UNIVERSIDADE FEDERAL DE SANTA CATARINA

CENTRO DE CIÊNCIAS FÍSICAS E MATEMÁTICAS

PROGRAMA DE PÓS-GRADUAÇÃO EM OCEANOGRAFIA

Lisiane Eble Heinzen de Liz

Matéria Orgânica Sedimentar na Baía de Todos os Santos. Bahia: Fontes, Distribuição e Caracterização por Pirólise de Rock-Eval

Florianópolis

2020

Lisiane Eble Heinzen de Liz

Matéria Orgânica Sedimentar na Baía de Todos os Santos. Bahia: Fontes, Distribuição e Caracterização por Pirólise de Rock-Eval

Dissertação submetida ao Programa de Pós Graduação em Oceanografia da Universidade Federal de Santa Catarina para a obtenção do título de Mestre em Oceanografia.
Orientador: Profa. Dra. Juliana Leonel.

Florianópolis

2020

Ficha de identificação da obra

Lisiane Eble Heinzen de Liz

Matéria Orgânica Sedimentar na Baía de Todos os Santos. Bahia: Fontes, Distribuição e Caracterização por Pirólise de Rock-Eval

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

Prof.(a) Alessandra Larissa D´Oliveira Fonseca. Dr.(a)
Universidade Federal de Santa Catarina

Prof. Felipe Sales de Freitas. Dr.
Bristol University

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

_____
Coordenação do Programa de Pós-Graduação

_____
Prof.(a) Juliana Leonel. Dr.(a)
Orientador(a)

Florianópolis. 2020.

AGRADECIMENTOS

Durante esses dois anos de Mestrado eu tenho muito para agradecer! Agradecer por tudo o que eu aprendi, vivi e amadureci. Agradecer por todas as pessoas que acompanharam essa jornada desde o início e também aquelas que chegaram durante o caminho. Que me mostraram que apesar dos desafios e dificuldades, eu seria capaz de concluir essa etapa na minha vida.

Agradeço meus pais, Eduardo e Sandra, e minha avó Darci por todo apoio e incentivo nas minhas escolhas, por sempre acreditarem em mim!

A professora Juliana Leonel por aceitar o desafio de me orientar durante esses dois anos. Sabemos como foi um processo de amadurecimento para mim. Foram muitos ensinamentos, desafios, desabafos, reflexões, dicas e ajudas. Obrigada por me inspirar como mulher, como professora & orientadora, como cientista e futura mãe. Aprendi a gostar da academia e de fazer ciência. Agradeço também ao Filipe Fernandes por toda paciência e ajuda com as aulas de Python.

A Banca Examinadora, Felipe e professora Carla Bonetti, por acompanharem o presente trabalho desde o projeto. Todas as dicas, críticas e sugestões foram fundamentais para o amadurecimento e a melhoria deste.

Agradeço por ter as melhores mulheres dessa Ilha ao meu lado desde a graduação: Natasha, Larissa e Marina.

O laboratório de Oceanografia Química e o nosso Laboratório de Poluição e Geoquímica Marinha (LapogeoMar) pela família que construímos e um ambiente com muita energia positiva, boas conversas, café e amor! Prof Ale, prof Ju, Alex, Gabi, Lari, Dani, Cami e Kalina.

As minhas amigas Vanessa, Tielle, Duda, Gabi, Maísa, Luana e Mari; e de infância Bel, Cy, Beta, Lele, Lu, Nanda, Paula, Kaka, Bia e Guinter que, mesmo de longe, estão sempre em energia me apoiando e acreditando em mim!

A Run Fitness Club por me proporcionar momentos de descontração da mente e me fazer gostar de exercícios físicos. Além disso, tive a sorte de encontrar pessoas loucas como eu, que amam um desafio: Dai, Ana Carol, Aninha, Carol, Fabi, Marina, Lu. Obrigada pelo incentivo diário! E claro, aos melhores profissionais que nos estimulam: prof. Anderson e prof Pri.

Ao pessoal dos laboratórios vizinhos pelos cafés, ar condicionado, conversas de corredor e claro, dias de bar.

RESUMO

Baías e estuários são importantes ambientes de transição entre o continente e os oceanos que exercem papel importante na produção, degradação e preservação da matéria orgânica (MO), que por sua vez influenciam nos ciclos biogeoquímicos e, consequentemente, no ciclo do Carbono. Testemunhos sedimentares foram coletados na Baía de Todos os Santos (BTS) com o objetivo de identificar as principais fontes, distribuição e composição da matéria orgânica sedimentar em sedimentos recentes (~100 anos), e relacionar com a evolução histórica da região, pioneira em atividades petrolíferas no Brasil. As amostras de sedimento foram analisadas por pirólise de Rock-Eval 6. Os parâmetros indicam uma MO predominante terrígena com grande contribuição dos mangues ao entorno e diagênese recente da MO na BTS.

Palavras-chave: Rock Eval. Matéria Orgânica Sedimentar. Baía de Todos os Santos.

ABSTRACT

Bays and estuaries are important environments between the continent and the oceans play an important role in the production, degradation and preservation of organic matter (OM). These processes influence the biogeochemical cycles and, consequently, the carbon cycle. Sedimentary cores were collected in Todos os Santos Bay (BTS), NE Brazil to identify main sources, distributions and composition of sedimentary OM in recent sediments (~ 100 years), and to relate to the historical evolution of the region, pioneer in oil activities in Brazil. Sediments were analyzed by pyrolysis Rock-Eval 6. The parameters suggest a predominantly terrestrial OM with large contribution from mangroves and recent diagenesis of OM in BTS.

Keywords: Rock Eval, Sedimentary Organic Matter, Todos os Santos Bay.

LISTA DE FIGURAS

LISTA DE ABREVIATURAS E SIGLAS

BTS – Baía de Todos os Santos / Todos os Santos Bay

CIA – Aratu Industrial Complex

CIC – Camaçari Industrial Complex

CIS – Subaé Industrial Complex

EA – Elemental Analysis

FID – Flame Ionization Detector

HB – Hudson Bay

HC - Hydrocarbon

HI – Hydrogen Index

IR –Infrared

MO – Matéria Orgânica

MOS – Matéria Orgânica Sedimentar

MinC(%) – Mineral Carbon

OI – Oxygen Index

OM - Organic Matter

PC – Pyrolyzed Carbon

PLUMBUM – Smelter PlumbumMineration

RE – Rock Eval

RC – Residual Carbon

RDM – Rio Doce Manganês Electrosurgery

RLAM - LandulphoAlves Refinery

SOM – Sedimentary Organic Matte

S1 - Free Hydrocarbons

S2 –Amount of Hydrocarbon released

TEMADRE – Madre de Deus Waterway Terminal

Tmax – Maximum Temperature

TOC – Total Organic Carbon

SUMÁRIO

INTRODUÇÃO GERAL

A matéria orgânica sedimentar (MOS) tem papel chave nos ciclos biogeoquímicos do ambiente marinho, pois representa a principal conexão entre o ciclo bioquímico do carbono, referente à produção primária, e o ciclo geoquímico do carbono, relacionado ao carbono preservado nas rochas sedimentares (BURDIGE, 2005; MOORE et al., 2013). Dessa forma, o transporte e soterramento de carbono no sedimento marinho exercem papel de sumidouro de CO_2 e tem importância fundamental na manutenção do clima a partir do controle entre a remoção líquida do CO_2 atmosférico e a entrada de O_2 atmosférico (HEDGES & KEIL, 1995; BURDIGE, 2007; JIAO et al., 2010; ARNDT et al., 2013).

A origem da MOS pode ser classificada em relação a sua natureza, natural ou antrópica, ou pelo seu aporte, autóctone ou alóctone (BUENO et al.. 2018; MARCHAND et al., 2008). A MOS de origem natural é oriunda principalmente da produção primária fitoplanctônica, e em menor escala, de plantas vasculares. Em ambientes mais rasos, pode-se ter a contribuição da produção fitobentônica. Ainda, em regiões específicas, também pode haver a contribuição oriunda de quimiossíntese (MEYERS, 1997; MIGNÉ et al., 2009; ARNDT et al., 2013; DRYLIE et al., 2018). Por outro lado, a origem antrópica é consequente de atividades humanas, resultante de compostos oriundos da queima de combustíveis fósseis e biomassa, atividades industriais e agricultura (SANTOS et al., 2013; HU et al., 2016; BUENO et al., 2018). Em relação ao seu aporte, a MOS autóctone é produzida diretamente no ambiente marinho, dessa forma, está relacionada à produtividade local do ambiente. Por outro lado, a MO alóctone origina-se fora do ambiente marinho e chega até este através do transporte eólico ou fluvial, podendo ter origem tanto natural quanto antrópica (ZONNEVELD et al., 2010; CANUEL & HARDISON, 2016). Ainda, a contribuição alóctone antrópica pode chegar até o ambiente marinho de forma direta ou indireta. O despejo direto ocorre quando há derramamento de óleo ou pelo lançamento de efluentes domésticos e industriais pontuais em determinadas regiões, enquanto que o despejo indireto está relacionado à drenagem urbana e pluvial, bem como despejo de efluentes e partículas transportados pelos rios e partículas carreadas pelo vento (BUENO et al., 2018; LIAO et al., 2018).

Consequentemente, a composição da MOS é uma mistura complexa de compostos oriundos de diferentes fontes e com reatividades variadas que sobreviveram aos processos de degradação, ainda que possam ter sofrido alterações (TISSOT & WELTE, 1984; KILLOPS &

KILLOPS, 2005). Dessa forma, a caracterização da composição da MOS é um descritor importante para estudos geoquímicos, pois é um registro que pode fornecer informações sobre o passado e o presente do ciclo do carbono através da caracterização de suas fontes, composição, distribuição espacial e variação temporal (DISNAR et al., 2003; KILLOPS & KILLOPS, 2005; HARE et al., 2014; CANUEL & HARDISON, 2016).

Entre os principais componentes da MOS, as proteínas e carboidratos são preferencialmente degradados devido à sua labilidade, enquanto que lipídios e lignina são mais refratários e tendem a serem preservados (ARNDT et al., 2013; BURDIGE, 2007; KILLOPS & KILLOPS, 2005). No entanto, é importante ressaltar que lipídios englobam uma classe com um número amplo e variado de compostos como alquenonas, esteroides, triterpenoides e ácidos graxos, entre outros que apresentam reatividades distintas de acordo com o tempo de exposição ao oxigênio, taxa de sedimentação, proteção mineral, etc (SINNINGHE-DAMSTÉ, RIJPSTRA & REICHART, 2002; HOEFS, RUPSTRA & DAMSTÉ, 2002, ARNDT et al., 2010). Da mesma forma, proteínas e carboidratos podem ser preservados por períodos mais longos devido à proteção física oriunda da interação com outros compostos orgânicos, como algininas e/ou com materiais inorgânicos, como carbonato de cálcio e sílica biogênica (BURDIGE, 2007; HEDGES & OADES, 1997). Portanto, a preservação e/ou degradação de grupos de compostos deve ser analisada e interpretada com cautela e considerando as peculiaridades de cada ambiente.

A MOS natural de origem terrígena é constituída principalmente por detritos vegetais ricos em carbono. A parede celular de plantas vasculares é composta de polímeros rígidos e complexos, como celulose e lignina, que são mais resistentes à degradação e possuem maior teor de oxigênio (EGLINTON et al., 1962; HEDGES, 1992; HEDGES, KEIL & BENNER, 1997). Por outro lado, a matéria orgânica de origem marinha é composta por material fitoplanctônico empobrecido em carbono quando comparados às plantas terrestres, mas com elevados teores de nitrogênio e hidrogênio devido a maior ocorrência de proteínas presentes em suas células (BURDIGE, 2007; MARCHAND et al., 2008; MEYERS, 1994). Tais diferenças composicionais influenciam na labilidade das MOS e permitem identificar suas distintas fontes (SUM & WAKEHAM, 1994)..

Estima-se que um terço da MOS é de origem terrígena, sendo que a maior parte sedimenta nas margens continentais e apenas uma pequena parcela (20% ou menos) chega ao oceano profundo (BURDIGE, 2005). Ao pressupor que a MO terrígena possui constituintes mais refratários que a MO marinha, essa proporção é relativamente baixa, fazendo com que

essa estimativa ainda seja questionada em relação a sua baixa ocorrência nos oceanos. Alguns quesitos devem ser considerados: a) a reatividade de cada componente varia conforme as propriedades físico-químicas do ambiente e da coluna d'água; b) as técnicas de caracterização da MOS podem estar subestimando a detecção do material terrígeno; c) a remineralização da matéria orgânica terrígena ser mais rápida do que se acredita; d) mecanismos de transporte e redistribuição aprisionam a maior parte desse material em deltas e margens continentais (SUN & WAKEHAN, 1994; BIANCHI, 2006; BURDIGE, 2007; SELVARAJ et al., 2015).

O estudo da MO sedimentar engloba estudos elementares e moleculares. Estudos elementares envolvem métodos de identificação e caracterização de elementos que compõem a MOS tais como C, N, O, S e seus respectivos isótopos (MEYERS, 1994; THORNTON & MCMANUS, 1994; BIANCHI & CANUEL, 2011). Por outro lado, estudos moleculares buscam identificar moléculas presentes na MOS e a assinatura isotópica dos elementos presentes nestes compostos (SUN & WAKEHAN, 1994; VOLKMAN et al., 1998; MEYERS, 2003; PETERS, WALTERS & MOLDOWAN, 2005; AFFOURI & SAHRAOUI, 2017; BAUDIN et al.,2017). Recentemente, diversos trabalhos vêm utilizando a técnica elementar pirólise de Rock Eval para estudos geoquímicos da MOS, por ser uma técnica mais rápida e econômica quando comparada às outras (MARCHAND et al., 2008; HARE et al., 2014; BAUDIN et al., 2017).

O RE é um instrumento que foi desenvolvido pelo Instituto Francês do Petróleo (IFP) na década de 1970 para estudos de geoquímica do petróleo. Desde então, diversas versões foram criadas e aprimoradas (LAFARGUE, MARQUIS & PILLOT, 1998), sendo a mais recente a versão 7 (LAMOUREUX-VAR et al., 2019). A técnica simula em laboratório o processo natural de maturação da matéria orgânica. Como não é possível reproduzir em laboratório o efeito do tempo geológico, utilizam-se temperaturas maiores do que as registradas no ambiente, que podem alcançar até 850°C em um curto intervalo de tempo para mimetizar o efeito da pressão e assim, obter resultados semelhantes aos encontrados naturalmente (MCCARTHY et al., 2011).

A MO passa por dois processos: pirólise e oxidação. A pirólise ocorre em atmosfera inerte com gás N_2 para que não ocorra combustão da amostra e, simultaneamente, ocorre à detecção dos hidrocarbonetos com detector de Ionização em Chama (FID) e a quantificação do CO e CO_2 pelo detector de Infravermelho (IR) (HARE et al., 2014). A parcela de amostra que sobrevive a pirólise é denominada carbono residual (CR), o qual segue para o processo de combustão em ar e são detectados somente pelo IR (BAUDIN et al., 2015).

Durante a queima da amostra, são gerados parâmetros que permitem a caracterização da MOS em relação a porcentagem de Carbono Orgânico Total (COT), fontes, transformação diagenética e maturação (MARCHAND et al., 2008; BEHAR et al., 2001; HARE et al., 2014; BAUDIN et al., 2017).

A pirólise de RE, inicialmente utilizada para estudos de geoquímica do petróleo, recentemente, tem sido aplicada para estudos de matéria orgânica em sedimentos recentes de solos, lacustres, marinhos, de mangues e baías (MARCHAND et al., 2008; DISNAR et al., 2003; HARE et al., 2014; AFFOURI & SAHRAOUI., 2017; BAUDIN et al., 2017).

A Baía de Todos os Santos (BTS), nordeste do Brasil, apresenta grande importância ecológica, histórica e socioeconômica para o Estado da Bahia e ao Brasil devido à sua riqueza ecossistêmica, atividades pesqueiras e extrativistas, tanto comerciais como de subsistência (HATJE & ANDRADE, 2009). A BTS é considerada o berço histórico das atividades petrolíferas no país devido à instalação da primeira refinaria do país em 1950, Refinaria Landulpho Alves (RLAM). A instalação da RLAM estimulou um amplo crescimento industrial na região, principalmente ao norte da BTS, e populacional, influenciando na qualidade ambiental da Baía (NASCIMENTO et al., 2017; HATJE & ANDRADE, 2009; ANDRADE et al., 2017).

O crescimento das atividades na época ainda não considerava a componente ambiental como parte integrante da tomada de decisões pelas empresas e órgãos ambientais bem como pelo poder público. Dessa forma, o presente estudo busca analisar a técnica de RE, bem como aplicá-la para caracterizar as principais fontes e estado de degradação da MOS na Baía de Todos os Santos bem e avaliar a variação temporal da composição da MOS em relação à evolução histórica da BTS. Com base nessas informações, o estudo também buscou verificar a hipótese de que essas pressões antrópicas, resultantes da expansão urbana e impulsionadas pela industrialização em torno do BTS, causaram mudanças nas fontes de MOS para o ambiente aquático adjacente, o que resulta em uma maior entrada de hidrocarbonetos livres e carbono refratário (carbono residual).

ARTIGO

Os resultados do presente trabalho serão apresentados a seguir na forma de artigo científico, submetido para revista *Marine Pollution Bulletin (Elsevier)* - qualis A1.

Sedimentary Organic Matter in Todos os Santos Bay, Bahia:

Sources, Distribution and Characterization by Rock Eval Pyrolysis

Lisiane Eble Heinzen de Liz[a,b] *; Juliana Leonel[b]

[b]Department of Oceanography, Federal University of Santa Catarina (UFSC), Brazil
*Address correspondence to lisiheinzendeliz@gmail.com and juoceano@gmail.com

Abstract

Bays and estuaries are important environments between the continent and the oceans play an important role in the production, degradation and preservation of organic matter (OM). These processes influence the biogeochemical cycles and, consequently, the carbon cycle. Sedimentary cores were collected in Todos os Santos Bay (BTS), NE Brazil to identify main sources, distributions and composition of sedimentary OM in recent sediments (~ 100 years), and to relate to the historical evolution of the region, pioneer in oil activities in Brazil. Sediments were analyzed by pyrolysis Rock-Eval 6. The parameters suggest a predominantly terrestrial OM with large contribution from mangroves and recent diagenesis of OM in BTS.

Keywords: Rock Eval, Sedimentary Organic Matter, Todos os Santos Bay.

1 INTRODUCTION

Sedimentary organic matter (SOM) represents an important descriptor for geochemical studies. It is a record that can provide information about the present and the past of carbon cycle, through the characterization their sources, composition, spatial distribution and temporal variation (HEDGES & KEIL, 1995; DISNAR et al., 2003; KILLOPS & KILLOPS, 2005; HARE et al., 2014; CANUEL & HARDISON, 2016).

Sources of SOM can be classified in relation to their nature (natural or anthropic) or source of their input (autochthonous or allochthonous) (BUENO et al., 2018;

MARCHAND et al., 2008). SOM of natural origin originates mainly from primary phytoplankton production, and to a smaller scale, from vascular plants. In shallower environments, there may be a contribution from primary phytobenthic production. Still, in specific regions, there may also be a contribution from chemosynthesis (MEYERS, 1997; MIGNÉ et al., 2009; ARNDT et al., 2013; DRYLIE et al., 2018). The anthropic origin is a consequence of human activities, resulting from compounds from the burning of fossil fuels and biomass, industrial activities and agriculture (SANTOS et al., 2013; HU et al., 2016; BUENO et al., 2018). Regarding their input, the autochthonous MO is produced directly in the marine environment, thus, it is related to the local productivity. While, allochthonous MO originates outside the marine environment and reaches it through wind or river transport, and may have both natural and anthropic origin (ZONNEVELD et al., 2010; CANUEL & HARDISON, 2016). Also, the anthropic allochtone contribution can reach the marine environment directly or indirectly. Direct discharge occurs when there is an oil spill or the discharge of punctual domestic and industrial effluents in certain regions, while indirect discharge is related to urban and rain drainage, as well as the discharge of effluents and particles carried by rivers and particles carried by the wind (BUENO et al., 2018; LIAO et al., 2018).

There are several procedures to characterize SOM divided in bulk and molecular studies (SUN & WAKEHAM, 1994; VOLKMAN et al., 1998; MEYERS, 2003). Bulk methods involve identification and characterization of SOM components, such as C, N, O, S, and their respective stable isotopes (MEYERS, 1994; THORNTON & MCMANUS, 1994; BIANCHI & CANUEL, 2011), while molecular studies search to identify the molecules present in SOM using biomarkers (PETERS, WALTERS & MOLDOWAN, 2005; AFFOURI & SAHRAOUI, 2017; BAUDIN et al., 2017). Recently, the elemental technique Rock Eval pyrolysis has been used for SOM studies since it is a faster and more economical technique when compared to the others. (DISNAR et al., 2003; MARCHAND et al., 2008; BAUDIN et al., 2017).

Although Rock Eval (RE) analyses were initially developed for petroleum geoscience studies by providing the hydrocarbon potential of sedimentary rocks (HARE et al., 2014), it has been largely used to determine content, sources, state of degradation and diagenetic transformation of OM in recent sediments (AFFOURI & SAHRAOUI, 2017; BAUDIN et al., 2017). RE technique simulates, in the laboratory, the natural maturation process of OM using high temperatures (up to 850 °C) in a short time interval to obtain

similar results to those found naturally (MCCARTHY et al., 2011). The technique was applied for studies in coastal areas and bays showing to be a good tool for SOM studies (HARE et al., 2014; AFFOURI & SAHRAOUI, 2017).

Todos os Santos Bay (BTS), northeast Brazil (Figure 1), presents great ecological, historical and socio-economic importance due to its ecosystem wealth, fishing and extractive activities, both commercial and subsistence. BTS is the pioneer of oil activities in Brazil after the discovery of the first oil well in 1939 (OLIVEIRA, 1997; HATJE & ANDRADE, 2009). Later, the first refinery in Brazil was established in 1950, the Landulfo Alves Refinery (RLAM). Since their construction, other industrial activities have developed in the area affecting the environmental quality of BTS (ANDRADE et al., 2017; DE SOUZA et al., 2017; HATJE et al., 2019).

Therefore, the present study aims to analyze the use of RE technique to study SOM, as well as its application to characterize the main sources and state of degradation of SOM at BTS. Based on this information, the study also wanted to verify the hypothesis that the anthropic pressures on BTS, resulting from urban expansion and driven by industrialization around BTS, caused changes in the sources of SOM for the adjacent aquatic environment that results in a higher input of free hydrocarbons and residual carbon.

2 METHODS

2.1 STUDY AREA

BTS is located on the northeastern coast of Brazil and is the second largest Brazilian coastal bay (~ 1200 km²) (DE SOUZA et al., 2017). The region has a rich and diverse ecosystem with estuaries, coral reefs, mangroves, islands and tidal flats (CIRANO & LESSA, 2007). BTS drainage basin, with 61.110 km², is composed of dozens of tributaries, but the main three are Paraguaçu, Jaguaripe and Subaé rivers, which contribute to 74% of the total freshwater discharge in the bay (LIMA & LESSA, 2002). Despite that, the volume of freshwater is approximately half the amount of saltwater that enters the bay and BTS has marine predominant characteristics (LEÃO & DOMINGUEZ, 2000). Paraguaçu River the main river of the region, had its regime altered in 1985 with the construction of the Pedra do Cavalo dam, decreasing its discharge from 91 m³ s^{-1} to approximately 64 m³ s^{-1} (CIRANO & LESSA, 2007). The water column of BTS is well mixed and internal circulation is controlled

by semidiurnal tides with a maximum range of 2.7 m (LESSA et al., 2001). The region is characterized by a tropical climate. Bottom sediments vary from predominance of mud in the northern area, sand-clay in the center and sand, from marine influence, in the southern region.

Approximately 3.5 million people live around BTS, being 2.9 million in Salvador (IBGE, 2017). The main economic activities include petrochemical and industrial activities, besides the tourism provided by the scenic beauty of its beaches and islands (SETUR, 2010). The first anthropogenic activity in the region dates back to 1500 with sugar cane plantations. Since then, the economy has evolved to more complex industries, such as, the implementation of an oil refinery, a maritime terminal for transport of petroleum products, three public harbors, the largest petrochemical complex of the Southern hemisphere (Camaçari Industrial Center), and two large industrial centers (Aratu Industrial Complex and Subaé Industrial Complex) with industries from several sectors such as food, metallurgy, electronics, thermoelectric (SILVA, 2010; SOUZA, 2014). All the anthropogenic pressure around the BTS, mainly originate from industrialization, population growth and tourism, impact the quality of the bay (HATJE & BARROS, 2012) and is a potential source of anthropogenic OM.
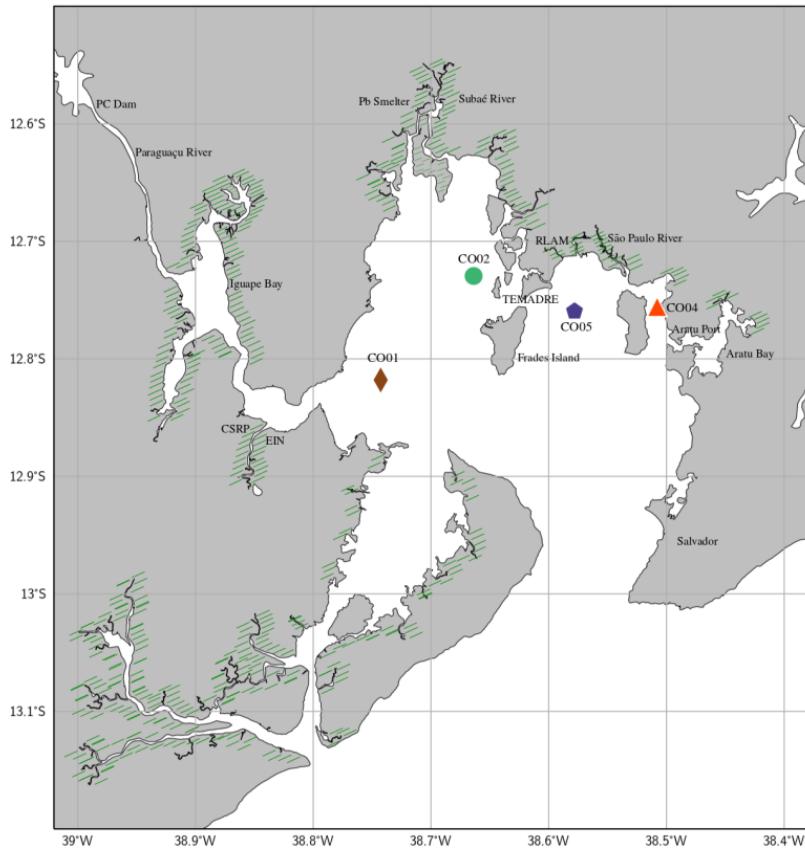
Figure 1: Location of Cores (CO01-CO05) at Todos os Santos Bay. Green lines represent mangrove areas. EIN: enseada indústria naval shipyard, CSRP: São Roque do Paraguaçu Shipyard, PC Dam: Pedra do Cavalo Dam, RLAM: Landulfo Alves Refinery, and TEMADRE: Madre de Deus Harbor Terminal. Green lines represent mangrove areas.

2.2 SAMPLE COLLECTION AND PROCESSING

Four sediment cores were collected from the northern region of BTS in October 2014. Details regarding sampling procedures, dating and granulometry have been described previously by Andrade et al. (2017).

Core CO01 (9.8 m depth) was collected close to the mouth of the Paraguaçu estuary. Core CO02 (7.7 m depth) close to Subaé estuary, region that may be under influence of the Subaé Industrial Complex (CIS) and Madre de Deus Waterway Terminal (TEMADRE). Core CO04 (6.6 m depth) next to the harbor and the Aratu Industrial Complex (CIA). Core CO05 (8.9 m depth) near RLAM refinery. More details about cores can be found at Table S2. Cores are approximately 100 cm long and were sub-sectioned at 1 cm intervals for the upper 20 cm, and then every 2 cm. Samples were stored frozen (-20 °C), then freeze-dried and powdering for further analysis.

2.3 ROCK EVAL ANALYSIS

Organic matter analysis was carried out with approximately 100 mg of sediment sample, previously washed to remove NaCl, using a Turbo Rock-Eval 6 device (Vinci Technologies). Sediment samples are submitted to two processes: pyrolysis and oxidation, respectively. First, during pyrolysis phase, carbon compounds were released from sediment by heating them from 300 to 650°C at a rate of 25 °C min^{-1} in an oxygen free atmosphere and quantification of hydrocarbon is carried out by a flame ionization detector (FID) while quantification of CO and CO_2 is carried out by an infrared detector (IR). The remaining organic and inorganic carbon content, called residual carbon, is further combusted in air from 300 - 850°C at a heat rate of 20 °C min^{-1}. The quantification is also made by an IR detector (Figure S1) (ESPITALIE et al., 1985; LAFARGUE et al., 1998; BEHAR et al., 2001; BAUDIN et al., 2015).

From RE analysis, the follow parameters were recorded/calculated, all from the pyrolysis phase:

- Pyrolyzed carbon (%PC): labile components of OM;
- Residual carbon (%RC): organic matter survive of pyrolysis;
- Total organic carbon (%TOC): sum all organic carbons (PC and RC);
- S1 (mg HC g^{-1} sediment): amount of free HC (gases and oil);
- S2 (mg HC g^{-1} sediment): amount HC released or potential hydrocarbon by kerogen cracking;
- S3 (mg CO_2 g^{-1} sediment): amount CO_2 released in pyrolysis;
- S3CO (mg CO g^{-1} sediment): amount CO released in pyrolysis;
- Hydrogen Index (mg HC g^{-1}TOC): quantity of pyrolyzable organic compounds in relation to TOC [(S2/TOC) x 100];
- Oxygen Index (mg HC g^{-1}TOC): quantify of S3 in relation TOC [(S3/TOC) x 100];
- Tmax (°C): maximum HC released in S2;
- MinC (%): amount of CO_2 released during pyrolysis and oxidation phases above 400°C and 600°C. respectively.

3 RESULTS AND DISCUSSION

Values of TOC, S1, S2, S3, Tmax, PC, RC, HI and OI from BTS cores were shown in Table S1, Table S2 and Figure S3.

3.1 SEDIMENTARY CHARACTERIZATION

In general, the sediments in cores from BTS consisted mainly of silt which favors organic matter preservation and suggests an environment with low hydrodynamic as already suggest by Hatje et al. (2019). More details regarding sedimentary characteristics of the samples were described in by Andrade et al, (2017).

3.2 TOC CONTENT: PYROLYZABLE X RESIDUAL CARBON

TOC values from Rock Eval analysis ranged from 0.63 to 2.74% in the sediment samples from Todos os Santos Bay and agree with values previously reported for the region (COSTA et al., 2011; DE SOUZA et al., 2017; HATJE et al., 2019). These values are characteristics of modern surface sediments (ORDONEZ et al., 2019) and consistent with an oligotrophic system with no severe anthropogenic influence (CIRANO & LESSA, 2007; LESSA & DIAS, 2009; HARE et al., 2014; PEREIRA et al., 2015; HATJE et al.,2019).

Rock Eval models prior RE6 were not a robust technique to measure TOC and these analyses were made, in general, by Elemental Analysis (EA) (BAUDIN et al., 2015). However, from model RE6, it is suggested that the TOC values provided can be reliable (DISNAR et al., 2003; MARCHAND et al., 2008; HARE et al., 2014). To test this hypothesis, the COT values generated by RE were compared with the TOC values generated by EA (ECS 4010 CHNS-O Analyzer Costech Instrument, Andrade et al., 2017). Statistically there is no difference between the two techniques ($p > 0.5$), as well as a good correlation ($r^2 = 0.95$) (Figure 2) was observed; even though RE values (Table S1) were slightly smaller than those generated by AE.

Differences in TOC values between the two techniques were also discussed by Dembicki (1992), Disnar et al. (2003). Hare et al. (2014) and Baudin et al. (2015), and may be related to: a) higher temperature reach by EA technique (1350°C) than RE (850°C) result in more complete burning of the MO; b) higher temperature can also result in loss of water

from the mineral matrix of clay-rich sediments (MATTHIESSEN et al., 2005; SMITH, 2003); c) FID has lower sensitivity to hydrogen-poor pyrolyzed compounds, thus, carbon-rich samples containing cellulose and other polysaccharides lose more easily theirs hydrogen as H_2O by dehydration reactions (DISNAR et al., 2013); and d) the presence of the mineral matrix, when associated to low TOC values (< 2%), can retains part of the material of S2 (HC generated from the decomposition of MO) and, consequently, decreases pyrolysis yield in S2 (DEMBICKI, 1992; PILLOT et al., 2013). BTS samples can be influenced by the hypotheses mentioned above, with the exception of hypothesis "d", since there is no interference of the mineral matrix in the samples (Fig 4 S2 x TOC).
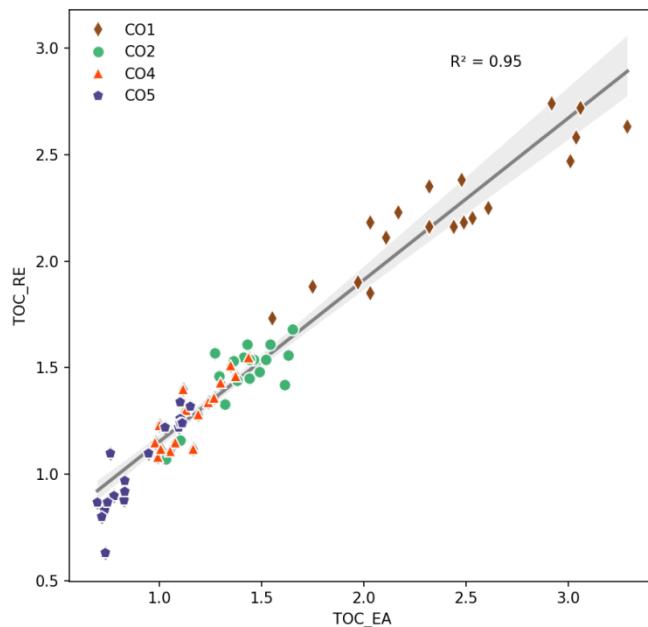
Figure 2: TOC content (%) in BTS sediments measured by Rock Eval Pyrolysis and Elemental Analysis.

Since TOC is the sum of pyrolyzed carbon (PC) plus residual carbon, it is possible to calculate the contribution of each of them. Overall RC represents around 83% of all TOC with values ranging from 76.2 to 87.9%. RC may be related to more resistant components of organic matter, such as cellulose and lignin, or possibly an indicative of the presence of black carbon (POOT et al., 2009; HARE et al., 2014; HATCHER et al., 2014; BAUDIN et al., 2015). The predominance of RC over PC was reported for other studies, such as Hare et al. (2004) and seems to be related to the input of terrigenous organic matter. Most labile components of PC, S1 e S2, presented low values and did not exceed 0.43 mg HC g^{-1}

sediment and 3.22 mg HC g^{-1} sediment, respectively, being S2 dominant in relation to S1 (Table S1). S1 and S2 values presented high positive linear correlation as well as S1 x S3 and S2 x S3 (Figure S2). However, when the S3 parameter is considered, there is a clear separation of CO01 from the other cores. Since S3 represents the oxygen-containing organic matter and CO01 was sampled close to the Paraguaçu River, main tributary to BTS, the separation appears to reflect the input of plant based OM (HARE et al., 2014). According to Affouri et al., 2017, a good correlation between S1x S2 suggests the presence of lipid compounds from local biomass.

S1, S2 and S3 values are relatively low in all cores (Table S1) and show a slightly gradual decrease toward the bottom (Figure S3), probably related to the digenetic processes that degrade or re-work the OM. It is especially noted for S1 and S2 values since they represent, respectively, the free hydrocarbon and low molecular weight compounds in the OM, and the relatively thermo-labile hydrogen rich OM; and all of them tend to degrade more efficiently during digenetic processes (SANEI et al., 2005; AFFOURI & SAHRAOUI, 2017). On the other hand, S3 represents more stable and resistant compounds rich in oxygen (HARE et al., 2014).

The values of MinC% at BTS were low (0.36 – 2.87%, Table S1), but consistent with that expected for a region with low occurrence of calcareous organisms (CRUZ, 2008 in HATJE & ANDRADE, 2009).

3.3 OM SOURCES AND STATE OF DEGRADATION

Hydrogen Index (HI) and Oxygen Index (OI) are determined from S2/TOC and S3/TOC ratios, respectively. HI refers to the amount of free hydrocarbons (mg HC g^{-1} TOC), especially those from hydrogen-rich OM, while OI refers to the amount of CO_2 released from OM (mg CO_2 g^{-1} TOC), reflecting the content of functional groups which preferably contains oxygen molecules (HATCHER et al., 2014).

Values of HI and OI for sediments from BTS ranged from 55 mg HC g^{-1} TOC to 128 mg HC g^{-1} TOC and from 145 mg CO_2 g^{-1} TOC to 350 mg CO_2 g^{-1}, respectively (Table S1). Even though HI values for all cores are low, they show a slight decrease downward suggesting dehydrogenation over time (Figure S3). For OI values all cores presented relatively constant profiles along the years, except for CO04 which presented a slight increase from the year 2000 to present (Figure S3).

HI values around 100 mg HC g^{-1} COT indicate an environment with a mixture of influences between marine and terrestrial, while the absence of HI value exceeding 200 mg HC g^{-1} COT suggest that no sample can be considered exclusively marine (HARE et al., 2014). Both are expected for a coastal bay such as BTS. Low values of HI can also indicate that the OM was not well preserved and suffered some degradation (HATCHER et al., 2014). Low values for HI/OI ratio (~0.45) also corroborate with these findings. Similar results (HI<150 mg HC g^{-1} TOC e HI/OI~0.5) were reported by Hare et al., (2014) in samples also close to river discharge from Hudson Bay, USA.

For studies of OM in recent sediments, the pseudo-Van Krevelen diagram can be applied to evaluate the sources and state of OM (DISNAR et al., 2003; BAUDIN et al., 2017). It describes HI and OI parameters in a manner akin to the atomic H/C and O/C ratios, respectively (HARE et al., 2014). In general, the organic matter may be classified in three types. Type I is related to OM from lacustrine origin, while type II represents marine materials derived from algae, hydrogen-rich and with higher proportions of aliphatic lipids. On the other hand, type III is characterized for oxygen-rich compounds, like cellulose and lignin, originating from land plants, but can also result from more degraded organic matter (MCCARTHY et al., 2011; AFFOURI & SAHRAOUI, 2017; BAUDIN et al., 2017).

Before applying the pseudo-Van Krevelen diagram for RE data or any interpretation using HI values, it is important to test if the mineral matrix is interfering with them, because they could be responsible for successive retention and dehydrogenation of pyrolysis products (LANGFORD & BLANC-VALLERON, 1990; HAZRA et al., 2018). The mineral matrix effect is indicated when the correlation curve of S2 x TOC intercepts the abscissa axis. However, if the correlation tends to the origin of the axis there is no significant mineral matrix effect and no alteration of HI values. This is the case for BTS samples (Figure S4). Additionally, the pseudo-Van Krevelen diagram also assumes that the OM thermal evolution is no further than moderate. Since Tmax values for all BTS samples were always low (377 - 427°C), the bulk OM did not undergo strong thermal maturation (PETERS, 1986) and the pseudo-Van Krevelen diagram can be used.

When RE values for BTS cores were plotted in a pseudo-Van Krevelen diagram (Figure 3), all samples were distributed in the type III, as already suggested by HI values. The predominance of terrestrial OM was specially expected for cores CO01, CO02 and CO04 due to their location close to river and/or mangrove areas. Even though high plants are poor in H-like compounds and rich in cellulose and lignin that result in low HI values, epicuticular wax

of terrestrial plants has H-rich compounds resulting in high HI values similar to those of algae (CARRIE et al., 2012; MCCARTHY et al., 2011; AFFOURI & SAHRAOUI, 2017). Therefore, the low values of HI in BTS samples could also be the result of OM oxidation that removes H-rich compounds at a greater rate than O-rich compounds (MARCHAND et al., 2008; HARE et al., 2014).
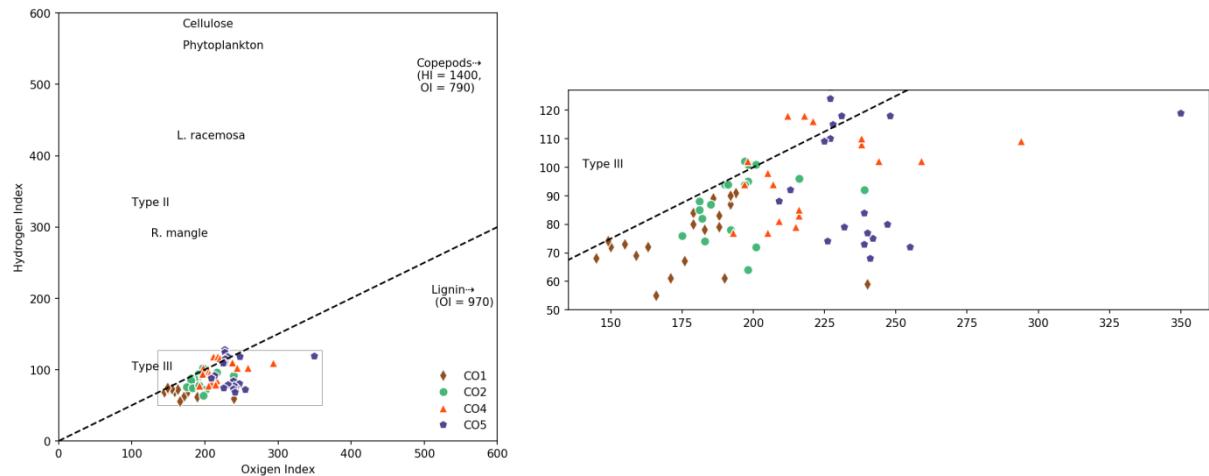

Figure 3: Pseudo-Van Krevelen-type diagram for sediments from BTS. Dashed line indicates HI/OI = 0.5. Values for cellulose.phytoplankton.copepods.and lignin are from Carrie et al.. 2012; Baudin et al. 2017.and for R. mangle and L. racemosa from. Type II and and Type III were defined according to Marchand et al.. 2008.

When HI and OI values from BTS samples were compared with those from pure biochemical compounds and biological standards and samples (CARRIE et al., 2012; MARCHAND et al., 2008; AFFOURI & SAHRAOUI., 2017), results indicated that the OM suffered alteration during transport and/or deposition. One important source of terrestrial OM to BTS is the mangroves (NASCIMENTO et al., 2017), but HI values from leaves and woods of mangrove species are much higher than those detected in BTS sediments and OI values are slightly lower (MARCHAND et al., 2008). Such differences can result from alteration during transport and deposition. For example, even though core CO01 is under the influence of the Paraguaçu River that has many mangrove forests, most of it is located in the Iguape Bay that also works as a buffer reducing the transport of material to the BTS (ANDRADE et al., 2017) and allowing more time for OM to be altered. Since a similar pattern is observed for HI and OI values for phytoplankton and zooplankton samples (CARRIE et al., 2012), it is no surprise that even for core CO05, where the marine influence is greater, some OM reworking is suggested.

Besides pseudo-Van Krevelen diagram to study OM nature from RE parameters, the S2xTOC (Figure 4) plot is also recommended (LANGFORD & BLANC-VALLERON, 1990; DAHL et al., 2004). In the S2-TOC cross-plot (Figure 4), two groups can be distinguished: a) BTS samples with TOC >2% from core CO01 distributed between the two lines that present typical values for type III OM (HI = 50 - 100 mg HC g^{-1} TOC); and b) samples from cores CO02, CO04 and CO05, distributed along lines with HI values from 50 to 150 mg HC g^{-1} TOC and with lower TOC values. It suggests that, although almost all samples are classified as type III, CO01 core received a larger contribution from terrestrial sources or has more reworked OM when compared to other cores.
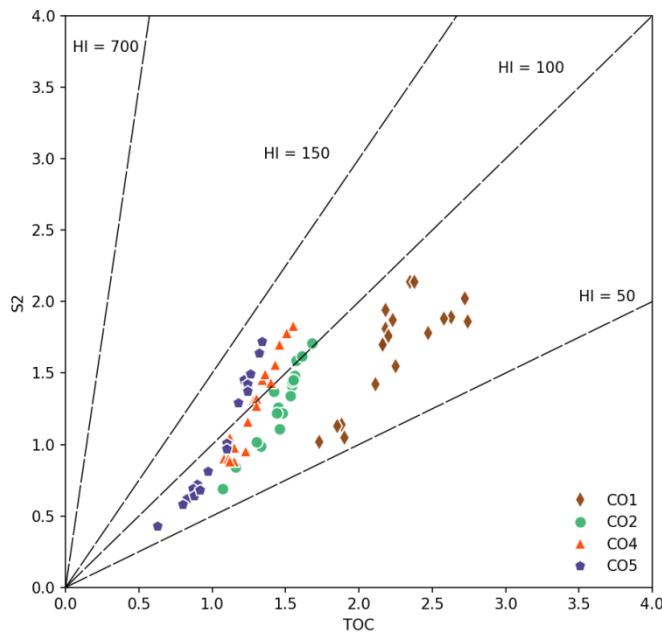
Figure 4: Cross-plot of S2 and TOC in BTS sediments. Dashed lines represent HI values.

Galimov (2004) and Hare et al (2014) used the HI/OI x $\delta^{13}C$ plot to explore sources of OM for a given region. In general, terrigenous OM presents low values of HI/OI and $\delta^{13}C$, while marine OM presents high values for these parameters. For BTS samples (Figure 5) and as reported by Leonel et. (in preparation), $\delta^{13}C$ values clearly separate BTS core in three groups: from CO01 with terrigenous predominance, to CO05 with marine predominance and CO02 and CO04 as a mixture of both OM sources. However, HI/OI did not show any similar distinction, with similar values among core. According to Galimov (2004), high values of $\delta^{13}C$ (~ -21‰ a -20‰) with low values of HI/OI (~ 0.5) may be associated

with the oxidative diagenesis process, in which part of the organic carbon is oxidized to CO_2 with preferential loss of H-rich moieties, but also with some oxygen atoms incorporation into the remaining organic compounds.
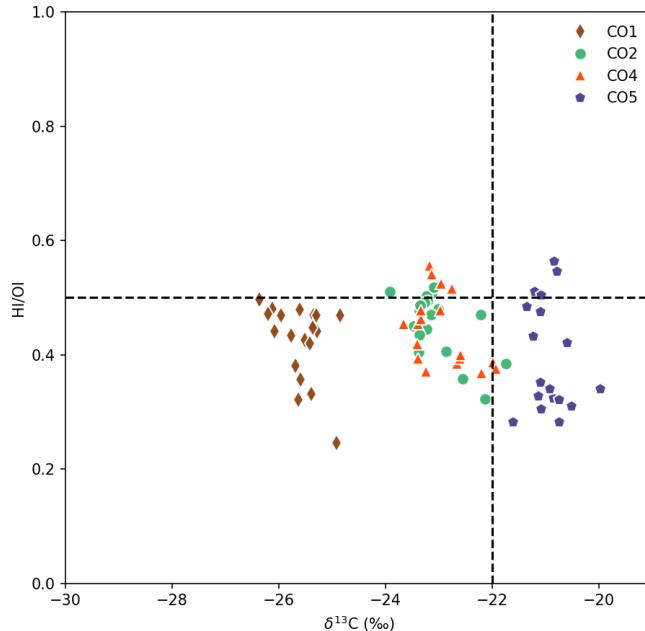
Figure 5: HI/OI x $\delta^{13}C$ for sediments in BTS. The vertical dashed line indicates $\delta 13C$ = -22‰, which represents the separation between marine and terrigenous isotopic signature, and the horizontal dashed line indicates HI/OI = 0.5.

Tmax is the temperature that occurs the maximum yield of hydrocarbons during the pyrolysis in S2, resulting from OM cracking. This parameter represents the thermal stability of organic compounds from original OM, providing information about their maturation state (HARE et al., 2014; BAUDIN et al., 2015).

According to DISNAR et al. (2003) values between 320-390°C are typical from thermal breakdown of biological compounds, such as lignin and polysaccharides, whereas between 420-470°C are typical from breakdown of immature humic substances. Besides, AFFOURI & SAHRAOUI, (2017) reported that values ≤ 440°C are associated with immature OM recently deposited and still in the beginning of its diagenesis. Tmax values in BTS sediments ranged from 377 to 427°C among the cores, with most temperatures higher than 400°C (Table S1; Figure 6). Therefore, Tmax values in the BTS suggest OM suffering recent diagenesis, as expected for recent sediments.

The fact that the recorded values are not close to those of autochthonous sources, together with C/N ratio and $\delta^{13}C$ data, suggests that BTS is an oligotrophic system (MARCHAND et al., 2008; HARE et al., 2014; BAUDIN et al., 2017). Some values of Tmax and OI recorded by Hare et al. (2014) in an oligotrophic area in HB, were similar to those at BTS.
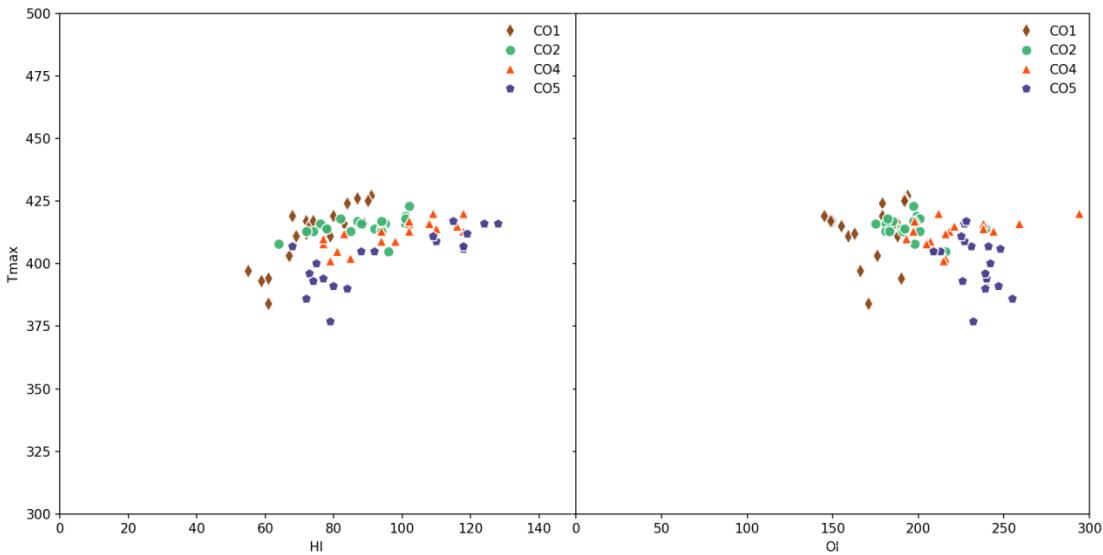
Figure 6: Tmax as a function of HI and OI in BTS sediments.

3.4 GENERAL CHARACTERISTICS IN BTS

Core CO01 showed the most distinct results probably due to its proximity to Paraguaçu River and, consequently, the area with the largest terrigenous influence. Paraguaçu River has both biological and social importance, because it has an extensive area of mangroves and provides a source of food and income through consumption and commercialization of fish and agropecuary activities (HATJE & ANDRADE, 2009). The major changes in the area happened after 1950 when two shipyards (CSRP and EIN) and a dam (Pedra do Cavalo Dam) were installed in the region (Figure 1). Overall CSRP (~1975) and PC Dam (1985) did not result in significant changes in RE parameters, except for a small increase in S1, S2 and H1 values. On the other hand, a spike in values for S1, S2, S3, PC and RC could be related to EIN (~2011) construction. Similar results were reported for ANDRADE et al. (2017) regarding trace elements analysis.

Even though RE parameters suggest a greater influence of terrigenous OM in core CO01 due to its proximity to Paraguaçu River, they also suggest that the material did not promptly reach BTS and suffers some degradation before being buried in the sediment. Without the influence of Paraguaçu River, cores CO02, CO04 and CO05 show lower values of TOC, still have some influence from terrigenous sources, probably due to their proximity to mangrove areas.

Cores CO02, CO04 and CO05 show an increase in S1 and S2 values since 1990, when all main anthropogenic sources were already well installed in the BTS region.

Therefore, it would be difficult to associate any change in RE parameters with a specific industry or construction. Since only data from the pyrolysis phase were used in this study, it is suggested that data from residual carbon, such as black carbon, should be included in future studies to detect anthropogenic influences regarding historic changes in BTS. Another hypothesis for not identifying the anthropic influence may be related to the internal hydrodynamics of the BTS. The less fluvial influence and the internal circulation forced by tides, causes a great exchange of water between the bay and the ocean, suggesting that possibly this material is transported out of the bay.

4 CONCLUSION

The Rock Eval technique initially developed for the petroleum geochemistry studies is being used to characterize organic matter in ancient and recent sediments. This technique proved to be a useful tool to determine content, sources, and state of degradation of organic matter as shown in analysis performed in sediment from BTS.

Van Krevelen-type diagram and HI/OI x δ^{13}C distribution indicates OM with significant terrigenous source influence for CO01, CO02 and CO04 cores, while CO05 core presents a larger mixture with OM from marine sources. Low Tmax and OI values indicate that OM suffered recent diagenesis, with some samples presenting similar values to those of mangrove plant species.

Although BTS suffered an intensification of human activities from mid-1900, the hypothesis relating the changes in the sources of OM from adjacent aquatic environments that results in a higher input of free hydrocarbons and residual carbon was not validated. RE parameters remained relatively constant over time and showed no changes in the sources of organic matter for BTS.

5 ACKNOWLEDGMENTS

6 REFERENCES

AFFOURI, H.; SAHROUI, O. The sedimentary organic matter from a Lake Ichkeul core (far northern Tunisia): Rock-Eval and biomarker approach. **Journal of African Earth Sciences**, 2017.

ANDRADE, R. L. B. et al. Chronology of anthropogenic impacts reconstructed from sediment records of trace metals and Pb isotopes in Todosos Santos Bay (NE Brazil). **Marine Pollution Bulletin**, v. 125, n. 1–2, p. 459–471, 2017.

ARBI, Iman et al. Detection of terrigenous and marine organic matter flow into a eutrophic semi-enclosed bay by $\delta 13C$ and $\delta 15N$ of intertidal macrobenthos and basal food sources. **Science of the Total Environment**, v. 613, p. 847-860, 2018.

ARNDT, Sandra et al. Quantifying the degradation of organic matter in marine sediments: a review and synthesis. **Earth-science reviews**, v. 123, p. 53-86, 2013.

BAUDIN, François et al. Guidelines for Rock–Eval analysis of recent marine sediments. **Organic Geochemistry**, v. 86, p. 71-80, 2015.

BAUDIN, François et al. Origin and distribution of the organic matter in the distal lobe of the Congo deep-sea fan–A Rock-Eval survey. **Deep Sea Research Part II: Topical Studies in Oceanography**, v. 142, p. 75-90, 2017.

BIANCHI, T. S. Biogeochemistry of Estuaries: Oxford University Press. 2006.

BIANCHI, Thomas S.; CANUEL, Elizabeth A. **Chemical biomarkers in aquatic ecosystems**. Princeton University Press, 2011.

BUENO, C. et al. Anthropogenic and natural variability in the composition of sedimentary organic matter of the urbanised coastal zone of Montevideo (Río de la Plata). **Marine Pollution Bulletin**, v. 126, p. 197-203, 2018.

BURDIGE, David J. Burial of terrestrial organic matter in marine sediments: A re-assessment. Global Biogeochemical Cycles, v. 19, n. 4, 2005.

CANUEL, Elizabeth A.; HARDISON, Amber K. Sources, ages, and alteration of organic matter in estuaries. **Annual review of marine science**, v. 8, p. 409-434, 2016.

CARRIE, Jesse; SANEI, Hamed; STERN, Gary. Standardisation of Rock–Eval pyrolysis for the analysis of recent sediments and soils. **Organic Geochemistry**, v. 46, p. 38-53, 2012.

CIRANO, Mauro; LESSA, Guilherme Camargo. Oceanographiccharacteristicsof Baía de Todos os Santos, Brazil. **Revista Brasileira de Geofísica**, v. 25, n. 4, p. 363-387, 2007.

COSTA, A. B. et al. Characterization of organic matter in sediment cores of the Todosos Santos Bay, Bahia, Brazil, by elemental analysis and 13C NMR. **Marine pollutionbulletin**, v. 62, n. 8, p. 1883-1890, 2011.

CRUZ, Igor Cristino Silva. **Recifes de corais da Baía de Todos os Santos, caracterização, avaliação e identificação de áreas prioritárias para conservação**. 2008. Tese de Doutorado. Dissertação de Mestrado, 102 p., Universidade Federal da Bahia, BA, Brasil.(não publicado).

DAHL, Birger et al.A new approach to interpreting Rock-Eval S2 and TOC data for kerogen quality assessment.**OrganicGeochemistry**, v. 35, n. 11-12, p. 1461-1477, 2004.

DE SOUZA, José Roberto Bispo et al. Geochemical markers of sedimentary organic matter in Todosos Santos Bay, Bahia–Brazil. Indicators of sources and preservation. **Marine pollution bulletin**, v. 119, n. 2, p. 239-246, 2017.

DE SOUZA, José Roberto Bispo et al. Geochemical markers of sedimentary organic matter in Todosos Santos Bay, Bahia–Brazil. Indicators of sources and preservation. **Marine pollution bulletin**, v. 119, n. 2, p. 239-246, 2017.

DEMBICKI JR, H. The effects of the mineral matrix on the determination of kinetic parameters using modified Rock Eval pyrolysis. **Organic Geochemistry**, v. 18, n. 4, p. 531-539, 1992.

DISNAR, Jean-Robert et al. Soil organic matter (SOM) characterization by Rock-Eval pyrolysis: scope and limitations. **Organicgeochemistry**, v. 34, n. 3, p. 327-343, 2003.

ESPITALIE, J.; DEROO, G.; MARQUIS, Fernand. Rock-Eval pyrolysis and its applications.**Revue De L InstitutFrancais Du Petrole**, v. 40, n. 5, p. 563-579, 1985.

GALIMOV, E. M. The pattern of δ13Corg versus HI/OI relation in recent sediments as an indicator of geochemical regime in marine basins: Comparison of the Black Sea, Kara Sea, and Cariaco Trench. **Chemical Geology**, v. 204, n. 3-4, p. 287-301, 2004.

HARE, A. A. et al. Organic Geochemistry Characterization of sedimentary organic matter in recente marine sediments from Hudson Bay, Canada, by Rock-Eval pyrolysis.**ORGANIC GEOCHEMISTRY**, V. 68, p. 52-60, 2014.

HATCHER, P. G. et al. Organic Geochemistry Diagenesis of organic matter in a 400 m organic rich sediment core from offshore Namibia using solid state 13 C NMR and FTIR.**ORGANIC GEOCHEMISTRY**, v. 75, p. 8–23, 2014.

HATJE, V. et al. Historical records of mercury deposition in dated sediment cores reveal the impacts of the legacy and present-day human activities in Todosos Santos Bay, Northeast Brazil. **Marine pollution bulletin**, v. 145, p. 396-406, 2019.

HATJE, Vanessa; ANDRADE, Jailson B. de. **Baía de Todos os Santos: aspectos oceanográficos**. EDUFBA, 2009.

HATJE, Vanessa; BARROS, Francisco. Overview of the 20th century impact of trace metal contamination in the estuaries of Todosos Santos Bay: past, present and future scenarios. **Marine pollution bulletin**, v. 64, n. 11, p. 2603-2614, 2012.

HEDGES, J. I.; OADES, J. M. Comparative organic geochemistries of soils and marine sediments.**Organicgeochemistry**, v. 27, n. 7-8, p. 319-361, 1997.

HEDGES, John I.; KEIL, Richard G. Sedimentary organic matter preservation: an assessment and speculative synthesis. **Marine chemistry**, v. 49, n. 2-3, p. 81-115, 1995.

IBGE. Disponível em <https://ww2.ibge.gov.br/home/estatistica/populacao/estimativa2015/estimativa_tcu.shtm> Acesso em 07/06/2018.

KILLOPS, S.; KILLOPS, V. Introduction to Organic Geochemistry, 2nd edn (paperback). **Geofluids**, v. 5, n. 3, p. 236-237, 2005.

KRISTENSEN, Erik et al. Organic carbon dynamics in mangrove ecosystems: a review. **Aquatic botany**, v. 89, n. 2, p. 201-219, 2008.

LAFARGUE, E.; MARQUIS, F.; PILLOT, D. Rock-Eval 6 applications in hydrocarbon exploration, production, and soil contamination studies. **Revue de l'institutfrançais du pétrole**, v. 53, n. 4, p. 421-437, 1998.

LANGFORD, F. F.; BLANC-VALLERON, M.-M.Interpreting Rock-Eval pyrolysis data using graphs of pyrolizable hydrocarbons vs. total organic carbon (1).**AAPG bulletin**, v. 74, n. 6, p. 799-804, 1990.

LEÃO, Zelinda MAN; DOMINGUEZ, José ML. Tropical coast of Brazil. **Marine Pollution Bulletin**, v. 41, n. 1-6, p. 112-122, 2000.

LESSA, Guilherme C. et al. The tides and tidal circulation of Todosos Santos Bay, Northeast Brazil: a general characterization. **Anais da Academia Brasileira de Ciências**, v. 73, n. 2, p. 245-261, 2001.

LESSA, Guilherme; DIAS, Kalina. Distribuição espacial das litofácies de fundo da Baía de Todos os Santos. **Quaternary and Environmental Geosciences**, v. 1, n. 2, 2009.

LIAO, Weisen et al. Sources and distribution of sedimentary organic matter in the Beibu Gulf, China: Application of multiple proxies. **Marine Chemistry**, 2018.

Lima, G. M. P. e Lessa, G. C. (2002) The freshwater discharge in Todosos Santos Bay and its significance to the general water circulation. **Revista Pesquisas**. Porto Alegre (RS), v. 28, p. 85-98.

MARCHAND, C.et al. Organic carbon sources and transformations in mangrove sediments: A Rock-Eval pyrolysis approach. **ORGANIC GEOCHEMISTRY**, v. 32, p. 408-421, 2008.

MATTHIESSEN, Mark K. et al. Influence of loss-on-ignition temperature and heating time on ash content of compost and manure. **Communications in soil science and plant analysis**, v. 36, n. 17-18, p. 2561-2573, 2005.

MCCARTHY, Kevin et al. Basic petroleum geochemistry for source rock evaluation. **Oilfield Review**, v. 23, n. 2, p. 32-43, 2011.

MEYERS, Philip A. Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. **Organicgeochemistry**, v. 34, n. 2, p. 261-289, 2003.

MEYERS, Philip A. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes.**Organic geochemistry**, v. 27, n. 5-6, p. 213-250, 1997.

MEYERS, Philip A. Preservation of elemental and isotopic source identification of sedimentary organic matter. **Chemicalgeology**, v. 114, n. 3-4, p. 289-302, 1994.

OLIVEIRA, W. F. Evolução Sócio-Econômica do Recôncavo Baiano. **Germen/UFBA-NIMA. Baía de Todos os Santos–DiagnósticoSócio-Ambiental e Subsídios para a Gestão. Parte I. Cap**, v. 3, p. 43-56, 1997.

ORDOÑEZ, Luis et al. Empowering conventional Rock-Eval pyrolysis for organic matter characterization of the siderite-rich sediments of Lake Towuti (Indonesia) using End-Member Analysis. **OrganicGeochemistry**, v. 134, p. 32-44, 2019.

PEREIRA, Taís de S. et al. Distribution and ecotoxicology of bioavailable metals and As in surface sediments of Paraguaçu estuary, Todosos Santos Bay, Brazil. **Marine pollution bulletin**, v. 99, n. 1-2, p. 166-177, 2015.

PETERS, K. E. Guidelines for evaluating petroleum source rock using programmed pyrolysis. **AAPG bulletin**, v. 70, n. 3, p. 318-329, 1986.

PETERS, Kenneth E.; WALTERS, C. C.; MOLDOWAN, J. M. The biomarker guide: Biomarkers and isotopes in the environment and human history, Vol. 1. **Cambridge, New York**, 2005.

PETROBRAS. Disponível em <http://www.petrobras.com.br/pt/nossas-atividades/principais-operacoes/refinarias/refinaria-landulpho-alves-rlam.html> Acesso em 07/06/18.

PILLOT, Daniel; DEVILLE, Eric; PRINZHOFER, Alain. Identification and quantification of carbonate species using Rock-Eval pyrolysis. **Oil & Gas Science and Technology–Revue d'IFP Energies nouvelles**, v. 69, n. 2, p. 341-349, 2014.

POOT, A. et al. Quantification methods of Black Carbon : Comparison of Rock-Eval analysis with traditional methods. **JournalofChromatography A**, v. 1216, p. 613–622, 2009.

SANEI, H.; STASIUK, L. D.; GOODARZI, F. Petrological changes occurring in organic matter from recent lacustrine sediments during thermal alteration by Rock-Eval pyrolysis. **Organic Geochemistry**, v. 36, n. 8, p. 1190-1203, 2005.

SETUR; Disponível em <http://www.setur.ba.gov.br/> Acesso em 07/06/18.

SILVA, Alex de Souza. **A influência do Centro Industrial do Subaé (CIS) no processo de urbanização do bairro do Tomba: um estudo de caso no município de Feira de Santana**. 2010. Tese de Doutorado. Dissertação de Mestrado. Salvador: Universidade Salvador.

SMITH, Jamie G. Aspects of the loss-on-ignition (loi) technique in the context of clay-rich, glaciolacustrine sediments. **GeografiskaAnnaler: Series A, PhysicalGeography**, v. 85, n. 1, p. 91-97, 2003.

SOUZA, Diego Silva de. **Centro industrial de Aratu: uma história cronológica de vicissitudes.**2014. Monografia. Faculdade de economia da Universidade Federal da Bahia.

SUN, Ming-Yi; WAKEHAM, Stuart G. Molecular evidence for degradation and preservation of organic matter in the anoxic Black Sea Basin.**GeochimicaetCosmochimicaActa**, v. 58, n. 16, p. 3395-3406, 1994.

THORNTON, S. F.; MCMANUS, J. Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: evidence from the Tay Estuary, Scotland. **Estuarine, Coastal and Shelf Science**, v. 38, n. 3, p. 219-233, 1994.

TISSOT, Bernard P.; WELTE, Dietrich H.From kerogen to petroleum. In: **Petroleum formation and occurrence**. Springer, Berlin, Heidelberg, 1984. p. 160-198.

VOLKMAN, John K. et al. Microalgal biomarkers: a review of recent research developments. **Organic Geochemistry**, v. 29, n. 5-7, p. 1163-1179, 1998.

ZONNEVELD, K. A. F. et al. Selective preservation of organic matter in marine environments; processes and impact on the sedimentary record. **Biogeosciences**, v. 7, n. 2, p. 483-511, 2010.

SUPLEMENTARY MATERIAL

Table S1. Rock Eval parameters from Todos os Santos Bay

Core	Year	S1 (mg HC g⁻¹)	S2 (mg HC g⁻¹)	S3 (mg HC g⁻¹)	PC (%)	RC (%)	TOC (%)	HI (mg HC g⁻¹ TOC)	OI (mg CO₂ g⁻¹ TOC)	Tmax (°C)	MinC (%)	EA
CO01	2012	0.18	2.14	4.55	0.39	1.96	2.35	91	194	427	0.45	2,32
CO01	2009	0.25	3.22	7.09	0.59	3.11	3.70	87	192	426	0.71	2,15
CO01	2005	0.18	2.14	4.58	0.39	1.99	2.38	90	192	425	0.44	2,48
CO01	2002	0.15	1.81	4.10	0.34	1.84	2.18	83	188	416	0.40	2,49
CO01	1995	0.16	1.87	4.00	0.35	1.88	2.23	84	179	424	0.40	2,17
CO01	1989	0.15	1.76	3.93	0.34	1.86	2.20	80	179	419	0.38	2,53
CO01	1981	0.14	1.69	3.96	0.33	1.83	2.16	78	183	414	0.43	2,32
CO01	1970	0.18	1.70	4.05	0.32	1.84	2.16	79	188	411	0.47	2,44
CO01	1960	0.12	1.42	3.71	0.29	1.82	2.11	67	176	403	0.45	2,11
CO01	1950	0.18	1.94	4.06	0.36	1.82	2.18	89	186	416	0.44	2,03
CO01	1934	0.10	1.14	3.22	0.25	1.63	1.88	61	171	384	0.60	1,75
CO01	1918	0.12	1.13	3.52	0.25	1.60	1.85	61	190	394	0.61	2,03
CO01	1891	0.10	1.05	3.15	0.23	1.67	1.90	55	166	397	0.72	1,97
CO01	1861	0.14	1.02	4.15	0.25	1.48	1.73	59	240	393	0.91	1,55
CO01	1827	0.12	1.55	3.58	0.30	1.95	2.25	69	159	411	1.10	2,61
CO01	1796	0.14	1.86	3.98	0.34	2.40	2.74	68	145	419	0.85	2,92
CO01	1763	0.16	1.78	4.02	0.33	2.14	2.47	72	163	412	1.00	3,01
CO01	1731	0.16	1.89	3.94	0.34	2.29	2.63	72	150	417	1.06	3,29
CO01	1692	0.17	1.88	4.00	0.34	2.24	2.58	73	155	415	1.17	3,04
CO01	1661	0.15	2.02	4.06	0.36	2.36	2.72	74	149	417	1.06	3,06
CO02	2014.5	0.16	1.63	3.20	0.29	1.32	1.61	101	199	419	0.51	1,43

CO02	2014.2	0.15	1.59	3.11	0.28	1.29	1.57	101	198	416	0.46	1,27
CO02	2013	0.14	1.37	3.07	0.25	1.17	1.42	96	216	405	0.50	1,61
CO02	2012.6	0.15	1.62	3.23	0.28	1.33	1.61	101	201	418	0.49	1,54
CO02	2012	0.14	1.71	3.31	0.29	1.39	1.68	102	197	423	0.42	1,65
CO02	2011	0.13	1.48	3.09	0.26	1.30	1.56	95	198	416	0.43	1,63
CO02	2010	0.18	1.41	3.68	0.28	1.26	1.54	92	239	414	0.36	1,46
CO02	2009	0.13	1.45	2.92	0.26	1.28	1.54	94	190	414	0.41	1,44
CO02	2008	0.11	1.44	2.94	0.26	1.28	1.54	94	191	413	0.44	1,52
CO02	2007	0.13	1.45	3.06	0.26	1.29	1.55	94	197	417	0.43	1,41
CO02	2006	0.12	1.26	2.68	0.23	1.22	1.45	87	185	417	0.40	1,44
CO02	2005	0.13	1.34	2.77	0.25	1.28	1.53	88	181	416	0.40	1,36
CO02	2003	0.12	1.22	2.70	0.23	1.25	1.48	82	182	418	0.40	1,49
CO02	2001	0.11	1.22	2.61	0.22	1.22	1.44	85	181	413	0.42	1,38
CO02	1999	0.10	1.11	2.55	0.22	1.24	1.46	76	175	416	0.39	1,29
CO02	1996	0.09	0.99	2.44	0.20	1.13	1.33	74	183	413	0.44	1,32
CO02	1994	0.09	1.02	2.49	0.20	1.10	1.30	78	192	414	0.43	1,13
CO02	1991	0.08	0.84	2.33	0.18	0.98	1.16	72	201	413	0.50	1,10
CO02	1988	0.06	0.69	2.12	0.16	0.91	1.07	64	198	408	0.60	1,03
CO04	2014	0.18	1.83	3.29	0.30	1.25	1.55	118	212	420	0.82	1,44
CO04	2013	0.18	1.78	3.29	0.30	1.21	1.51	118	218	413	0.82	1,35
CO04	2012	0.16	1.70	3.23	0.29	1.17	1.46	116	221	415	0.86	1,37
CO04	2011	0.23	1.56	4.21	0.30	1.13	1.43	109	294	420	0.73	1,30
CO04	2009	0.17	1.45	3.19	0.25	1.09	1.34	108	238	416	0.85	1,24
CO04	2007	0.16	1.49	3.24	0.26	1.10	1.36	110	238	414	0.81	1,27
CO04	2005	0.14	1.31	3.32	0.25	1.03	1.28	102	259	416	0.85	1,19
CO04	2003	0.14	1.32	3.17	0.24	1.06	1.30	102	244	413	0.80	1,12
CO04	2000	0.13	1.43	2.77	0.24	1.16	1.40	102	198	417	0.69	1,11
CO04	1996	0.13	1.27	2.67	0.22	1.08	1.30	98	205	409	0.68	1,13

CO04	1992	0.10	1.16	2.44	0.21	1.03	1.24	94	197	413	0.62	1,10
CO04	1988	0.10	1.05	2.32	0.19	0.93	1.12	94	207	409	0.73	1,16
CO04	1977	0.08	0.90	2.33	0.18	0.90	1.08	83	216	412	0.42	0,99
CO04	1972	0.09	0.98	2.48	0.20	0.95	1.15	85	216	402	0.38	1,08
CO04	1967	0.08	0.90	2.32	0.18	0.93	1.11	81	209	405	0.51	1,05
CO04	1962	0.08	0.88	2.36	0.18	0.97	1.15	77	205	408	0.44	0,98
CO04	1958	0.08	0.88	2.41	0.18	0.94	1.12	79	215	401	0.55	1,00
CO04	1952	0.08	0.95	2.38	0.19	1.04	1.23	77	193	410	0.47	1,00
CO05	2013	0.15	1.72	3.04	0.29	1.05	1.34	128	227	416	1.62	1,10
CO05	2011	0.16	1.64	2.99	0.28	1.04	1.32	124	227	416	1.61	1,15
CO05	2008	0.14	1.44	3.02	0.26	0.96	1.22	118	248	406	1.73	1,03
CO05	2004	0.19	1.45	4.27	0.29	0.93	1.22	119	350	412	1.64	1,09
CO05	1999	0.15	1.49	2.91	0.26	1.00	1.26	118	231	407	1.59	1,10
CO05	1995	0.13	1.42	2.83	0.25	0.99	1.24	115	228	417	1.67	1,10
CO05	1990	0.13	1.37	2.82	0.24	1.00	1.24	110	227	409	1.46	1,11
CO05	1984	0.14	1.29	2.66	0.24	0.94	1.18	109	225	411	1.61	nan
CO05	1963	0.11	1.01	2.34	0.20	0.90	1.10	92	213	405	1.56	0,95
CO05	1947	0.09	0.81	2.32	0.17	0.80	0.97	84	239	390	1.58	0,83
CO05	1932	0.09	0.72	2.22	0.16	0.74	0.90	80	247	391	1.66	0,77
CO05	1911	0.09	0.97	2.30	0.18	0.92	1.10	88	209	405	0.45	0,76
CO05	1887	0.06	0.62	2.01	0.15	0.68	0.83	75	242	400	1.97	0,73
CO05	1862	0.08	0.67	2.09	0.16	0.71	0.87	77	240	394	1.93	0,70
CO05	1837	0.06	0.58	2.04	0.14	0.66	0.80	72	255	386	1.93	0,72
CO05	1813	0.08	0.69	2.02	0.16	0.71	0.87	79	232	377	1.90	0,74
CO05	1789	0.06	0.64	2.10	0.15	0.73	0.88	73	239	396	1.85	0,83
CO05	1757	0.07	0.68	2.08	0.16	0.76	0.92	74	226	393	1.95	0,83
CO05	1732	0.06	0.43	1.52	0.11	0.52	0.63	68	241	407	2.87	0,73

Table S2. Maximum and minimum of the parameters values of each core in BTS.

	COT(%) - RE		COT(%) - AE		MinC(%)		HI (mg HC g^{-1})		OI (mg CO2 g^{-1})		Tmax (°C)	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
CO01	1,73	3,7	1,55	3,29	0,38	1,17	50	95	140	240	384	427
CO02	1,07	1,03	1,03	1,65	0,36	0,6	60	100	160	220	405	423
CO04	1,08	0,98	0,98	1,44	0,38	0,86	70	120	150	290	401	420
CO05	0,63	0,7	0,7	1,15	0,45	2,87	65	130	200	250	377	417

Table S3. Details of cores collected in BTS.

Core	Depth water column (m)	Long	Lat	Number of samples
CO01	9.8	-38.742.305	-12.811.794	20
CO02	7.7	-38.663.694	-12.729.472	19
CO04	6.6	-38.507.722	-12.755.416	18
CO05	8.9	-38.577.833	-12.759.583	19
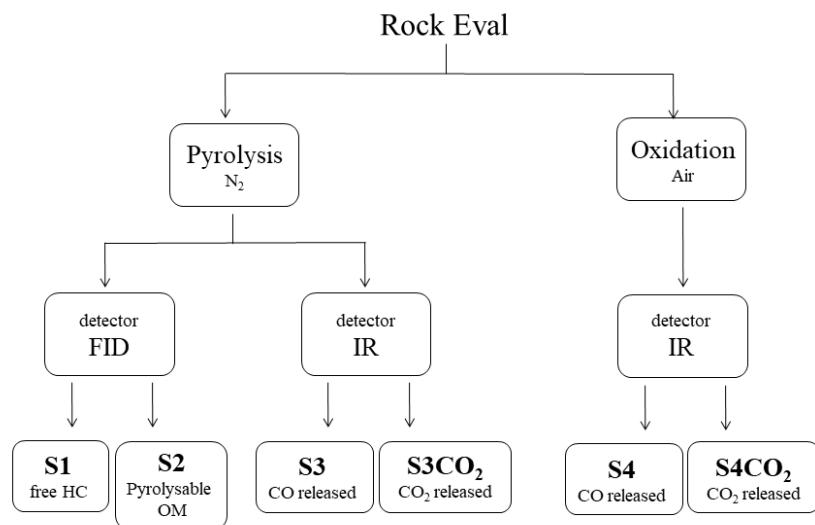
Figure S1: Main parameters generated by Rock Eval 6
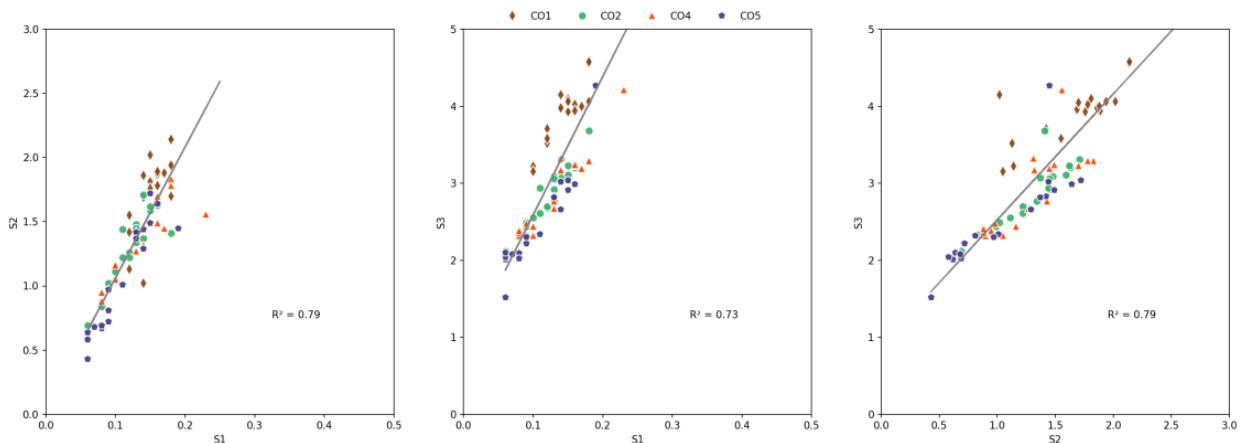
Figure S2. Correlations between S1xS2. S1xS3 and S2xS2. S1: free hydrocarbons in the sample (mg HC g^{-1} sediment). S2: amount of potential hydrocarbons (S2. mg HC g^{-1} sediment). S3: amount of CO_2 (mg CO_2 g^{-1} sediment).

A)
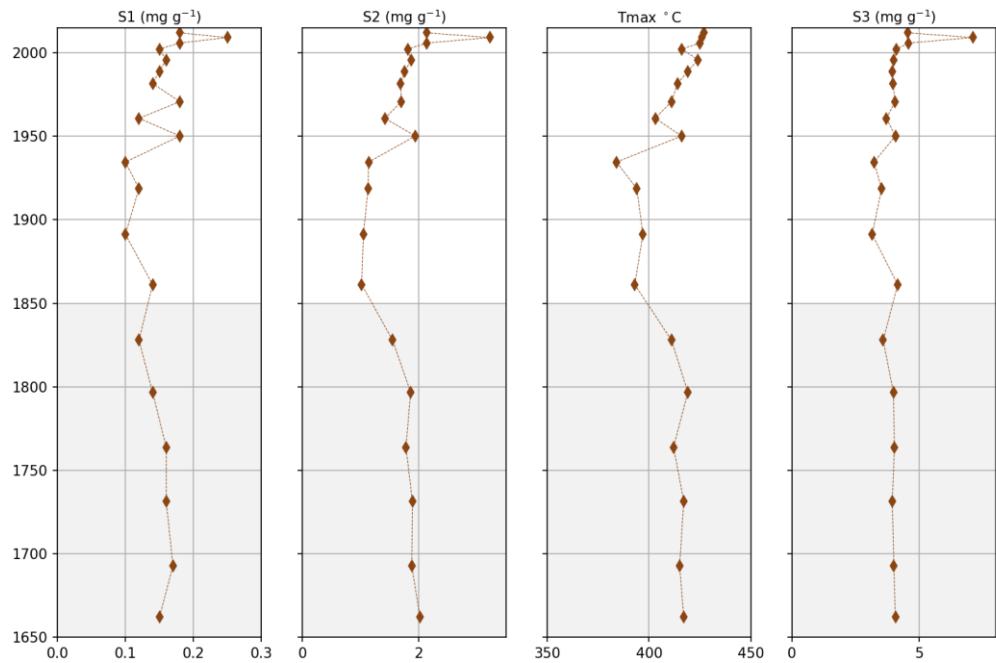

B)
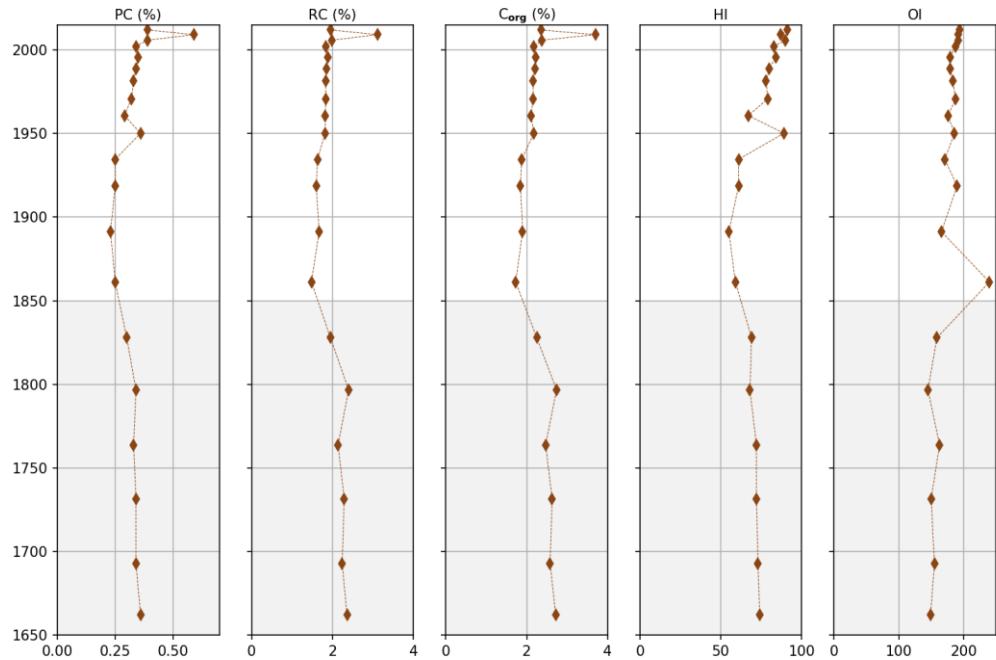
C)
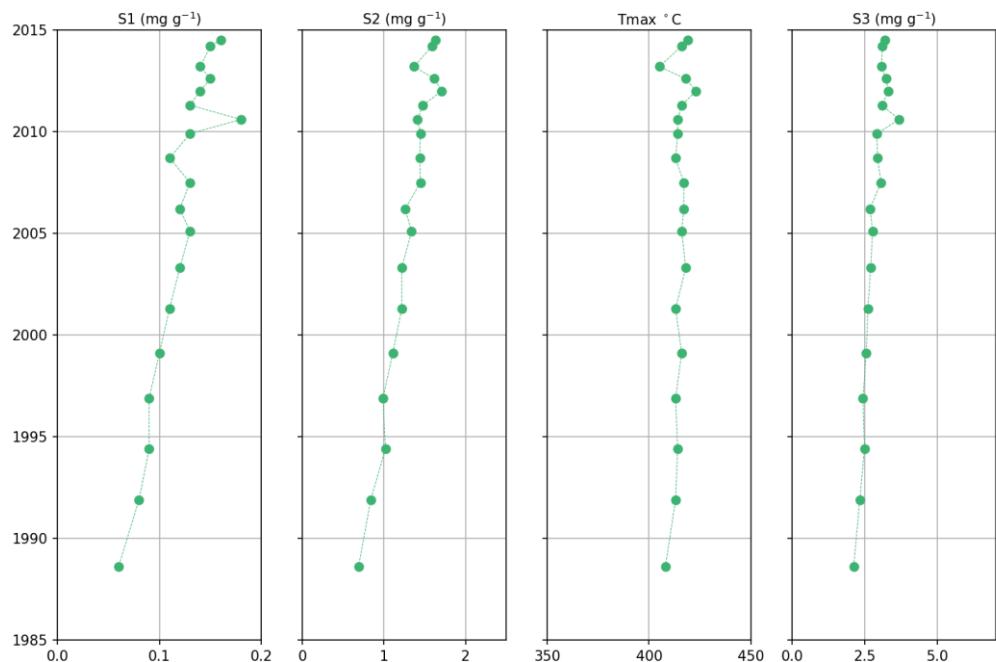
D)
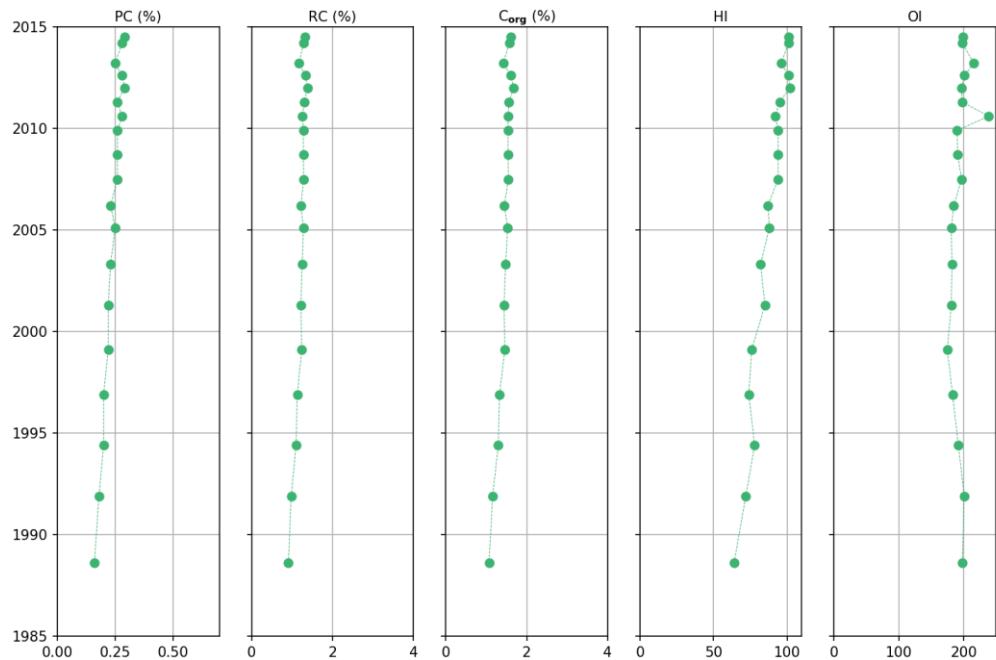
E)
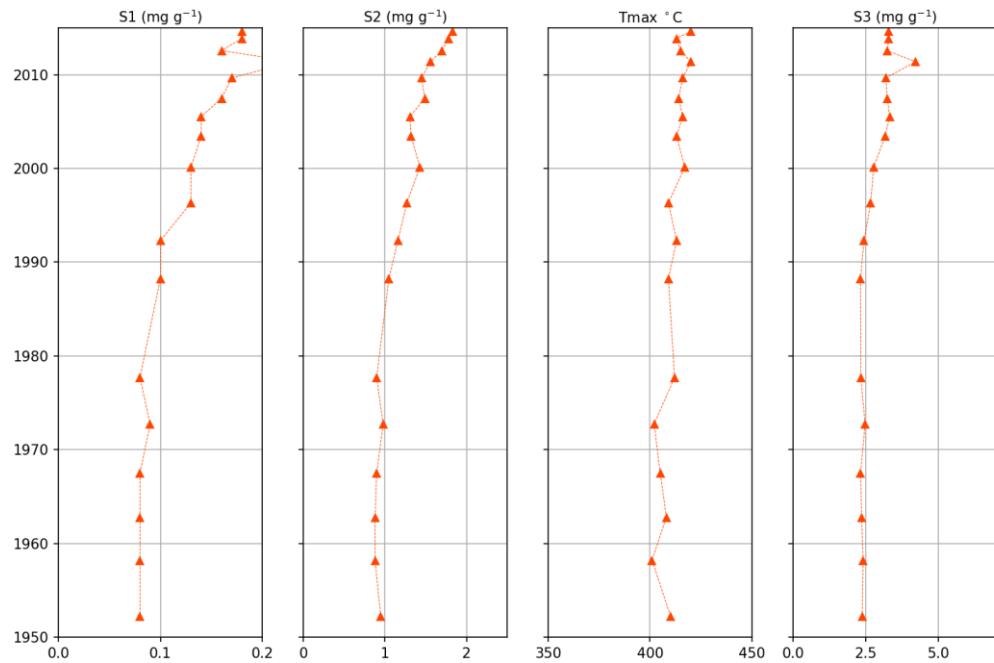
F)
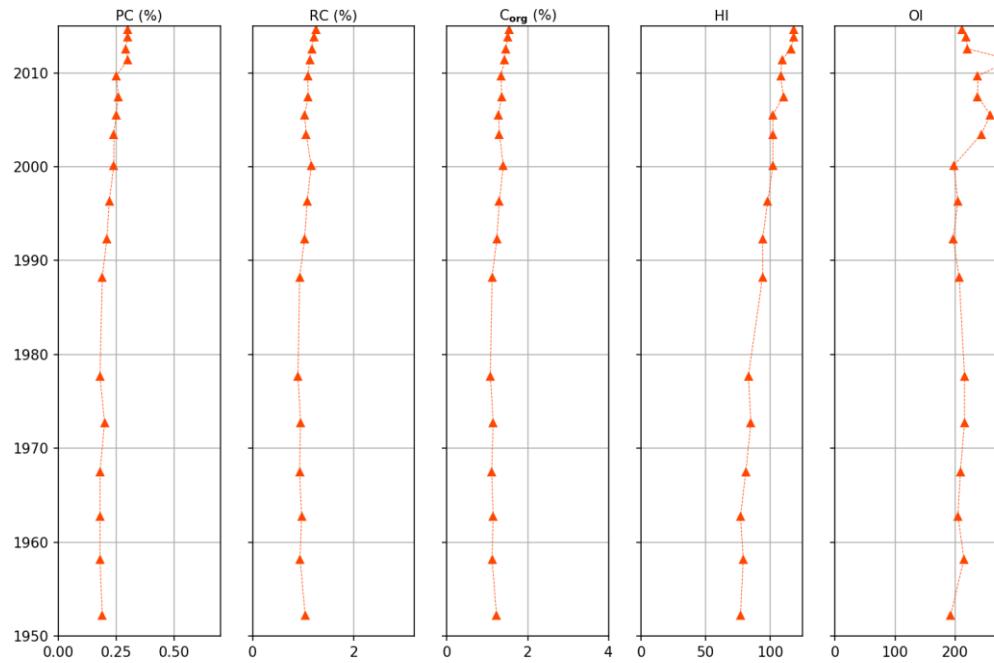
G)
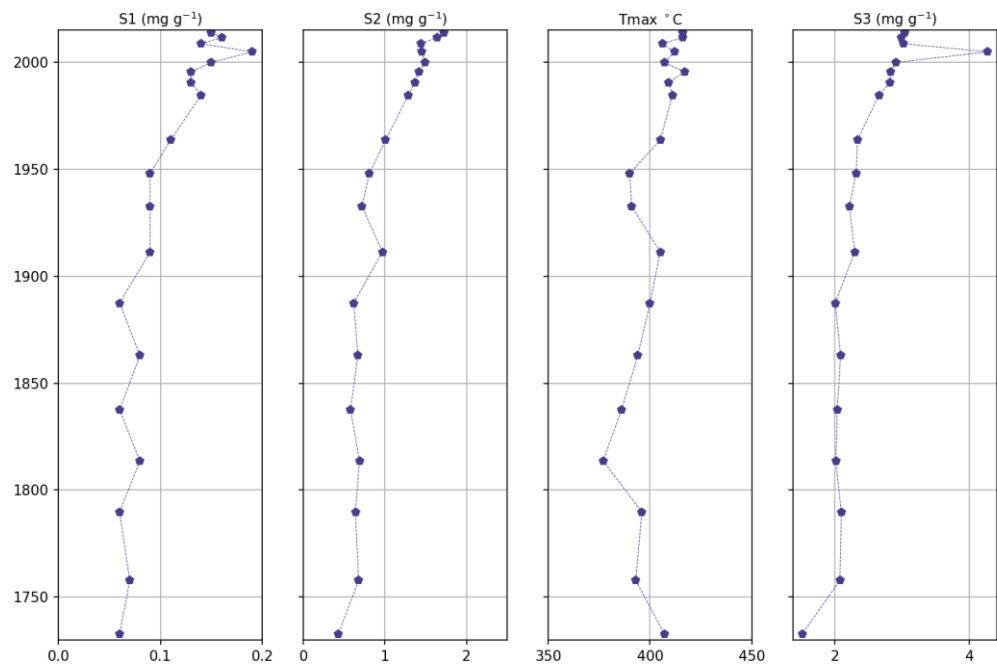
H)
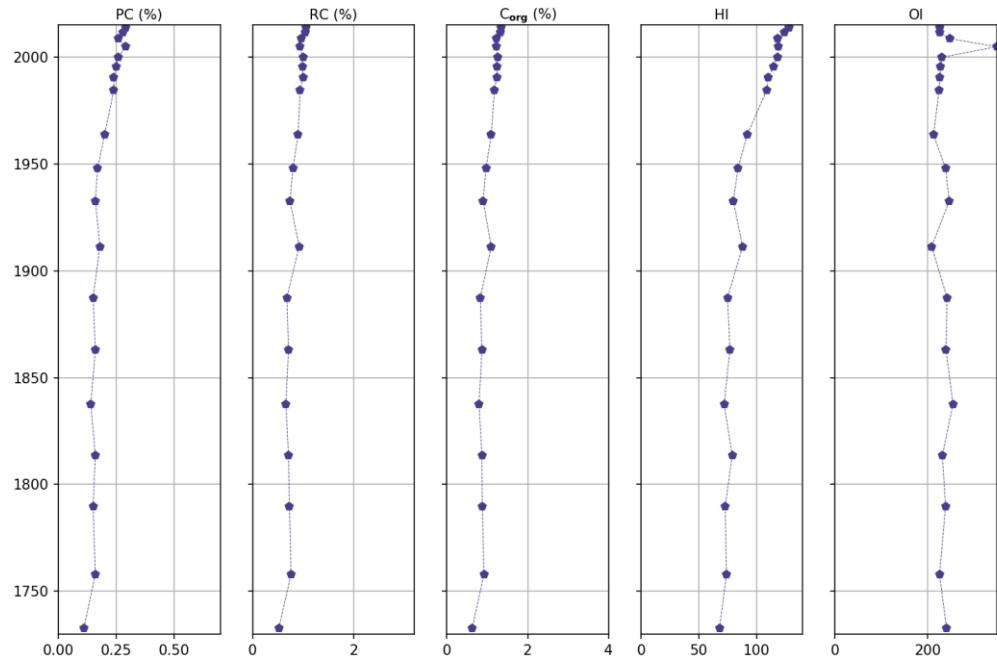
Figure S3. Vertical distribution of Rock Eval parameters of the Todosos Santos Bay. A, B represents core CO01; C, D CO02; E, F CO04 and G, H CO05.
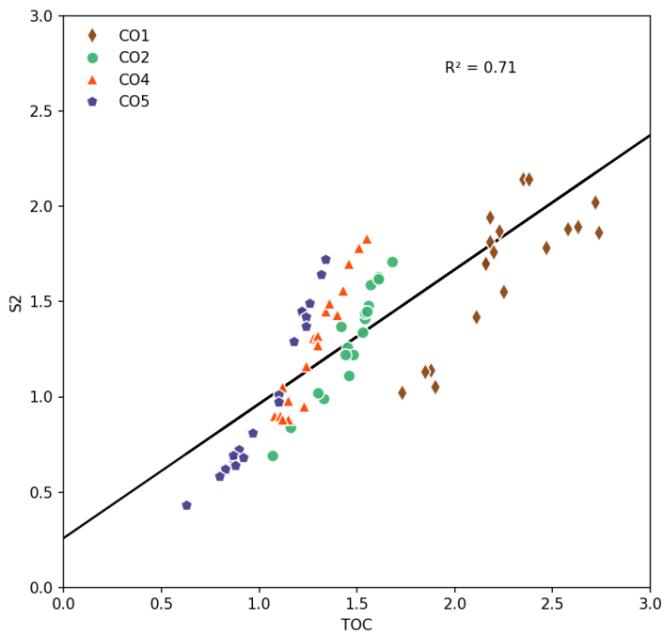

Figure S4: Correlation between S2xTOC. The BTS samples don't suffering inorganic matrix influence.

CONCLUSÕES E CONSIDERAÇÕES FUTURAS

- A técnica pirólise Rock Eval é uma boa ferramenta para estudos de caracterização da MO;
- A partir do diagrama de Van Krevelen e 13C x HI/OI pode se observar que os testemunhos CO01, CO02 e CO04 possuem maior influência de fontes terrígenas, enquanto que CO05 apresenta uma mistura de fontes marinhas e terrígenas;
- Os baixos valores de Tmax e de OI indicam que a MO sofreu diagênese recente, com algumas amostras apresentando valores semelhantes aos valores registrados para plantas de mangue;
- A partir dos parâmetros utilizados pelo presente estudo (TOC, HI, OI, Tmax) pode-se observar a variação espacial entre os testemunhos da BTS;
- A hipótese relacionada à mudança das fontes de MO para o ambiente aquático adjacente, com aumento no *input* de hidrocarbonetos livres e de carbono residual não foi validada. Embora a intensificação das atividades humanas na BTS a partir do

século XIX, os parâmetros do RE permaneceram relativamente constantes ao longo do tempo e não houve mudanças nas fontes de MO para o ambiente;

- Embora a técnica de Rock Eval seja uma boa ferramenta, análises complementares como de biomarcadores, podem auxiliar numa melhor compreensão e interpretação dos dados, a fim de complementar e dar maior robustez aos resultados fornecidos pelos parâmetros.

REFERÊNCIAS BIBLIOGRÁFICAS UTILIZADAS NA INTRODUÇÃO GERAL

AFFOURI.H.; SAHRAOUI. O. The sedimentary organic matter from a Lake Ichkeul core (far northern Tunisia): Rock-Eval and biomarker approach. **Journal of African Earth Sciences**. 2017.

ANDRADE. R. L. B. et al. Chronology of anthropogenic impacts reconstructed from sediment records of trace metals and Pb isotopes in Todosos Santos Bay (NE Brazil). **Marine Pollution Bulletin**. v. 125.n. 1–2. p. 459–471. 2017.

ARNDT. Sandra et al. Quantifying the degradation of organic matter in marine sediments: a review and synthesis. **Earth-science reviews**. v. 123. p. 53-86. 2013.

BAUDIN.François et al. Guidelines for Rock–Eval analysis of recent marine sediments. **Organic Geochemistry**. v. 86. p. 71-80. 2015.

BAUDIN.François et al. Origin and distribution of the organic matter in the distal lobe of the Congo deep-sea fan–A Rock-Eval survey. **Deep Sea Research Part II: Topical Studies in Oceanography**. v. 142. p. 75-90. 2017.

BEHAR.F.; BEAUMONT.V.; PENTEADO. HL De B. Rock-Eval 6 technology: performances and developments. **Oil & Gas Science and Technology**. v. 56. n. 2. p. 111-134. 2001.

BIANCHI. T. S. Biogeochemistry of Estuaries: Oxford University Press. 2006.

BIANCHI.Thomas S.; CANUEL.Elizabeth A. **Chemical biomarkers in aquatic ecosystems**.Princeton University Press. 2011.

BUENO. C. et al. Anthropogenic and natural variability in the composition of sedimentary organic matter of the urbanised coastal zone of Montevideo (Río de la Plata). **Marine Pollution Bulletin**. v. 126. p. 197-203. 2018.

BURDIGE. David J. Burial of terrestrial organic matter in marine sediments: A re-assessment. Global Biogeochemical Cycles. v. 19. n. 4. 2005.

BURDIGE. David J. Preservation of organic matter in marine sediments: controls.mechanisms.and an imbalance in sediment organic carbon budgets?. **Chemical reviews**. v. 107. n. 2. p. 467-485. 2007.

DAMSTÉ.Jaap S. Sinninghe; RUPSTRA.W. Irene C.; REICHART.Gert-jan.The influence of oxic degradation on the sedimentary biomarker record II.Evidence from Arabian Sea sediments.**GeochimicaetCosmochimicaActa**. v. 66. n. 15. p. 2737-2754. 2002.

DISNAR. Jean-Robert et al. Soil organic matter (SOM) characterization by Rock-Eval pyrolysis: scope and limitations. **Organic geochemistry**. v. 34. n. 3. p. 327-343. 2003.

DRYLIE. Tarn P. et al. Benthic primary production in emerged intertidal habitats provides resilience to high water column turbidity. **Journal of sea research**. v. 142. p. 101-112. 2018.

EGLINTON. Geoffrey et al. Hydrocarbon constituents of the wax coatings of plant leaves: a taxonomic survey. **Phytochemistry**. v. 1. n. 2. p. 89-102. 1962.

HARE. A. A. et al. Organic Geochemistry Characterization of sedimentary organic matter in recente marine sediments from Hudson Bay. Canada.by Rock-Eval pyrolysis. **ORGANIC GEOCHEMISTRY**. V. 68. p. 52-60. 2014.

HATJE. Vanessa; ANDRADE.Jailson B. de.**Baía de Todos os Santos: aspectos oceanográficos**. EDUFBA.2009.

HEDGES. J. I.; KEIL. R. G.; BENNER. Ronald. What happens to terrestrial organic matter in the ocean?. **Organic geochemistry**. v. 27.n. 5-6. p. 195-212. 1997.

HEDGES. J. I.; OADES.J. M. Comparative organic geochemistries of soils and marine sediments.**Organic geochemistry**. v. 27.n. 7-8. p. 319-361. 1997.

HEDGES. John I. Global biogeochemical cycles: progress and problems. **Marine chemistry**. v. 39.n. 1-3. p. 67-93. 1992.

HEDGES.John I.; KEIL. Richard G. Sedimentary organic matter preservation: an assessment and speculative synthesis. **Marine chemistry**. v. 49.n. 2-3. p. 81-115. 1995.

HOEFS. Marcel JL; RIJPSTRA. W. Irene C.; DAMSTÉ.Jaap S. Sinninghe. The influence of oxic degradation on the sedimentary biomarker record I: Evidence from Madeira Abyssal Plain turbidites. **GeochimicaetCosmochimica Acta**.v. 66.n. 15.p. 2719-2735. 2002.

HU.Limin et al. Distribution.input pathway and mass inventory of black carbon in sediments of the Gulf of Thailand. SE Asia. **Estuarine.Coastal and Shelf Science**. v. 170. p. 10-19. 2016.

JIAO.Nianzhi et al. Microbial production of recalcitrant dissolved organic matter: long-term carbon storage in the global ocean. **Nature Reviews Microbiology**. v. 8. n. 8.p. 593. 2010.

KILLOPS.S.; KILLOPS. V. Introduction to Organic Geochemistry.2nd edn (paperback). **Geofluids**. v. 5. n. 3. p. 236-237. 2005.

LAFARGUE. E.; MARQUIS. F.; PILLOT.D. Rock-Eval 6 applications in hydrocarbon exploration.production.and soil contamination studies. **Revue de l'institutfrançais du pétrole**. v. 53. n. 4. p. 421-437. 1998.

Lamoureux-Var, Violaine & Espitalié, J. & Daniel, Pillot & Bouton, N. & Garcia, B. & Antonas, R. & Aboussou, A. & Wattripont, A. & Ravelojaona, H. & Noirez, S. & Valérie, Beaumont. (2019). ROCK-EVAL 7S: TECHNOLOGY AND PERFORMANCE. 10.3997/2214-4609.201902941.

LIAO.Weisen et al. Sources and distribution of sedimentary organic matter in the Beibu Gulf. China: Application of multiple proxies. **Marine Chemistry**. 2018.

MARCHAND. C.et al. Organic carbon sources and transformations in mangrove sediments: A Rock-Eval pyrolysis approach. **ORGANIC GEOCHEMISTRY**. v. 32. p. 408-421. 2008.

MCCARTHY.Kevin et al. Basic petroleum geochemistry for source rck evaluation.**Oilfield Review**. v. 23. n. 2. p. 32-43. 2011.

MEYERS. Philip A. Applications of organic geochemistry to paleolimnological reconstructions: a summary of examples from the Laurentian Great Lakes. **Organic geochemistry**. v. 34. n. 2. p. 261-289. 2003.

MEYERS.Philip A. Organic geochemical proxies of paleoceanographic.paleolimnologic.andpaleoclimatic processes. **Organic geochemistry**. v. 27.n. 5-6. p. 213-250. 1997.

MEYERS.Phillip A. Preservation of elemental and isotopic source identification of sedimentary organic matter.**Chemical geology**. v. 114.n. 3-4. p. 289-302. 1994.

MIGNÉ.Aline et al. Annual budget of benthic production in Mont Saint-Michel Bay considering cloudiness.microphytobenthos migration.and variability of respiration rates with tidal conditions. **Continental Shelf Research**. v. 29. n. 19. p. 2280-2285. 2009.

MOORE. C. M. et al. Processes and patterns of oceanic nutrient limitation. Nat. Geosci.. 6. 701–710. 2013.

PETERS.Kenneth E.; WALTERS. C. C.; MOLDOWAN. J. M. The biomarker guide: Biomarkers and isotopes in the environment and human history.Vol. 1. **Cambridge. New York**. 2005.

SANTOS. Elisângela Costa et al. Source and distribution of organic matter in surface sediments from mangroves on the island of Itaparica.Bahia/Brazil. **Environmental monitoring and assessment**. v. 185. n. 12. p. 9857-9869. 2013.

SELVARAJ. K. et al. Stable isotopic and biomarker evidence of terrigenous organic matter export to the deep sea during tropical storms. **Marine Geology**. v. 364. p. 32-42. 2015.

SUN.Ming-Yi; WAKEHAM.Stuart G. Molecular evidence for degradation and preservation of organic matter in the anoxic Black Sea Basin.**GeochimicaetCosmochimica Acta**.v. 58.n. 16.p. 3395-3406. 1994.

THORNTON. S. F.; MCMANUS.J. Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: evidence from the Tay Estuary. Scotland. **Estuarine.Coastal and Shelf Science**. v. 38. n. 3. p. 219-233. 1994.

TISSOT.Bernard P.; WELTE.Dietrich H.From kerogen to petroleum. In: **Petroleum formation and occurrence**. Springer. Berlin. Heidelberg. 1984. p. 160-198.

VOLKMAN. John K. et al. Microalgal biomarkers: a review of recent research developments. **Organic Geochemistry**. v. 29.n. 5-7. p. 1163-1179. 1998.

ZONNEVELD.K. A. F. et al. Selective preservation of organic matter in marine environments; processes and impact on the sedimentary record. **Biogeosciences**. v. 7. n. 2. p. 483-511.2010