UNIVERSIDADE FEDERAL DA BAHIA
INSTITUTO DE GEOCIÊNCIAS
PROGRAMA DE PESQUISA E PÓS-GRADUAÇÃO EM GEOLOGIA
ÁREA DE CONCENTRAÇÃO: MARINHA, COSTEIRA E SEDIMENTAR

TESE DE DOUTORADO

ASSINATURA GEOQUÍMICA DA MATERIA ORGÂNICA NA BAÍA DE TODOS OS SANTOS: EVIDÊNCIAS DO ANTROPOCENO E SUAS IMPLICAÇÕES AMBIENTAIS

CARINE SANTANA SILVA

SALVADOR
2024

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Orientador: Prof. Dr. José Maria Landim Dominguez

Tese de Doutorado apresentada ao Programa de Pós-Graduação em Geologia do Instituto de Geociências da Universidade Federal da Bahia como requisito à obtenção do Título de Doutora em Geologia, Área de Concentração: Marinha, Costeira e Sedimentar.

SALVADOR
2024

Ficha catalográfica elaborada pela Biblioteca Universitária de Ciências e Tecnologias Prof. Omar Catunda, SIBI – UFBA.

S586 Silva, Carine Santana

Assinatura geoquímica da matéria orgânica na Baía de Todos os Santos: evidências do antropoceno e suas implicações ambientais. / Carine Santana Silva. – Salvador, 2024.

119 f.

Orientador: Prof. Dr. José Maria Landim Dominguez

Tese (Doutorado) – Universidade Federal da Bahia. Instituto de Geociências, 2023.

1. Hidrocarbonetos. 2. Geoquímica. 3. isótopo estável. I. Dominguez, José Maria Landim. II. Universidade Federal da Bahia. III. Título.

CDU 550.4

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TESE APROVADA PELA BANCA EXAMINADORA:

José Maria Landim Dominguez

Dr. José Maria Landim Dominguez
Orientador – PPGG/UFBA

Dr. Gilvan Takeshi Yogui
Examinador externo – ORGANOMAR/ UFPE

Drª. Márcia Caruso Bícego
Examinadora externa – IO/USP

Tatiane Combi

Drª. Tatiane Combi
Examinadora externa – LAGPOM/ UFPR

Dr. Renato da Silva Carreira
Examinador externo – LabMAM / PUC - RIO

Salvador – BA
2024

A meu filho, Guilherme, pelo maior amor do mundo.

AGRADECIMENTOS

Escrever uma tese implica em pedir muita paciência aos mais próximos e, ao mesmo tempo, precisar de muito apoio. Nenhuma vitória é individual. Esse trabalho só foi possível com o suporte de muitas pessoas e instituições.

A meus pais, por mesmo sem terem tido a oportunidade de seguir no ensino superior, terem a sabedoria e determinação de ter os estudos como prioridade na nossa casa. Obrigada pelo incentivo e apoio.

Ao meu orientador José Maria Landim Dominguez, pelo apoio e colaboração. Por escolher acreditar diversas vezes no meu potecial. Aos companheiros do Laboratório de Estudo Costeiro (LEC): Nara, Clarinha, Marcelinha, Rafa, Milena e Didica, pelo ótimo ambiente de trabalho.

Ao laboratório Laboratório de Compostos Orgânicos em Ecossistemas Costeiros e Marinhos (OrganoMAR) pelo apoio nas análises de hidrocarbonetos. Agradeço especialmente ao prof. Gilvan Takeshi Yogui pela confiança, pelo apoio, pelo conhecimento passado e pela gentileza. A Lino, pela paciência e apoio nas análises.

A Marcos de Almeida e Lucas Guimarães, pelo apoio fundamental nas análises de hidrocarbonetos, pela hospedagem e companhia em Recife. Pela amizade, suporte e estímulo ao longo desses anos.

Ao laboratório de Física Nuclear Aplicada (LFNA) pelo apoio nas análises de isótopos. Agradeço em especial ao Dr. José Roberto pela agilidade, boa vontade e educação.

Ao laboratório de Estudos do Petróleo (LEPETRO), em especial prof. Antônio Fernando, Sarinha, Juci, Gisele e Larissa, pelo apoio nas análises granulométricas, conselhos e resoluções burocráticas.

Ao Dr. Renato Campello por ter disponibilizado a estrutura do Laboratório de Geoquímica da UFF e seus colaboradores para o pré-tratamento das amostras de sedimento para determinação do black carbon. Em especial, ao Dr. Libério Júnior e ao técnico Leandro pela disponibilidade e gentileza.

Ao prof. Marcos Godoy pelo apoio com a datação dos testemunhos.

A Carlos Purificação, pelo suporte no campo, pelo desenvolvimento dos mapas, pelo apoio e incentivo nessa jornada.

Ao grande amor da minha vida, meu pequeno Guilherme, que nasceu no final dessa longa trajetória e que me encheu de amor, força e determinação para finalizar essa etapa.

Um provérbio africano diz que "É preciso uma aldeia inteira para educar uma criança". Então agradeço especialmente aos avós Ana, Nilton e Sr. Antônio, e a Nara, pelo suporte, disponibilidade e amor com meu neném.

À banca, pela oportunidade enriquecer e melhorar este trabalho, pois pelos olhares mais distantes é que se encontram diferenças na paisagem. Obrigado!

Ao Programa de Pós-Graduação em Geologia da UFBA pela oportunidade.

Ao CNPq, pela bolsa concedida. Por permitir que tantos estudantes se dediquem integralmente às suas pesquisas e incentivar o exercício da pós-graduação no país.

À CAPES. O presente trabalho foi realizado com o apoio da CAPES - Código de financiamento 001.

Á UFBA. Universidade pública, gratuita e de qualidade.

Meus sinceros agradecimentos a todos.

RESUMO

Mudanças significativas no aporte ou no tipo de matéria orgânica (MO) podem resultar em alterações no nível de trofia do ambiente, no grau de labilidade, na liberação de contaminantes adsorvidos, bem como no armazenamento e na ciclagem biogeoquímica do carbono. Nesse contexto, a Baía de Todos os Santos (BTS) tem sido submetida a múltiplas atividades antrópicas com potencial de alterar a natureza e o conteúdo da MO sedimentar: indústria petrolífera, química e, secundariamente, urbanização. A reconstrução das variações históricas do carbono, nitrogênio e seus respectivos isótopos, hidrocarbonetos (alifáticos, policíclicos aromáticos e alquilados) e do carbono negro (BC) com base em registros sedimentares é significativa para a compreensão das emissões de poluentes de longo prazo, o rastreamento de fontes e o estabelecimento de estratégias eficazes para o controle da poluição. Ao comparar dois testemunhos de sedimentos coletados na região norte da BTS as variações históricas foram reconstruídas e comparadas com o desenvolvimento socioeconômico local. Em linhas gerais, os resultados indicam que os perfis temporais da MO depositada nos testemunhos podem diferir significativamente em uma pequena escala espacial. No testemunho T2, coletado mais offshore, os parâmetros analisados indicam melhores condições ambientais com fontes naturais de MO. As concentrações de carbono orgânico total - COT e nitrogênio total – NT variaram de 0,66 a 1,98% e 0,12 a 0,19%, respectivamente. O modelo de mistura isotópico mostrou uma contribuição marinha média de 70,23%, relativamente uniforme, com exceção do período entre as décadas de 1930 e 1980, quando houve um aumento da contribuição de marinho possivelmente associada à expansão de um banco de algas. Os baixos teores de ALC$_{TOT}$ (0,25 a 2,23 µg g^{-1}), $\sum$ALI (0,36 a 2,90 µg g^{-1}), HPA$_{TOT}$ (7,62 a 354,45 ng g^{-1}), HPA$_{ALK}$ (1,11–77,50 ng g^{-1}), associados à ausência de UCM, pristano e fitano, mostram pouco ou não há influência de contaminação por fontes antrópicas nas áreas da MO. Os índices diagnósticos indicaram as fontes pirolíticas como as principais fontes de HPAs no testemunho T2. Os teores de BC variaram de 0,0800 a 0,440 mg g^{-1} e foi produzido partir da queima incompleta de biomassa do tipo C4. No testemunho T4, as concentrações de COT (1,17 a 2,23%) e NT (0,13 a 0,26%) aumentaram ao longo do tempo, mas ainda indicam um sistema oligotrófico. O modelo de mistura isotópica mostrou mudanças nas proporções das fontes dominantes de MO, com o aumento gradual da contribuição terrestre (alóctone) a partir da década de 1950, provavelmente relacionado com mudanças no uso do solo. A partir da década de 1970, os teores de hidrocarbonetos em geral aumentaram de maneira abrupta alcançando o nível de poluição elevada, apesar da redução verificada nas últimas décadas. Nesse período, houve também uma mudança nas fontes de BC, com as contribuições da queima da biomassa dando lugar às emissões veiculares. A partir de 1980, uma clara assinatura petrogênica foi vista com a presença de uma mistura complexa não resolvida (nd para 349,94 µg g^{-1}), concentrações aumentadas de $\sum$ALI (0,35 a 380,34 µg g^{-1}), ALC$_{TOT}$ (0,25 a 5,84 µg g^{-1}), HPA$_{TOT}$ (3,05 a 1096,37 ng g^{-1}) e HPA$_{Alk}$ (0,40 a 329,23 ng g^{-1}). A partir da década de 1990 houve um aumento mais pronunciado nas concentrações de BC. Os efeitos da implementação de políticas ambientais para melhorar a qualidade da água da BTS começaram a refletir-se na qualidade dos sedimentos no início do século XXI.

Palavras-chave: isótopo estável, carbono orgânico, carbono negro, hidrocarbonetos.

ABSTRACT

Significant changes in the transport or composition of organic matter (OM) can lead to alterations in trophic environments, the degree of lability, the release of adsorbed contaminants, as well as the storage and biogeochemical cycling of carbon. In this context, Baía de Todos os Santos (BTS) has been subject to multiple human activities with the potential to modify the nature and content of sedimentary OM: oil and chemical industries, and to a lesser extent, urbanization. Reconstructing historical variations in carbon, nitrogen, their respective isotopes, hydrocarbons (aliphatic, polycyclic aromatic, and alkylated), and black carbon (BC) based on sedimentary records is significant for understanding long-term pollutant emissions, tracing sources, and establishing effective pollution control strategies. By comparing two sediment cores collected in the northern region of the BTS, historical variations were reconstructed and compared with local socioeconomic development. Overall, the results indicate that the temporal profiles of OM deposited in cores can vary significantly on a small spatial scale. In core T2, collected further offshore, the analyzed parameters indicate better environmental conditions with natural sources of OM. The concentrations of total organic carbon (TOC) and total nitrogen (TN) ranged from 0.66% to 1.98% and 0.12% to 0.19%, respectively. The isotopic mixing model showed an average marine contribution of 70.23%, relatively uniform, with the exception of the period between the 1930s and 1980s, when there was an increase in the marine contribution possibly associated with the expansion of an algal bed. The low levels of ALC_{TOT} (0.25 to 2.23 µg g^{-1}), ∑ALI (0.36 to 2.90 µg g^{-1}), HPA_{TOT} (7.62 to 354.45 ng g^{-1}), HPA_{ALK} (1.11–77.50 ng g^{-1}), associated with the absence of UCM, pristane, and phytane, indicate little or no influence of contamination by anthropogenic sources in the OM areas. The diagnostic indices indicated pyrolytic sources as the main contributors of PAHs in the T2 core. The BC contents ranged from 0.0800 to 0.440 mg g^{-1} and were produced from the incomplete combustion of C4 type biomass. In core T4, the concentrations of total organic carbon (TOC) (1.17 to 2.23%) and total nitrogen (TN) (0.13 to 0.26%) increased over time but still indicate an oligotrophic system. The isotopic mixing model revealed changes in the proportions of the dominant sources of organic matter (OM), with a gradual increase in terrestrial (allochthonous) contribution from the 1950s onwards, likely associated with changes in land use. From the 1970s onwards, hydrocarbon levels increased abruptly, reaching high pollution levels, despite the reduction observed in recent decades. During this period, there was also a shift in BC sources, with contributions from biomass burning being replaced by vehicle emissions. From 1980 onwards, a clear petrogenic signature was observed with the presence of an unresolved complex mixture (nd to 349.94 µg g^{-1}), increased concentrations of ΣALI (0.35 to 380.34 µg g^{-1}), ALC_{TOT} (0.25 to 5.84 µg g^{-1}), HPA_{TOT} (3.05 to 1096.37 ng g^{-1}), and HPA_{Alk} (0.40 to 329.23 ng g^{-1}). From the 1990s onwards, there was a more pronounced increase in BC concentrations. The effects of implementing environmental policies to improve water quality in the BTS began to be reflected in sediment quality at the beginning of the 21st century.

Keywords: stable isotopes, organic carbon, black carbon, hydrocarbons.

APRESENTAÇÃO

Conforme indicado pelo regimento do Programa de Pós-Graduação em Geologia – PPGEO, da Universidade Federal da Bahia, através da Resolução nº 01/2015, a tese está dividida em capítulos e os resultados são expressos na forma artigos científicos.

O primeiro capítulo é a **Introdução Geral** na qual é apresentado o tema pesquisado, sua relevância, a localização da área de trabalho, bem como objetivos geral e específicos. Os capítulos 2 e 3 têm o objetivo de apresentar o desenvolvimento do trabalho sob forma de artigos:

- Artigo 1, intitulado “**Changes in the nature of organic matter in a large tropical urban bay: temporal variations and environmental implications**”, escrito em colaboração com o Dr. José Maria Landim Dominguez, Dr. Gilvan Takeshi Yogui e Msc Marcos de Almeida, foi publicado na revista *Regional Studies in Marine Science,* classificada como Qualis A3 para Geociências (Fator de Impacto: 2.1).

- Artigo 2, intitulado “**Deposição histórica de carbono negro e hidrocarbonetos policíclicos aromáticos em sedimentos de uma baía tropical: exploração de petróleo, impactos da urbanização e agricultura**”, escrito em colaboração com o Dr. José Maria Landim Dominguez e Dr. Gilvan Takeshi Yogui, está no formato de submissão para a revista *Regional Studies in Marine Science*.

Na seção **Conclusões** são feitas considerações finais a cerca do trabalho, seguidas de sugestões para novas pesquisas na área. As regras de formatação de submissão da revista *Regional Studies in Marine Science* constam no ANEXO C. O Apêndice 1 descreve a participação dos coautores dos artigos.

SUMÁRIO

CAPÍTULO 1

INTRODUÇÃO GERAL

A magnitude, extensão e velocidade das mudanças climáticas, geoquímicas e sedimentológicas verificadas no registro geológico recente são únicos na história do planeta. Nesse sentido, uma nova Era geológica vem se consolidando na comunidade científica — o Antropoceno — na qual a humanidade tornou-se uma força significativa para a modificação global (Crutzen; Stoermer, 2000). Enquanto o Holoceno representa cerca de 11.700 anos de estabilidade climática favorável ao desenvolvimento humano, o Antropoceno destaca os impactos da industrialização, urbanização e globalização na transformação dos sistemas terrestres (Steffen et al., 2007).

O debate sobre a oficialização do Antropoceno como uma época geológica ainda está em curso na comunidade científica. Alguns argumentam que o início do Antropoceno deve ser marcado pela Revolução Industrial (Crutzen; Stoermer, 2000; Zalasiewicz et al., 2011), enquanto outros propõem datas mais recentes, como meados do século XX (Lewis; Maslin, 2015). De fato, desde a década de 1950, a influência da atividade humana no sistema terrestre aumentou acentuadamente. Esse período vem sendo chamado de ‘Grande Aceleração’ e é marcada por uma grande expansão da população humana, aumento acentuado do uso de produtos químicos sintéticos, disseminação global de materiais radioativos resultantes das explosões de bombas atômicas durante a Segunda Guerra Mundial, além de grandes mudanças nos processos naturais (Lewis; Maslin, 2015).

O século XX foi marcado por uma perturbação dos ciclos dos nutrientes sem precedentes, ultrapassando fronteiras planetárias definidas como um ‘espaço operacional seguro para a humanidade’ (Rockström et al., 2009; Steffen et al., 2019). Essa ciclagem acelerada dos nutrientes reflete o rápido crescimento populacional, a mudança uso do solo, o uso de fertilizantes agrícolas, o descarte de esgoto, a queima de combustíveis fósseis e outros processos antrópicos (Steffen et al., 2019). Colocando em perspectiva, durante o século passado, a entrada estimada de nitrogênio reativo pelas atividades humanas (210 Tg N^{-1}) ultrapassou a fixação natural (203 Tg N^{-1}) (Stevens, 2019). Já referente ao ciclo do carbono, o uso em escala industrial de fluxos de energia derivados do carbono fóssil causou um aumento exponencial de carbono liberado para os reservatórios atmosférico, terrestre e oceânico (Le Quéré etal., 2017). As emissões globais de CO_2 eram cerca de 5 bilhões de toneladas por ano em 1950. Em 2020, esse número mais do que triplicou, atingindo aproximadamente 37 bilhões de toneladas por ano (Global Carbon Atlas, 2023).

A matéria orgânica (MO) é composta principalmente por carbono, hidrogênio, oxigênio e nitrogênio. Sua função é indispensável na natureza, servindo como fonte de energia na teia alimentar terrestre e marinha, além de atuar como elo de ligação entre diversos ciclos biogeoquímicos (Lehmann; Kleber, 2015). A MO também é reconhecida por sua importância na distribuição, mobilidade, solubilidade, toxicidade e biodisponibilidade de diversos poluentes (Derrien et al., 2017).

A MO pode carregar impressões digitais dos fluxos hidrológicos e processos sedimentares, incluindo modificações antropogênicas no sistema natural (Liu et al., 2022). Mudanças significativas no aporte ou no tipo de MO podem resultar em alterações no nível de trofia do ambiente, no grau de labilidade, na liberação de contaminantes adsorvidos, bem como no armazenamento e na ciclagem biogeoquímica do carbono (Heredia et al., 2022).

Alguns efeitos imediatos desses processos nos corpos hídricos são conhecidos e bem documentados, como a eutrofização, acidificação, alteração do teor de oxigênio dissolvido e outros, que por fim produzem desequilíbrios nos ecossistemas e, não raro, inviabilizam o aproveitamento desses corpos d’água (Dang et al., 2018; Cabral et al., 2019; Liu et al., 2020). No entanto, o entendimento sobre os demais efeitos do desequilíbrio entre o aporte natural e antropogênico nos ciclos biogeoquímicos precisa ser melhor elaborado.

Em função disso, a composição e a determinação de fontes da MO tem sido amplamente descritas em todo o mundo a partir de métodos que identificam e/ou quantificam seus componentes a nível elementar (e.g. C, N, CN - carbono negro), isotópico (e.g. $\delta^{13}C$, $\delta^{15}N$, a assinatura isotópica do carbono negro - $\delta^{13}C_{CN}$) e molecular (e.g. HPA – Hidrocarboneto Policíclico Aromático) (Derrien et al., 2017; Dang et al., 2018; Liu et al., 2020). No entanto, alguns desses compostos sofrem degradação diferencial, especialmente em ambientes tropicais, onde processos físicos, químicos e biológicos afetam frequentemente sua composição, dificultando a identificação das fontes. Para superar essas limitações, abordagens *multiproxy* têm sido utilizadas, principalmente em sistemas com um grande número de fontes e quando as assinaturas dessas fontes se sobrepõem (Yunker et al., 2015; Liu et al., 2020).

A Baía de Todos os Santos (BTS) é a segunda maior baía do Brasil e possui uma importância histórica, econômica e ecológica para o país. A BTS foi a primeira região produtora de petróleo no país, em 1939, e recebeu a primeira refinaria nacional (atual Refinaria Mataripe - RM) em 1950, hoje a segunda do país em capacidade (ACELEN, 2022). Em 1956, foi inaugurado o Terminal Marítimo Almirante Alves Câmara (TEMADRE) para o escoamento da produção da RM. Atualmente, a BTS abriga dez terminais portuários de grande porte, complexos industriais (incluindo metalurgia, têxtil, química e petroquímica), estaleiros, tanques de carcinicultura, além de atividades de mineração (Hatje; De Andrade, 2009). É também a região de maior concentração demográfica e industrial do estado, com quatorze municípios em seu entorno e abrigando uma população superior a 3 milhões de habitantes (IBGE, 2022). Além disso, a baía recebe esgoto industrial/doméstico tratado e não tratado (Hatje; De Andrade, 2009). Essa situação tornou a BTS uma grande receptora da carga de compostos químicos continentais e atmosféricos. O setor nordeste da BTS, em particular, é considerado um ponto significativo de pressão antrópica, sendo um *hotspot* de contaminação para diversos poluentes (Silva et al., 2014; Oliveira et al., 2018; Do Ó Martins et al., 2020, Eça et al., 2021).

Esses processos podem ter levado a mudanças ambientais tão marcantes que podem caracterizar o início do Antropoceno na BTS. A análise de testemunhos sedimentares, registros históricos e indicadores geoquímicos poderia confirmar essa hipótese, identificando uma ruptura nos padrões do aporte e composição da matéria orgânica a partir desse período.

O presente trabalho utilizou uma abordagem *multiproxy* (C, N, $\delta^{13}C$, $\delta^{15}N$, HPAs parentais e alquilados, n-alcanos, CN e $\delta^{13}C_{CN}$) para descrever a variação espaço-temporal da MO nos níveis elementar, isotópico e molecular, quantificando a contribuição das fontes e avaliando os processos que regulam a distribuição e a origem da matéria orgânica no sedimento da BTS.

Os objetivos específicos foram:

- Caracterizar a variação temporal da matéria orgânica sedimentar;
- Quantificar as contribuições marinha e terrestre no balanço de nutrientes através de um modelo simples de mistura de membros finais;
- Avaliar o destino e preservação da MO depositada;
- Determinar o histórico de contaminação e a identificação de suas possíveis fontes de emissão por meio de razão diagnósticas e análise isotópica;
- Fornecer a primeira avaliação do conteúdo de carbono negro de sedimentos da BTS;
- Discutir a adequação dos *proxies* utilizados como indicadores para fontes naturais e antropogênicas das entradas de MO no sedimento em ambientes tropicais.

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CAPÍTULO 2

ARTIGO 1

Submetido e aceito pela: *Regional Studies in Marine Science*

CHANGES IN THE NATURE OF ORGANIC MATTER IN A LARGE TROPICAL URBAN BAY: TEMPORAL VARIATIONS AND ENVIRONMENTAL IMPLICATIONS

Carine Santana Silva[1]; José Maria Landim Dominguez[1]; Gilvan Takeshi Yogui[2]; Marcos de Almeida[3]

[1] LEC- Coastal Studies Laboratory - Geoscience Institute, Federal University of Bahia, Rua Barão de Jeremoabo, s/n, 40170-020, Salvador, BA, Brazil

[2] OrganoMAR - Laboratory of Organic Compounds in Coastal and Marine Ecosystems - Federal University of Pernambuco - Av. Architecture, s/n - University City, 50740-550, Recife, PE, Brazil

[3] LOQUIM - Laboratory of Chemical Oceanography, Federal University of Pernambuco - Av. Architecture, s/n - University City, 50740-550, Recife, PE, Brazil

∗Corresponding author at: Coastal Studies Laboratory - Geoscience Institute, Federal University of Bahia, Rua Barão de Jeremoabo, s/n, 40170-020, Salvador, BA, Brazil

Email address: carine.sntn@outlook.com (Carine Santana Silva)

ABSTRACT

We used information on the elemental (C/N ratio), isotopic ($\delta^{13}C$ and $\delta^{15}N$) and molecular (aliphatic hydrocarbons) composition of organic matter in sediments from two cores collected in the Todos os Santos Bay to investigate the sources, distribution and fate of organic matter (OM). TOC (0.66–2.23%) and TN (0.12–0.26%) concentrations increased over time but still indicate an oligotrophic system. A simple isotopic mixing model shows a mixture of sources, with autochthonous OM dominating (47.1–93.2% of TOC). ALC_{TOT} concentrations in the sediments varied from 0.25 to 5.84 µg g^{-1}. The ACL (27.79 to 29.89) and AI (0.02 to 0.57) indices show the dominance of the terrestrial contribution coming from C3 vascular plants, such as the mangrove vegetation present on the BTS tidal flats. In core T2, collected at a more offshore site, the parameters analyzed indicate better environmental conditions with natural sources of hydrocarbons. At the T4 core collection site, which was close to the shoreline, a gradual and persistent increase in terrestrial input from 1950 onward was detected, probably related to changes in land use. From 1980 onward, a clear petrogenic signature is seen with the presence of a complex unresolved mixture (nd to 349.94 µg/g) and increased concentrations of total resolved aliphatic hydrocarbons (0.35 to 380.34 µg/g) and normal alkanes (0.25 to 5.84 µg/g). Three decades of moderate chronic contamination are revealed in the T4 core, reflecting the history of economic development of the region, including extraction, refining, transportation and burning of fossil fuels and changes in land use. The effects of implementing environmental policies to improve the Bay's water quality began to be reflected in the sediment quality at the beginning of the 21st century.

Keywords: organic carbon; hydrocarbons; nitrogen, n-alkanes; isotopes; Todos os Santos Bay;

Abbreviations: OM: organic matter; BTS: Todos os Santos Bay; IBGE: Brazilian Institute of Geography and Statistics; TOC: total organic carbon; TN: total nitrogen; CRA: Environmental Resource Center; USGS: United States Geological Survey; RM: Mataripe Refinery; TEMADRE: Maritime Terminal of Madre de Deus; CIA: Aratu Industrial Center; COPEC: Camaçari Petrochemical Complex; CIC: constant initial concentration; GC-FID: Gas chromatography with a flame ionization detector; QA/QC: Quality Assurance/Quality Control; United States Geological Survey (USGS); atmospheric air (AIR); $ALC_{TOT:}$ Total n-alkane concentrations; LMW: low molecular weight; HMW: high molecular weight; PCA: principal component analysis; ALI: resolved aliphatic hydrocarbons; UCM: unresolved complex mixture; Pr: pristane; Ph:phytane; PC: Principal component; C/N: Carbon/Nitrogen; ACL: average chain length; AI: alkane index, TAR: Terrigen Aquatic Ratio; CPI: Preferred Carbon Index; InctAmbTropic: National Institute on Science and Technology for Tropical Marine Environments; CAPES: Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, CNPq: Conselho Nacional de Desenvolvimento Científico e Tecnológico; FAPESB: Fundação de Amparo à Pesquisa do Estado da Bahia.

1. INTRODUCTION

Changes in organic matter (OM) deposited over time in coastal marine sediments related to variations in the input or type of OM can result in changes in the degree of trophicity of the environment, in the degree of OM lability, in the solubility, toxicity, bioavailability, mobility and distribution of pollutants and, ultimately, can influence the natural biogeochemical cycling and carbon storage (Derrien et al., 2017).

Studies using multiple biogeochemical techniques, mainly biomarkers in combination with isotopic analyses of carbon and nitrogen, have been successful in elucidating OM sources in coastal environments (Ke et al., 2017, Oliveira et al., 2018, da Costa et al., 2021). Straight-chain alkanes (n-alkanes) are common geochemical markers found in sedimentary organic matter. The identification of the OM source using these molecular markers is based on variations in the length of the carbon chain for specific organic sources, whether natural or anthropogenic (Derrien et al., 2017; Abdulla et al., 2023). In natural alkanes, there is a dominance of the odd number of carbons, where higher plants are characterized by long chains (C_{27}-C_{35}) and aquatic algae by shorter chains (C_{15}, C_{17}, and C_{19}). On the other hand, petroleum n-alkanes have little or no predominance of even or odd chain lengths (Meyers et al., 1984). Similarly, the elemental signatures of carbon and nitrogen and their respective isotopes ($\delta^{13}C$ and $\delta^{15}N$) also tend to be specific for terrestrial, marine and anthropogenic OM sources (Vilhena et al., 2018, Cabral et al., 2019, Pang et al., 2021).

Todos os Santos Bay (BTS) is one of the largest and most important bays in Brazil. BTS is situated in a historical context of anthropogenic actions, being subjected to strong industrial, port and urban pressures. As a highlight, it has the second largest petrochemical complex in the Southern Hemisphere, the second largest and oldest oil refinery in Brazil, and two large ports (Hatje and Andrade, 2009) (Fig. 1). These activities have the potential to alter the nature of the OM in the sedimentary deposits of the Bay and therefore to impact the Bay's ecosystem services.

Distinguishing the effects resulting from anthropogenic nutrient enrichment and the natural variability of the system in urban bays is challenging due to i) the multiplicity of natural and anthropogenic sources, ii) the hydrodynamic complexity of the environment and iii) the occurrence of complex biogeochemical processes capable of altering the original compositions (Lamb et al., 2006). In this sense, the present research has the potential to contribute to a greater understanding of the impact of anthropogenic activities on the quality of sedimentary OM deposited in BTS.

In this study, we evaluated the vertical variation in the concentrations of stable isotopes of carbon and nitrogen ($\delta^{13}C$ and $\delta^{15}N$), total organic carbon (TOC), total nitrogen (TN) and aliphatic hydrocarbons to investigate the sources, fate and changes in OM deposited in the region. In addition, we used a simple final element mix model (Shultz and Calder, 1976) to assess the relative contributions of OM sources.

2. MATERIALS AND METHODS

2.1 STUDY AREA

The BTS, located on the east coast of Brazil, has a total area of 1223 km2. It is an environment protected from wave action, with circulation dominated by tides and salinity varying between 28 and 36 (Lessa et al., 2009). The main rivers in the region include the Paraguaçu, Jaguaribe and Subaé. However, the Mataripe, São Paulo and Caípe rivers also stand out (Fig. 1), then have activities such as oil exploration/transportation in their basins (Environmental Resource Center - CRA, 2004). Sediments in the northern half of the bay tend to be muddy (Fig. 1).

Its surroundings include tropical forests, beaches, coral reefs and mangrove swamps (Hatje and Andrade, 2009). The latter are mainly composed of the species

Avicennia schaueriana, *Rhizophora mangle* L. and *Laguncularia racemosa* R. (Ramos et al., 2023).

Historically, several human activities have influenced the environmental quality of the BTS. In the most recent period, at least four economic cycles can be identified. The first economic cycle (1950s) was driven by the start of operations at the Landulpho Alves Refinery – Mataripe, in 1950 (current Mataripe Refinery - RM) and the Maritime Terminal of Madre de Deus (TEMADRE) in 1956 (Hatje and Andrade, 2009). Currently, the RM is the second largest in the country, with a refining capacity of 300,000 barrels of oil per day (ACELEN, 2022). In 1967, the Aratu Industrial Center (CIA) was established, with enterprises in chemicals, fertilizers, nonmetallic minerals, plastics, textiles, services and commerce segments, and others.

The second economic cycle (1975-1986) was marked by the installation of the largest industrial complex in the Southern Hemisphere (Camaçari Petrochemical Complex – COPEC), which housed more than 90 chemical, petrochemical and other branches of activity. In the third economic cycle (1992-2000), the economy diversified, including tourism, manufacturing, and automotive industries. Starting in 2000 (fourth cycle), in addition to the strengthening of the chemical industry and gas and oil extraction, other industries emerged (for example, the footwear and automotive sectors) (Pessoti and Silva, 2011).

These activities resulted in impacts on the environmental quality of the bay (Hatje and Andrade, 2009). The northern portion is considered the most polluted sector of the BTS (CRA, 2004). Studies have indicated chronic oil contamination (Silva et al., 2014, Oliveira et al., 2018, Almeida et al., 2018, do Ó Martins et al., 2020), as well as the presence of metals at concentration levels that may cause adverse effects on the biota (Hatje et al., 2009).

2.2 SAMPLING

Two cores (T2 - 76 cm long and T4 - 68 cm long) were collected in June 2017 in the northeastern region of the BTS (Fig. 2) at water depths of 8.9 m and 8.3 m, respectively (Fig. 2).

At the T4 core site, the surficial sediment is muddy, covered with a biofilm and has low species diversity (Oliveira et al., 2020) (Fig. 2), whereas the T2 core was collected at a site where the surficial sediment is sandier and rich in bioclasts (Fig. 2), with biota characterized by soft and calcareous macroalgae, hard corals, and Polychaeta (Oliveira et al., 2020).

After collection, the cores were frozen immediately upon arrival at the laboratory and sampled at 2-cm intervals. Subsequently, the samples were lyophilized.

2.3 GEOCHEMICAL ANALYSIS

The sediment grain size was determined in a laser diffraction particle analyzer (CILAS 1064). Samples were pretreated with hydrogen peroxide to degrade the OM, followed by stirring for 24 h with sodium hexametaphosphate. The classification of granulometric fractions was performed using GRADISTAT v 5.0® software (Garcia et al., 2014).

For the determination of total organic carbon, total nitrogen, $\delta^{13}C$ and $\delta^{15}N$, approximately 10 mg of dry sediment was weighed into tin capsules after removal of carbonates by acidification (detailed in Guimarães et al., 2019). The determination was made in an elemental analyzer (Costech Instruments Elemental System) coupled to an isotopic ratio mass spectrometer (Thermo Finnigan Delta Plus). The international reference standards for isotopic analyses were Vienna Pee Dee Belemnite for $\delta^{13}C$ and atmospheric air (AIR) for $\delta^{15}N$. The reference materials for the TOC and TN isotopic analysis were two standards certified by the United States Geological Survey (USGS): USGS-40 (L-glutamic acid: $\delta^{13}C_{VPDB}$ = -26.39‰ and $\delta^{15}N_{AIR}$= -4.52‰) and USGS-41 (L-glutamic acid enriched in ^{13}C ($\delta^{13}C_{VPDB}$ = +37.63‰) and ^{15}N ($\delta^{15}N_{AIR}$ = +47.57‰)).

The sedimentation rate of the T2 core was established by measuring the ^{210}Pb activity, according to the procedures described in detail by Godoy et al. (1998). The concentration of ^{210}Pb was determined based on its secondary decay product, ^{210}Bi, after a two-week growth period by beta counting with a low-level proportional counter and ten-channel Perkin–Elmer Prof. Berthold. LB-750. The detection limit of this technique is 1 Bq kg^{-1} per 1000 minutes of counting time. The calculation of ages and sedimentation rates was performed using the constant initial concentration (CIC) model applied to excess ^{210}Pb. Sedimentation rates for core T4 were not determined because, in the immediate vicinity, previous works have determined it to be approximately 0.61 cm $year^{-1}$ (CRA, 2004-0.62 cm $year^{-1}$ and Wagener et al., 2010-0.60 cm $year^{-1}$, located 1.41 km and 1.74 km away, respectively).

Aliphatic hydrocarbons were extracted using the method described by Costa et al. (2021). Briefly, approximately 5-10 g of dry sediment from each sample was weighed into glass cartridges, internal standards were added (80 µg 1-hexadecene and 70 µg 1-eicosene), and the samples were placed in a Soxhlet extractor with 80 mL of a mixture of dichloromethane/n-hexane (1:1, v/v) and extracted for 8 h. Samples were treated with activated copper to remove elemental sulfur. The organic extracts were concentrated to 1 mL on a rotary vacuum evaporator under gentle N_2 flow. Then, the extracts were purified using column adsorption chromatography. The column was packed (bottom to top) with 3.2 g of silica gel (5% deactivated), 1.8 g of alumina (5% deactivated) and 1 cm of anhydrous sodium sulfate. Each extract was eluted with 10 mL of n-hexane through the column. The purified extracts were concentrated to 1 mL, and a recovery standard (70 µg 1-tetradecene) was added. Finally, the samples were stored in a freezer at -20 °C.

Quantification of n-alkanes and isoprenoid alkanes was performed using a gas chromatograph (Agilent 7820A) equipped with a flame ionization detector (GC-FID). The injector temperature was 300 °C, and helium was used as a carrier gas with a constant flow rate of 1.4 mL min^{-1} through the column. The injection of the extracts was performed in split mode at a ratio of 3:1. The capillary column installed in the furnace was a DB-5 column (30 m long, 0.25 mm internal diameter and 0.25 µm film thickness). The oven temperature program was as follows: 40 °C; ramp at 20 °C min^{-1} to 60 °C; ramp at 5 °C min^{-1} to 290 °C (isothermal for 5 min); and ramp at 10 °C min^{-1} to 300 °C (isothermal for 15 min).

2.3.1 Quality Assurance/Quality Control (QA/QC)

In the laboratory procedures, ultrapure solvents of pesticide grade were used. Laboratory standard solutions were prepared from the following commercially available primary standards: tetradecene-1 (AccuStandard, catalog number PS-241D-10-1ML); hexadecene-1 (AccuStandard, catalog number PS-241D-11-1ML); eicosene-1 (AccuStandard, catalog number PS-241D-13-1ML); and hydrocarbon window defining standard (AccuStandard, catalog number DRH-008S-R2). For each batch of 15 field samples, an instrument blank (solvent), a laboratory blank (Na_2SO_4) and a spiked matrix were analyzed together to check the accuracy of the method. In two batches, duplicate samples were also analyzed to check the accuracy of the method. As an additional analytical control, all standard solutions used in laboratory processes were analyzed together to verify their integrity. To monitor the efficiency of the extraction and cleaning processes, internal standards (hexadecene and eicosene) were added to all samples. Recovery of internal standards was monitored by adding tetradecene to the final extract after completion of laboratory procedures. Standard solutions of n-alkanes were periodically injected into the GC-FID to verify the validity of the calibration curve. Each set of samples was run in sequence with a solvent blank, calibration curve check standard solution, quality control samples, and field samples. The calculation of target analytes was based on internal standards and a six-point linear calibration curve, with a coefficient of determination (R^2) greater than or equal to 0.995. The mean recovery of internal standards was 84 ± 10% (standard deviation). The blanks had only 2% of analytes above the quantification limit, which varied between 0.02 and 0.03 µg g^{-1} (dry weight). The coefficient of variation (CV) of duplicates was 4.3 ± 3.2%, revealing excellent method repeatability. The recovery of analytes in the spiked matrix was 82 ± 14%, showing excellent method accuracy.

2.3.2 Diagnostic ratios for n-alkanes

Several diagnostic ratios reflecting the relative abundance of individual compounds are widely applied to characterize the origin of OM (Szymczak-Żyła and Lubecki, 2022, Liu et al., 2022; Abdulla et al., 2023). The proxies used in this study are shown in Table 1. Total n-alkane concentrations (ALC_{TOT}) were obtained by summing the concentration (in µg g^{-1}) of each individual n-alkane from C_{12} to C_{40}. The total of even and odd n-alkanes refers to the sum of even n-alkanes from C_{12} to C_{40} and odd n-alkanes from C_{13} to C_{39}, respectively. Low molecular weight (LMW) and high molecular weight (HMW) n-alkanes are defined as C_{12} to C_{22} and C_{23} to C_{40}, respectively.

2.4 STATISTICAL ANALYSIS

Student's t test assuming unequal variances was used to compare hydrocarbon concentrations between cores. The normality of variables was verified using the Kolmogorov–Smirnov test, and descriptive statistical analyses and nonparametric statistical tests were performed using STATISTICA 9.0® software (STATSOFT 2009).

Values below the limit of quantification were replaced by half of this limit for the purpose of statistical calculations, and the concentrations were dimensionally normalized. Principal component analysis (PCA) was applied to the concentrations to determine the main variables influencing the dataset. Spearman correlation analysis was performed to evaluate linear relationships between sediment variables.

3. RESULTS

3.1. SEDIMENTATION RATES

Excess ^{210}Pb activity concentrations ranged from 7.9 Bq kg^{-1} to 52.8 Bq kg^{-1}, with higher values found in the upper sedimentary layers. The T2 core sedimentation rate was 0.44 ± 0.2 cm year^{-1}, and the cover period was 173 years, starting from 1844 (bottom) to 2017 (top). As mentioned in Section 3.2, the sedimentation rate in the T4 core was assumed to be 0.61 cm year^{-1}. This value is the average of the sedimentation rates of nearby cores (CRA, 2004-0.62 cm yr^{-1} and Wagener et al., 2010-0.60 cm yr^{-1}, at distances of 1.41 km and 1.74 km, respectively). Thus, the coverage period of the T4 core was 113 years, starting from 1904 (bottom) to 2017 (top).

3.2 DOWNCORE VARIATIONS IN CARBON, NITROGEN AND GRAIN SIZE

Downcore variations in the percentage of fines and geochemical parameters (TOC, TN, C/N ratio, δ^{13}C, δ^{15}N) in the T2 and T4 cores are shown in Figures 3 and 4, respectively and are detailed in the Supplementary Material (Table S1).

The T2 core had a lower mud content (53.18 ± 0.09%) than the T4 core (64.03 ± 0.07%). In the T2 core, the average clay, silt and sand percentages were 8.58 ± 0.02%, 44.60 ± 0.07% and 45.94 ± 0.09%, respectively. In the T4 core, the clay, silt and sand percentages were 12.05 ± 0.02%, 51.98 ± 0.06% and 35.94 ± 0.07%, respectively. There were no large downcore variations in sediment texture, with the exception of some mud peaks at 20 and 26 cm depth that exceeded 80% in the T2 core and at depths of 14, 30, 34, 40 and 46 cm in the core T4 where the mud percentage exceeded 70% (Figs. 3 and 4).

The TOC and TN percentages in the T4 core (Fig. 4) were higher than those found in the T2 core (Fig. 3). In T2, the TOC and TN contents ranged from 0.66 to 1.98% (mean of 1.29 ± 0.39%) and from 0.12 to 0.19% (mean of 0.15 ± 0. 02%), respectively. From the base of the core until 1925, a downward trend in TOC percentages can be observed, except for a few slight fluctuations. From this depth to the top, there was a shift in this pattern, with TOC percentages increasing, reaching the highest values in most of the top layers. TN showed a uniform distribution along the core (0.15 ± 0.2%) and a moderate correlation with TOC ($r_s = 0.50$, $p < 0.05$, $n = 39$).

In the T4 core, the TOC and TN percentages ranged from 1.17 to 2.23% (mean of 1.59 ± 0.32%) and from 0.13 to 0.26% (mean of 0.18 ± 0. 04%), respectively. The TN content showed a strong positive correlation with TOC ($r_s = 0.86$, $p < 0.05$, $n = 35$), implying that the vast majority of sedimentary nitrogen is of organic origin. It is possible to identify three distinct patterns in the distribution of TOC and TN: i) from the base of the core (1906) to 1948, the TOC and TN concentrations tended to increase (TOC = 1.69 ± 0.21%; TN = 0.18 ± 0.03%); ii) from 1991 to 1951, there was a reduction in the percentages compared to the lower and upper intervals (TOC = 1.27 ± 0.10%; TN = 0.15 ± 0.01%), and these values remained approximately constant, accompanied by an increase in fine sediment content; and iii) from 1994 to 2017, the highest concentrations of TOC and TN were found, averaging 1.94 ± 0.22% for TOC and 0.22 ± 0.03% for TN.

3.3 CARBON AND NITROGEN ISOTOPES ($\delta^{13}C$ and $\delta^{15}N$)

In core T2, $\delta^{13}C$ ranged from -15.26‰ to -21.80‰ (mean -20.21 ± 1.56‰) (Fig. 3), and $\delta^{15}N$ ranged from 2.84 to 7.40‰, with an average of 5.35 ±1.32‰. Similar to the TOC, the $\delta^{15}N$ values showed a remarkable increasing trend from 1925 onward.

In core T4, $\delta^{13}C$ ranged from -22.53 to -16.77‰, with an average of -20.50 ± 1.53‰ (Fig. 4). In the interval between 1935 and 1950, there was an increasing trend in $\delta^{13}C$ values from -22 to -16‰. The $\delta^{15}N$ ranged from 0.57 to 9.03‰, with an average of 4.18 ± 2.04‰. A clear increasing trend in these values from the bottom to the top is observed, with a more abrupt increase starting in 2004.

3.4. ALIPHATIC HYDROCARBONS

A total of 29 n-alkanes were detected in the BTS sediments. The complete table with molecular data is presented in the Supplementary Material (Tables S2 and S3). A synthesis with the values of total n-alkanes (ALC_{TOT}), sum of low molecular weight n-alkanes (LMW), sum of high molecular weight n-alkanes (HMW), resolved aliphatic hydrocarbons (ALI), mixture unresolved complex (UCM), pristane (P) and phytane (F) is presented in Table 2.

ALC_{TOT} concentrations in the sediments of the T2 and T4 cores ranged from 0.25 to 2.23 µg g^{-1} and from 0.66 to 5.84 µg g^{-1}, respectively. The LMW ranged from 0.04 to 0.22 µg g^{-1} at T2 and from 0.07 to 2.17 µg g^{-1} at T4. The HMW in both cores represented the largest fraction of normal alkanes. HMW concentrations in the T2 and T4 samples ranged from 0.27 to 2.02 µg g^{-1} and 0.53 to 4.35 µg g^{-1}, respectively.

The n-alkanes also showed a dominance of odd over even homologs in both cores and at all depths. The mean concentrations of the sum of odd n-alkanes in the T2 and T4 samples were 0.45 ± 0.28 µg g^{-1} and 0.73 ± 1.09 µg g^{-1}, respectively. The sum of even n-alkanes in T2 and T4 was 0.25 ± 0.19 µg g^{-1} and 0.22 ± 0.86 µg g^{-1}, respectively. The maximum concentration for C_{29} was observed in both cores. Generally, C_{27}, C_{29} or C_{31} as maximum n-alkanes are indicative of epicuticular waxes of higher plants (Chen et al., 2017). The sum of aliphatic hydrocarbons ranged from 0.36 to 2.90 µg g^{-1} in T2 and from 0.96 to 380.34 µg g^{-1} in T4.

The analysis of total aliphatic hydrocarbons and total alkanes showed statistically significant differences between the samples ($p < 0.05$). In fact, there was a general trend toward a decrease in the total concentrations of aliphatic hydrocarbons and n-alkanes from core T4 (close to the continent) to core T2 (away from the continent) (Table 2; Fig. 5). ALC_{TOT} concentrations gradually increased upcore in T2 (Fig. 5). HMW concentrations varied synchronously with the ALC_{TOT} ($r_s = 0.94$, $p < 0.05$, $n = 39$). In contrast, LMW concentrations showed no correlation with other components and a more homogeneous distribution. In T4, an increase in ALC_{TOT} concentration occurred abruptly from the 1980s onward. The LMW and HMW concentrations showed a similar trend (Fig. 5).

3.5. INTEGRATED STATISTICAL ANALYSIS

The result of the PCA, based on the elemental, molecular and isotopic markers characteristic of OM sources, in addition to accessory data, is shown in Fig. 6. A combination of the two main PCA axis, which accounted for approximately 70% of the variance in the data, allowed the distinction of three large groups. Principal component 1 (PC1) explained 42.34% of the total variance and was strongly influenced by ALC_{TOT}, ALI_{TOT}, COT and UCM. High values of hydrocarbons in general are indicative of the presence of crude oil and/or petroleum input, and high UCM concentrations suggest the presence of degraded oil. Thus, PC1 was attributed to the anthropogenic contribution. PC1 separated the samples of the T2 core (36 to 74) from those of the T4 core (1 to 35).

TOC showed a high correlation with ALC_{TOT} ($r_s = 0.72$, $p < 0.05$, $n = 75$), especially with HMW components ($r_s = 0.72$, $p < 0.05$, $n = 75$). ALI_{TOT} also showed a significant correlation with ALC_{TOT} ($rs = 0.95$, $p < 0.05$, $n = 75$), and indeed, the latter represent a considerable fraction of the total aliphatic hydrocarbons.

Principal component 2 (PC2) explained 26.97% of the total variance. It was associated with $\delta^{13}C$, C/N ratio and $\delta^{15}N$. These parameters showed a strong correlation with lipids of autochthonous marine origin. Thus, PC2 is considered herein as an indicator of biogenic contribution.

Interestingly, the T4 core samples were separated into two groups. The most recent samples (1994 to 2017) showed a strong anthropogenic contribution, while the older samples (dated from 1909 to 1991) had a dominant biogenic contribution.

4. DISCUSSION

4.1. SOURCES OF ORGANIC MATTER BASED ON ELEMENTAL AND ISOTOPIC COMPOSITIONS OF CARBON AND NITROGEN

The TOC and TN values in the core samples collected at the BTS showed an increasing trend over time (Figs. 3 and 4). Although the highest concentrations were observed near the coast (core sample T4), it is worth noting that TOC concentrations in the upper layers of core T2 are almost double those found in the 1940s and 1950s. This trend in part may be a response to the low degradation of OM in young sediments, but above all to the increased mobilization of carbon from continental origin through the intensification of land use in more recent years.

Conversely, it is noteworthy that regardless of the depth, the nitrogen contents in the BTS are low (Figs. 3 and 4). This indicates that the OM in the sediments has a reduced nutritive value for detritivorous benthic organisms, reflecting the low density and diversity of benthos found in this portion of the Bay (CRA, 2004). However, even if nitrogen is clearly a limiting nutrient for productivity, in recent years, at least two episodes of algal blooms have been recorded at the BTS associated with high rainfall events and anthropogenic contributions, with the occurrence of harmful algal species (Santos et al., 2020). In 2007, for example, an enormous bloom of *Akashiwo sanguinea* produced anoxic conditions in the water column, causing the death of more than seven tons of fish (Argôlo and Carmel, 2007). However, the values of TOC, TN, $\delta^{13}C$ and $\delta^{15}N$ in the sediments are still typical of an oligotrophic system. It is likely that primary production is preferentially maintained by recycling the OM synthesized in the photic zone of the water column. The values found are close to the concentrations reported in other studies carried out in the BTS and lower than the levels found in other bays affected by strong eutrophication (e.g., Guanabara, Toulon and Bohai Bays) (Table 3).

In general, the isotopic composition of terrestrial OM (C/N > 20, $\delta^{13}C \approx -28‰$ and $\delta^{15}N \approx 4-5‰$) is distinct from that of marine OM (C/N ≈ 4-10, $\delta^{13}C \approx -18$ to $-22‰$ and $\delta^{15}N \approx 5-7‰$) (Meyers et al., 1984, Ramaswamy et al., 2008, Barros et al., 2010, Cabral et al., 2019). A C/N ratio between 12 and 14 indicates a mixture of marine and terrestrial sources typically found in estuaries (Meyers et al., 1984). These differences result from the biochemistry of the plants. Nonvascular plants (e.g., algae) contain a large proportion of nitrogen-rich proteinaceous material. In contrast, terrestrial vascular plants that require physical support structures show a high concentration of carbon-rich polymeric materials (cellulose, hemicellulose and lignin) (Meyers, 1997, Sun et al., 2016). Intermediate values are usually attributed to a mixture between marine and terrestrial sources.

The isotopic composition of OM in cores T2 ($\delta^{13}C$: -21.80 to -15.26‰, $\delta^{15}N$: 2.84 to 7.40‰, C/N: 8.42 ± 2.24) and T4 ($\delta^{13}C$: -22.53 to -16.77‰, $\delta^{15}N$: 0.57 to 9.03‰, C/N: 9.01 ± 1.10) indicates a mixing of marine and terrestrial sources. An isotopic mass balance mixing model, proposed by Shultz and Calder (1976), was used to assess the relative contributions of OM in the BTS. Since there is no significant post-depositional fractionation of $\delta^{13}C$, it is possible to quantify the relative contribution of terrestrial organic carbon in marine sediments. In the mixing model, constant end-member values are used, representing the isotopic signature of the considered sources, according to the following equation:

$$\delta^{13}C_{Sample} = [f\ \delta^{13}C_{terrestrial} + (1\text{-}f)\ \delta^{13}C_{marine}] \times 100\% \quad (1)$$

where f is the fraction of terrestrial organic carbon and $\delta^{13}C_{terrestrial}$ and $\delta^{13}C_{marine}$ are the isotopic signatures of terrestrial and marine organic carbon sources, respectively.

It is worth noting that the choice of end members is complex because a single value must represent a mixture of biological components occurring in an environment. In this work, we chose to use a value of -26‰ as the end member of the terrestrial $\delta^{13}C$, following the average values obtained for mangroves and other terrestrial sources (Souza et al., 2017). For the marine end-member, a value of -18.6‰ was used, which is the average $\delta^{13}C$ in phytoplankton samples from the region (Souza et al., 2017). The resulting estimates for the contribution of terrestrial and marine organic carbon in the sedimentary cores of the BTS are summarized in Fig. 7. The isotopic mixing model shows that the sedimentary OM deposited in the study area is dominated by autochthonous (marine) organic carbon. The terrestrial (allochthonous) component exerts a secondary influence. The marine OM in BTS is derived from phytoplankton (in general, phytoflagellates, diatoms and cyanobacteria) and zooplankton (copepods). Indeed, the $\delta^{13}C$ and $\delta^{15}N$ of phytoplankton vary from -22.0 to -15.6‰ and 5.0 to 11.2‰, respectively. For zooplankton, $\delta^{13}C$ varies from -19.6 to -15.0‰, and $\delta^{15}N$ varies from 5.5 to 12.8‰ (Lopes et al., 2009; Souza et al., 2017). In addition, sea grasses (genera *Thalassia* and *Halodule*) (CRA, 2004) located in extensive areas in the study region (Figure 2) are also a source of OM for the BTS. Seagrass $\delta^{13}C$ values reported in the literature range from −24 to −3‰ (Hemminga and Mateo, 1996). The allochthonous/natural terrestrial material has a signature typical of a C3 photosynthetic pattern. This may be associated with the tropical forest and mangrove swamps that occur around the BTS (Fig. 1).

Core T2, farther from the coast, had an average marine contribution of 70.23%, which was slightly higher than the percentage found in core T4 (67.06%). The relative contribution of different sources in T2 is relatively uniform, with an average proportion of terrestrial OM of 33.38 ± 8.39% along the profile, with the exception of the period between the 1930s and 1980s, when there was greater variability and a greater contribution from marine OM (Fig. 7). Oliveira et al. (2020) identified the presence of patches of reef with soft and calcareous macroalgae near the T2 core collection region (Fig. 2). It is possible that the expansion of these seaweeds in the past contributed to the increase in the autochthonous contribution to OM in this period.

In core sample T4, the mixing model shows changes in the proportions of the dominant sources of OM (Fig. 7) that are consistent with the changes found in the TOC and TN contents (Fig. 4; Section 4.1). The gradual increase in the terrestrial (allochthonous) contribution to OM from the 1950s onward, reaching its maximum in the 1990s, stands out.

4.2. SOURCES OF ORGANIC MATTER BASED ON MOLECULAR MARKERS

To further characterize the different OM sources in the sediments, we used the parameters and indices presented in Table 2. Although the contributions of natural n-alkanes are similar in both cores, marked differences in the parameters and indices listed in Table 2 are observed.

In general, these indices are based on the fact that short-chain n-alkanes are derived from bacteria, phytoplankton and zooplankton, while long-chain n-alkanes (C_{24} to C_{34}) originate from terrigenous hydrocarbons, but are also produced by bacterial reprocessing of OM (Bray and Evans, 1961; Abdulla et al., 2023).The average chain length (ACL) is an index describing the average number of carbon atoms present in n-alkanes. Lower values (C_{23}-C_{25}) show a higher contribution of macrophytes to the OM. In contrast, values between C_{27}-C_{33} indicate the dominance of terrestrial plants (Ficken et al., 2000). Considering terrestrial plants, n-alkanes derived from vascular plants with a C3-type photosynthetic pattern show a higher abundance of C_{27} and C_{29}. Plants with the C4 photosynthetic pattern produce more normal alkanes with chains of C_{31} and C_{33} (Rommerskirchen et al., 2003). This difference is the principle of the alkane index (AI). Values higher than 0.5 indicate C4 grasses, and values lower than 0.5 indicate the predominance of C3 plants (Ficken et al., 2000). In core T2, the ACL and AI values vary from 27.79 to 29.89 and 0.03 to 0.22, respectively. In T4, the same proxies vary from 27.97 to 29.52 and 0.02 to 0.57, respectively. The contribution of vascular plants with a photosynthetic pattern of type C3, such as the abundant mangrove vegetation present on the banks of the bay, generated a dominant signature in agreement with the isotopes. This result shows that although plants of the C4 type (e.g. sugar cane) occupied vast areas of the BTS in the 16th century, these crops are currently reduced (de Araújo, 2000) and have a smaller contribution to the sedimentary organic matter, a few hundred meters from the coast.

The TAR (Terrigen Aquatic Ratio) index has been used to distinguish between terrestrial and aquatic sources from differences in the distribution of HMW and LMW n-alkanes. The mean TAR values in cores T2 and T4 were 8.07 ± 4.68 and 6.47 ± 3.82, respectively. Thus, the TAR indicates a predominance of terrestrial sources for both cores in disagreement with the isotopes and the ACL and AI indices. Such inconsistencies indicate the need for caution in the application and interpretation of these molecular ratios. Knowledge of the coastal system is imperative, along with consideration of more sensitive parameters (e.g., isotopes) to better understand the origins of n-alkanes.

To investigate the anthropogenic contribution of OM deposited in the BTS, the concentrations of ALI and UCM, as well as the UCM/ALI, pristane/phytane and CPI (Preferred Carbon Index) ratios, were investigated (Table 2).

Unpolluted sediments normally have average concentrations of total aliphatic hydrocarbons of 5 µg g^{-1} and this value may reach 10 µg g^{-1} in sediments where there is a significant contribution of higher plants (Volkman et al., 1992). Concentrations lower than 2.90 µg g^{-1} are found in the T2 core, although an upcore increase in these values is observed. In contrast, in core T4, values lower than 10 µg g^{-1} were found only until 1984. Subsequently, the values increased, reaching a maximum of 380 µg g^{-1} in 1997 and a downward trend thereafter (but maintaining concentrations above 100 µg g^{-1}). Concentrations higher than 100 µg g^{-1} are frequently associated with oil contamination (Readman et al., 2002).

UCM represents a number of compounds that cannot be resolved by traditional chromatographic methods, including isomers and homologs of branched and cyclic hydrocarbons that cannot be identified and quantified individually (Readman et al. 2002). Low concentrations of UCM (< 10 µg g^{-1}), accompanied by a bimodal configuration, with a second elevation between C_{16} and C_{22}, are related to bacterial degradation of OM (Venkatesan and Kaplan, 1982). On the other hand, elevated UCM concentrations are often a robust indicator of weathered petroleum residues (Volkman et al., 1992). UCM was not detected in the T2 core, but in the T4 core, it was present in the sedimentary layers from 1984 onward. It reached a maximum value of 349.94 µg g^{-1} in the late 1990s, when it accounted for up to 40% of the ALI. Thus, the UCM values indicate that the T4 core OM is enriched in compounds of petrogenic origin. Furthermore, the UCM/ALI ratio greater than 4 from 1987 also suggests the presence of degraded oil in the region (Table 2).

Pristane (Pr) and phytane (Ph) are isoprenoid hydrocarbons produced from the degradation of phytol ($C_{20}H_{40}O$), a constituent of chlorophyll-a. The formation of pristane and phytane is associated with an oxidizing or reducing environment, respectively. In the marine environment, pristane occurs in higher concentrations and is present in phytoplankton, zooplankton and bacteria (Volkman et al., 1992). In addition, pristane and phytane are commonly found in equal proportions in most crude oils, so they are often considered good indicators of oil contamination (Readman, et al., 2002). Isoprenoids were detected only in the top of the T2 core (2008-2017) and with Pr/Ph ratio > 1, suggesting the presence of uncontaminated sediments and a predominantly biogenic source. On the other hand, in T4, these compounds were recorded together in the early 1990s, with a greater abundance of phytane and a Pr/Ph ratio < 1, indicating a petrogenic source.

The CPI is an index used to assess the potential contributions of OM sources to sediments based on the analysis of the ratio of odd and even n-alkane concentrations. High CPI values reflect the dominant presence of biogenic n-alkanes, while values close to 1 indicate petrogenic origin (Aboul-Kassim and Simoneit, 1996) or erosion of sedimentary rocks (Zhang et al., 2019). The continental or marine origin of the biogenic fraction can be determined using the CPI calculation between light (< n-C_{24}) and heavy (> n-C_{24}) compounds.

In cores T2 and T4, light n-alkanes (< n-C_{24}) were often less abundant than heavy n-alkanes (> n-C_{24}). The CPI for the lower molecular weight compounds indicates that there is a low incidence of n-alkanes of planktonic origin, confirming the low primary production in the BTS. The C_{17} values were also low, ranging from nd (not detected) to 0.08 µg g^{-1} and from 0.01 to 0.12 µg g^{-1} in cores T2 and T4, respectively. This is an indication of the low contribution of phytoplankton to the sedimentary OM (Table 2).

The CPI values calculated in the range of C_{24} to C_{34} (Table 2), in contrast, showed higher values in core T4 (1.52 to 19.52) than in core T2 (1.01 to 4.75). In general, C_{29} and C_{31} were the main n-alkanes in the cores, which is indicative of terrigenous inputs (Supplementary Material, Tables S2 and S3). However, assuming that alkanes containing even carbon numbers in the C_{19} to C_{33} range are mostly of petroleum origin, the concentrations found suggest that there is also an impact of petrogenic input.

The use of indexes indicative of the origin of n-alkanes in older sediment samples is more complex. Once deposited, OM may undergo early diagenetic changes. These processes can mask the results of the indices, as these ratios between the concentrations of individual compounds or sets of compounds are affected by the different rates of degradation (Meyers, 1997).

4.3. Historical changes in om contribution and environmental implications

The greatest differences in the geochemical parameters measured in the two cores derive from the locations where these cores were collected.

The T2 core, located further away from the coastline, is subject to less restricted tidal circulation. Although there is a gradual increase in the concentrations of total aliphatic hydrocarbons and n-alkanes from the bottom to the top of this core, the low contents of these components, associated with the absence of a measurable UCM, pristane and phytane, show little or no influence of contamination from anthropogenic sources areas of OM.

Core T4 is located closer to the coast, where tidal circulation is more restricted, and close to an important oil refinery. In addition, the low renewal of the water mass in the BTS (Cirano and Lessa, 2007) favors the retention of contaminants. The absence of UCM in the sedimentary layers deposited in the first half of the 20th century is a strong indication that there were no significant contributions of hydrocarbons of anthropogenic origin, mainly of petrogenic origin.

From 1950 onward, there was a gradual increase in the terrestrial fraction (allochthonous) as a component of the OM in the T4 core. Using the average sedimentation rate of 6.1 mm year^{-1} reported for this area (CRA, 2004, Wagener et al., 2010), this depth corresponds to the 1950s, when the first cycle of industrial expansion took place in the BTS, marked by the construction of the Mataripe Refinery (RM) and

TEMADRE. A similar change in the OM pattern in the region was described by Costa et al. (2011).

The lack of environmental legislation at the time allowed the deforestation and landfill of extensive areas of mangroves, which were used for the construction of port terminals, refineries, pipelines, roads and various types of industries. As a consequence, the BTS mangroves were drastically reduced (CRA, 2004). These land use changes may have increased the export of soil-derived organic carbon to the BTS. However, these past changes in land use have not been accompanied by an increase in aliphatic hydrocarbon or n-alkane concentrations.

An abrupt change in the concentrations of ALC_{TOT}, LMW, HMW, and $\sum$ALI occurred in the 1980s. The presence of UCM was also recorded. The UCM is an indicator of the presence of petrogenic hydrocarbons in an advanced degree of degradation; that is, it is a marker of past contamination (Readman et al., 2002). The presence of petrogenic compounds is also evidenced by UCM/ALI ratio values always greater than 4 in the T4 core, also indicative of the existence of petrogenic compounds with a high degree of degradation.

During this period, the Camaçari Industrial Center (CIA) and the Camaçari Petrochemical Complex (COPEC) (Figure 1) were already fully operational. In addition, a series of incentive policies culminated in the second economic cycle (1975 to 1986), which accelerated urban–industrial growth in the region and further altered land use and human occupation in the region. Although there is no detailed historical survey of the occurrence of hydrocarbon leaks to the BTS, from 1988, there are some records (CRA, 2004). This time was also marked by a significant demographic increase in the area. From 1980 to 1991, the population in the municipalities surrounding the BTS increased from 1.8 to 2.5 million inhabitants (IBGE, 2020).

From the 1990s onward, concentrations of total aliphatic hydrocarbons and UCM greater than 100 µg g^{-1} represent the geochemical record of chronic contamination in the area. The presence of petrogenic compounds is also evidenced by the UCM/ALI ratio values always greater than 4, characterizing the existence of petrogenic compounds with a high degree of degradation. In this interval, the allochthonous fraction of OM exceeds 50% and is accompanied by an increase in the percentage of fine sediment.

The highest values of total aliphatic hydrocarbons, normal alkanes and UCM in the T4 core occurred in the late 1990s and early 2000s. These high values suggest severe contamination at the T4 site.

In the 1990s, environmental policies began to be implemented to improve water quality in the BTS, which included sanitation and industrial pollution control actions (Bahia Azul Program – Bahia, 2005). Another important intervention was the implementation of a water and oil separation system for the liquid effluents generated by the asphalt plant (RM refinery) in 1998, which contributed to reducing the operational impacts caused by the refinery. In 2004, the Bahia Azul Program was completed.

These actions may possibly be responsible for the decrease in hydrocarbon concentrations in the upper layers of the T4 core. However, until 2017, when the T4 core was collected, there was still chronic contamination at this location.

Despite these improvements, the synergistic effect related to the introduction of other contaminants may affect the local biota. In this sense, several sectors of the BTS, including the investigated region, already present poor benthic fauna as a reflection of this contamination (Venturini et al., 2004, Pires-Vanin et al., 2011, Eça et al., 2021). In addition, moderate PAH values have been found in mollusks from the region (do Ó Martins et al., 2020, Eça et al., 2021).

5. CONCLUSIONS

Although environmental changes in the BTS date back to colonization by the Portuguese in 1550, the OM geochemical parameters investigated in this study indicate that important changes took place only starting in the mid-20th century.

Our results indicated an increase in OM contents over time, with an increasing input of allochthonous contributions near the coast (T4 core), driven by oil sector activities and evidencing at least three decades of chronic contamination at moderate levels. However, actions to control organic pollution apparently contributed to improving the quality of sediments during the 21st century.

The region furthest from the BTS coastline, where the T2 core was collected, is a more preserved area from the viewpoint of the organic contaminants studied, in which the contributions of natural hydrocarbons are more significant.

As a strategy for future monitoring and considering the complexity of a large urban bay with multiple OM sources such as the BTS, we suggest the use of isotopes of specific n-alkane compounds, the development of indices adapted to the local diversity of OM sources, and the combined use of polycyclic aromatic hydrocarbons and black carbon to better characterize anthropogenic inputs.

ACKNOWLEDGEMENTS

The authors are grateful for the support of Professor José Marcos Godoy Institute of Radioprotection and Dosimetry of the Pontifical University of Rio de Janeiro, Brazil. JML Dominguez thanks CNPq for a research fellowship.

FUNDING SOURCES

This work was supported by the InctAmbTropic (National Institute on Science and Technology for Tropical Marine Environments), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) – Brazil and Fundação de Amparo à Pesquisa do Estado da Bahia (FAPESB) (565054/2010-4, 8936/2011, 465634/2014-1 and inc004/2019).

FIGURES

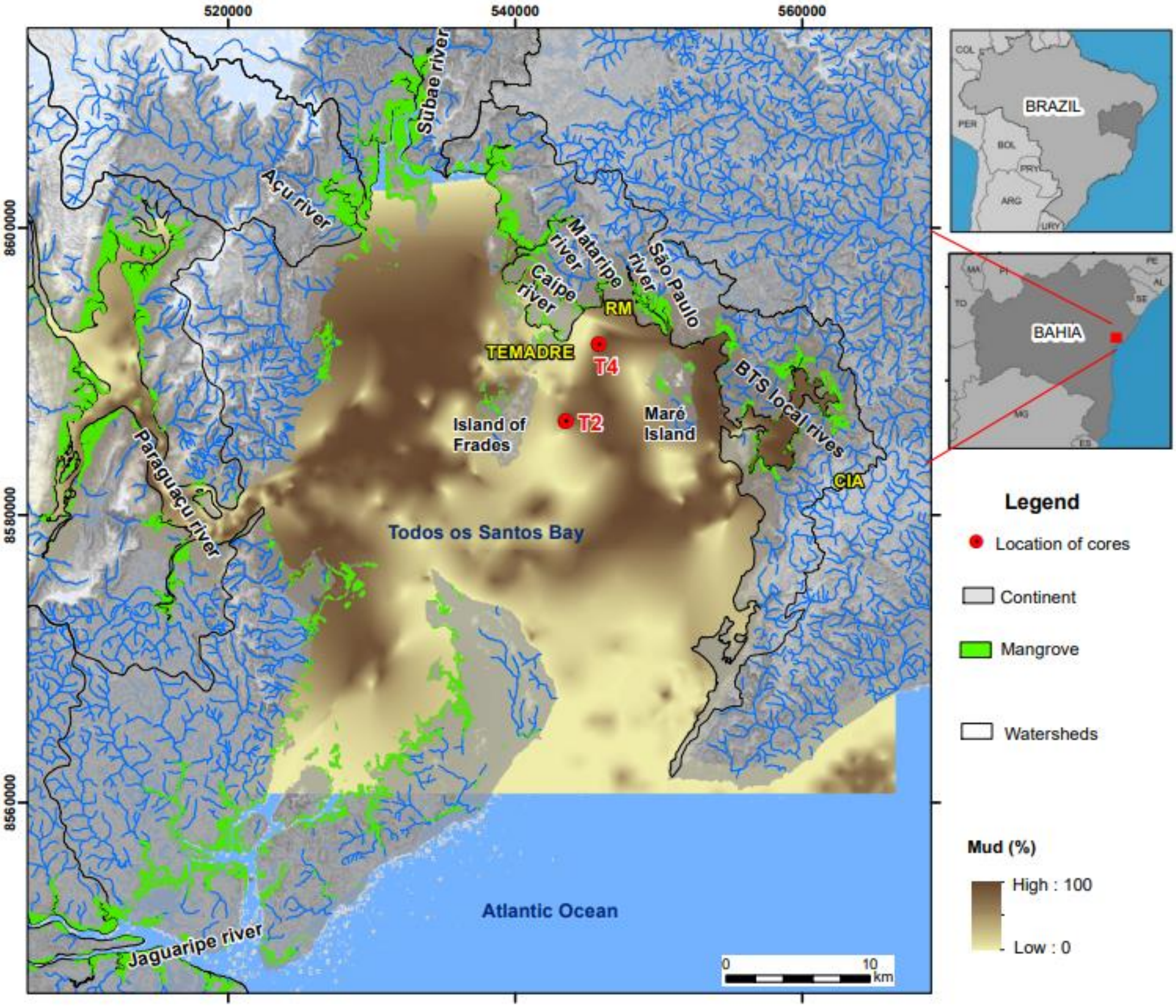

Figure 1. Map of Todos os Santos Bay (BTS), Brazil, with the sampling location of T2 and T4 sediment cores. Locations of the Mataripe Refinery (RM), Madre de Deus Port Terminal (TEMADRE), Aratu Industrial Center (CIA) and main rivers flowing into the Todos os Santos Bay.

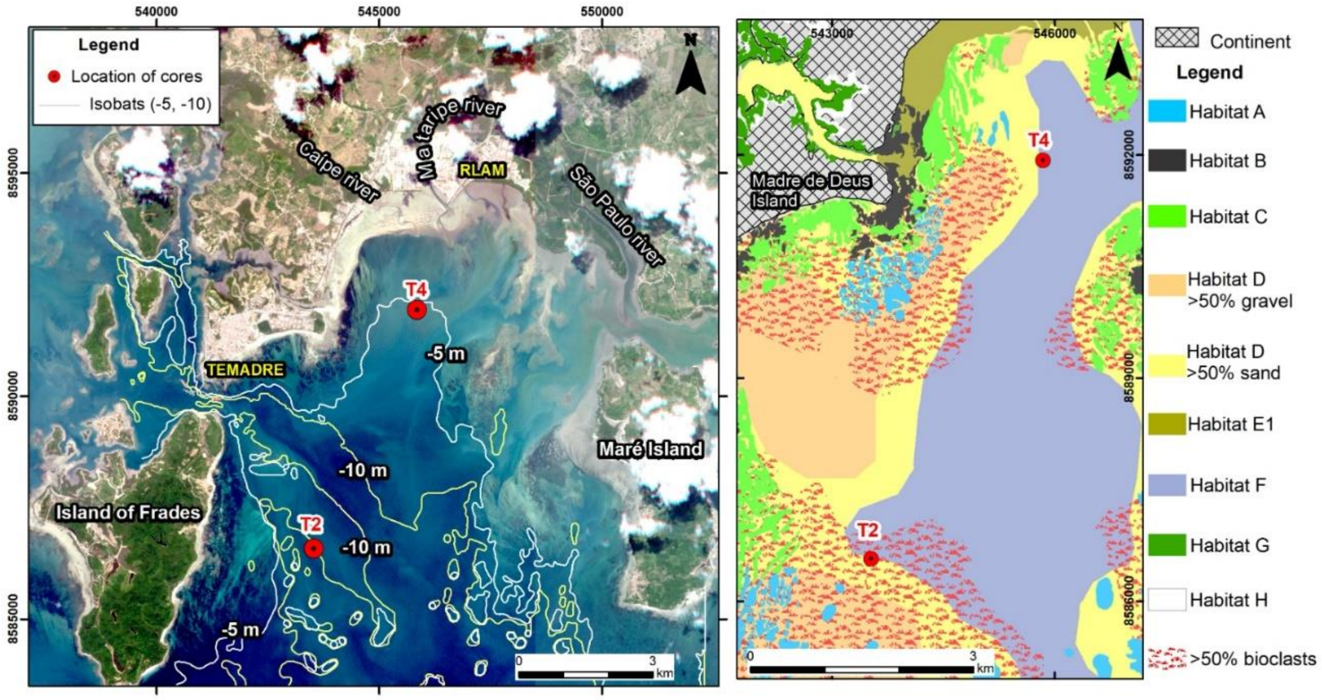

Figure 2. A – Satellite image of the northeastern portion of the BTS showing the location of cores T2 and T4. Also indicated are the locations of the Mataripe Refinery (RM) and the Madre de Deus Port Terminal (TEMADRE). B - Epibenthic marine habitat map (source: Oliveira et al., 2020) with the locations of cores T2 and T4. Habitat A—Reef patches (Porifera, Zoantharia, and calcareous macroalgae dominant); Habitat B—Intertidal abrasion terraces (soft macroalgae and Mollusca dominant); Habitat C—Sandy bottom densely covered by soft macroalgae; Habitat D—Bioclastic bioturbated sandy bottom; Habitat E1—Sandy tidal flat, and Habitat E2—Muddy tidal flat; Habitat F—Bioturbated subtidal muddy bottom; Habitat G—Mangrove forests; Habitat H—Supratidal flats (Apicum).

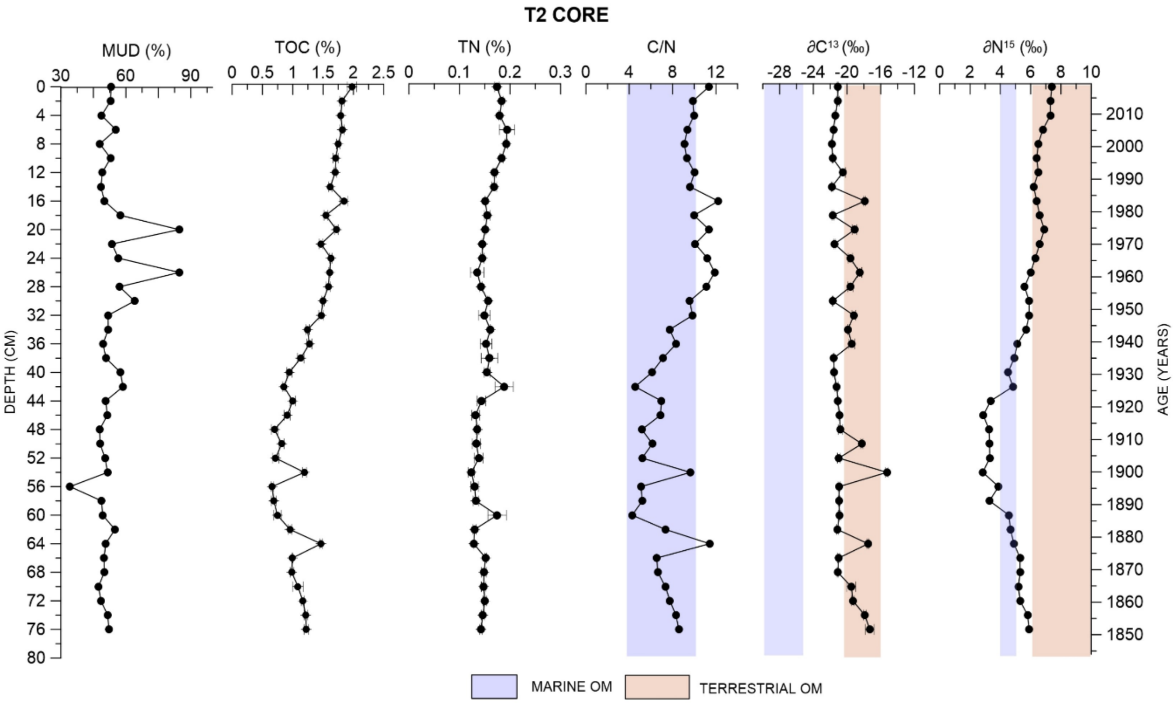

Figure 3. Time variation of mud, total organic carbon (TOC), total nitrogen (TN), C/N ratio, $\delta^{13}C$ and $\delta^{15}N$ in the T2 core collected in Todos os Santos Bay, Brazil. Vertical bars indicate the typical value range of marine and terrestrial sources of organic matter.

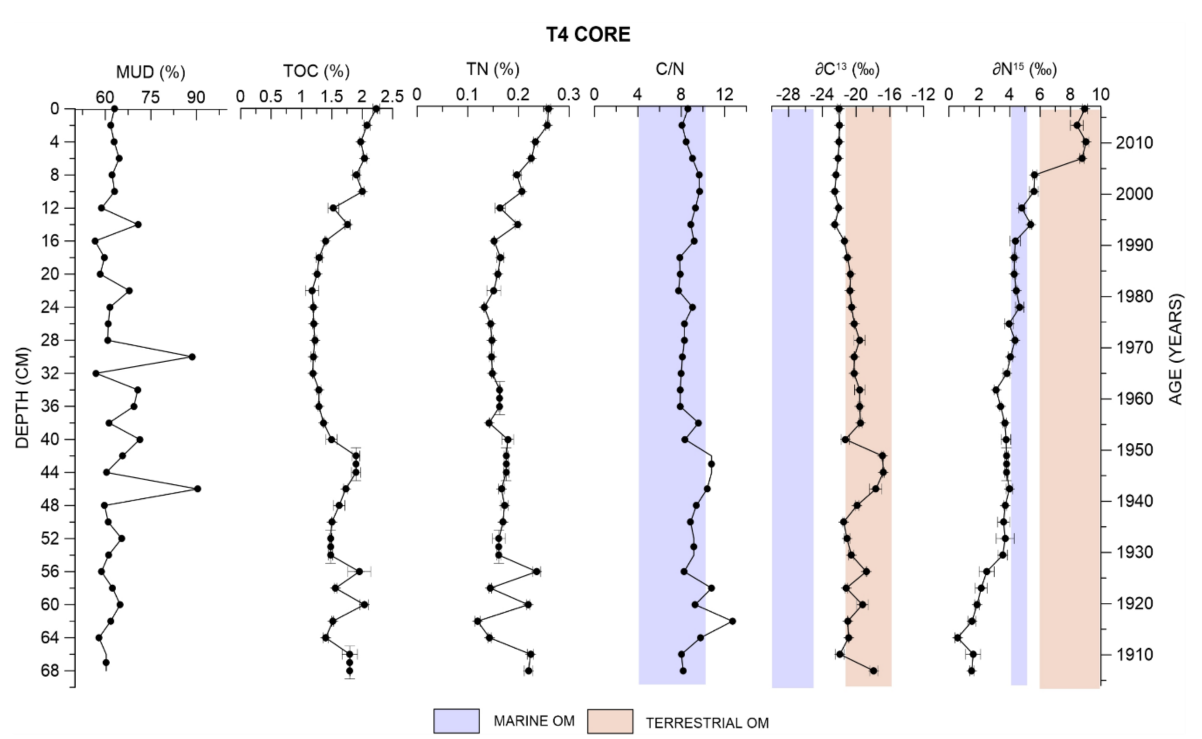

Figure 4. Time variation of mud, total organic carbon (TOC), total nitrogen (TN), C/N ratio, $\delta^{13}C$ and $\delta^{15}N$ in the T4 core collected in Todos os Santos Bay, Brazil. Vertical bars indicate the typical value range of marine and terrestrial sources of organic matter.

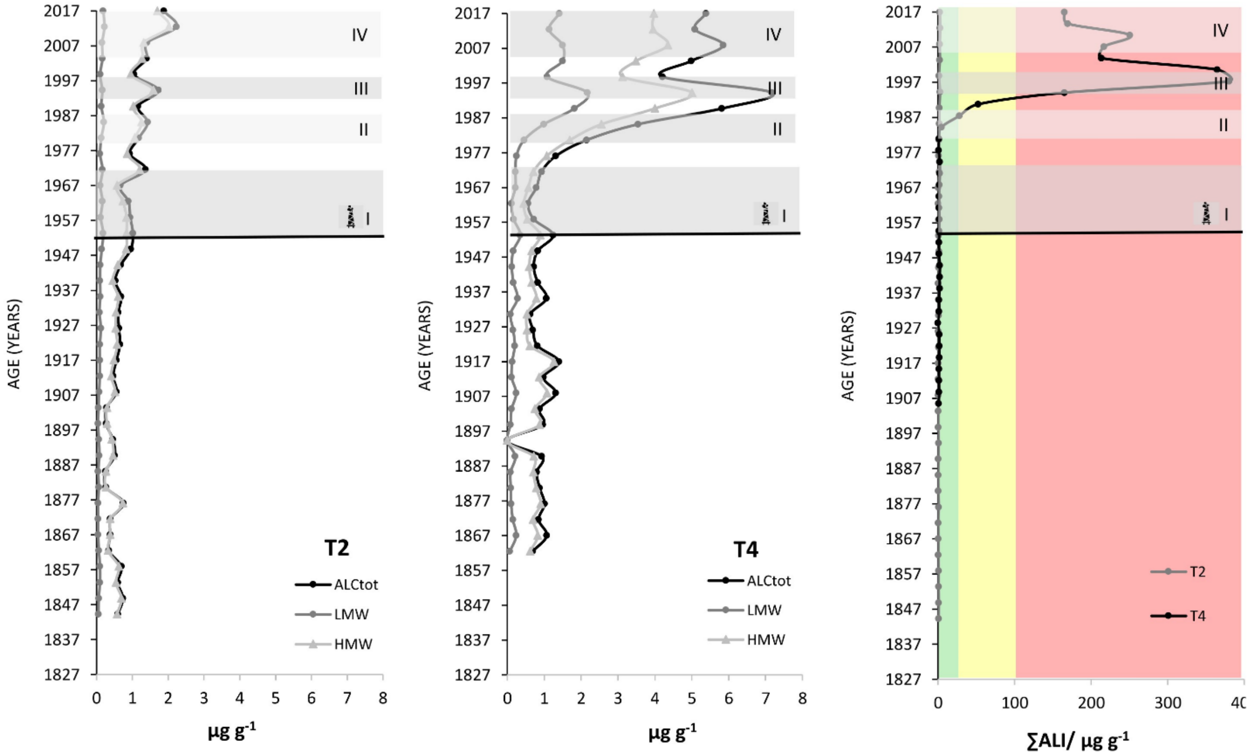

Figure 5. Vertical variations in the concentrations of total n-alkanes (ALC$_{TOT}$) and low molecular weight (LMW) and high molecular weight (HMW) n-alkanes in the samples studied. The vertical colored bars indicate oil contamination levels according to Volkman et al. (1992) and Readman et al. (2002): green (nonpolluted sediments), red (polluted sediments) and yellow (moderate concentrations). Horizontal bands indicate the four economic cycles identified in the region and detailed in Section 2.

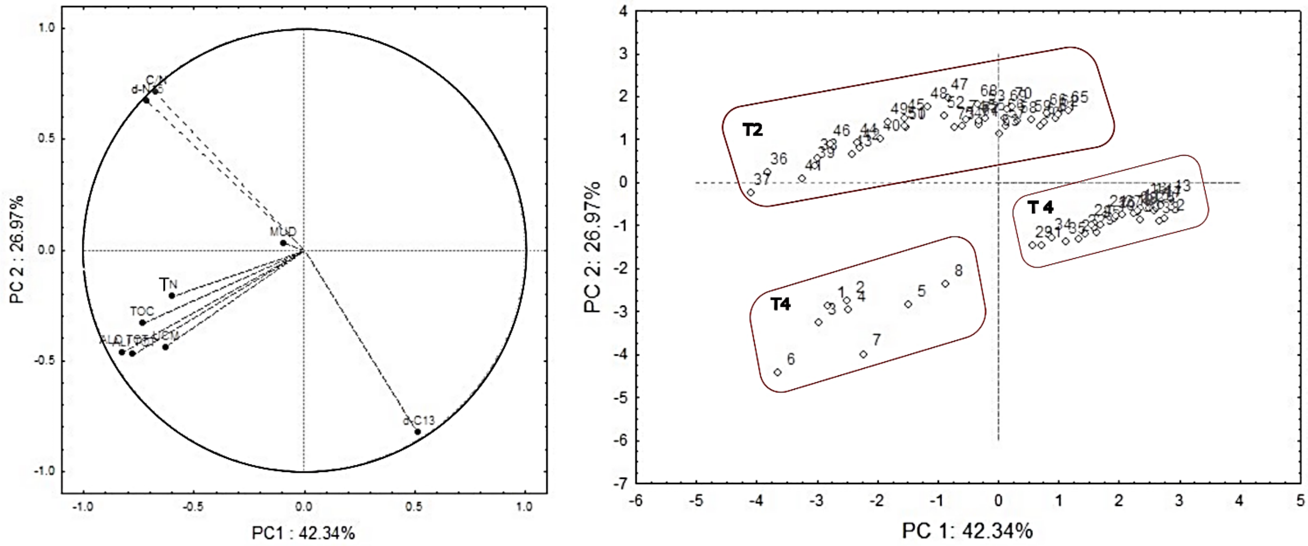

Fig. 6. Principal component analysis (PCA) based on the parameters: Mud, TOC, TN, C/N, δ^{13}C, δ^{15}N, ALC$_{TOT}$, ALI$_{TOT}$, and UCM. The PCA loadings plot is shown on the left, and the sample scoring plot is shown on the right.

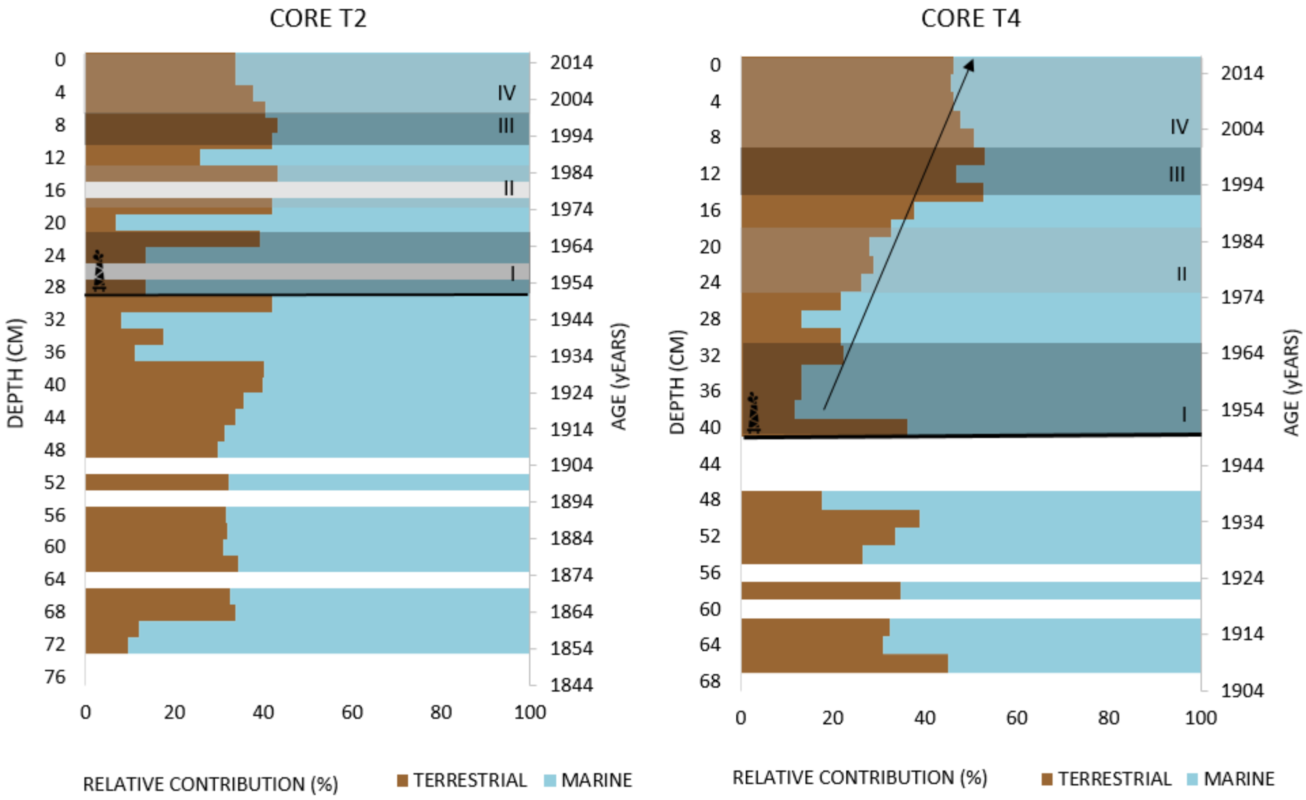

Figure 7. Relative contribution of terrestrial and marine organic carbon based on an isotopic mixing model (Shultz and Calder, 1976), applied to the sediments of cores T2 and T4. The dashed lines indicate important economic cycles in the Todos os Santos Bay, with the first cycle driven by the oil sector. Horizontal bands indicate the four economic cycles identified in the region and detailed in Section 2.

TABLES

Table 1. Organic matter source identification proxies used in this study.

Index	Interval	Source	Reference
Average Chain Length (ACL)	23 e 25	Biogenic: macrophytes	Zhang et al., 2006
	27 e 33	Terrigen	
Terrigen Aquatic Ratio (TAR)	< 1	Aquatic	Bourbonniiere; Meyer, 1996
	> 1	Terrigen	
Alkane Index (AI)	> 0.5	Biogenic: C4 type grasses	Rommerskirchen et al., 2003
	< 0.5	Terrestrial: vascular plants (type C3)	
Total Aliphatic Hydrocarbons (HA)	5.0 – 10.0	Predominance of biogenic sources	Volkman et al., 1992
	>100	Oil contaminated sediments	Readman et al., 2002
UCM	Absence	Sediments not contaminated by oil	Volkman et al., 1992
	Presence	Oil contaminated sediments	
UCM/ALI	> 4	Oil contaminated sediments	Volkman et al., 1992
	< 4	Sediments not contaminated by oil	
PRISTANE / PHYTANE	~ 1	Petrogenic	Steinhauer; Boehm, 1992
	>1 (3 e 5)	Predominance of biogenic sources	
Preferred Carbon Index (CPI)	≤1	Petrogenic	Aboul-Kassim; Simoneit, 1996
	4 a 7	Biogenic and Terrigen	Hedges; Prahl, 1993
	> 1	Biogenic	

$$\mathrm{TAR}=\left[\frac{n\mathrm{C}_{27}+n\mathrm{C}_{29}+n\mathrm{C}_{31}}{n\mathrm{C}_{15}+n\mathrm{C}_{17}+n\mathrm{C}_{19}}\right];\ ACL=\frac{\sum[n\mathrm{C}_i\times i]}{\sum[n\mathrm{C}_i]};\ AI=\frac{[n\mathrm{C}_{31}]}{[n\mathrm{C}_{29}+n\mathrm{C}_{31}]};\ CPI=0{,}5\ x\ \left[\frac{n\mathrm{C}_{25}+n\mathrm{C}_{27}+n\mathrm{C}_{29}+n\mathrm{C}_{31}+n\mathrm{C}_{33}}{n\mathrm{C}_{24}+n\mathrm{C}_{26}+n\mathrm{C}_{28}+n\mathrm{C}_{30}+n\mathrm{C}_{32}}+\frac{n\mathrm{C}_{25}+n\mathrm{C}_{27}+n\mathrm{C}_{29}+n\mathrm{C}_{31}+n\mathrm{C}_{33}}{n\mathrm{C}_{26}+n\mathrm{C}_{28}+n\mathrm{C}_{30}+n\mathrm{C}_{32}+n\mathrm{C}_{34}}\right]$$

Table 2. Concentrations of total n-alkanes (ALC_{TOT}), sum of low molecular weight n-alkanes (LMW), sum of high molecular weight n-alkanes (HMW), resolved aliphatic hydrocarbons (ALI), mixture unresolved complex (UCM), pristane (P) and phytane (F) in sediment cores from Todos os Santos Bay, Brazil, with mean, standard deviation, maximum and minimum values.

T2 CORE												T4 CORE											
AGE (YEARS)	**Alc Tot** [a]	**LMW** [b]	**HMW** [c]	**ALI** [d]	**UCM** [e]	**UCM/ ALI** [f]	**ACL** [g]	**AI** [h]	**Pr/Ph** [i]	**CPI (C_{12} - C_{24})** [j]	**CPI (C_{24} - C_{34})** [l]	**AGE (YEARS)**	**Alc Tot** [a]	**LMW** [b]	**HMW** [c]	**ALI** [d]	**UCM** [e]	**UCM/ ALI** [f]	**ACL** [g]	**AI** [h]	**Pr/Ph** [i]	**CPI (C_{12} - C_{24})** [j]	**CPI (C_{24} - C_{34})** [l]
2017	1.88	0.19	1.70	2.50	nd	0.00	29.05	0.10	1.42	0.78	1.56	2017	5.36	1.41	3.97	23.44	141.69	6.04	27.97	0.33	nd	1.90	1.56
2012	2.23	0.22	2.02	2.90	nd	0.00	28.32	0.08	0.00	0.84	1.62	2014	5.07	1.13	3.96	32.40	136.96	4.23	28.57	0.39	0.50	2.17	2.21
2008	1.41	0.16	1.32	2.34	nd	0.00	28.58	0.07	nd	0.82	1.91	2010	5.84	1.50	4.35	29.70	221.30	7.45	28.90	0.33	0.47	1.74	2.34
2003	1.40	0.16	1.28	2.50	nd	0.00	28.94	0.03	nd	0.71	1.82	2007	4.96	1.50	3.49	21.85	195.01	8.93	28.65	0.48	0.44	2.02	1.52
1999	1.05	0.10	0.96	1.47	nd	0.00	28.69	0.08	nd	0.90	1.67	2004	4.21	1.08	3.13	26.54	187.09	7.05	28.16	0.06	0.42	1.37	1.79
1994	1.73	0.16	1.59	2.67	nd	0.00	28.59	0.06	nd	0.80	1.43	2001	7.16	2.17	5.01	37.40	327.34	8.75	28.11	0.57	0.38	2.61	2.31
1990	1.16	0.13	1.03	1.89	nd	0.00	28.84	0.05	nd	0.62	1.63	1997	5.82	1.82	4.00	30.40	349.94	11.51	28.16	0.35	0.31	1.90	2.00
1985	1.42	0.20	1.26	1.91	nd	0.00	28.98	0.05	nd	0.57	1.40	1994	3.52	0.99	2.55	13.94	151.43	10.87	28.37	0.31	0.46	1.49	1.59
1981	1.18	0.13	1.06	1.56	nd	0.00	28.63	0.03	nd	0.62	1.09	1991	2.14	0.45	1.70	6.70	45.99	6.86	28.14	0.17	nd	1.05	1.55
1976	0.93	0.10	0.86	1.06	nd	0.00	28.93	0.03	nd	0.79	1.49	1987	1.31	0.25	1.07	2.52	25.87	10.27	28.36	0.24	nd	1.31	1.72
1972	1.37	0.17	1.21	1.83	nd	0.00	28.43	0.12	0.00	0.67	1.27	1984	0.91	0.22	0.71	1.63	3.04	1.87	29.18	0.06	nd	0.77	3.49
1967	0.67	0.11	0.57	0.43	nd	0.00	28.74	0.22	nd	0.86	1.53	1981	0.76	0.22	0.57	1.28	nd	0.00	29.21	0.12	nd	0.55	6.55
1962	0.89	0.16	0.74	0.35	nd	0.00	28.92	0.13	nd	0.72	2.00	1978	0.55	0.11	0.45	1.04	nd	0.00	29.52	0.10	nd	1.07	19.52
1958	0.94	0.12	0.84	1.20	nd	0.00	28.81	0.03	nd	0.69	1.27	1974	0.69	0.18	0.54	2.35	nd	0.00	29.47	0.09	nd	0.97	3.38
1953	1.01	0.19	0.83	1.03	nd	0.00	28.90	0.04	0.00	0.56	1.29	1971	1.24	0.35	0.89	2.58	nd	0.00	28.72	0.07	nd	0.73	1.88
1949	0.96	0.15	0.82	1.23	nd	0.00	28.94	0.04	0.00	0.53	3.31	1968	0.80	0.16	0.67	1.95	nd	0.00	29.25	0.06	nd	0.53	2.95

1944	0.68	0.10	0.60	0.79	nd	0.00	28.63	0.00	nd	0.56	1.14	1965	0.70	0.12	0.60	1.51	nd	0.00	29.52	0.07	nd	0.75	4.02
1940	0.52	0.10	0.45	0.52	nd	0.00	28.87	0.05	nd	0.62	1.38	1961	0.81	0.17	0.66	1.68	nd	0.00	29.41	0.09	nd	0.79	3.72
1935	0.69	0.10	0.60	0.99	nd	0.00	28.95	0.09	nd	0.66	1.35	1958	1.05	0.28	0.79	1.92	nd	0.00	29.04	0.07	nd	0.64	2.44
1931	0.60	0.08	0.55	0.79	nd	0.00	28.92	0.05	nd	0.62	1.15	1955	0.59	0.09	0.53	1.47	nd	0.00	29.31	0.03	nd	0.87	3.11
1926	0.63	0.12	0.53	0.67	nd	0.00	29.33	0.05	nd	0.53	1.19	1951	0.68	0.16	0.54	1.56	nd	0.00	29.52	0.08	nd	0.8	4.62
1922	0.65	0.09	0.58	0.83	nd	0.00	28.79	0.05	nd	0.57	1.23	1948	0.80	0.20	0.62	1.39	nd	0.00	29.33	0.11	nd	0.81	4.05
1917	0.56	0.09	0.49	0.56	nd	0.00	29.69	0.00	nd	0.44	1.31	1945	1.40	0.13	1.27	2.58	nd	0.00	28.56	0.07		0.42	2.24
1912	0.46	0.09	0.41	0.57	nd	0.00	29.27	0.05	nd	0.67	1.69	1942	0.95	0.12	0.86	2.25	nd	0.00	28.91	0.05	nd	1.73	2.82
1908	0.55	0.07	0.51	0.70	nd	0.00	29.25	0.05	4.86	0.41	1.92	1938	1.31	0.24	1.08	2.21	nd	0.00	28.90	0.05	nd	0.62	2.76
1903	0.28	0.06	0.29	0.48	nd	0.00	29.20	0.07	nd	0.49	4.01	1935	0.84	0.12	0.75	1.54	nd	0.00	29.21	0.06	nd	1.02	3.86
1899	0.27	0.04	0.29	0.54	nd	0.00	29.62	0.07	nd	0.36	3.11	1932	0.93	0.08	0.88	1.68	nd	0.00	29.17	0.04	nd	2.06	4.13
1894	0.45	0.06	0.43	0.92	nd	0.00	29.21	0.06	1.00	0.38	1.62	1928									nd		
1890	0.51	0.08	0.46	0.74	nd	0.00	28.91	0.07	0.00	0.30	1.84	1925	0.91	0.22	0.72	1.79	nd	0.00	28.97	0.03	nd	0.54	2.16
1885	0.25	0.05	0.27	0.36	nd	0.00	29.21	0.08	nd	0.41	4.45	1922	0.76	0.09	0.71	1.75	nd	0.00	28.75	0.03	nd	1.24	1.94
1881	0.26	0.06	0.27	0.66	nd	0.00	29.25	0.09	nd	0.36	2.34	1919	0.84	0.09	0.79	1.92	nd	0.00	28.84	0.02	nd	0.73	2.28
1876	0.75	0.04	0.73	1.06	nd	0.00	27.79	0.05	nd	0.60	0.92	1915	0.97	0.10	0.90	1.52	nd	0.00	28.33	0.03	nd	0.9	1.57
1872	0.39	0.04	0.38	0.44	nd	0.00	29.89	0.06	nd	0.45	2.82	1912	0.82	0.15	0.70	1.37	nd	0.00	28.78	0.03	nd	1.06	2.01
1867	0.39	0.04	0.39	0.74	nd	0.00	29.05	0.06	1.00	0.41	2.08	1909	1.05	0.24	0.83	1.57	nd	0.00	28.95	0.06	nd	0.46	2.43
1862	0.35	0.06	0.33	0.68	nd	0.00	29.66	0.07	1.00	0.34	2.98	1906	0.66	0.07	0.62	0.96	nd	0.00	29.35	0.07	nd	1.62	4.28
1858	0.69	0.09	0.62	0.94	nd	0.00	28.80	0.10	0.00	0.50	1.49												
1853	0.59	0.09	0.54	0.89	nd	0.00	29.08	0.04	0.37	0.52	1.99												
1849	0.73	0.06	0.69	1.12	nd	0.00	28.59	0.04	nd	0.61	1.31												
1844	0.60	0.05	0.57	0.97	nd	0.00	28.38	0.05	nd	0.50	1.25												
Mean	0.68	0.10	0.60	0.92			28.92	0.05		0.57	1.56	Mean	0.94	0.21	0.81	1.92	151.43	0.00	28.90	0.07		1.00	3.26
Standard Deviation	0.47	0.05	0.42	0.69			0.40	0.04		0.16	0.80	Standard Deviation	1.94	0.58	1.37	11.31	98.84	3.95	0.47	0.15		0.57	3.09
Maximum	2.23	0.22	2.02	2.90			29.69	0.22		0.90	4.45	Maximum	5.84	2.17	4.35	37.40	349.94	8.75	28.16	0.35		2.61	19.52
Minimum	0.25	0.04	0.27	0.36			27.79	0.03		0.30	1.14	Minimum	0.66	0.07	0.53	0.96	nd	0.00	29.35	0.07		0.42	1.56

[a] Total concentration of n–alkanes (C_{12}-C_{40}).
[b] Concentrations of low molecular weight n-alkanes (≤ C_{22})
[c] Concentrations of high molecular weight n-alkanes (≥ C_{23})
[d] Total concentration of resolved aliphatic hydrocarbons
[e] Total concentration of unresolved complex mixture
[f] Ratio between unresolved complex mixture and resolved aliphatic hydrocarbons
[g] Mean chain length of n-alkanes
[h] Alkanes index
[i] Pristane to phytane ratio
[j] Preferential carbon index calculated for C_{12}-C_{24}
[l] Preferential carbon index calculated for C_{24}-C_{34}

Table 3. Total organic carbon (TOC), total nitrogen (TN) and carbon isotopes ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) contents found in sediments from the BTS and in other bays in Brazil and worldwide.

	TOC (%)	**TN (%)**	**$\delta^{13}C$ (‰)**	**$\delta^{15}N$ (‰)**	**Reference**
Todos os Santos Bay, Brazil	0,66 - 2,23	0,12 - 0,26	-15,26 a - 21,80	2,84 - 7,40	Present study
Todos os Santos Bay, Brazil	0,7 - 1,6	0,10 - 0,30	-19,5 a - 22,8	3,8 - 6,3	Souza et al., 2017
Todos os Santos Bay, Brazil	0,95 - 2,72	0,10 - 0,33	**	**	Costa et al., 2011
Guanabara Bay, Brazil	2,97 - 3,97	0,33 - 0,48	**	**	Lazzari et al., 2019
Babitonga Bay, Brazil	0,07 - 3,82	0,01 - 3,82	-24,9 a - 22,6	3,6 - 6,4	Barros et al., 2010
Bohai Bay, China	0,85 – 7,24	0,03 - 0,47	-25,69 a - 18,23	6,06 ± 2,81	Gao et al., 2012
Zhelin Bay, China	0,46 - 1,23	0,08 -0,20	-22,07 a - 21,13	5,28 - 7,14	Gu et al., 2017
Arabian Sea, Pakistan	0,65 - 4,77	0,08 -0,59	-21,03 a - 19,14	6,85 - 8,86	Cowie et al., 2009
Arctic Ocean	0,34 - 1,90	0,05 - 0,22	-24,2 a - 22,0	5,1 - 6,8	Schubert; calvert, 2001

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CAPÍTULO 3

ARTIGO 2

A ser submetido a *Regional Studies in Marine Science*

DEPOSIÇÃO HISTÓRICA DE CARBONO NEGRO E HIDROCARBONETOS POLICÍCLICOS AROMÁTICOS EM SEDIMENTOS DE UMA BAÍA TROPICAL: EXPLORAÇÃO DE PETRÓLEO, IMPACTOS DA URBANIZAÇÃO E AGRICULTURA

Carine Santana Silva[1]; José Maria Landim Dominguez[1]; Gilvan Takeshi Yogui[2]

[1]LEC- Laboratório de Estudos Costeiros - Instituto de Geociências, Universidade Federal da Bahia, Rua Barão de Jeremoabo, s/n, 40170-020, Salvador, BA, Brasil

[2]OrganoMAR – Laboratório de Compostos Orgânicos em Ecossistemas Costeiros e Marinhos, Departamento de Oceanografia, Universidade Federal de Pernambuco, Av. Arquitetura s/n, Cidade Universitária, 50740-550, Recife, PE, Brasil

∗Autor correspondente para: Laboratório de Estudos Costeiros - Instituto de Geociências, Universidade Federal da Bahia, Rua Barão de Jeremoabo, s/n, 40170-020, Salvador, BA, Brasil

Endereço de e-mail: carine.sntn@outlook.com (Carine Santana Silva)

RESUMO

A deposição histórica de carbono negro (BC) e hidrocarbonetos policíclicos aromáticos (HPAs) foi estudada pela primeira vez nos sedimentos da Baía de Todos os Santos (BTS). Dois testemunhos de sedimentos da região norte da BTS foram analisados, comparando suas variações históricas com o desenvolvimento socioeconômico local. A concentração de BC variou de 0,08 a 0,44 mg g^{-1}, representando até 4% do carbono orgânico total (COT). O testemunho T2 indicou BC proveniente da queima incompleta de plantas C4, enquanto próximo à costa (T4), esse padrão foi observado apenas antes de 1960, devido à agricultura de cana-de-açúcar. Com a urbanização, fontes veiculares passaram a predominar no BC depositado, aumentando significativamente após 1990. As concentrações de HPA_{TOT} nos testemunhos T2 e T4 variaram de 33,6 a 185 ng g^{-1} e de 2,90 a 1066 ng g^{-1}, respectivamente, com fontes pirolíticas sendo as principais fontes de HPAs. No entanto, T4 refletiu mudanças históricas locais, com um aumento abrupto de hidrocarbonetos a partir de 1980, coincidindo com a intensificação da exploração de petróleo e derramamentos acidentais. A poluição foi moderada após esse período, exceto por um pico elevado em 2010. A implementação de políticas ambientais melhorou a qualidade da água e reduziu a poluição.

Palavras – chave: Baía de Todos os Santos, carbono orgânico, emissão antropogênica, matéria orgânica.

1. Introdução

Nas últimas décadas, o desenvolvimento industrial e tecnológico, aliado ao aumento da população mundial, destruição de habitats, extinção de espécies e exploração massiva dos recursos naturais resultaram em mudanças profundas no planeta conceitualizadas como o Antropoceno (Crutzen, 2002). Essa unidade não oficial de tempo geológico tem sido usada para descrever o período mais recente da história da Terra. Durante este período, a liberação de contaminantes químicos tem causado graves problemas ambientais em diversas escalas (Cao et al., 2020; Sharifi et al., 2022).

Nesse contexto, os hidrocarbonetos policíclicos aromáticos (HPAs) parentais e alquilados são compostos ubíquos e representam uma grande preocupação ambiental devido ao seu caráter tóxico, carcinogênico, mutagênico e bioacumulativo (Han et al., 2021; Pang et al., 2022). Esses compostos são introduzidos no ambiente marinho por diferentes fontes, incluindo fontes pirolíticas (resultantes da combustão incompleta de matéria orgânica, incluindo combustíveis fósseis), petrogênicas (originadas do aporte direto de petróleo e seus derivados) e processos diagenéticos (transformações que ocorrem após a deposição de precursores biogênicos) (Li et al., 2023). Embora exista um aporte natural, seu aumento inequívoco está associado a introduções antrópicas, especialmente nas regiões costeiras (Pang et al., 2022).

Juntamente com os HPAs de origem pirolítica, a combustão incompleta de combustíveis fósseis e biomassa gera o carbono negro (no inglês, Black Carbon – BC). O BC é uma fração aromática altamente refratária do carbono orgânico (Goldberg, 1985) que alcança os sistemas costeiros através da descarga fluvial e/ou pela deposição atmosférica úmida ou seca (Khan et al., 2017). Dessa forma, o BC presente no ambiente marinho se destaca como marcador por ser proveniente de fontes alóctones exclusivamente terrestres (Bond et al., 2013). Sua assinatura isotópica ($\delta^{13}C_{BC}$) tem sido usada para identificar as fontes de BC no aerossol e em sedimentos (Gao et al., 2018).

Os HPAs leves, presentes em maior abundância em óleos, se degradam mais rapidamente que os de alto peso molecular, o que pode levar a interpretações ambíguas quando baseadas apenas neles (Yunker et al., 2002). Portanto, a análise dos homólogos alquilados dos HPAs, predominantes em resíduos de petróleo, oferece uma base mais sólida para estimar as contribuições pirolíticas e petrogênicas de HPAs (Wagener et al., 2012). Além disso, o BC, com sua baixa taxa de degradação, é gerado principalmente por fontes pirolíticas como tráfego, carvão, indústria e queima de biomassa (Gao et al., 2018). Assim, os HPAs (parentais e alquilados) e o BC podem, em conjunto, ser uma ferramenta poderosa na distinção de fontes de MO em sistemas costeiros complexos.

A Baía de Todos os Santos (BTS) é uma das primeiras áreas de exploração de petróleo no Brasil. Ao longo do tempo esse ambiente tem sido submetido a diversas atividades potencialmente impactantes, principalmente a indústria petroquímica e, secundariamente, a urbanização. Um estudo anterior (Silva et al., 2024) com a análise das tendências temporais da MO depositada no sedimento da BTS reveladas através de alcanos e isótopos de carbono e nitrogênio mostraram tendências consistentes de mudança no tipo da MO depositada, com um aumento da MO alóctone/terrestre próximo à costa, refletindo os ciclos econômicos na BTS. No entanto, não está claro a natureza dessa MO alóctone e as contribuições das fontes locais.

A fim de investigar melhor a MO depositada na baía esse estudo analisou nos mesmos testemunhos a variação dos teores de BC e HPAs parentais e alquilados. O registro histórico do BC e HPAs que abrangem a era pré-industrial local e contemporânea foi caracterizado. Os períodos críticos de aumento foram identificados e as principais fontes e causas da variação da deposição do BC e dos HPAs foram discutidas. Esses dados históricos constituem a primeira avaliação da deposição do BC na BTS e, portanto, fornecem informações relevantes sobre o impacto do aumento das emissões na região.

2. Materiais e métodos

2.1 Área de estudo

A Baía de Todos os Santos (BTS) (Fig. 1), a segunda maior baía do Brasil com 1.223 km², é reconhecida por seu valor ecológico e abriga ecossistemas como recifes de coral, estuários, manguezais, ilhas e planícies de maré (Hatje; De Andrade, 2009). Com uma profundidade média de 9,8 m, a BTS apresenta características oceânicas e circulação impulsionada por marés (Lessa et al., 2009). Sedimentos de lama predominam na metade norte, enquanto sedimentos arenosos são comuns na parte sul (Lessa; Dias, 2009). Os principais rios afluentes são Paraguaçu, Subaé e Jaguaripe, enquanto os menores, Mataripe, São Paulo e Caípe, estão próximos a uma refinaria de petróleo (CRA, 2004).

A influência humana significativa na BTS começou nas décadas de 1940 e 1950, com o desenvolvimento industrial ligado ao setor petrolífero. Desde então, indústrias metalúrgicas, têxtil, química, petroquímica, carcinicultura, mineração e atividades portuárias aumentaram as pressões antropogênicas. A região norte/nordeste da BTS é fortemente impactada por contaminação orgânica e inorgânica devido a efluentes industriais e domésticos não tratados (Felizzola et al., 2007; Silva et al., 2014; Nascimento et al., 2017; Andrade et al., 2017; de Almeida et al., 2018; Santos et al., 2020).

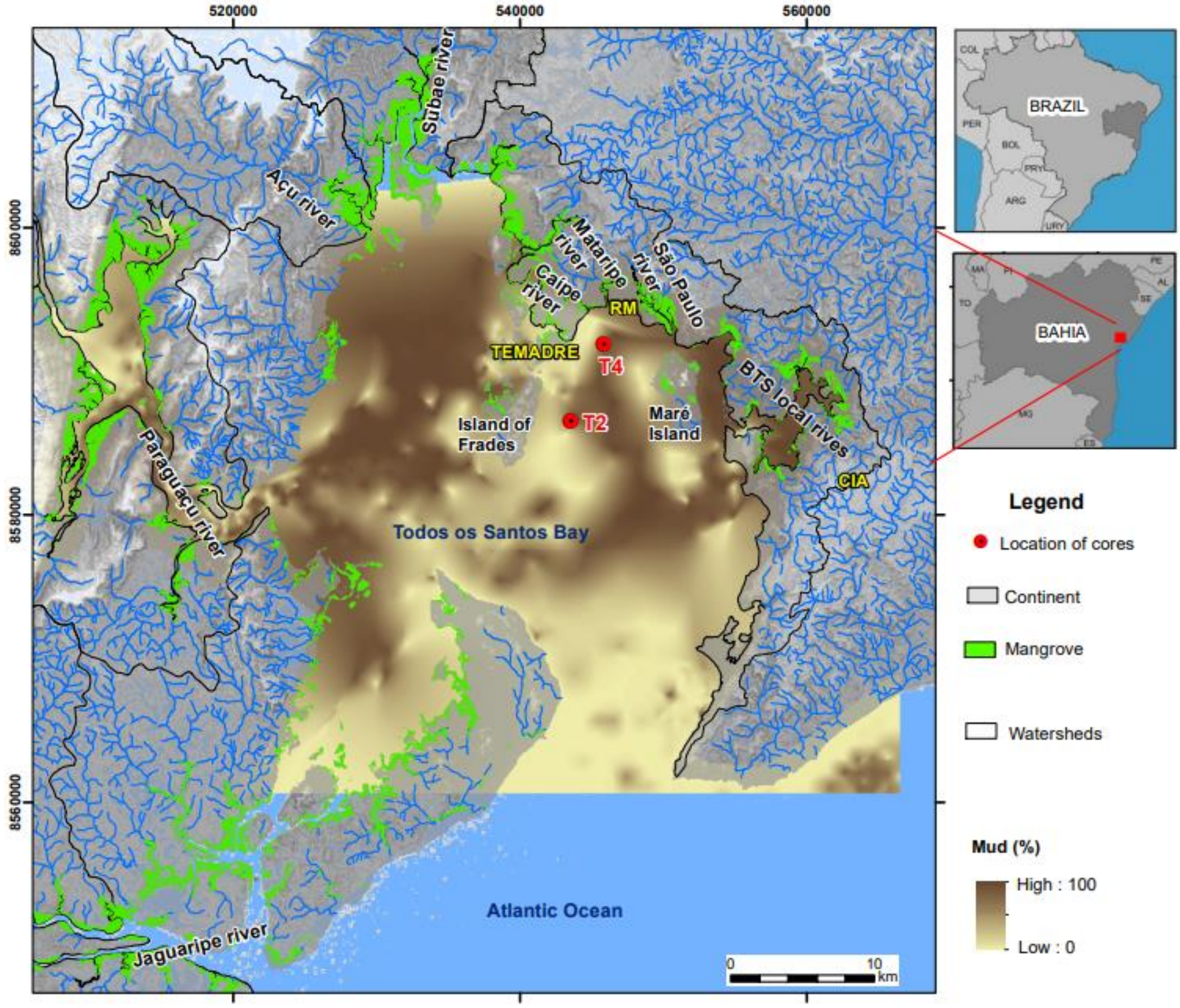


Figura 1. Mapa da Baía de Todos os Santos (BTS), Brasil, com a localizações de amostragem dos testemunhos de sedimentos T2 e T4. As localizações da Refinaria Mataripe (RM) e do Terminal Portuário Madre de Deus (TEMADRE) também são mostrados.

2.2. Amostragem

Em 2017, dois testemunhos foram coletados na região norte da BTS (Fig.1). O testemunho T2, foi coletado mais distante da costa, em um local de maior hidrodinâmica e mais afastado de fontes diretas de contaminação. Já o testemunho T4 foi coletado mais próximo à costa, sob uma potencial influência de uma refinaria de petróleo e outras fontes antrópicas continentais. Em laboratório, os testemunhos foram mantidos a -4ºC, sendo posteriormente abertos e seccionados em intervalos de 2 cm. As subamostras foram liofilizadas e armazenadas até as análises químicas.

2.3 Preparação das amostras e análises instrumentais

Detalhes das análises de granulometria, datação/taxa de sedimentação, carbono orgânico total (COT) e da extração de hidrocarbonetos podem ser encontrados em Silva et al. (2024). A granulometria foi obtida com um analisador de partículas por difração a laser (CILAS 1064) e classificada com o software GRADISTAT V 5.0®. A datação do testemunho T2 foi feita com ^{210}Pb, utilizando o modelo de concentração inicial constante (CIC) para calcular a taxa de sedimentação e idades (Godoy et al., 1998). A taxa de sedimentação do testemunho T4 foi estimada em 0,61 cm ano^{-1}, com base em dados de CRA (2004) e Wagener et al. (2010). A determinação do COT foi realizada em um analisador elementar acoplado a um espectrômetro de massas de razão isotópica (EA-IRMS), após acidificação para remover carbonatos.

A análise de carbono negro (BC) seguiu o método de oxidação térmica (CTO-375) de Gustafson et al. (1997). Em resumo, ~10mg de sedimento foi pesada após a remoção dos carbonatos por acidificação com ácido clorídrico. Adicionalmente, o sedimento seco passou por uma etapa de oxidação térmica em uma mufla (NABERTHERM) com fluxo de oxigênio constante. O programa de temperatura utilizado foi de 10 ºC min^{-1} até 300 ºC e 0,5 ºC min^{-1} até 375 ± 5 ºC, permanecendo nesta temperatura durante 24 horas. Após o tratamento térmico considera-se que o todo COT foi removido, restando apenas o BC. Posteriormente, foi realizada a quantificação no analisador elementar conforme descrito acima, com ~10 mg de sedimento seco em cápsulas de prata.

A extração de HPAs utilizou um método adaptado do EPA 3540C, com 5-10 g de sedimento extraído em Soxhlet usando diclorometano/n-hexano (1:1, v/v) por 8 horas. Padrões internos deuterados (acenafteno-D_{10}, fenantreno-D_{10} and criseno-D_{12}; concentração de 1000 ng mL^{-1} cada) foram adicionados antes da extração, e o sedimento foi tratado com cobre ativado para remover enxofre. Os extratos foram concentrados e purificados em colunas de sílica gel e alumina, eluidos com n-hexano e diclorometano. Padrões de recuperação deuterados (fluoreno-D_{10} e benzo[a]antraceno-D_{12}; concentração de 1000 ng mL^{-1} cada) foram adicionados aos extratos concentrados.

A quantificação dos HPAs foi realizada usando um cromatógrafo a gás (Agilent Technologies, modelo 7820A) acoplado a um espectrômetro de massas (Agilent Technologies, modelo 5975C). O cromatógrafo a gás foi equipado com uma coluna capilar de sílica fusionada HP-5ms (comprimento de 30 m, 0,25 mm de diâmetro interno e 0.25 µm de espessura de filme). A temperatura do injetor e da interface do GC-MS foi de 300 °C. A temperatura do forno foi programada da seguinte forma: 60 °C, taxa de 15 °C min^{-1} até 150 °C, taxa de 5 °C min^{-1} até 220 °C e taxa de 10 °C min^{-1} até 300 °C, com um período isotérmico final de 10 min. Hélio foi usado como gás de arraste em fluxo constante (1.2 mL min^{-1}), e 1 µL do extrato foi injetado no modo splitless com um amostrador automático.

Um total de 16 HPAs parentais foram identificados: naftaleno (NaF), acenaftileno (Ac), acenafteno (Acl), fluoreno (Fl), fenantreno (Fen), antraceno (Ant), fluoranteno (Flu), pireno (Pir), benzo[a]antraceno (BaA), criseno (Cri), benzo[b]fluoranteno (BbF), benzo[k]fluoranteno (BkF), benzo[a]pireno (BaP), indeno [1,2,3,cd] pireno (IP), dibenzo[a,h]antraceno (DahA) e benzo[g,h,i]perileno (BghiP). Além disso, cinco grupos de HPAs alquilados também foram identificados, incluindo naftalenos (C2–C4 NaF), fluorenos (C1–C3 Fl), fenantrenos/antracenos (C1–C4 Fen/Ant), fluorantenos/pirenos (C1–C3 Flu/Pir) e benzo[a]antracenos/crisenos (C1–C3 BaA/Cri).

2.4 Garantia de qualidade/controle de qualidade (QA/QC)

Detalhes do procedimento são descritos por Silva et al., 2024. A cada lote de 15 amostras de campo, foram analisados um branco de instrumento, um branco de laboratório, uma duplicata de amostra e duas amostras do material de referência certificado (NIST SRM 1941b). Solventes de grau pesticida foram utilizados, e todas as soluções padrão foram analisadas para garantir sua integridade. A quantificação dos analitos seguiu o método de padronização interna, com recuperação dos padrões internos de 79 ± 16%, dentro dos limites aceitos (Lauenstein e Cantillo, 1998). O limite de quantificação dos HPAs variou de 0,09 a 0,19 ng g^{-1} (peso seco). Apenas 5,4% dos analitos nos brancos de laboratório estavam acima do LQ e foram subtraídos das amostras. A recuperação média dos analitos foi de 105%, com um coeficiente de variação de 8%, indicando boa exatidão e precisão.

3. Estatística

A normalidade das variáveis foi verificada pelo teste de Kolmogorov-Smirnov, e as análises estatísticas descritivas e não-paramétricas foram realizadas com o software STATISTICA 9.0® (STATSOFT 2009). Valores abaixo do limite de detecção foram substituídos por metade desse limite. A análise de correlação de Spearman foi realizada, com significância estabelecida em $p = 0,05$.

4. Resultados

4.1. Taxas de sedimentação

A taxa de sedimentação do testemunho T2 foi de 0,44 ± 0,2 cm ano^{-1}, abrangendo o período de 1844 (base) a 2017 (topo). Em contrapartida, o testemunho

T4 apresentou uma taxa estimada de 0,61 cm ano^{-1}, abarcando um período de 113 anos, desde 1904 (base) até 2017 (topo). Os métodos utilizados para datação e cálculo das taxas de sedimentação podem ser encontrados em Silva et al., 2024.

4.2. Concentração, composição e perfil temporal dos HPAs

As concentrações de HPAs nos testemunhos T2 e T4 são mostradas na Figura 2. No testemunho T2, os HPA_{TOT} (HPA_{16} e HPA_{Alk}) variaram de 33,6 a 185 ng g^{-1}, com HPA_{16} variando de 32,5 a 109 ng g^{-1}. Os HPAs de baixo peso molecular (LMW), isto é, a soma de HPAs com 2 e 3 anéis, variaram de 2,93 a 14,5 ng g^{-1}, enquanto os HPAs de alto peso molecular (HMW), somatório de HPAs com 4, 5 e 6 anéis, variaram de 26,9 a 95,1 ng g^{-1}. Os homólogos alquilados (HPA_{Alk}) variaram de 1,11 a 77,5 ng g^{-1}, contribuindo em média com 24,5% do total de HPAs identificados. As concentrações se mantiveram relativamente constantes ao longo do perfil temporal.

A composição dos HPAs nos testemunhos é mostrada na Figura 3. No T2, os HPAs de cinco e seis anéis (BbF, BkF, BaP, IP, DahA e BghiP) dominaram, compondo 17,6 a 70,5% dos HPAs. Os HPAs de quatro anéis (fluoranteno, pireno, benzo[a]antraceno e criseno) constituíram de 9,34 a 39,5%. Compostos com dois e três anéis representaram de 3,72 a 73,8% do HPA_{TOT}. O BbF (3,49 a 23,6%, média = 15,4%) foi o principal componente dos HPAs no testemunho T2. Acenafteno foi o HPA menos comum (0 a 0,16%). Para os HPA_{Alk}, benzo[a]antraceno/criseno foi a série mais abundante, seguido por fluoranteno/pireno, fenantreno/antraceno, fluoreno e naftaleno.

No testemunho T4, HPA_{TOT} e HPA_{16} variaram de 2,90 a 1066 ng g^{-1} e 2,70 a 878 ng g^{-1}, respectivamente. LMW variou de 1,47 a 45,6 ng g^{-1} e HMW de não detectados a 833 ng g^{-1}. HPA_{Alk} variou de 0,63 a 329 ng g^{-1}, compondo 27,4% dos HPAs. As concentrações aumentaram abruptamente desde 1980.

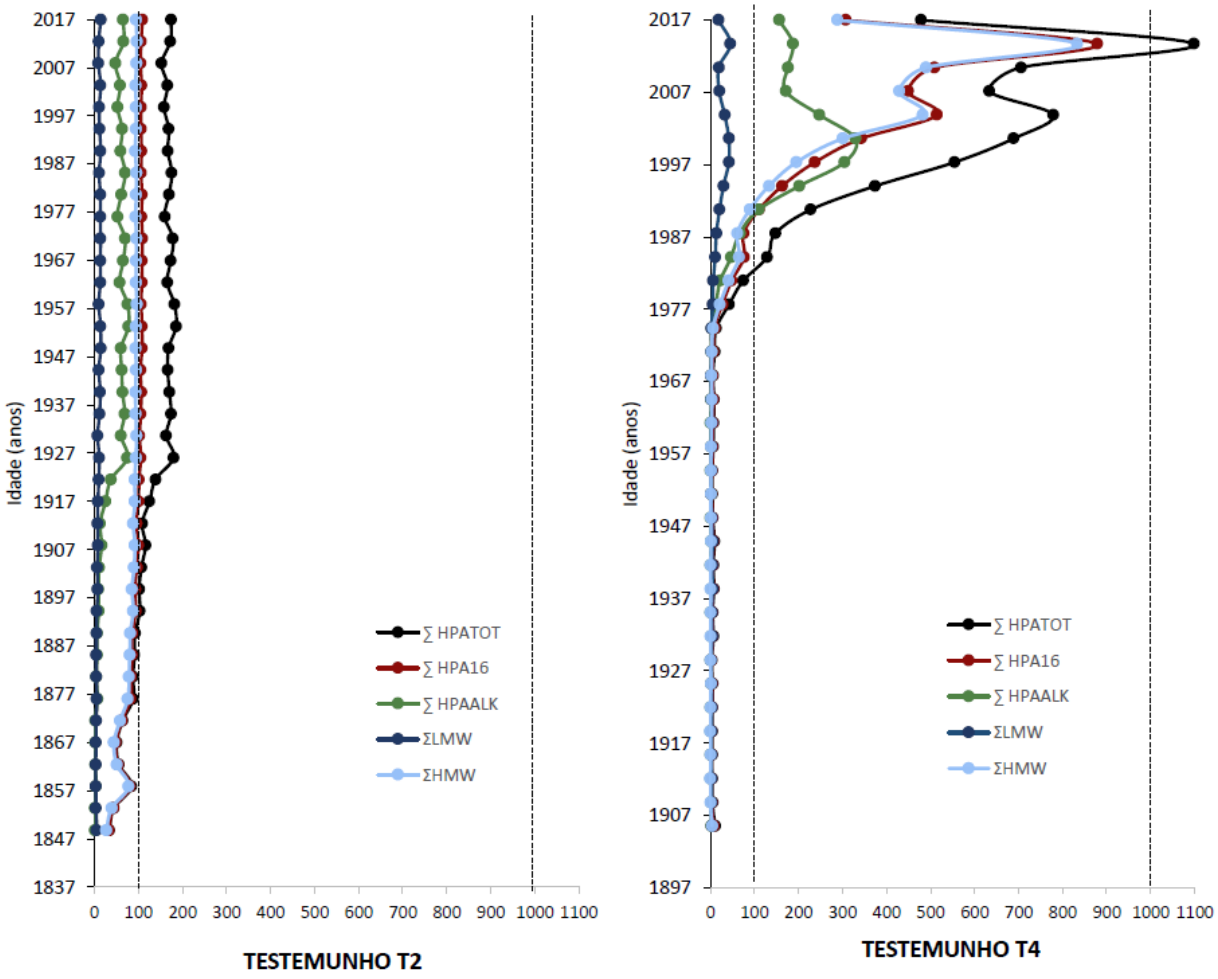
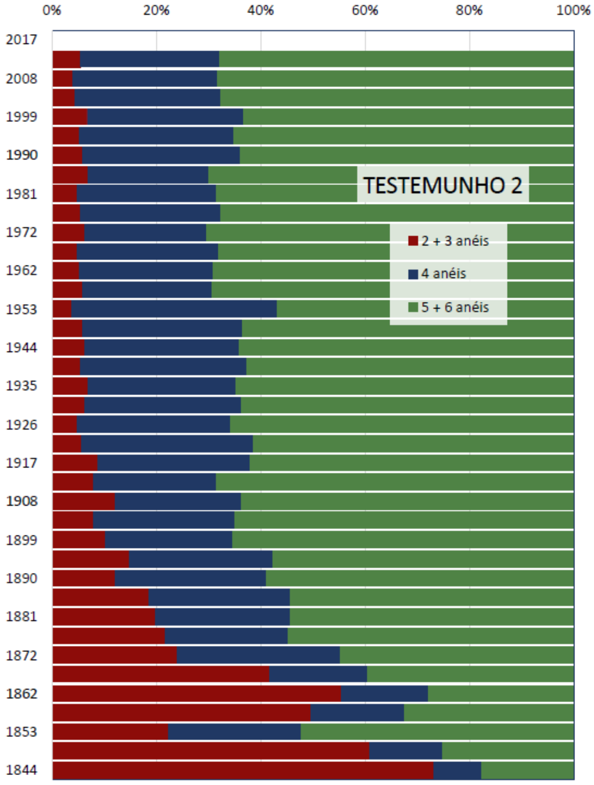


Figura 2. Variações das concentrações de HPA_{TOT}, HPA_{16}, LMW, HMW e HPA_{Alk} dos testemunhos T2 e T4. HPA_{16} se refere aos 16 HPAs prioritários da Agência de Proteção Ambiental dos EUA. As linhas tracejadas indicam os níveis de referência onde HPA_{TOT} < 100 ng g^{-1} indicam uma contaminação baixa, valores entre 100 a 1000 ng g^{-1} indicam um nível moderado e HPA_{TOT} entre 1000 a 5000 ng g^{-1} indica um nível alto de contaminação (Baumard et al.,1998).

Com relação à composição dos HPAs, compostos com cinco e seis anéis responderam por 0 a 79,1% do HPA_{TOT}, já a frequência de ocorrência dos compostos com quatro anéis variou de 0 a 31,2%. Por sua vez, os compostos de dois + três anéis dominaram o testemunho T4, respondendo por 3,78 a 100% dos compostos. NaF esteve presente em todas as amostras e foi responsável por 0,36 a 95,8% do HPA_{Tot}. Por outro lado, o acenafteno foi o HPA menos comum, contribuindo com 0 a 0,200% do HPA_{Tot}. Para os HPA_{Alk} foram registrados a seguinte ordem de abundância: Fen/Ant > BaA/Cri > Flu/Pir > Fl > NaF.



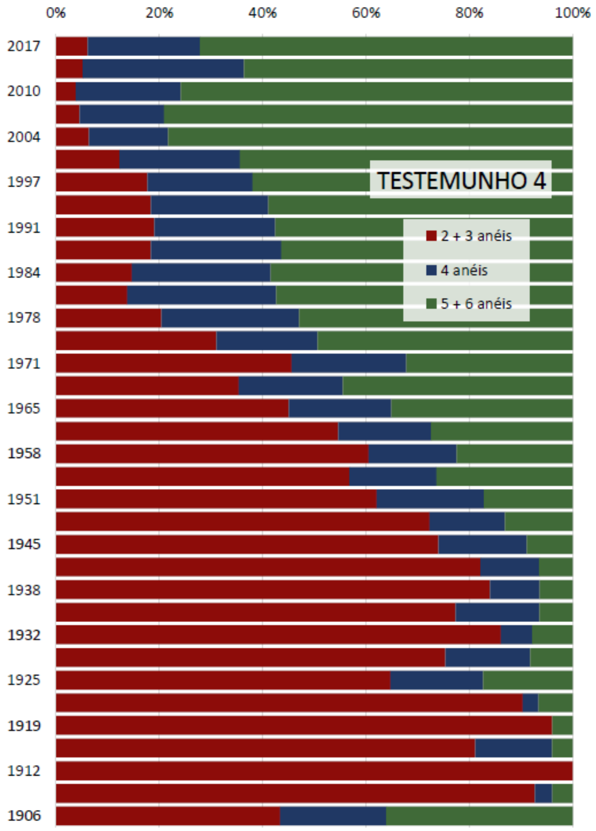


Figura 3. Padrão de distribuição de HPAs com 2 a 6 anéis em sedimentos dos testemunhos T2 e T4 coletados na Baía de Todos os Santos, Brasil.

4.3. Concentração e perfil temporal do BC e COT

As concentrações de BC, COT, $\delta^{13}C_{-BC}$ e $\delta^{13}C_{-OC}$ nos testemunhos coletados na BTS são apresentados no Material Suplementar (Tabela S1 e S2). A Figura 4 mostra os perfis sedimentares das concentrações do BC e COT. As concentrações de BC foram < 0,5 mg g^{-1} em todos os estratos dos testemunhos, variando de 0,08 a 0,44 mg g^{-1} em T2 e 0,14 a 0,43 mg g^{-1} em T4.

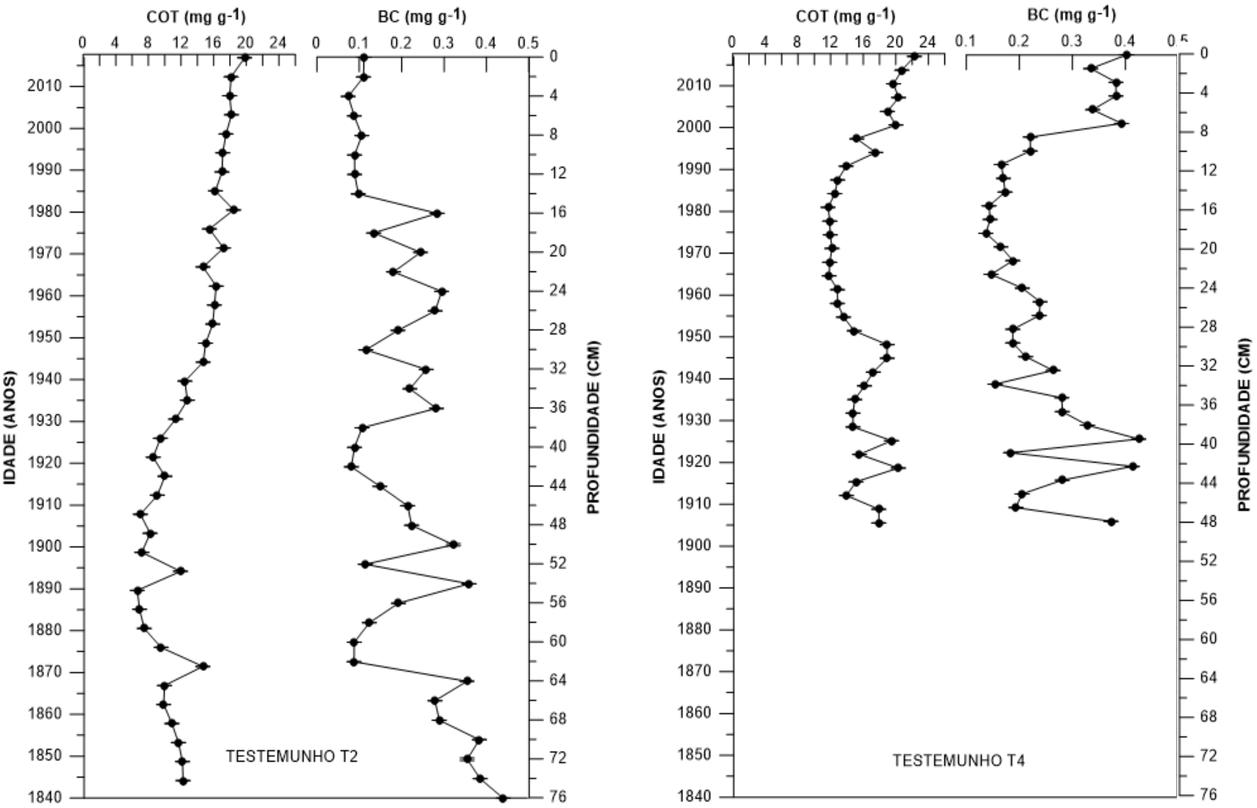


Figura 4. Concentrações de carbono negro (BC) e carbono orgânico total (COT) no sedimento dos testemunhos T2 e T4, coletados na Baía de Todos os Santos, Brasil.

No testemunho T2, o BC diminuiu da base para o topo, estabilizando em 0,1 mg g^{-1}a partir da década de 1980. Em T4, o BC foi mais variável antes de 1950, com um padrão mais constante de 1950 até o final da década de 1990. A partir dos anos 2000, houve um aumento significativo, quando as concentrações passaram de 0,220 para 0,400 mg g^{-1}.

Os resultados de COT foram descritos por Silva et al. (2024) (Material Suplementar – Tabela S1 e S2). As concentrações de COT variaram de 6,60 a 19,8 mg g^{-1} em T2, aumentando a partir da década de 1920. Já em T4, variaram de 11,7 a 22,3 mg g^{-1}, com as concentrações mais elevadas entre 1990 e 2017 (14 a 22,3 mg g^{-1}).

O BC representou de 0,420 a 3,95% do COT em T2 e de 0,95 a 2,22% em T4.

4.4 . Isótopos de COT e BC

A Figura 5 mostra os perfis sedimentares das concentrações do $\delta^{13}C_{OC}$ e $\delta^{13}C_{BC}$ em T2 e T4. Os *valores de* $\delta^{13}C_{OC}$ variaram de -21,8 a -15,3‰ em T2 e de -22,53 a -16,77 no testemunho T4. Entre 1935 e 1950, houve uma tendência crescente nos valores de $\delta^{13}C_{OC}$ de -22 a -16‰ em T4. Já os *valores de* $\delta^{13}C_{BC}$ variaram de −23,6 a −9,83‰ em T2 e de -23,7 a -10,2‰ em T4.

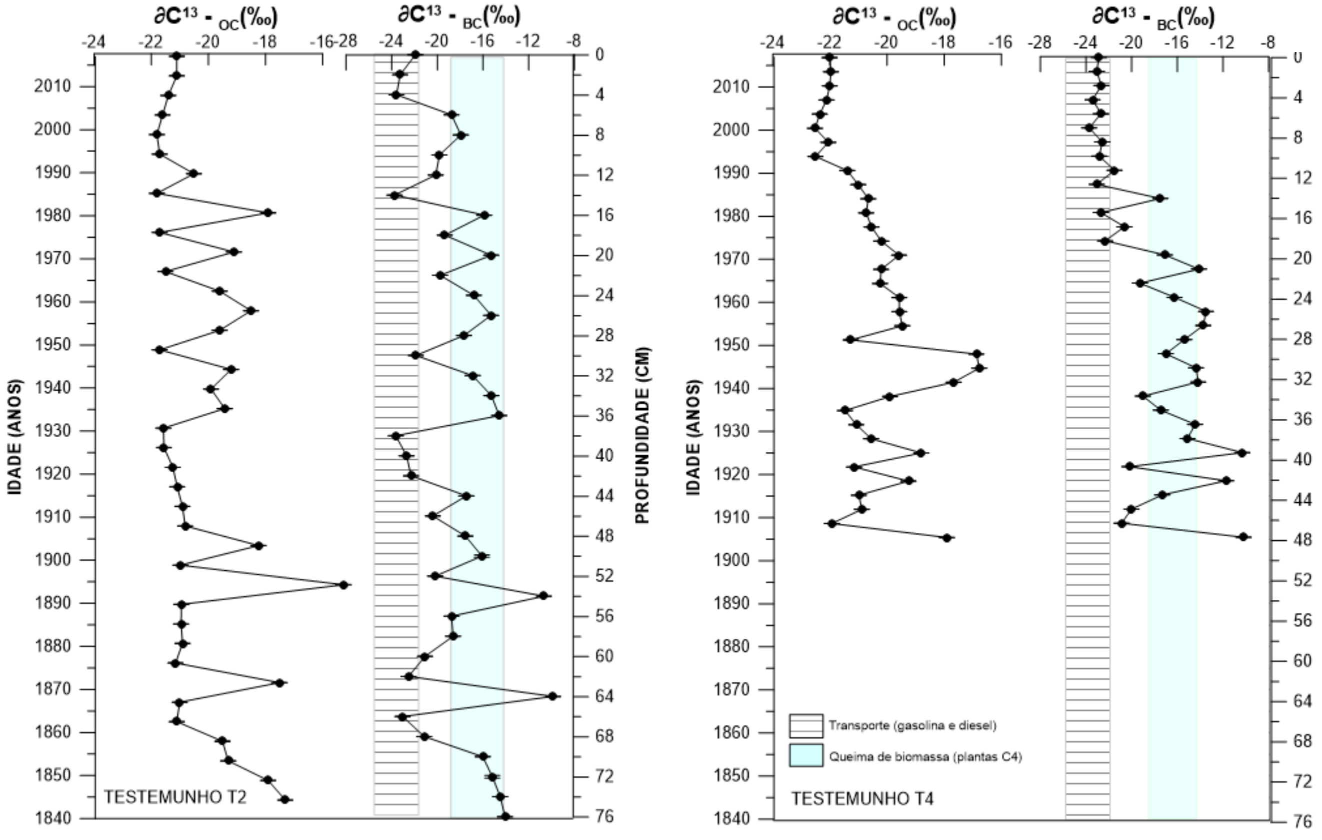


Figura 5. Valores de $\delta^{13}C_{CO}$ e $\delta^{13}C_{BC}$ no sedimento dos testemunhos T2 e T4, coletados na Baía de Todos os Santos, Brasil.

4.5 . Correlação entre TOC, BC e HPAs

A matriz de correlação de Spearman (Tabela 1) mostra as associações entre COT e BC com as demais variáveis. Em T2, o COT foi significativamente correlacionado ($r_s \geq 0{,}50$) com todos os HPAs com quatro, cinco e seis anéis de origem pirolítica (Flu, Pir, BaA, Cri, BbF, BkF, BahP, DahA, IP, BghiP), além do ∑HPA e $\sum HPA_{16}$. Já o BC mostrou correlação elevada apenas com $\delta^{13}C_{OC}$. Compostos alquilados revelaram correlação significativa entre COT e HPA_{ALK}, C3 NaF, C1–Fl, C3-Flu+Pir, C1-BaA+Cri, C2-BaA+Cri e C3-BaA+Cri.

Em T4, houve alta correlação entre COT e BC e entre $\delta^{13}C_{OC}$ e $\delta^{13}C_{BC}$. O COT foi significativamente correlacionado ao NaF, Fl e Ant além dos HPAs com cinco e seis anéis, ∑HPA e $\sum HPA_{16}$. Entre os alquilados, correlações significativas foram encontradas entre COT e C1-Fl, C1-BaA+Cri, C2-BaA+Cri e C3-BaA+Cri. Já o BC foi significativamente relacionado aos compostos de origem pirolítica BkF, IP e BghiP. Dentre os HPA_{ALK}, apenas o C2-BaA+Cri revelou uma importante correlação com o BC.

Tabela 1. Matriz de correlação de *Spearman* com os dados de COT e BC para os componentes individuais de HPA, $\delta^{13}C_{OC}$, $\delta^{13}C_{BC}$, $\sum HPA_{TOT}$, $\sum HPA_{16}$, $\sum HPA_{ALK}$ obtidos no sedimento dos testemunhos T2 e T4, coletados na Baía de Todos os Santos, Brasil. Valores em negrito indicam correlações significativas para $p< 0.05$.

	TESTEMUNHO T2		**TESTEMUNHO T4**	
	Correlação com COT	Correlação para BC	Correlação com COT	Correlação para BC
COT	1.00	-0.12	1.00	**0.78**
$\delta^{13}C$ - OC	0.02	**0.82**	-0.07	-0.13
BC	-0.12	1.00	**0.78**	1.00
$\delta^{13}C$ - BC	0.49	-0.41	-0.08	0.18
NaF	0.01	-0.07	**0.56**	0.47
Ac	0.39	-0.32	0.23	-0.12
Acl	0.40	-0.16	0.34	0.30
Fl	0.20	-0.28	**0.52**	0.44
Fen	**0.57**	-0.34	0.47	0.36
Ant	0.43	-0.39	**0.50**	0.39
Flu	**0.57**	-0.37	0.30	0.22
Pir	**0.55**	-0.37	0.48	0.37
BaA	**0.53**	-0.42	**0.50**	0.39
Cri	**0.61**	-0.45	**0.50**	0.39
BbF	**0.60**	-0.35	**0.54**	0.45
BkF	**0.64**	-0.45	**0.56**	**0.50**
BahP	**0.54**	-0.38	**0.57**	**0.50**
DahA	**0.51**	-0.25	**0.52**	0.43
IP	**0.61**	-0.38	**0.58**	**0.51**
Bgp	**0.64**	-0.37	**0.55**	**0.50**
$\sum HPA_{TOT}$	0.37	-0.40	**0.57**	0.46
$\sum HPA_{16}$	0.12	-0.39	**0.56**	0.47
HPA_{ALK}	**0.54**	-0.43	0.46	0.39
C2 Naf	0.49	-0.41	**0.54**	0.46
C3 Naf	**0.56**	-0.48	**0.54**	0.47
C4 Naf	0.42	-0.41	**0.50**	0.41
C1 - Fl	**0.54**	-0.41	**0.50**	0.40
C2 - Fl	0.22	-0.20	**0.50**	0.42
C3 - Fl	0.18	-0.38	0.42	0.35
C1 Fen + Ant	0.44	-0.40	0.34	0.27
C2 Fen + Ant	0.46	-0.40	0.35	0.28
C3 Fen + Ant	0.49	-0.40	0.39	0.33
C4 Fen + Ant	0.36	-0.22	**0.50**	0.42
C1- Flu+Pir	**0.50**	-0.38	**0.53**	0.44
C2- Flu+Pir	0.48	-0.37	0.48	0.40
C3- Flu+Pir	**0.51**	-0.37	0.44	0.37
C1-BaA+Cri	**0.55**	-0.44	**0.54**	0.47
C2-BaA+Cri	**0.64**	-0.45	**0.58**	**0.50**
C3-BaA+Cri	**0.59**	-0.36	**0.56**	0.48

5. Discussão

5.1 Fontes de contaminação para a BTS

Para formular estratégias adequadas de controle de poluentes, é necessário determinar as fontes desses compostos. A razão entre os isótopos estáveis do carbono ($\delta^{13}C$) tem sido uma ferramenta bastante utilizada não apenas para identificar fontes de COT, mas também para identificar vias de produção do BC.

Em um estudo anterior nos mesmos testemunhos, Silva et al. (2024) relataram de uma dominância do carbono orgânico autóctone (fitoplâncton, zooplâncton e gramíneas). No testemunho T2, a contribuição da MO terrestre foi de 33,38 ± 8,39%. Destaca-se o período entre as décadas de 1930 e 1980, quando houve maior contribuição da MO marinha por uma possível expansão de macroalgas moles e calcárias hoje presentes no local. Já no testemunho T4, houve um aumento nos teores de MO ao longo do tempo, com um aporte crescente de contribuições alóctones a partir da década de 1950, impulsionada por mudanças no uso da terra.

Alguns estudos tiveram sucesso em utilizar valores $\delta^{13}C_{BC}$ para discriminar essas fontes. Os valores de $\delta^{13}C_{BC}$ na fuligem de carvão variam de -23‰ a -26‰ (Glaser et al., 2005; Widory, 2006), no entando não são fontes significativas para área estudada. Já partículas geradas a partir queima de combustíveis fósseis estão na faixa de -27‰ a -30‰ para óleo combustível (Widory, 2006) e -22‰ a -26‰ para disel e gasolina (Glaser et al., 2005; López-Veneroni, 2009). Foram relatados valores de $\delta^{13}C$ a partir de rochas intemperizadas no intervalo de -19,4‰ a -21,3‰ (Dickens et al., 2004). Saiz et al (2015) a partir de queimadas experimentais em savanas do norte da Austrália determinou um $\delta^{13}C_{BC}$ variando de −29‰ a −33‰ em uma biomassa lenhosa (tipo C3) e variando de −15‰ a −19‰ para gramíneas (tipo C4). Mas é importante notar que o $\delta^{13}C_{BC}$ produzido durante a queima depende do $\delta^{13}C$ da biomassa original (Gao et al., 2018) e que não existem valores estabelecidos para a flora da região.

Os valores de $\delta^{13}C_{BC}$ variaram de −23,6 a −9,83‰ (média de -18,4 ± 3,46‰) no testemunho T2. Em geral, esses valores estão associados a queima de biomassa (gramíneas – C4). Para o testemunho T4, o $\delta^{13}C_{BC}$ variou entre -23,7 a -10,2‰ (média de -18,4 ± 4,11‰) (Fig. 5). Da base do testemunho até meados da década de 1980 esses valores sugerem queima de biomassa (C4). Desse período até o topo do testemunho a depleção de ^{13}C implica que as contribuições de BC para os sedimentos se originam principalmente de emissões veiculares (queima de gasolina, diesel).

A composição dos diferentes HPAs também desempenha um papel importante na atribuição da fonte. Vários estudos aplicaram razões diagnósticas entre isômeros de HPAs para identificar possíveis fontes de HPAs para o meio ambiente (Cao et al., 2020, Vaezzadeh et al., 2021, Li et al., 2023). Neste estudo, foram aplicadas as seguintes razões: Ant/(Ant+Fen), Flu/(Flu+Pir), IP/(IP+BghiP) e BaA/(BaA+Cri). Os resultados estão resumidos no material suplementar (Tabela S3).

Todas as relações indicaram origem pirolítica dos HPAs para os dois testemunhos em todos os estratos sedimentares. A razão Ant/(Ant+Fen) foi superior a 0,1 em todas as amostras indicando a presença de uma fonte pirolítica, porém não discrimina o tipo de material queimado.

A relação Flu/(Flu + Pir) indicou uma origem pirolítica dos HPAs como derivados da queima de biomassa (> 0,5) no testemunho T2. Já no testemunho T4 também indicaram fonte pirolítica proveniente da combustão de biomassa, com exceção de alguns períodos com presença de HPAs associados à queima de petróleo (> 0,4 e < 0,5).

Os valores da relação IP/(IP + BghiP) variaram de 0,47 a 0,61 e de 0,33 a 0,72 nos testemunhos T2 e T4, respectivamente. Para esta relação, valores superiores a 0,5 indicam a queima de carvão e biomassa como fontes de HPAs e foram predominantes no testemunho T2. Já índices inferiores a 0,5 sugeriram a queima de petróleo e combustíveis como fontes de HPAs (Fig. 6a) e ocorreram com maior frequência no testemunho T2 durante o início dos anos 2000, enquanto no testemunho T4 a frequência aumentou no final da década de 1970.

Já a relação BaA/(BaA + Cri) indicou a presença fontes pirolíticas para os testemunhos T2 (0,38 a 0,53) e T4 (0,37 a 0,54) sem discriminar o tipo de combustão (> 0,35).

Os produtos pirolíticos aparecem mais amplamente disseminados nos sedimentos da BTS, possivelmente em decorrência do caráter difuso de sua principal via de introdução, a deposição atmosférica. A deposição de partículas secas é um mecanismo muito importante nos fluxos ar-mar na BTS e as emissões de contaminantes por veículos e/ou indústrias são apontadas como uma das principais fontes de partículas finas em processos de transporte de longa distância (Mkoma et al., 2014). Por outro lado, compostos de origem petrogênica, sedimentam preferencialmente nas proximidades de suas fontes.

Ressaltamos que as concentrações de HMW nos testemunhos foram sempre superiores ao LMW. Nota-se, entretanto, que no testemunho T4 houve um aumento da proporção de compostos HMW em direção ao topo (Fig. 3). Uma vez que os LMW estão principalmente associados a fontes petrogênicas e os HMW são predominantemente pirolíticos (Yunker et al., 2002), esses dados sugerem a predominância de fontes pirolíticas para os HPAs no testemunho T2 e, diferente das razões diagnósticas, aponta para uma mudança de fontes no testemunho T4 (de petrogênica para pirolítica).

A presença de grande quantidade compostos alquilados é representativa de introdução recente de óleo, enquanto que compostos parentais podem inferir processos de combustão e/ou introdução mais antiga. O testemunho T2 apresentou um padrão com baixa variabilidade para HPA_{ALK} e uma concentração média de 39,24 ng g^{-1}. A razão Fenantreno + Antraceno/ Fenantreno + Antraceno + C1Fe (Yunker et al., 2002) indicou a origem pirolítica dos HPAs (> 0,5) em todo perfil, com exceção de 2 amostras.

Já no testemunho T4, da base até a década de 1970 as concentrações são baixas (< 4 ng g^{-1}) e uniformes. Após esse período observa-se um aumento significativo das concentrações de HPA_{ALK} que persiste até o topo, com o máximo ocorrendo na década de 2000 (329,23 ng g^{-1}) e que chega a representar quase 50% dos HPAs. Esse intervalo é acompanhado do aumento de HPA_{TOT}, $HPA_{16,}$ LMW e HMW. A razão (Fen + Ant)/(Fen + Ant + C1Fe) da base até a década de 1970 indica a presença de fonte pirolítica, após esse período os valores < 0,5 podem indicar características tanto de combustão quanto de petróleo.

Outras evidências detalhadas por Silva et al., 2024 mostram a presença de compostos de origem petrogênica no testemunho T4. A alta concentração de UCM (valor máximo = 349,94 ng g^{-1}) e a relação UCM/n-alcanos > 4 são inequivocamente característicos de material petrogênico altamente degradado. Essas condições indicam um aporte pretérito significativo de hidrocarbonetos, possivelmente associado à indústria de petróleo instalada na região.

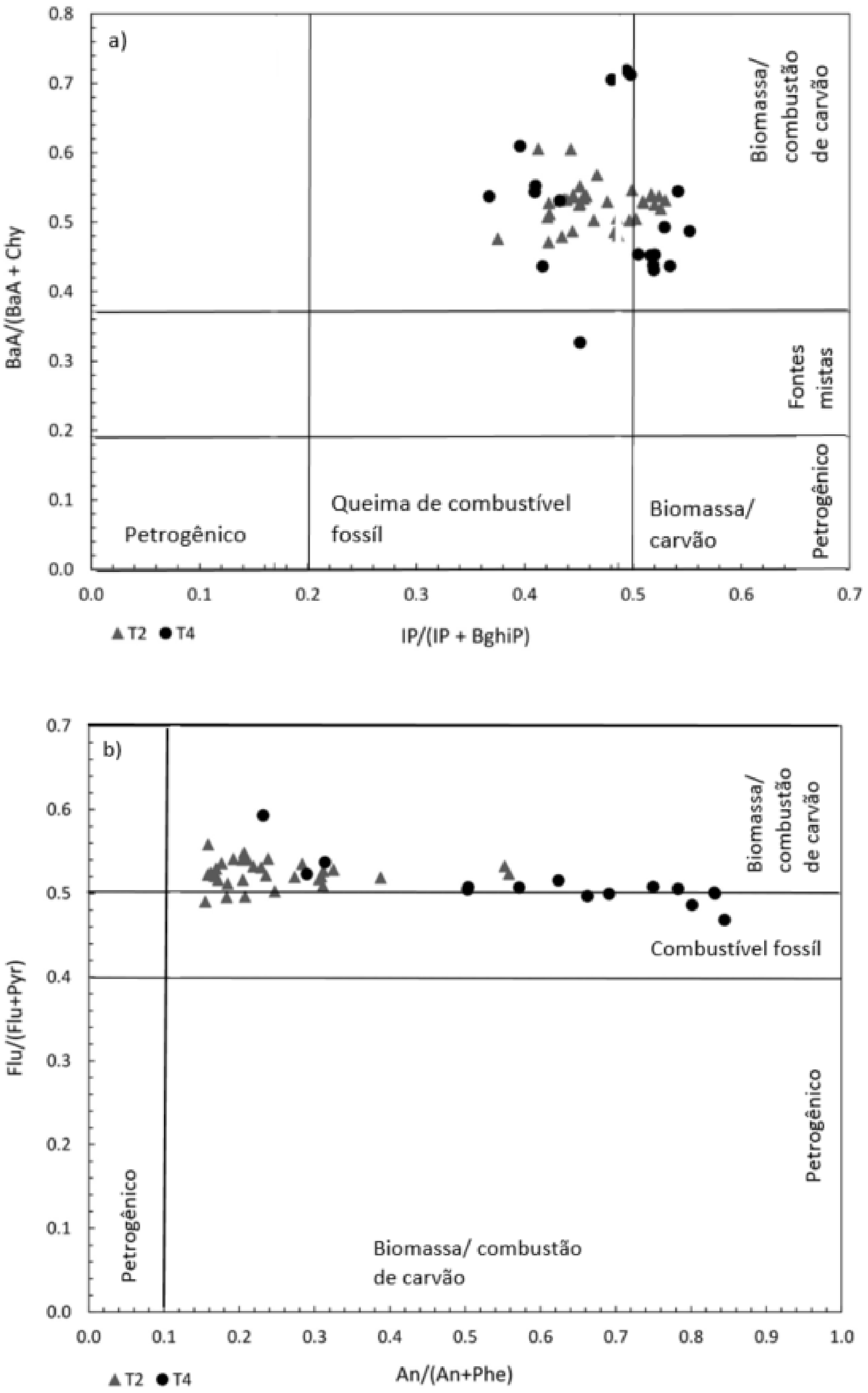


Figura 6. a) Diagrama cruzado entre as razões diagnósticas BaA/(BaA + Cri) versus IP/(IP + BghiP) e b) Diagrama cruzado entre as razões Ant/(Ant +Fen) versus Flu/(Flu + Pir). Legenda: BaA: benzo[a]antraceno; Cri: criseno; IP: indeno[1,2,3-cd]pireno; BghiP: benzo[ghi]perileno; Flu: fluoranteno; Pir: pireno; Ant: antraceno; Fen: fenantreno.

5.2. BC e HPAs em baías costeiras

O BC emitido a partir de processos de combustão pode ser transportado através descarga fluvial ou deposição atmosférica úmida ou seca até alcançar os sistemas costeiros (Mitra et al., 2014). Contudo, seu alcance é variável e depende essencialmente do tamanho da partícula. Partículas de carvão mineral e vegetal (maiores que 2 µm), costumam se acumular no solo, refletindo apenas a história de queima de ecossistemas locais. Por outro lado, partículas como a fuligem liberadas a partir de emissões veiculares, como descritas nesse estudo, costumam ser menores que 2 µm e assim, podem ser transportadas por longas distâncias (Han et al., 2009).

A circulação atmosférica da região é dominada pelo anticiclone móvel do Atlântico Sul, com ventos alíseos de sudeste e leste de grande penetração no continente. De acordo com Tavares (1997), o padrão de circulação local favorece o transporte dos poluentes produzidos pelo Complexo Petroquímico de Camaçari (COPEC) e Centro Industrial de Aratu (CIA) para a BTS (Figura 1), tornando a baía uma grande receptora de compostos químicos atmosféricos resultantes das atividades antropogênicas. Estudos já reportaram a presença dos HPA_{16} no material particulado depositado na Ilha de Maré, localizado a leste da área de estudo. O fluxo de deposição de 2,49 µg m^{-2} dia^{-1} foi associado a queima de diesel em navios e barcos menores, fuligem doméstica, combustão de madeira para produção de energia (da Rocha et al., 2009).

Neste estudo, observamos níveis mais altos de BC no testemunho T4, situado próximo a costa, provavelmente transportado por escoamento urbano e dos rios. No entanto, a presença do BC ainda que em baixas concentrações ao longo do testemunho T2, sugerem que a deposição atmosférica também seja uma rota de disseminação do BC para a BTS.

Não há outros estudos do BC nos sedimentos da BTS. Os dados também são escassos no Brasil e o sistema costeiro estudado de maior semelhaça é a baía de Guanabara (BG), no estado do Rio de Janeiro. De maneira geral, as concentrações encontradas no topo dos testemunhos coletados na BTS (0,11 a 0,44 mg g^{-1}) ainda são significativamente inferiores quando comparados com concentrações obtidas nos sedimentos superficiais da baía de Guanabara (0,3 a 3,1 mg g^{-1}) (Luz et al., 2008). O mesmo acontece em comparação com três testemunhos coletados em regiões de manguezal da BG, onde as concentrações variaram de 0,3 a 4,7 mg g^{-1} (Luz et al., 2010). É importante destacar que a BG é uma uma baía cerca de quatro vezes menor que a BTS e mais severamente antropizada.

Os teores encontrados no topo dos testemunhos da BTS são comparáveis com amostras superficiais de outras regiões marinhas costeiras menos impactadas como o Golfo de Cádiz (0,1 – 1,1 mg g^{-1}) (Sánchez-García et al., 2013), a Malásia (0,2 – 0,36 mg g^{-1}) (Vaezzadeh et al., 2021) e a baía de Daya, na China, (0,5 – 1,8 mg g^{-1}) utilizada para maricultura (Dan et al., 2022). No entanto, ainda são significativamente baixos quando comparados com regiões densamente urbanizadas e industrializadas como Beijing (0,37–12,7mg g^{-1}) (Liu et al., 2011) e aos sedimentos na área portuária de Boston e Nova York (3,40 – 6,00 mg g^{-1}) (Lohmann et al., 2005).

É crucial, entretanto, considerar que mesmo concentrações relativamente baixas de BC são relevantes do ponto de vista ambiental e o aumento significativo das concentrações de BC registrado em T4 a partir dos anos 2000, associado ao aumento dos processos de combustão, merece atenção. A alta capacidade de sorção do BC e seu caráter recalcitrante e resistente à degradação favorece o acúmulo no ambiente (Lian e Xing, 2017). Por outro lado, o BC compreendido no COT de solos e sedimentos pode reduzir a assimilação de poluentes pela biota em até duas ordens de magnitude. Isso justifica a necessidade de um estudo detalhado dessa fração carbonácea, a fim de evitar avaliações errôneas dos riscos ambientais (Koelmans et al., 2006).

Com relação aos HPAs, embora comparações quantitativas sejam difíceis devido à variação no número e tipo de HPAs individuais, estudos anteriores realizados em sedimentos superficiais na BTS mostram concentrações mais elevadas próximas às margens da baía, com destaque para a região próximo a RM (Silva et al., 2014; de

Almeida et al., 2018). Já registros históricos de HPA na BTS também são escassos. Wagener et al. (2010) relataram concentrações elevadas próximo a RM, com o HPA_{TOT} (24 HPAs parentais e alquilados) variando de 112 - 3765 ng g^{-1} (peso seco). Também foi verificado que os compostos alquilados constituiam a maior fração da concentração total concorrendo com a presença de resíduos petrogênicos nas amostras e que as séries completas de naftaleno e fenantreno estiveram presentes em todos os segmentos depositados após a década de 1950.

5.3. Efeitos do BC e dos HPAs sobre o COT e a matéria orgânica

As relações entre BC e COT podem ser explicadas pela natureza da MO depositada na BTS. Silva et al., 2024 mostraram que o testemunho T2 registrou ao longo de todo perfil uma dominância da MO autóctone, derivada do fitoplâncton marinho, zooplâncton e gramíneas marinhas. Nesse sentido, é importante notar que a entrada reduzida da MO alóctone diminui automaticamente a possibilidade de contribuição do BC, de origem exclusivamente terrestre (Bond et al., 2013). Esta observação é consistente com a fraca correlação entre o COT e o BC no testemunho T2. Um padrão semelhante foi encontrado por Dan et al. (2022) na Baía de Daya (China), uma baía com grandes áreas destinadas à maricultura. Destacamos também que as correlações indicam que os HPAs, em maior abundância pirolíticos, foram regulados pelo COT no testemunho T2.

Já no testemunho T4, foi registrado o aumento gradativo e consistente da MO terrestre a partir da década de 1950 e de maneira mais acelerada a partir da década de 1980 (Silva et al., 2024). Esse processo também coincide com uma mudança na composição dos HPAs, a partir de década de 1950, com o aumento da proporção relativa de compostos de alto peso molecular, tais como pireno, fluoranteno, indeno[1,2,3- cd]pireno, benzo[b]fluoranteno, benzo[k]fluoranteno e benzo[ghi]perileno.

Esses compostos podem ter sido gradualmente introduzidos no ambiente pelo processo de refino na RM, contudo, em parte podem ser associados a deposição atmosférica de partículas de fuligem resultante de emissões veiculares, principalmente nas últimas décadas. Essa suposição é sustentada pelo aumento expressivo do aporte do BC, associado a essas fontes, a partir da década de 1990.

5.4. Mudanças históricas na contribuição da MO na BTS

Até meados do século XX, a região ao redor da BTS era predominantemente rural, com foco em atividades primárias como pesca artesanal e cultivo de culturas como cana-de-açúcar, café, fumo, cacau e algodão. Nessa época, a prática comum de "corte e queima" era utilizada para colheita ou limpeza dos campos, o que pode explicar as concentrações mais elevadas de BC associadas à combustão de biomassa no testemunho T2 (o período não foi abrangido pelo testemunho T4) (Figura 4). Por outro lado, poucas dezenas de ng/g de HPA_{TOT} e dos HPA_{ALK} foram registrados (Figura 2). Em conjunto com a ausência de UCM e de pristano e fitano reportadas por Silva et al., 2024, há um forte indício de que não haviam aportes significativos de hidrocarbonetos de origem petrogênica.

Uma transformação significativa na região foi impulsionada pela descoberta, exploração, refino e transporte de petróleo na BTS. A Figura 7 resume os principais eventos relacionados à indústria petrolífera na área. A descoberta e o início da exploração de petróleo no Brasil ocorreram na BTS entre 1939 e 1941, e até a década de 1980, a região foi a única produtora de petróleo do país. Em 1950, a construção da Refinaria Mataripe (RM) marcou o primeiro ciclo de expansão industrial na BTS.

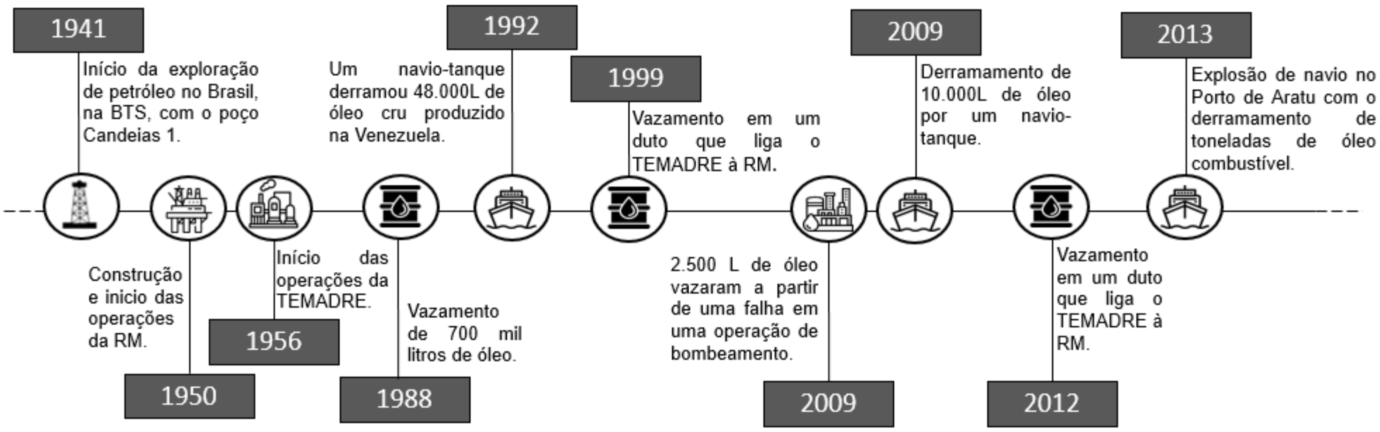


Figura 7. Linha do tempo dos principais eventos relacionados à indústria petrolífera na Baía de Todos os Santos, Bahia - Brasil, incluindo derramamentos de petróleo e derivados.

Muitas fazendas foram desapropriadas para dar lugar à infraestrutura complementar ao complexo petrolífero. Além disso, foram implantadas centenas de unidades industriais, infraestrutura de transporte, abastecimento de água, energia elétrica e terminais marítimos, como o TEMADRE em 1956, juntamente com rotas de navegação conectando os terminais e as empresas produtoras (Brito, 2008). A construção de estradas, por sua vez, impulsionou o aumento da ocupação humana nas proximidades da BTS. Todas essas mudanças ocorreram ao longo de poucas décadas.

O testemunho T4 foi mais impactado por essas atividades antrópicas. Silva et al., 2024 verificaram um aumento gradual da MO terrestre a partir de 1950, associado a mudanças do uso da terra. Contudo, essas alterações não foram acompanhadas de mudanças imediatas nos hidrocarbonetos. Na verdade, antes da década de 1970 as concentrações de HPAs ($HPA_{TOT,}$ HPA_{ALK}) permaneceram relativamente baixas (< 50 ng g^{-1}), não mostrando indícios da presença de compostos de petróleo no sedimento.

O aumento nas concentrações de $HPA_{TOT,}$ HPA_{ALK} no testemunho T4 no final da década de 1970 podem estar relacionados as ampliações da capacidade de produção da RM (CRA, 2004) e a alguns eventos de contaminação ao longo do tempo de operação da refinaria (Figura 7). Silva et al. (2024) analisando essas amostras verificaram um aumento substancial dos hidrocarbonetos alifáticos nesse período, alcançando um nível de contaminação considerado alto (> 100 µg g^{-1}), bem como a detecção da UCM a partir do início da década de 1980. Para a mesma região, o CRA (2004) e Wagner et al., 2016 também observaram valores elevados de HPA_{TOT} a partir da década de 1970 que foram associados a uma fonte petrogênica.

No entanto, observa-se uma mudança na composição dos HPAs ao longo do tempo (Figura 3), com a fonte petrogênica sendo gradualmente substituída pela combustão. Os dados de BC também indicam uma mudança nas fontes de combustão após a década de 1980, com a indústria e o transporte emergindo como as principais fontes de BC, ao invés da queima de biomassa. As concentrações de BC aumentaram a partir da década de 1990 até o topo do testemunho, refletindo a crescente influência humana e o acúmulo de fuligem produzida na região metropolitana ao redor da área de estudo. De fato, em 2017, as 13 cidades ao redor da BTS possuíam uma frota de aproximadamente 993 mil veículos (DENATRAN, 2017). Isso sugere que o BC e os HPAs pirolíticos provenientes dessas emissões podem representar uma importante fonte de contaminantes para a baía por meio do transporte atmosférico.

O perfil de concentração de HPA_{TOT} revela uma redução dos valores que pode ser explicada em parte pela implementação de políticas ambientais na década de 1990, como o Programa Bahia Azul (Bahia, 2005), pelo uso de um sistema de separação de água e óleo gerados pela usina de asfalto da RM e, em parte, pela redução da frequência de eventos de contaminação de maior porte (Fig. 7). No entanto, em 2014, o perfil de concentração de HPA_{TOT} no testemunho T4 atingiu seu valor máximo (1066,43 ng g^{-1}), seguido de um declínio, indicando uma possível contaminação aguda associada ao derramamento de 10.000 litros de óleo por um navio-tanque na região (CRA, 2004).

O testemunho T2 revelou-se mais bem preservado. Distante de atividades industriais e da influência de aportes dos rios, as entradas de HPAs são afetadas possivelmente apenas pelo transporte atmosférico. Em geral, as contribuições de HPA ao longo do último século parecem ter permanecido relativamente constantes. Ao longo de todo o perfil as contribuições de HPA_{TOT} e dos homólogos alquilados são baixas. Silva et al., 2024 não encontraram assinaturas petrogênicas ao longo do testemunho T2 (ausência de UCM, pristano e fitano).

Com relação ao BC, os valores de $\delta^{13}C_{BC}$ oscilaram, mas permaneceram dentro da faixa associada à combustão de biomassa. Isso pode refletir a natureza transitória da prática de corte e queima para atividades agrícolas, além do caráter dinâmico do transporte eólico. No final da década de 1990, houve uma diminuição nas concentrações de BC no testemunho T2 que reflete a redução das práticas de queimadas agrícolas. A importância das fontes pirolíticas é confirmada pelos índices diagnósticos de HPAs.

6. CONCLUSÕES

Este estudo mostra que o BC e HPAs na BTS são eficientemente dispersos pelo transporte eólico. Em tempos remotos, a combustão de biomassa contribuiu significativamente para os sedimentos, enquanto, desde a década de 1980, as emissões veiculares predominaram próximo à costa. A área urbanizada ao redor da BTS influencia a poluição dos sedimentos. O aumento recente de BC próximo à costa destaca a necessidade de controlar emissões industriais e veiculares. A presença de BC por mais de um século nos testemunhos sugere que ele pode se acumular em sedimentos marinhos por muito tempo.

As atividades de produção, refino e transporte de petróleo na BTS impactaram diretamente a qualidade dos sedimentos desde a década de 1970. Foi observada poluição moderada a partir dos anos 1980, com um pico elevado em torno de 2010. As fontes pirolíticas predominam nos HPAs, enquanto os índices diagnósticos tradicionais não discriminam eficientemente o aporte petrogênico histórico.

Os dados aqui apresentados fornecem uma quantificação valiosa de HPAs e BC, essencial para avaliar impactos futuros e definir metas de remediação em casos de poluição ambiental. Estudos adicionais sobre deposição atmosférica desses contaminantes e monitoramento contínuo a longo prazo são necessários para garantir que os níveis não excedam os atuais.

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Material Suplementar

Tabela S1. Concentrações total dos HPAs (HPAs$_{TOT}$), os 16 HPAs prioritários da Agência de Proteção Ambiental dos EUA (HPA$_{16}$), soma de n-alcanos de baixo peso molecular (LMW), soma de n-alcanos de alto peso molecular (HMW), Hidrocarbonetos alquilados (HPA$_{ALK}$), carbono negro (BC, do inglês black carbono), isótopo do carbono negro ($\delta^{13}C_{BC}$), carbono orgânico total (COT) e o isótopo do carbono (δ^{13}Co$_{C}$) no testemunho T2, coletado na Baía de Todos os Santos, Brasil.

ANO	PROFUNDIDADE	**HPA$_{TOT}$**	**HPA$_{16}$**	**LMW**	**HMW**	**HPA$_{ALK}$**	**COT**	**δC^{13}_{CO}**	**BC**	**δC^{13}_{BC}**
2017	0						1.98	0.08	0.11	-21.89
2012	2	173.91	108.88	14.24	251.47	65.03	1.81	0.17	0.11	-23.22
2008	4	172.52	106.12	10.04	246.21	66.40	1.79	0.09	0.07	-23.54
2003	6	152.63	104.74	9.18	197.57	47.89	1.81	0.10	0.09	-18.72
1999	8	165.93	107.24	14.02	192.86	58.69	1.75	0.05	0.11	-17.91
1994	10	158.30	105.77	10.95	200.57	52.53	1.71	0.07	0.09	-19.78
1990	12	168.65	105.74	11.65	185.31	62.92	1.70	0.32	0.09	-20.11
1985	14	166.80	107.17	14.14	188.68	59.63	1.62	0.09	0.10	-23.72
1981	16	175.67	105.93	10.82	210.55	69.74	1.84	0.10	0.28	-15.86
1976	18	169.23	107.95	13.36	233.69	61.28	1.54	0.10	0.14	-19.32
1972	20	159.75	107.00	13.31	197.64	52.75	1.72	0.27	0.25	-15.25
1967	22	178.47	109.07	13.98	271.07	69.40	1.47	0.10	0.18	-19.72
1962	24	173.61	108.19	13.50	240.65	65.43	1.63	0.26	0.30	-16.76
1958	26	165.36	107.55	13.34	216.83	57.81	1.61	0.26	0.28	-15.26
1953	28	181.69	106.35	10.07	260.75	75.34	1.58	0.31	0.19	-17.63
1949	30	185.58	108.07	14.00	222.22	77.50	1.50	0.06	0.12	-21.84
1944	32	168.66	108.15	14.46	214.53	60.51	1.47	0.23	0.26	-16.88
1940	34	166.54	104.69	10.18	175.08	61.85	1.24	0.00	0.22	-15.24
1935	36	170.15	106.41	13.25	180.56	63.73	1.27	0.33	0.28	-14.55
1931	38	173.95	105.36	11.53	175.42	68.58	1.13	0.05	0.11	-23.61
1926	40	163.26	102.55	7.40	145.02	60.71	0.94	0.12	0.09	-22.65
1922	42	179.98	105.25	10.95	181.11	74.73	0.85	0.17	0.08	-22.27
1917	44	138.80	101.31	10.00	105.03	37.50	1.00	0.03	0.15	-17.42
1912	46	125.16	100.05	7.94	92.67	25.11	0.91	0.08	0.22	-20.36
1908	48	108.54	95.28	7.26	53.36	13.25	0.70	0.25	0.22	-17.51
1903	50	115.98	99.74	7.73	88.99	16.24	0.82	0.14	0.32	-16.06
1899	52	106.72	95.99	6.11	54.25	10.73	0.72	0.18	0.11	-20.16
1894	54	101.79	92.46	7.27	41.82	9.33	1.19	0.16	0.36	-10.63
1890	56	103.14	93.41	5.47	39.89	9.73	0.66	0.14	0.19	-18.73
1885	58	92.45	86.39	4.99	21.82	6.06	0.69	0.11	0.12	-18.59
1881	60	91.00	84.76	4.59	18.55	6.24	0.75	0.13	0.09	-21.05
1876	62	87.46	82.98	4.63	16.76	4.48	0.95	0.11	0.09	-22.49
1872	64	88.28	81.54	5.60	18.06	6.74	1.47	0.11	0.35	-9.83
1867	66	64.32	62.18	3.95	5.51	2.14	0.99	0.12	0.28	-20.00
1862	68	50.72	48.33	3.73	3.00	2.39	0.98	0.08	0.29	-20.11
1858	70	55.80	53.35	2.93	2.98	2.45	1.08	0.55	0.38	-15.98
1853	72	84.31	80.67	3.03	10.52	3.64	1.16	0.16	0.36	-15.14
1849	74	44.23	42.82	3.78	2.42	1.41	1.21	0.16	0.39	-14.46
1844	76	33.58	32.47	5.54	2.04	1.11	1.22	0.53	0.44	-14.04

HPAs$_{TOT}$, HPA$_{16}$, LMW, HMW, HPA$_{ALK}$ (ng g^{-1})

BC (mg g^{-1}), COT (‰)

δ^{13}Co$_{C}$ e $\delta^{13}C_{BC}$ (‰)

Tabela S2. Concentrações total dos HPAs ($HPAs_{TOT}$), os 16 HPAs prioritários da Agência de Proteção Ambiental dos EUA (HPA_{16}), soma de n-alcanos de baixo peso molecular (LMW), soma de n-alcanos de alto peso molecular (HMW), Hidrocarbonetos alquilados (HPA_{ALK}), carbono negro (BC, do inglês black carbono), isótopo do carbono negro ($\delta^{13}C_{BC}$), carbono orgânico total (COT) e o isótopo do carbono ($\delta^{13}Co_{C}$) no testemunho T4, coletado na Baía de Todos os Santos, Brasil.

ANO	PROFUNDIDADE	**HPA_{TOT}**	**HPA_{16}**	**LMW**	**HMW**	**HPA_{ALK}**	**COT**	**δC^{13}_{CO}**	**BC**	**δC^{13}_{BC}**
2017	0	464.02	307.61	18.77	288.84	156.42	2.23	-22.02	0.40	-22.89
2014	2	1066.43	878.97	45.58	833.40	187.46	2.08	-21.97	0.33	-23.08
2010	4	685.37	509.38	19.27	490.10	176.00	1.98	-22.01	0.38	-22.67
2007	6	620.58	449.33	20.32	429.01	171.25	2.04	-22.13	0.38	-23.44
2004	8	763.01	514.92	32.76	482.16	248.08	1.90	-22.36	0.34	-22.71
2001	10	671.86	342.63	42.04	300.59	329.23	2.00	-22.53	0.39	-23.74
1997	12	542.15	237.40	41.98	195.43	304.75	1.52	-22.06	0.22	-22.59
1994	14	364.94	163.08	29.84	133.24	201.86	1.76	-22.51	0.22	-22.86
1991	16	220.63	110.48	20.99	89.49	110.14	1.40	-21.40	0.17	-21.52
1987	18	142.22	75.36	13.82	61.54	66.85	1.29	-21.01	0.17	-23.08
1984	20	123.89	76.69	11.26	65.42	47.20	1.26	-20.66	0.17	-17.50
1981	22	70.96	48.41	6.65	41.76	22.54	1.17	-20.74	0.14	-22.71
1978	24	40.03	27.20	5.54	21.66	12.83	1.20	-20.55	0.14	-20.65
1974	26	12.50	8.76	2.72	6.04	3.75	1.20	-20.21	0.14	-22.34
1971	28	8.45	6.36	2.90	3.46	2.09	1.22	-19.58	0.17	-17.12
1968	30	5.48	4.16	1.47	2.69	1.32	1.19	-20.21	0.19	-14.13
1965	32	7.83	6.33	2.85	3.48	1.50	1.19	-20.25	0.15	-19.30
1961	34	6.51	5.54	3.02	2.51	0.98	1.29	-19.58	0.21	-16.27
1958	36	5.91	4.69	2.84	1.85	1.22	1.29	-19.58	0.24	-13.51
1955	38	4.04	3.61	2.05	1.56	0.43	1.36	-19.47	0.24	-13.75
1951	40	3.93	2.86	1.77	1.09	1.07	1.49	-21.27	0.19	-15.41
1948	42	5.14	4.38	3.16	1.21	0.76	1.90	-16.87	0.19	-17.03
1945	44	7.86	6.51	4.94	1.74	1.35	1.90	-16.77	0.21	-14.39
1942	46	5.94	5.06	4.24	0.92	0.88	1.73	-17.67	0.26	-14.19
1938	48	7.36	6.10	5.21	1.00	1.26	1.62	-19.90	0.15	-19.04
1935	50	4.50	3.74	2.97	0.87	0.76	1.50	-21.48	0.28	-17.48
1932	52	6.09	4.64	3.99	0.64	1.46	1.48	-21.08	0.28	-14.47
1928	54	2.90	2.50	1.89	0.62	0.40	1.48	-20.56	0.33	-15.13
1925	56	4.51	3.38	2.19	1.19	1.13	1.95	-18.80	0.43	-10.33
1922	58	4.27	3.36	3.03	0.33	0.91	1.56	-21.16	0.18	-20.21
1919	60	3.70	2.72	2.61	0.11	0.98	2.03	-19.26	0.41	-11.75
1915	62	3.50	2.73	2.22	0.51	0.76	1.52	-20.99	0.28	-17.35
1912	64	3.34	2.70	2.70	0.00	0.63	1.40	-20.89	0.20	-20.04
1909	66	4.44	3.09	2.87	0.23	1.34	1.80	-21.94	0.19	-20.90
1906	68	10.03	7.10	3.08	4.02	2.94	1.80	-17.91	0.37	-10.22

$HPAs_{TOT}$, HPA_{16}, LMW, HMW, HPA_{ALK} (ng g^{-1})

BC (mg g^{-1}), COT (‰)

$\delta^{13}Co_{C}$ e $\delta^{13}C_{BC}$ (‰)

Tabela S3. Índices diagnósticos de origem dos HPAs.

T2 CORE							
Age (yers)	Depth(cm)	Phen/Ant	Ant/(Ant + Phen)	Fluo/Pi	Fluo/[Fluo + Pyr]	BaA/(BaA + Cri)	InP/(InP + BgP)
2017	0	nc	nc	nc	nc	nc	nc
2015	2	5.31	10.53	1.26	0.56	0.41	0.61
2013	4	3.84	5.71	1.21	0.55	0.44	0.60
2011	6	3.73	5.62	1.17	0.54	0.45	0.52
2009	8	0.81	13.15	1.14	0.53	0.43	0.48
2007	10	4.67	7.51	1.15	0.54	0.42	0.47
2005	12	3.20	7.75	1.18	0.54	0.49	0.48
2003	14	0.79	12.63	1.10	0.52	0.44	0.49
2001	16	2.66	6.52	1.08	0.52	0.49	0.51
1999	18	4.21	8.09	1.18	0.54	0.50	0.55
1997	20	3.90	7.00	1.17	0.54	0.45	0.55
1995	22	3.36	8.25	1.13	0.53	0.50	0.50
1993	24	3.25	8.13	1.09	0.52	0.50	0.50
1991	26	3.57	7.28	1.14	0.53	0.48	0.49
1989	28	nc	10.94	nc	nc	nc	nc
1987	30	2.21	8.99	1.11	0.53	0.51	0.53
1985	32	3.87	10.62	1.18	0.54	0.48	0.53
1983	34	2.52	7.66	1.15	0.53	0.53	0.52
1981	36	2.24	9.14	1.08	0.52	0.51	0.53
1979	38	2.08	7.69	1.12	0.53	0.53	0.53
1977	40	1.58	7.25	1.08	0.52	0.52	0.54
1975	42	2.21	7.14	1.04	0.51	0.52	0.52
1973	44	2.27	5.01	1.07	0.52	0.52	0.54
1971	46	3.04	2.90	1.01	0.50	0.52	0.54
1969	48	3.88	2.12	1.07	0.52	0.45	0.53
1967	50	4.42	2.70	1.05	0.51	0.47	0.57
1965	52	3.81	1.73	0.99	0.50	0.42	0.51
1963	54	4.90	2.46	1.12	0.53	0.43	0.53
1961	56	5.32	1.70	1.09	0.52	0.44	0.53
1959	58	4.46	1.17	0.98	0.50	0.44	0.53
1957	60	4.96	1.01	1.09	0.52	0.45	0.53
1955	62	4.82	0.87	1.07	0.52	0.45	0.54
1953	64	5.45	1.00	0.96	0.49	0.42	0.53
1951	66	nc	nc	1.25	0.56	0.46	0.50
1949	68	nc	nc	1.35	0.57	0.45	0.54
1947	70	nc	nc	1.22	0.55	0.44	0.54
1945	72	5.17	0.86	1.10	0.52	0.42	0.51
1943	74	nc	nc	1.27	0.56	0.38	0.48
1941	76	nc	nc	1.74	0.64	0.46	0.54

T4 CORE							
Age (yers)	Depth(cm)	Phen/Ant	Ant/(Ant + Phen)	Fluo/Pir	Fluo/[Fluo + Pyr]	BaA/(BaA + Cri)	InP/(InP + BgP)
2017	0	0.99	20.34	1.02	0.50	0.42	0.44
2014	2	2.18	50.44	1.16	0.54	0.54	0.54
2010	4	0.98	22.84	1.03	0.51	0.50	0.71
2007	6	0.75	25.11	1.03	0.51	0.48	0.70
2004	8	0.45	46.77	1.00	0.50	0.49	0.72
2001	10	0.33	66.36	1.03	0.51	0.51	0.45
1997	12	0.20	68.75	1.00	0.50	0.52	0.44
1994	14	0.20	47.41	1.00	0.50	0.52	0.43
1991	16	0.18	32.40	0.88	0.47	0.53	0.44
1987	18	0.25	17.82	0.94	0.49	0.52	0.45
1984	20	0.28	13.86	1.02	0.51	0.55	0.49
1981	22	0.51	5.25	0.99	0.50	0.53	0.49
1978	24	0.60	2.85	1.06	0.52	0.52	0.45
1974	26	3.31	1.16	1.46	0.59	0.41	0.55
1971	28	nc	nc	1.46	0.59	0.41	0.54
1968	30	nc	nc	1.58	0.61	0.43	0.53
1965	32	nc	nc	1.33	0.57	0.37	0.54
1961	34	nc	nc	1.37	0.58	0.40	0.61
1958	36	nc	nc	1.77	0.64	0.37	nc
1955	38	nc	nc	1.63	0.62	nc	nc
1951	40	nc	nc	1.55	0.61	nc	nc
1948	42	nc	nc	1.24	0.55	nc	nc
1945	44	nc	nc	1.19	0.54	0.33	nc
1942	46	nc	nc	1.52	0.60	0.47	nc
1938	48	nc	nc	1.66	0.62	0.44	nc
1935	50	nc	nc	1.34	0.57	0.48	nc
1932	52	nc	nc	nc	nc	nc	nc
1928	54	nc	nc	1.34	0.57	nc	nc
1925	56	nc	nc	1.25	0.56	0.52	nc
1922	58	nc	nc	nc	nc	nc	nc
1919	60	nc	nc	nc	nc	nc	nc
1915	62	nc	nc	0.58	0.37	nc	nc
1912	64	nc	nc	nc	nc	nc	nc
1909	66	nc	nc	nc	nc	nc	nc
1906	68	2.45	0.58	1.09	0.52	0.45	0.33

CAPÍTULO 4

CONCLUSÃO GERAL

A Baía de Todos os Santos é um sistema costeiro altamente complexo, onde a distribuição do material orgânico nos sedimentos depende de uma variedade de fatores como produção primária, aporte terrígeno, profundidade, hidrodinâmica, taxas de sedimentação, fontes antropogênicas etc. No presente trabalho, a MO foi caracterizada nos níveis elementar, isotópico e molecular. As principais contribuições e conclusões são as seguintes:

Com relação ao histórico de deposição da MO e suas fontes:

- O alcance cronológico obtido neste trabalho permitiu analisar o contexto histórico da alteração da MO na região norte da BTS, antes do período de maiores mudanças significativas ocorridas a partir do desenvolvimento urbano e industrial (1950) nessa região.

- Em relação à abundância de matéria orgânica de origem natural, prevalece a MO marinha, no entanto, os n-alcanos mostram uma contribuição pequena dos derivados de fitoplâncton (baixa contribuição do C_{17}). Isto decorre da maior labilidade da MO marinha, mas também é um indicativo da baixa produtividade primária na baía. A BTS ainda pode ser considerada um sistema oligotrófico em função principalmente da escassez de nutrientes.

- Embora a amostragem no estudo seja limitada, a comparação entre os testemunhos mostra que a proximidade das fontes de contaminação e o agente de transporte influenciam o alcance dos contaminantes. O transporte eólico é um importante agente para compostos pirogênicos.

- As atividades de produção, refino e transporte de petróleo às margens da Baía de Todos os Santos tiveram um impacto direto na qualidade dos sedimentos marinhos a partir da década de 1970. As emissões veiculares também contribuíram com o aporte antropogênico da MO nos testemunhos.

- Apesar das diversas indústrias e complexos urbanos existentes no entorno da BTS, em geral, os níveis de poluição são considerados moderados em comparação a outras baías do Brasil e do mundo. Isso possivelmente ocorre devido a troca de água constante com os oceanos, através do canal de Salvador, resultando em um curto tempo de residência de partículas sedimentares em seu interior, portanto reduzindo a quantidade de sedimento e contaminantes no ambiente.

Com relação ao uso dos marcadores e índices:

- Os índices de diagnóstico frequentemente aplicados podem fornecer informações ambíguas em ambientes tropicais. As altas temperaturas e intensidade solar, bem como a atividade microbiana intensa podem desempenhar um papel importante na determinação da taxa de degradação dos hidrocarbonetos e assim modificar as concentrações dos compostos nos quais dependem as taxas de diagnóstico. Somente o uso dos 16 HPAs prioritários podem não produzir resultados confiáveis. A verificação cruzada com o máximo de indicadores possíveis permite uma interpretação mais fiável e precisa.

- A determinação da UCM na fração alifática, dos HPAs alquilados e do BC foram importantes para a caracterização das fontes de MO na BTS.

- A maior resistência do BC à alteração em relação a outras formas de matéria orgânica o torna um rastreador útil para reconstruir a história da combustão local.

Antropoceno:

- Ao reconhecer o Antropeceno, também nos confrontamos com questões éticas e práticas urgentes, como a necessidade de adotar práticas sustentáveis de desenvolvimento. O Antropeceno pode representar uma nova maneira de entender a relação entre os seres humanos e o planeta, destacando nossa responsabilidade coletiva de agir de maneira consciente e sustentável para preservar a saúde e a diversidade da vida na Terra.

- Embora o ano de 1950 seja indicado como um limite provável para marcar o início do Antropoceno, a industrialização tardia da Baía de Todos os Santos resultou em mudanças nos padrões de deposição para os marcadores geoquímicos analisados nesse estudo apenas na década de 1980.

- Nossos resultados mostram a importância de recorrer a múltiplos marcadores para restringir as fontes de matéria orgânica durante o Antropoceno.

Para futuros trabalhos recomenda-se:

- Ampliar a determinações de BC para outras áreas críticas da BTS como a Baía de Aratu e a região sob influência de Salvador;

- Determinar o BC em outros compartimentos (água, atmosfera) para se compreender sua dinâmica na BTS;
- Considerar a fração BC em estudos ambientais de avaliação de risco à biota;
- Determinar a razão isotópica em n-alcanos específicos e o desenvolver índices adaptados à diversidade local de fontes de MO;
- Utilizar biormarcadores como hopanos e esteranos para melhor caracterizar os insumos antrópicos.

APÊNDICE A - JUSTIFICATIVA DA PARTICIPAÇÃO DOS COAUTORES

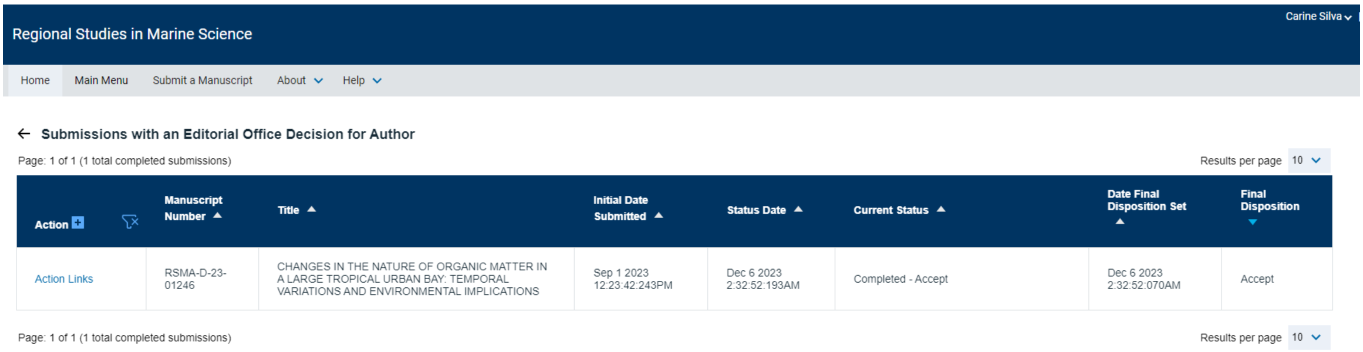
Artigos 1 e 2: Carine Santana Silva. Administração de projeto; Análise formal; Conceituação; Curadoria de dados; Escrita - rascunho original; Escrita - revisão e edição; Investigação; Metodologia; Visualização. Graduada em oceanografia, mestre em Geoquímica: Petróleo e Meio Ambiente (POSPETRO/ UFBA). Faz parte do Laboratório de Estudos Costeiros. Tem experiência em projetos de monitoramento ambiental de ambientes aquáticos e costeiros (nutrientes, metais e compostos orgânicos, biomarcadores de petróleo), coleta e análise de dados ambientais, avaliação e recuperação de áreas impactadas por atividades petrolíferas e avaliação de sedimento para dragagem.

Artigos 1 e 2: José Maria Landim Dominguez. Concluiu a graduação em geologia pela Universidade Federal da Bahia, onde também obteve o Mestrado em Geologia, área de concentração em Sedimentologia. Concluiu seu doutorado em Geologia e Geofísica Marinha pela Rosenstiel School of Marine and Atmospheric Sciences da Universidade de Miami em 1987. Atualmente é professor titular em Geologia Costeira e Sedimentar da Universidade Federal da Bahia e coordena o inct AmbTropic - Ambientes Marinhos Tropicais. Sua participação justifica-se por: Administração de projeto; Conceituação; Escrita - revisão e edição; Supervisão, Aquisição de financiamento.

Artigo 1 e 2: Gilvan Takeshi Yogui. Possui graduação em Oceanologia pela Universidade Federal do Rio Grande (1998), mestrado em Oceanografia Química e Geológica pela Universidade de São Paulo (2002) e doutorado em Oceanografia pela Texas A&M University (2008). Atualmente é professor associado no Departamento de Oceanografia da Universidade Federal de Pernambuco. Tem experiência em programas de monitoramento ambiental e estudos biogeoquímicos de compostos orgânicos, tais como hidrocarbonetos do petróleo, poluentes orgânicos persistentes, isótopos estáveis e marcadores geoquímicos de lignina. Sua participação justifica-se por: Metodologia, Validação, Supervisão, Escrita - revisão e edição.

Artigo 1: Marcos de Almeida. Doutorando em Oceanografia pela Universidade Federal de Pernambuco (UFPE). Estuda mudanças climáticas e acidificação oceânica em recifes de corais oceânico (Reserva Biológica de Atol das Rocas - Brasil) e costeiro (Área de Proteção Ambiental Marinha Recifes Serrambi - Brasil). Bacharelado em Oceanografia (2014) e mestrado em Geoquímica do Petróleo e Meio Ambiente pela Universidade Federal da Bahia (UFBA) (2017). Atuou como Técnico químico especializado no projeto "Formação do Centro de Excelência em Geoquímica do Petróleo do Instituto de Geociências da UFBA -GEOQPETROL" (2014 - 2018). Possui experiência em análises químicas de água e sedimento em monitoramento ambiental de ambientes marinhos oceânico e costeiro. Sua participação justifica-se por: Conceituação; Metodologia; Visualização; Metodologia; Escrita - revisão e edição.

ANEXO A
- COMPROVANTE DE PUBLICAÇÃO DO ARTIGO 1



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Action Links	RSMA-D-23-01246	CHANGES IN THE NATURE OF ORGANIC MATTER IN A LARGE TROPICAL URBAN BAY: TEMPORAL VARIATIONS AND ENVIRONMENTAL IMPLICATIONS	Sep 1 2023 12:23:42:243PM	Dec 6 2023 2:32:52:193AM	Completed - Accept	Dec 6 2023 2:32:52:070AM	Accept

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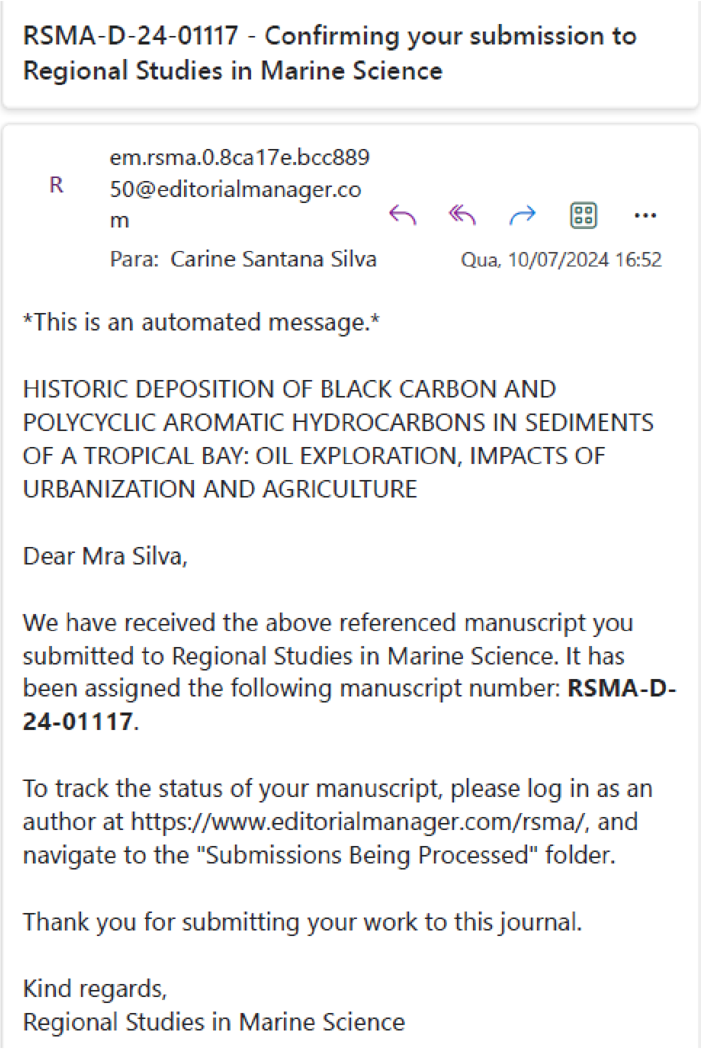
ANEXO B

- COMPROVANTE DE SUBMISSÃO DO ARTIGO 2



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- REGRAS DE FORMATAÇÃO DA REVISTA 2

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