UNIVERSIDADE FEDERAL DE SANTA CATARINA
CENTRO DE CIÊNCIAS FÍSICAS E MATEMÁTICAS
PROGRAMA DE PÓS-GRADUAÇÃO EM OCEANOGRAFIA

ALEX CABRAL DOS SANTOS

EFEITO DOS EVENTOS METEOROLÓGICOS E OCEANOGRÁFICOS NA BIOGEOQUÍMICA DA BAÍA DA ILHA DE SANTA CATARINA:
IMPLICAÇÕES PARA AVALIAÇÃO E CONTROLE DA EUTROFIZAÇÃO

FLORIANÓPOLIS
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Dissertação submetida ao Programa de Pós-Graduação em Oceanografia da Universidade Federal de Santa Catarina para obtenção do título de Mestre em Oceanografia.
Orientadora: Profa. Dra. Alessandra Larissa D'Oliveira Fonseca
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Florianópolis
2019

Ficha de identificação da obra elaborada pelo autor,
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Cabral dos Santos, Alex
EFEITO DOS EVENTOS METEOROLÓGICOS E OCEANOGRÁFICOS NA BIOGEOQUÍMICA DA BAÍA DA ILHA DE SANTA CATARINA: : IMPLICAÇÕES PARA AVALIAÇÃO E CONTROLE DA EUTROFIZAÇÃO / Alex Cabral dos Santos ; orientadora, Alessandra Larissa D'Oliveira Fonseca, coorientadora, Carla Van Der Haagen Custodio Bonetti, 2019.
56 p.

Dissertação (mestrado) - Universidade Federal de Santa Catarina, Centro de Ciências Físicas e Matemáticas, Programa de Pós-Graduação em Oceanografia, Florianópolis, 2019.

Inclui referências.

1. Oceanografia. 2. Nutrientes. 3. Clorofila-a. 4. Qualidade da Água. 5. El Niño. I. D'Oliveira Fonseca, Alessandra Larissa. II. Van Der Haagen Custodio Bonetti, Carla. III. Universidade Federal de Santa Catarina. Programa de Pós-Graduação em Oceanografia. IV. Título.

Alex Cabral dos Santos

Efeito dos Eventos Meteorológicos e Oceanográficos na Biogeoquímica da Baía da Ilha de Santa Catarina: Implicações para Avaliação e Controle da Eutrofização

O presente trabalho em nível de mestrado foi avaliado e aprovado por banca examinadora composta pelos seguintes membros:

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Certificamos que esta é a **versão original e final** do trabalho de conclusão que foi julgado adequado para obtenção do título de Mestre em Oceanografia.

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Data: 16/12/2019 16:05:31-0300
CPF: 873.350.779-15

Profa. Dra. Alessandra Larissa D'Oliveira Fonseca
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Florianópolis, 16 de dezembro de 2019.

AGRADECIMENTOS

Agradeço a todos que contribuíram para a realização desta dissertação, que só foi possível devido ao esforço coletivo de muitas pessoas. Os dados utilizados neste estudo são resultados de diversas pesquisas que vêm sendo realizadas na Baía da Ilha de Santa Catarina e entorno desde a década de 1990, através de coleta de amostras *in situ*. Sabendo o quão laborioso é este processo e posterior análise, gostaria de agradecer a todos que trabalharam comigo ao longo destes anos no Laboratório de Biogeoquímica Marinha da UFSC, principalmente a Ana Paula da Silva, Georgia de Barros, Aichely Silva, Manuel Bercovich, Jaqueline Prudêncio, Maria Luiza Fontes, Sonia Kaminski e Vítor Pereira.

Agradeço a professora Alessandra Fonseca, que me orienta desde a iniciação científica, TCC e agora no mestrado. Muito obrigado por todos os ensinamentos (foram muitos!), não só pelos conhecimentos científicos, mas também pelas reflexões sociais e políticas. Obrigado também por todos os trabalhos de campo, pela paciência ao ensinar e por, literalmente, a minha iniciação na vida acadêmica. Agradeço a professora Carla Bonetti pela co-orientação e pelas excelentes explicações sobre análises estatísticas. Agradeço a todos os professores que participaram da minha formação, principalmente às professoras Juliana Leonel e Sarah Rodrigues e aos professores Paulo Pagliosa e Leonardo Rörig.

Agradeço as minhas colegas do Laboratório de Oceanografia Química da UFSC pelo apoio e conversas, Gabriela Souza, Lisiane de Liz, Camila Andreussi, Larissa Jaques, Daniela Zanetti e Kalina Brauko. Agradeço ao pessoal do curso de graduação e pós-graduação em Oceanografia da UFSC. Agradeço a Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) e a Fundação de Amparo à Pesquisa e Inovação do Estado de Santa Catarina (FAPESC) pela bolsa de mestrado. Agradeço a minha família, principalmente a minha mãe, Francisca Cabral, e a minha vó, Nolicia Cabral, pelo apoio incondicional. Gostaria de agradecer a todos que participaram desta importante etapa da minha vida. Muito Obrigado! Agora novos mares me aguardam!

“NO WATER, NO LIFE. NO BLUE, NO GREEN”
“NO OCEAN, NO US”

Sylvia Earle

RESUMO

Compreender as diferentes escalas da variabilidade espaço-temporal é fundamental para o melhor entendimento dos processos biogeoquímicos que ocorrem na interface continente-oceano. O objetivo deste estudo foi avaliar o papel do fluxo das bacias hidrográficas e da intrusão de massas de água oceânicas no estado trófico da Baía da Ilha de Santa Catarina ao longo das três últimas décadas (1993-2019), utilizando modelos biogeoquímicos para a avaliação da eutrofização. Os rios que drenam para as baías apresentaram altas concentrações de nutrientes, coliformes fecais e clorofila-a, diretamente correlacionadas ao número de habitantes das bacias hidrográficas. Os piores cenários foram encontrados durante o verão e outono, devido ao turismo em massa associado à ineficiência ou ausência de sistemas de tratamento de esgoto. As intrusões de massas de água, como a Água Central do Atlântico Sul e a Pluma do Rio da Prata, favoreceram condições autotróficas no verão e heterotróficas no inverno, concomitante a um baixo e alto tempo de residência da água, respectivamente. Eventos de El Niño aumentaram as taxas de precipitação e as descargas fluviais, exportando elevada concentração de nutrientes e biomassa fitoplanctônica dos rios eutróficos para a plataforma continental. Este cenário mudou durante eventos de La Niña, quando as maiores concentrações de nutrientes e clorofila-a ocorreram dentro das baías. Os métodos para avaliação da eutrofização indicaram que o estado trófico variou de moderado a alto e que essas condições tendem a permanecer as mesmas na próxima década devido ao tempo moderado de residência da água (~ 40 dias), às pressões antrópicas, frequentes florações de algas tóxicas e à intrusão de massas de água oceânicas ricas em nutrientes. Políticas públicas para o controle e mitigação da eutrofização são necessárias para evitar a perda dos bens e serviços ecossistêmicos.

Palavras chave: Nutrientes, Clorofila-a, ENSO, Qualidade da Água, TRIX, LOICZ, ASSETS.

ABSTRACT

Understand the different scales of temporal variability is crucial to improve the knowledge of the biogeochemical processes in the land-ocean interface. In this study, we evaluated the role of continental runoff and intrusion of oceanic water masses in the trophic state of the Bay of Santa Catarina Island (BSCI) over the last three decades (1993-2019) by using multiple biogeochemical and eutrophication assessment tools. The sub-watersheds of BSCI showed high concentration of nutrients, fecal coliform and chlorophyll-a, directly correlated to the number of inhabitants. Worst-case scenarios were found in summer and fall seasons due to sewage inputs caused by mass tourism and the inefficiency or even absence of treatment systems, boosted by strong rainfall. The intrusion of the South Atlantic Central Water and the Plata Plume Water favored autotrophy in the summer and heterotrophy in the winter, coupled with low and high residence time, respectively. El Niño events enhanced rainfall and continental runoff, exporting elevated nutrients and phytoplankton biomass loads from the eutrophic rivers to the continental shelf. The pattern reverses during La Niña, where chlorophyll-a and nutrients peaks were detected inside the bay. Methods for eutrophication evaluation indicated that the trophic state ranged from moderate to high and that these conditions tend to remain the same in future scenarios due to the moderate residence time of the water (~ 40 days), anthropogenic pressures, frequent toxic algal blooms and the intrusion of nutrient-rich ocean water masses. Management practices are needed in order to control eutrophication and loss of ecosystem services and functions.

Keywords: Nutrients, Chlorophyll, ENSO, Water Quality, TRIX, LOICZ, ASSETS.

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LISTA DE ABREVIATURAS E SIGLAS

ACAS – Água Central do Atlântico Sul
ANOVA – Analysis of Variance
ASSETS – Assessment of Estuarine Trophic Status model
AOU – Apparent Oxygen Utilization
BISC – Baía da Ilha de Santa Catarina
BSCI – Bay of Santa Catarina Island
DIN – Dissolved Inorganic Nitrogen
DIP – Dissolved Inorganic Phosphorus
DO – Dissolved Oxygen
EC – Efficiency Coefficient
ENSO – El Niño Southern Oscillation
GAM – Generalized Additive Model
HAB – Harmful Algal Bloom
KW – Kruskal-Wallis analysis
LOICZ – Land Ocean Interactions in the Coastal Zone model
MEI – Multivariate ENSO Index
MPN – Most Probable Number
NEM – Net Ecosystem Metabolism
N_{FIX}-D – Nitrogen fixation minus denitrification
NTU – Nephelometric Turbidity Unit
OM – Organic Matter
PCO – Principal Coordinate Analysis
PERMANOVA – Permutational Multivariate Analysis of Variance
PPW – Plata Plume Water
PRP – Pluma do Rio da Prata
SACW – South Atlantic Central Water
SC – Santa Catarina
TRIX – Trophic Index
TSS – Total Suspended Solids
VP – Rainfall flux
VQ – River flux
VR – Residual flux
VX – Mixing flux
WRT – Water Residence Time
WWTP – Wastewater Treatment Plant

SUMÁRIO

INTRODUÇÃO GERAL

Diversos estudos indicam que a capacidade de suporte dos sistemas naturais tem sido ultrapassada em função das demandas da sociedade humana (Rockström et al., 2009; Weinzettel et al., 2018). O aumento da população, das atividades agrícolas e da pecuária, devido à alta demanda global por alimentos e combustíveis, vem causando diversas pressões nos ecossistemas, principalmente na zona costeira dos países em desenvolvimento (e.g. Brasil, China e Índia), onde o tratamento de esgoto e águas residuais ainda é precário (Nixon, 2009). Dentre os diversos estressores locais e globais que impactam os sistemas aquáticos, a eutrofização é um dos mais recorrentes, sendo que a variabilidade deste processo está condicionada, além da pressão antrópica, à efeito sinergéticos e de retroalimentação (Cloern, 2001). O processo de eutrofização é definido como uma mudança nos fluxos de matéria orgânica em um determinado ecossistema, podendo ser causado, por exemplo, pelo aumento da entrada autóctone ou alóctone de nutrientes, da produção primária ou do tempo de residência da água e resultando em hipoxia (oxigênio < 2.0 mg.L^{-1}), floração de algas, mortalidade de espécies nativas e aumento da turbidez (Breitburg et al., 2018; Nixon, 2009).

As metodologias para avaliar o estado trófico de um determinado ecossistema geralmente tratam de uma combinação de variáveis indicadoras dos processos físicos e biogeoquímicos, que, associadas a um monitoramento de longo prazo, são essenciais para determinar se o sistema está em processo de eutrofização (Devlin et al., 2011). O índice TRIX foi inicialmente desenvolvido para o Mar Adriático por Vollenweider et al. (1998), porém devido a sua flexibilidade quanto ao ajuste dos coeficientes para uma determinada região, através de correções logarítmicas, vem sendo aplicado em escala global. O TRIX é calculado pela relação linear entre quatro variáveis que indicam sintomas primários (fósforo e nitrogênio) e secundários (clorofila-a e consumo de oxigênio) da eutrofização, onde o resultado classifica desde condições ultra-oligotróficas até hiper-eutróficas (Giovanardi & Vollenweider, 2004). O modelo ASSETS avalia a suscetibilidade à eutrofização a partir de variáveis indicadoras da pressão (vulnerabilidade natural do sistema), estado (sintomas primários e secundários da eutrofização) e resposta (previsões futuras), indicando uma condição geral da expressão da eutrofização, que varia de baixa a alta (Ferreira et al., 2007). O modelo biogeoquímico LOICZ quantifica os fluxos de água e nutrientes na interface continente-oceano, gerando estimativas do tempo de residência da água e das condições metabólicas do ecossistema, as quais podem ser usadas para estimar o estado trófico do sistema, seguindo a metodologia do suprimento de carbono orgânico proposta por Nixon (1995) (Gordon et al., 1996; Ramesh et al., 2015).

As regiões estuarinas são importantes áreas de transição na interface continente-oceano, as quais são moduladas por fatores ambientais e antrópicos (Nixon, 2009). Estuários são ecossistemas complexos, apresentando alta variabilidade espacial e temporal, além de comunidades biológicas e processos biogeoquímicos únicos, que os diferem dos rios, lagos e oceanos (Cloern et al., 2017). Os padrões climáticos e morfológicos de cada região determinam as condicionantes ambientais que atuam na hidrodinâmica estuarina, influenciando a dinâmica biogeoquímica e o estado trófico (Bricker et al., 2008). Alguns estudos sugerem que, por exemplo, sistemas com maior tempo de residência da água tendem a heterotrofia, já sistemas com maior fluxo de mistura parecem apresentar condições autotróficas (Swaney et al., 2011; Bricker et al., 2008). Nos sistemas costeiros do sul do Brasil, o regime de precipitação e o padrão de ventos influenciam nas trocas de água e no estado trófico dos sistemas estuarinos e lagunares (Abreu et al., 2010; Cabral & Fonseca, 2019). A intrusão de massas de água oceânicas nesta região também está relacionada ao padrão de ventos, desempenhando um papel importante nos processos físicos e biogeoquímicos (Brandini et al., 2018). Dentre estas massas de água, a ressurgência da Água Central do Atlântico Sul (ACAS) é comumente reportada durante a passagem de ventos persistentes do quadrante norte-nordeste, enquanto que a Pluma do Rio da Prata (PRP) é transportada ao longo da costa sul-sudeste do Brasil pelos ventos do quadrante sul, principalmente no inverno, ambas com elevada concentração de nutrientes, potencializando a produtividade da região (Bordin et al., 2019; Möller et al., 2008; Rörig et al., 2018).

A Baía da Ilha de Santa Catarina (BISC) está localizada na região subtropical do Brasil, onde os fenômenos meteorológicos e oceanográficos descritos acima são observados, porém até o momento, ainda não foi avaliado a influência destes processos na biogeoquímica do sistema em escala espacial (rios-baía-plataforma) e temporal (1993-2019). Além disto, as bacias hidrográficas que drenam para a BISC sofrem alta pressão antrópica pela entrada de esgoto devido à precariedade ou falta de saneamento e também pelo fluxo de contaminantes proveniente das atividades agrícolas, que se desenvolvem principalmente nas bacias da região continental (Garbossa et al., 2017; Pagliosa et al., 2005; Silva et al., 2016). Deste modo, o melhor entendimento do comportamento sazonal e espacial dos processos físicos e biogeoquímicos da BISC se mostra fundamental para uma compreensão holística da variabilidade espaço-temporal do estado trófico deste sistema, onde os resultados poderão ser utilizados nas políticas públicas de gerenciamento costeiro para o controle e mitigação da eutrofização e a melhora da qualidade de água.

Neste contexto, o objetivo deste estudo foi investigar a variabilidade espacial, sazonal e interanual (1993-2019) das propriedades biogeoquímicas e do estado trófico da BISC em relação aos eventos meteorológicos e oceanográficos, buscando entender o papel do fluxo de nutrientes proveniente das bacias hidrográficas, passível de ser minimizado pelas ações da gestão costeira, e dos fluxos via fenômenos sazonais de mesoescala. Com base nestas informações, serão testadas as seguintes hipóteses: i) O aumento do estado trófico está diretamente associado a urbanização das bacias hidrográficas, principalmente no verão, devido ao aumento da população pelo turismo e a precariedade das políticas públicas de saneamento; ii) a produção primária e a regeneração da matéria orgânica são controladas pela sazonalidade das massas de água oceânicas e pelos fluxos das bacias hidrográficas; e iii) eventos de El Niño e La Niña modulam as condições tróficas na BISC e na plataforma continental. Estas questões são abordadas no artigo apresentado a seguir, a ser submetido na revista *Science of the Total Environment (Elsevier)*.

Water masses seasonality and meteorological patterns drive the biogeochemical processes of a subtropical and urbanized watershed-bay-shelf continuum

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Abstract

Understand the different scales of temporal variability is crucial to improve the knowledge of the biogeochemical processes in the land-ocean interface. In this study, we evaluated the role of continental runoff and intrusion of oceanic water masses in the trophic state of the Bay of Santa Catarina Island (BSCI) over the last three decades (1993-2019) by using multiple biogeochemical and eutrophication assessment tools. The sub-watersheds of BSCI showed high concentration of nutrients, fecal coliform and chlorophyll-a, directly correlated to the number of inhabitants. Worst-case scenarios were found in summer and fall seasons due to sewage inputs caused by mass tourism and the inefficiency or even absence of treatment systems, boosted by strong rainfall. The intrusion of the South Atlantic Central Water and the Plata Plume Water favored autotrophy in the summer and heterotrophy in the winter, coupled with low and high residence time, respectively. El Niño events enhanced rainfall and continental runoff, exporting elevated nutrients and phytoplankton biomass loads from the eutrophic rivers to the continental shelf. The pattern reverses during La Niña, where chlorophyll-a and nutrients peaks were detected inside the bay. Methods for eutrophication evaluation indicated that the trophic state ranged from moderate to high and that these conditions tend to remain the same in future scenarios due to the moderate residence time of the water (~ 40 days), anthropogenic pressures, frequent toxic algal blooms and the intrusion of nutrient-rich ocean water masses. Management practices are needed in order to control eutrophication and loss of ecosystem services and functions.

Keywords: Nutrients, Chlorophyll-a, ENSO, TRIX, LOICZ, ASSETS.

1. Introduction

Estuaries are important transitional ecosystems and biogeochemical hotspots, where primary productivity and organic matter remineralization are enhanced by continental and oceanic fluxes (Bricker et al., 2008; Cloern et al., 2017). Disruptions in the natural processes are found when these systems are surrounded by urban or agricultural areas, activities that input high amounts of nutrients and other pollutants, mainly when wastewater treatment is not enforced or poor-regulated (Cloern et al., 2016; Nixon, 2009). The allochthonous or autochthonous production of organic matter induced by anthropogenic nutrients influx is the main cause of eutrophication worldwide, especially in systems with low water exchange, such as lagoons and bays (Le Moal et al., 2019; Rabalais et al., 2010). Eutrophication can be identified by some symptoms (e.g. algal blooms and deoxygenation), leading to water quality degradation, losses of biodiversity and ecosystem services and threat to food security (Breitburg et al., 2018; Bricker et al., 2008).

The biogeochemical processes of coastal areas depends on multiple environmental and anthropic conditions, such as the meteorological and hydrological variability and watershed land-uses (Cloern et al., 2017; Dan et al., 2019; Li et al., 2012). Meteo-oceanographic events play an important role in this variability, for example, when precipitation events induce pulses of continental discharges, increasing the trophic status of coastal systems (Brugnoli et al., 2019; Netto et al., 2018). Sometimes these events are coupled with large-scale phenomena (e.g. El Niño and La Niña), producing effects over weeks to months (Abreu et al., 2010; Cloern et al., 2016). In the subtropical region of Brazil, Ekman transport associated with persistent northerly winds drive surface waters away from the coast, triggering coastal upwelling events of the South Atlantic Central Water (SACW) in the euphotic zone (Bordin et al., 2019; Brandini et al., 2018). Southerly winds, on the other hand, force downwelling of surface ocean waters and storm surges over the coast, mainly in the winter (Möller et al., 2008). Southerly winds are also the main mechanism driving the meridional (from 34ºS to ~24ºS) displacement of the Plata Plume Water (PPW) through subtropical Brazil, producing strong physical and biogeochemical cross-shore gradients (Fontes et al., 2018; Pimenta and Kirwan, 2014).

Assessing the biogeochemistry dynamics of coastal systems can be challenging due to the complex mechanisms described above. Long-term studies are essential to better understand the different scales of temporal and seasonal variability; however, there are few studies like that in South America (Abreu et al., 2010; Barrera-Alba et al., 2019; Cloern and Jassby, 2010; Ovalle et al., 2013). The Bay of Santa Catarina Island (BSCI, Fig. 1) has shown eutrophication symptoms in the watersheds and shallow regions, such as algal blooms and hypoxia (Alves et al., 2010; Pagliosa et al., 2006; Silva et al., 2016). In addition, the sewage treatment systems are not effective or nor existent in most of the sub-watersheds that drain to the bay, where population growth rates are two times higher than the country's average (Garbossa et al., 2017). Associated with this condition, we must also consider the multiple protected areas around and inside the BSCI, where endangered species and coastal traditional communities rely on to survive (Alves and Hanazaki, 2015) and the fact that the system is economically important due to the summer tourism (~1.5 million visitors per year) and bivalve mollusks aquaculture (~70% of the Brazilian production) (Souza et al., 2017).

Here we examine, for the first time, how oceanographic and meteorological events affect the biogeochemical properties of the BSCI ecosystem, using a dataset covering the last three decades (1993-2019). Besides the seasonal variability, we also investigated the fate and processes associated with the nutrients and chlorophyll-a in the land-ocean interface, from the BSCI's main watersheds to the adjacent continental shelf. We hypothesize that i) the number of inhabitants in each sub-watershed is directly associated to water quality degradation, mainly during summer, due to the increase of tourism and precipitation; iii) new primary production and regeneration of organic matter are controlled by water masses seasonally and watersheds runoff; and iii) El Niño and La Niña events modulate the trophic conditions in the watershed-bay-shelf continuum. Our approach was to apply multiple biogeochemical and eutrophication assessment tools in order to better understand the role of nutrient fluxes from the continental runoff and the oceanic water masses in the ecosystem metabolism. In this way, we aim that the results of this study will draw attention about the environmental issues of this region and support better coastal management strategies to restore and preserve this important ecosystem.

2. Material and Methods

2.1. Study Area

The BSCI is shaped by two water bodies, named as North and South Bay, which are connected in the middle by a narrow (~ 500 m) channel (Fig. 1). It is a well-mixed semi-enclosed system, where the waters are exchange with the continental shelf in the extremes (Simonassi et al., 2010). The bay area and length are around 430 km^2 and 50 km, respectively. The drainage basin area is about 1875 km^2. The tidal regime is semi-diurnal, with measured daily amplitudes from 0.2 to 1.7m (Garbossa et al., 2014). Tidal heights are lower than 1 m, but it can significantly increase during strong southerly winds events, concomitant with the spring tide. Local depths are less than 4 m in most of the bay, increasing up to 30m in the central and south straits, where strong currents are observed (Silveira and Bonetti, 2019). Low-energy areas are usually found in the central region of the bay, due to the overlap of the tidal waves that came from both sides, generating a standing wave node (Garbossa et al., 2014).

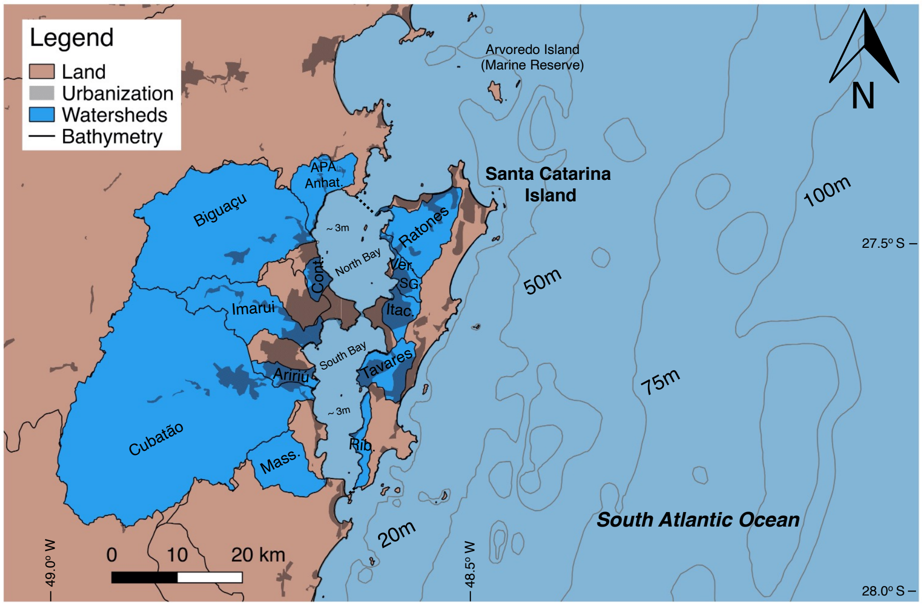

Figure 1. Map of the watershed-bay-shelf continuum. The dotted lines in the extremes and the channel in the middle were defined as the limits among the North and South Bays and the continental shelf for modeling purposes. Watersheds: Mass. (Massiambú), Cubatão, Aririú, Imarui, Cont. (Continental), Biguaçu, APA Anhat. (Anhatomirim), Ratones, Ver. (Veríssimo), SG (Saco Grande), Itac. (Itacorubi), Tavares and Rib. (Ribeirão).

2.2. Data Acquisition

2.2.1. Water Column

All available data, both new and already published, about the water quality of the watersheds, bays, and continental shelf were compilated in order to evaluate the spatial and seasonal variability (Tab. S1, supplemental material). In all studies, depth, salinity, temperature, pH and turbidity were acquired by sensors or multiparameter probes, previously calibrated. Dissolved oxygen (DO) concentration and saturation were measured by pre-calibrated sensors or the Winkler method (Labasque et al., 2004). The apparent oxygen utilization (AOU) was calculated between the difference of the equilibrium saturation (depending on temperature, salinity, and pressure) and the *in situ* oxygen saturation (Benson and Krause, 1984). In all studies, water samples were collected to analyze the dissolved inorganic nutrients, chlorophyll-a and total suspended solids (TSS) by standard methods, using Van Dorn or Niskin bottles. The water samples were conditioned in previously acid-washed (HCl 10%) polyethylene bottles, cooled in a thermal box with ice, and kept in the dark until arrival in the laboratory.

The water was vacuum filtered in glass fiber filters of 0.45 or 0.7 µm of porosity and 47 mm of diameter to photosynthetic pigments and TSS analyzes. Chlorophyll-a and pheophytin-a were determined spectrophotometrically, after 24 hours extraction with acetone, following Strickland and Parsons (1972). TSS was determined gravimetrically, by weighing the dry filters in analytical balances (Grasshoff et al., 1983). Nutrients (phosphate, nitrate+nitrite, ammonium+ammonia and silicate) were determined by the colorimetric method (Grasshoff et al., 1983), reading the absorbances in spectrophotometers. In order to check the quality of the reagents and equipment, standard curves were run daily prior to each nutrient analysis. Dissolved inorganic nitrogen (DIN) was calculated by sum nitrate+nitrite and ammonium+ammonia concentrations. It was assumed that phosphate is equal to the concentration of dissolved inorganic phosphorus (DIP). Ammonia (NH_3) and ammonium (NH_4^+) concentrations were determinate as a function of pH, temperature and salinity (Bell et al., 2007; Whitfield, 1974). Fecal coliform data from 2002 to 2019 of the 16 sites inside the BSCI was provided by the state environmental agency (IMA-SC).

2.2.2. Meteorological Variables

The main meteorological variables (temperature, precipitation, evaporation, and wind) were extracted from a meteorological station (number 83897) of the National Institute of Meteorology

(INMET-Brazil), located at the South Bay margin. The multivariate ENSO index (MEI) is a method to identify the frequency and intensity of the El Niño Southern Oscillation in both phases, negative (La Niña) and positive (El Niño) (Wolter and Timlin, 2011). The index fluctuates from -3 to 3, categorizing the ENSO events as weak (0.5-1), moderate (1-1.5), strong (1.5-2) and very strong (>2). The data was extracted from the website https://www.esrl.noaa.gov/psd/enso/mei/, in order to give an index for each day of sampling.

2.3. Land-Ocean Interactions in the Coastal Zone (LOICZ) Biogeochemical Model

The LOICZ model uses a biogeochemical mass-balance approach to quantify water and nutrient fluxes and to estimate the metabolism of estuarine systems (Gordon et al., 1996; Swaney et al., 2011). In this study, we modeled the South and North Bay separately, since sampling in those sites were made mostly in different days. Daily averages of salinity and nutrients from multiple sampling points of each bay were used to build a single box, following LOICZ guidelines (Gordon et al., 1996). In the North Bay, 46 days were selected from 2005 to 2018. In the South Bay, we compiled a larger dataset (86 days), from 1996 to 2017. Salinity and nutrient data from the continental shelf and the main rivers were retrieved from our dataset. Meteorological data (precipitation and evaporation) were acquired from a nearby meteorological station, as described in section 2.2.2. DIN and DIP concentration in the rain were obtained from Hoinaski et al. (2014) and Mizerkowski et al. (2012), respectively. Daily freshwater runoff of BSCI main watersheds (N=13) was calculated following LOICZ guidelines (Dupra et al., 2000) and calibrated with *in situ* water flow measurements (Garbossa et al., 2017). Non-conservative budgets (Δ_{DIN} and Δ_{DIP}) were calculated considering the rivers (V_Q), precipitation (V_P), residual (V_R) and oceanic (V_X) fluxes as sources and sinks of nutrients between the bays and the continental shelf. The net ecosystem metabolism (NEM), phytoplankton primary production minus mineralization (p – r), and the relative importance of N fixation or denitrification (N_{FIX}–D) were calculated through CNP (carbon, nitrogen and phosphorus) Redfield stoichiometry (Swaney et al., 2011).

2.4. Eutrophication Assessment Methods

2.4.1. Assessment of Estuarine Trophic Status (ASSETS)

The ASSETS method was designed to evaluate the susceptibility to eutrophication of coastal ecosystems by the influencing factors-IF (pressure), eutrophic conditions-EuC (state) and future outlook-FO (response) (Bricker et al., 2003). Those three parameters are used to calculate the overall assessment or level of expression, which is given by a trophic status classification: bad (worsen), poor, moderate, good and high (better). All the calculations were made in the ASSETS software (http://www.eutro.org), following the recommendations of Ferreira et al. (2007). We used the coastal bay equations, considering just the seawater zone indicated by the model (salinity >

25). Physical parameters, such as mean tidal prism and tidal range, were obtained from Garbossa et al. (2017). We generated a model for each bay (North and South) separately, during the 1990's, 2000's and 2010's. The decadal medians of DIN concentration in the main rivers and continental shelf were obtained from our dataset. N loads decadal medians of the rivers were estimated by the LOICZ model (VQ_{DIN}). Chlorophyll-a and DO were calculated by 90th and 10th decadal percentile, respectively, as recommended by Ferreira et al. (2007). Toxic blooms duration and frequency were obtained from the Santa Catarina farming development company (CIDASC). As for the future outlook, we considered that the agriculture and urbanization correspond to 20% and 80% of the land-uses, following Fonseca et al. (*in prep.*), which used the Municipality Plan of BSCI's watersheds for population and agricultural growth in the next decades.

2.4.2. Trophic Index (TRIX)

The trophic index TRIX is used to characterize the trophic status of coastal waters, by the linear relation of chlorophyll-a ($mg.m^{-3}$), DIN ($mg.m^{-3}$), DIP ($mg.m^{-3}$) and the absolute percentage of deviation (100%) from oxygen saturation values (aD%DO) (Vollenweider et al., 1998). The index covers a spectrum of 5 trophic conditions: ultra-oligotrophic (0–2), oligotrophic (2–4), mesotrophic (4–6), eutrophic (6–8), and hypertrophic (8–10) (Giovanardi and Vollenweider, 2004). The index is also used to classify the water quality in 4 categories: elevated (<4), good (4-5), poor/mediocre (5-6) and bad (>6) (Rinaldi and Giovanardi, 2011). An index was calculated for each sample of BSCI (N = 590) and the watersheds (N = 365), following equation 1. Where "k" is the sum of the minimum logarithmic value of each variable (ΣLogMin) and "m" is the scale factor [(ΣLogMax – ΣLogMin)*(0.1)]. The TRIX formula was calibrated for both the bay (k = -1.49; m = 1.31) and the rivers (k = -1.00; m = 1.00).

Equation 1.

$$\mathrm{TRIX} = \left[\frac{\mathrm{Log10}\ (\mathrm{Chlorophyll{-}a} * \mathrm{DIN} * \mathrm{DIP} * \mathrm{aD\%DO}) - \mathrm{k}}{\mathrm{m}}\right]$$

The efficiency coefficient (EC) was also used as complement information of TRIX (Eq. 2) (Giovanardi and Vollenweider, 2004). EC indicates if the trophic status is dominated by nutritional factors (DIN and DIP) or biological symptoms (chlorophyll-a and DO). EC values lower than -2.0 indicate "low degree of nutrient utilization" or no incorporation of these nutrients by primary producers. High degree of nutrient utilization (EC > -2.0) suggests potential intake of nutrients by the biological components.

Equation 2.

$$\mathrm{EC} = \mathrm{Log10}\left[\frac{(\mathrm{Chlorophyll{-}a} * \mathrm{aD\%DO})}{(\mathrm{DIN} * \mathrm{DIP})}\right]$$

2.5. Statistical Analyses

The boxplot graphs and correlation analyses were performed using the RStudio software (R Core Team, 2015). Kruskal-Wallis (KW) test was applied to verify significant ($p<0.05$) univariate differences between groups. When KW was significant, the Dunn's post-hoc test was used to obtain pairwise comparison results. The *p* values were adjusted with the Bonferroni method. Principal coordinates analysis (PCO) was used to explore seasonal and spatial variability and the main indicators. Samples were previously transformed by log (x+1). The resemblance matrix was calculated by the Gower coefficient. The permutational multivariate analysis of variance (PERMANOVA) was applied in the same resemblance matrix used in the PCOs to verify significant differences ($p<0.001$) among the groups (classified by seasonal and/or spatial factors). PCO and PERMANOVA were performed in the PRIMER-E software (Anderson, 2017; Clarke and Warwick, 2001). The generalized additive model (GAM) was used to verify which variables (water temperature, salinity, DO, year and MEI) drive the chlorophyll-a variability in the bays. The dataset was standardized before GAM analysis. The GAM model was performed in the RStudio software using the "gam" and "mgcv" packages, AIC model, "tw" family and the gaussian function (R Core Team, 2015). The Ocean Data View (ODV) software was used to plot the water masses over the continental shelf of South Bay (Fig. 6).

3. Results

3.1. Spatial variability pattern across the watershed-bay-shelf continuum

The rivers showed the highest concentrations of nutrients and lowest levels of DO among all the systems (Tab. 1). Considering the watershed-bay-shelf continuum**,** the main descriptors of axis 1 of PCO (Fig. 2) were salinity ($r = 0.59$), silicate ($r = -0.50$) and ammonium ($r = 0.42$) (Fig. 2). The main descriptor of axis 2 (Fig. 2) was chlorophyll-a ($r = -0.76$), indicating that the highest phytoplankton biomass is found in the estuarine zone of the rivers, concomitantly with the pheophytin-a and TSS peaks (Tab. 1). The NP ratio indicated that the system was limited by P in the freshwater domain and by N in the seawater zone (Tab. 1). The efficiency coefficient (EC) showed lower ($p < 0.05$, KW test) values in the freshwater zone (-2.4 ± 1.5), indicating low nutrient utilization by primary producers, when compared to the estuarine (-1.5 ± 1.4) and seawater (-1.2 ± 0.8) regions. The PERMANOVA, applied on the same dataset used to perform the PCO (salinity, oxygen saturation, chlorophyll-a, ammonium, DIP, nitrate and silicate) (Tab. S2), indicated that all the systems are significant ($p < 0.05$) different from each other, strong dissimilarities were observed between the shelf and rivers and slight differences between the bay systems and the rivers (estuarine zone) and shelf waters. Ammonium was the main nutrient in the DIN pool, both in the North Bay (62 ± 29%), South Bay (74 ± 24%), continental shelf (56 ± 23%) and rivers (63 ± 32%). Ammonia contribute with only 0.2 ± 0.8% of the total DIN but increases up to 7.7 µM in the rivers. The watershed population was associated with high DIN, chlorophyll-a, coliform and TRIX (Fig. 3). Also, in the rivers, Secchi disk depth was highly correlated with TRIX ($r = -0.97$; $p < 0.05$).

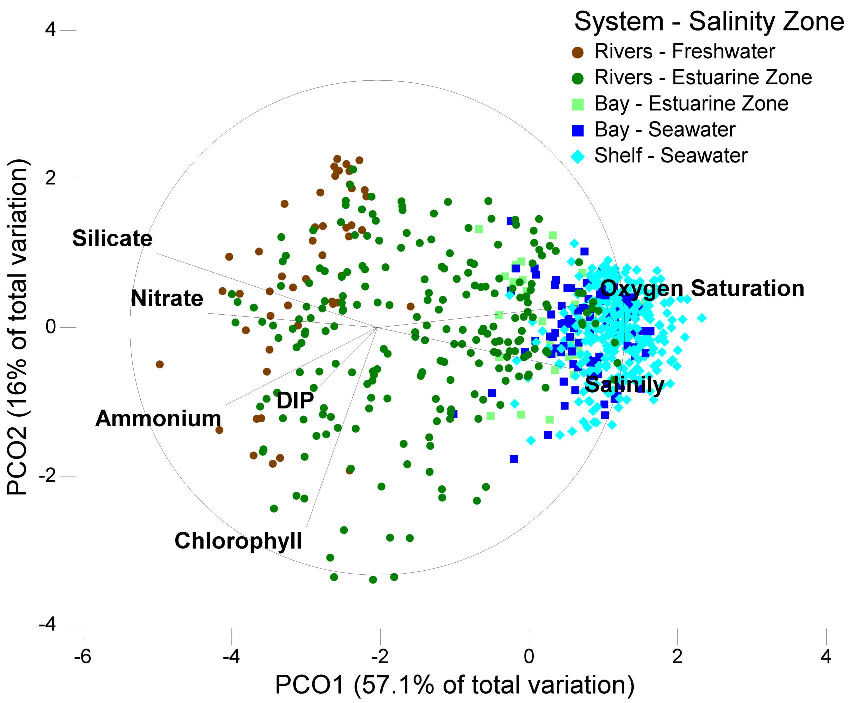

Figure 2. Principal coordinates analysis (PCO) emphasizing the biogeochemical pattern across the watershed-bay-shelf continuum (N=715). Freshwater (Salinity < 0.5), Estuarine Zone (0.5 < Salinity < 30) and Seawater (Salinity > 30).

Table 1. Median, minimum and maximum values of the biogeochemical variables across the watershed-bay-shelf continuum, considering all the dataset. Freshwater (Salinity < 0.5), Estuarine Zone (0.5 < Salinity < 30) and Seawater (Salinity > 30). When significative ($p < 0.05$), lower-case letters indicate the Kruskal-Wallis pairwise comparison test results, where A>B>C>D>E.

System	Rivers		Bay		Shelf
Salinity Zone	Freshwater	Estuarine Zone	Estuarine Zone	Seawater	Seawater
pH	7.0 (5.5-8.4)^{C}	7.4 (5.8-11.0)^{B}	8.2 (6.7-8.8)^{A}	8.1 (6.1-9.9)^{A}	8.2 (6.1-8.9)^{A}
DO (mg.L$^{-1)}$	4.4 (0.0-11.5)^{C}	4.4 (0.0-12.4)^{C}	7.1 (4.3-10.9)^{A}	6.8 (1.8-11.4)^{B}	6.7 (1.6-11.5)^{B}
DIP (µmol.L^{-1})	1.9 (0.1-159.4)^{A}	0.9 (0.1-123.2)^{A}	0.4 (0.1-5.9)^{B}	0.5 (0.1-6.5)^{B}	0.4 (0.1-2.1)^{B}
Ammonium (µmol.L^{-1})	40.4 (0.4-284.5)^{A}	9.0 (0.1-256.8)^{B}	4.7 (0.3-108.0)^{C}	3.1 (0.2-85.2)^{C}	1.3 (0.1-13.5)^{D}
Nitrate (µmol.L^{-1})	12.8 (0.3-123.4)^{A}	3.9 (0.1-77.3)^{B}	2.1 (0.1-9.3)^{C}	1.3 (0.1-10.0)^{D}	1.0 (0.1-8.6)^{E}
NP Ratio	26.5 (0.1-1402.0)^{A}	14.0 (0.1-336.0)^{B}	14.7 (0.3-691.0)^{B}	8.2 (0.1-999.1)^{C}	5.9 (0.6-770.9)^{D}
Silicate (µmol.L^{-1})	89.3 (0.4-365.2)^{A}	57.0 (0.4-720.8)^{A}	19.5 (2.2-106.3)^{B}	14.2 (0.2-144.5)^{C}	7.4 (0.3-42.7)^{D}
Chlorophyll-a (µg.L^{-1})	1.8 (0.1-197.8)^{B}	4.8 (0.1-180.9)^{A}	3.0 (0.2-66.1)^{A}	3.1 (0.1-68.5)^{A}	1.6 (0.1-79.2)^{B}
Pheophytin-a (µg.L^{-1})	0.1 (0.1-77.0)^{B}	17.5 (0.1-176.0)^{A}	9.7 (0.1-96.6)^{A}	5.6 (0.1-80.9)^{A}	0.7 (0.1-70.9)^{B}
TSS (mg.L^{-1})	15.4 (0.7-899.6)^{B}	36.0 (0.3-490.2)^{A}	27.0 (0.3-1498.2)^{A}	20.0 (0.1-1078.6)^{B}	17.5 (1.3-1094.1)^{B}

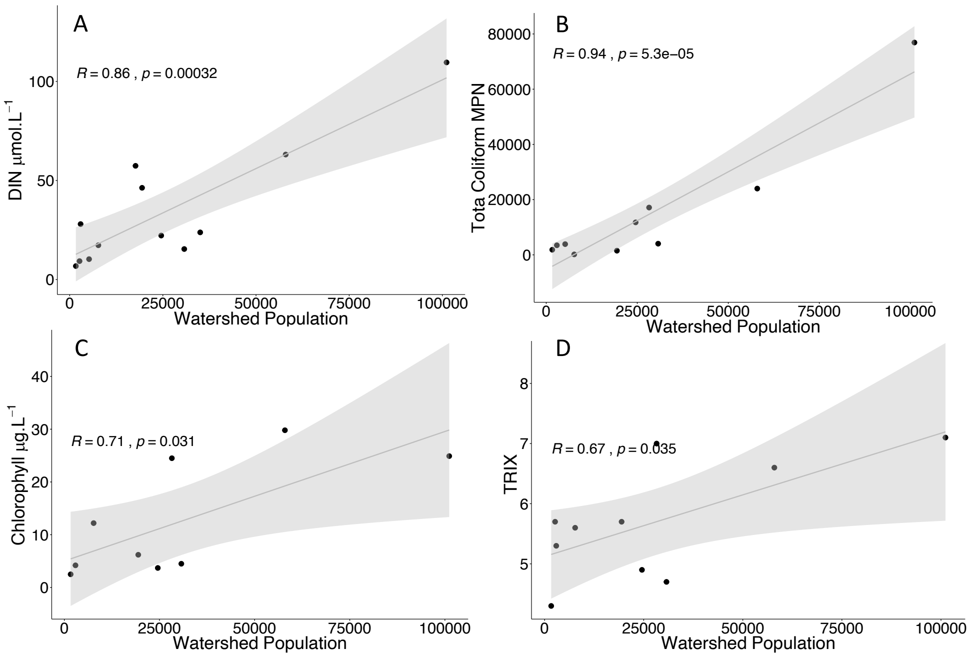

Figure 3. Scatter plot between a) DIN (Dissolved Inorganic Nitrogen), b) total coliform (MPN – Most Probable Number in 100 mL^{-1}), c) Chlorophyll-a and d) TRIX and the number of inhabitants of the BSCI main sub-watersheds. Pearson correlation algorithm was used to obtain the p and R values. The grey lines indicate 95% confidence intervals.

3.2. Seasonal variability

3.2.1. Rivers

Overall, salinity and DO were significantly higher ($p < 0.05$) in the winter, compared to summer, while temperature, DIN, fecal coliform and turbidity were lower ($p < 0.05$) in winter than summer, as indicated by Kruskal-Wallis tests (Fig. 4). DIP didn't show a clear pattern through the seasons of the year (Fig. 4e). Chlorophyll-a and turbidity showed an inverse correlation ($r = -0.32$, $p < 0.05$). Considering the Brazilian water quality legislation (CONAMA 357/2005), worst-case scenarios were found during summer and fall, whereas in the winter there was a slight improvement. Oxygen was bellow limits in 27% of the samples during winter, whereas 66% of the samples were above limits in the other seasons. Hypoxic conditions (<2.0 mg.L^{-1}) were found in 20% of the cases, especially in fall. DIP and DIN were above limits in 25% of the samples. As for chlorophyll-a, 28% of the samples were above limits, mainly during fall. Fecal coliform concentrations were above limits in 43% of samples during winter and in 66% during the other seasons.

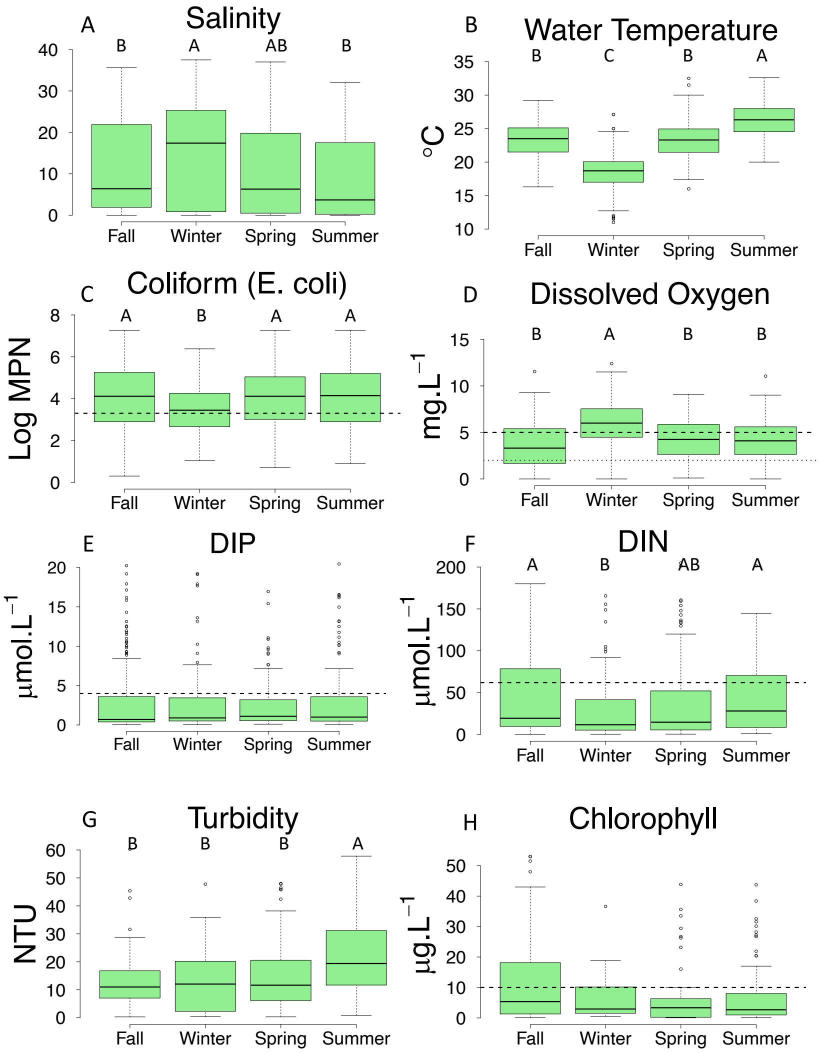

Figure 4. Boxplot (minimum, maximum, median, first quartile, third quartile, and outliers) of the physical and biogeochemical proprieties of all main watersheds (N=13) of BSCI by the seasons of the year. The dashed line indicates the maximum (Coliform, DIP, DIN, and Chlorophyll-a) and minimum (Dissolved Oxygen) thresholds according the Brazilian water quality legislation (CONAMA 357/2005) for estuarine waters. The dotted line (Fig. 3d) indicates the threshold for hypoxia (2.0 mg.L^{-1}). Salinity (N=676), Water Temperature (N=675), Fecal Coliform (N=1146), Dissolved Oxygen (N=623), DIP (Dissolved Inorganic Phosphorus, N=610), DIN (Dissolved Inorganic Nitrogen, N=616), Turbidity (N=298) and Chlorophyll-a (N=369). When significative ($p < 0.05$), lower-case letters indicate the Kruskal-Wallis pairwise comparison test results, where A>B>C.

3.2.2. Bays and Continental Shelf

The water column seasonality of BSCI was driving mainly by temperature, as indicated by its strong correlation (r = -0.99) with axis 1 of PCO (Fig. 5). The spatial distribution was driving by salinity, positively correlated (r = 0.80) with axis 2. In the negative side of both axes of PCO (Fig. 5), it is, samples inside the bays in the spring-summer seasons and also some samples of South Bay during winter, high DIN and chlorophyll-a values were concentrated (Fig. 5). Whereas the lowest concentrations of nutrients and chlorophyll-a were observed in the continental shelf during all seasons (positive side of axis 2). Considering the same dataset used in the Fig. 5, the PERMANOVA showed that the differences between regions are dependent on the seasonality (Tab. S3). When the seasons were analyzed separately, there were no significative differences (p = 0.054) between the North and South bays during the spring-summer (Table S2). In the winter-fall, however, the South and North bays showed significant ($p<0.05$) differences. Moreover, the continental shelf and the bays were significant different ($p<0.05$) during all seasons (Table S2). Three water masses were identified over the continental shelf of South Bay, both in the fall and winter seasons (Fig. 6). Strong influence of continental plumes over the shelf was observed in both seasons, the South Bay plume in the fall and the Plata Plume Water (PPW) in the winter (Fig. 6).

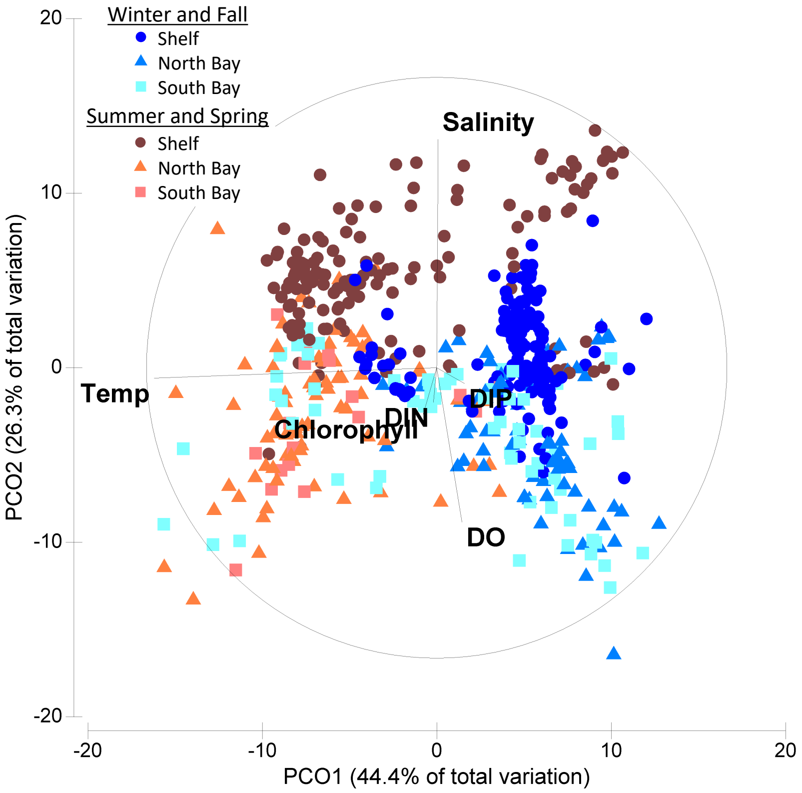

Figure 5. Principal coordinate analysis (PCO) emphasizing the seasonal and spatial variability of the water column (Temperature (Temp), Salinity, Dissolved Oxygen (DO), DIP, DIN and chlorophyll-a) of the South and North bays, and the continental shelf (N=584).

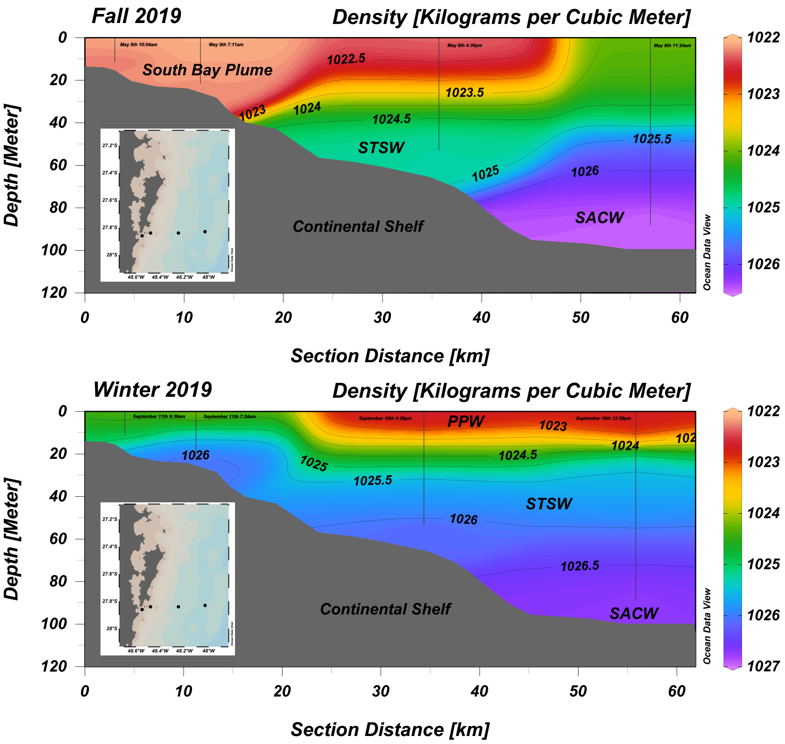

Figure 6. Water mass seasonality over the continental shelf of South Bay in the fall (May 8-9th) and winter (September 10-11th) of 2019. The vertical and horizontal lines indicate the CTD profiles and isopycnals, respectively. The STSW (Subtropical Shelf Water), SACW (South Atlantic Central Water) and PPW (Plata Plume Water) water masses were characterized according to Möller et al. (2008).

Considering the LOICZ results, the residence time (WRT) observed in the winter were 6 and 3 times higher than in the summer in the North and South bay, respectively (Tab. 2). WRT was inversely correlated ($p < 0.05$) with rain ($r = -0.77$) and water temperature ($r = -0.72$), while pheophytin-a ($r = 0.66$) and apparent oxygen utilization ($r = 0.52$) showed positive correlation with WRT. Residual (VR) and riverine (VQ) nutrient fluxes were higher in the summer than winter, both for DIP and DIN. P exchanges with the continental shelf (VX) were more important in the South Bay, while in the North Bay, it was the N flux. The riverine nutrient inputs (VQ) were the main nutrient source for the bays (Tab. 2). The North Bay exported 4.5% and 12.4% of all N and P inputs to the continental shelf, respectively (Tab. 2). In the South Bay, 5.6% of N and 21.9% of P were exported. Both systems behaved as a sink of nutrients most of the time, shifting to sources of P and N during winter in the North and South bays, respectively (Tab. 2). Autotrophic conditions prevail in 63% of the sampled days in both systems throughout the year. Heterotrophic metabolism or near balance was mostly observed in the winter. The NEM ($p - r$) was correlated ($p < 0.05$) to rain ($r = 0.88$), WRT ($r = -0.71$) and TRIX ($r = -0.51$). The LOICZ model indicates that denitrification predominates over N fixation in the North Bay (Tab. 2), removing about 60% of all N inputs and limiting primary productivity. N fixation predominates in the South Bay (Tab. 2), where about 13% of all DIN came from this process.

Table 2. Median of the water residence time (WRT, days), DIP and DIN budgets (10^3.mol.day^{-1}), Net Ecosystem Metabolism (NEM, production – respiration, gC.m^{-2}.day^{-1}) and the relative importance of N fixation and denitrification (N_{FIX} – D, mmolN.m^{-2}.day^{-1}) for the North (2005-2018) and South (1996-2017) bays during the seasons of the year. VR (nutrient residual flux), VX (nutrient oceanic flux), VQ (watershed nutrient flux) and Δ (nutrient internal production – consumption).

Region	Season	WRT	VRDIP	VXDIP	VQDIP	ΔDIP	NEM	VRDIN	VXDIN	VQDIN	ΔDIN	N_{FIX}-D
North Bay	Fall	34.73	-0.05	-0.25	0.94	-0.76	0.06	-0.33	0.14	7.42	-10.06	0.02
	Winter	55.96	-0.12	-1.08	1.13	0.27	-0.02	-0.59	-0.15	9.00	-8.85	-0.11
	Spring	32.62	-0.45	-4.07	3.33	-0.20	0.02	-2.64	25.50	26.43	-67.85	-0.67
	Summer	9.27	-1.10	-1.12	6.33	-1.55	0.13	-8.70	10.42	50.19	-47.97	-0.12
	System	26.34	-0.55	-1.27	3.35	-0.78	0.07	-2.79	6.14	26.53	-27.04	-0.13
South Bay	Fall	11.28	-1.39	2.46	2.00	-3.76	0.31	-6.71	-143.56	146.14	-7.69	0.67
	Winter	27.53	-0.10	-0.22	0.28	0.02	-0.01	-1.02	-81.49	20.41	29.59	0.05
	Spring	9.90	-0.90	-0.01	1.57	-0.76	0.06	-14.34	-129.24	113.13	1.88	0.50
	Summer	8.81	-2.02	2.20	2.11	-3.62	0.30	-10.57	-99.75	153.86	-6.09	-0.06
	System	14.92	-0.88	0.36	1.34	-1.09	0.09	-8.35	-97.94	97.63	10.52	0.19

3.3. Interannual, Decadal and El Niño-Southern Oscillations

The NP ratio seems to be decreasing over the years in the BSCI, shifting the system from P to N limiting (Fig. 7b). Considering the median values above and below and the long-term mean, fecal coliform, DIP and TSS appear to be increasing, whereas DIN and silicate are decreasing (Fig. 7). The trophic index varied between mesotrophic and eutrophic conditions (Fig. 7f). Giving the importance of chlorophyll as a predictor of harmful algal blooms, a generalized additive model (GAM) was applied to better understand its variability (Tab. 3). GAM results showed that ENSO events and temperature have strong control over chlorophyll-a concentrations in the bays, following by salinity, DO and year sampled (Tab. 3).

Table 3. Generalized additive model (GAM) results for the bays between 1993 and 2019 (N=349 days). Chlorophyll-a as the dependent variable and the MEI (multivariate ENSO index), water temperature, salinity, DO (dissolved oxygen) and year as predictors. R^2 (adjusted) = 0.14, Deviance explained = 14.9%, GCV = 0.34, and Scale est. = 0.34.

Chlorophyll-a	Estimate	Std. Error	t value	p value	F value	p value
(Intercept)	-333.9	147.3	-2.3	0.024000	ANOVA	
MEI	-0.9	0.2	-4.4	0.000017	19.0	0.00002
Temperature	0.9	0.2	4.6	0.000007	18.7	0.00002
Salinity	-2.3	0.5	-4.8	0.000003	13.4	0.00029
DO	0.4	0.2	2.0	0.049400	5.6	0.01807
Year	44.8	19.4	2.3	0.021500	4.3	0.03888

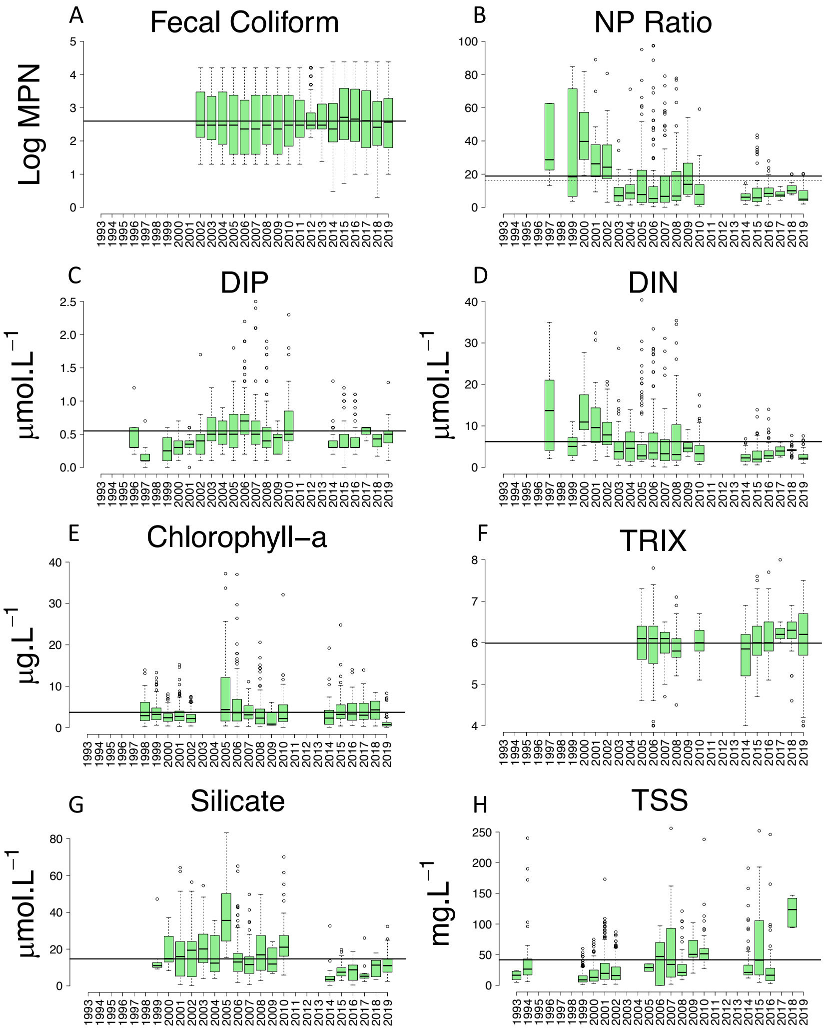

Figure 7. Long-term time-series boxplot (minimum, maximum, median, first quartile, third quartile, and outliers) for the Fecal Coliform (N=8084), NP Ratio (N=1034), DIP (N=1193), DIN (N=1152), Chlorophyll-a (N=1748), TRIX (N=653), Silicate (N=878) and TSS - Total Suspended Solids (N=1565) in the bays. The line represents the historical average of each variable. The dashed line indicates the Redfield ratio (16N:1P) in the Fig 7b.

El Niño events increased precipitation rates (Fig. 8) and affected the bays and continental shelf in different ways. In the bays, there was a tendency to low nutrients and chlorophyll-a during El Niño, whereas the opposite was observed in the continental shelf (Fig. 9 and 10). This pattern seems to shift during La Niña (Fig. 9 and 10). However, both systems showed high AOU and low salinity during El Niño events (Fig. 11). Chlorophyll-a was correlated ($p < 0.05$) with the MEI in the bays (r = -0.49) and shelf (r = 0.54). Other meteorological patterns, wind intensity, was tied ($p<0.05$) with the TRIX (r = -0.82) in the extreme sector South Bay, however, no significant correlation was found in other regions.

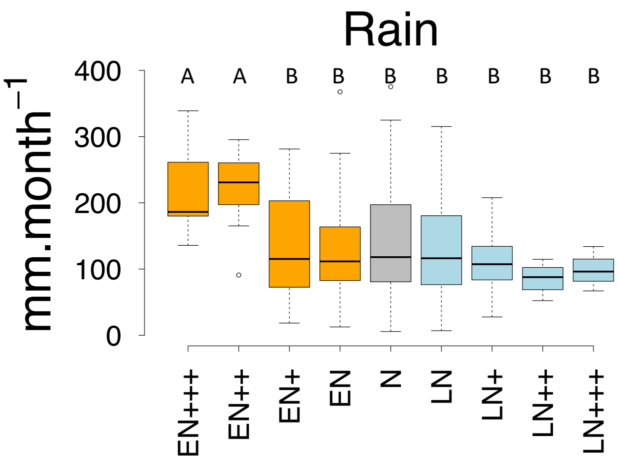

Figure 8. Boxplot (minimum, maximum, median, first quartile, third quartile, and outliers) of accumulated precipitation across ENSO events. EN (El Niño, orange), N (Neutral, grey) and LN (La Niña, blue). The signals represent the intensity, according the Multivariate ENSO Index (MEI): +++ (very strong, MEI > 2), ++ (strong, 1.5 < MEI < 2), + (moderate, 1 < MEI < 1.5) and no signal (weak, 0.5 < MEI < 1). All the sampled days with MEI between -0.5 and 0.5 were classified as neutral phase (N). When significative ($p < 0.05$), lower-case letters indicate the Kruskal-Wallis pairwise comparison test results, where A>B>C.

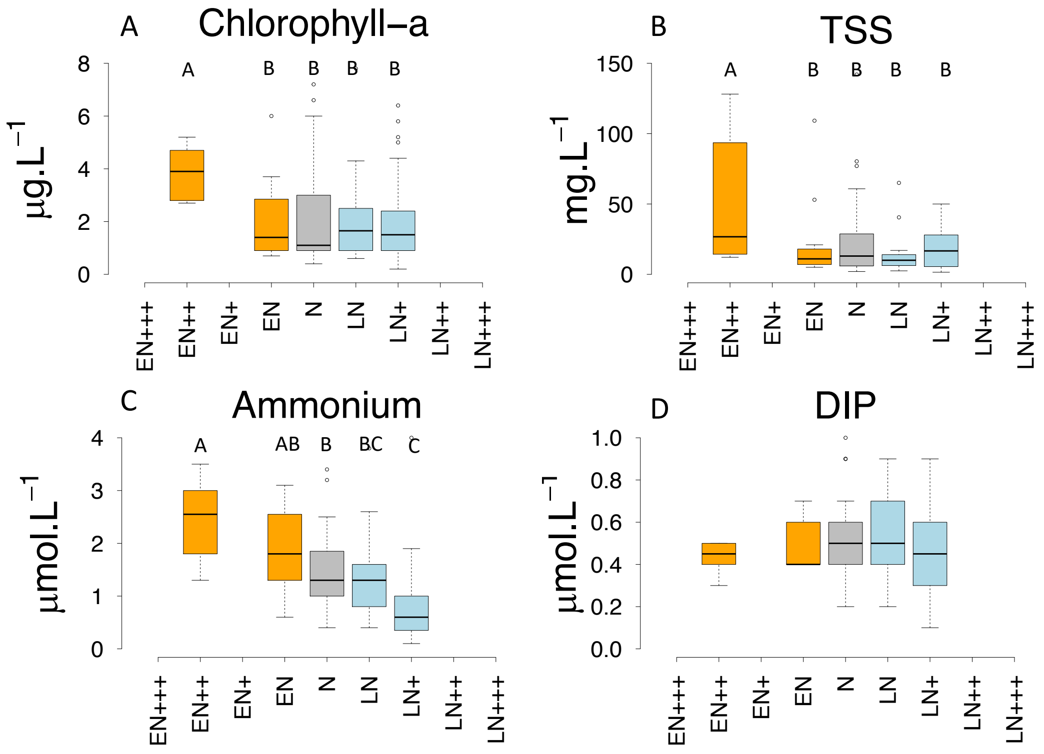

Figure 9. Boxplot (minimum, maximum, median, first quartile, third quartile, and outliers) of the chlorophyll-a, TSS, ammonium and DIP in the continental shelf across ENSO events. Legend information in the Fig. 8.

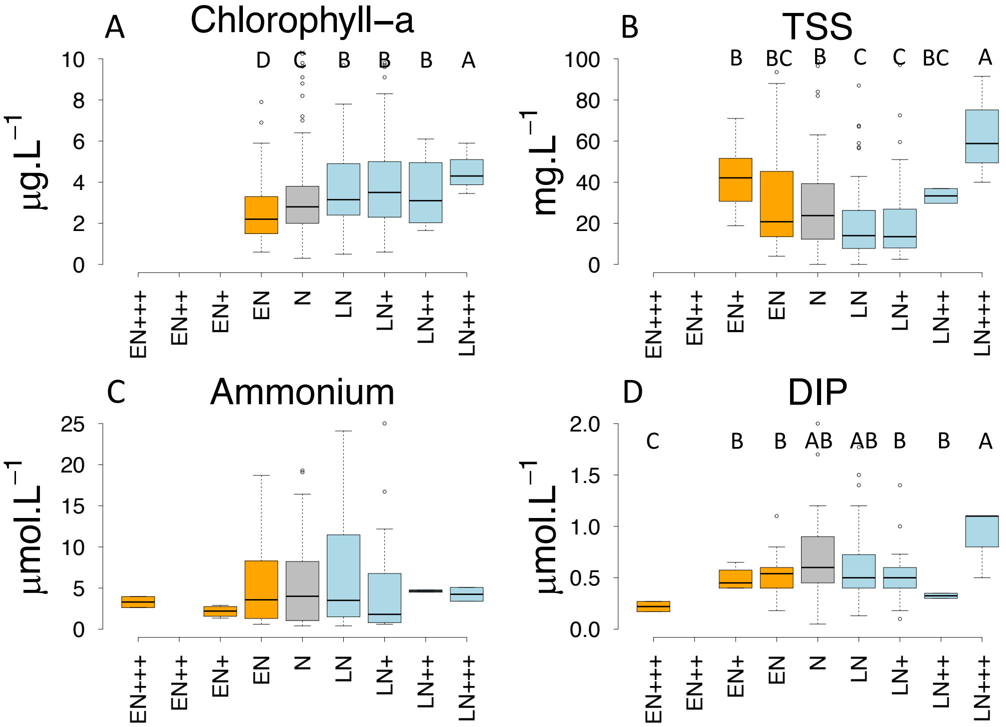

Figure 10. Boxplot (minimum, maximum, median, first quartile, third quartile, and outliers) of the chlorophyll-a, TSS, ammonium and DIP in the bay across ENSO events. Legend information in the Fig. 8.

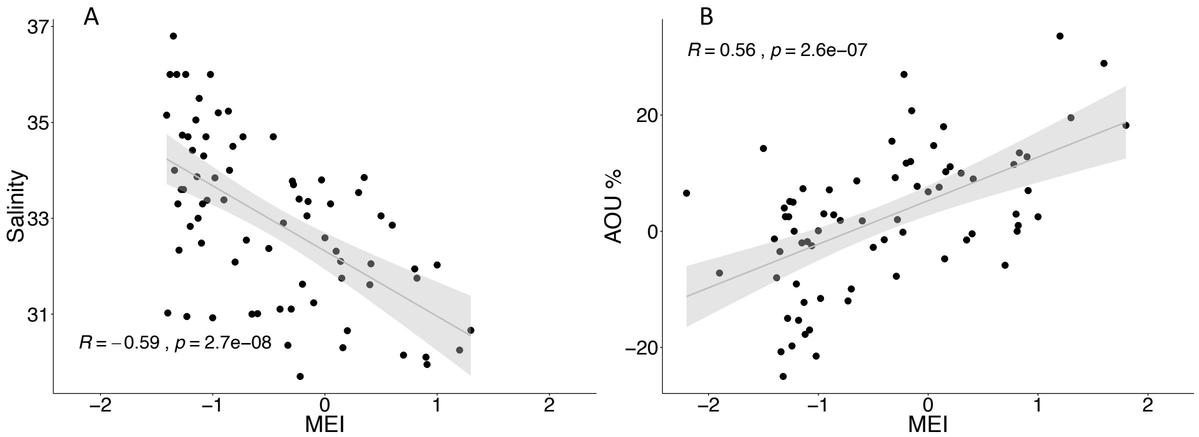

Figure 11. Scatter plot between a) Salinity and b) AOU (Apparent Oxygen Utilization) and the multivariate ENSO index, considering MEI mean values, both in the bays and continental shelf. Pearson correlation algorithm was used to obtain the *p* and R values. Positive and negatives MEI values indicate El Niño and La Niña events, respectively.

The ASSETS model overall grade showed poor and bad trophic status for the North and South bay, respectively, which agreed with other methodologies (TRIX and LOICZ) (Tab. 4). Considering the influencing factors (IF) to natural susceptibility to eutrophication (e.g. nutrient dilution and flushing potential), the systems showed moderate-high to high pressure. As for the eutrophic conditions (EuC), moderate-high state was observed, except in the South Bay during the 2010's, mostly due to the increase of 90th percentile of chlorophyll-a (primary symptom) from 5.3 µg.L^{-1} in the 90's to 6.8 in the 00's and 8.9 in the 10's. The 10th percentile of DO (secondary eutrophication symptom) indicated biological stressful conditions (<5 mg.L^{-1}) just in the North Bay in the 10's. The analysis of the future outlook (FO) showed that the susceptibility to eutrophication will likely remain the same, considering three different scenarios and the assumptions detailed on section 2.4.1 (Tab. 4).

Table 4. Level of susceptibility to eutrophication by the pressure (IF), state (EuC) and response (FO) components and the overall classification grade by the ASSETS model for the North and South Bays by decade. FO1 (population increasing by 25% and same effluent treatment), FO2 (population increasing by 25% and 100% of effluent treatment) and FO3 (same population and 100% of effluent treatment). TRIX and LOICZ decadal trophic classification were also included, following Giovanardi and Vollenweider (2004) for TRIX and Nixon (1995) for the organic carbon production, here estimated by the LOICZ model (NEM, gC.m^{-2}.year^{-1}).

System	North Bay			South Bay		
Decade	1990's	2000's	2010's	1990's	2000's	2010's
Influencing Factors (IF)	Moderate High	Moderate High	Moderate High	High	High	High
Eutrophic Conditions (EuC)	Moderate High	Moderate High	Moderate High	Moderate High	Moderate High	High
Future Outlook (FO1)	-	-	No Change	-	-	No Change
Future Outlook (FO2)	-	-	No Change	-	-	No Change
Future Outlook (FO3)	-	-	No Change	-	-	No Change
ASSETS Overall Score	Poor	Poor	Poor	Bad	Bad	Bad
TRIX (index)	-	Bad Eutrophic (6.1)	Bad Eutrophic (6.1)	-	Poor Mesotrophic (5.8)	Bad Eutrophic (6.2)
LOICZ (NEM)	-	Good Oligotrophic (53)	Poor Mesotrophic (129)	Very Bad Hypereutrophic (695)	Poor Mesotrophic (133)	Bad Eutrophic (376)

4. Discussion

4.1. Anthropogenic pressures

The BSCI is under moderate to high eutrophication pressure due to the poor-regulations and enforcement of land-uses, especially with those related with urban planning and sanitation. Disposal of effluents from rural activities or untreated domestic and industrial sewage is a generalized problem in the estuaries of South America (Barletta et al., 2019). BSCI is no exception, although there are wastewater treatment plants (WWTPs) in the region, they are not enough to prevent the input of pollutants to the rivers and the bay, since there are several watersheds that are not covered by the sewage treatment. Moreover, the existing ones cover primary and secondary treatment only, threatening human and ecosystem health (Garbossa et al., 2017; Silva and Fonseca, 2016). The pressure over the existing WWTPs increase during summer, when the population rises up to 208% in some watersheds and rainfall events overload the WWTPs (Silva et al., 2016). Nonetheless, just about 46% of the households have access to the sewerage system, most of the population uses septic tanks or dump raw sewage into the small streams that drain to the bays. Risks of contamination are high since some of these rivers and also groundwater are used for human consumption, where waterborne diseases were already associated water quality degradation and elevated trophic status (Silva and Fonseca, 2016)

This study demonstrates that the number of inhabitants of each sub-watershed of BSCI is directly correlated to the increase of nitrogen, chlorophyll-a, and coliform in the water column, also increasing the trophic state from mesotrophic to eutrophic. Our data also showed that the impact is extended to the estuarine and seawater zones. For example, even though the worst-case scenarios were found in the rivers, high nutrients concentrations were measured in the surface waters of the South Bay emissary (ETE Insular) in the winter of 2012, where DIP (5.3 µM) was above the regulations (4.0 µM), indicating sewage contamination. High DIP (1.0 µM) and DIN (22.7 µM) were also measured ~1km away from the emissary, almost two and three times the long-term mean concentration found in the bay's estuarine waters, respectively. The content of organic matter (14.0 ± 1.2 %) and carbon (3.1 ± 0.9 %) in the sediment next to the emissary was also above the average values found in the South Bay (Sewald et al., 2012; Vianna and Bonetti, 2018), of 2.5% and 1.1%, respectively. This indicates that the WWTPs technology and coverage needs improvement in order to control eutrophication.

Several studies have stated that aquaculture activities can significantly damage the water quality and biodiversity of coastal ecosystems, although some others indicated that shellfish culture can help to reduce eutrophication by removing chlorophyll and increasing water transparency (Silva et al., 2011; Zimmer-Faust et al., 2018). In the BSCI, bivalve aquaculture might be suppressing phytoplankton growth, keeping concentrations below 10 $\mu g.L^{-1}$ most of the time, which is the threshold for eutrophication risk (Devlin et al., 2011). In other systems, such as the San Francisco Bay (SFB-USA), the introduction of a non-native species of clam (*Potamocorbula amurensis*) is reported to be the main cause of phytoplankton biomass loss due to the rapid grazing pressure (Cloern, 2019). *P. amurensis* and other filter feeders (e.g. *M. arenaria*) also changed the nutrient dynamics and disturbed the biological community structure of SFB (Cloern, 2019). In the BSCI, aquaculture farms start to establish in the l980's, introducing the Pacific oyster *Crassostrea gigas* and the brown mussel *Perna perna*. Nowadays, the region produces up to 21,000 $ton.year^{-1}$, encompassing about 70% of all bivalve aquaculture produced in Brazil (Netto et al., 2018). There is no chlorophyll-a data before the implementation of aquaculture in the BSCI, but the filter feeders might be controlling phytoplankton biomass, although other factors, such as nutrient limitation and turbidity may be influencing as well.

Despite the importance of aquaculture, tourism has also a major role in the economy of Santa Catarina island, mainly in the summer. However, during this season most of the beaches inside the bays are in non-compliance with regulations for bath and other recreational uses, due to high fecal coliform concentrations, periodically monitored by the state environmental agency (IMA-SC) since the 2000's. Fecal coliforms usually are associated with other pathogens that can concentrate in the shellfish tissues, favoring the risks of food poisoning since they are frequently eaten raw (Zimmer-Faust et al., 2018). In the BSCI, 54% of the samples showed proper conditions for bath, considering all the time series (2002-2019) and the 16 sites monitored in the bays by IMA-SC. However, since the system is used by shellfish farms, there is more restrictive legislation (CONAMA 274/2000), that, when applied, indicates that only 26% of the water samples in the monitored areas are suitable for bivalve aquaculture. In the rivers, just 36% of the samples agreed with the legislation for bath and other recreational uses (<2000 MPN/100mL). When considering more restrictive regulations, such as the US Environmental Protection Agency (<235 MPN/100mL), just 15% of the samples presented conditions for primary contact recreation. Therefore, sewage is dumped in the watersheds without adequate or any treatment, a common practice in the coastal systems of South Brazil, fueling eutrophication (Cabral et al., 2019; Garbossa et al., 2017; Netto et al., 2018).

4.2. Seasonal variability across the watershed-bay-shelf continuum

Meteorological events and the water masses seasonality had strong control over the biogeochemistry and ecosystem metabolism of BSCI. The net ecosystem metabolism of BSCI fluctuated from autotrophic in the summer to heterotrophic in the winter. In the summer, the synergetic effects of multiple eutrophic rivers outflow (enhanced by the rainfall and sewage discharges) and SACW upwelling boosted the biogeochemical processes and an autotrophic metabolism inside the bays. Oceanic P inputs occurred mainly to the South Bay in the summer and fall, while N inputs predominated in the North Bay during summer and spring. Interestingly, since these nutrients limit phytoplankton production in each bay, respectively, they favored autotrophy and new primary production. Concomitantly, maximum concentrations of chlorophyll-a in the bays were found mostly in the summer, and also during winter in the South Bay, similar to other systems in Brazil under the influence of nutrient-rich water masses and anthropogenic runoff (Abreu et al., 2010; Barrera-Alba et al., 2019). In the rivers, primary productivity seems to be limited by turbidity in the summer. Pan et al. (2016) established a maximum threshold of 12 NTU for phytoplankton growth since chlorophyll-a was close to zero above those values. Turbidity equal or above 12 NTU was found in 76% of the samples in the rivers during summer, suggesting that phytoplankton might be inhibited, as observed in other systems (Cloern, 1999; Xu et al., 2013). In the fall, however, decreasing in precipitation, the relative stability of water column and still high concentration of nutrients and abundant sunlight allowed phytoplankton growth. High chlorophyll-a (>10 $\mu g.L^{-1}$) and hypoxia were observed in 39% and 33% of the samples in the rivers during fall, respectively, the highest frequencies between all seasons.

Although primary production seems to be occurring mainly in the summer and fall, regeneration of organic matter was mostly observed during the winter in the bays, concomitantly with high residence time, pheophytin-a and TRIX. The fluctuations of the NEM in estuarine systems appear to be regulated by the exchange time, where heterotrophic conditions are directly correlated with high water residence time (Bricker et al., 2008; Swaney et al., 2011). In the winter, cold fronts associated to southerly winds transport ocean waters into the coast by Ekman pumping, favoring water retention and organic matter (OM) mineralization in the estuaries and lagoons of south Brazil (Abreu et al., 2010; Cabral and Fonseca, 2019; Möller et al., 2008). The same variation in the net metabolism was observed in the continental shelf of SC, where new production was enhanced in the summer, associated to the SACW upwelling up to the 20 m isobath, and OM regeneration in the winter, related to the PPW (Bordin et al., 2019; Brandini et al., 2014). Moreover, bacterioplankton abundance and biomass in the shelf of SC is 10 times higher in the winter than summer, mostly concentrated in the areas under the influence of the PPW (Fontes et al., 2018), fueling net heterotrophy and corroborating our results. Although the main nutrient pool of PPW is assimilated in higher latitudes (>30°S), the residual DIP and silicate, combinate with OM remineralization, can stimulate primary productivity and algal blooms in the SC shelf during winter (Brandini et al., 2014).

Denitrification predominates in both bays during summer, removing N out of the water column and limiting primary production, especially in the North Bay. Denitrification also increases over the summer in the SC continental shelf, associated with OM mineralization in the oxygen-depleted SACW (Bordin et al., 2019). In the BSCI, sediment characteristics might be influencing denitrification, since the North Bay is composed by mud enriched with organic matter and nitrogen, whereas the bottom of South Bay is mostly formed by sand (Bonetti et al., 2007). The carbon to sulfur ratio also indicated a more reduced state in the sediments of North Bay (11.6 C/S) than the South Bay (19.0 C/S) (Bonetti et al., 2007), contributing to sediment denitrification in the North. Although we estimated denitrification by the LOICZ model, our results oscillated between zero and -2 $\text{mmolN.m}^2.\text{day}^{-1}$, consistent with the values found in 20 other estuaries and coastal lagoons around the world, where denitrification was measured by membrane inlet mass spectrometry (Cornwell et al., 2014). N fixation contributed with just 13% of total DIN, indicating little contribution of diazotrophs, however *Trichodesmium* colonies, including some toxic species, have been reported close to the BSCI and in the continental shelf of SC, suggesting autochthonous N inputs (Proença et al., 2009; Rörig et al., 2018).

The effects of oceanic waters intrusion during winter were detected up the estuarine zone of the rivers, associated with the Ekman transport driving by southerly winds and low freshwater runoff, also observed in other systems of South Brazil (Netto et al., 2018). Salinity levels were three times higher in the winter than other seasons, improving the rivers water quality due to the decrease of continental runoff and the enhance of mixing processes with marine waters. The wintertime was also the only season where most of DO and fecal coliform were in compliance with regulations thresholds. DIN also decreases in winter, but DIP has not changed between seasons, probably due to the strong control over P fluxes by the sediment, as previously reported for different estuaries within the BSCI (Pagliosa et al., 2005). Overall, the estuarine zone of the rivers showed a clear pattern, where the worst-case scenarios were found in the summer and fall due to high wastewater runoff, precipitation rates and population fluctuation pressure, as well as discussed by Silva et al. (2016). Eutrophic conditions were sustained until late fall, when the intrusion of oceanic waters gained strength, boosting water renew. However, the low oxygen levels and high pheophytin-a concentrations indicated that the estuarine zones of the rivers are potentially heterotrophic most of the time, acting as a source of nutrients to the BSCI. The LOICZ model showed that nutrient inputs from the rivers are metabolized inside the bays, except during winter, when heterotrophic conditions shift the system from sink to source of nutrients, also increasing the trophic state. A conceptual model about the interactions among the meteorological patterns, water masses seasonality and the biogeochemical processes in watershed-bay-shelf continuum is showed in the Fig. 12.

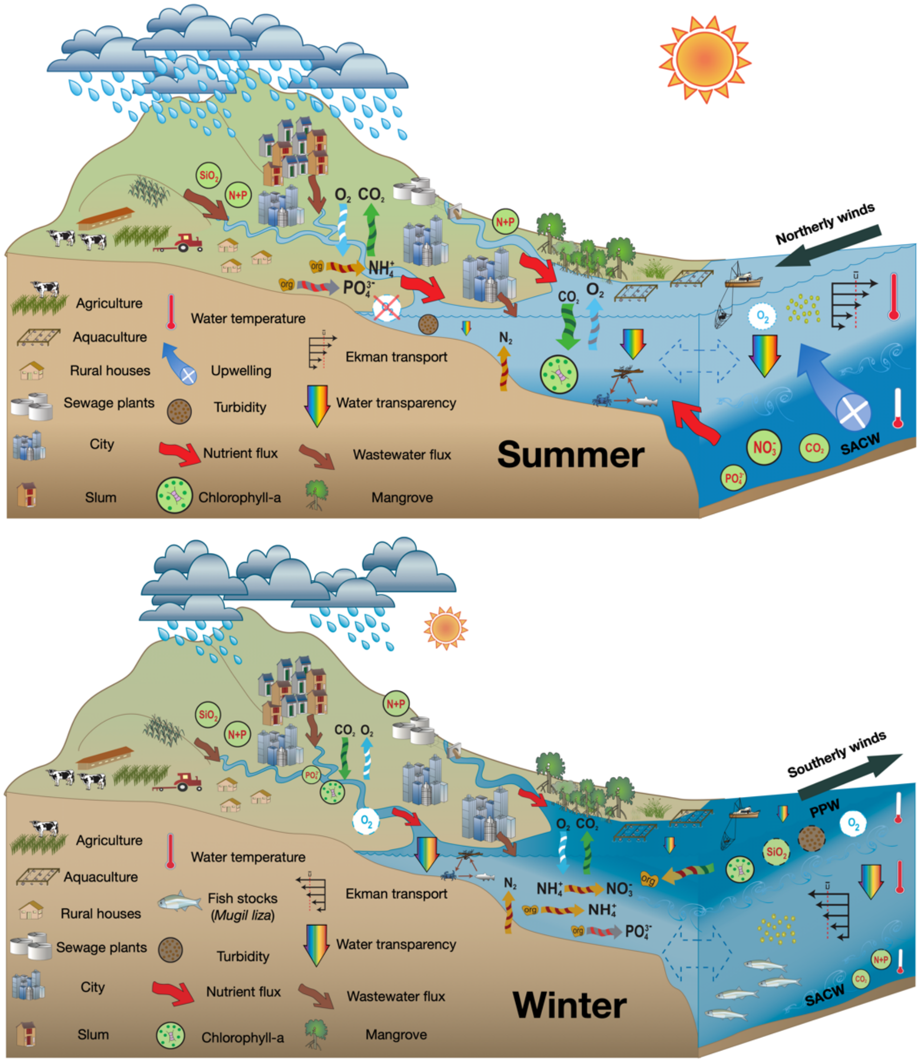

Figure 12. Conceptual model of the physical and biogeochemical seasonality in the watershed-bay-shelf continuum. Symbols and images are courtesy of the Integration and Application Network, University of Maryland Center for Environmental Science (https://ian.umces.edu).

4.3. ENSO effects in the biogeochemistry

The El Niño Southern Oscillation (ENSO) plays an important role in the meteorological patterns of South America, also affecting the physical and biogeochemical characteristics of the estuarine systems of South Brazil (Abreu et al., 2010; Netto et al., 2018). There were nine El Niño and eight La Niña events between 1993 and 2019, persisting from weeks to years and showing different levels of intensity. Extreme rainfall in the southeastern sector of South America is expected during El Niño months, whereas abnormally long droughts usually occurs on La Niña events (Grimm and Tedeschi, 2009). Considering all the main rivers that drain to the BSCI and all the dataset used in this study, mean freshwater runoff into the North and South bay were about 12 and 20 $m^3.s^{-1}$, respectively. However, we found that during extreme rainfall (> 250 $mm.month^{-1}$), observed in 13% of the months between 1993-2019, freshwater runoff can increase up to 114 $m^3.s^{-1}$ in the North bay and 273 $m^3.s^{-1}$ in the South bay, approximately ten times more than normal conditions. One of the effects of high runoff in estuarine systems is an abrupt drop of residence time and chlorophyll-a, such as observed in the San Francisco Bay when outflows exceed 200-300 $m^3.s^{-1}$ (Cloern, 2019).

Similar outflow effects were observed in the Patos Lagoon (Brazil), Jiulong River Estuary (China), Ilha Grande Bay (Brazil) and Plata River (Argentina) during El Niño or strong storm events, where the high rainfall exported or induced high phytoplankton biomass in the continental shelf (Abreu et al., 2010; Barrera-Alba et al., 2019; Chen et al., 2018; Odebrecht et al., 2015; Sathicq et al., 2015). The same pattern might be occurring in the BSCI, where low chlorophyll-a and nutrients were measured during El Niño, especially in the 1997-1998 event, one of strongest ENSO ever recorded, shifting meteorological patterns worldwide (Wolter and Timlin, 2011). Moreover, the GAM model indicated that the ENSO (inferred from intensity of the MEI) and salinity have strong controls on chlorophyll-a variability inside de bay, supporting our hypothesis. In the San Quintín Bay (Mexico), benthic respiration and clam excretion were associated with high nitrogen levels during the 1997-1998 El Niño (Hernández-Ayón et al., 2004). As previously mentioned, the BSCI hosts several mollusks' aquaculture farms, which might be contributing as a source of ammonium to the water column, as well as the discharges of the eutrophic rivers. However, since the BSCI is open on both sides, elevate exportation to the adjacent regions occurs when environmental conditions are favored, such as during El Niño due to the extreme rainfall, explaining the high concentration of chlorophyll-a, TSS and ammonium measured in the continental shelf. High nutrient and chlorophyll-a from the discharge of San Francisco Bay was also observed in the Gulf of Farallones (USA) during the 1997-1998 El Niño, sustaining the primary productivity in the continental shelf during a period of weak upwelling (Wilkerson et al., 2002).

The influence of the South Bay's plume over the continental shelf can reach up the 100 m isobath, such as measured in a transect perpendicular to the coast in the fall of 2019 (Fig. 6), which was under a weak El Niño event. The plume of the North Bay, as well as of other eutrophic coastal systems of SC (e.g. Itajaí river, Tijucas river, Camboriú river, and Babitonga Bay) have been reported to modify the plankton food web structure over the continental shelf, also driving harmful algal blooms, but little is known about the coupled effects of ENSO in these processes (Becker et al., 2018; Menezes et al., 2019; Rörig et al., 2018). The combined effect of estuarine waters with the intrusion of nutrient-rich water masses, such as the PPW, have also been described as a major mechanism driving dinoflagellate (e.g. *Dinophysis acuminata*) blooms in the BSCI and other coastal ecosystems of South Brazil (Alves et al., 2018). These organisms produce okadaic acid and dinophysistoxins, which causes diarrheic shellfish poisoning (DSP), the main reason for mollusks aquaculture and extraction bans in SC, since these toxins accumulate in mussels, oysters and fishes (Alves et al., 2018).

The PPW transport different phytoplankton species, especially during El Niño events, since the extreme rainfall strength the overflow of Plata river watershed (~ 3 million Km^2), the second largest in South America (Machado et al., 2013; Sathicq et al., 2015). The longest (~ 55 days) HAB reported in Brazil occurred in SC during the fall-winter of 2016, associated with a strong PPW intrusion and the 2015-2016 El Niño, when economic losses of shellfish aquaculture where up to 4 million US dollars (Proença et al., 2017). The estuarine systems of SC have elevated nutrient concentration and residence time, favoring episodic blooms of opportunistic phytoplankton species, such as *Dinophysis* ssp. and *Pseudo-nitzschia* spp., this last produces domoic acid, related to amnesic shellfish poisoning (Alves et al., 2018; Rörig et al., 2018). While dinoflagellate blooms are found in the winter, diatoms blooms usually occur in the late-spring and late-summer in south Brazil, both causing the embargo of shellfish aquaculture for a period of weeks to months (Fernandes et al., 2013). Although there is less water runoff during La Niña events, continuously wastewater runoff keeps coming from the watersheds, fertilizing the bay with nutrients. The highest levels of chlorophyll-a inside the bays were found during very strong La Niña events, as also observed in Babitonga bay (~ 100 Km North of BSCI) and Patos Lagoon (~ 400 Km South of BSCI), associated with high water residence time (Alves et al., 2018; Odebrecht et al., 2015).

4.4. Long-term trends and eutrophication management approaches

Although the water quality parameters in estuarine systems change continually and vary across multiple time scales (Cloern, 2019), some trends were observed in the BSCI, such as the NP ratio shift from P to N limiting and the increase of TSS in the most recent years. Silicate, on the other hand, seems to be decreasing, indicating that the TSS might be composed of organic materials from sewage, corroborating with the DIP and coliform increases. HABs have also been increasing over the coast of SC in the last years and, although the actual cause is not clear yet, it was suggested that aquaculture and sewage runoff might be contributing to this trend, especially for *Pseudo-nitzschia* spp. blooms (Rörig et al., 2018). The GAM model suggested that chlorophyll-a has increased through the years, also associated with high temperatures. The frequency of extreme events, such as heat waves and intense rainfall, have increased over the coast of SC, favoring

HABs (Gouvêa et al., 2017; Nunes and Silva, 2013). Moreover, the future outlook of the ASSETS model indicated that the BSCI is showing susceptibility to eutrophication since the 1990's and that this condition will likely remain the same in the next decade as a result of high nutrient loads and periodically HABs. It is worth mentioning that even considering 100% of effluent treatment, the bays remained susceptible to eutrophication given its moderate flushing time (~ 40 days) and seasonal influence of nutrient-rich oceanic water masses. Furthermore, the reduction of anthropogenic nutrient loads alone might not be able to shortly revert eutrophication, since other mechanisms, such as sediment nutrient release and environmental characteristics, may sustain eutrophic conditions for years or even decades (Duarte et al., 2009; Smith and Schindler, 2009).

While our dataset starts in 1993, previous studies using sediment cores traced carbon and nutrient levels in the BSCI back to 1880 through isotope techniques (Lamego et al., 2017). They found that total carbon, nitrogen and phosphorus increased towards the most recent years, concomitantly with population and urbanization growth, showing a gradual evolution of eutrophication. Major increases in sedimentation rates were also found from the 1960's onwards, caused by sediment load from rivers draining human settlements. Also, the $\delta^{15}N$ shifted to more enriched values since the 1990's in the North Bay, while the $\delta^{13}C$ indicated that the main source of organic matter is the phytoplankton. The increase of $\delta^{15}N$ may be related to denitrification rates in the recent decades, as the LOICZ model showed, about 60% of N is removed by this process in the North Bay, similar to the rates found in coastal systems of New Zealand (Zeldis and Swaney, 2018). Denitrification removes the lighter ^{14}N faster than the ^{15}N isotope, being an important mechanism to regulated eutrophication (Abreu et al., 2006). In the shelf of SC, sediment core indicates that carbon and nutrients concentrations were stable in the last decades (Oliveira et al., 2014), suggesting that the organic matter is retained and more preserved in the bays.

Ammonia is the most toxic form of DIN, causing chronic and/or acute toxicity effects in many estuarine species and inhibit primary and secondary production when soluble in high concentrations (Livingston et al., 2002). In the rivers, we found N as ammonia up to 549 $\mu gNH_3\text{-}N.L^{-1}$, well above the recommended for waters of high conservation value (160 $\mu gNH_3\text{-}N.L^{-1}$), but near 460 $\mu gNH_3\text{-}N.L^{-1}$, considered as moderately disturbed (Batley and Simpson, 2009). High concentrations of copper were also reported in the water of the bays and rivers of BSCI, up to 213 $nmol.L^{-1}$, associated with anti-fouling paints and industrial activities (Mello et al., 2005). Toxic compounds in the water column are worrying, since, besides aquaculture, the BSCI is a nursery ground for several fish species, such as the whitemouth croaker (*Micropogonias furnieri*), catfish (*Genidens genidens*) and mullet (*Mugil liza*) (Cattani et al., 2018). It is also the southern limit of the Guiana dolphin (*Sotalia guianensis*) occurrence in Brazil. *S. guianensis* stays inside of BSCI about 70% of its lifetime, increasing the risk of contamination (Rossi-Santos and Flores, 2009; Wedekin et al., 2007).

The most southern coralline algal bank along the Brazilian coast occurs near the North Bay (Arvoredo island), providing substrate for numerous species and supporting artisanal fisheries on its surroundings (Rocha et al., 2006). However, local (continental runoff) and global stressors (acidification and warming) have been reported to induce rhodolith beds decalcification (Gouvêa et al., 2017; Horta et al., 2016). As also demonstrated by the spatial distribution of benthic foraminifera associations, organically enriched waters from North Bay could reach the Arvoredo island, which might threaten the sensitive marine species established there (Paquette et al., 2016). TRIX results indicate that the BSCI has shown eutrophic status since 2005, contributing to ecosystem degradation and increasing the susceptibility to long-term eutrophication. Considering the TRIX and hydrodynamics of BSCI, the least susceptible region to eutrophication is the outer area of South Bay, where strong currents and high grain size sediments were observed (Bonetti et al., 2007; Vianna and Bonetti, 2018). We found that in this area, persistent wind events (3-day mean), with velocities greater than 3.0 $m.s^{-1}$, decreases the TRIX from eutrophic to mesotrophic, indicating that the improvement of circulation or the intrusion of oceanic waters are strong mechanisms to increase the water quality, which was not observed in the others sectors of the bay.

The coastal zone of Santa Catarina has shown susceptibility to erosion and flood, mainly in the most urbanized areas during storm surges events, such as the central region of Santa Catarina State, where the BSCI is located (Serafim et al., 2019). Although the bays are semi-enclosed systems with low exposure to waves and tides, they were classified as moderate vulnerable to erosion and flood due to the low declivity of coastal plain and degree of urbanization (Silveira and Bonetti, 2019). There are five remain mangroves patches in the BSCI (Ratones, Saco Grande, Itacorubi, Tavares, and Aririú) that could help to reduce flood during storm surges. However, wetlands deforestation compromised these functions, resulting in episodic floods, especially on the roads built over the mangroves and susceptible areas. Among the 13 rivers considered in this study, five of them drains towards these mangroves and, as our study showed, the watersheds of BSCI are in eutrophication process, compromising the environmental quality of these systems. Ratones and Tavares are inside protected areas due to their ecological and social importance. The Pirajubaé extractive reserve is in the Tavares mangrove, where traditional communities collect cockles (*Anomalocardia brasiliana*) to market and subsistence. However, dramatically decrease of *A. brasiliana* has been occurring and some studies already indicate that the mass mortality reported in 2015 (~95% of the population died) might be related to heat waves and eutrophication (Sampaio, 2018; Carneiro et al., *in prep.*). The synergetic effects of local and global stressors might compromise the biodiversity, water quality and food security of BSCI since this system is susceptible to eutrophication and to other factors as well.

5. Conclusions

The BSCI watersheds are under high anthropic pressure, where the most urbanized systems are more susceptible to eutrophication due to wastewater runoff. Worst-case scenarios in the rivers were found in the summer and fall, associated with sewage inputs boosted by rainfall, mass tourism, WWTPs overloads and the lack of sewage treatment systems. In the bays, the eutrophication assessment methods resulted in similar feedbacks, indicating that trophic status oscillated from moderate to high over the last three decades and that management intervention is needed in order to avoid dramatically loss of ecosystem services and functions. The seasonal effect of water masses (SACW and PPW) and rainfall events drive the ecosystem metabolism and the water residence time of BSCI, from new primary production in the summer to regeneration of organic matter in the winter, coupled with low and high residence time, respectively. Large-scale events, such the ENSO, had strong controls over the transport of materials in the watershed-bay-shelf continuum. The overall synergetic effects of the continental runoff associated with meso-scale phenomena (e.g. oceanic water masses) have important implications for the occurrence of HABs in south Brazil, both during summer and winter. Effective actions to mitigate eutrophication include address sewage and fertilizer sources, upgrade the WWTPs with tertiary treatment, expand wastewater treatment coverage for densely populated watersheds, wetlands restoration and long-term monitoring. In this way, the anthropic pressures might decrease, also providing better water quality to sustain the rich biodiversity and ecosystem services of BSCI.

6. Acknowledgments

We would like to thank all the people, researches and students who collaborate in any way to produce all the data used in this article. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) and the Fundação de Amparo à Pesquisa e Inovação do Estado de Santa Catarina - Brasil (FAPESC) - Finance Code Edital 3/2017.

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Supplemental materials

Table S1. Description of the data sources for the watersheds, bays and continental shelf. Variables: Depth (D), Salinity (Sal), Temperature (Temp), pH, Dissolved Oxygen (DO), Dissolved Inorganic Nutrients (Nutri), Chlorophyll-a and Pheophytin-a (CP), Turbidity (Turb) and Total Suspended Solids (TSS).

Source	Sampling period	System	Variables	Number of samples
(Cerutti, 1996)	1993-1994	North bay	Sal, Temp, pH, DO, TSS	94
(Ferreira et al., 2006)	1998-2002	North and South bays, shelf	Sal, Temp, pH, DO, Turb, C, TSS	970
This Study	1996-2008	South bay	Sal, Nutri	264
(Pagliosa et al., 2006)	2002	Watershed	Sal, Temp, pH, DO, Nutri, CP, TSS	54
(Souza, 2008)	2006	North and South bays	D, Sal, Temp, pH, DO, Nutri, CP, TSS	133
(Parizotto, 2009)	2007-2008	North and South bays and watershed	Sal, Temp, pH, DO, Nutri, CP, Turb	194
(Alves et al., 2010)	2006-2008	South bay	Sal, Temp, Nutri, CP	221
(Simonassi et al., 2010)	2006-2008	North bay and shelf	Sal, Temp, pH, DO, Nutri, CP, TSS	71
(Rodrigues, 2016)	2005-2006 2011-2012	Watershed	Sal, Temp, pH, DO, Nutri, CP, TSS, Turb	229
(Silva et al., 2016)	2013-2014	Watershed	Sal, Temp, DO, Nutri, CP, TSS, Turb	82
(Fonseca et al., *in prep.*)	2005-2010	Bays, watershed and shelf	D, Sal, Temp, pH, DO, Nutri, CP, TSS	376
This Study	2010	North bay and shelf	D, Sal, Temp, pH, DO, Nutri, CP, TSS, Turb	21
(Garbossa et al., 2017)	2012-2013	Watershed	Fecal coliform (*E. coli*), watershed population and water flow	1147
This Study	2012	North and South bays	Sal, Temp, pH, Nutri, TSS	21
This Study	2014	North and South bays	D, Sal, pH, Temp, DO	33
(Bordin et al., 2019)	2014-2016	Shelf	D, Sal, Temp, DO, Nutri, CP, TSS	219
This Study	2017	North and South bays	D, Sal, Temp, pH, DO, Nutri, CP	43
This Study	2018-2019	North bay	Sal, Temp, pH, DO, Nutri, CP, TSS	14
(Gomes et al., *in prep.*)	2017-2018	Shelf	Sal, Temp, pH, DO, Nutri, CP	39
(Cabral et al., *in prep.*)	2018-2019	Shelf	D, Sal, Temp, pH, DO, Nutri, CP	85

Table S2. PERMANOVA results considering the same samples and variables (salinity, oxygen saturation, chlorophyll-a, ammonium, DIP, nitrate and silicate) used to perform the PCO at figure 2 of the manuscript. Df = degrees of freedom, SS = sum of squares, MS = mean square, perms= permutations. The data was standardized before resemblance analysis (Gower coefficient).

Source	**df**	**SS**	**MS**	**Pseudo-F**	**P(perm)**	**perms**
Salinity Zone	2	178.78	89.4	35.1	0.001	998
System	2	144.92	72.4	28.5	0.001	998
Residual	655	1666	2.5			
Total	569	3052				

PAIR-WISE TESTS

Groups	**t**	**P(perm)**	**perms**
Rivers – Freshwater vs. Rivers – Estuarine	6.7	0.001	998
Rivers – Estuarine vs. Bays – Estuarine	4.9	0.001	998
Bays – Estuarine vs. Bays - Seawater	2.7	0.001	998
Bays – Seawater vs. Shelf - Seawater	4.7	0.001	998

Table S3. PERMANOVA results considering the same samples and variables (salinity, temperature, DIP, DIN, dissolved oxygen and chlorophyll-a) used to perform the PCO at figure 5 of the manuscript. Df = degrees of freedom, SS = sum of squares, MS = mean square, perms = permutations. The data was standardized before resemblance analysis (Gower coefficient).

Source	**df**	**SS**	**MS**	**Pseudo-F**	**P(perm)**	**perms**
Region	2	5355.9	2677.9	29.035	0.001	999
Season	1	3665.7	3665.7	39.745	0.001	999
Region vs. Season	2	975.59	487.8	5.2889	0.002	998
Residual	578	53309	92.23			
Total	583	65010				

PAIR-WISE TESTS

Within level “Fall-Winter” of factor “Season of the Year”

Groups	**t**	**P(perm)**	**perms**
North Bay vs. South Bay	25.403	0.002	997
North Bay vs. Shelf	4.339	0.001	998
South Bay vs. Shelf	56.924	0.001	999

Within level “Spring-Summer” of factor “Season of the Year”

Groups	**t**	**P(perm)**	**perms**
North Bay vs. South Bay	1.72	0.054	999
North Bay vs. Shelf	53.666	0.001	999
South Bay vs. Shelf	39.923	0.001	998

Within level “Shelf” of factor “Region”

Groups	**t**	**P(perm)**	**perms**
Spring-Summer vs. Fall-Winter	6.3082	0.001	999

Within level “North Bay” of factor “Region”			
Groups	**t**	**P(perm)**	**perms**
Spring-Summer vs. Fall-Winter	5.1009	0.001	999
Within level “South Bay” of factor “Region”			
Groups	**t**	**P(perm)**	**perms**
Spring-Summer vs. Fall-Winter	2.2845	0.002	999

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CONCLUSÕES

As bacias hidrográficas da BISC estão sob elevada pressão antrópica, onde as regiões mais urbanizadas estão mais susceptíveis a eutrofização devido à entrada de esgoto e águas residuais. Em escala sazonal, os piores cenários foram encontrados no verão e no outono devido ao aumento da entrada de efluentes em função do turismo em massa, o que potencializa as entradas de esgoto, tanto pelas descargas difusas, quanto pela sobrecarga das estações de tratamento de esgoto, as quais não possuem capacidade para atender a demanda atual, principalmente concomitante aos períodos de intensa precipitação que ocorrem no verão. Os métodos de avaliação da eutrofização indicaram resultados similares durante as últimas três décadas, variando, principalmente, de condições mesotróficas a eutróficas. Para a próxima década, estas condições tendem a permanecer as mesmas devido ao moderado tempo de residência da água, pressões antrópicas e as frequentes florações de algas tóxicas que ocorrem nas baías. A intrusão de massas de água oceânicas (ACAS e PRP) e o padrão de precipitação da região, favoreceram autotrofia no verão e heterotrofia no inverno, concomitante a um menor e maior tempo de residência da água, respectivamente. Na interface continente-oceano da BISC, os eventos de El Niño aumentaram a exportação de materiais para a plataforma continental devido ao aumento da descarga fluvial, potencializadas pelo aumento anômalo da precipitação. Já durante os eventos de La Niña, as maiores concentrações de nutrientes e biomassa fitoplanctônica foram observadas dentro das baías. O efeito acoplado da entrada de nutrientes pelos rios eutrofizados e dos fenômenos de mesoescala têm um papel importante para a ocorrência de florações de algas tóxicas no sul do Brasil, tanto no verão quando no inverno. Algumas ações para mitigar a eutrofização incluem: identificar as fontes de esgotos e fertilizantes, implementar estações de tratamento de esgoto com sistema terciário, restauração e conservação das áreas úmidas (manguezais, mata ciliar, marismas, etc.) e monitoramento de longa duração. Desta maneira, as pressões antrópicas podem diminuir, favorecendo a melhora da qualidade das águas, preservação da biodiversidade e dos serviços ecossistêmicos.

CONTRIBUIÇÃO CIENTÍFICA DA DISSERTAÇÃO

1. Melhor entendimento da influência da sazonalidade na biogeoquímica do sistema.
2. Avaliação ambiental espaço-temporal da qualidade da água.
3. Quantificação do estado trófico utilizando diferentes metodologias em escala temporal.
4. Influência de eventos de meso- e macro-escala na biogeoquímica do sistema.
5. Compilação de base de dados de longa duração de uma região ainda pouco amostrada.

RESUMO EM LINGUAGUEM ACESSÍVEL AOS LEIGOS

A Baía da Ilha de Santa de Catarina (BISC) recebe drenagem da região mais urbanizada do Estado de SC, cerca de 1,2 milhão de pessoas habitam as bacias hidrográficas, onde o tratamento de esgoto é precário ou não existente. Somado a isto, as cidades no entorno das baías recebem cerca de 1,5 milhões de turistas anualmente, principalmente no verão, aumentando a entrada de efluentes. Além das perdas do potencial turístico, a poluição deste ambiente também pode impactar a maricultura nas baías, responsável por mais de 70% da produção nacional, e as áreas protegidas, como a Ilha do Arvoredo e os manguezais, que sustentam alta biodiversidade e recursos pesqueiros, nos quais algumas comunidades tradicionais ainda dependem para sobreviver. Este estudo teve como objetivo avaliar a qualidade da água das baías ao longo das últimas três décadas. Os resultados indicaram que os rios que drenam para as baías estão poluídos e que essa condição piora no verão, em resposta ao aumento do turismo e a baixa qualidade dos sistemas de tratamento dos esgotos. No entanto, uma melhora na qualidade da água foi observada durante o inverno, devido a menor entrada de esgoto e a maior intensidade dos ventos de sul, que trazem a água do mar para dentro dos rios, “limpando” momentaneamente estes sistemas. As chuvas são mais fortes no período de El Niño, aumentando a descarga dos rios, que carrega para o mar aberto as águas poluídas. Já durante meses de La Niña, a descarga dos rios diminui, retendo os compostos químicos e microalgas dentro das baías. O cenário futuro para a qualidade da água das baías tende a se manter inalterado, pois o sistema é sensível à entrada de compostos químicos vindo do continente. No entanto, algumas medidas podem ser tomadas para tentar melhorar este cenário, como: identificar as fontes poluidoras, implementar estações de tratamento de esgoto com sistema terciário (as quais removem nutrientes), restaurar a vegetação no entorno dos ambientes aquáticos e monitoramento da qualidade de água de longa duração.

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