence and waves. Despite high pCO_2, the high alkalinities above 2300 µmol kg^{-1} are found close to the river mouths, which may constitute an additional buffer to the ocean acidification process in the area.

Keywords: Biogeochemical models; ocean acidification; tropical coastal environments

RESUMO

As plataformas continentais de ambientes tropicais são consideradas fontes de CO_2 para a atmosfera, mas ainda há muito poucos dados para estas áreas. Este estudo teve como objetivo avaliar a variabilidade espacial e sazonal dos parâmetros de carbonato na plataforma continental do estado de Pernambuco, por meio da análise de alcalinidade total

(TA) e carbono inorgânico total (TCO_2) no rio e em seções marinhas da plataforma continental do estado Pernambuco. A distribuição espacial do TCO_2 foi semelhante a todas as áreas estudadas com média global de 2.057,9 ± 21,9 umol kg^{-1}. No entanto, ele mostrou uma variabilidade sazonal, com os valores mais baixos ocorrendo durante a estação chuvosa para as estações na plataforma interna. A pCO_2 foi maior na seção fluvial com média de 463,8 ± 72,2 μatm, enquanto os menores valores foram registrados na quebra da plataforma com média de 412,8 ± 8,6 μatm. A pCO_2, o pH e o TCO_2 mostraram variabilidades sazonais somente na seção plataforma interna ribeirinha, com menor pCO_2 e TCO_2 e pH mais elevado durante a estação chuvosa, devido ao aumento da descarga fluvial e sua influência sobre a plataforma proximal. A estabilidade térmica e as profundidades rasas da plataforma continental parecem ser os principais mecanismos que mantém a pCO_2 elevada, enquanto o transporte direto de CO_2 pelos rios estão restritos à área proximal das bocas dos rios. A correlação com a longitude utilizada nos modelos pode explicar a interferência de parâmetros não medidos durante o estudo, como atividade biológica, turbulência e ondas. Apesar da alta pCO_2, as altas alcalinidade acima de 2,300 mol kg^{-1} são encontrados perto das bocas de rio, que podem constituir um tampão adicional para o processo de acidificação do oceano na área.

Palavras-chave: modelos biogeoquímicos; acidificação oceânica; ambientes costeiros tropicais.

INTRODUCTION

The coastal oceans are considered areas with intense biogeochemical activity, which links fluxes of energy and matter between land, the open ocean and the atmosphere (THOMAS *et al.*, 2009). Despite the great variability of partial pressure of carbon dioxide (pCO_2) in coastal oceans, the actual global CO_2 fluxes estimates are based on literature compilations with insufficient data to cover the full spatial extent of the coastal ocean adequately and the diversity of biogeochemical carbon cycling related to contrasting physical and biogeochemical settings (BORGES, 2011).

It is expected that the absorption of atmospheric CO_2 in coastal zones may be minor compared to the input of all land-derived materials, particularly within eutrophic regions where excessive nutrient loading and organic matter production have been associated with large hypoxic events (WALLACE *et al.*, 2014). Compared to distal

continental shelf areas, the proximal shelf usually exhibits much steeper biogeochemical gradients. Therefore, higher resolution surveys are warranted to understand the biogeochemical processes on inner shelf environments (JIANG *et al*., 2013).

Despite of the large area represented by the Brazilian continental shelf, it is still neglected by the scientific community and there is a huge lack of knowledge on what concerns the carbon biogeochemical cycle. Recent studies in the Brazilian coast have shown that estuaries in north and northeast Brazil are net sources of CO_2 to the atmosphere throughout the year (NORIEGA; ARAUJO, 2014; GASPAR *et al.* (in press). While in southeast Brazil an estuarine embayment acts as a sink of atmospheric CO_2 enhanced by eutrophication (COTOVICZ *et al.*, 2015).

Here, we assessed the spatial and seasonal variability of the carbonate parameters over the Pernambuco state's continental shelf, by the analysis of total alkalinity and total inorganic carbon (TCO_2) in river and marine dominated sections of the continental shelf in order to provide reliable data for the regional and global biogeochemical models and carbon budgets. Regional empiric biogeochemical models were developed to identify long term trends and patterns of the pCO_2 variability in large temporal scale.

METHODS

Study site

The study area is located in the eastern portion of the Brazilian continental shelf (Figure 1) which encompasses the Pernambuco state between the latitudes -7.5 to -9.0 in northeastern Brazil. The continental shelf in this area is relatively narrow and shallow, with ≈ 35km wide, 50–65 m deep and has a steep continental slope ≈ 1:600 (MANSO *et al.*, 2004). The bottom is covered by large areas of benthic macrophytes until the 10 m isobath. There are also more than 300 species of benthonic macroalgaes spread until the shelf break, with predominance of calcareous algaes from the genre *Halimeda* and *Melobesiacea* (ESKINAZI-LEÇA *et al.*, 2004). Sediments in this area are mainly in-situ biogenic carbonates and, at a less extent, continental terrigenous and relict sediments (MARQUES *et al.*, 2008).

The surface hydrography of the outer shelf (> 40 m deep) area is dominated by the northward flowing South Atlantic boundary current (North Brazil Current, NBC).

Starting at around 10° S as a relatively weak current (North Brazilian Undercurrent " NBUC), the NBC is mainly supplied by South Equatorial Current (SEC) waters and its flow is closely connected to the shelf edge (PETERSON; STRAMMA, 1991)

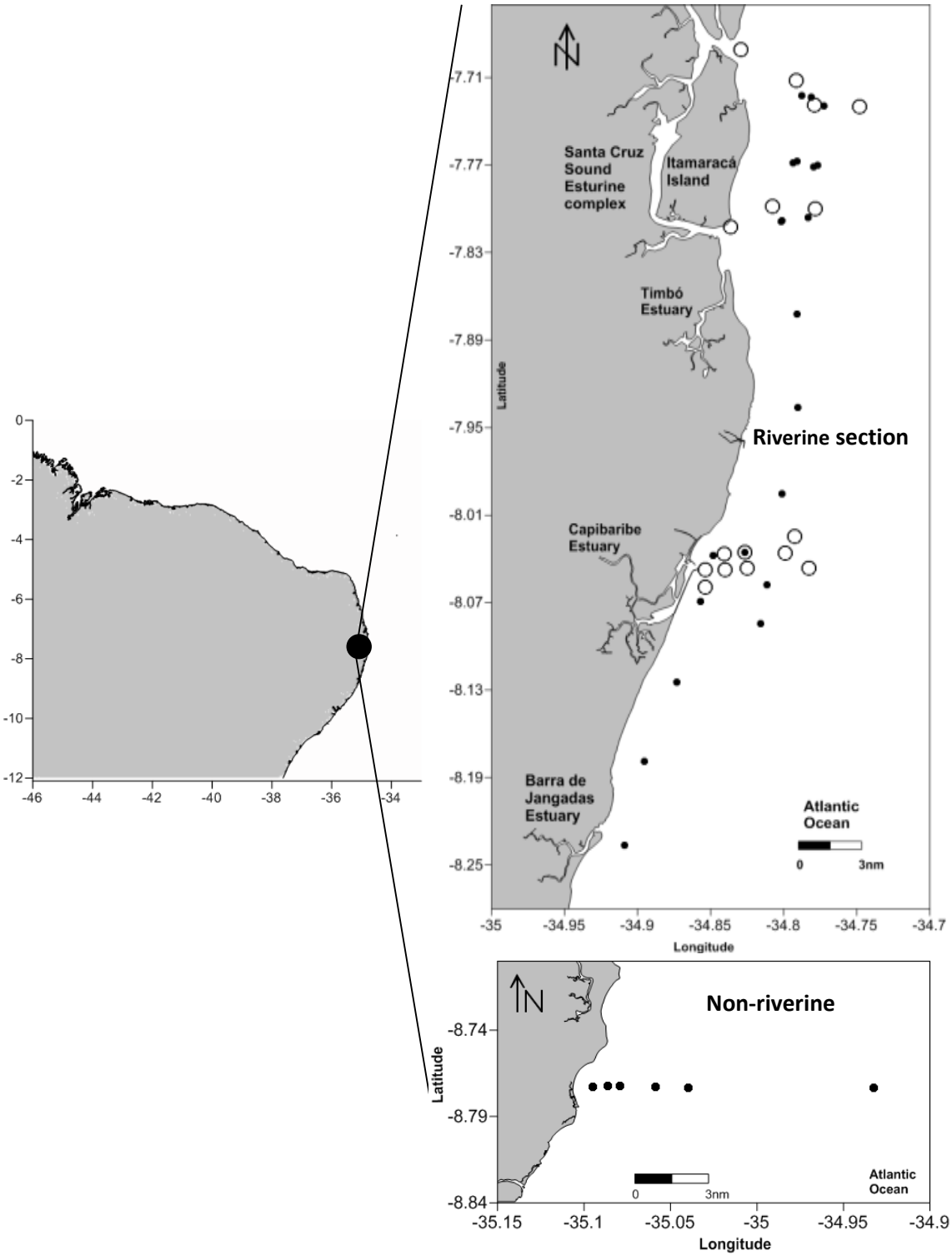
The northeastern Brazilian continental shelf waters present a mean annual sea surface temperature (SST) of ≈ 27° C and the seasonal amplitude is in the order of ≈ 2°C, while the average sea surface salinity (SSS) is around 36 (MACEDO *et al.* 2004).

The inner shelf (<20m) circulation is more influenced by the seasonality of the wind regime and thus wave climate. During the rainy season, when the prevailing winds are stronger, steadier and from SE, the near-shore net transport in the entire water column is mainly northwards. On the other hand, during the dry season, the winds are more variable and blow mainly from NE-E, with a prevailing net transport of the surface water to the south with a not well clear pattern near the bottom. The area also experiences semi-diurnal tides, with a mean range of 1.67m, a neap tide range of 0.97m, and a spring tide range of 2.07m. In addition to the tidal cycles, reef lines are present in the nearshore which further modifies the coastal circulation, reflecting, attenuating or increasing the net transport of water and materials (ROLLNIC *et al.*, 2011).

The city of Recife is the capital of the Pernambuco state and, along with its metropolitan region, it is considered the 6th most populated area of Brazil with approximately 3,743,854 inhabitants and a population density of about 1,352.53 inhabitants / km^2 (IBGE, 2010).

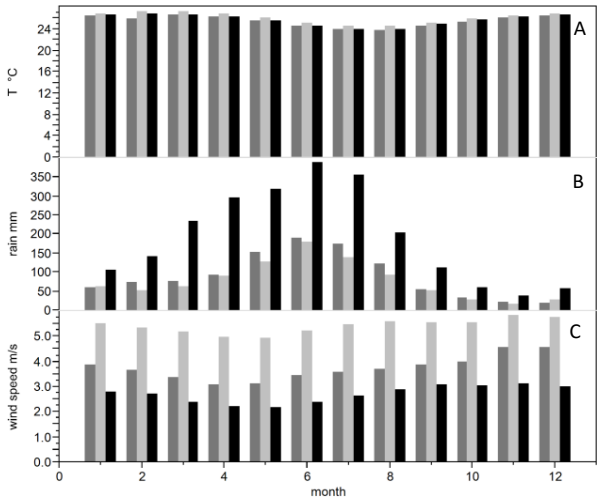
The climate of the Metropolitan Region of Recife (MRR) is tropical humid, or Am, according to the Köppen classification (PEEL *et al.*, 2007). The mean air temperatures are high throughout the year, ranging between 24°C and 29°C (Figure 2A). The wet season occurs from May to July (Figure 2B) and concentrates about 50% of the total annual rainfall, which on average is greater than 2000 mm. Consequently, the months with the highest rivers discharge are also from May to July.

Figure IV.1: Map of the study site with the location of the sampling stations. Riverine area- full markers represents dry season; Non-riverine: same transect during wet and dry season).



Source: The author

Figure IV.2: monthly average temperature (A), precipitation (B) and wind speed (C) for the south coast (dark gray), north coast (light gray) and the central coast (black) of the Pernambuco state.



Source: The author

Sampling

The outter shelf samples were taken in 2012 during a cruise aboard the Research Vessel Cruzeiro do Sul of the Brazilian navy. The sampling was held in two transects parallel to the coast, over the shelf break area (Figure 1). For the inner shelf evaluation the sampling was conducted in three different locations over the Pernambuco shore.

The northern section (Itamaracá Island) is strongly influenced by inputs from an estuarine complex with approximately 100 Km^2, with extended areas of mangrove and some Atlantic forest reminescents. The central section, close to the city of Recife, is influenced by the largest river of the area (Capibaribe river) which receives substantial amounts of wastewater from the MRR. In addition, there is the Barra de Jangadas estuary which also receives wastewater from MRR, but still preserves large mangrove areas.

The sampling campaigns in these two areas were conducted in July 2013 and October 2013 in front of Recife and Itamaracá (Figure 1). In December 2014 an alongshore sampling was held from Itamaracá down to the Barra de Jangadas estuary (Figure 1).

The southern sampling area was located inside the no-take zone from the marine protected area “Costa dos Corais”, in the city of Tamandaré, an area rich in coral reefs where riverine inputs are negligible. The sampling was held bimonthly from April 2013

to March 2014, comprising a seasonal cycle; in a transect perpendicular to the coast (Figure 1).

Chemical analysis

The samples for the simultaneous determination of TCO_2 and TA were preserved with $HgCl_2$ and sent to analysis in the Laboratoire d´Océanographie et du Climat: Expérimentation et Approches Numériques – LOCEAN, Service National d'Analyse des paramètres Océaniques du CO_2 - University Pierre et Marie Curie - France. The analysis was performed according to the titration methodology reported by Edmond, (1970) and the equivalence points were calculated according to Doe (1994). The reproducibility of the method was tested against certified reference materials for DIC and TA seawater measurements from the Scripps institute with ± 3 μmol kg^{-1} for both parameters.

CO_2 solubility in the water was calculated according to Weiss (1974). The pCO_2 and saturation states of calcite (ΩCa) and aragonite (ΩAr) were calculated with the CO_2SYS macro, using TA, TCO_2, temperature, salinity, total phosphorus and reactive silica data. We used the dissociation constants of carbonic acid according to (MILLERO *et al.*, 2006), and the dissociation constants of sulfate according to Dickson (1990).

Samples for analysis of total phosphorus and silica were collected and kept in a cool box, then stored frozen for analysis The precision and accuracy of the method is respectively 0.1 μmol kg sw^{-1} and 0.5% for the TP and 2 μmol kg sw^{-1} and 1% for the silicate.

in the Laboratory of Chemical Oceanography of the Federal University of Pernambuco – Recife, Brazil. The sea surface temperature (SST) and salinity (SSS) values were obtained with CTD.

Statistics

A *Kolmogorov-Smirnov* test was performed to check the normality of the data and the *Levene* test the homoscedasticity of the variances. It was assumed a significance level of 0.05. When the data showed a normal distribution with equal variances we used the analysis of variance, ANOVA to examine the seasonal and spatial variation in the carbonate chemistry parameters. When the data did not follow a normal distribution, we used the Kruskall-Wallis test.

RESULTS

Due to the difference in freshwater discharge along the Pernambuco state coast, it was considered the north and central areas as riverine region and the south as non-riverine. The salinities registered in the transect located in the non-riverine region were very similar to the shelf break stations, with average values of 36.4 ± 0.57 and 36.53 ± 0.09 respectively (mean ± sd). In the other hand, the freshwater inputs to the coastal area of the riverine section decreased the SSS annual mean to less than 36. The annual and seasonal means of SST, SSS, TA, TCO_2, pCO_2, pH, ΩCa and ΩAr for the riverine, non-riverine and shelf break areas are summarized in Tables 1 and 2.

TableIV.1: overall average ± standard deviations for the analyzed parameters. * p<0.05 among locations.

	Riverine *n=34*	Non-riverine *n=30*	Shelfbreak *n=6*	Overall *n=70*
SSS	35.82 ± 0.76*	36.41 ± 0.56	36.53 ± 0.09	36.14 ± 0.71
SST °C	27.59 ± 0.86*	28.28 ± 1	26.23 ± 0.13	27.78 ± 1.05
TA µmolkg^{-1}	2358 ± 28*	2385 ± 31	2390 ± 3	2373 ± 31
TCO_2 µmolkg^{-1}	2050 ± 21	2061 ± 18	2064 ± 3	2056 ± 19.9
pCO_2 µatm	456 ± 56.3	449.6 ± 30.2	412 ± 8.6	449.5 ± 45
pH $_{sw}$	7.995 ± 0.043	8.00 ± 0.02	8.033 ± 0.007	8.00 ± 0.03
ΩCa	5.2 ± 0.4	5.5 ± 0.3	5.5 ± 0.1	5.4 ± 0.3
ΩAr	3.5 ± 0.2	3.7 ± 0.2	3.6 ± 0.06	3.6 ± 0.2

Source: The author

The SST between riverine and non-riverine sections was significantly different (ANOVA, p=0.0132), the non-riverine section was the warmest area with annual average temperature of 28.28 ± 1°C, followed by the riverine section and the shelf break (Table 1). There were also significant seasonal variabilities in SST and SSS over the inner shelf sections with the highest values of both parameters occurring during the dry season (Table2).

The alkalinity showed a good correlation with salinity r^2= 0.81, the lowest values were found at the riverine section, with average value of 2358 ± 28 µmol kg^{-1} and was significantly different in relation to the non-riverine (ANOVA, p=0.0004) and shelf break area (ANOVA, p=0.0162) (Table 1). The average for the non-riverine section was 2385 ± 31 µmol kg^{-1} and did not differ from the shelf break. As the alkalinity was correlated with SSS, it also followed the same seasonal pattern with significantly lower TA during

the wet season, as seen by the seasonal comparisons of the non-riverine (p=0.0008) and riverine (p=0.0001) sections respectively (Table 2). The values of ΩCa and ΩAr followed the alkalinity distribution and were lower in the riverine section during the wet season (Table 2).

Table IV.2: Seasonal average values ± standard deviation of the analyzed parameters in the shelf break (outer shelf), the riverine and non-riverine inner shelf sections. * p<0.05 between seasons.

	Inner shelf			
	Riverine Section		Non-riverine Section	
	dry *n=22*	wet *n= 12*	dry *n= 20*	wet *n=10*
SSS	36.15 ± 0.49*	34.26 ± 2.43	36.69 ± 0.45*	35.83 ± 0.3
SST °C	28.16 ± 0.52*	26.61 ± 0.21	28.63 ± 0.97*	27.59 ± 0.71
TA µmolkg^{-1}	2370± 24*	2334 ± 21	2393 ± 30*	2365 ± 22
TCO_2 µmolkg^{-1}	2065± 16*	2027± 7	2064 ± 19*	2053.5 ± 12.6
pCO_2 µatm	475.3 ± 60.6*	420.5 ± 19.4	450.8 ± 34.6	447.8 ± 22.6
pH_{sw}	7.98 ± 0.04	8.02 ± 0.02	8 ± 0.03	8 ± 0.02
ΩCa	5.2 ± 0.5	5.26 ± 0.26	5.59 ± 0.28*	5.34 ± 0.22
ΩAr	3.47 ± 0.35	3.48 ± 0.18	3.74 ± 0.19*	3.55 ± 0.15

Source: The author

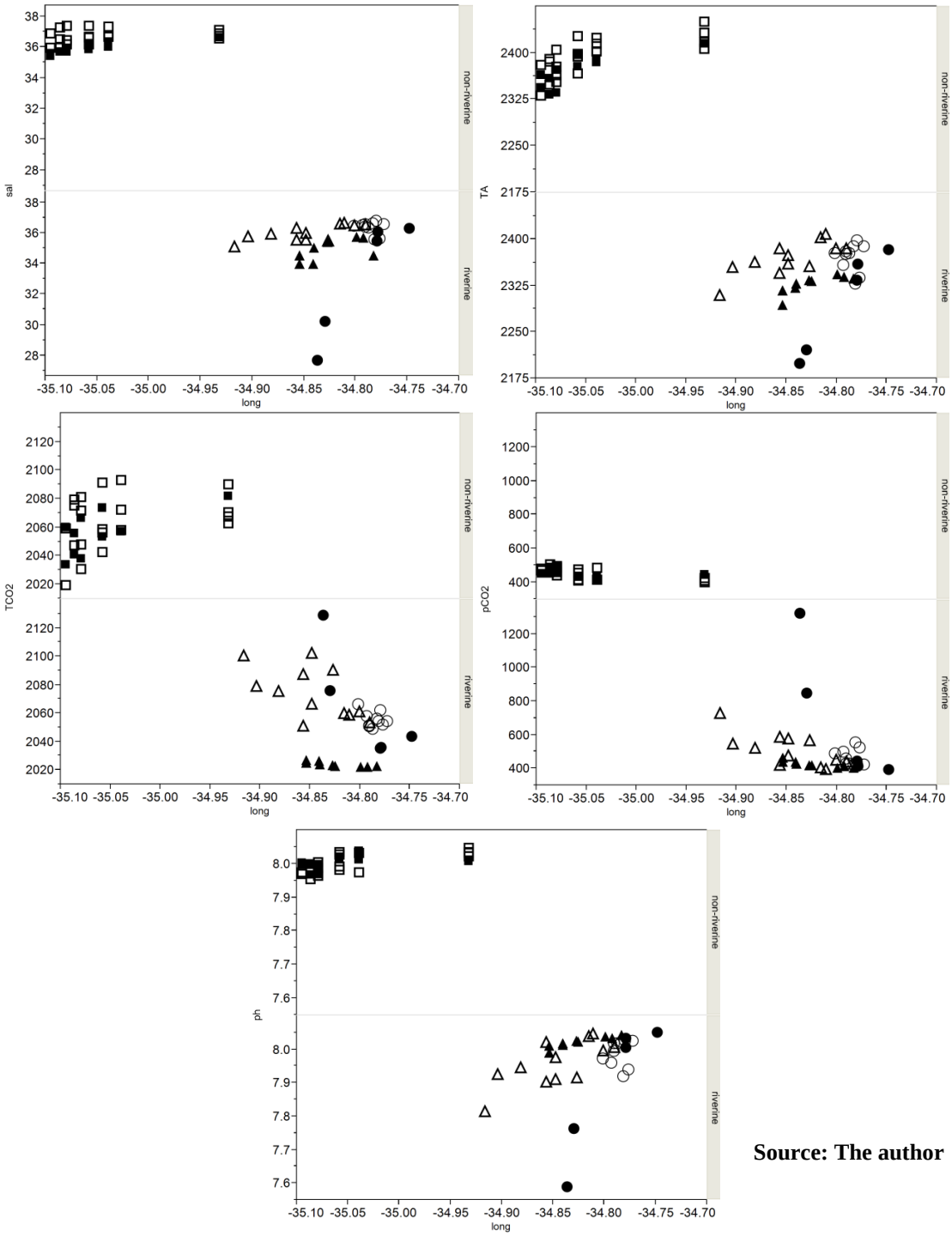
The TCO_2 spatial distribution did not differed between locations (p>0.05) with an overall mean of 2057.9 ± 21.9 µmol kg^{-1}. However, it showed a seasonal variability (ANOVA, p <0.0001) with the lower values occurring during the wet season at the inner shelf stations (Table 2).

The pCO_2 was higher in the riverine section with an average of 456 ± 56.3 µatm, while the lowest partial pressures were registered in the shelf break with an average of 412.8 ± 8.6 µatm. However no significant difference among areas was identified because of the high variability of pCO_2 in the riverine area. The pH distribution followed the pCO_2 and was lower in the riverine section 7.99 ± 0.05, and decreased toward the shelf break 8.033 ± 0.007. There was no annual significant difference between riverine and non-riverine sections of pCO_2, pH and TCO_2 (Table 1). However, these parameters showed seasonal variabilities only in the riverine inner shelf section, mainly due to the variability in the stations located closer to the coast, with lower pCO_2 (K-W, p= 0.0044), TCO_2 (p<0.0001) and higher pH (p=0.0074) during the wet season, due the increased fluvial discharge and its influence over the proximal shelf (Table 2).

Longitudinal distribution

The SSS and TA increased with longitude (Figure 3) in both studied sections. However, the TCO2 showed a different distribution between areas, it increased towards the ocean in the non-riverine section and conversely in the riverine section. The pCO_2 values in both shelf sections decreased with longitude, the Figure 3 summarizes the longitudinal distribution of all analyzed parameters.

Figure IV.3: Longitudinal distribution of SSS, TA µmol kg^{-1}, TCO_2 µmol kg^{-1}, pCO_2 µatm pH_{sw}. (Triangles represent Recife, circles Itamaracá and squares Tamandaré. Full markers represent the wet season).



Source: The author

All the seasonal predictive models are presented in Figure 4 for the riverine inner shelf section and Figure 5 for the non-riverine area; the equations are summarized in Table 3.

Table IV.3: Predictive seasonal equations for the estimation of TA µmol kg^{-1}, TCO_2 µmol kg^{-1}, pH seawater, pCO_2 µatm, ΩCa and ΩAr in riverine and non-riverine inner shelf sections of the Pernambuco coast.

	Dry season	Wet season
Riverine inner shelf section		
TA =	-2485.277 +44.7457*S -13.779*T -104.128*long	9963.401 +18.551*S +7.956*T +243.984*long
TCO_2=	-3516.603 -16.323*S – 4.056*T -180.546*long	14166.013 +13.066*S -11.349*T +326.843*long
pCO_2 =	-4569 -124.994*S +28.787*T -251.765*long	53836.584 -111.528*S -153.183*T +1304.819*long
pH =	5.24 +0.097*S -0.028*T	-12.92 +0.0562*S +0.044*T -0.511*long
ΩCa =	-25.932 +0.977*S -0.149*T	-18.816 +0.436*S +0.329*T
ΩAr =	-17.795 +0.657*S -0.088*T	-12.743 +0.292*S +0.223*T
Non-riverine inner shelf section		
TA =	9286.824 +51.976*S -6.674*T +245.676*long	45634.583 -30.252*S -20.943*T +1186.355*long
TCO_2=	697.814 +41.554*S -5.536*T	1702.855 + 17.764*S -10.359*T
pCO_2 =	-12779.532 +9.960*S +17.428*T -352.887*long	-64613.339 +82.753*S +28.405*T -1748.202*long
pH =	19.507 -0.002*S -0.016*T +0.313*long	65.652 -0.072*S -0.027*T +1.549*long
ΩCa =	130.888 +0.143*S -0.014*T +3.714*long	637.351 -0.690*S -0.143*T +17.203*long
ΩAr =	86.55 +0.1*S +0.004*T +2.471*long	421.777 -0.449*S -0.081*T +11.403*long

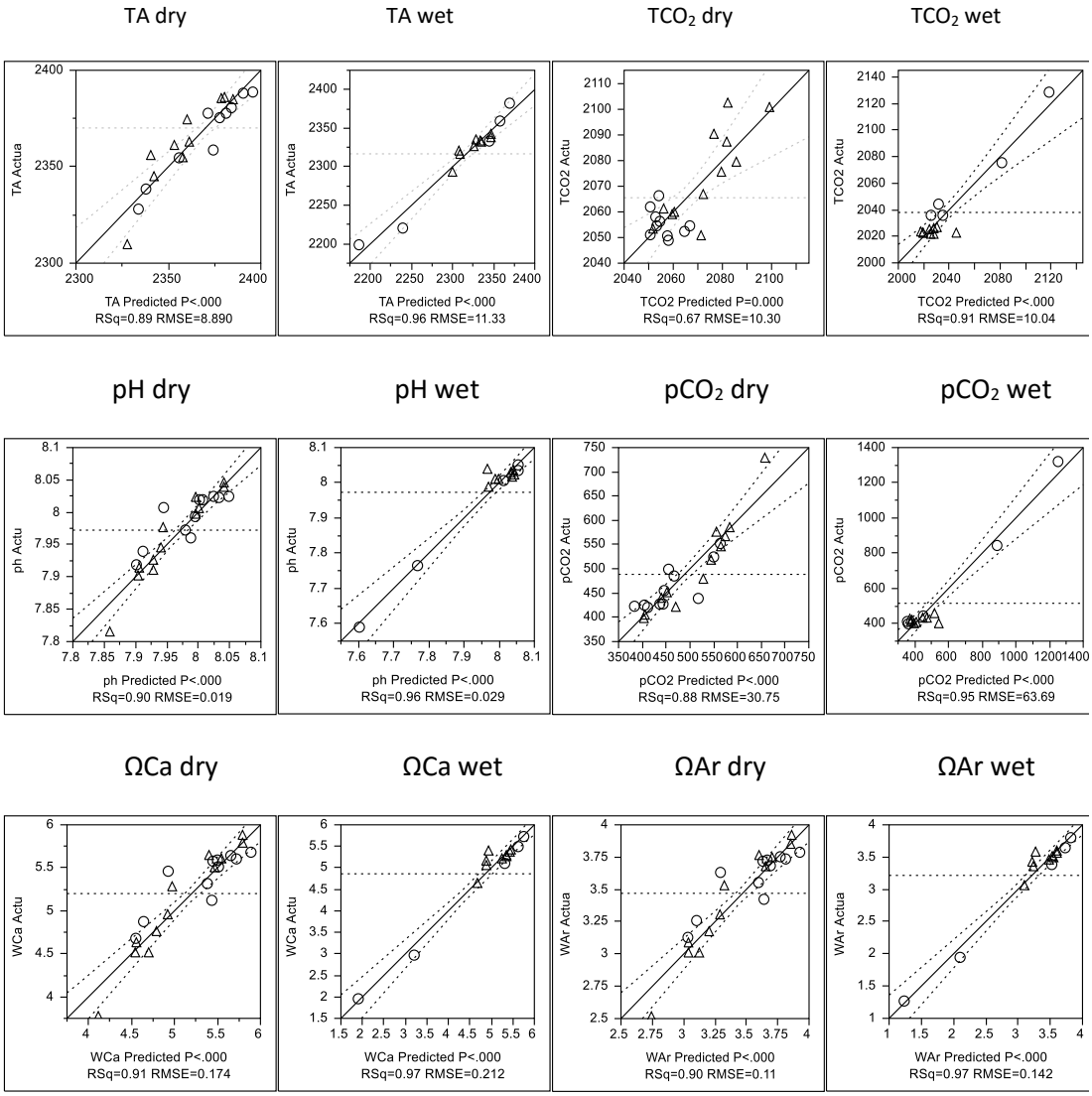
Source: The author

DISCUSSION

The TCO_2 in the non-riverine inner shelf section accompanied the salinity variability and was less subjected to external inputs of inorganic carbon. The predominance of the oceanic influence over this area resulted in the development of a good model only with thermodynamic parameters to explain its variability in both seasons. In the other hand, the riverine shelf section showed a different pattern, decreasing with longitude, similarly to the one reported by Jiang *et al.* (2013).

Most of the parameters showed better correlation with SST, SSS and longitude than with SSS and SST only. The use of the longitude in the most part of the models here proposed seems to compensate the riverine inputs, the biological activity, as well as the tidal mixing in the inner shelf of Pernambuco. It is reported that exists strong region-specific relationships between marine inorganic carbon and hydrographic (SSS, SST) and/or biological (e.g. nutrients, chl-*a*) parameters (LEE *et al.*, 2008). In this way, the relationship with longitude for the Pernambuco coast turns to be an easier short-term option for researchers who evaluate ecological implications without the need of further chemical analysis. However, this kind of approach must be improved with the discovery of the real drivers of the inorganic carbon variability in the nearshore.

Figure IV.4: Seasonal prediction models of the TA µmol kg^{-1}, TCO_2 µmol kg^{-1}, pH seawater, pCO_2 µatm, ΩCa and ΩAr, for the riverine shelf sections as a function of SSS, SST and longitude. The solid line is the 1:1 value.



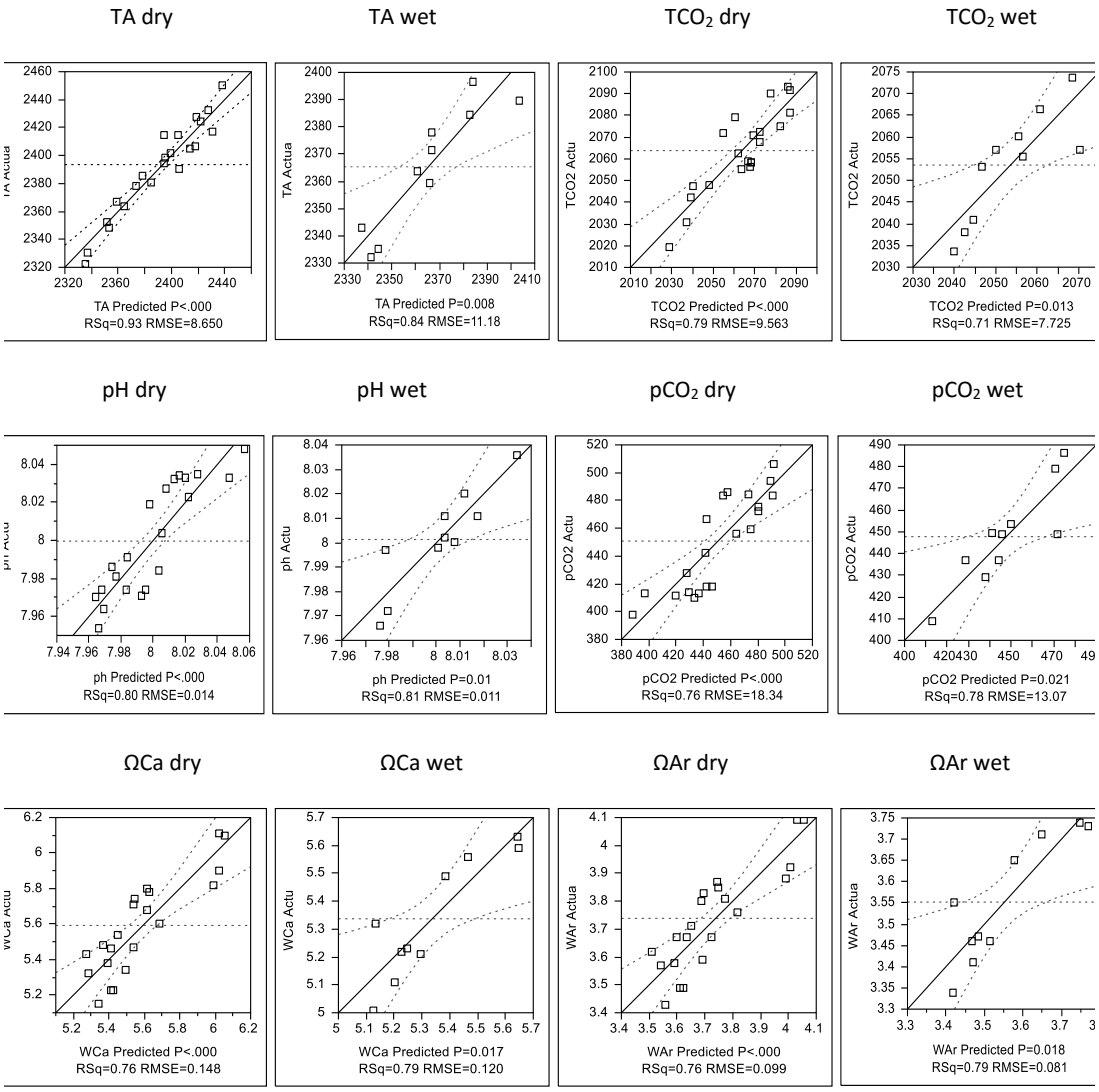
Source: The author

In the non-riverine inner shelf section, inside the marine protected area, the highest pCO_2 values are found in the waters over the coral reefs, between the longitudes -35.096 and -35.062 (Figure 3). This area also exhibits the lowest alkalinities and TCO_2, suggesting the influence of the coral reef metabolism over the carbonate parameters, increasing pCO_2 and decreasing TCO_2 and TA (ALBRIGHT *et al.*, 2015). Nevertheless the ΩCa and ΩAr were always above the values considered ideal for coral reefs >3.5 and >5 (KLEYPAS *et al.*, 1999)

The overall annual temperature average of 27.93 ± 0.97 °C found in the inner shelf of Pernambuco evidences a high thermal stability that must be the main factor controlling the pCO_2 over the study site. The permanent high temperature allows the organic carbon

respiration over the continental shelf throughout the year in the hot and shallow shelf environment. In addition, the coastal waters fertilization promoted by the inputs of the largest river in the Pernambuco's shore, the Capibaribe river, cannot sustain high phytoplankton productivities as far as 5nm from the coast (ESKINAZI-LEÇA *et al.*, 1997)

Figure IV.5: Seasonal prediction models of the TA, TCO_2, pH, pCO_2, ΩCa and ΩAr, for the non-riverine shelf section as a function of SSS, SST and longitude, the solid line is the 1:1 value.



Source: The author

The eutrophication hosted by the excessive amount of nutrients exported by the Capibaribe and Barra de Jangadas estuaries are not enough to significantly decrease the pCO_2 in the inner shelf of the MRR as reported by Gaspar *et al.*, (unpublished). They found a mean fCO_2 of 474.33 ± 66.57 µatm by performing underway pCO_2 measurements and registered a minimum fCO_2 value of 376.6 µatm in an small area under the influence

of the Capibaribe river plume, with a maximum chl-*a* value of 8.3 mg m^{-3} and. The average value of 474.33 µatm is practically the same average found in the present study for the dry season in the riverine section (475.3 ± 60.6 µatm; Figure 3) using TA and TCO_2 for pCO_2 calculation during a longer period of time in a broader area.

It seems that the continental shelf of Pernambuco is always supersaturated in CO_2 even in the areas under continental inputs from the rivers. This latter is not enough to host a significant primary productivity able to drawn down the pCO_2 similarly to what occurs in large river plumes and river dominated continental shelves, like the Amazon River, Southern North Sea, Changjiang river and Gulf of Mexico (TERNON *et al.*, 2000; KÖRTZINGER, 2003; GYPENS *et al.*, 2009; LEFÉVRE *et al.*, 2010; CHOU *et al.*, 2013; HUANG *et al.*, 2015; IBÁNHEZ *et al.*, 2015).

According to Oviatt *et al.*, (1986) and Nixon *et al.*, (2014), who worked with mesocosmos experiments evaluating the primary productivity response to nutrient enrichment, incremental changes in nutrients increases the productivity and also the respiration rates. Furthermore the productivity growth does not respond linearly to nutrient enrichment. Such metabolic response may aid to understand the inability of the primary production to decrease the pCO_2 in the area, especially close to the Capibaribe river plume (GASPAR *et al.*, unpublished, FLORES-MONTES *et al.*, 2011)

The main mechanism controlling the variability of pCO_2 in the study area is the temperature and the organic carbon oxidation over the continental shelf, as observed by Jiang *et al.* (2013) for the US South Atlantic Bight (SAB). Such pattern with intense signal of pCO_2 from the oxidation over the continental shelf may be valid to explain the variability observed in our study site, subjected to small temperature changes. They described that the influence of direct DIC transport by the rivers in the SAB are confined to the proximal areas of the shelf. The above authors have identified the own pCO_2 from organic matter oxidation over the shelf and the seasonal cycle of temperature as the main drivers of the pCO_2 distribution over the SAB. The temperature varies annually ±20 °C and ± 10 °C in the proximal and distal shelf respectively, oscillating among seasons and changing the status of the SAB from a CO_2 sink in winter, to a CO_2 source to the atmosphere during summer.

Similar findings are reported by Ibánhez *et al.*, (2015) in the oceanic waters adjacent to the Amazon river plume (SSS >35). They credited the CO_2 source outside the direct influence of the Amazon river plume to biological and physical processes without influence of seasonal cycles of temperature, with net outgassing throughout the year.

Despite the increased river discharge, the pCO_2 as well as the alkalinity in the riverine section were lower during the wet season accompanied by a raise in pH as a consequence of the increased fluvial water discharge. During the wet season the river flow transports more nutrients and organic matter to the continental shelf instead of being respired inside the estuaries (Gaspar *et al.* in press). Such process decreases the direct transport of CO_2 with a probably increase in the organic matter transport to the nearshore where will be respired throughout the year.

Despite the relatively high pCO_2 observed, the area exhibits high alkalinity even close to river mouths, which resulted in no pH difference among areas, with only a seasonal variability in the riverine section. According to Nixon *et al.*, (2014) there is an asymmetry in the response of pH to pCO_2 which seems to buffer the coastal waters at high dissolved inorganic carbon concentrations. This relation has an exponential decay shape and is attributable to pH being measured on a log scale, so shifts in pH are more readily seen in low pCO_2 waters.

However, future trends are hard to predict as the increasing atmospheric pCO_2 may cause a decrease in the CO_2 flux to the atmosphere in tropical areas (CAI, 2011). Nevertheless, increases in the SST may also counterbalance the increased atmospheric pCO_2 and sustain the CO_2 efflux in non-upwelling tropical shelves.

CONCLUSION

The coast of Pernambuco is supersaturated in CO_2 throughout the year. The inner shelf areas under continental influence from the rivers do not host a significant primary productivity able to decrease the pCO_2 to undersaturation values. The thermal stability and the shallow depths of the continental shelf seem to be the main mechanisms which keep the elevated pCO_2, while the direct transport of CO_2 by the rivers are restricted to the proximal area of the river mouths. Furthermore, the organic carbon oxidation over the well mixed water column may increase the pCO_2 over the continental shelf waters, where

we identified an overall average of 449.5 ± 45 µatm, which is above the actual global averages for tropical open shelf areas.

The correlation of the inorganic carbon parameters with the longitude may explain the interference of variables not investigated during the study, such as biological activity, bottom stress, turbulence and waves. These models are a good short-term option to evaluate the inorganic carbon variability in the Pernambuco coast. Despite high pCO_2, high alkalinities above 2300 µmol kg^{-1} are found close to the river mouths which may constitute an additional buffer to the ocean acidification process in the area.

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10 CONCLUSÃO GERAL

Predomina sobre a plataforma continental pernambucana as características hidrológicas das águas quentes e ricas em CO_2 vindas do Atlântico Tropical, trazidas pela

corrente norte do Brasil. Desta maneira, a costa pernambucana apresenta estabilidade térmica durante todo o ano devido às pequenas variações de temperatura do ar.

O desenvolvimento de equipamentos específicos para a medição direta da pCO_2 na água do mar, assim como a aplicação de metodologias com certificação internacional, possibilitaram a elucidação de algumas questões relacionadas à dinâmica do carbono inorgânico na região costeira de Pernambuco.

Os rios e estuários da região costeira do estado não possuem descarga suficiente para produzir grandes alterações na plataforma continental, de maneira que as influências sobre as características hidrológicas da região estão restritas às áreas mais próximas da costa. Entretanto a produtividade primária, sustentada por esses aportes continentais, não é suficientemente grande para diminuir de maneira significativa a pressão parcial de CO_2 na região da plataforma interna, onde apenas pequenas áreas de subsaturação de CO_2 em relação à atmosfera foram identificadas.

Os estuários de Pernambuco são fontes de CO_2 para a atmosfera durante todo o ano, com médias de pCO_2 e fluxos comparáveis às de estuários poluídos de altas e médias latitudes. As regiões de Itamaracá e de Barra de Jangadas apresentam maior transporte direto de $CO_{2(aq)}$, provavelmente oriundo do solo das áreas de mangue presentes nestes estuários. No entanto, para os estuários avaliados, a principal causa de variabilidade da pCO_2 está ligada à oxidação da matéria orgânica dentro destes ambientes, que por sua vez estão submetidos a elevadas cargas orgânicas provenientes do lançamento de esgoto sem tratamento.

Nesse contexto, destaca-se o estuário do rio Capibaribe, que apresenta frequentes episódios de *blooms* fitoplanctônicos. Neste estuário, diferentemente dos demais, a pCO_2 diminui consideravelmente durante o período chuvoso, pois suas margens estão imobilizadas e sua porção estuarina encontra-se completamente inserida em ambiente urbano. Dessa forma, diminui a entrada lateral de $CO_{2(aq)}$ proveniente do solo de áreas alagáveis. Ainda neste estuário, são encontradas as maiores alcalinidades, evidenciando processos geradores de alcalinidade ligados à oxidação anaeróbica do carbono orgânico. Tais processos, juntamente com a água doce alcalina que entra nos estuários, constituem um tampão extra para o excesso de prótons proveniente da respiração da matéria orgânica, diminuindo a vulnerabilidade ao processo de acidificação oceânica na região costeira.

A região da plataforma continental de Pernambuco apresenta elevada alcalinidade, além de um gradiente longitudinal em relação aos parâmetros do sistema carbonato, o que possibilitou o desenvolvimento de modelos descritivos para distribuição da TA, TCO_2, pCO_2, pH, TA, ΩAr e ΩCa em áreas da plataforma com e sem influência dos aportes fluviais. Os valores de pCO_2 encontrados para a plataforma continental de Pernambuco estão acima das médias descritas para plataformas continentais abertas tropicais, evidenciando que as médias globais de fluxos na interface ar-água dos oceanos podem estar subestimadas.

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ANEXOS

ANEXO 1.

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(ver rodapé)

O artigo deve ser redigido com no máximo 30 folhas incluindo o texto, figuras e tabelas (espaçamento simples de linhas)

ABSTRACT e RESUMO

(artigo em inglês ou português) contendo no máximo 150 palavras.

A …..

O abstract deve conter o Key Word com três a seis palavras que não conste no título.

O Resumo deve conter as palavras chave com três a seis palavras que não conste no título.

INTRODUCTION/INTRODUÇÃO

A….

STUDY AREA/ÁREA ESTUDADA

A…. Texto (Fig.1).

As figuras – preferencialmente coloridas (mapas, gráficos, fotografias) devem se colada em uma tabela (ver abaixo). As legendas das figuras devem ser inserida abaixo de cada figura e numerada consecutivamente em algarismos arábico.

Observação: cada figura deve esta referenciada no texto.

Colar a figura em cola especial (imagem - PNJ) e inserir no local definitivo do corpo do texto.

Figura 1 – Study área...

MATERIAL AND METHODS/MATERIAO E METODOS

RESULTS/RESULTADOS

As **figuras** – preferencialmente coloridas (gráficos, fotografias, organismos. etc) devem se colada em uma tabela (ver abaixo). As legendas das figuras devem ser inserida abaixo de cada figura e numerada consecutivamente em algarismos arábico.

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Figura 2 – Legenda...

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A **legenda** fica acima de cada tabela.

Table/Tabela 1 – Legenda ....

Quadro 1 - Legenda .... (se for necessário).

DISCUSSION/DISCUSSÃO

A…

CONCLUSION/CONCLUSÃO

A….

1. a ……;
2. a ……;

AKNOWLEDGEMENTS/AGRADECIMENTOS

A….

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ANEXO 2

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1 ESTUARINE, COASTAL AND SHELF SCIENCE

In association with the Estuarine Coastal Sciences Association (ECSA)

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Estuarine, Coastal and Shelf Science is an international multidisciplinary journal devoted to theanalysis of saline waterphenomena ranging from the outer edge of the continental shelfto theupper limits of the tidal zone. The journal provides a unique forum, unifying the multidisciplinaryapproaches to the study of the oceanography of estuaries, coastal zones, and continental shelf seas. It features original research papers, review papers and short communications treating such disciplines as zoology, botany, geology, sedimentology, physical oceanography. Data reports of mainly local interest are discouraged. Research areas include:

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