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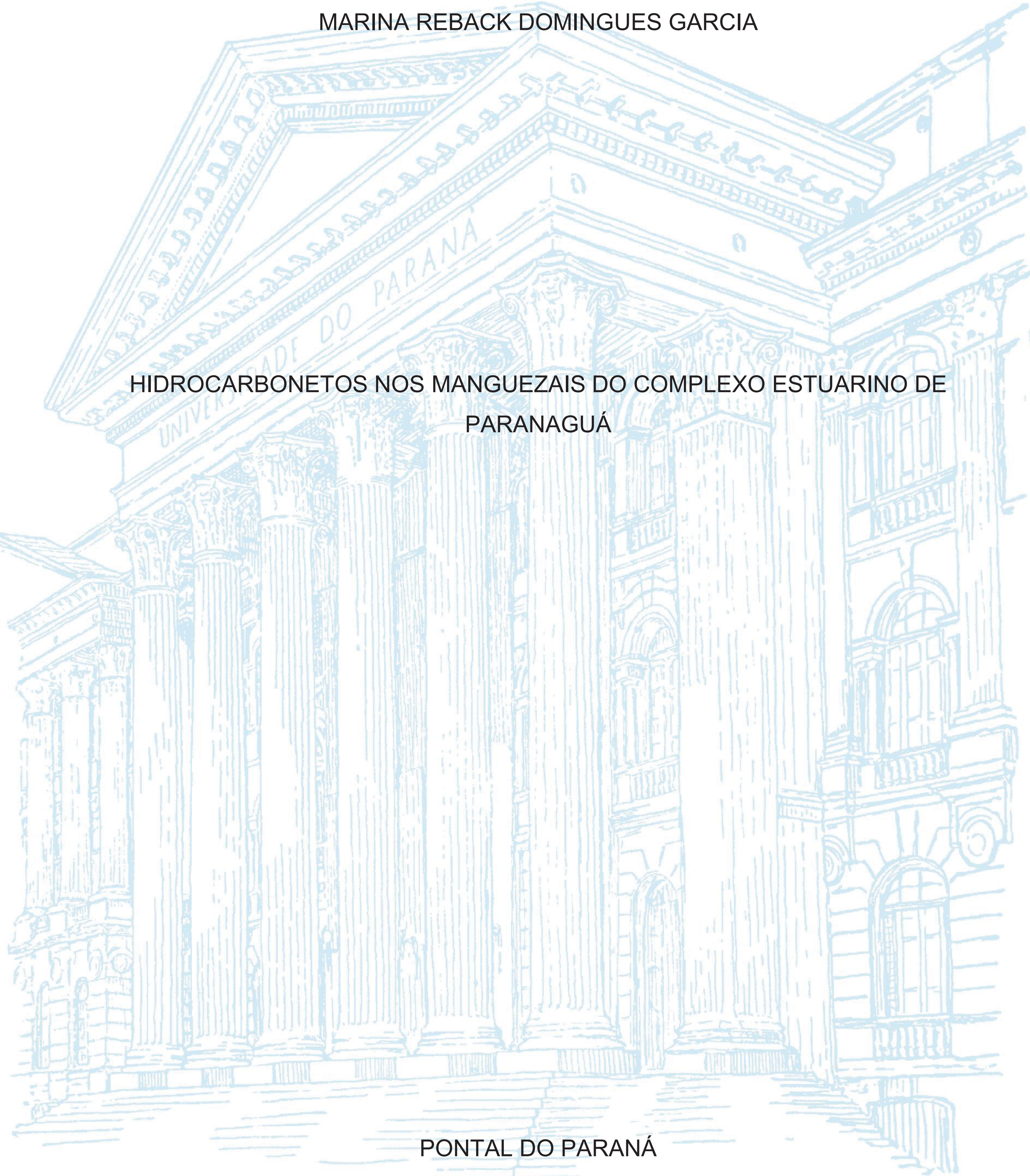

HIDROCARBONETOS NOS MANGUEZAIS DO COMPLEXO ESTUARINO DE PARANAGUÁ

PONTAL DO PARANÁ
2019

MARINA REBACK DOMINGUES GARCIA

HIDROCARBONETOS NOS MANGUEZAIS DO COMPLEXO ESTUARINO DE PARANAGUÁ

Tese apresentada ao curso de Pós-Graduação em Sistemas Costeiros e Oceânicos, Centro de Estudos do Mar, Setor Reitoria, Universidade Federal do Paraná, como requisito parcial à obtenção do título de Doutor em Sistemas Costeiros e Oceanicos.

Orientador: Prof. Dr. César de Castro Martins

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TERMO DE APROVAÇÃO

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Curitiba, 28 de Maio de 2019.

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Dedico esta tese aos professores e cientistas brasileiros e aos estrangeiros
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RESUMO

Hidrocarbonetos são compostos orgânicos formados por cadeias de átomos de carbono e hidrogênio. Estão amplamente distribuídos nos ambientes costeiros e marinhos, apresentando diferentes classes com propriedades e origens diversas (tanto antrópicas quanto naturais). O presente trabalho realizou, pela primeira vez, a caracterização e a quantificação dos hidrocarbonetos (*n*-alcanos, hidrocarbonetos policíclicos aromáticos (HPAs) e biomarcadores de petróleo) nos ambientes de manguezal do Complexo Estuarino de Paranaguá (CEP). O estudo foi dividido em três capítulos, em formato de artigos. O primeiro artigo buscou verificar a distribuição dos hidrocarbonetos em dois transectos (um em uma área impactada e o outro em uma área de controle), dispostos ao longo do gradiente de zonação manguezal-marisma-planície não vegetada. As zonas mais elevadas, com menor tempo de imersão (marismas e manguezais) se mostraram mais propícias para acúmulo de hidrocarbonetos. Os *n*-alcanos revelaram a predominância de aportes naturais, porém HPAs e biomarcadores de petróleo (atribuídos a aportes crônicos de petróleo e derivados, provenientes principalmente das atividades de navegação) indicaram sinais de contaminação. O somatório de *n*-alcanos variou entre 0,640 e 11,930 μg g^{-1}(*n*-C_{12} a *n*-C_{39}); o somatório de 16 HPAs entre 1,28 e 78,60 ng g^{-1}; os hopanos totais entre 3,69 e 282,30 ng g^{-1} (19 compostos); os terpanos totais entre < LD e 75,30 ng g^{-1} (7 compostos); e os esteranos totais entre 1,41 e 48,60 ng g^{-1} (19 compostos). O segundo artigo teve como objetivo estudar os compostos triterpenoides naturais e catagênicos (de petróleo) nos sedimentos de manguezal do CEP. Os compostos naturais predominantes foram identificados como terpenoides provenientes de vegetais superiores (oleanoides, lupanoides, ursanoides and taraxeroides) com sinais de degradação anaeróbica (configuração 'des-A'), além de hopanoides bacterianos. Compostos catagênicos estiveram distribuídos por todo o estuário e evidenciaram as fontes preferenciais de contaminação quando presentes em uma razão > 1 em relação aos compostos biogênicos. As Baías de Antonina e de Guaraqueçaba foram áreas preferenciais de acumulação dos terpanos e hopanos naturais. Analogamente, essas regiões internas do CEP podem ser apontadas como locais de alta vulnerabilidade para contaminação por compostos hidrofóbicos e possuem baixo potencial de remobilização/recuperação. O terceiro artigo estudou a distribuição espacial dos HPAs nos sedimentos superficiais do CEP. O somatório dos 16 HPAs variou entre < LD e 234,3 ng g^{-1}. A maior concentração esteve localizada na Baía das Encantadas (Ilha do Mel), seguida de pontos localizados nas Baías de Paranaguá e Antonina, e na Ilha da Gamela (Baía das Laranjeiras). Em linhas gerais, o impacto antrópico causado por hidrocarbonetos nos manguezais do CEP pode ser considerado baixo, porém foram observados sinais de impacto nas Baías de Antonina e de Paranaguá e no entorno da Ilha do Mel. O eixo Leste-Oeste do CEP apresentou evidências de aportes crônicos de hidrocarbonetos, provenientes das ocupações urbanas e das atividades portuárias. Já o eixo Norte-Sul apresentou baixa evidência de aportes antrópicos de hidrocarbonetos, sendo identificados níveis aumentados apenas para o grupo dos HPAs em um dos locais avaliados (Vila da Gamela). Tais condições devem ser consideradas no planejamento de novos empreendimentos na região.

Palavras-chave: Atlântico Sul. HPAs. Terpanos. Hopanos. Esteranos.

ABSTRACT

Hydrocarbons are organic compounds formed by chains of carbon and hydrogen atoms. They are ubiquitous in coastal and marine environments, having many classes with different properties and origins (anthropic or natural). This work aimed to characterize and quantitate hydrocarbons (*n*-alkanes, polycyclic aromatic hydrocarbons (PAHs) and petroleum biomarkers) in the mangrove sediment of the Paranaguá Estuarine Complex (PEC). The study was comprised of three papers. The objective of the first paper was to verify the distribution of hydrocarbons in two transects (one in an impacted area and another in a control area), distributed along the zonation gradient (mudflat - salt marsh - mangrove). Hydrocarbons were preferentially accumulated in higher areas with shorter immersion time (salt marshes and mangroves). The *n*-alkanes were dominated by natural inputs. However, contamination was evidenced by PAHs and mainly petroleum biomarkers (attributed to chronic inputs of petroleum and byproducts, mainly from navigation). The sum of *n*-alkanes in the sediments (d.w.) ranged between 0,64 and 11,930 µg g^{-1} (*n*-C_{12} to *n*-C_{39}); the sum of 16 HPAs, between 1,28 and 78,60 ng g^{-1}; total hopanes, between 3,69 and 282,30 ng g^{-1} (19 compounds); total terpanes, between < DL and 75,30 ng g^{-1} (7 compounds); and total steranes, between 1,41 and 48,60 ng g^{-1} (19 compounds). The second paper aimed to study the distribution of natural and catagenic triterpenoids in the mangrove sediments of PEC. Natural compounds were identified mainly as terpenoids from higher plants (oleanoids, lupanoids, ursanoids, and taraxeroids) with signs of anaerobic degradation ('des-A' configuration), as well as bacterial hopanoids. Catagenic compounds were also distributed throughout the estuary and could reveal the preferential source areas of contamination when present in a ratio > 1, in relation to the biogenic compounds. Antonina and Guaraqueçaba Bays were preferential areas for the accumulation of natural terpanes and hopanes. These inner, sheltered areas of PEC can be identified as highly vulnerable sites for contamination with hydrophobic compounds having low remobilization/recovery potential. The third paper presents the spatial distribution of PAHs in the superficial sediments of PEC. The sum of 16 PAHs ranged from < LD to 234,3 ng g^{-1}. The highest concentration was located in Encantadas Bay (Mel Island), followed by sites located at Paranaguá and Antonina Bays and Gamela Village (Laranjeiras Bay). In general terms, the anthropic impact by hydrocarbons in the PEC mangroves can be considered low but signs of impact were observed in Antonina and Paranaguá Bays and around Mel Island. The East-West axis of the PEC showed evidence of chronic hydrocarbon inputs from urban occupations and port activities. The North-South axis showed low evidence of anthropogenic hydrocarbon inputs but increased levels of PAHs were identified in one site (Gamela Village). Such conditions are relevant for impact studies and must be considered for the assessment of impacts of new ventures in the area.

Keywords: Hydrocarbons. South Atlantic. PAHs. Hopanes. Terpanes.

SUMÁRIO

1 INTRODUÇÃO

1.1 HIDROCARBONETOS NOS ESTUDOS AMBIENTAIS

Hidrocarbonetos são compostos orgânicos formados por átomos de carbono e hidrogênio. Apesar da simplicidade de sua composição elementar, esses compostos apresentam muitas classes com propriedades e origens diferentes, devido a grande variação estrutural que pode ser assumida. São compostos muito comuns no ambiente, incluindo os ecossistemas costeiros e marinhos, onde estão associados principalmente à fração orgânica dos sedimentos, devido as suas características hidrofóbicas (KILLOPS e KILLOPS, 2005; VOLKMAN *et al.*, 1997).

Os hidrocarbonetos nos ambientes costeiros e marinhos podem ter origens tanto naturais quanto antrópicas (UNEP, 1992; GESAMP, 1993; LIBES, 2009) e os principais grupos avaliados em estudos ambientais são os *n*-alcanos, os alcanos isoprenoides e os hidrocarbonetos policíclicos aromáticos (HPAs). Além de apresentarem importância ecotoxicológica (no caso dos HPAs), os hidrocarbonetos podem fornecer indícios a respeito das fontes naturais e antrópicas da matéria orgânica para o ambiente, sendo considerados marcadores moleculares pois podem ser diretamente relacionados a sua origem (EGANHOUSE, 1997). Outro grupo de hidrocarbonetos com aplicação em estudos ambientais são os biomarcadores de petróleo (BMPs), onde se incluem as classes dos esteranos, hopanos e terpanos. Os BMPs têm sido aplicados para realizar o diagnóstico específico do aporte de petróleo, pois são moléculas com elevada resistência aos processos de intemperismo e biodegradação, sendo possível correlacioná-las especificamente às fontes de introdução (WANG e FINGAS, 1995; WANG e STOUT, 2007).

Assim, o estudo do aporte de hidrocarbonetos para os ecossistemas costeiros e marinhos fornecem informações sobre as fontes, o transporte e destino dessas substâncias que são introduzidas de forma aguda ou crônica no ambiente, sendo fundamentais para avaliação de impactos ambientais. Como a maioria da população mundial está estabelecida na zona costeira, os impactos humanos são intensos nessa região, decorrentes da construção de infra-estrutura e outros impactos associados, tais como lançamento de esgoto e de resíduos sólidos, atividades extrativistas, dentre diversas outras (SPALDING, 2001).

Um dos ecossistemas costeiros mais impactados são os manguezais, que sofreram nas últimas décadas um rápido declínio de sua cobertura vegetal, já tendo perdido mais de 20% de sua cobertura total (ALONGI *et al.*, 2008; SPALDING *et al.*, 2010). Alguns autores chegam a prever a destruição total dos mangues nos próximos 100 anos (DUKE *et al.*, 2007). Além dos impactos diretos do desmatamento e extrativismo, os impactos da poluição nos manguezais merecem particular atenção pois suas condições fisico-químicas favorecem a deposição de sedimentos finos e a degradação lenta da matéria orgânica, sendo considerados bastante vulneráveis à contaminação orgânica, inclusive por hidrocarbonetos do petróleo (BOUILLON *et al.*, 2008; NOERNBERG & LANA, 2002; DUKE, 2016). Os manguezais têm, portanto, uma baixa capacidade de recuperação, pois os compostos tóxicos são removidos muito lentamente dos sedimentos e a degradação dos hidrocarbonetos é baixa em sedimentos anóxicos, mesmo em zonas de clima tropical (BURNS *et al.*, 1993).

Outros aspectos, incluindo alta produtividade, abundância de detritos e alta concentração de carbono orgânico fazem dos manguezais ambientes preferenciais para captação e acúmulo de petróleo e outras substâncias hidrofóbicas lançadas de forma crônica no ambiente, como os HPAs (LI *et al.*, 2014; LEWIS *et al.*, 2011; DUKE, 2016). Certos manguezais foram diagnosticados como severamente contaminados por HPAs, com concentrações mais altas que 10 $\mu g\ g^{-1}$ (peso seco) (KLEKOWSKI *et al.*, 1994). Em locais onde ocorreram processos de urbanização de forma rápida e desordenada como, por exemplo, em Hong Kong, os manguezais se encontram contaminados e com concentrações mais altas do que as verificadas nas áreas portuárias adjacentes (TAM *et al.*, 2001). Dessa forma, diversos estudos têm demonstrado que níveis de hidrocarbonetos relativamente altos podem ser encontrados nos sedimentos de manguezal, inclusive no Brasil (FARIAS *et al.*, 2008; SANTOS *et al.*, 2013), onde foi possível identificar locais impactados, principalmente próximos a grandes centros urbanos e sujeitos a aportes crônicos e agudos de petróleo e derivados.

Além dos *n*-alcanos e HPAs, os biomarcadores de petróleo têm sido estudados em locais sujeitos a influência de aportes de petróleo em diversas áreas do mundo, tanto em sedimentos superficiais quanto em testemunhos. Em sedimentos estuarinos de locais sujeitos a intensas atividades antrópicas (navegação e transporte de petróleo e derivados e próximo a assentamentos urbanos) são reportados valores da ordem de µg g^{-1} de somatório total de biomarcadores de petróleo (hopanos e esteranos) (MEDEIROS e BÍCEGO, 2004; MEDEIROS *et al*., 2005; FARIAS *et al*., 2008; SILVA e BÍCEGO, 2010). Em locais relacionados a atividades de extração de hidrocarbonetos, como na província de Alberta, no Canadá, são relatados valores até dez vezes maiores (WANG *et al.*, 2014). No entanto, estudos sobre o acúmulo de biomarcadores de petróleo em manguezais são escassos, estando na maioria restritos a distribuição e concentração de *n*-alcanos e HPAs.

1.2 HIDROCARBONETOS NO LITORAL DO PARANÁ

O litoral do Estado do Paraná, apesar de ser um dos menos extensos do Brasil, possui muitas reentrâncias, totalizando 1.675 km de linha de costa. De toda essa extensão, 80% é classificada como área de alta sensibilidade ambiental, compreendendo áreas de marisma e manguezal (SOUSA, 2008). Assim, a avaliação dos níveis e perfis de hidrocarbonetos desses ecosssistemas é fundamental para o diagnóstico ambiental da região. Além dessa abordagem, a determinação de testemunhos em áreas adjacentes aos manguezais busca indícios de eventos da introdução de hidrocarbonetos na área de estudo tanto de forma crônica como acidental.

A principal feição geomorfológica do litoral do Estado é o Complexo Estuarino de Paranaguá (CEP), onde os primeiros estudos sobre a introdução de hidrocarbonetos na zona costeira foram realizados por SEYFFERT (2008) a partir de coletas realizadas em 2003, 2004 e 2006, com amostras de sedimento superficial. Em geral, os níveis reportados de *n*-alcanos e HPAs foram baixos, compatíveis com áreas consideradas livres de contaminação petrogênica. A contribuição de fontes biogênicas é predominante para a região, tendo sido verificada influência urbana, petrogênica e pirolítica nos sedimentos apenas: (1) em locais próximos a atividades portuárias; (2) onde ocorre lançamento de petróleo e derivados (locais com intensa movimentação de embarcações), e; (3) zonas urbanas. As maiores concentrações de hidrocarbonetos foram encontradas nas baías de Antonina e Paranaguá, enquanto as baías de Guaraqueçaba e Pinheiros apresentaram níveis relativamente baixos.

Posteriormente, foram realizados outros estudos sobre hidrocarbonetos no CEP, em fundos predominantemente arenosos (ABREU-MOTA *et al.*, 2014; BET *et al.*, 2015), além de dois testemunhos curtos obtidos em áreas próximas das cidades de Paranaguá e Antonina (MARTINS *et al.*, 2015). As áreas de manguezal ainda não haviam sido avaliadas, nem haviam sido efetuadas determinações de BMPs em amostras de sedimento superficial do CEP.

No CEP, além da influência das fontes difusas de hidrocarbonetos antropogênicos originadas das atividades humanas realizadas na área, ocorreram acidentes ambientais que envolveram aportes agudos de hidrocarbonetos para o estuário (ALBARELLO, 2012; IAP, 2004). Os principais foram: (1) em 2000, no porto de Paranaguá, ocorreu vazamento de 450 litros de óleo diesel, dentro do terminal, atingindo a linha de costa, devido ao rompimento de uma válvula durante uma operação de rotina; (2) ainda em 2000, em torno de 4.000 m^3 de diesel vazaram de um trem na cidade de Morretes, atingindo o rio Nhundiaquara; (3) em 2001, um acidente no Oleoduto Araucária-Paranaguá (OLAPA) que liga a Refinaria Presidente Getúlio Vargas, em Araucária (REPAR), ao Porto de Paranaguá, levou ao vazamento de 145 m^3 de óleo diesel (dados estimados), atingindo o rio Nhundiaquara e seus afluentes e manguezais na desembocadura do rio na Baía de Antonina; (4) em 2004, no píer da empresa Cattalini Terminais Marítimos, em Paranaguá, ocorreu o vazamento de 4.000 t de metanol e 1.400 m^3 de óleo combustível devido à explosão do navio chileno Vicuña, durante o descarregamento de sua carga de metanol. Estima-se que 400 m^3 de óleo bunker não puderam ser recolhidos e se dispersaram no ambiente, atingindo as baías de Paranaguá, Antonina e Laranjeiras e 170 km da linha de costa no entorno do navio, das Ilha da Cotinga e do Mel. A área estimada de manguezal atingido foi de, no mínimo, 135 km^2 (APPA, 2017; IAP e FATMA, 2005), tendo sido considerado o maior desastre ambiental ocorrido no CEP,

1.3 OBJETIVOS

O objetivo geral deste trabalho foi realizar a caracterização, distribuição e quantificação dos hidrocarbonetos (*n*-alcanos, HPAs e biomarcadores de petróleo) nos ambientes de manguezal do Complexo Estuarino de Paranaguá, a fim de:

- Estudar a distribuição dos hidrocarbonetos ao longo do gradiente de zonação: planície entre marés – marisma – manguezal em dois locais com distintos graus de contaminação (Item 2);
- Realizar a determinação e identificação dos biomarcadores de petróleo (terpanos e hopanos) nos sedimentos superficiais de manguezal da área de estudo, como ênfase na caracterização geoquímica dos principais hidrocarbonetos naturais cíclicos eramificados (Item 3);
- Avaliar o aporte recente de HPAs através da determinação desses compostos nos sedimentos superficiais dos manguezais distribuídos na área de estudo (Item 4).

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2 PETROLEUM BIOMARKERS AS TRACERS OF LOW-LEVEL AND CHRONIC OIL CONTAMINATION OF COASTAL ENVIRONMENTS: A SYSTEMATIC STUDY IN A SUBTROPICAL ESTUARINE MANGROVE

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Petroleum biomarkers as tracers of low-level chronic oil contamination of coastal environments: A systematic approach in a subtropical mangrove[☆]

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ABSTRACT

Petroleum biomarkers (hopanes, terpanes and steranes) are frequently assessed in estuarine sediments as tracers of oil input. In order to compare distinct patterns of hydrocarbon accumulation in mudflats, salt marsh and mangrove, sediments from two transects (control and impacted areas) were sampled in Paranaguá Bay, SW Atlantic. Concentrations of *n*-alkanes, polycyclic aromatic hydrocarbons (PAHs) and petroleum biomarkers (hopanes, terpanes and steranes) were determined, as well as bulk parameters (TOC, grain size and $\delta^{13}C$). *N*-alkanes concentrations were similar between control and impacted sites (respectively, $3.03 \pm 1.20\ \mu g\ g^{-1}$ and $4.11 \pm 3.02\ \mu g\ g^{-1}$) and reflected a high biogenic input. Conversely, PAHs and petroleum biomarker concentrations were three to six times higher in impacted site than the control site (respectively, $60.4 \pm 23.3\ ng\ g^{-1}$ and $22.0 \pm 25.0\ ng\ g^{-1}$ for PAHs and $197.7 \pm 51.8\ ng\ g^{-1}$ and $40.2 \pm 32.\ ng\ g^{-1}$ for hopanes). Despite these differences, concentrations were lower than those reported for highly impacted areas worldwide. Diagnostic ratios and hydrocarbon parameters (e.g. total PAHs and total petroleum biomarkers) helped to distinguish human impact in the ecological zones, suggesting different sources and/or levels of weathering, confirmed by ANOVA tests. TOC played a fundamental role to the concentration of hydrocarbons, showing similar distributions along the transects. Petroleum biomarkers could clearly indicate the preferential sites of deposition and assign different levels of anthropic contamination by hydrocarbons, thus providing clear information about the chronic petroleum pollution in coastal sediments.

1. Introduction

Hydrocarbons are ubiquitous compounds in the marine environment with several biogenic sources, being produced mainly by marine organisms like planktonic algae or delivered from terrigenous sources by drainage basin runoff (Volkman et al., 1992; Cardoso et al., 2016). In addition, human activities can contribute to the environmental inventory of hydrocarbons by means of petrogenic, pyrogenic and domestic sewage sources (Medeiros and Bícego, 2004; Vaezzadeh et al., 2015).

The exploration of petroleum reserves and their use as fossil fuels and other by-products are responsible for the removal of massive amounts of immobilized organic matter (OM) from sedimentary deposits, introducing high concentrations of hydrocarbons and CO_2, to the different natural compartments of the planet, including marine ecosystems (Ciais et al., 2014). Actually, the chronic input of hydrocarbons to marine and coastal areas has a higher load than that from accidental oil spills (GESAMP, 1993; Tarr et al., 2016).

Estuaries are among the most densely populated areas in the world. As such, they suffer from chronic pollution of urban and industrial diffuse sources and are the destination of loads of

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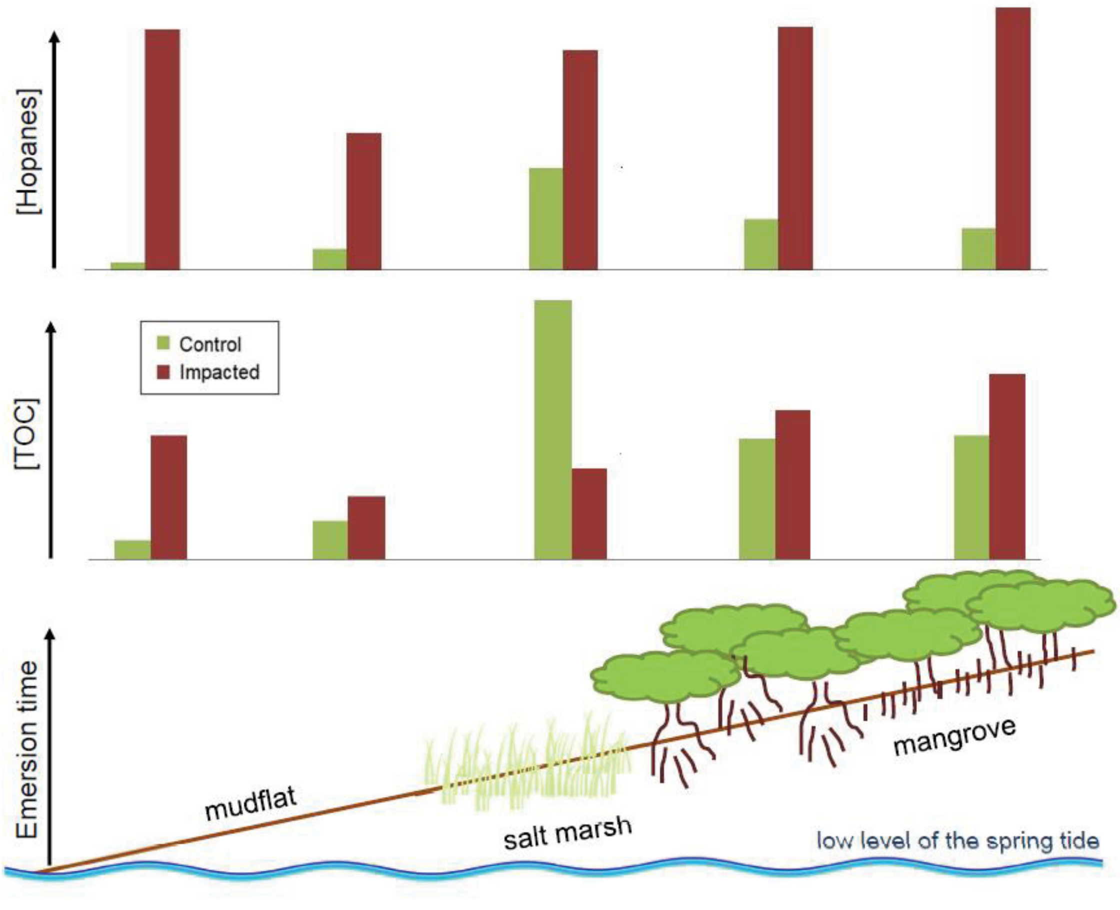
HIGHLIGHTS

- Hydrocarbons assessed in mudflat, salt marsh and mangrove of a subtropical estuary
- Hydrocarbon levels varied in correlation to organic carbon and fine sediments
- PAHs and petroleum biomarkers in the impacted site were higher (3-6 fold)
- *N*-alkanes reflected biogenic hydrocarbon input in control and impacted sites
- Petroleum biomarkers evidenced HCs contamination under a high biogenic background

Graphical abstract



Abstract

Petroleum biomarkers (hopanes, terpanes and steranes) are frequently assessed in estuarine sediments as tracers of oil input. In order to compare distinct patterns of hydrocarbon accumulation in mudflats, salt marsh and mangrove, sediments from two transects (control and impacted areas) were sampled in Paranaguá Bay, SW Atlantic. Concentrations of *n*-alkanes, polycyclic aromatic hydrocarbons (PAHs) and petroleum biomarkers (hopanes, terpanes and steranes) were determined, as well as bulk parameters (TOC, grain size and $\delta^{13}C$). *N*-alkanes concentrations were similar between control and impacted sites (respectively, 3.03 ±1.20 µg g^{-1} and 4.11 ± 3.02 µg g^{-1}) and reflected a high biogenic input. Conversely, PAHs and petroleum biomarker concentrations were three to six times higher in impacted site than the control site (respectively, 60.4 ± 23.3 ng g^{-1} and 22.0 ± 25.0 ng g^{-1} for PAHs and 197.7 ± 51.8 ng g^{-1} and 40.2 ± 32. ng g^{-1} for hopanes). Despite these differences, concentrations were lower than those reported for highly impacted areas worldwide. Diagnostic ratios and hydrocarbon parameters (e.g. total PAHs and total petroleum biomarkers) helped to distinguish human impact in the ecological zones, suggesting different sources and/or levels of weathering, confirmed by ANOVA tests. TOC played a fundamental role to the concentration of hydrocarbons, showing similar distributions along the transects. Petroleum biomarkers could clearly indicate the preferential sites of deposition and assign different levels of anthropic contamination by hydrocarbons, thus providing clear information about the chronic petroleum pollution in coastal sediments.

Keywords: hydrocarbons; hopanes; steranes; terpanes; mudflat; salt marsh; SW Atlantic.

Capsule: Petroleum hydrocarbons are reliable molecular markers to assess low-level hydrocarbon contamination in salt marshes and mangroves, along the terrestrial-aquatic gradient

2.1. Introduction

Hydrocarbons are ubiquitous compounds in the marine environment with several biogenic sources, being produced mainly by marine organisms like planktonic algae or delivered from terrigenous sources by drainage basin runoff (Volkman et al., 1992; Cardoso et al., 2016). In addition, human activities can contribute to the environmental inventory of hydrocarbons by means of petrogenic, pyrogenic and domestic sewage sources (Medeiros and Bícego, 2004; Vaezzadeh et al., 2015).

The exploration of petroleum reserves and their use as fossil fuels and other by-products are responsible for the removal of massive amounts of immobilized organic matter (OM) from sedimentary deposits, introducing high concentrations of hydrocarbons and CO_2, to the different natural compartments of the planet, including marine ecosystems (Ciais et al., 2014). Actually, the chronic input of hydrocarbons to marine and coastal areas has a higher load than that from accidental oil spills (GESAMP, 1993; Tarr et al., 2016).

Estuaries are among the most densely populated areas in the world. As such, they suffer from chronic pollution of urban and industrial diffuse sources and are the destination of loads of contaminants from the drainage of the river basins (United Nations, 2018a, b). Consequently, coastal sediments act as a sink and a repository of hydrophobic compounds, such as hydrocarbons, that can pose environmental risks (Maioli et al., 2010).

Mangroves are among the most remarkable coastal ecosystems playing a key role to the OM environmental balance due to their high capacity of carbon sequestration (termed “blue carbon”) despite being critically sensitive to human impact (Mcleod et al., 2011). The rapid decline in mangrove coverage areas and associated biological productivity is of global concern, reinforcing the importance to develop new strategies to evaluate hydrocarbon in these coastal systems (Duke, 2016; Ferreira and Lacerda, 2016).

Mangrove sediments tend to accumulate hydrophobic compounds, due to low hydrodynamic energy, low oxygen levels, fine grain size and high organic carbon content (Bernard et al., 1996; Bayen, 2012; Wagener et al., 2012). They are rich in OM from multiple biogenic sources including autochthone mangrove litter and suspended OM from terrigenous, riverine and marine sources. Several organic markers such as *n*-alkanes derived from plant waxes (*n*-C_{27}, *n*-C_{29} and *n*-C_{31}) are typically associated to mangroves (Kristensen et al., 2008). *N*-alkanes are also associated with anthropogenic inputs that can be overlapped by the natural hydrocarbons, posing a challenge to the discrimination of chronic loads from different sources.

Once hydrocarbons reach the estuarine environment, most compounds can be rapidly degraded but some can be preserved. Remarkably, petroleum biomarkers are recalcitrant compounds that represent a major component of natural oil, being highly reliable as markers of petroleum contamination (Peters et al., 2005; Tarr et al., 2016). The best known and widely studied petroleum biomarkers are terpanes, hopanes (derived from prokaryots) and steranes (from eukaryotic cells) (Volkman, 2005; Zhang et al., 2015). Despite the high source specificity of these molecular markers, the determination of petroleum biomarkers in subtropical mangrove and adjacent environments has not been totally explored, especially in areas under a high biogenic hydrocarbon input together with anthropogenic contributions.

Therefore, the main purpose of this study is to determine the concentrations of different classes of hydrocarbons, with special attention to petroleum biomarkers, in the sediments along two transects (mudflat – salt marsh – mangrove) from two locations exposed to different levels of anthropogenic impact (control *vs* impacted site).

The sites are located in Paranaguá Bay, SW Atlantic, a subtropical estuary affected by intensive tourism and high contamination risk (e.g. Combi et al., 2013; Souza et al., 2016) due to extensive urban development and harbors activities (e.g. Martins et al., 2015). Based on an integrated approach of multivariate statistics, bulk parameters, multiple groups of hydrocarbons and diagnostic ratios, we hypothesized that the chronic hydrocarbon contamination may affect mudflat, saltmarshes and mangrove zones in distinct ways. Finally, we aim to define the best strategy to achieve an effective assessment of environmental impacts of hydrocarbon input in the intertidal area.

2.2. Material and Methods

2.2.1. Sampling and studied sites

Sediments (n = 30) were collected along a sea-to-land transect in the intertidal zone from a subtropical estuary, the Paranaguá Bay (25°30’S; 48°25’W) (Fig. 1). The estuarine system is the larger bay of South Brazil with 552 km² of open water area (Lana et al., 2018). The study site was on the mesohaline sector of Paranaguá Bay, where the main human settlements are located, including Paranaguá city, the largest urban center established in the bay margins with more than 140,000 inhabitants (IBGE, 2010). The study area has no oil and gas deposits or any other significative deposit of fossil organic matter. The Bay is comprehended in the geological barrier system of Paranaguá coastal plain with Pleistocene and Holocene sedimentary deposits, surrounded by prominent mountain ranges, consisting of granitic massifs, intruded into the paleoproterozoic basement (Lessa et al., 2000; Nascimento et al., 2016).

Samples were collected along two different transects according to the impact from human activities as assessed in previous studies (e.g. Abreu-Mota et al., 2014; Souza et al., 2016). The first one was located in Paranaguá city (T1), near to Paranaguá harbor (Fig. S1), the main grain terminal and the third most important port of South America in terms of loading and unloading operations (Martins et al., 2015). This place is considered to be more influenced by human activities, receiving effluents from several sources (sewage and fertilizer plants), urban runoff and residues from the intense cargo harbor activity. The second transect (T2), located near the mouth of Maciel River, 12 km away from Paranaguá city can be considered semi-pristine and much less influenced by anthropogenic activities (Egres et al., 2012).

In each transect, 15 samples of surface sediments (0 - 2 cm) were collected in five different zones (Fig. 2), according to the absence or nature of plant cover –, which is ultimately the result of how long the sediments are subject to flooding during the tidal cycles (Spier et al., 2016). Sampling was performed during a low spring tide, when the whole intertidal zone was exposed. The transects started at non-vegetated mud bottoms, followed by *Spartina alterniflora* marshes and finally in mangrove woodland (mixed stands of *Laguncularia racemosa* and *Rhizophora mangle*). Due to their large extension, both the upper and lower zones of the mudflat and mangrove were sampled, whereas only one zone was sampled at the narrow salt marsh belt. Each sample was composed from equal parts of sediments taken from three different quadrats (1 m^2 each) in order to minimize short-scale spatial variation (Fig. 2). Sediment temperature, pH and Eh were measured *in situ* in each quadrat (thermometer Instrutherm TE 300, pH meter Instrutherm 710, with combined electrode; and Eh meter Instrutherm ORP-896 with platinum electrode ORP-897). The sediments were frozen (-20 °C), freeze-dried and stored in cleaned glass jars until analysis.

2.2.2. Bulk parameters

Particle size of the sediment samples was determined in the dried total sediment by a laser particle size analyzer (CILAS 1064 L, CILAS, Orleans, France). Bulk OM (total organic carbon; TOC, total nitrogen; TN, and carbon isotope ratio; $\delta^{13}C$) was determined using an EA-Costech elemental analyzer coupled with an isotope ratio mass spectrometrer Thermo Scientifc Delta V Advantage MS (EA-IRMS). The detailed procedure is described as supplementary material.

2.2.3. Sample extraction and instrumental analysis of hydrocarbons

The analytical procedure used for the hydrocarbons in the marine sediments analysis was based on the United Nations Environment Programme method (UNEP, 1992) with adaptations described in Wisnieski et al. (2016). Approximately 20 g of sediment were extracted over 8 h using 80 mL of a mixture of dichloromethane and *n*-hexane (1:1, v/v). Activated copper was added in order to remove elemental sulfur. A surrogate standard mixture of deuterated compounds (naphtalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12} and 5α-cholestane-d_4) and two aliphatic hydrocarbons (1-hexadecene and 1-eicosene) were added before each blank and sample extraction. The DCM/*n*-hexane extract was concentrated using rotary evaporation until 2 mL and purified by column chromatography using 5% deactivated alumina (1.8 g) and silica (3.2 g). Elution was performed with 10 mL of *n*-hexane (fraction 1: aliphatic hydrocarbons and petroleum biomarkers) and 15 mL of a mixture of dichloromethane and *n*-hexane (3:7, v/v) (fraction 2: PAHs). The resulting extract (500 µL) was stored in glass vials. Internal standard (1-tetradecene, benzo(*b*)fluoranthene-d_{12} and pregnane-d_4) was added prior to the gas chromatographic analysis. The quantification of organic compounds, detailed instrumental analyses and quality assurance are described as supplementary material.

2.2.4. Statistical analyses

Statistical data analyses were performed with TIBCO Statistic Academic software and R Studio (GAD package). As a first approach, the relationship between the studied parameters was analyzed with Spearman correlation (*r*). Following, the normality of data was checked by the Shapiro's test and the homogeneity of the variances was verified by the Cochran's test. Data was transformed to ln(x+1) whenever necessary (Underwood, 1997) and the mean bulk parameters (% of fine sediments and TOC), aliphatic hydrocarbons (∑*n*-alkanes) and petroleum biomarkers (hopanes, terpanes and steranes) were separately analyzed by a two-factor analysis of variance with the following model: Transect (fixed, 2 levels: T1 -impacted; T2 - control) and Zones (fixed, 5 levels crossed with Transect: LF - lower mudflat; UF - upper mudflat; SM - salt marsh; LM - lower mangrove and UM - upper mangrove). *A posteriori* comparison in significant terms of interest ($\alpha = 0.05$) were conducted by the Student-Newman-Keuls procedure (SNK). Each dependent variable from aliphatic hydrocarbons, polycyclic aromatic hydrocarbons and petroleum biomarkers were selected according to local contamination sources.

2.3. Results and Discussion

2.3.1. Field and bulk parameters

Field and bulk parameters (mean ± standard deviation) for each site are presented in Table 1 and Fig. 3a. Both sites (T1, impacted and T2, control) presented similar contents of TOC and TN that are within the lower limits of values reported elsewhere for mangrove sediments (Holmer and Bachmann, 2002; Kristensen et al., 2008; Resmi et al., 2016). The percentage of fine sediments

(% silt + clay) remained in similar ranges in both transects. In general, T2 presented lower values of pH and Eh than T1, probably due to the influence from the riverine input.

A prevalent organic origin of total nitrogen is suggested by the TOC/TN ratio ($R^2 = 0.88$, Fig. S2) which in association to the $\delta^{13}C$ shows a predominance of terrigenous OM in both transects (mean values at T1: $\delta^{13}C$ of -25.1‰ and TOC/TN of 8.68 and T2: -25.8‰ and 10.6, respectively) (Bouillon et al., 2008; Kristensen et al., 2008). The depositional and weathering sediment conditions can be considered similar in both sites, with $\delta^{13}C$ indicating a dominance of C_3-plants (-23.4 to -26.5‰) (Meyers, 1997; Kelleway et al., 2018).

2.3.2. Levels and ratios of hydrocarbons for impacted vs control sites

2.3.2.1. Aliphatic hydrocarbons

Total *n*-alkanes (∑*n*-alkanes) and resolved aliphatic hydrocarbons (∑AHs_R) concentrations (mean ± standard deviation) were similar in both transects, with T2 presenting a slightly higher level of ∑*n*-alkanes than T1 (Table 1, Fig. 3b). On the other hand, unresolved complex mixture (UCM) and total aliphatic hydrocarbons were almost two times higher in T1, probably as a result of human impact. In general, the UCM in T2 samples presented a hump in the range of medium-length carbon chain *n*-alkanes (C_{18} to C_{26}) while in T1 also presented a bimodal hump in the range of medium-length and long carbon chain *n*-alkanes (C_{26} to C_{33}) (Fig. S3). According to Tolosa et al. (2009), the UCM related to short/middle carbon chain *n*-alkanes can be related to light oils as fossil fuels (gasoline and diesel) and the long one can be associated to crude oils characterized by an asphaltic content. In this study, the UCM was determined by GC-MS so it must be examined as a general trend, but a similar UCM hump in the long-chain *n*-alkanes range can be identified in fresh lube oil as Bunker C diesel, commonly associated to ship traffic in harbor areas (Wang et al., 1999). Also, similar UCM bi-modal humps were observed by Oliveira and

Madureira (2011) in the sediments from a nearby impacted coastal area (~200 km south). Another possible source for the UCM can be the degradation and weathering of biogenic terrigenous OM contributions (Zaghden et al., 2005). However, the differences between T1 and T2 sites and the presence of the petroleum biomarkers suggest that the anthropogenic activities are the main sources of the UCM.

The predominance of odd carbon numbered *n*-alkanes was evident, with *n*-C_{29} representing the most abundant compound in all samples (Fig. S3). The long chain *n*-alkanes (*n*-C_{25} to *n*-C_{35}) with odd number of carbon atoms are characteristically synthetized by mangrove trees (Kristensen et al., 2008) acting as a protection to the leaves (epicuticlar waxes). Specifically, *n*-C_{29} is the most abundant lipid on the epicuticle layer of *Rizophora sp.* (Mead et al., 2005). Therefore, mangrove forests can be inferred as the main source of *n*-alkanes to the local sediments, confirmed by similar distributions reported in pristine mangroves (Resmi et al., 2016). As a result, the anthropic influence is not evident in the *n*-alkanes distribution. The concentrations of *n*-alkanes found in Paranaguá Bay mangroves compared to levels found in previous studies in the Paranaguá Bay bottom sediments and several locations of the world are presented as supplementary material.

Total aliphatic hydrocarbons (∑AHs) in unpolluted sediments are expected to be lower than 10 $\mu g\ g^{-1}$ (Volkman et al., 1992; Readman et al., 2002). In T1 site, 100% of sediment samples had concentrations higher than this threshold while in T2 only 20% of the samples were above this level. This parameter cannot be directly related to human impact in the study area due to the intensive biogenic input, mainly from mangrove trees. High levels (> 100 $\mu g\ g^{-1}$) of total aliphatic hydrocarbons have indeed been attributed to natural sources (Volkman et al., 1992; Oliveira and Madureira, 2011). However, the total aliphatic hydrocarbons are not a conclusive source indicator of hydrocarbons and complimentary parameters are required.

Diagnostic ratios based on the hydrocarbon concentrations are widely used to assess the contribution of different sources of OM as well as degradation processes (Medeiros and Bícego, 2004; Massone et al., 2013; Martins et al., 2015). The CPI $_{25–35}$ (carbon preference index) for odd-to-even *n*-alkanes with high molecular weight can sign plant wax contribution (CPI > 1.0, typically 4.0 – 6.0) or fossil fuel contamination (CPI < 1.0) (Aboul-Kassim and Simoneit, 1996; Wang et al., 2009; Abreu-Mota et al., 2014). CPI values in both transects (4.94 – 10.5) reflect the predominance of terrigenous OM source of long-chain *n*-alkanes over petroleum contamination.

In order to further examine the terrigenous contribution, the TAR (terrigenous-to-aquatic ratio) can be applied $[(n\text{-C}_{27} + n\text{-C}_{29} + n\text{-C}_{31})/(n\text{-C}_{15} + n\text{-C}_{17} + n\text{-C}_{19})]$ with values above 1.0 being diagnostic of terrigenous material (Silliman et al., 1996; Vaezzadeh et al., 2015). In this study, TAR values ranged between 4.45 and 54.7, with average values increasing progressively from the lower mudflat to the upper mangrove, showing the increasing contribution of terrigenous hydrocarbons (Fig. S4).

Overall, the high natural levels of *n*-alkanes observed in the salt marshes and mangroves may be superimposed on the anthropic inputs of hydrocarbons to the sediments. Therefore, additional parameters such as PAHs and petroleum biomarkers could provide key information to the environmental assessment and must be included in these studies.

2.3.2.2. Polycyclic aromatic hydrocarbons

The concentration of total PAHs (∑PAHs) (mean ± standard deviation) were about three times higher in T1 than in T2 (Table 1, Fig. 3c). The concentrations of PAHs found in Paranaguá Bay mangroves compared to levels found in previous studies in the Paranaguá Bay bottom sediments and several locations of the world are presented as supplementary material.

Despite the low levels of PAHs, the semi-pristine T2 site presented signs of a recent contribution of petroleum hydrocarbons, with alkylated PAHs showing levels close to T1. The PAHs (4-6 rings) were prevalent in T1 that can be preliminary assigned to pyrogenic sources and pyrene presented the highest level of an individual compound in this site.

Perylene, a diagenetic-related PAH, was detected in higher concentrations if compared to other individual PAH in the majority of sediments analyzed, representing 50-100% of the 5-ring PAHs in T2 and 24-52% in T1. Perylene represented the most abundant PAH in the T2 sample, and the lower predominance of this compound in the T1 can be linked to the relatively higher contribution of the other anthropogenic PAHs.

The PAH isomer pair ratios (Yunker et al., 2002) calculated for the sediment samples are shown in Fig. S5, and the results indicate the predominance of PAHs from combustion processes as the main source of PAHs in both transects. Despite this general trend, samples in the control site showed a tendency towards the range of petrogenic sources (Fig. S5b). However, the majority of the PAHs ratios in both sites remained in the petroleum or biomass combustion range (Fig. S5a, c and d). Similar results were verified in Shantou wetlands, China, where pyrolytic PAHs were also prevalent in an impacted environment (Cao et al., 2009).

2.3.2.3. Petroleum biomarkers

The concentrations of petroleum biomarkers are presented in Table 1. Hopanes were predominant, followed by terpanes and steranes, the latter two having similar concentrations (Fig. 3d). The concentrations of PAHs found in Paranaguá Bay mangroves compared to levels found in previous studies in several locations of the world are presented as supplementary material.

Total hopanes (∑Hopanes) concentrations were on average five-fold higher in T1 compared to T2. The C_{30}-17α(H),21β(H)-hopane was the predominant hopane in the T1 while the

C_{31}-17α(H),21β(H)-hopane (22R) was dominant in the T2 transect (Fig. S6a). Both hopanes are characteristically sourced from crude oil, with the thermodynamically stable 17α(H),21β(H) configuration (Peters et al., 2005). However, 17α,21β(H)-homohopane (22R) can be quickly formed through diagenetic processes in acidic environments (Inglis et al., 2018). So, the diagenetic formation of this compound in the sediments may be suggested as an additional source of this specific compound to the T2.

Furthermore, extended hopanes (C_{31}-C_{35} S and R homohopanes) found in the T1 samples are also unequivocal indications of petrogenic contamination of marine sediments (Babcock-Adams et al., 2017). These typical doublets of extended hopanes found in crude oil are not apparent in the T2 chromatograms, but present other biological hopanes such as C_{30}-17β,21β-hopane (Silva and Bicego, 2010). The presence of biogenic compounds in the m/z 191 and 217 fragmentograms in sediment samples with recent OM inputs have been reported (e.g. Meniconi and Barbanti, 2007) and high peaks observed in the T2 site may be linked to ‘fresh’ bacterial contribution in the m/z 191 related to hopenes (such as diploptene) (Bieger et al., 1996; Le Dréau et al., 1997; Tolosa et al., 2009) or other biologically-produced hopanes derived from polyhydroxyhopanoids of bacterial origin that are ubiquitous in immature sediments (Volkman, 2005). Also, mangrove sediments can have multiple triterpenoid compounds from high-plants (He et al., 2018) and many biogenic compounds have m/z 191 fragments such as unsaturated hopanes, lupenes, oleanenes (Simoneit, 1996; Shiojima et al., 1992).

Terpanes were prominent in T2, as expressed by higher values of diagnostic ratios (iv) and (v) (Table 2). It can be attributed to the fuel used by small boats and ships around Paranaguá Bay since these compounds are common in diesel fuel and in lubricating oils (Simoneit, 2005). The occurrence of an UCM related to medium-carbon chain length (C_{15} – C_{25}) is also characteristic of this oil source. The T2 site presented terpanes that are less resistant to environmental degradation than pentacyclic terpanes (Bieger et al., 1996), suggesting a more recent (or less degraded) input of hydrocarbons.

Total steranes (∑Steranes) concentrations were on average six-fold higher in T1 than in T2, with levels similar to locations under chronic pollution, such as the Gulf of Mexico sediments before the Deepwater Horizon accident (Babcock-Adams et al., 2017). The most abundant compounds were stigmastanes (C_{29}) (24-ethyl-5α,14α,17α-cholestane 20S and 20R; and 24-ethyl-5α,14β,17β-cholestane 20S and 20R) indicating mainly terrigenous matured OM (Fig. S6b). The C_{29}-ααα/C_{29}-αββ ratio values for site T1 were around 1.0, typical of mature sedimentary OM (Volkman et al., 1997). At the T2 site, only four compounds were detected, limiting the use of diagnostic ratios. Steranes have relatively poor chromatographic resolution in one-dimensional gas chromatography due to the variety of homologous series and stereoisomers (Araújo and Azevedo, 2016). In spite of these limitations, total steranes could provide qualitative information about petroleum hydrocarbon inputs and are a reliable specific molecular marker to the study area since no expected biogenic inputs of matured OM with m/z 218 and specific 5α,14β,17β configuration from matured hydrocarbons was presented (Wang et al., 2007).

According to Bayona and Albaiges (2006) and references therein, the sterane 20S/S + R epimeric ratio (e.g. ratio (x), Table 2) are indicators of primary maturity and they usually reach the thermodynamic equilibrium values in mature crude oils. While studying oil spills fingerprint, these ratios would be of limited interest because all oils would present similar values, resulting in no differentiation from one potential source to another. However, these ratios can provide signals of the extension of oil biodegradation in environmental conditions, since the biological isomer 20R is removed faster than 20S compounds; the same tendency occur with 14α(H),17α(H) isomers in relation to the 14β(H),17β(H). In the T2 sites, the main compound has 'αααR' configuration, considered as the more degradable sterane, and in the T1 site, the prevailing components were 'αββR' (9 samples) and 'αααS' (6 samples), considered to be the more resistant steranes (Chosson et al., 1992).

Furthermore, the calculated ratios for C_{29} steranes isomers shows higher values of C_{29} ααα (S/S + R) and lower values for the C_{29} αββ/(αββ+ααα) (ratios (vii) and (viii), Table 2) in T1 sites. These differences can be a reflex of a decrease in ααα and R isomers, expected to be preferentially attacked by microbial degradation (Bayona and Albaiges, 2006). Additionally, the carbon number also affects the degradation rate of steranes ($C_{27} > C_{28} > C_{29}$); so, the absence of C_{27} and C_{28} isomers may be a signal of preferential degradation by the local microbiota (Bayona and Albaiges, 2006).

Petroleum biomarkers diagnostic ratios are often used in petroleum geochemistry and forensic studies of oils spills (Peters et al., 2005; Wang et al., 2009). In contrast, where contamination sources are considered to be diffuse, it is a challenge to assign sources using the calculated diagnostic ratios (Wagener et al., 2012; Keshavarzifard et al., 2015). In this study, most of the calculated ratios for each of the sites were in different ranges, suggesting that there are distinct petroleum biomarkers sources or, alternatively, hydrocarbons have suffered distinct levels of weathering processes (Table 2).

The fundamentals of fingerprinting methods for identification of oil spills is that each oil is unique in terms of petroleum biomarkers composition. However, if sources are diffuse as in the case of chronic pollution the result can be a sum of many possible sources (Wagener et al., 2012). Therefore, an exact match is not always possible, as observed in other chronically impacted sites (Le Dréau et al., 1997; Tolosa et al., 2009) and there is no single diagnostic ratio that can be used to identify the source of unknown spilled oil by itself without matching it to known oils (Wang et al., 2007).

The weathering of oil may change the characteristics of the original input, although hopanes are considered to be stable in environmental conditions and the C_{29}/C_{30} hopanes (ratio (iii), Table 2) is apparently independent of weathering effects (Wang and Fingas, 1995). However, incubation studies have shown that C_{30} hopanes may be degraded if environmental temperature is high or around 30 ^{o}C (Frontera-Suau et al., 2002) as observed in the studied sites (Table 1). In the incubation conditions used by Frontera-Suau et al. (2002) the biomarker Tm had a relatively faster rate of biodegradation than its homolog Ts, resulting in higher Ts/(Tm + Ts) values for heavily biodegraded samples. Homohopane index was also affected by degradation with higher values verified for degraded oils. A similar tendency was observed for the studied sites (ratios (i) and (x), Table 2).

In general, tricyclic terpanes are considered to be very resistant compared to other petroleum biomarkers (Head et al., 2003; Larter et al., 2012). However, some degradation may occur, mostly in the lighter compounds. In the C_{23}/C_{24} tricyclic terpanes ratio (ii), Table 2), both of these terpanes are biodegradable, but the degradation rate of C_{23} is higher than C_{24}, since lower C_{23}/C_{24} values are observed for degraded oils (Wang and Fingas, 1995).

Aeppli et al. (2014) studied the biodegradation in the Deepwater Horizon oil spill and compiled several studies with different time scales. Some groups of petroleum biomarkers may undergo biodegradation only in longer time scales (more than 5 years); so, the observed alteration in petroleum biomarkers ratios in T1 and T2 sites can be a result of some years of accumulation and degradation of the chronic inputs of hydrocarbons. In the case of T1, it is possible that the oil may be biodegraded even before being released to the environment (inside the ships in wastewater tanks), since the autochthonous microbiota consortium may possess high potential for hydrocarbon degradation (Nievas et al., 2006; Chandrasekaran et al., 2011).

Navigation activities can be an important widespread source of petroleum biomarkers to the marine coastal sediments (Volkman et al., 1992; Bieger et al., 1996). In the study area, there was clear evidence of contamination from the ship traffic from Paranaguá port (T1) and small touristic and fishing boats (T2). These sources of hydrocarbon contamination are coherent with the distribution of petroleum biomarkers and UCM humps detected mostly in the T1 site, that are similar to oil and derivatives used in the local fleet (Peters et al., 2005). Large ships that use maritime oil as the main source of energy and oil lubricants and grease that contains petroleum biomarkers may be an important source of hydrocarbon pollution to the coastal areas. They are recognized worldwide as a relevant source of chronic oil pollution, as the result of the continuous stream of smaller and larger oil spills and operational discharges of oily waste (bilge water) from vessels (USNRC, 2003; Wiese and Ryan, 2003; García-Borboroglu et al., 2006). These residues may contain petroleum biomarkers, as maritime fuel is the result of the highest boiling residues of crude oil distillation and inherits most biomarkers. Then, the chemical fingerprint of an oily waste will be a mixture of the fuels, lubricants, and solvents that are used on board (Wang et al., 2007) and they are very difficult to identify individually.

Another expected source of hydrocarbons to the estuary is Paranaguá city, with contributions from urban runoff, sewage and atmospheric deposition – that may as well contain petroleum biomarkers. The lubricant oils used in the cars at coastal urban centers can leave their fingerprint on coastal sediments (Zakaria et al., 2000) provided that lubricating oils largely reflect the biomarker distributions in the original crude oil (Wang et al., 2007). Additionally, the predominance of high molecular weight PAHs (4-6 rings) found in T1 zones can also be related to urban runoff (Wang et al., 1999).

In contrast, T2 zones presented different PAHs, showing signs of low molecular weight compounds associated to 'fresh' petrogenic sources and significative contribution of perylene, a diagenetic-related PAH. Despite the fact that the studied mangrove margins are unoccupied, the local traffic of boats moved by gasoline or diesel engines may contribute to low level, chronic inputs of fuel, lubricant, engine wastes and soot that are released to the environment and ultimately are adsorbed to the suspended material and deposited in the sediments (Bieger et al., 1996).

2.3.3. Statistical analyses

The correlation coefficients (*r*) between silt+clay, TOC and hydrocarbons classes are shown in Table S1. Some groups of hydrocarbons exhibited a highly significant correlation to each other ($p < 0.05$, n = 30): ∑PAHs *vs* ∑PAHs (2-3 rings) and ∑PAHs (4-6 rings); ∑Hopanes *vs* ∑Steranes. Other groups presented a significant correlation ($p < 0.10$, n = 30): ∑AHs_R *vs* TOC; ∑AHs_R *vs* ∑*n*-alkanes; ∑PAHs (2-3 rings) *vs* ∑PAHs (4-6 rings); ∑PAHs (4-6 rings) *vs* ∑Terpanes, ∑Hopanes and ∑Steranes; ∑Terpanes *vs* ∑Steranes.

The correlation between Resolved AHs and *n*-alkanes point to a predominant biogenic origin to these groups, with an influence of the TOC in the distribution of these compounds. In contrast, the correlation between PAHs with 4-6 rings and the petroleum biomarkers indicates the influence of oil contamination in association to pyrolytic origins of PAHs, suggesting another source of hydrocarbons to the sediments linked to contamination/anthropic sources.

The ANOVA results showed significant differences in interaction between factors for all mean dependent variables analyzed (Table S2). For the fine sediments and TOC, all zones followed the same pattern, except for TOC in the salt marsh zone (SM) where significantly lower concentrations were found in the impacted transect (T1). Considering the aliphatic hydrocarbons, PAHs and petroleum biomarkers analyzed in the five zones within the transects, all hydrocarbons concentrations in the lower mudflat zone (LF) were significantly higher in T1, except for ∑Alkyl PAHs which had significantly higher values detected in T2. In the upper mudflat zone (UF), ∑PAHs, ∑Alkyl PAHs, ∑PAHs (4-6 rings), ∑Terpanes, ∑Hopanes and ∑Steranes showed significantly higher concentrations in T1. However, for ∑PAHs (2-3 rings) the differences were not significant between the two transects. In salt marshes zone (SM) the differences were not significant for ∑PAHs, ∑PAHs (2-3 rings), ∑PAHs (4-6 rings) and ∑Terpanes. For ∑n-alkanes and ∑Alkyl PAHs significantly lower means were found in T1 and for ∑PAHs, ∑PAHs (2-3rings) and ∑Terpanes the differences were not significant between transects. Significantly higher means were found for ∑Hopanes and ∑Steranes in T1. In the lower mangrove zone (LM), significantly lower concentrations were observed in T1 for ∑*n*-alkanes but the differences were not significant for ∑Alkyl PAHs; and the means were significantly higher in T1 for all the other hydrocarbon groups. In the upper mangrove zone (UM) the significantly higher for ∑PAHs, ∑PAHs (2-3rings), ∑PAHs (4-6rings), ∑Terpanes, ∑Hopanes and ∑Steranes in T1. No significant differences were observed for ∑*n*-alkanes and ∑Alkyl PAHs. In general, the results evidenced a higher impact in T1 in most zones, mainly for ∑Hopanes and ∑Steranes since all zones from this transect were significantly different when compared to T2.

2.3.4. Hydrocarbon distribution along transects

In general, the concentration of different classes of hydrocarbons increased as immersion time decreased, despite within-transect differences (Fig. 4). However, as a similar trend for both sites, aliphatic hydrocarbons presented higher levels of total aliphatic hydrocarbons in the lower mangrove (LM), with a noticeable UCM contribution. The lower mudflat zone (LF) also presented a high UCM but the lowest hydrocarbons concentrations were always observed in the upper mudflat (UF) (Fig. 4c and 4d).

PAHs distribution along the transect also increased with decreasing time of immersion (Fig. 4d and 4e). A similar distribution was reported by Cao et al. (2009) in the human-impacted Shantou wetlands, China. However, there were exceptions to this general distribution trend, as the in lower mudflat (LF) in T1 and the salt marsh (SM) in T2. The PAHs distribution trends were similar to the TOC and fine grain size (Fig. 4a and 4b). Salt marsh (SM) presented the highest levels of PAHs in T2 with an important contribution of alkyl PAHs. Conversely, in T1 the upper mangrove (UM) was the most impacted environment but the lower mudflat (LF) also showed high PAHs concentrations.

The distribution of petroleum biomarkers along the transect was similar to the distribution of PAHs, with concentrations increasing towards the land (Fig. 4g and 4h). Exceptions to this trend were seen for the lower mudflat (LF) in T1 and salt marsh (SM) in T2, both with relatively higher levels of petroleum biomarkers.

Overal, hydrocarbon levels tend to increase as flooding time decreases. This might be a result of the remobilization of compounds by the water preventing the accumulation of OM in the zones more exposed to wave energy, such as the upper mudflat. In contrast, more protected zones such as the salt marsh and mangrove seem to possess a higher capacity of accumulation of chronic inputs of hydrocarbons. This is a matter of concern, since these environments may be subjected to pollution even in remote areas, considered to be away from the major expected sources of hydrocarbons. These environments should be treated as preferential places for environmental monitoring of hydrophobic compounds, including hydrocarbons.

2.4. Conclusions

This was the first study focusing on the petroleum biomarkers at Paranaguá Bay mangroves, an important subtropical environment in South Hemisphere. Hydrocarbon levels varied along the transects (mudflat, salt marsh and mangrove) in accordance to the organic carbon and fine sediments content. Differences between sites (control *vs* impacted) were not evidenced by *n*-alkanes levels which had a predominant biogenic input. In contrast, PAHs and petroleum biomarkers revealed the contribution from anthropic sources with concentrations at least three times higher in the impacted site than in the semi-pristine site. Petrogenic inputs could be assigned by the presence of alkyl PAHs and petroleum biomarkers, while combustion sources were evidenced by high molecular weight PAHs.

Petroleum biomarkers are a reliable tool to assess petroleum inputs to subtropical mangroves being able to reveal preferential sites of deposition and assign different levels of chronic oil contamination (particularly the hopanes, that were found in relatively higher concentrations). Despite the high background levels of natural hydrocarbons from biogenic source (both normal and cyclic hydrocarbons), the anthropic inputs could be clearly assigned. Petroleum biomarkers provided evidences that the deposition of hydrocarbons is different for each zone along the terrestrial-aquatic gradient and salt marshes and mangroves are the preferential environments for the accumulation of hydrocarbons. As such, monitoring for oil pollution must be considered as a priority in areas subjected to chronic contamination.

The recalcitrance and source-specificity of these compounds are the main characteristics that provide high reliability for the assessment of chronic petroleum pollution to coastal sediments. Although diagnostic ratios of petroleum biomarkers could not be linked unequivocally to any specific type of oil, the calculated values for T1 and T2 sites provided information about two possible different sources of hydrocarbons and/or different levels of degradation. This methodology will be applied to further investigations in the study area and can also be extended to other salt marshes and mangrove swamps to provide a reliable assessment of these ecosystems.

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Figures

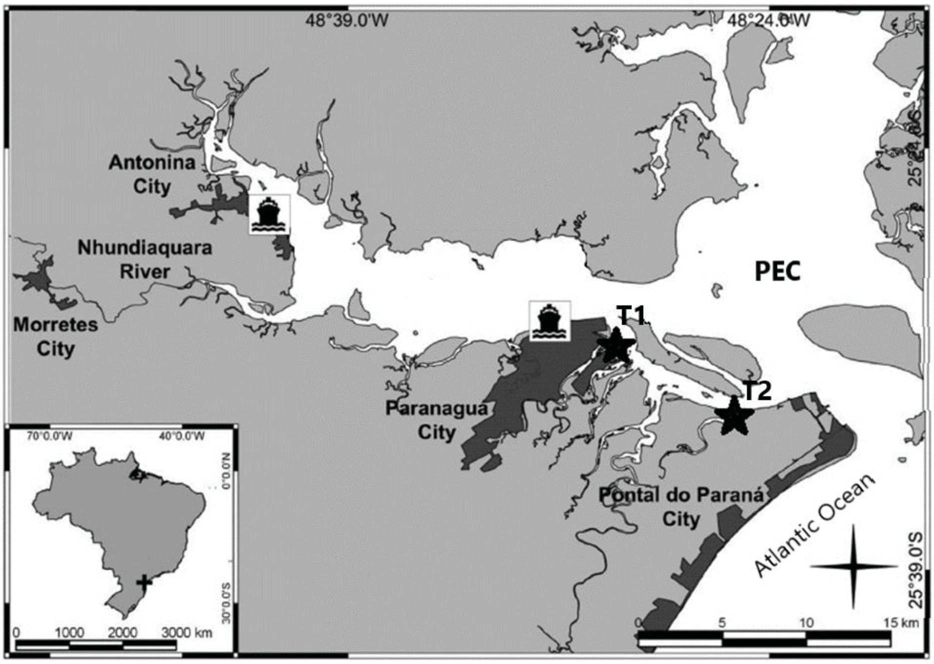

Fig. 1. Paranaguá Bay with T1 and T2 sampling sites (black stars).

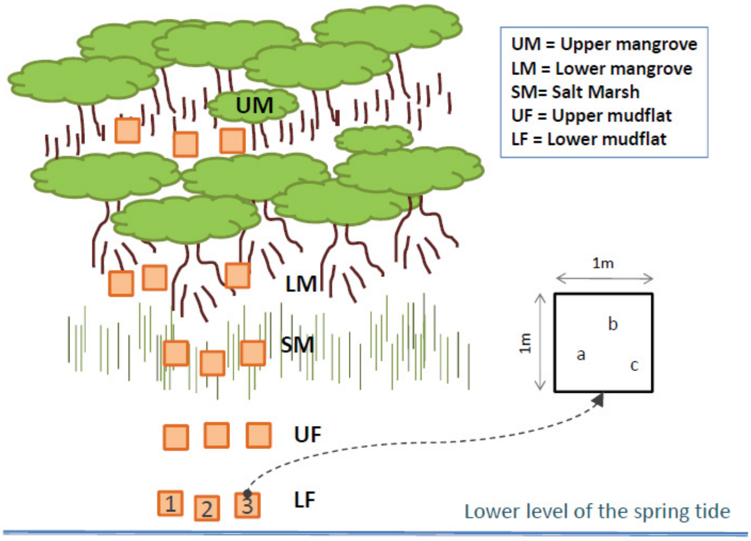

Fig. 2. Sampling design diagram.

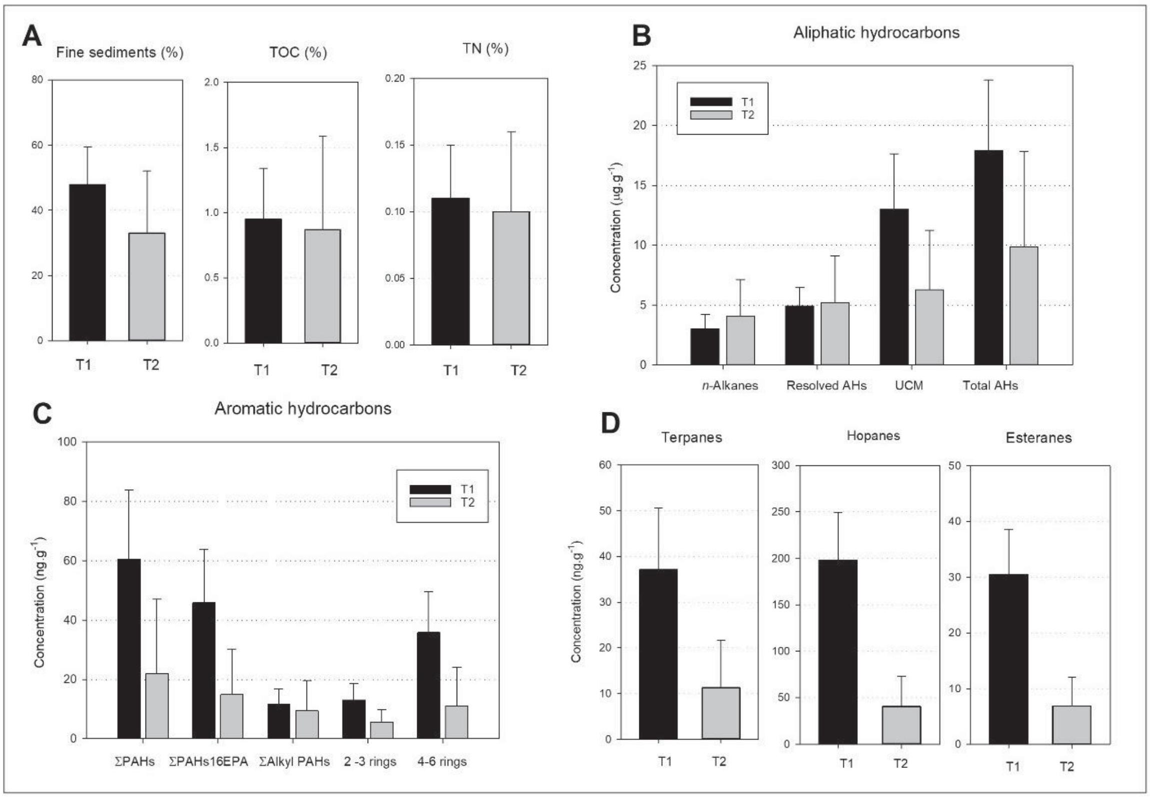

Fig. 3. Average results for control *vs* impacted site: bulk results (A); aliphatic hydrocarbons (B); polycyclic aromatic hydrocarbons (C), and; petroleum biomarkers (D) (error bars = standard deviation).

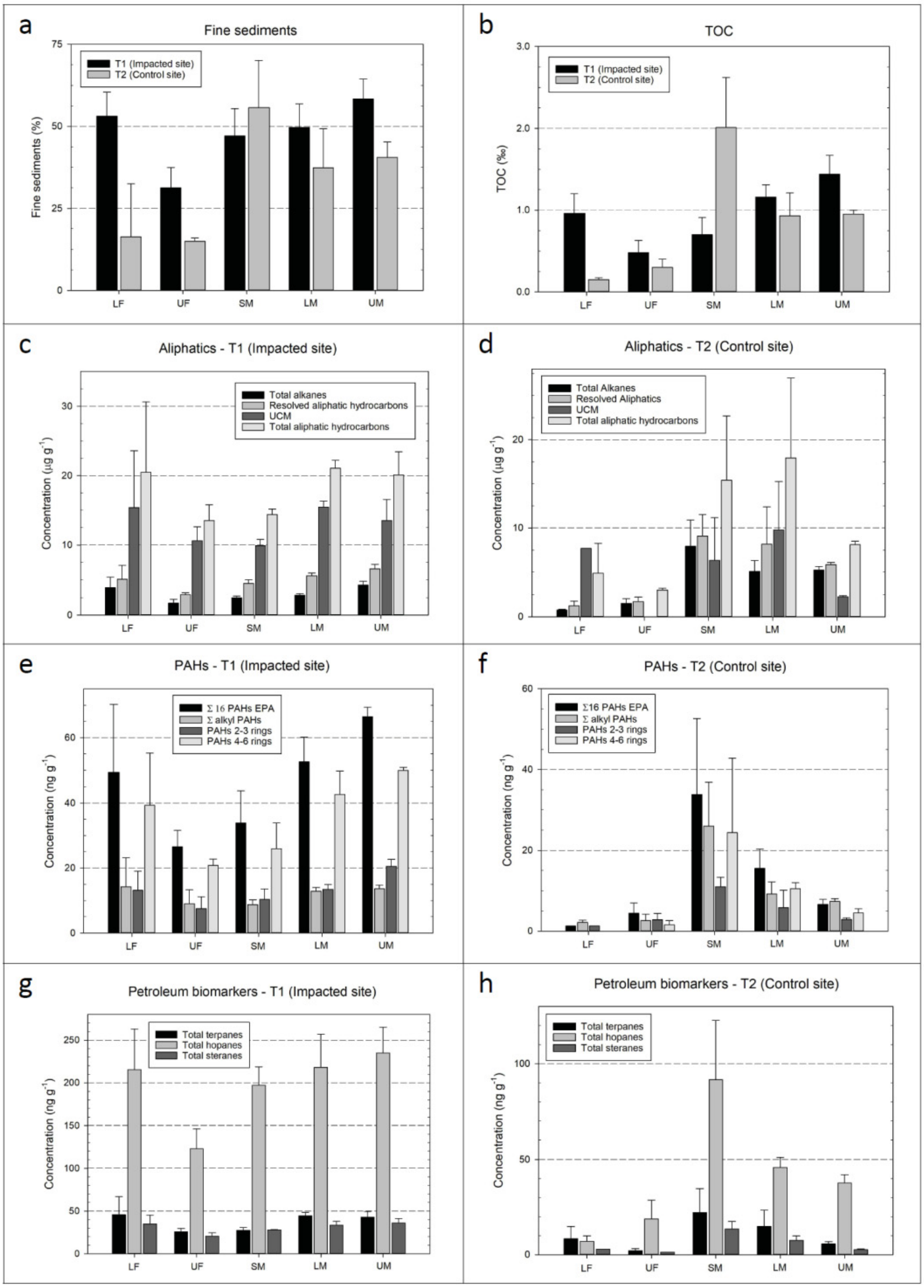

Fig. 4. Average results for groups of hydrocarbons along the transects. LF - lower mudflat; UF - upper mudflat; S - salt marsh; LM - lower mangrove, and; UM - upper mangrove.

Tables

Table 1. Summary of the results for field/bulk parameters and hydrocarbon concentrations. SD: standard deviation; <DL: below detection limit.

	Parameters	**Impacted (T1)**		**Control (T2)**	
		Min − Max	Mean (± SD)	Min − Max	Mean (± SD)
Field parameters	Temperature (°C)	28.5 − 31.3	30.1 ± 1.0	25.9 − 27.5	26.8 ± 0.6
	pH	6.1 − 6.6	6.3 ± 0.1	4.8 − 6.2	5.5 ± 0.4
	Eh (mV)	-178.0 − 50.0	-81.6 ± 64.0	-310.0 − 117.0	-7.1 ± 96.5
Bulk parameters	Fine sediment (% silt+clay)	23.7 − 67.0	47.9 ± 11.6	4.3 − 66.6	33.0 ± 19.1
	TOC (%)	0.37 − 1.76	0.95 ± 0.39	0.13 − 2.71	0.87 ± 0.72
	$\delta^{13}C/\delta^{12}C$	-26.0 − -23.4	-25.1 ± 0.7	-26.5 − -24.4	-25.6 ± 0.6
	TN (%)	0.06 – 0.20	0.11 ± 0.4	n.d. – 0.24	0.10 ±0.06
Aliphatic hydrocarbons (µg g^{-1})	∑*n*-alkanes	1.29 – 6.00	3.03 ±1.20	0.64 – 11.9	4.11 ± 3.02
	∑AHs_R	2.55 – 7.91	4.93 ±1.57	0.69 – 14.2	5.21 ± 3.91
	UCM	7.28 – 26.6	13.0 ± 4.66	2.13 – 15.2	6.28 ± 4.98
	∑AHs	10.8 – 34.5	17.9 ± 5.90	2.27 – 29.4	9.86 ± 7.97
Aromatic hydrocarbons (ng g^{-1})	∑PAHs	27.4 – 109.8	60.4 ±23.3	0.64 – 95.8	22.0 ± 25.0
	∑16 PAHs EPA	21.1 – 78.6	45.8 ±18.0	<DL – 59.8	14.9 ± 15.4
	∑Alkyl PAHs	4.69 – 26.9	11.7 ± 5.12	0.64 – 33.8	9.48 ± 10.1
	∑PAHs (2-3rings)	4.63 – 22.3	13.0 ± 5.67	<DL – 13.1	5.51 ± 4.28
	∑PAHs (4-6rings)	18.1 – 61.4	35.7 ±13.8	<DL – 49.1	11.0 ± 13.1
Petroleum biomarkers (ng g^{-1})	Total Terpanes	21.8 – 75.3	37.1 ± 13.5	<DL – 39.6	11.3 ±10.4
	Total Hopanes	103.4 – 282.3	197.7 ± 51.8	3.69 – 133.3	40.2 ± 32.7
	Total Steranes	15.9 – 48.6	30.4 ± 8.17	1.41 – 18.7	6.89 ± 5.19

Table 2. Ranges for petroleum biomarkers ratios in the sampling sites of Paranaguá Bay.

Code	Diagnostic ratio	Impacted (T1)	Control (T2)	Expected effect of biodegradation	References
i	Ts/(Ts+Tm)	0.77 – 0.83	0.58 – 0.67	↑	Wang and Fingas (1995); Munoz et al. (1997); Frontera-Suau et al. (2002)
ii	C_{23}/C_{24} tricyclic	1.66 – 1.88	1.46 – 2.32	↓	Wang and Fingas (1995)
iii	C_{29}/C_{30} hopane	0.57 – 0.92	0.74 – 1.10	↓	Frontera-Suau et al. (2002)
iv	C_{31}-C_{35} α,β S/(S+R)	0.51 – 0.56	0.28 – 0.53	↑	Munoz et al. (1997), Bost et al. (2001)
v	C_{30}-β,α/(C_{30}-β,α + C_{30}-α,β)	0.16 – 0.23	0.23 – 0.50	-	
vi	C_{31}-22S/(C_{31}-22S + C_{31}-22R)	0.45 – 0.51	0.29 – 0.34	↑	Munoz et al. (1997)
vii	C_{29} ααα (S/S + R)	0.66 – 1.00	0.30 – 0.41	↑	Bayona and Albaiges (2006)
viii	C_{29} αββ/(αββ+ααα)	0.48 – 0.64	0.31 – 0.47	↑	Bayona and Albaiges (2006)
ix	ΣC_{31}-C_{35}/C_{30}	1.56 – 2.07	2.00 – 3.54	↓	Aeppli et al. (2014); Wang et al. (2001)
x	Homopane index	3.06 – 7.81	0.00 – 5.12	↑	Frontera-Suau et al. (2002)

Appendix A. Supplementary data

Material and Methods

1. Bulk parameters

Approximately 6-8 mg of dry sediment was decarbonated with HCl solution (1 mol L^{-1}) (Costa *et al*., 2016) and total nitrogen was determined in the same amount of bulk sediment (Ryba and Burgess, 2002). Standards (USGS-40, glutamic acid, United States Geological Survey, and IAEA-600, caffeine, International Atomic Energy Agency) were determined before each bath of 40 samples to verify the analytical accuracy. The standard deviation for the calibration of $\delta^{13}C$ was equal to 0.01% (USGS-40) and 0.03% (IAEA-600). The standard used for determination of carbon and nitrogen contents was Soil LECO (LECO Corporation, USA) (estimated levels of 13.6% and 0.81%, respectively).

2. Instrumental analyses and quality assurance procedures

Hydrocarbons analysis was performed with a gas chromatograph (Agilent Model 7890A) coupled to a mass spectrometer (Agilent 5973N inert MSD with Triple-Axis Detector) using a fused silica capillary column coated with 5% diphenyl/dimethyl siloxane (30 m, 0.25 mm internal diameter, 0.25 µm film thickness). A 2 µL aliquot of each extract (fraction 1 and 2) was injected in splitless mode with the injector temperature at 280°C. Oven temperature ramp was programmed from 40 to 60°C at 20 °C min^{-1}, then to 290 °C at 5 °C min^{-1}, and finally to 300 °C at 6 °C min^{-1}, with a final hold for 20 min. The interface with the detector was conditioned at 300 °C and the ion source at 230 °C. Data acquisition was performed in selected ion monitoring (SIM) mode (Table S3).

Individual *n*-alkanes and PAHs were identified by matching their retention times and ion mass fragments (m/z) with those from standard mixtures (*n*-C_{12} to *n*-C_{39}, DRH-008S-R2 and Z-014G-FL respectively, both from AccuStandard). The calibration range used in the quantification were 0.25 to 15.0 and 0.10 to 2.00 ng μL^{-1} respectively. Petroleum biomarkers were quantified based on response factor of 17α(H),21β(H)-Hopane-C_{30}-αβ and 5α-cholestane-C_{27}-ααα-20R, both from Chiron, with concentrations range from 0.10 to 2.00 ng μL^{-1}, and identified by their ion mass fragments compared to m/z chromatograms obtained in the literature (Wang et al., 2009; Tolosa et al., 2009; Yang et al., 2011) and from injected oil samples (commercial Arab Light, MF 380 and Marlim Blend). Total aliphatic hydrocarbons were determined by the total area of the chromatogram of the aliphatic fraction. Unresolved Complex Mixture (UCM) was calculated by the total aliphatic hydrocarbons minus the area of the unidentified peaks in the aliphatic fraction (resolved aliphatic hydrocarbons) and the *n*-alkanes, pristane and phytane peaks.

Quality assurance procedures included analyses of procedural blanks, matrix spikes, precision tests and certified reference material (Wade and Cantillo, 1994). Blanks were performed for each extraction batch of 11 samples and did not show interference with the analyses of the target compounds. Mean standard recoveries for the spiked sediments were 60 ± 8% for 1-hexadecene, 83 ± 10% for 1-eicosene, 40 ± 9% for naphthalene-d_8, 60 ± 10% for acenaphtene-d_{10}, 83 ±15 % for phenantrene-d_{10}, 86 ± 11% for chysene-d_{12}, 84 ± 13% for perylene-d_{12} and 80 ± 13% for 5α-cholestane-d_4.

The detection limit (DL) and repeatability were obtained by analyzing the samples spiked with known concentration of standards (Table S4). The DL was determined by the addition of known standards in concentrations 10 times lower than expected for the samples and was considered as the highest value obtained in comparison to the instrumental detection limit (IDL) of 0.001 µg g^{-1} for individual *n*-alkanes and 0.50 ng g^{-1} for PAHs and petroleum biomarkers. Precision for aliphatic hydrocarbons was 90% within the target (< 15% of the average values), while 100% of the PAHs and petroleum biomarkers attended this threshold. Additionally, target hydrocarbon concentrations in the sediment reference material (IAEA-417; International Atomic Energy Agency) were satisfactory, with recoveries in agreement to ±35% within the certified values.

Results and Discussion

1. Levels of hydrocarbons compared to other locations

The concentrations of *n*-alkanes found in Paranaguá Bay mangroves showed similar or slightly higher concentrations when compared to previous studies in the Paranaguá Bay bottom sediments (0.28 – 8.19 µg g^{-1}, Martins et al., 2012; 0.01 – 1.23 µg g^{-1}, Abreu-Mota et al., 2014); <DL – 3.45 µg g^{-1}, Bet et al., 2015; 6.04 – 12.98 µg g^{-1}, Martins et al., 2015). When compared to other mangrove forests, the *n*-alkanes levels in the Paranaguá bay sediments are lower or similar to pristine places such as Camamu Bay, Brazil (0.8 – 55.2 µg g^{-1}, Paixão et al., 2011), Itaparica, Brazil (0.1 – 5.7 µg g^{-1}, Santos et al., 2013), Pichavaram, India (0.0 – 9.4 µg g^{-1}, Ranjan et al., 2015) and Kerala, India (10.3 – 221.4 µg g^{-1}, Resmi et al., 2016). Impacted mangroves located in Santa Catarina State, Brazil presented similar levels of *n*-alkanes (0.53 – 18.14 µg g^{-1}, Oliveira and Madureira, 2011; 4.2 – 55.6 µg g^{-1}, Assunção et al., 2017). However, most of the impacted mangroves presented higher *n*-alkanes levels, as those reported for Guanabara Bay, Brazil (3 – 318 µg g^{-1}, Farias et al., 2008); the Strait of Malacca, Malaysia (28.0 – 254.5 µg g^{-1}, Vaezzadeh et al., 2015) and the Caribbean (0.7 – 382.8 µg g^{-1}, Bernard et al., 1996).

Considering the sixteen prioritary PAHs listed by USEPA (∑16PAHs EPA), previous studies in the Paranaguá Bay bottom sediments showed similar levels of PAHs (3.85 – 89.2 ng g^{-1}, Martins et al., 2012; <DL – 57.2 ng g^{-1}, Abreu-Mota et al., 2014; 0.6 – 63.8 ng g^{-1}, Cardoso et al., 2016) and in areas near Paranaguá Port the levels were 10 times higher (15 – 812 ng g^{-1}, Martins et al., 2015). Also, the concentrations were low if compared to impacted mangroves such as Guanabara Bay, Brazil (10 – 240,394 ng g^{-1}, Farias et al., 2008; 4,400 – 1,387,000 ng g^{-1}, Fontana et al., 2012); Florianópolis, South Brazil (25.9 – 434.2 ng g^{-1}, Assunção et al., 2017); Fortaleza, Brazil (3,040 – 2,234,760 ng g^{-1}, Cavalcante et al., 2009); Guadeloupe Island, the Caribbean (103 – 1,657 ng g^{-1}, Bernard et al., 1996); Puerto Rico coast (500 – 58,800 ng g^{1}, Klekowski et al., 1994) and Shantou wetlands, China (57– 238 ng g^{-1}, Cao et al., 2009).

Concentrations found in Paranaguá Bay mangrove sediments were 1-2 orders of magnitude lower than those reported for highly impacted Brazilian coastal mangrove areas, such as Guanabara Bay (up to 64,68 μg g^{-1}, Farias et al., 2008); São Sebastião Channel (<LD – 2.20 μg g^{-1}, Silva and Bícego, 2010) and Santos Bay (0.05 – 2.56 μg g^{-1}, Medeiros and Bícego, 2004) and also the Athabasca River, Canada (0.22 – 30.00 μg g^{-1}, Wang et al., 2014). Concentrations were similar to those reported for the human impacted area of Pearl River Delta, China (0.01 – 0.40 μg g^{-1}, Yang et al., 2011) and the pristine Hecate Strait, Canada (0.01 – 0.06 μg g^{-1}, Yunker et al., 2014), where natural background prevails.

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Table S1. Spearman correlation coefficients correlating hydrocarbons classes, grain size (% silt+clay) and TOC in the sediments collected in Paranaguá Bay. Bold values mean significant correlation at the 95% level ($p < 0.05$) and underlined values mean significant correlations at the 90% level ($p < 0.10$)

	% silt+clay	**TOC**	**∑*n*-alkanes**	**∑AHs_R**	**∑AHs**	**∑PAHs**	**∑Alkyl PAHs**	**∑PAHs (2-3rings)**	**∑PAHs (4-6rings)**	**∑Terpanes**	**∑Hopanes**	**∑Steranes**
% silt+clay	**x**											
TOC	0.67	**x**										
∑*n*-alkanes	0.57	0.86	**x**									
∑AHs_R	0.57	0.93	0.94	**x**								
∑AHs	0.47	0.66	0.46	0.66	**x**							
∑PAHs	0.74	0.78	0.53	0.66	0.83	**x**						
∑Alkyl PAHs	0.66	0.88	0.71	0.79	0.73	0.89	**x**					
∑PAHs (2-3rings)	0.62	0.75	0.48	0.63	0.79	**0.95**	0.85	**x**				
∑PAHs (4-6rings)	0.71	0.67	0.42	0.54	0.83	**0.97**	0.79	0.92	**x**			
∑Terpanes	0.61	0.57	0.30	0.48	0.86	0.88	0.67	0.84	0.92	**x**		
∑Hopanes	0.69	0.57	0.34	0.49	0.76	0.90	0.70	0.89	0.93	0.88	**x**	
∑Steranes	0.65	0.55	0.29	0.47	0.81	0.88	0.68	0.88	0.92	0.94	**0.97**	**x**

Table S2: Summary of analysis of variance (n = 3 replicate per zone) for mean of main parameters. For SNK pair-wise a posteriori comparison: LF = Lower Mudflat, UF = Upper Mudflat, SM = Salt Marsh, LM = Lower Mangrove, UP = Upper Mangrove. “>” indicates $p < 0.05$ and “=” indicates $p > 0.05$. Significant terms of interest (α =0.05) are highlighted in bold. Data transformed to 1ln(x +1) before analysis

		% of fine sediments		**TOC**		**∑n-alkanes**	
Source	df	MS	F	MS	F	MS	F
Transect = Tr	1	1672.68	12.65**	0.08	3.02	0.06	1.18
Zone = Zn	4	816.11	6.17**	0.41	15.73***	0.84	16.46***
Tr x Zn	4	394.32	**2.98***	0.28	**10.76*****	0.72	**14.07*****
Residual	20	132.21		0.03		0.05	
SNK tests		Among levels of Tr, within Zn LF: T1 > T2; UF: T1 = T2 SM: T1 = T2; LM: T1 = T2 UP: T1 = T2		Among levels of Tr, within Zn LF: T1 > T2; UF: T1 = T2 SM: T1 < T2; LM: T1 = T2 UP: T1 = T2		Among levels of Tr, within Zn LF: T1 > T2; UF: T1 = T2 SM: T1 < T2; LM: T1 < T2 UP: T1 = T2	

		∑PAHs		**∑Alkyl PAHs**		**∑PAHs (2-3 rings)**	
Source	df	MS	F	MS	F	MS	F
Transect = Tr	1	25.81	115.68***	1.81	10.44**	551.69	39.28***
Zone = Zn	4	2.65	11.89***	1.13	6.54**	50.39	3.59*
Tr x Zn	4	2.46	**11.01*****	1.20	**6.93****	73.02	**5.20****
Residual	20	0.22		0.17		14.04	
SNK tests		Among levels of Tr, within Zn LF: T1 > T2; UF: T1 > T2 SM: T1 = T2; LM: T1 > T2 UP: T1 > T2		Among levels of Tr, within Zn LF: T1 < T2; UF: T1 > T2 SM: T1 < T2; LM: T1 = T2 UP: T1 = T2		Among levels of Tr, within Zn LF: T1 > T2; UF: T1 = T2 SM: T1 = T2; LM: T1 > T2 UP: T1 > T2	

		∑PAHs (4-6 rings)		**∑Terpanes**		**∑Hopanes**	
Source	df	MS	F	MS	F	MS	F
Transect = Tr	1	5724.2	53.39***	17.69	76.68***	185990	182.57***
Zone = Zn	4	279.3	2.60	1.44	6.24**	5242	5.15**
Tr x Zn	4	452.8	**4.22***	1.03	**4.48****	3734	**3.66***
Residual	20	107.2		0.23		1019	
SNK tests		Among levels of Tr, within Zn LF: T1 > T2; UF: T1 > T2 SM: T1 = T2; LM: T1 > T2 UP: T1 > T2		Among levels of Tr, within Zn LF: T1 > T2; UF: T1 > T2 SM: T1 = T2; LM: T1 > T2 UP: T1 > T2		Among levels of Tr, within Zn LF: T1 > T2; UF: T1 > T2 SM: T1 > T2; LM: T1 > T2 UP: T1 > T2	

		∑Steranes	
Source	df	MS	F
Transect = Tr	1	31.18	247.21***
Zone = Zn	4	1.80	14.26***

Table S3: List of monitored ions (m/z) for the hydrocarbons analyses by gas chromatography coupled to mass spectrometer

Classes of hydrocarbons	**Monitored Ions (m/z)**	**Compounds**
N-alkanes and linear isoprenoids	83	*n*-C_{12} to *n*-C_{39}, pristane and phytane
Petroleum biomarkers	191	terpanes
	191	hopanes
	217/218	steranes
PAHs	128/127	naphthalene
	142/141	C_1-naphthalene
	156/141	C_2-naphthalene
	152/153	acenaphtylene
	153/154	acenaphtene
	170/155	C_3- naphthalene
	166/165	fluorene
	178/179	phenanthrene
	178/179	anthracene
	192/191	C_1-phenanthrene
	202/200	fluoranthrene
	202/200	pyrene
	228/226	benzo(*a*)anthracene
	228/226	crysene
	252/253	benzo(*b*+*j*+*k*)fluoranthrene
	252/253	benzo(*e*+*a*)pyrene
	252/253	perylene
	276/138	indeno(1,2,3-*c,d*)pyrene
	276/138	benzo(*g,h,i*)perylene
	279/139	dibenz(*a,h*)anthracene

Table S4: List of individual compounds and detection limits (DL)

***N*-alkanes, pristane, phytane**	**DL**
n-C$_{12}$	0.004
n-C$_{13}$	0.002
n-C$_{14}$	0.002
n-C$_{15}$	0.016
n-C$_{16}$	0.005
n-C$_{17}$	0.009
n-C$_{18}$	0.004
n-C$_{19}$	0.008
n-C$_{20}$	0.012
n-C$_{21}$	0.005
n-C$_{22}$	0.006
n-C$_{23}$	0.005
n-C$_{24}$	0.009
n-C$_{25}$	0.019
n-C$_{26}$	0.010
n-C$_{27}$	0.019
n-C$_{28}$	0.017
n-C$_{29}$	0.017
n-C$_{30}$	0.019
n-C$_{31}$	0.019
n-C$_{32}$	0.012
n-C$_{33}$	0.018
n-C$_{34}$	0.006
n-C$_{35}$	0.017
n-C$_{36}$	0.005
n-C$_{37}$	0.004
n-C$_{38}$	0.004
n-C$_{39}$	0.002
pristane	0.011
phytane	0.006

Aromatic hydrocarbons	**DL**
PAHs (2-3 rings)	
naphthalene	0.67
acenaphthylene	1.79
acenaphthene (*)	0.50
fluorene (*)	0.50
phenanthrene	0.82
anthracene (*)	0.50
PAHs (4-6 rings)	
fluoranthene	1.44
pyrene	1.92
benzo[a]anthracene (*)	0.50
chrysene	0.52
benzo[b]fluoranthene	1.02
benzo[j+k]fluoranthene	0.69
benzo[e]pyrene	0.60
benzo[a]pyrene	1.02
indene[1,2,3-c,d]pyrene	0.66
dibenzo[a,h]anthracene (*)	0.50
benzo[g,h,i]perylene (*)	0.50
Alkyl PAHs	
2-methynaphthalene (*)	0.50
1-methylnaphtalene (*)	0.50
C$_2$-naphthalene (*)	0.50
C$_3$- naphthalene (*)	0.50
C$_1$-phenanthrene (*)	0.50
Natural PAH	
Perylene	0.91

(*) instrumental DL > method DL

Table S4 (continued): List of individual compounds and detection limits (DL)

Terpanes and hopanes	DL
(1) C_{20}-Tricyclic Terpane (*)	0.50
(2) C_{21}-Tricyclic Terpane (*)	0.50
(3) C_{23}-Tricyclic Terpane	0.92
(4) C_{24}-Tricyclic Terpane	0.66
(5) C_{25}-Tricyclic Terpane	1.51
(6) C_{24}-Tetracyclic Terpane	0.90
(7) C_{26}-Tricyclic Terpane (*)	0.50
(8) C_{27}-18α,21β Hopane (T_s) (*)	0.50
(9) 22,29,30-Trisnorhop-17(21)-ene (T_e)	0.53
(10) C_{27}-17α,21β Hopane (T_m) (*)	0.50
(11) 17b(H)-22,29,30-Trisnorhopane (T_b) (*)	0.50
(12) C_{29}-17α,21β Hopane	2.60
(13) C_{29}-17β,21α Hopane (*)	0.50
(14) C_{30}-17α,21β Hopane	1.78
(15) C_{30}-17β,21α Hopane	1.09
(16) C_{31}-17α,21β Hopane (22S)	1.86
(17) C_{31}-17α,21β Hopane (22R)	1.93
(18) C_{30}-17β,21β Hopane	0.55
(19) C_{32}-17α,21β Hopane (22S)	0.71
(20) C_{32}-17α,21β Hopane (22R) (*)	0.50
(21) C_{33}-17α,21β Hopane (22S) (*)	0.50
(22) C_{33}-17α,21β Hopane (22R) (*)	0.50
(23) C_{34}-17α,21β Hopane (22S) (*)	0.50
(24) C_{34}-17α,21β Hopane (22R) (*)	0.50
(25) C_{35}-17α,21β Hopane (22S) (*)	0.50
(26) C_{35}-17α,21β Hopane (22R) (*)	0.50

Steranes	DL
(1) 13β,17β-diacholestane (20S) (*)	0.50
(2) 13β,17β- diacholestane (20R) (*)	0.50
(3) 13α,17β- diacholestane (20S) (**)	0.50
(4) 13α,17β- diacholestane (20R) (**)	0.50
(5) 24-methyl-13β,17α- diacholestane (20S) (*)	0.50
(6) co-eluted compounds: 24-methyl-13 α,17β-diacholestane (20S) and 5α,14α,17α-cholestane (20S) (*)	0.50
(7) co-eluted compounds: 24-ethyl-13β,17α-diacholestane (20S) and 5α,14β,17β-cholestane (20R) (*)	0.50
(8) co-eluted compounds: 5α,14β,17β-cholestane (20S) and 24-methyl-13 α,17β- diacholestane (20R) (*)	0.50
(9) 5α,14α,17α-cholestane (20R)	0.59
(10) 24-ethyl-13β,17α- diacholestane (20R) (*)	0.50
(11) 24-ethyl-13α,17β- diacholestane (20S) (*)	0.50
(12) 24-methyl-5α,14α,17α-cholestane (20S) (*)	0.50
(13) co-eluted compounds: 24-ethyl-13α,17β-diacholestane (20R) and 24-methyl-5α,14β,17β-cholestane (20R) (*)	0.50
(14) 24-methyl-5α,14β,17β-cholestane (20S) (*)	0.50
(15) 24-methyl-5α,14α,17α-cholestane (20R) (**)	0.50
(16) 24-ethyl-5α,14α,17α-cholestane (20S) (*)	0.50
(17) 24-ethyl-5α,14β,17β-cholestane (20R) (*)	0.50
(18) 24-ethyl-5α,14β,17β-cholestane (20S) (*)	0.50
(19) 24-ethyl-5α,14α,17α-cholestane (20R) (*)	0.50

(*) instrumental DL > method DL

(**) not detected

Fig. S1. Sampling site T1

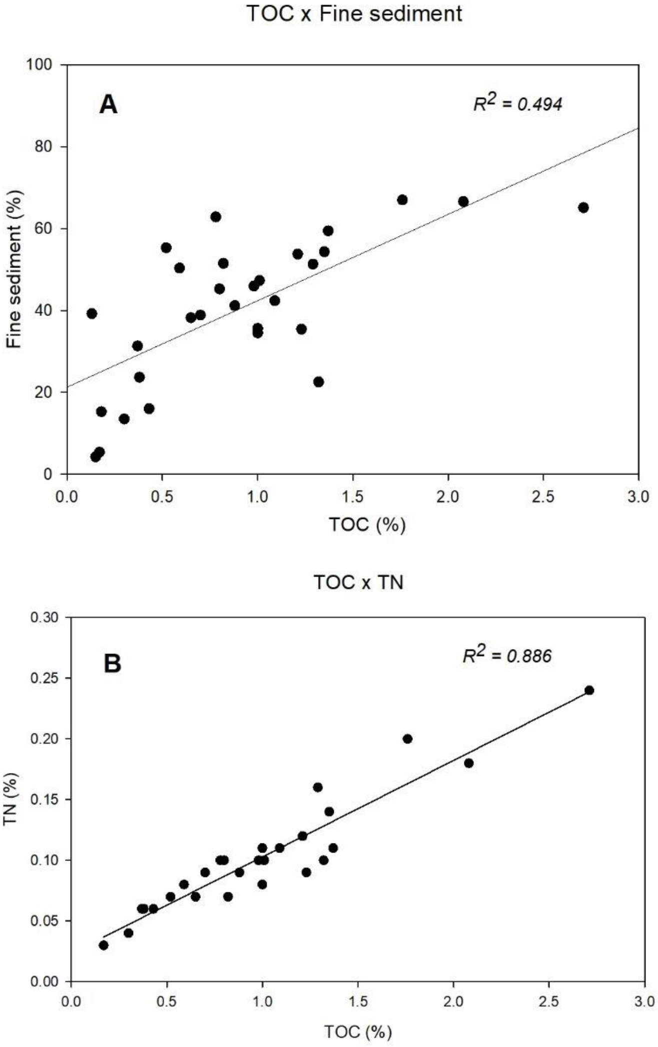

Fig. S2. Bulk data cross plots. A: Total organic carbon *vs* percentage of fine sediments. B: Total organic carbon *vs* Total nitrogen

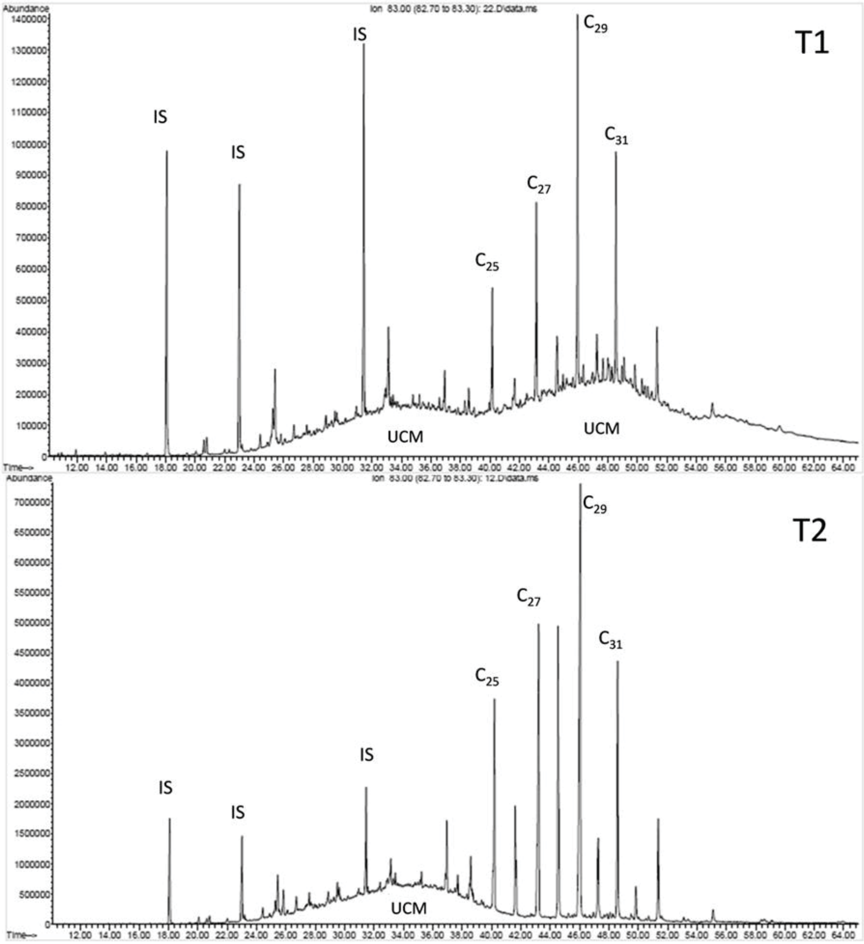

Fig. S3. Representative chromatograms (m/z 83) from T1 and T2 sites (IS = internal standard).

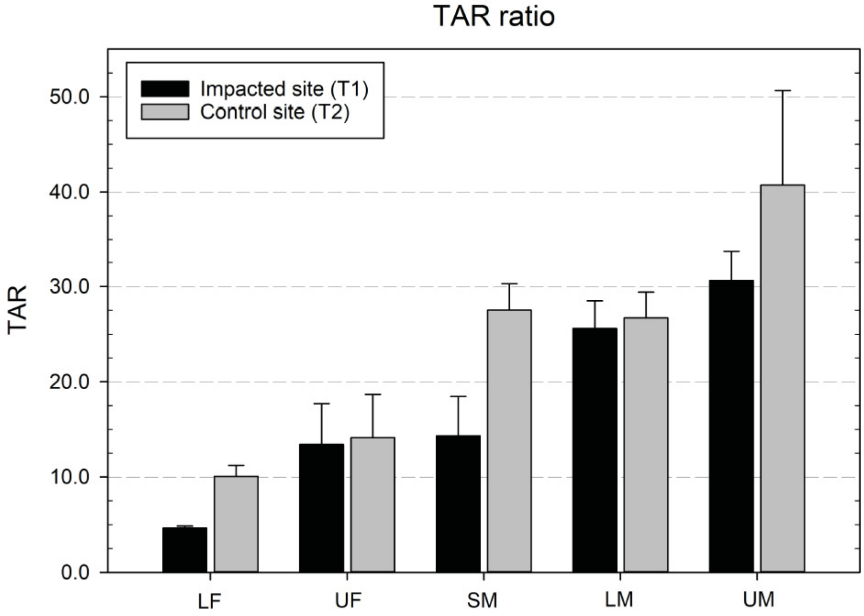

Fig. S4. Terrigenous-to-aquatic ratio (TAR): (n-C_{27} + n-C_{29} + n-C_{31})/ (n-C_{15} + n-C_{17} + n-C_{19})

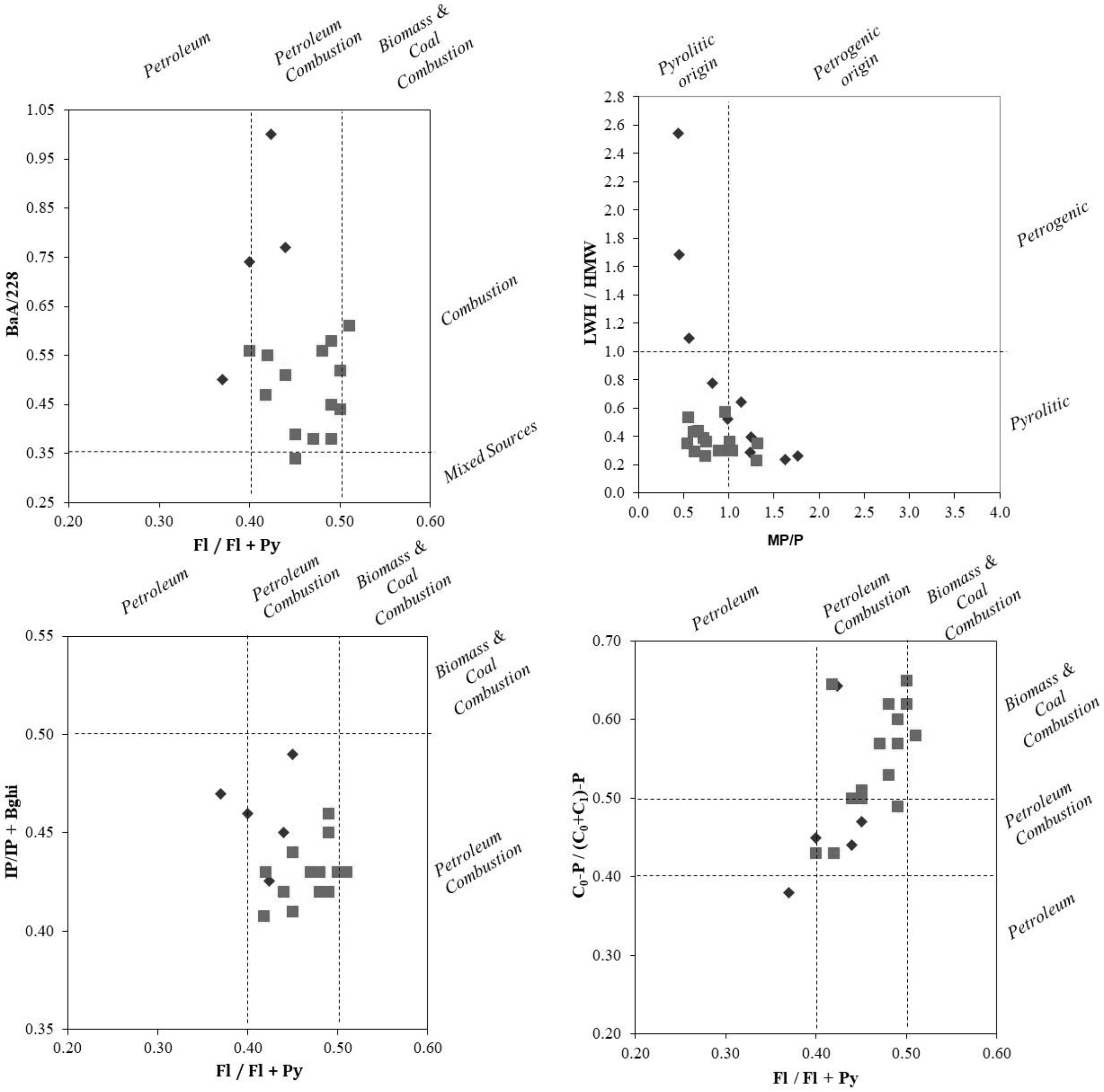

Fig. S5. PAH cross plots for the diagnostic ratios of (a) BaA/228 vs Fl/Fl+Py, (b) LMW/HMW vs MP/P, (c) IP/IP+Bghi vs Fl/Fl+Py and (d) C_0-P/(C_0+C_1)-P vs Fl/Fl+Py of sediments from mangroves of Paranaguá Bay, Brazil. T1 = squares; T2 sites = diamonds.

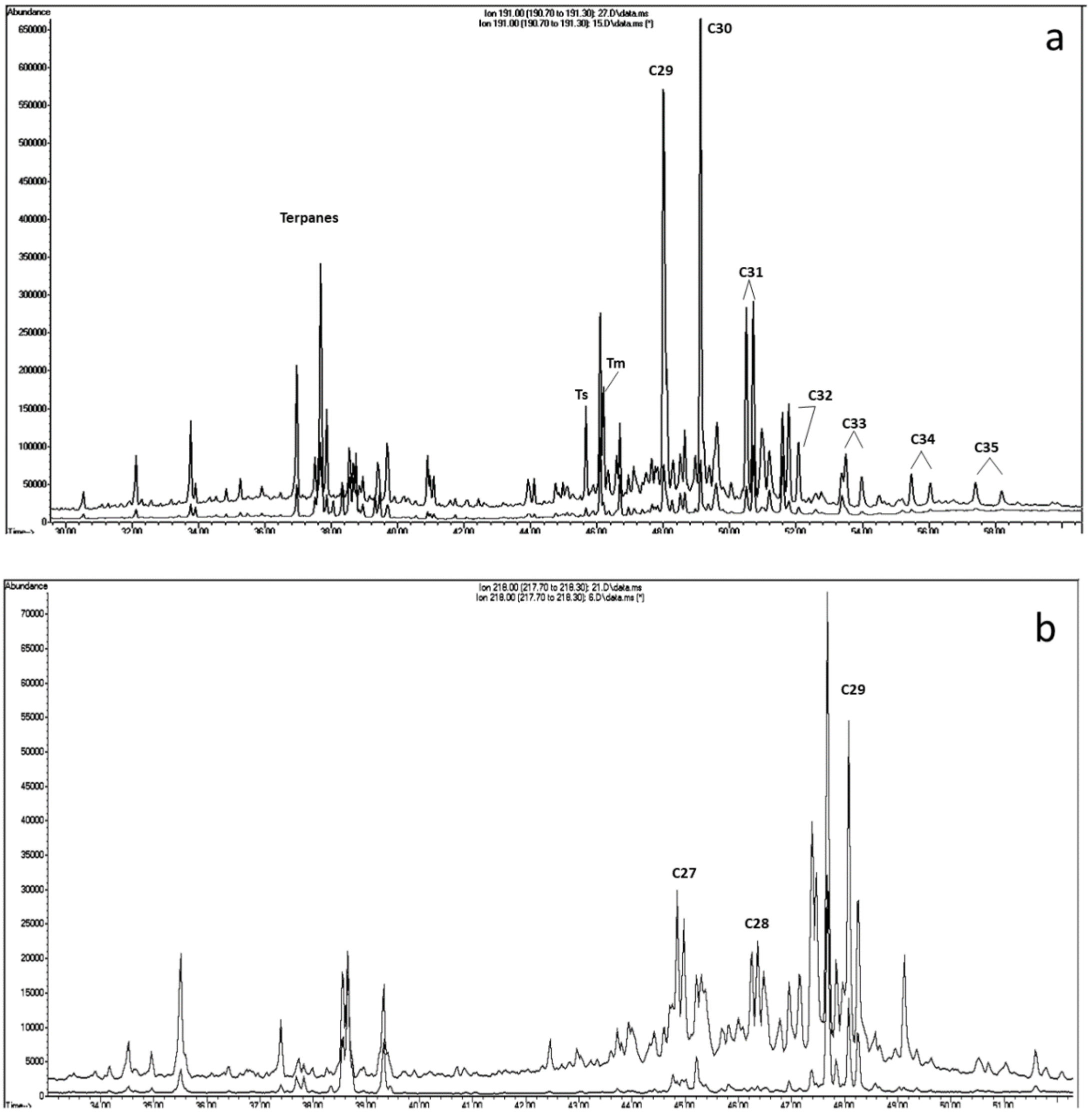

Fig. S6. Typical chromatograms for m/z 191 (a) and m/z 218 (b), showing T1 (top line) *vs* T2 (bottom line) samples.

3 BIOGENIC AND CATAGENIC CYCLIC TERPENOID HYDROCARBONS AS TOOLS TO THE STUDY OF ORGANIC MATTER ACCUMULATION IN SUBTROPICAL MANGROVE SEDIMENTS

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ABSTRACT

Terpenoid hydrocarbons are ubiquitous compounds in the marine environment and can be linked to natural synthetic activities, as the structure of the original carbon skeleton from the biological precursor is kept. In pristine environments, the terpenoid profile is expected to have a biogenic signature. However, the widespread use of petroleum derivatives can contribute to the inventory of hydrocarbons found in recent sediments, introducing cyclic hydrocarbons with a catagenic signature. Terpenoid hydrocarbons were examined in the mangrove sediments of Paranaguá Estuarine System, the largest bay of South Brazil, affected by intensive tourism and high contamination risk due to extensive urban development and harbors activities. Biological terpenoids were predominantly composed by high plant unsaturated derivatives (oleanoids, lupanoids, ursanoids and taraxeroids) with des-A configuration, as well as bacterial hopanoids.

Catagenic compounds were distributed throughout the estuary and both groups presented a similar distribution, with significant correlation (R^2=0.66). In order to better assess anthropic sources of hydrocarbons to the mangrove, a ratio of catagenic/biogenic terpanes is proposed. Ratios higher than 1.0 were found near Paranaguá Port and in Paranaguá Bay area. An important touristic destination, Mel Island, also presented ratios higher than 1.0 in two locations. The proposed ratio of catagenic/biogenic terpenoids could accurately assess the low-level chronic inputs of anthropic hydrocarbons in the study area. This innovative approach can be applied to areas with high natural inputs of organic matter, where chronic low-level hydrocarbon inputs are not evident through *n*-alkanes and PAHs analyses.

3.1 INTRODUCTION

Cyclic aliphatic hydrocarbons, such as cycloalkanes and cycloalkenes, are organic markers frequently found in sediments being assumed to be derived from biological precursors. During sedimentation, the original products undergo chemical processes leading to the degradation and loss of the original reactive functional groups (e.g. biological hopanoids lead to hopanoid acids and, finally, hydrocarbons) (RIES-KAUTT and ALBRECHT, 1989, MEYERS and ISHIWATARI, 1993; HE *et al.*, 2018). Despite these changes, the ‘carbon skeleton’ of the original molecules formed by a hydrocarbon cyclic chain is recalcitrant to degradation. Therefore, it keeps information about its sources, being applied as geochemical tracers in the reconstruction of paleoenvironments and petroleum exploration (PETERS *et al.*, 2005; JACOB *et al.*, 2007; VAN BREE, *et al.*, 2016).

After sedimentation, the organic matter undergoes further transformations during diagenesis and catagenesis. In the case of hopanoids, biogenic precursors present a 17βH,21βH configuration assuming a 17αH,21βH configuration and, to a lesser extent, a 17βH,21αH configuration, during sedimentary maturation process. Extended hopanes, that present an additional chiral center at C22 (originally with a 22R configuration) may be altered to a mixture of 22R and 22S epimers (RIES-KAUTT and ALBRECHT, 1989, RUSHDI *et al.*, 2017; INGLIS *et al.*, 2018). Other compounds such as triterpenes from higher plants, also undergo transformation processes in order to reach a thermodynamically stable configuration (PETERS *et al.*, 2005; SAMUEL *et al.*, 2010).

In environments where deposits of mature organic matter do not occur, recent sediments are expected to have a predominance of cyclic hydrocarbons from biogenic sources, such as oleananes, lupanes, taraxeranes (TRENDEL *et al.*, 1989; VAN BREE *et al.*, 2016) and hopanoids (MEREDITH *et al.*, 2008; ISHIWATARI *et al.*, 2014). However, cyclic hydrocarbons with a catagenic signature can effectively contribute to the inventory of hydrocarbons found in recent sediments, derived from the widespread use of petroleum derivatives (CHANDRU *et al.*, 2008; KAO *et al.*, 2015; RUSHDI *et al.*, 2017).

In sediments with high content of organic matter such as those found in mangrove swamps, both ‘anthropic’ and ‘biogenic’ inputs may be overlapped (GARCIA *et al.*, 2019). Mangrove swamps have proper conditions for the deposition of fine sediments including biogenic debris and a slow degradation of the organic matter (BOUILLON *et al.*, 2008; DUKE, 2016). Therefore, natural recalcitrant compounds as well as chronic inputs of hydrophobic contaminants from anthropogenic sources are favorably accumulated in these conditions. Also, recently efforts have been made to better understand the carbon storage in mangrove soils, since it presents an important carbon sequestration rate in the earth surface (termed “blue carbon”; HOWARD *et al*., 2014).

Despite its importance, mangroves are considered to be critically sensitive to human impact (MCLEOD *et al.*, 2011). There is a global concern on the rapid decline in mangrove coverage areas and the associated biological productivity (DUKE, 2016; FERREIRA and LACERDA, 2016) therefore it is urgent to study this ecosystem. The blue carbon stock of mangroves is mostly stored belowground usually constituting 50% to over 90% of the total carbon in the ecosystem (DONATO et al. 2011; KAUFFMAN et al. 2011). According to HOWARD et al. (2014), carbon soil storage can reach many meters deep and remain for long times, but their vulnerability to land-use is poorly understood. Recalcitrant organic compounds contribute to the carbon storage.

The presence, accumulation and persistence of anthropogenic hydrocarbons in mangrove sediments have been frequently reported in the literature (OYO-ITA *et al*., 2013; LI *et al*., 2014; SOUZA *et al*., 2018). However, the high level of natural compounds found in mangrove sediments may pose a challenge on the identification of the catagenic compounds in the same matrix since the structures of the natural molecules are very similar, providing a similar spectral signature (e.g., high signals in the m/z 191 fragmentograms) which may lead to mistake in the identification. Therefore, this study aims to (1) characterize the natural background cyclic aliphatic hydrocarbons in the mangrove sediments from a subtropical estuarine system; (2) map the chronic low-level inputs of catagenic terpanes and hopanes under a high biogenic background in order to identify anthropogenic inputs, and; (3) associate the occurrence of selected biogenic and anthropogenic hydrocarbons as tracers of organic matter ('blue carbon') accumulation in the mangrove swamps.

3.2 MATERIAL AND METHODS

PES is a subtropical estuary (25°30'S; 48°25'W) affected by intensive tourism and high contamination risk (e.g. COMBI *et al*., 2013; SOUZA *et al*., 2016) due to extensive urban development and harbors activities (e.g. MARTINS *et al*., 2015). The estuarine system is the larger bay of South Brazil with 552 km² of open water area (LANA *et al*., 2018). The E-W axis comprise the main human settlements, including Paranaguá city, the largest urban center established in the Bay margins with more than 140,000 inhabitants (IBGE, 2010). PES is comprehended in the geological barrier system of Paranaguá coastal plain with Pleistocene and

Holocene sedimentary deposits. It is surrounded by prominent mountain ranges, consisting of granitic massifs, intruded into the Paleoproterozoic basement (LESSA *et al*., 2000; NASCIMENTO *et al*., 2016). The study area has no oil and gas deposits with mature organic matter, so all catagenic compounds present in the sediments are therefore attributed to anthropogenic inputs.

Mangrove areas have a high complexity of structures that do not enable a regular mapping, requiring an irregular distribution of the samples defined according to the existent natural mosaic of vegetation coverage. Thirty-six sediment samples were distributed amongst well developed forests (NOERNBERG *et al.*, 2008), representing different structural types (NAIZOT, 1993) (Fig. 3.1).

Forests formed by *Rizophora sp.* were preferentially sampled, corresponding to recent areas of swamp that are favorable to retain sedimentary organic carbon (CUNHA-LIGNON *et al.*, 2009). Also, this species of mangrove tree can resist longer periods of flooding and anoxia, conditions expected to provide better preservation of hydrocarbons (SANDERS *et al.*, 2010). If *Rizophora* forests could not be found in the target location, sampling was performed in *Avicennia sp*. or mixed forests (*Rizophora* and *Avicennia*).

Each sample was composed from equal parts of sediments taken from three different quadrats (1 m^2 each) in order to minimize short-scale spatial variation (GARCIA *et al.*, 2019). Sediment pH and Eh were measured in situ in each quadrat (pH meter Instrutherm 710, with combined electrode and Eh meter Instrutherm ORP-896 with platinum electrode ORP-897). The sediments were frozen (-20 °C), freeze-dried and stored in cleaned glass jars until analysis.

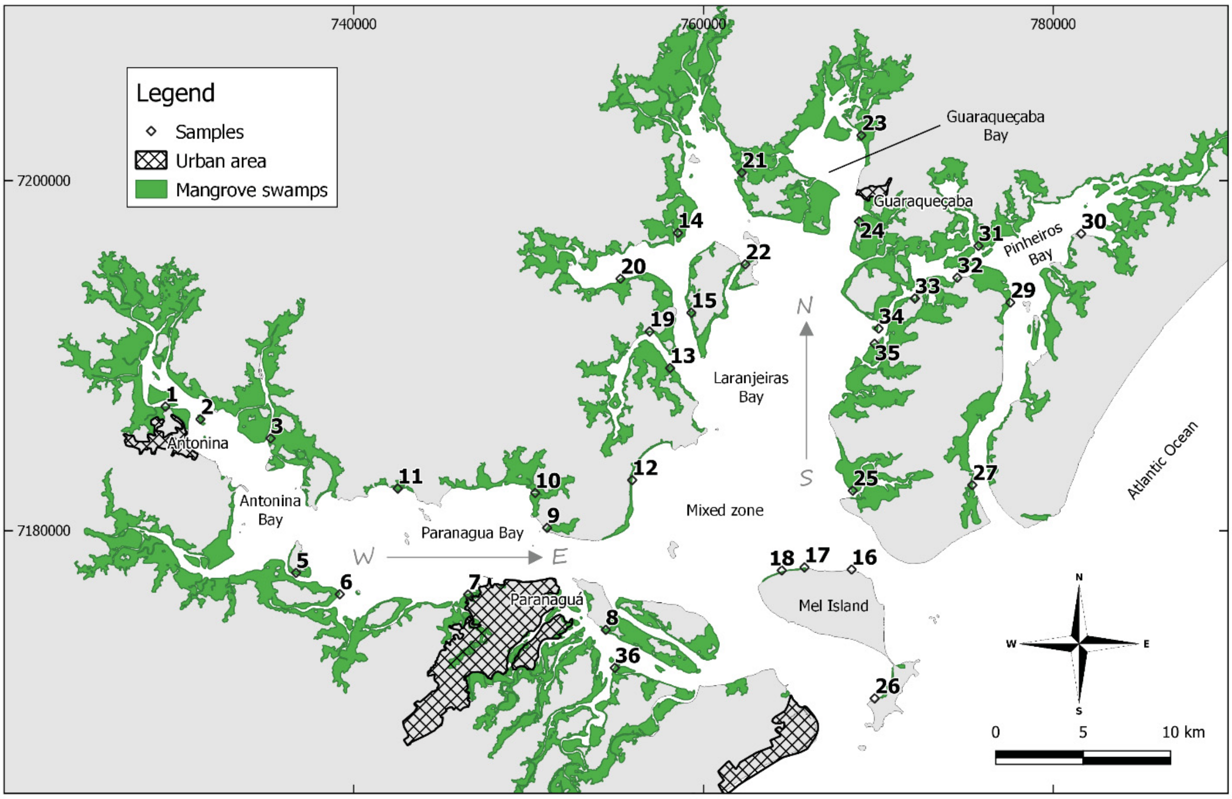

FIGURE 3.1: Sampling sites in Paranaguá Estuarine System (PES) with sub-areas and main axes (N-S and E-W).

Fine sediments content was determined in the dried total sediment by sieving method (<0,062 mm particle size). Bulk organic matter (total organic carbon; TOC, total nitrogen; TN, and carbon isotope ratio; $\delta^{13}C$) was determined using an EA-Costech elemental analyzer coupled to an isotope ratio mass spectrometry Thermo Scientific Delta V Advantage MS (EA-IRMS). Approximately 6-8 mg of dry sediment was decarbonated with HCl solution (1 mol L^{-1}) and total nitrogen was determined in the same amount of bulk sediment. Standards were determined before each group of 40 samples to verify the analytical accuracy (USGS-40/glutamic acid, United States Geological Survey, and IAEA-600/caffeine, International Atomic Energy Agency). The standard deviation for the calibration of isotopic ratios was equal to 0.01% for both ratios (USGS-40 standard) and 0.03% for $\delta^{13}C$ (IAEA-600 standard). The standard used for determination of carbon and nitrogen contents was Soil LECO (LECO Corporation USA) (estimated levels of 13.55% and 0.81%, respectively).

The analytical procedure used for the hydrocarbons in the marine sediments analysis was based on the United Nations Environment Program method (UNEP, 1992) with adaptations described in WISNIESKI *et al.* (2016). Approximately 20 g of sediment were extracted over 8 h using 80 mL of a mixture of dichloromethane and *n*-hexane (1:1). Activated copper was added in order to remove elemental sulfur. A surrogate standard deuterated (5α-cholestane-d_4) was added before each blank and sample extraction. The DCM/$_n$-hexane extract was purified by column chromatography using 5% deactivated alumina (1.8 g) and silica (3.2 g). Elution of the saturate fraction was performed with 10 mL of *n*-hexane (fraction 1: aliphatic hydrocarbons and petroleum biomarkers). The resulting extract (500 µL) was stored in glass vials.

The extracts of five samples (#1, 2, 3, 10 and 11) were molecular-sieved for removal of *n*-alkanes with the adsorbent S-115 (Honeywell/UOP, dry at 85 °C). A glass pipette was packed with approximately 2 g of the adsorbent and eluted with approximately 3x5 mL of *n*-pentane (Honeywell, ≥95.0% GC). The *n*-alkanes were retained in the sieve while the branched and cyclic (B/C) were eluted from the column (VILLALBA, 2016).

Following fractionation (or purification in the case of B/C alkanes extracts), the chromatographic analyses were performed in a GC Agilent 7890 paired with an Agilent 5975C MSD quadrupole with a DB-5 column (60 m x 250 µm x 0.25 µm). Injections were made manually (1 µL) in splitless mode (front inlet temperature: 300°C). Helium was used as a carrier gas. Oven program was 40 °C for 1.5 min then 4 °C min^{-1} to 300 °C for 34 min. The detector was set to a 70 eV energy impact.

The saturate fractions were scanned in multiple ion detection mode (including m/z 191 for terpanes and hopanes), while the five molecular-sieved extracts were injected in full scan mode. The results for these selected samples were qualitatively similar, then only one sample with the highest quantity of extractable organic matter (# 10) was used in order to primarily characterize the natural/catagenic compounds by mass spectrometry. This sample was assumed as being representative of the study area.

Compounds in B/C fraction of # 10 were identified by comparison with mass spectra and retention times from known catagenic compounds found in Lower Pennsylvanian Morrow shale and published data (PHILP, 1985; SHIOJIMA *et al.*, 1992; DAMSTÈ *et al.*, 1995; JACOB *et al.*, 2007; HE *et al.*, 2018).

The estimated concentrations of the compounds identified (semiquantitative analysis) was based on the integrated areas of specific ions (m/z 191 for the terpanes and hopanes and m/z 221 for the surrogate 5α-cholestane-d_4) in the saturate fraction extracts. This procedure aims to assess the variations of concentrations in the study area, and although this cannot provide a real concentration it provides an estimative facing the unknown individual response factors for each compound (JACOB *et al.*, 2007).

3.3 RESULTS AND DISCUSSION

3.3.1Bulk results

PES has a geographic configuration that allows it to be divided into subareas (NAIZOT, 1993; LANA *et al.*, 2001; MANTOVANELLI *et al.*, 2004; Tab. 3.1). According to the geographic location, a progressive increase of marine influences towards the mixed zone is expected. The lowest average content of fine sediments and TOC was observed in areas near the ocean, suggesting a stronger marine influence with a higher energy depositional environment. In contrast, inner bay areas (Antonina and Guaraqueçaba) present average bulk results that may reflect a stronger influence of continental apportions in a lower energy depositional environment, such as relatively high fine sediment content and TOC and TN. In between, there is Paranaguá, Laranjeiras and Pinheiros Bay - presenting intermediate results to these parameters.

For $\delta^{13}C$, the results ranged from -28.4 to -23.1 with all results corresponding to terrigenous inputs (ZHOU *et al*., 2006). The spatial distribution of $\delta^{13}C$ throughout the PES mangroves was apparently random, not following the expected terrestrial-marine gradient. Regarding C/N ratios, this gradient was not clear, but it presented average values corresponding to terrigenous O.M. in Antonina Bay (> 15). All other sub-areas presented lower values – with averages remaining in the mixed range (8 – 15). Results corresponding to marine inputs (< 8) were observed in isolated samples in Paranaguá Bay, Pinheiros Bay and Mixed zone (PREMUZIC *et al.,* 1982). TOC and $\delta^{13}C$ were not significantly correlated ($R^2 = 0.10$) with $\delta^{13}C$ suggesting the same source of OM for all TOC levels. For TOC and TN, these parameters presented good correlation ($R^2 = 0.80$) indicating similar sources for both elements.

TABLE 3.1 – AVERAGE BULK RESULTS IN EACH SUBAREA OF PEC

	PEC Subareas					
	Inner zone		**Intermediate zone**			**Outer zone**
	Antonina	**Guaraqueçaba**	**Paranaguá**	**Laranjeiras**	**Pinheiros**	**Mixed zone**
N	5	2	5	7	9	8
pH	6.1 (5.50 – 6.64)	5.8 (5.78 – 5.89)	6.8 (6.26 – 7.33)	6.1 (5.70 – 6.40)	6.2 (5.66 – 6.80)	6.5 (6.22 – 6.98)
Eh (mV)	+62 (-24 – +145)	+99 (+58 – +140)	+25 (-192 – +141)	+22 (-178 – +124)	+42 (-127 – +150)	+11 (-296 – +194)
% fine sed	76.5 (14.9 – 96.0)	54.6 (24.3 – 85.0)	30.9 (2.1 – 87.3)	21.2 (4.7 – 48.6)	33.0 (3.3 – 72.5)	14.1 (1.1 – 45.7)
% TOC	5.9 (3.32 – 9.14)	3.5 (1.74 – 5.30)	2.5 (0.27 – 5.35)	1.5 (0.51 – 3.67)	2.2 (0.60 – 4.03)	1.1 (0.13 – 3.08)
% TN	0.37 (0.12 – 0.45)	0.30 (0.12 – 0.48)	0.21 (0.04 – 0.43)	0.13 (0.05 – 0.34)	0.21 (0.06 – 0.49)	0.14 (<LOD – 0.22)
$\delta^{13}C$	-26.9 (-27.43 – -26.36)	-26.6 (-27.16 – -26.09)	-25.5 (-26.62 – - 24.86)	-26.8 (-28.36 – -25.77)	-25.8 (-26.78 – -24.96)	-25.7 (-27.29 – -23.10)
C/N	17.7 (12.1 – 27.5)	12.9 (11.1 – 14.8)	10.0 (6.2 – 13.8)	12.1 (8.1 – 18.9)	11.45 (5.2 – 21.3)	10.85 (4.5 – 16.2)

3.3.2Identification of the mass spectra of biogenic compounds

The TIC chromatogram of # 10 obtained in full scan mode after molecular sieving is presented in Fig. 3.2 and the peaks correspondence with probable compounds identified are listed in Table 3.2. The compilated mass spectra of selected compounds area presented as Supplementary Material (‘Anexo 1’). In the terpanes group (retention time: 56 - 62 min), all identified peaks are natural compounds, with inferred molecular structures derived from ursane, oleanane, lupane and taraxerane (Fig. 3.2). These hydrocarbon skeletons are common in higher plants and are ubiquitous in marine sediments, being typically used as markers of higher plant inputs (PANCOST and BOOT, 2004).

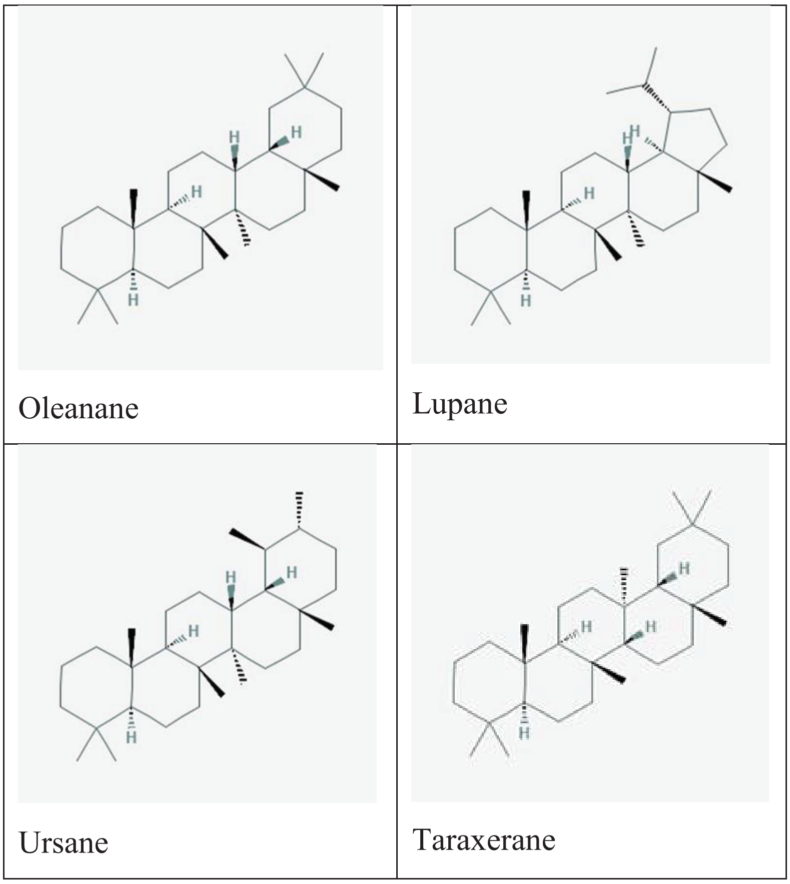
Oleanane
Lupane
Ursane
Taraxerane

FIGURE. 3.2. COMMON TRITERPENOID CARBON STRUCTURES FROM HIGHER PLANTS IN RECENT SEDIMENTS ($C_{30}H_{52}$) (structures after: pubchem.ncbi.nlm.nih.gov)

The occurrence of oleanoids and lupanoids in marine sediments are interpreted as being tracers from angiosperms (TEN HAVEN and RULLKOTTER, 1988; RULLKOTTER *et al.*, 1994; MOLDOWAN *et al.* 1994). Compounds with the taraxer-14-ene carbon skeleton as presented in taraxerol are common in higher plants (PANCOST *et al.*, 2002), being abundant in mangrove leaves and seagrass. The taraxeroids are classically applied as tracers of mangrove swamps (KILLOPS and FREWIN, 1994; VERSTEEG *et al.*, 2004; KOCH *et al.*, 2011).

The identified molecules present 22 or 24 carbons and different degree of unsaturation. All compounds showed an early stage of degradation/diagenesis with a 'broken' A ring ('Des-

A configuration') which are considered to be diagenetic products of microbial degradation of plant triterpenoids under anoxic conditions (HUANG *et al.*, 2008; TRENDEL *et al.*, 1989; MILLE *et al.*, 2006; JACOB *et al.*, 2007).

With exception from compound 7 (10β(H)-Des-A-lupane), the identified molecules presented one, two, five or six unsaturations on the cyclic chain. Most of the peaks were identified as oleanane by-products. The presence of these unsaturated molecules suggests the early diagenesis of the of organic matter in an anaerobic environment leading to aromatization, since the original oleanane carbon 'skeleton' present a Δ^2 configuration (KILLOPS and FREWIN, 1994; TEN HAVEN *et al.*, 1992; JACOB *et al.*, 2007).

Des-A-triterpenoids are reported in sediments with the dominating type of carbon skeletons being unsaturated oleananoids, ursanoids and lupanoids. In contrast, for saturated compounds, des-A-lupane is in most cases the only ring A-degraded diagenetic triterpenoid identified in Holocene deposits as well as in ancient sediments (JAFFÉ *et al.*, 1996; OTTO *et al.*, 2005; BECHTEL *et al.*, 2007; JACOB *et al.*, 2007; HUANG *et al.*, 2008). This compound probably results from its preferential formation or peculiar resistance to diagenetic transformations (JACOB *et al.*, 2007). However, in the studied environment, unsaturated compounds are much more abundant, what is probably an indication of the diagenesis of organic matter in a reduced environment.

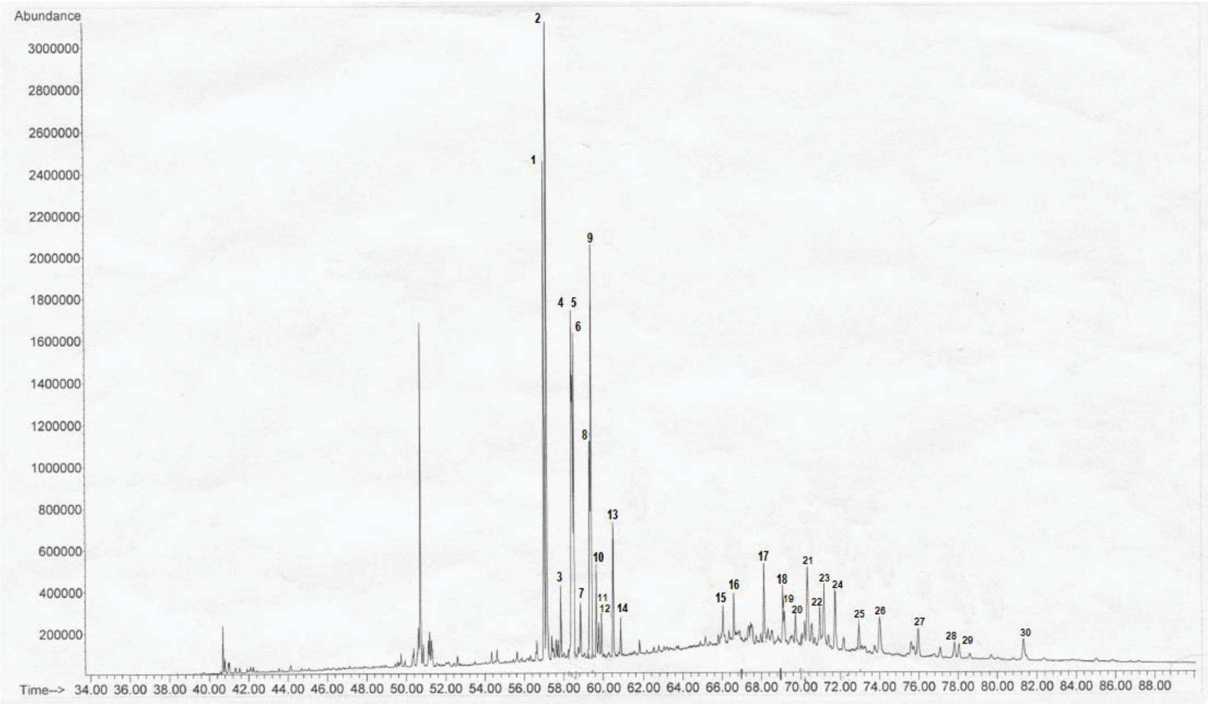

FIGURE 3.3: TIC chromatogram on full scan (branched and cyclic fraction of # 10).

TABLE 3.2 – SELECTED TERPANES IDENTIFIED IN FULL SCAN MODE (FIG. 3.3)

ID number	Compound name	M^+ ion	Formula	Retention time (min)
1	Des-A-oleana-9,18-diene	326	$C_{24}H_{38}$	57.026
2	Des-A-oleana-9,13(18)-diene	326	$C_{24}H_{38}$	57.166
3	Des-A-lupana-9,22(29)diene	326	$C_{24}H_{38}$	57.861
4	Des-A-traxera-5(10),14-diene	326	$C_{24}H_{38}$	58.418
5	Des-A-oleana-5(10),12-diene	326	$C_{24}H_{38}$	58.480
6	Des-A-oleana-5(10),13(18)-diene	326	$C_{24}H_{38}$	58.532
7	10β(H)-Des-A-lupane	330	$C_{24}H_{42}$	58.861
8	Des-A-ursana-5(10), 12-diene	326	$C_{24}H_{38}$	59.331
9	Des-A-26,27-bisnoroleana-5,7,9,11,13-pentaene (*)	292	$C_{22}H_{28}$	59.414
10	Des-A-26,27-bisnorursana-5,7,9,11,13-pentaene	292	$C_{22}H_{28}$	59.659
11	Des-A-lup-5(10)-ene	328	$C_{24}H_{40}$	59.778
12	Des-A-26,27-bisnorlupana-5,7,9,11,13-pentaene	292	$C_{22}H_{28}$	59.921
13	Des-A-26,27-bisnoroleana 5,7,9,11,13-hexaene	290	$C_{22}H_{26}$	60.458
14	di-unsaturated des-A-triterpene	326	$C_{24}H_{38}$	60.835

* Chromatographic standard coeluted (pregnane-d_4)

In the 'hopanes group' (retention time: 65 - 82 min), natural and catagenic compounds had similar signal intensities and were distributed along the TIC chromatogram. The identification of the petroleum biomarkers obtained in TIC could provide information for the disambiguation of the peaks identified in the SIM. Many compounds could not be completely identified (Table 3.3), since natural compounds can have many different configurations, and some of them may still unknown. But some effort is still being made to include more compounds and their specific information, regarding molecular masses and/or structural groups. However, the identifications obtained may be so far sufficient to provide the disambiguation of catagenic and biogenic compounds, what is still a valuable information in order to assess the low-level anthropic inputs to the study area.

Among the natural compounds, some higher plant six-carbon E-rings could be identified, such as oleanane and taraxerane derivatives (compounds 20, 21 and 28; Table 3.3). These are synthetized by high plants (KILLOPS and FREWIN, 1994; HE *et al.*, 2018). Other group of identified compounds were hopanoids, that are a group of pentacyclic triterpenoids produced by bacteria. The mass spectrum presented fragments derived from a biological configuration - such as hop-17(21)-ene. It is a product from acidic dehydration of the diplopterol, a biological product (SUMMONS and JAHNKE, 1990).

The catagenic C_{33}-22S (Compound 29, Table 3.3) appears close to a compound that has an ion with m/z 205 as the base peak, identified as $C_{31}\beta\beta$-22R (Compound 30; Table 3.3). The 17β(H),21β (H) stereochemistry in ring-E is characteristic from most bacteriohopanoids (SUMMONS and JAHNKE, 1990). After sedimentation, the rapid loss of reactive functional groups (-OH) leads to the formation of a hydrocarbon molecule that inherits the biological configuration of the cyclic chain (DAMSTÉ *et al.*, 1995).

A specific case occurs in the extended hopane C_{31}-22R that may have the contribution both from natural and catagenic sources. According to INGLIS *et al.* (2018) and references therein, in modern settings hopanoids mostly occur with the biological 17β,21β(H) configuration. But the 'mature' 17α,21β(H) stereoisomer C_{31} hopane is frequently found in modern peatlands since it is formed in early stages of the transformation of organic matter during diagenesis. In this case, the isomerization of the hydrogen atom at the C17 position is not caused by the long-term maturation of the organic matter during catagenesis, being quickly catalyzed by the acidic environment (RIES-KAUTT and ALBRECHT, 1989; INGLIS *et al.*, 2018).

TABLE 3.3 – HOPANES IDENTIFIED IN FULL-SCAN MODE (Sample 10)

ID number	**Compound name**	**M^+ ion**	**Formula**	**Retention time (min)**
15	Unknown formula	407	?	66.043
16	Natural compound *	370	$C_{27}H_{46}$	66.598
17	Tm	368	$C_{27}H_{44}$	68.131
18	Natural compound	396	$C_{29}H_{48}$	69.082
19	Natural compound	400	$C_{29}H_{52}$	69.160
20	Taraxera-14-diene	408	$C_{30}H_{48}$	69.726
21	24-nor-taraxerane	398	$C_{29}H_{50}$	70.333
22	17α(H),21β(H)-30-Norhopane	398	$C_{29}H_{50}$	70.964
23	Natural compound	408	$C_{38}H_{48}$	71.169
24	Hop-17(21)-ene (diploptene)	410	$C_{30}H_{50}$	71.733
25	17α (H),21β (H)-Hopane	412	$C_{30}H_{52}$	72.939
26	Glutin-18-ene	410	$C_{30}H_{50}$	74.006
27	C_{31} R extended hopane	426	$C_{31}H_{54}$	75.957
28	Oleanane	412	$C_{30}H_{52}$	77.820
29	C_{32} S extended hopane	440	$C_{32}H_{56}$	78.056
30	C_{31} ββ hopane	426	$C_{31}H_{54}$	81.313

* Surrogate coeluted (5α-cholestane-d4)

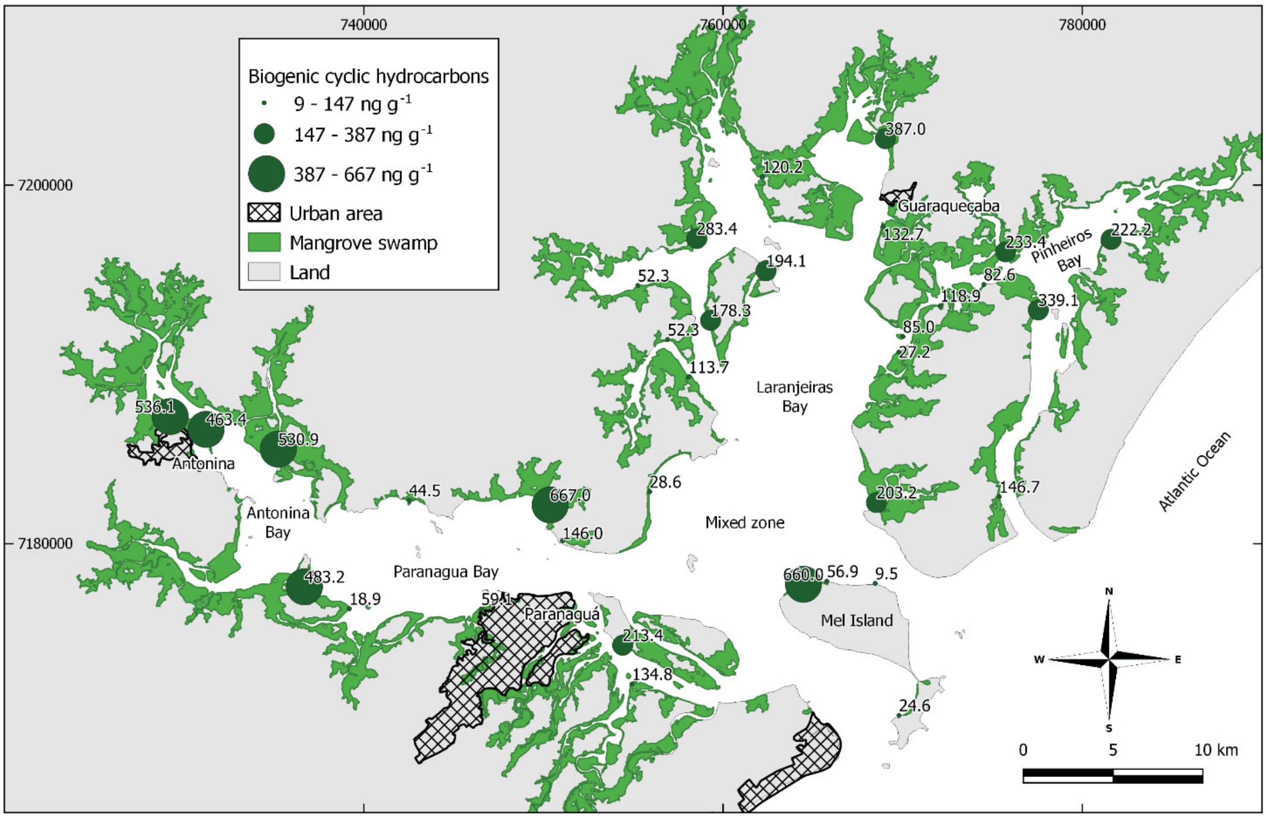

FIGURE 3.4 – CONCENTRATION OF BIOGENIC CYCLIC HYDROCARBONS (TERPANES AND HOPANES) IN ng g^{-1} IN THE MANGROVE SEDIMENTS OF PARANAGUÁ ESTUARINE SYSTEM

The biogenic compounds were distributed in all the sampled mangrove forests with higher concentrations in E-W axis of the estuarine system (Antonina and Paranaguá Bay) and in one specific sample of the mixed zone (# 18, Figure 3.4). Lower concentrations were observed in the N-S axis of the bay, with some sampling points presenting higher concentrations (# 23 in Guaraqueçaba Bay, # 29, # 30 and #31 in Pinheiros Bay, and # 14, # 15, # 22 and # 25 in Laranjeiras Bay). The hydrocarbon concentration according to spatial distribution seems to be an apparently random distribution in the PES.

3.3.3. Distribution of the catagenic terpanes and hopanes as molecular markers of anthropic inputs

Some catagenic compounds could be identified exclusively in the SIM mode, using the m/z 191 chromatogram, such as C_{24} tetracyclic and C_{26} tricyclic terpanes (Fig. 3.5; Table 3.4). On the full-scan mode, some natural compounds with prominent peaks (mainly in the terpanes range) may help in the identification of the mass spectra of petroleum biomarkers since they occurred in a specific retention time and are presented in the samples of the study area. Full scan and SIM chromatograms may have different retention times, due to normal fluctuations in the GC-MS equipment so an exact correspondence of the retention times in the tables are not expected. These are shown as a general indication. Retention times were evaluated and corrected while the identification of the peaks was performed.

FIGURE 3.5: M/Z 191 FRAGMENTOGRAM (# 01)

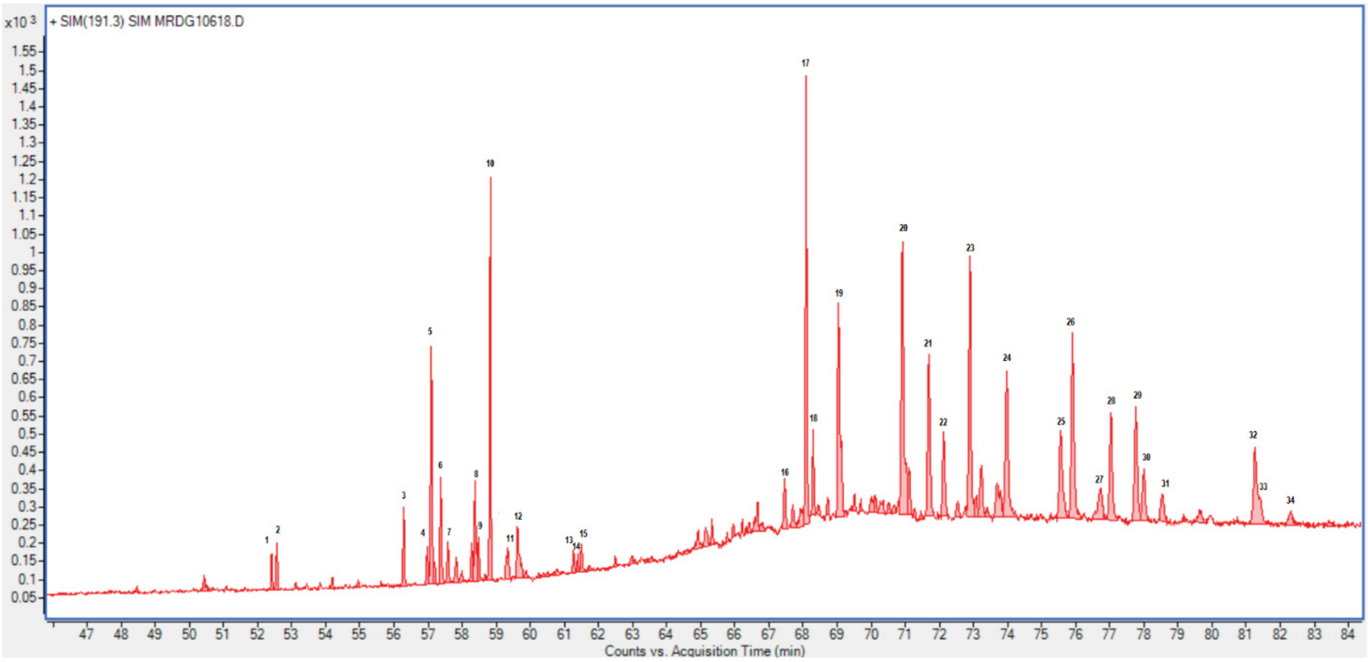

TABLE 3.4: IDENTIFIED COMPOUNDS IN M/Z 191 (# 01). IN GREEN: BIOLOGIC CONFIGURATION; IN GRAY: CATAGENIC CONFIGURATION.

ID	Name	Retention time (min)
1	Peak unidentified	-
2	C_{20} tricyclic terpane	52.585
3	C_{21} tricyclic terpane	56.309
4	Des-A-oleana-9,18-diene	57.017
5	Des-A-oleana-9,13(18)-diene	57.157
6	C_{22} tricyclic terpane	57.403
7	Des-A-lupana-5(10),22(29)-diene	57.860
8	Des-A-taraxera-5(10),14-diene	58.414
9	Des-A-oleana-5(10),13(18)-diene	58.525
10	10β (H)-Des-A-lupane	58.861
11	Des-A-26,27-bisnoroleana-5,7,9,11,13-pentaene	59.410
12	Des-A-26,27-bisnorursana-5,7,9,11,13-pentaene	59.661
13	C_{24} tetracyclic hopane	59.917
15	C_{25} tetracyclic hopane	61.528
16	T_s	67.491
17	1,2,3-Trisnortaraxera-5(10),14-diene	68.129
18	T_m	68.334
19	Monounsaturated triterpene (?)	69.079
20	17α(H), 21β (H)-30-Norhopane	70.964
21	Hop-17(21)-ene (diploptene)	71.728
22	Moretane C_{29} (?)	72.175
23	17α (H), 21b(H)-Hopane	72.947
24	C_{29} ββ hopane or Moretane C_{30} (?)	74.023
25	C_{31} S extend hopane	75.610
26	C_{31} R extend hopane	75.950
27	C_{30} ββ hopane (immature OM) (?)	76.769
28	C_{30} ββ hopane (immature OM)	77.095
29	Oleanane	77.831
30	C_{32} S extend hopane	78.050
31	C_{32} R extend hopane	78.599
32	C_{31} methyl hopanoid (or C_{31} ββ hopane)	81.308
33	C_{33} S extend hopane	81.485
34	C_{33} R extend hopane	82.370

Catagenic compounds were identified in all samples (Supplementary Material, ‘Anexo 2’). The higher concentrations of individual compounds were C_{29} αβ hopane or C_{30} αβ hopane. The extended C_{31} R αβ hopane were also a prominent compound and it corresponded to the more abundant in 30% of samples analyzed. However, despite the αβ configuration compounds, as cited previously, this compound must be a result of both catagenic (anthropogenic) and diagenetic (natural) inputs resulting in a higher concentration provided the sum of both sources.

An interesting pattern was observed in # 26 where a catagenic terpane (C_{21} tricyclic terpane) had the higher concentration, followed by C_{22} tricyclic terpanes - compounds characteristic from diesel (SIMONEIT, 2005; GARCIA *et al.*, 2019). A hydrodynamically protected mangrove with low supply of fine sediments and an intense boat traffic from tourism provided the favorable conditions to the accumulation of diesel exhaust products and/or chronic small oil spills. This site also presented pyrolytic PAHs and an abrupt UCM hump in the diesel range (unpublished data) that corroborates the identification of hydrocarbon contamination in this mangrove.

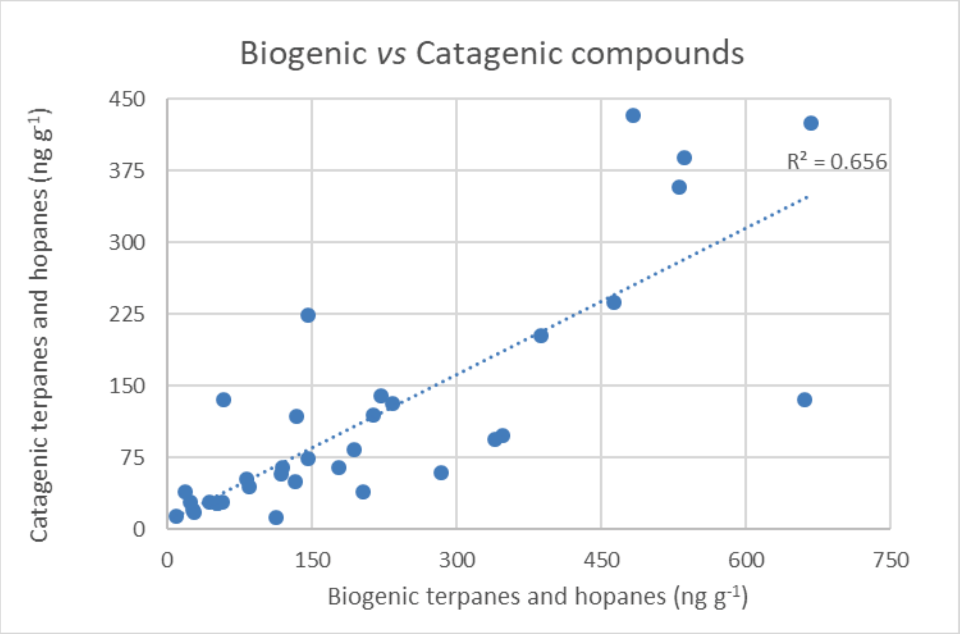

FIGURE 3.6 – CORRELATION BETWEEN BIOGENIC *VS* CATAGENIC TERPANES AND HOPANES

Catagenic and biogenic terpanes and hopanes were correlated to each other (R^2= 0.66, Fig. 3.6) and to TOC (R^2 = 0.50 for both groups). Assuming that both groups have different sources, this can be interpreted as an indication of similar ‘depositional behavior’ (e.g. affinity for TOC, fine sediments and lower energy sites).

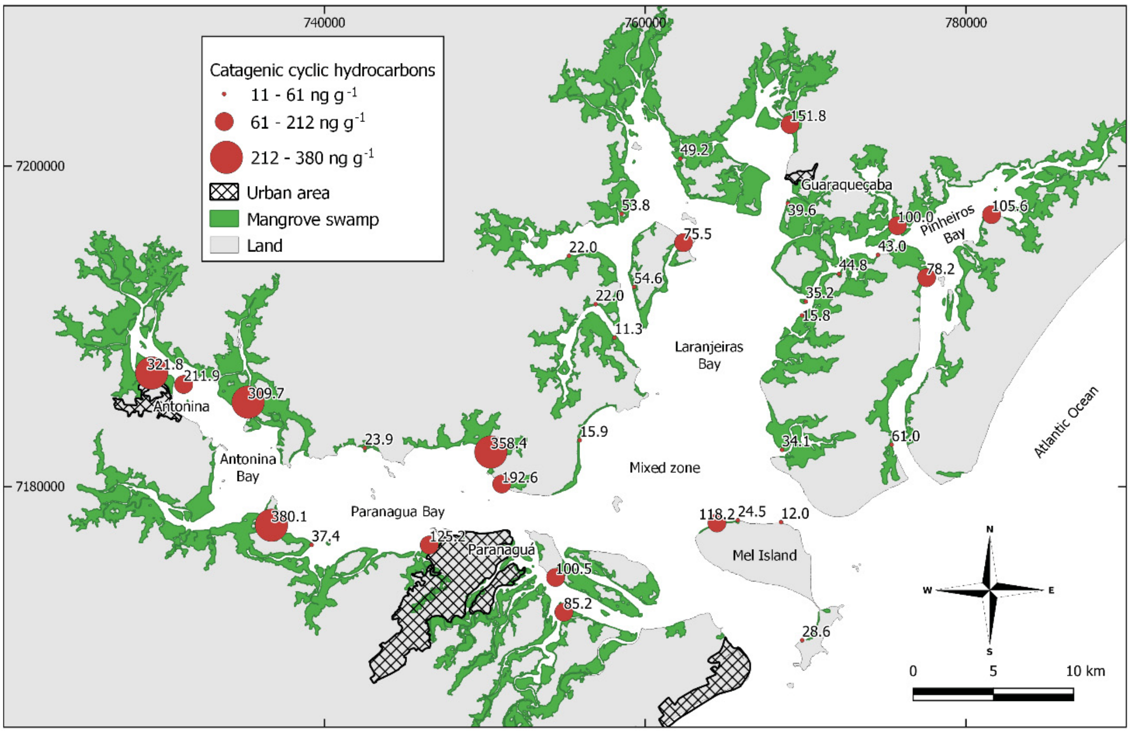

FIGURE 3.7 – CONCENTRATION OF CATAGENIC CYCLIC HYDROCARBONS (TERPANES AND HOPANES) IN ng g^{-1} IN MANGROVE SEDIMENTS OF PARANAGUÁ ESTUARINE SYSTEM

Catagenic compounds were distributed throughout the estuarine system (Fig. 3.7). Higher concentrations were observed in the E-W axis of the system (Antonina and Paranaguá Bay) and in one specific sample of the mixed zone (# 18), similar than the distribution of biogenic compounds. Lower concentrations were observed in the N-S axis of the system, with some sites presenting relatively high concentrations in the same sites verified to the biogenic cyclic terpanes and hopanes. This result may represent the preferential depositional sites since there is no evident sources nearby.

As presented above, the total concentrations of catagenic compounds seems to be mostly dependent from local depositional conditions, varying according to the TOC and having a similar distribution to the biogenic compounds. Therefore, the ratio of catagenic/biogenic terpanes and hopanes is proposed in this study as a useful proxy to distinguish the contribution of organic matter to the mangrove sediments, to better assign the anthropogenic sources of the chronic contamination of petrogenic hydrocarbons. Additionally, areas with high TOC in the sediments are favorable to the accumulation of 'blue carbon' (HOWARD *et al.*, 2014) so it must be assessed and preserved.

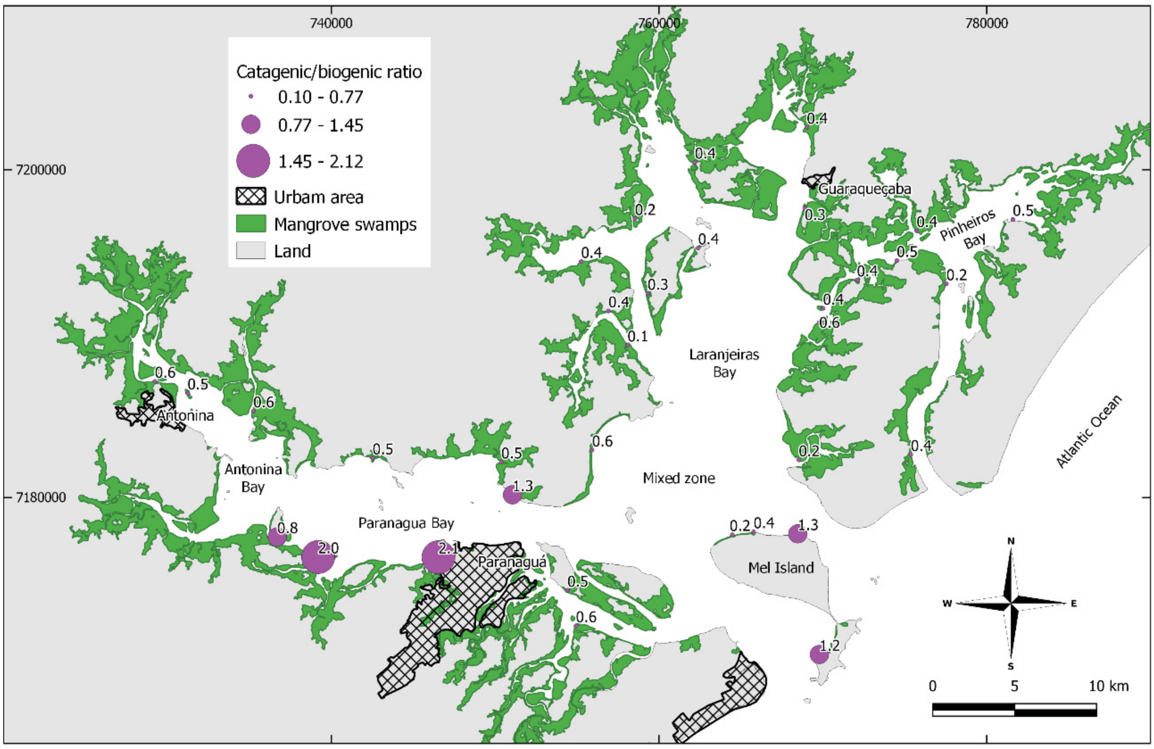

FIGURE 3.8 –CATAGENIC/BIOGENIC HOPANES AND TERPANES RATIO CALCULATED TO THE MANGROVE SEDIMENTS OF PARANAGUÁ ESTUARINE SYSTEM.

Catagenic/biogenic terpanes and hopanes ratios presented values higher than 1.0 in five samples (Fig. 3.8; Supplementary Material 'Anexo 2'). The highest values were observed near Paranaguá Port (# 07) and nearby in Paranaguá Bay area (# 06 and # 09). The other two places were in Mel Island: the first one in Encantadas pier (# 26) and the other one in a site far from any human settlement (# 16). This should be a result of the influence from the chronic small oil spills from Paranaguá Port, the runoff from Paranaguá City and/or from chronic inputs from the local boat traffic.

In particular, the Mel Island site has an urban occupation of around 1,000 inhabitants (IBGE, 2010) and is the main touristic destination in PES. In Encantadas beach, there is a touristic pier and in the North of the Island with an intense route of boats to the Guaraqueçaba bay, where a small city is established (approximately 7,800 inhabitants; IBGE, 2010). Also, tidal currents in Paranaguá Bay have a net transport towards the open sea and northward (NOERNBERG *et al.*, 2007); so, considering Paranaguá Port/City as a main source for local inputs of anthropogenic hydrocarbons, there may be an influence from Paranaguá as well.

The assumption of Paranaguá Port/City as the main source of anthropogenic hydrocarbons is also evidenced by the average ratios in each of the sub-areas of the estuary. The average catagenic/biogenic terpanes and hopanes ratios for Paranaguá Bay suggest that this area is the main contributor of catagenic hydrocarbons to the PES (Table 3.4). Laranjeiras, Guaraqueçaba and Pinheiros Bay can be considered on average as the less contaminated sites in this estuarine system, based on low values of this ratio.

TABLE 3.4 – CATAGENIC AND BIOGENIC TERPANES AND HOPANES IN SUB-AREAS OF THE PES (AVERAGE AND MIN – MAX)

	PES Zones					
	Inner zone		**Intermediate zone**			**Outer zone**
	Antonina	**Guaraqueçaba**	**Paranaguá**	**Laranjeiras**	**Pinheiros**	**Mixed zone**
N	5	2	5	7	9	8
CAT/BIO	0.6 (0.3 – 0.9)	0.4 (0.4 – 0.5)	1.4 (0.6 – 2.3)	0.4 (0.1 -0.5)	0.5 (0.3 – 0.7)	0.7 (0.2 – 1.4)
Total BIO (ng g^{-1})	472.2 (347.5 – 536.1)	259.8 (132.7 – 387.0)	187.1 (18.9 – 667.0)	142.0 (52.3 – 283.4)	156.9 (27.2 – 339.1)	166.4 (9.5 – 660.0)
Total CAT (ng g^{-1})	302.7 (97.3 – 432.3)	125.8 (49.5 – 202.2)	170.1 (28.3 – 423.9)	47.9 (12.7 – 82.7)	76.5 (19.7 – 139.4)	62.3 (13.5 – 134.8)

CAT= catagenic terpanes and hopanes /BIO = biogenic terpanes and hopanes

3.4 CONCLUSIONS

Mangroves of PES presented cyclic hydrocarbons from natural sources in the terpanes range (mostly from higher plants) and in the hopanes range (mostly from bacteria). Catagenic compounds were widespread through the study area, superimposed in the natural ‘profile’. Catagenic terpanes and hopanes concentrations varied according to the depositional conditions (TOC and fine sediments). Catagenic compounds varied coherently with the distribution of natural compounds.

The inner portion of the estuary, including hydrodynamically protected areas of PES (Paranaguá and Guaraqueçaba), presented in average higher levels of biogenic compounds, decreasing towards open areas. Higher levels of biogenic cyclic hydrocarbons can be interpreted as an indication of higher sensibility of the environment to inputs of hydrophobic contaminants, since the deposition processes are expected to be very similar. This approach can be applied to predict the sensibility/vulnerability of specific areas of coastal ecosystems to pollution by organic contaminants such as POPs and emerging hydrophobic contaminants. Also, areas with high TOC content in the sediments would emit more CO2 to the atmosphere in case of being degraded.

The proposed ratio of catagenic/biogenic compounds could accurately assess the low-level chronic inputs of anthropic hydrocarbons in the study area. It is another innovative approach and can be applied to areas with high natural inputs of organic matter, where chronic low-level hydrocarbon inputs are not evident through regular hydrocarbon analyses (such as *n*-alkanes and PAHs).

Coastal ecosystems including mangroves provide several services and benefits that are vital to mitigate the impacts of climate change and human occupation, including the storage of significant amounts carbon, known as coastal blue carbon, from the atmosphere and oceans (HOWARD *et al*., 2014). In contrast, these ecosystems are severely threatened by anthropogenic activities and mangroves are historically the most devastated (MURRAY *et al.* 2011). Therefore, it is essential to provide and apply tools to assess human impacts on mangroves in order to provide data to management, preservation and restoration of these important components of the biosphere.

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4 SPATIAL DISTRIBUTION AND MAIN SOURCES OF POLYCICLIC AROMATIC HYDROCARBONS IN MANGROVE SEDIMENTS FROM A SOUTH AMERICAN SUBTROPICAL ESTUARINE SYSTEM

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4.1 INTRODUCTION

Estuaries are a coastal ecosystem formed in the transitional areas from continental to marine environments. Among the estuarine ecosystems, mangrove swamps have a remarkable importance for coastal protection, food supplies, carbon storage, among other features (FAO, 2007; SPALDING *et al.*, 2010; PRIMAVERA *et al.*, 2019). This biome typically occurs in tropical and subtropical coasts that are subjected to the action of tides and human activities (SCHAEFFER-NOVELLI, 1999).

Mangrove sediments can be formed by particles from both marine and continental sources (COOPER, 2001; TREMBLAY *et al.*, 2007) with proper conditions for the deposition of fine sediments and a slow degradation of the organic matter. The mangrove ecosystems are considered vulnerable to the contamination by organic hydrophobic compounds such as petroleum hydrocarbons (BOUILLON *et al.*, 2008; NOERNBERG and LANA, 2002; DUKE, 2016), since they present low rates of recovery from accidental oil spills and the degradation of aromatic compounds are especially slow in these environments (BURNS *et al.*, 1993). Due to the high rates of organic matter preservation and anoxic conditions, the recovery of a mangrove ecosystem after an oil spill may last from 2 to more than 20 years (BOLLMANN *et al.*, 2010).

Some characteristics of the mangrove ecosystem provide favorable conditions for the accumulation of hydrophobic compounds from chronic inputs, such as a high biological productivity, the abundance of detritus and a high content of organic carbon. As a result, polycyclic aromatic hydrocarbons (PAHs) associated to multiple sources from human activities has been one of the most frequent group of pollutants accumulated in worldwide mangrove sediments (LI *et al.*, 2014; LEWIS *et al.*, 2011; DUKE, 2016). Many mangrove swamps have been reported as being heavily contaminated by PAHs, with concentrations higher than 10 $\mu g\ g^{-1}$ (dry weight) (KLEKOWSKI *et al.*, 1994; TAM *et al.*, 2001; CELINO and QUEIROZ, 2006; FARIAS *et al.*; 2008; FONTANA *et al.* 2012).

PAHs contamination is a reason of special concern due to their toxicity, mutagenic and carcinogenic effects to living organisms. They are relatively persistent in the environment and may accumulate in biological tissues with possible implications for human consumption of seafood (BAUMARD *et al.*, 1998a; ALMEIDA *et al.*, 2018).

In Brazil there are extensive areas of mangrove forests, especially in North Brazil with one of the biggest mangrove areas worldwide (SPALDING *et al.*, 2010). In contrast, remaining mangrove forests linked to the one of the better-preserved Atlantic Rainforests of South America are located on Paraná State, South Brazil, that encompasses a shoreline with 1,675 km and high environmental sensibility (SOUSA, 2008).

The main geomorphologic feature of Paraná State coast is Paranaguá Estuarine System (PES) (25°30’S; 48°25’W) (Fig. 4.1). This is the larger bay of South Brazil with 552 km² of open water area (LANA *et al.*, 2001). The main human settlements are located in the South area of this system, including Paranaguá city, the largest urban center established in the bay margins with more than 140,000 inhabitants (IBGE, 2010). Antonina is the second most important urban/port area in PEC, with approximately 19,000 inhabitants (IBGE, 2010).

PES has extensive mangrove areas as part of a biosphere reserve established by the United Nations Educational, Scientific and Cultural Organization (UNESCO) since 1993, that are considered to be under threat despite of having economic and nutritional relevance mainly due to crab fishing (*Ucides cordatus*) (BORGES *et al.*, 2006; FARACO *et al.*, 2010) and oyster harvesting (*Crassostrea sp.*) (MONTANHINI and MONTANHINI NETO, 2015). The main expected source of anthropogenic hydrocarbons for the study area are navigation activities (port and local boats) and urban occupation (MARTINS *et al.*, 2015). PAHs levels of bottom sediments in the study area have been considered low (ABREU-MOTA *et al.*, 2014; BET *et al.*, 2015). However, a large spatial evaluation of PAHs in mangrove sediments from PES have not been previously established despite of imminent risk of incidental oil spills during harbor operations and chronic input from direct discharge of sewage and petroleum by-products and also residues from combustion of biomass and fossil fuels.

The present study aims to assess the recent deposition of PAHs in the mangrove swamps of PES and (i) verify the spatial distribution of PAHs throughout the mangroves widespread in this subtropical estuarine system; (ii) elucidate the main sources of PAHs to the mangrove swamps based on diagnostic ratios of individual compounds and the previously studies in sediments and suspended particulate material, and; (iii) determine preferential depositional sites of PAHs accumulation in order to find potential sensitivity areas of past and future hydrocarbon contamination.

4.2 MATERIAL AND METHODS

PES is a subtropical estuary (25°30’S; 48°25’W) affected by intensive tourism and high contamination risk (e.g. COMBI et al., 2013; SOUZA et al., 2016) due to extensive urban development and harbors activities (e.g. MARTINS et al., 2015). The estuarine system is the larger bay of South Brazil with 552 km² of open water area (LANA et al., 2018). The E-W axis comprise the main human settlements, including Paranaguá city, the largest urban center established in the Bay margins with more than 140,000 inhabitants (IBGE, 2010). PES is comprehended in the geological barrier system of Paranaguá coastal plain with Pleistocene and Holocene sedimentary deposits. It is surrounded by prominent mountain ranges, consisting of granitic massifs, intruded into the Paleoproterozoic basement (LESSA et al., 2000; NASCIMENTO et al., 2016).

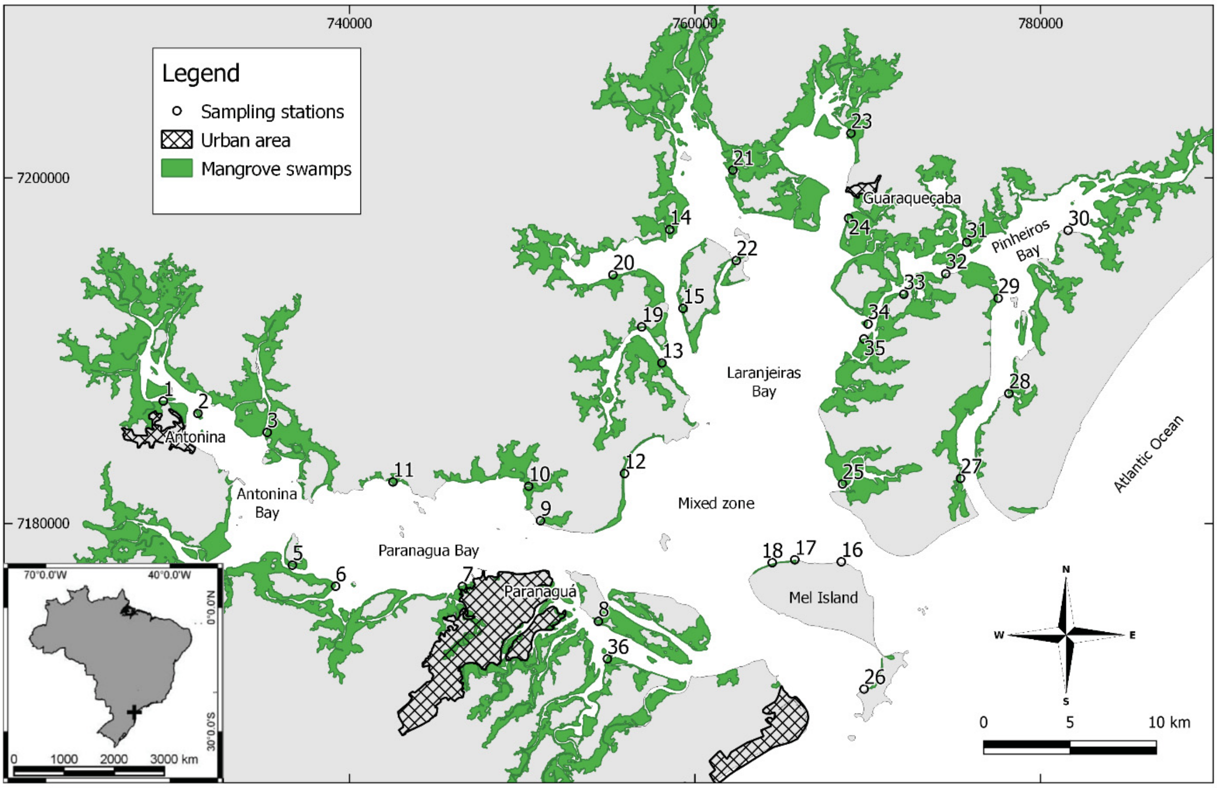

FIGURE 4.1 – SAMPLING SITES IN PARANAGUÁ ESTUARINE SYSTEM (PES)

Sampling was performed in December, 2017 in well-developed mangrove forests

(NOERNBERG *et al.*, 2008) covering different structural types and sub-areas (NAIZOT, 1993; LANA *et al.*, 2001; MANTOVANELLI et al., 2004). As shown in Figure 4.1, thirty-six sediment samples were collected preferentially in *Rizophora sp.* forests, corresponding to recent areas of swamp, being favorable to retain sedimentary organic material (CUNHA-LIGNON *et al.*, 2009). In case *Rizophora* forests could not be found in the target location, sampling was performed in *Avicennia sp*. or mixed forests (*Rizophora* and *Avicennia*).

Each sample was composed from equal parts of sediments taken from three different quadrats (1 m² each) in order to minimize short-scale spatial variation (GARCIA *et al.*, 2019). Collected sediments were frozen (-20 °C), freeze-dried and stored in cleaned glass jars until analysis.

Fine sediments content was determined in the dried total sediment by sieving method (<0,062 mm particle size). Bulk organic matter (total organic carbon; TOC, total nitrogen; TN, and carbon isotope ratio; $\delta^{13}C$) was determined using an EA-Costech elemental analyzer coupled to an isotope ratio mass spectrometry Thermo Scientific Delta V Advantage MS (EA-IRMS). Approximately 6-8 mg of dry sediment was decarbonated with HCl solution (1 mol L^{-1}) and total nitrogen was determined in the same amount of bulk sediment. Standards were determined before each group of 40 samples to verify the analytical accuracy (USGS-40/glutamic acid, United States Geological Survey, and IAEA-600/caffeine, International Atomic Energy Agency). The standard deviation for the calibration of isotopic ratios was equal to 0.01% for both ratios (USGS-40 standard) and 0.03% for $\delta^{13}C$ (IAEA-600 standard). The standard used for determination of carbon and nitrogen contents was Soil LECO (LECO Corporation USA) (estimated levels of 13.55% and 0.81%, respectively).

Analytical procedure of PAHs analysis in the marine sediments was based on the United Nations Environment Program method (UNEP, 1992) with adaptations described in WISNIESKI *et al.* (2016). Approximately 20 g of sediment were extracted over 8 h using 80 mL of a mixture of dichloromethane and *n*-hexane (1:1). Activated copper was added in order to remove elemental sulfur. A surrogate standard mixture of deuterated compounds (naphtalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}) was added before each blank and sample extraction. The DCM/*n*-hexane extract was purified by column chromatography using 5% deactivated alumina (1.8 g) and silica (3.2 g). Elution was performed with 10 mL of *n*-hexane (fraction 1: aliphatic hydrocarbons and petroleum biomarkers, with results not presented in this study) and 15 mL of a mixture of dichloromethane and *n*-hexane (3:7) (fraction 2: PAHs). The resulting extract (500 μL) was stored in glass vials. Internal standard (benzo[*b*]fluoranthene-d_{12}) was added prior to the gas chromatographic analysis.

Hydrocarbon determination was performed with a gas chromatograph (Agilent Model 7890A) coupled to a mass spectrometer (Agilent 5973N inert MSD with Triple-Axis Detector) using a fused silica capillary column coated with 5% diphenyl/dimethyl siloxane (30 m, 0.25 mm internal diameter, 0.25 μm film thickness). A 2 μL aliquot of each extract (fraction 1 and 2) was injected in splitless mode with the injector temperature at 280°C. Oven temperature ramp was programmed from 40 to 60°C at 20 °C min^{-1}, then to 290 °C at 5 °C min^{-1}, and finally to 300 °C at 6 °C min^{-1}, with a final hold for 20 min. The interface with the detector was conditioned at 300 °C and the ion source at 230 °C. Data acquisition was performed in selected ion monitoring (SIM) mode (Tab. 4.1).

TABLE 4.1 – MONITORED IONS FOR PAHs ANALYSIS

Monitored Ions (m/z)	**Compounds**
128/127	Naphthalene
142/141	C_1- naphthalene
156/141	C_2- naphthalene
152/153	Acenaphthylene
153/154	Acenaphthene
170/155	C_3- naphthalene
166/165	Fluorene
178/179	Phenanthrene and anthracene
192/191	C_1-phenanthrene
202/200	Fluoranthene and pyrene
228/226	Benzo(a)anthracene and chrysene
252/253	Benzo(*b*)fluoranthene, benzo(*j*+*k*)fluoranthene, benzo(*e*)pyrene, benzo(*a*)pyrene, perylene
276/138	Indeno[1,2,3-*c,d*]pyrene, benzo(*g,h,i*)perylene
279/139	Dibenzo(*a,h*)anthracene

Individual PAHs were identified by matching their retention times and ion mass fragments (m/z) with those from standard mixtures (Z-014G-FL, AccuStandard). The calibration range used in the quantification was 0.10 to 2.00 ng μL^{-1}. Quality assurance procedures included analyses of procedural blanks, matrix spikes, precision tests and certified reference material (WADE and CANTILLO, 1994). Blanks were performed for each extraction batch of 11 samples and did not show interference with the analyses of the target compounds. Mean standard recoveries for the spiked sediments were 60 ± 8% for 1-hexadecene, 83 ± 10% for 1-eicosene, 40 ± 9% for naphthalene-d_8, 60 ± 10% for acenaphtene-d_{10}, 83 ±15 % for phenantrene-d_{10}, 86 ± 11% for chysene-d_{12}, 84 ± 13% for perylene-d_{12} and 80 ± 13% for 5α-cholestane-d_4.

4.3 RESULTS AND DISCUSSION

4.3.1Bulk results

Sampling stations can be divided into sub areas according to the geographic configuration of the PES (NAIZOT, 1993; LANA *et al*., 2001; MANTOVANELLI *et al*., 2004; Tab. 4.2). There is an expected gradient from continental to marine influences varying according to the geographic location. Inner bay areas (Antonina and Guaraqueçaba) present average bulk results that suggests a stronger influence of continental apportions in a lower energy depositional environment, such as relatively high fine sediment content and TOC and TN. Paranaguá, Laranjeiras and Pinheiros Bay present intermediate results to these parameters. Among all areas of the estuarine complex, the lowest average content of fine sediments and TOC was observed in the Mixed zone. These results suggest a stronger marine influence with a higher energy depositional environment.

TABLE 4.2 – AVERAGE BULK RESULTS BY GEOGRAPHIC SUBZONES OF PEC

	PEC Subareas					
	Inner zone		**Intermediate zone**			**Outer zone**
	Antonina	**Guaraqueçaba**	**Paranaguá**	**Laranjeiras**	**Pinheiros**	**Mixed zone**
N	5	2	5	7	9	8
pH	6.1 (5.50 – 6.64)	5.8 (5.78 – 5.89)	6.8 (6.26 – 7.33)	6.1 (5.70 – 6.40)	6.2 (5.66 – 6.80)	6.5 (6.22 – 6.98)
Eh	+62 (-24 – +145)	+99 (+58 – +140)	+25 (-192 – +141)	+22 (-178 – +124)	+42 (-127 – +150)	+11 (-296 – +194)
% fine sed	76.5 (14.9 – 96.0)	54.6 (24.3 – 85.0)	30.9 (2.1 – 87.3)	21.2 (4.7 – 48.6)	33.0 (3.3 – 72.5)	14.1 (1.1 – 45.7)
% TOC	5.9 (3.32 – 9.14)	3.5 (1.74 – 5.30)	2.5 (0.27 – 5.35)	1.5 (0.51 – 3.67)	2.2 (0.60 – 4.03)	1.1 (0.13 – 3.08)
$\delta^{13}C$	-26.9 (-27.43 – -26.36)	-26.6 (-27.16 – -26.09)	-25.5 (-26.62 – - 24.86)	-26.8 (-28.36 – -25.77)	-25.8 (-26.78 – -24.96)	-25.7 (-27.29 – -23.10)
% TN	0.37 (0.12 – 0.45)	0.30 (0.12 – 0.48)	0.21 (0.04 – 0.43)	0.13 (0.05 – 0.34)	0.21 (0.06 – 0.49)	0.14 (0.05 – 0.22)

4.3.2PAHs levels and distribution

The complete set of results is presented in the Supplementary Material ('Anexo 3'). Concentrations of the 16 priority PAHs according to U.S. Environmental Protection Agency (EPA) (∑16 PAHs EPA: <DL – 234.3 ng g^{-1}) observed in mangrove sediments of PES are higher than those observed in previous studies for bottom sediments: 0.6 – 63.8 ng g^{-1}

(CARDOSO *et al*., 2016); <DL – 57.2 ng g^{-1} (ABREU-MOTA *et al*., 2014); 3.85 – 89.2 ng g^{-1} (MARTINS *et al*., 2012). However, in places near Paranaguá Port, the ∑16 PAHs in bottom sediments reached higher levels (max. 812 ng g^{-1}, MARTINS *et al*., 2015) than mangroves swamps studied.

Mangrove sediments in other locations considered as being human impacted presented levels of ∑16 PAHs in the same order of magnitude, as reported for Sundarban Mangrove Wetland, India (3.3 – 630 ng g^{-1}, MITRA et al., 2019); Florianópolis, Brazil (25.9 – 434.2 ng g^{-1}, ASSUNÇÃO *et al*., 2017) and Shantou wetlands, China (57 – 238 ng g^{-1}, CAO *et al*., 2009). On the other hand, concentrations observed in the study area are low if compared to heavily impacted mangroves such as Guanabara Bay, Brazil (10 – 240,394 ng g^{-1}, FARIAS *et al*., 2008; 4,400 – 1,387,000 ng g^{-1}, FONTANA *et al*., 2012); Fortaleza, Brazil (3,040 – 2,234,760 ng g^{-1}, CAVALCANTE *et al*., 2009) and Guadeloupe Island, the Caribbean Sea (103 – 1,657 ng g^{-1}, BERNARD *et al*., 1996).

There is a high correlation between TOC *vs* TN and also between TOC *vs* fine sediments ($R^2 \approx 0.8$, n = 36, $p < 0.01$). These parameters present similar trends of distribution, with similar sources and preferential depositional sites (Fig. 4.2). Also, the correlation of TOC *vs* Total PAHs ($R^2 = 0.66$, n = 35, $p < 0.01$) indicates that PAHs concentrations in the study area are dependent to TOC content, as long as # 26 is not considered in the cross plot. This site presented the highest concentration of Total PAHs found in this study (273.4 ng g^{-1}) despite of having low contents of TOC (0.18%) and fine sediments (1%). It suggests that there is local anomalous input of PAHs as well as proper hydrodynamic conditions that permit the deposition of PAHs in this specific mangrove forest placed in the more important touristic place (Mel Island) located in the PES.

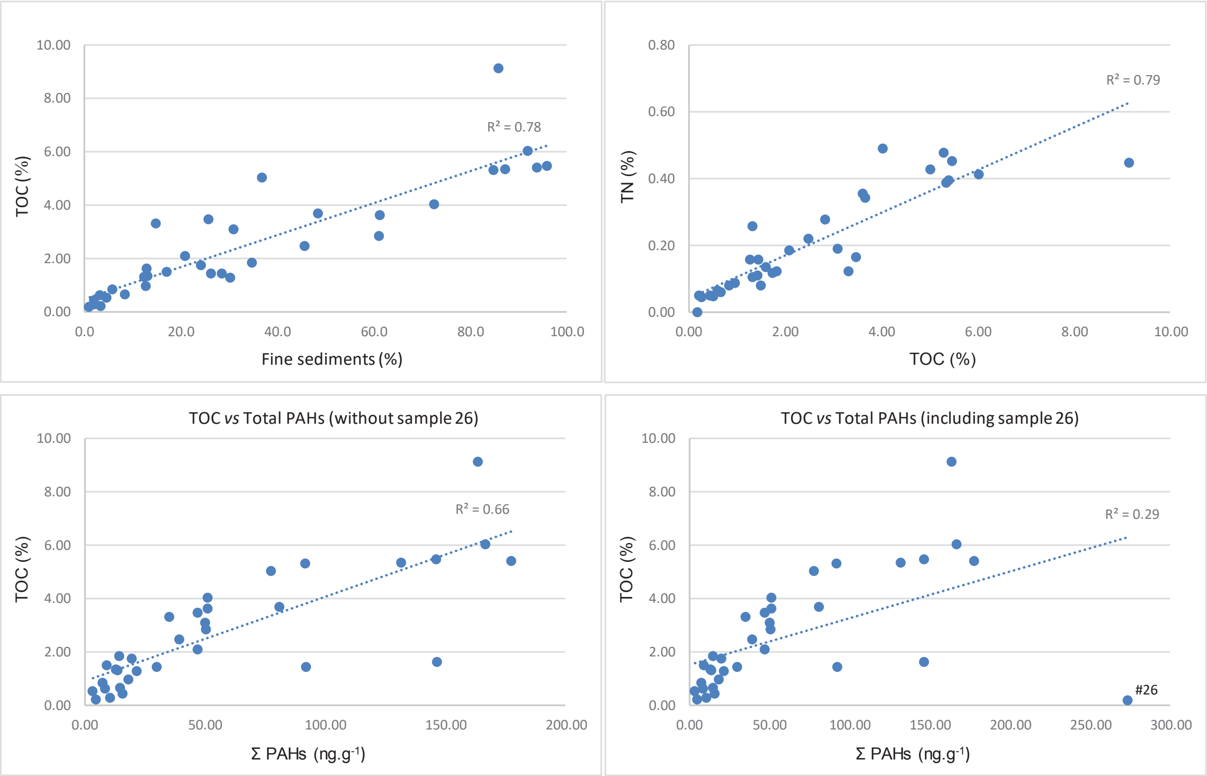

FIGURE 4.2 – LINEAR CORRELATIONS OF BULK PARAMETERS AND TOTAL PAHs IN MANGROVE SEDIMENTS OF PES

In general, total PAHs followed a trend of higher concentrations in the inner zone, medium average levels in the intermediate zone and lower values for the outer zone (Tab. 4.2). Due to the intensive anthropogenic activities in Antonina and Paranaguá bays, higher average levels were observed in specific locations, being different than general pattern observed in each zone. Also, there are punctual influences in the mixed zone (# 26, 273.4 ng g^{-1}) and in Laranjeiras Bay (# 22, 146.5 ng g^{-1}) (Fig. 4.3). Excluding the results of these sites, the average values are sensibly reduced (mixed zone= 24.3 ng g^{-1}, n = 7 and Laranjeiras Bay = 25.4 ng g^{-1}, n = 6).

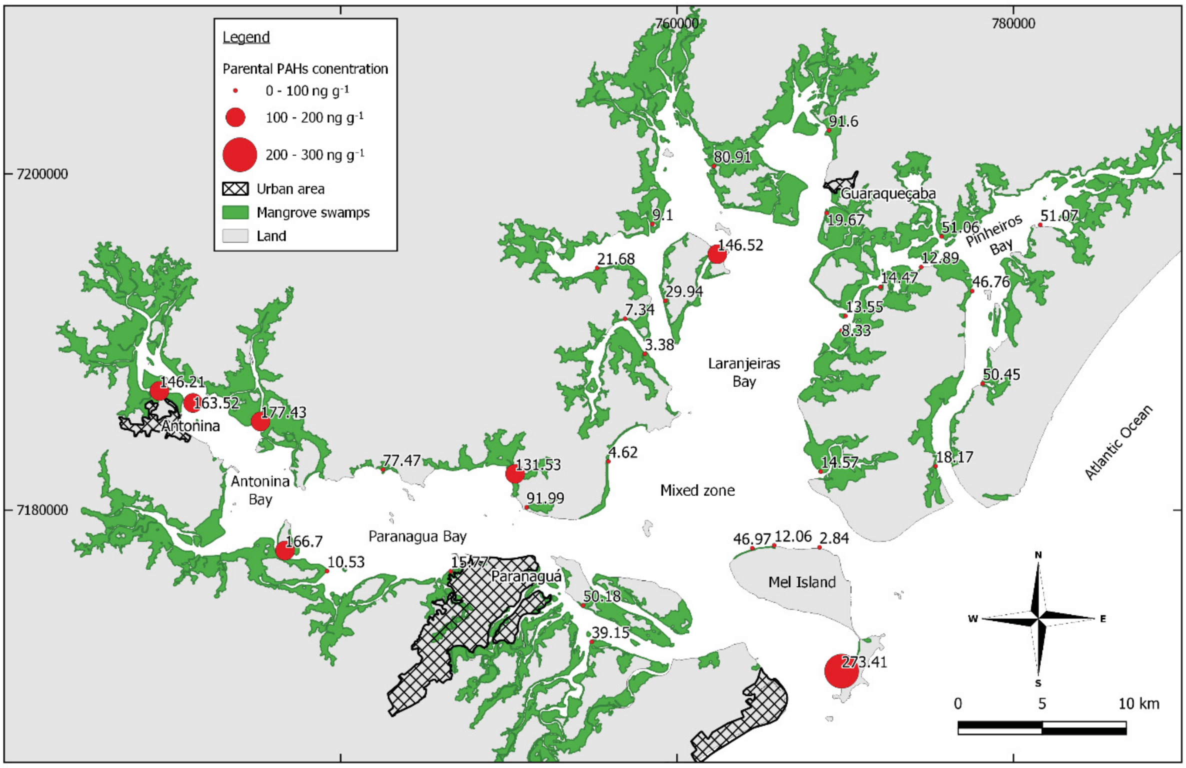

FIGURE 4.3 – SPATIAL DISTRIBUTION OF TOTAL PAHs CONCENTRATIONS (IN ng g^{-1}) IN PES MANGROVE SEDIMENTS.

Therefore, marine hydrodynamics and/or dilution processes seems to drive a major influence in the transport and deposition of PAHs in the mangrove swamps of PES. Inner areas of the estuarine system, sheltered from the effects of the energy of the open sea are a preferential site for the deposition and accumulation of chronic inputs of PAHs making these areas particularly vulnerable to long term contamination.

The predominant individual compounds can also be an indication of measurable anthropogenic impacts by PAHs. In samples with high levels of total PAHs (# 22 and # 26) pyrene and benzo(*a*)pyrene were the most prominent abundant compounds. In site # 07, near Paranaguá Port/City low levels of total PAHs were observed but the main compound was pyrene, as a result of human impact to this mangrove forest.

According to BAUMARD *et al.* (1998a), the level of sediment pollution can be assigned by the sum of parental PAHs as being low (0 – 100 ng g^{-1}), moderate (100 – 1,100 ng g^{-1}), high

(1,000 – 5,000 ng g^{-1}) and very high (> 5,000 ng g^{-1}). According to this classification, most of the studied sites presented a low level of contamination n = 28). However, some of the mangrove sediments presented a moderate level of contamination, located in Antonina Bay (# 01, # 02, # 03 and # 05), in Paranaguá Bay (# 10), in Laranjeiras bay (# 22) and in the mixed area (# 26). Sites # 10, # 22 and # 26 are located in sheltered bays and near human settlements that have possible sources of PAHs such as navigation (e.g. touristic terminal of Encantadas, # 26) and sewage (Gamela village, # 22).

4.3.3Perylene distribution

Perylene is a diagenetic-related PAH frequently found in marine and freshwater sediments and is frequently interpreted as being naturally formed in situ (VENKATESAN, 1988; BAUMARD et al., 1998b; ISHIWATARI *et al.*, 2004; MARTINS *et al.*, 2015; CARDOSO *et al.*, 2016). The formation of this compound was proposed to be controlled by in situ microbial processing of non-specific OM (SILLIMAN *et al.*, 1998, SILLIMAN *et al.*, 2000, SILLIMANN *et al.*, 2001), however its origin therefore remains unsolved. This compound may present a distribution pattern different from other combustion-derived PAHs (ISHIWATARI *et al.*, 2004).

The effect of anthropogenic inputs is reflected in the proportion of perylene relative to total 5-rings PAHs (Tab. 4.2). Perylene represented ~70% or more of the 5-rings PAHs in less human-impacted areas (Guaraqueçaba, Pinheiros and Laranjeiras Bay); whereas in Paranaguá Bay, the most human impacted sub-area in the PES, perylene roughly represented 50% of the total 5-rings PAHs.

Regarding individual compounds, perylene was the most abundant compound in 86% of the samples. Concentrations ranged from <DL to 214.5 ng g^{-1} corresponding from 4.7 to 100% of the Total 5 ring PAHs. The highest concentrations of this compound were found in

Antonina and Guaraqueçaba bays (Fig. 4.4). These also presented higher TOC in low energy environments and near to river's discharge, that may be an important source of natural terrigenous organic matter and precursors of this compound. Therefore, perylene in the study area can be attributed mostly to natural sources (VENKATESAN, 1988; BAUMARD et al., 1998b; ISHIWATARI *et al*., 2004; MARTINS *et al*., 2015).

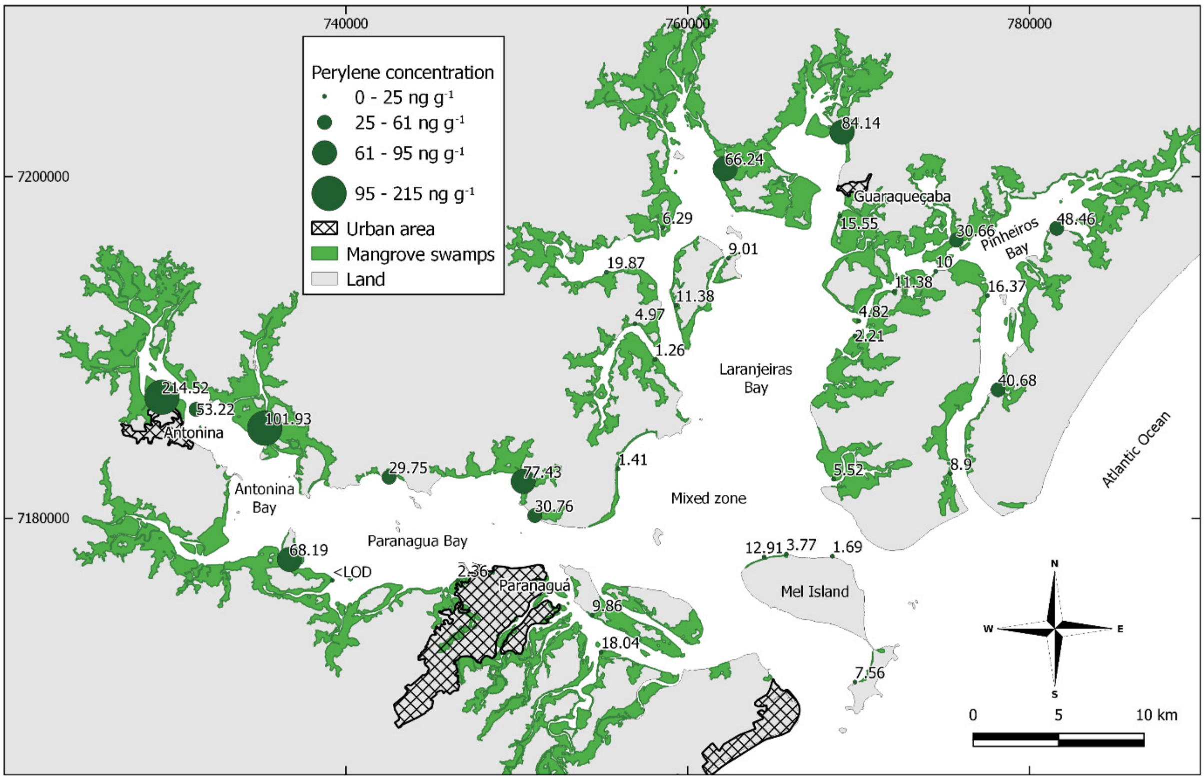

FIGURE 4.4 – SPATIAL DISTRIBUTION OF PERYLENE CONCENTRATIONS (IN ng g^{-1}) IN MANGROVE SEDIMENTS OF PES

Perylene correlation to TOC does not present the same pattern in all areas of PES. If Antonina Bay is not considered in the linear regression, the correlation of TOC *vs* perylene is increased to significant levels ($R^2 = 0.70$; n = 31). Further studies are needed in order to clarify the processes involved in this distribution, since the mangrove in Antonina has specific conditions such as high TOC content (max. 9.14%), low energy environment, riverine contributions and anthropic activities (city and port) that can result in a particular depositional environment.

4.3.4Sources of PAHs based on diagnostic ratios

Diagnostic ratios of individual PAHs (Fig. 4.5) suggest that combustion is the main source of PAHs to PES's mangroves. Despite some ratios point to biomass and coal combustion as the main contributors, most of the calculated values remain in the range of petroleum combustion (YUNKER *et al.*, 2002). Sites with this type of source signature are widespread throughout the studied estuary.

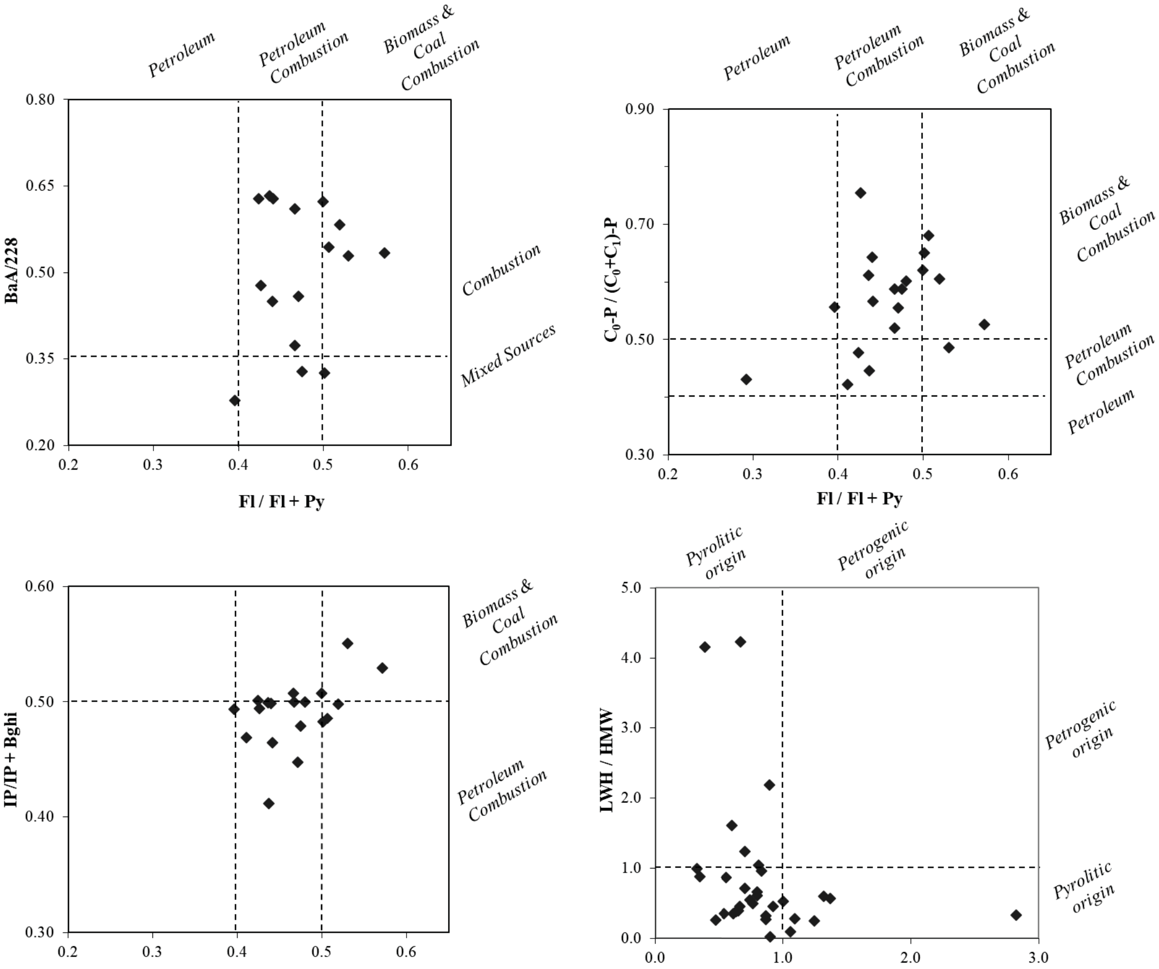

FIGURE 4.5 – DIAGNOSTIC RATIOS TO INDIVIDUAL PAHs CALCULATED FOR PES MANGROVE SEDIMENTS

The petroleum and by-products combustion are in accordance to the main expected anthropogenic source of PAHs to the studied area. Boat and cargo ship traffic can significantly contribute to PAHs inputs for aquatic environments, since exhaustion and chronic leakages of lubricant are rich in PAHs (SMITH *et al*., 1985; GARCIA *et al*., 2010; KAO *et al*., 2015). The PES margins are occupied by artisanal fisherfolk (distributed in approx. 40 villages with 2,100 families; FARACO *et al*., 2010) that depend almost exclusively on boats for transportation. Furthermore, Paranaguá and Antonina have intense port activities, Paranaguá being the main South American grain terminal and the third most important Brazilian port in terms of loading and unloading operations (MARTINS *et al*., 2015). Biomass and coal combustion seem to be another important source of PAHs to the study area.

4.4 CONCLUSIONS

This study assessed for the first time the PAHs distribution in the superficial sediments of the mangrove swamps of PEC, corresponding to the recent deposition of these compounds. PAHs were distributed throughout the mangroves of the study area with the most prominent compound being perylene, that was attributed to diagenetic processes and therefore is tracer for natural sources of organic matter.

Calculated ratios of PAHs point to combustion of petroleum and by-products as the main source of PAHs to the studied area, suggesting that navigation is the main source of PAHs to the study area. Biomass and coal combustion are also an important source. This study is a contribution for the study of PAHs in mangrove sediments being the first attempt to map these compounds in the study area. Despite of being one of the most a well-preserved estuary in Brazil and comprised on a World Heritage Listed area (POSSATO et al., 2014; SA et al., 2006), the results obtained in this study showed evidences of anthropogenic inputs. Mangrove sediments are therefore extremely vulnerable to chronic impacts that can pose cumulative amounts of carcinogenic compounds, such as benzo(a)pyrene.

Since mangroves are an important food source for the population and sustain fundamental economic activity (crabs and oyster extraction) the results deserve special attention, focusing on environmental quality to assure the security for food consuming of the traditional communities in PES and its customers. Future entrepreneurships in the area have the potential to increase the chronic loads of PAHs as well as the probability of accidents with hydrocarbons in the area, what should be a matter of concern to decision-makers, regulation agencies and the affected population.

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5 CONSIDERAÇÕES FINAIS

O presente trabalho buscou realizar a caracterização e quantificação e verificar a distribuição dos hidrocarbonetos (*n*-alcanos, HPAs e biomarcadores de petróleo) nos ambientes de manguezal do Complexo Estuarino de Paranaguá (CEP). O estudo foi dividido em três itens, com as principais conclusões de cada capítulo sendo resumidas a seguir.

Foi verificada a distribuição dos hidrocarbonetos ao longo do gradiente de zonação: planície entre marés – marisma – manguezal em dois locais com distintos graus de contaminação. Os marismas e manguezais se mostraram os locais mais propícios para acumulação dos hidrocarbonetos. Os *n*-alcanos revelaram a predominância de aportes naturais, em ambos locais. Já os HPAs apresentaram níveis até três vezes mais altos no local impactado e os biomarcadores de petróleo (hopanos e esteranos) apresentaram níveis até seis vezes maiores. Assim, foi evidenciada a aplicação dos biomarcadores de petróleo para a avaliação de aportes crônicos de petróleo e derivados em áreas com alto aporte natural de hidrocarbonetos.

Em uma segunda etapa do trabalho, foi realizado o mapeamento dos manguezais do CEP para hidrocarbonetos. Foi realizada a identificação dos principais hidrocarbonetos cíclicos naturais (terpanos e hopanos), a fim de obter uma caracterização inicial dos principais compostos aportados ao CEP. Este foi o primeiro trabalho desta natureza realizado para o local e permitiu diferenciar os compostos naturais dos compostos catagênicos com origem no petróleo (considerados como sendo de origem antrópica na área de estudo).

Foram identificadas áreas preferenciais de acumulação dos terpanos e hopanos naturais (Baías de Antonina e Guaraqueçaba), o que pode ser interpretado como uma indicação de áreas com tendência a acumular hidrocarbonetos e outros contaminantes hidrofóbicos. Esses sub-estuários, apesar de não serem atualmente considerados como contaminados por hidrocarbonetos, possuem evidências de grande sensibilidade a aportes dessa natureza e portanto demandam especial atenção sob o ponto de vista de prevenção à poluição e planejamento de ocupação e uso dessas áreas.

Diante dos resultados obtidos, é possivel concluir que os manguezais do CEP possuem níveis de hidrocarbonetos naturais (*n*-alcanos) similares a outros bosques de mangues subtropicais. Tais níveis podem ser considerados baixos quando comparados a ambientes similares que se desenvolvem em menores latitudes (áreas tropicais). Os grau de desenvolvimento dos bosques provavelmente exerce influência sobre os níveis de hidrocarbonetos verificados nos sedimentos.

Em geral, o grau de impacto antrópico por hidrocarbonetos observado para os manguezais do CEP pode ser considerado baixo. Os locais mais impactados foram localizados na Baía de Paranaguá, evidenciados pelos níveis de HPAs e presença de biomarcadores de petróleo de origem petrogênica. A Baía de Antonina também mostrou evidências de impactos, confirmando que o eixo Leste-Oeste do Complexo Estuarino recebe maiores cargas de contaminação crônica por hidrocarbonetos, sendo onde se encontram as maiores ocupações urbanas e atividades portuárias.

O eixo Norte-Sul apresentou evidências de baixos aportes crônicos de hidrocarbonetos, sendo que foi identificado impacto localizado (pela concentração de HPAs) proximo a um local com ocupação humana (Vila da Gamela). Apesar de ser um caso isolado, é valido ressaltar que os locais de despejo dos efluentes dessas vilas ainda não foram avaliados, e que o CEP possui diversas ocupações urbanas de pequeno porte em suas margens, com ausência de saneamento básico.

Na Zona de Mistura, próximo da desembocadura do estuário, foi evidenciado aporte significativo por HPAs na Baía das Encantadas (Ilha do Mel) próximo ao porto de turismo. No lado Norte da Ilha, próximo à Ponta do Hospital, apesar de não haver ocupação urbana ou outra fonte evidente, existem indícios de contaminação crônica por hidrocarbonetos.

Portanto, é possivel afirmar que a principal fonte de hidrocarbonetos antrópicos para a áea de estudos são as atividades de navegação. Os processos hidrodinâmicos e de deposição sedimentar no CEP ainda são pouco conhecidos, mas é possivel inferir através dos estudos realizados com os hidrocarbonetos que os manguezais das margens do CEP são a área mais provável para o acúmulo de contaminantes orgânicos hidrofóbicos porventura lançados em suas águas. Os compostos podem ser dispersados para áreas mais distantes das fontes - principalmente onde existe hidrodinâmica mais intensa (Zona de Mistura).

De modo geral, o ambiente estudado pode ser considerado como tendo alto potencial de acumulação de compostos hidrofóbicos, tanto de natureza natural como antrópica. As áreas mais protegidas do CEP (Baías de Antonina e Guaraqueçaba) podem ser apontadas como locais de alta vulnerabilidade para contaminação e baixo potencial de remobilização/recuperação. Tais condições devem ser levadas em conta no planejamento de novos empreendimentos na região.

5.1 RECOMENDAÇÕES PARA TRABALHOS FUTUROS

- Ampliar a caracterização dos hidrocarbonetos naturais, incluindo um mapeamento do CEP para esses compostos e também compostos aromáticos (por exemplo, triterpenos mono, di e triaromáticos) e HPAs naturais (reteno, coroneno). O ambiente estudado possui fontes abundantes de matéria orgânica e condições de sedimentação propícias para o aprisionamento desses materiais. Tais estudos podem elucidar novas vias de diagênese precoce de compostos, fornecer novos proxies para o estudo de alterações antropicas e climaticas, entre outras aplicações;
- Estudar o impacto local das ocupações urbanas (vilas) e o respectivo lançamento de efluentes. Tendo em vista o alto potencial de acumulação de contaminantes do manguezal, esses lançamentos crônicos podem ocasionar degradação ambiental e potencial risco para a população tendo em vista o consumo de pescado;
- Avaliar os processos de deposição e diagênese da matéria orgânica na Baía de Antonina. As condições deposicionais da Baía e o aporte direto de rios parece propiciar um ambiente estuarino diferenciado do restante do CEP, com alto potencial de acúmulo de materia orgânica;
- Realizar estudos com testemunhos para avaliar a evolução histórica dos aportes de hidrocarbonetos naturais e antrópicos para o CEP, com foco na identificação de acidentes que ocorreram no passado recente nas Baías de Antonina e de Paranaguá;
- Avaliar, nos sedimentos de manguezal, outros tipos de biomarcadores de petróleo resistentes a degradação (esteranos mono e triaromáticos - MAS, TAS) assim como outros tipos de contaminantes (metais, POPs e contaminantes emergentes);
- Estudar a dispersão de contaminantes na Baía de Paranaguá, incluindo a Ilha do Mel (Comunidade do Amparo, Ponta do Hospital e Baía das Encantadas). Tais estudos são imprescindíveis para a avaliação de impacto diante da ampliação de atividades antrópicas nas suas margens (tais como ocupações urbanas e portos) que possuem evidente potencial de aumento da carga de contaminação crônica para o ambiente, além da probabilidade de ocorrência de derrames acidentais.

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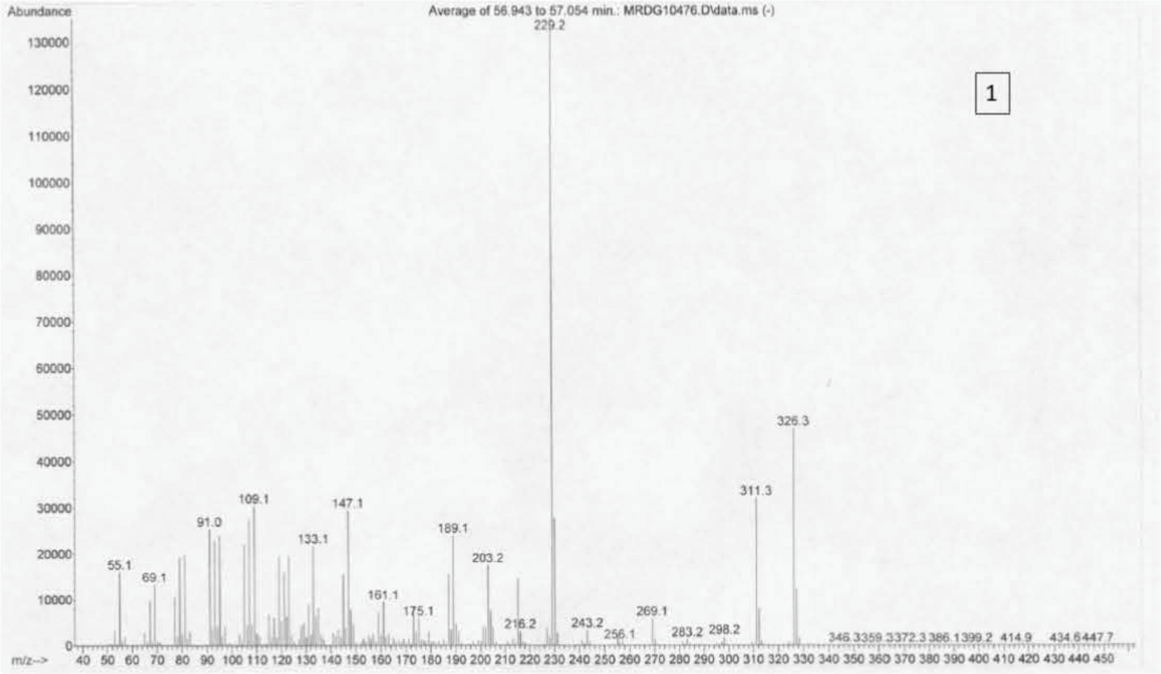
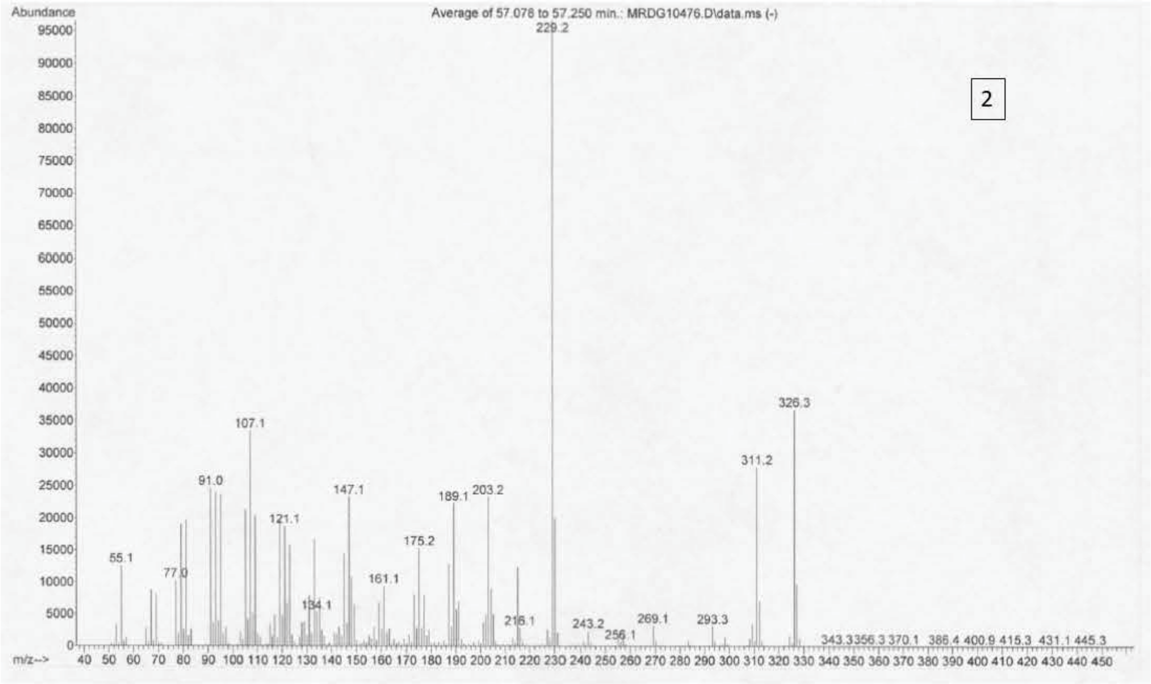
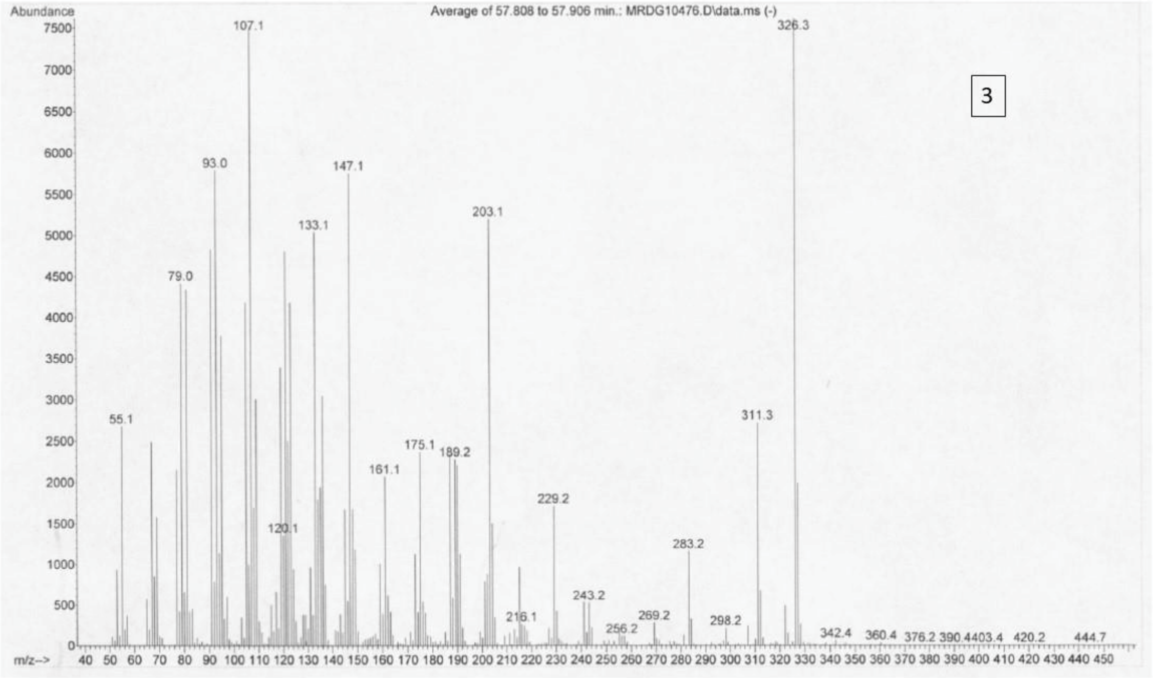
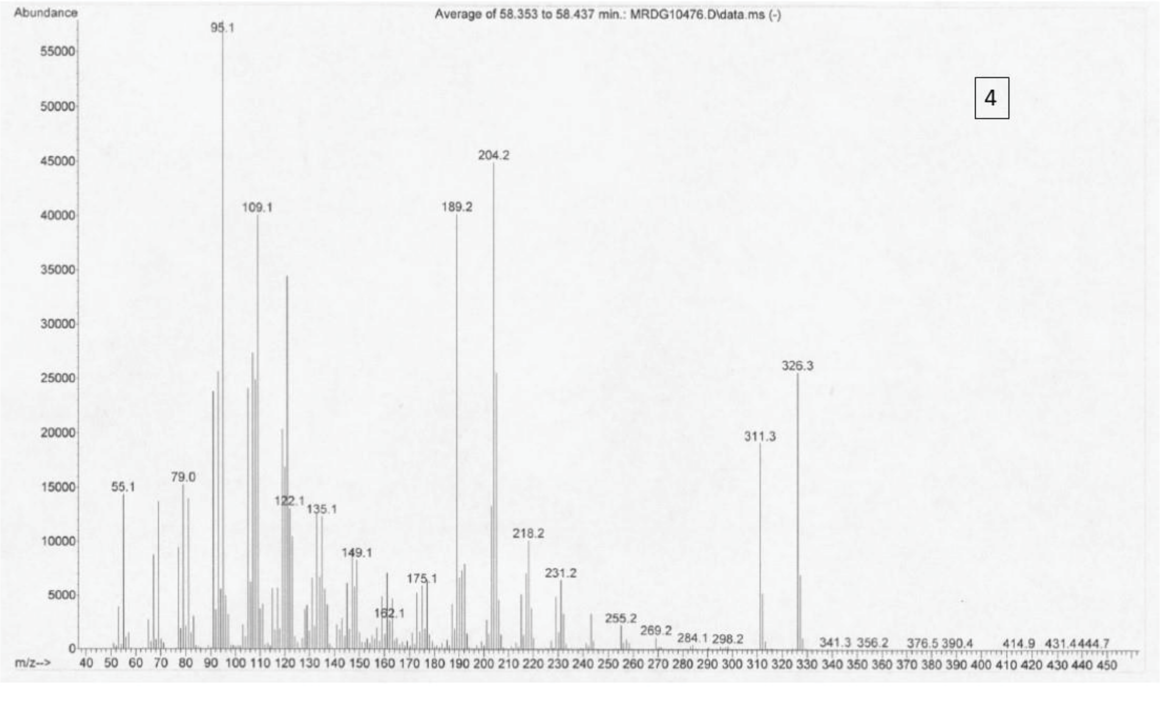
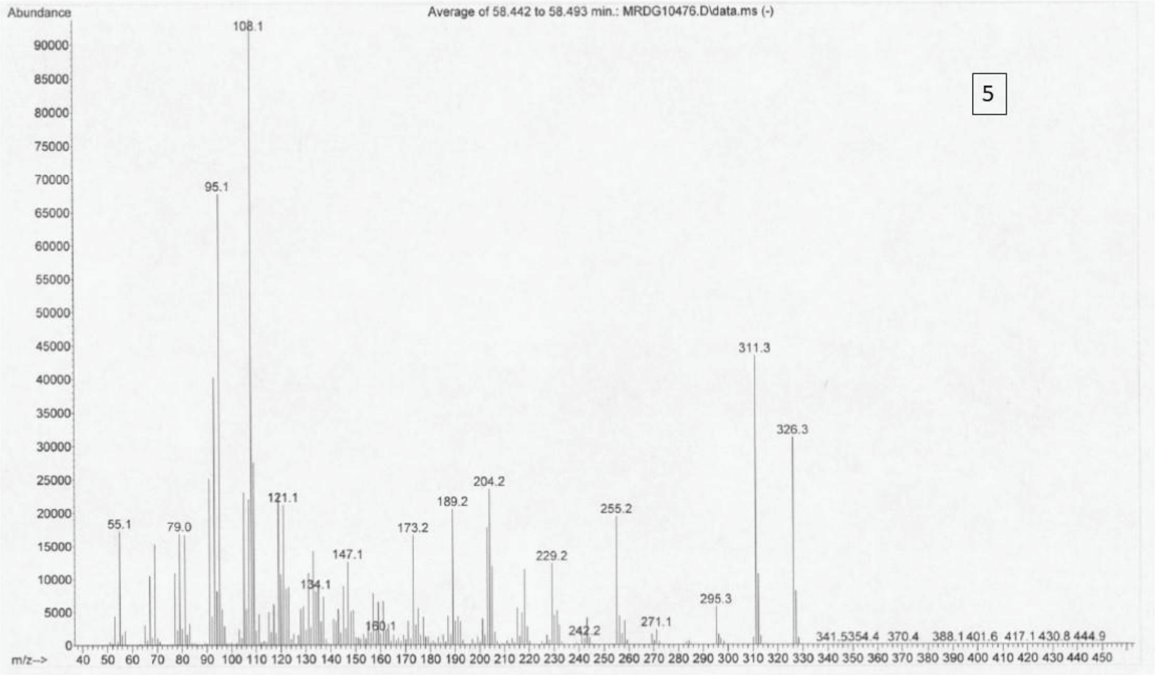
ANEXO 1 – ESPECTROS DE MASSA DOS COMPOSTOS SELECIONADOS NO ITEM 3

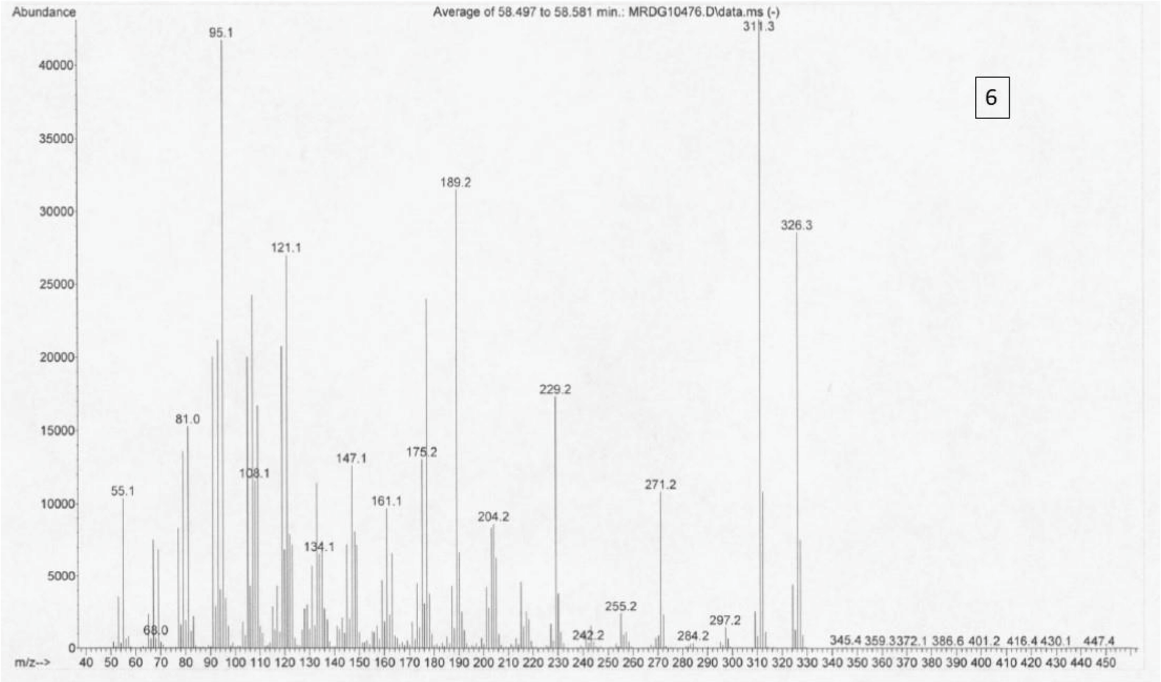


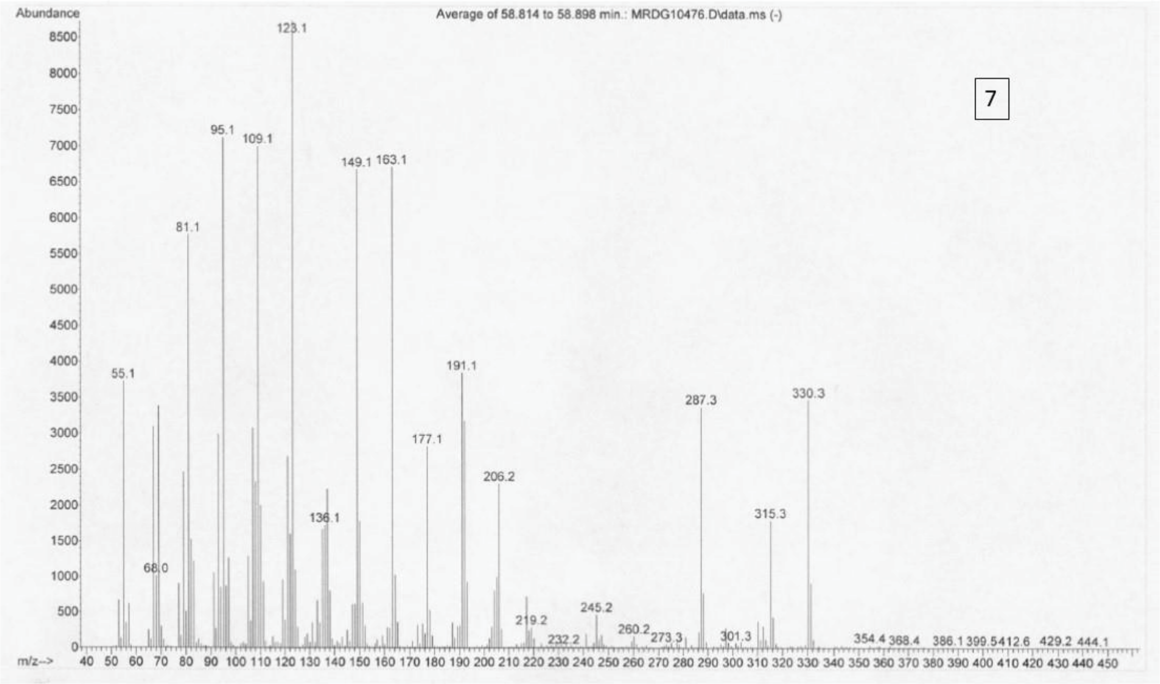


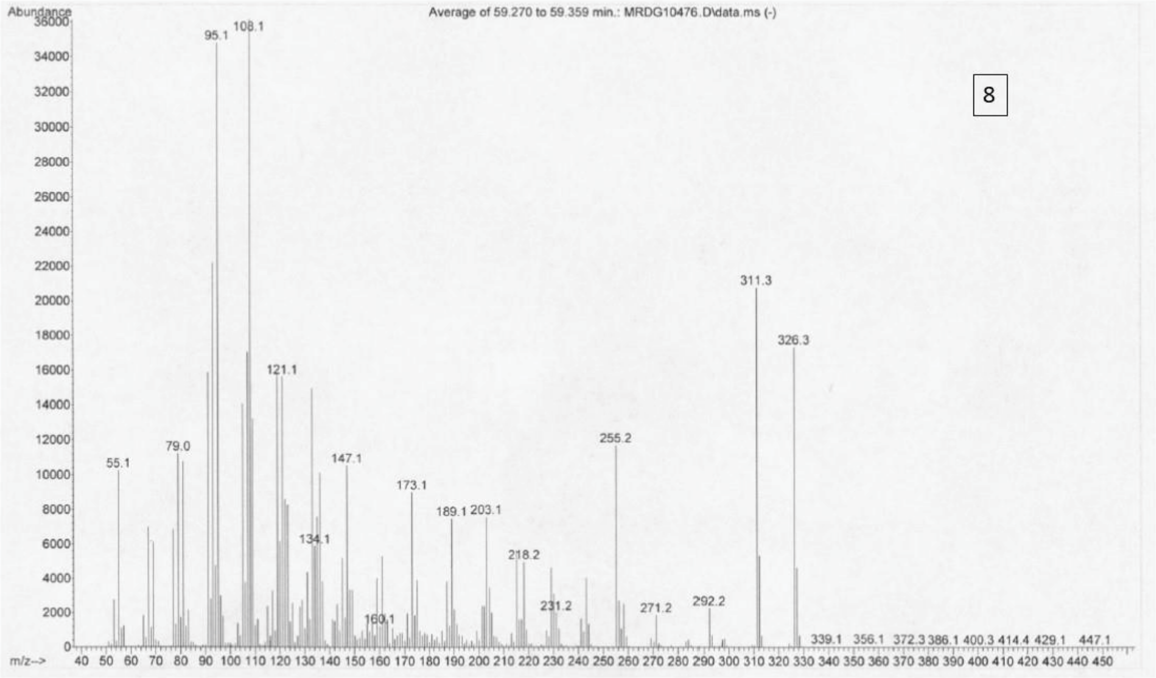

Abundance
Average of 57.808 to 57.906 min.: MRDG10476.D\data.ms (-)
3
107.1
326.3
93.0
147.1
203.1
133.1
79.0
55.1
311.3
175.1
189.2
161.1
229.2
120.1
283.2
243.2
216.1
269.2
256.2
298.2
342.4
360.4
376.2
390.4403.4
420.2
444.7
m/z-->

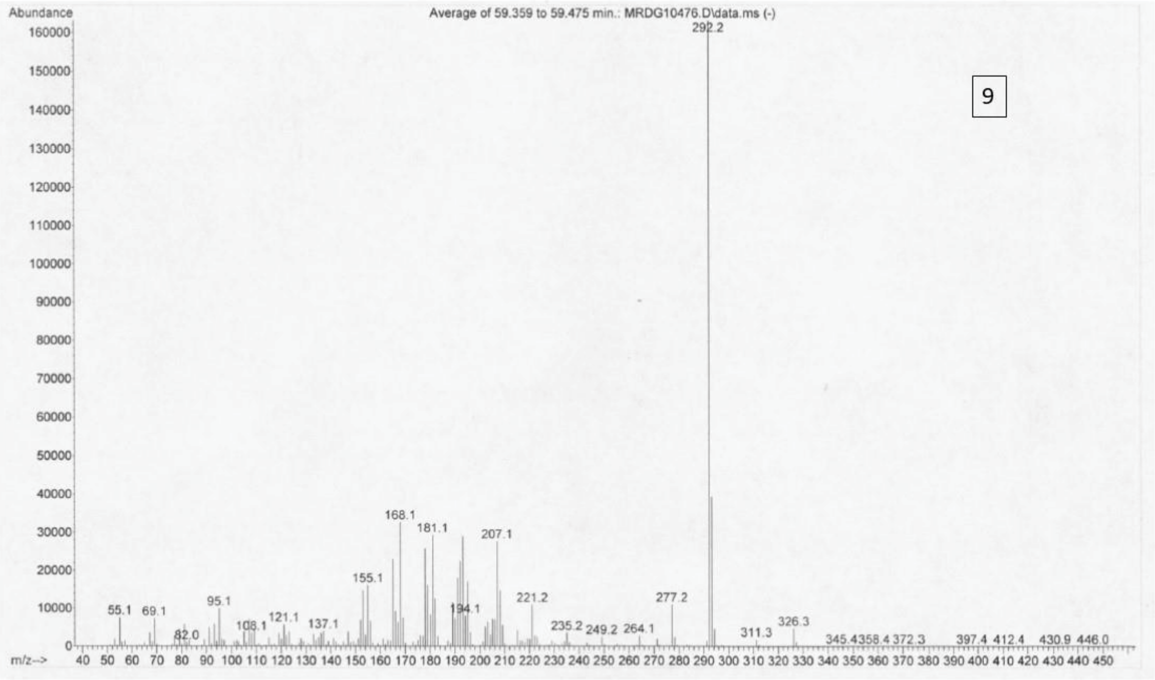

Abundance
Average of 58.353 to 58.437 min.: MRDG10476.D\data.ms (-)
4
95.1
204.2
109.1
189.2
326.3
311.3
55.1
79.0
122.1
135.1
218.2
149.1
231.2
175.1
162.1
255.2
269.2
284.1
298.2
341.3
356.2
376.5
390.4
414.9
431.4444.7
m/z-->

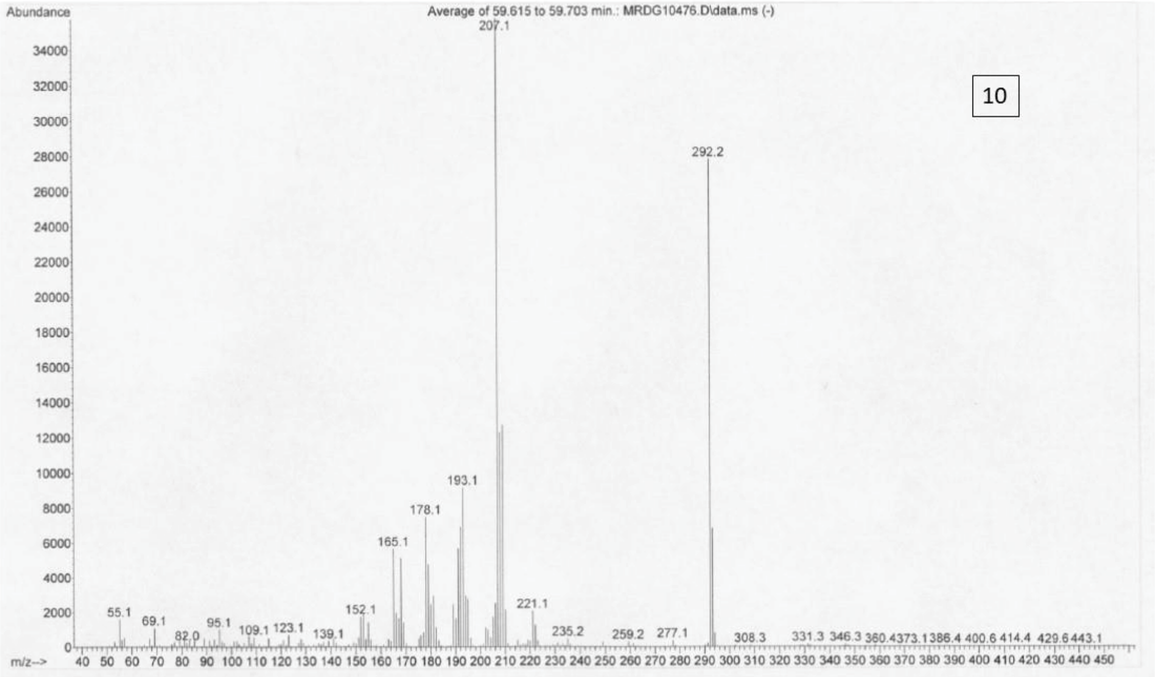

Average of 58.442 to 58.493 min.: MRDG10476.D\data.ms (-)
Abundance
m/z-->
5
108.1
95.1
311.3
326.3
121.1
204.2
189.2
255.2
55.1
79.0
173.2
147.1
229.2
134.1
295.3
160.1
242.2
271.1
341.5
354.4
370.4
388.1
401.6
417.1
430.8
444.9
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
50000
55000
60000
65000
70000
75000
80000
85000
90000
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450

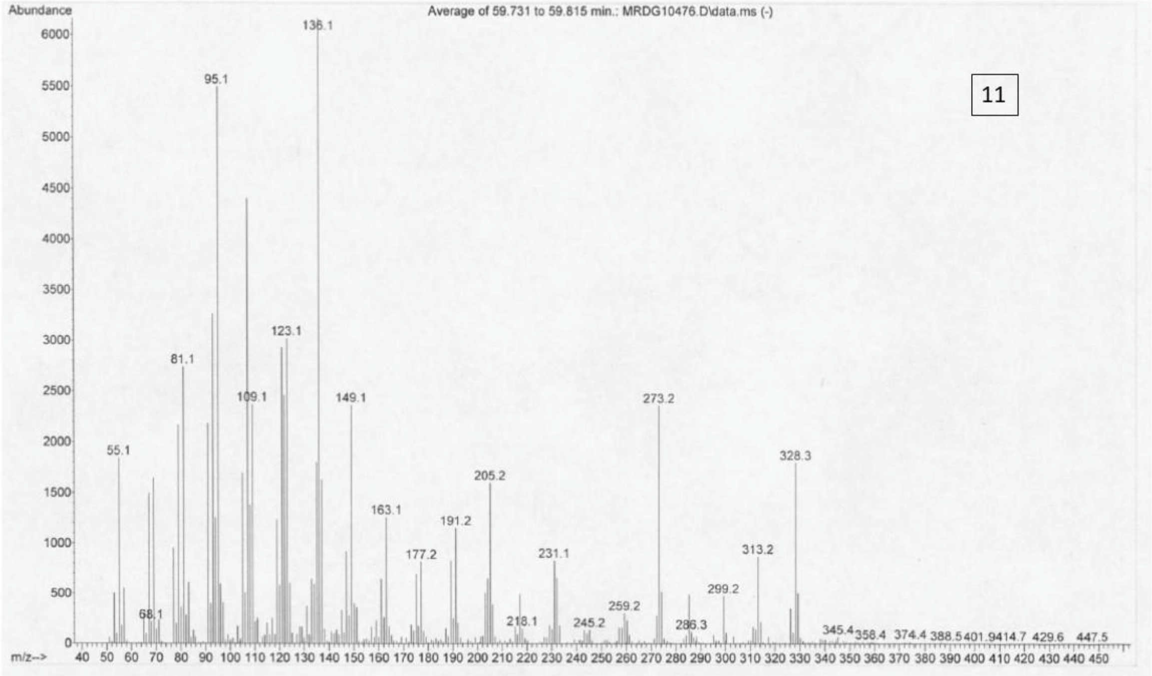

Average of 58.497 to 58.581 min.: MRDG10476.D\data.ms (-)
Abundance
m/z-->
6
95.1
311.3
189.2
326.3
121.1
229.2
81.0
175.2
147.1
108.1
271.2
55.1
161.1
204.2
134.1
255.2
297.2
68.0
242.2
284.2
345.4
359.3
372.1
386.6
401.2
416.4
430.1
447.4
0
5000
10000
15000
20000
25000
30000
35000
40000
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450

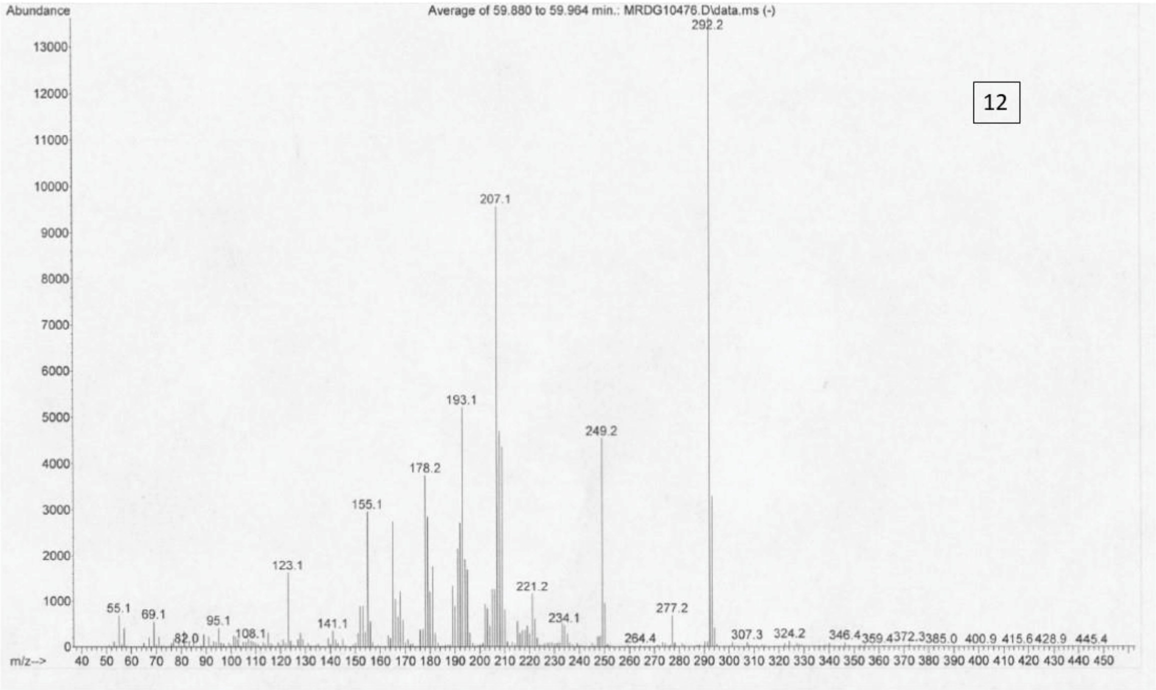

Abundance
Average of 58.814 to 58.898 min.: MRDG10476.D\data.ms (-)
7
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
123.1
95.1
109.1
149.1
163.1
81.1
55.1
191.1
287.3
330.3
177.1
206.2
315.3
136.1
68.0
219.2
245.2
232.2
260.2
273.3
301.3
354.4
368.4
386.1
399.5
412.6
429.2
444.1
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450

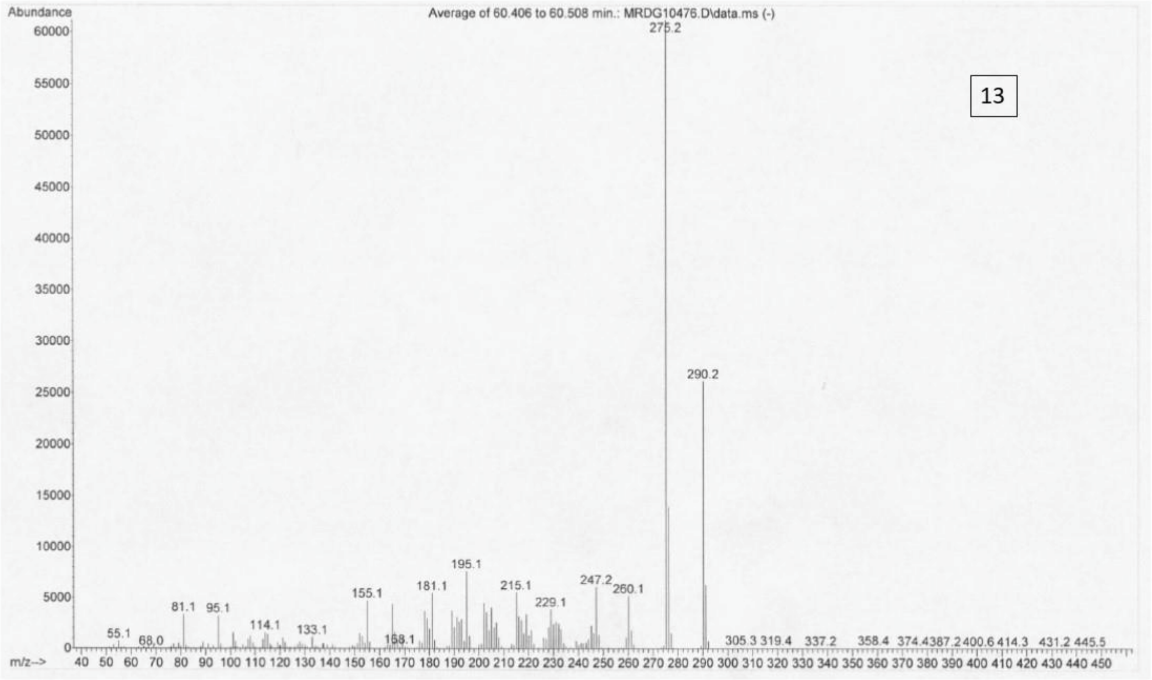

Abundance
Average of 59.270 to 59.359 min.: MRDG10476.D\data.ms (-)
8
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
95.1
108.1
311.3
326.3
121.1
255.2
79.0
55.1
147.1
173.1
189.1
203.1
134.1
218.2
231.2
160.1
271.2
292.2
339.1
356.1
372.3
386.1
400.3
414.4
429.1
447.1
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450


Abundance
Average of 59.359 to 59.475 min.: MRDG10476.D\data.ms (-)
9
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
292.2
168.1
181.1
207.1
155.1
194.1
221.2
277.2
55.1
69.1
95.1
82.0
108.1
121.1
137.1
235.2
249.2
264.1
311.3
326.3
345.4
358.4
372.3
397.4
412.4
430.9
446.0


Abundance
Average of 59.615 to 59.703 min.: MRDG10476.D\data.ms (-)
10
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
207.1
292.2
193.1
178.1
165.1
221.1
152.1
55.1
69.1
82.0
95.1
109.1
123.1
139.1
235.2
259.2
277.1
308.3
331.3
346.3
360.4
373.1
386.4
400.6
414.4
429.6
443.1

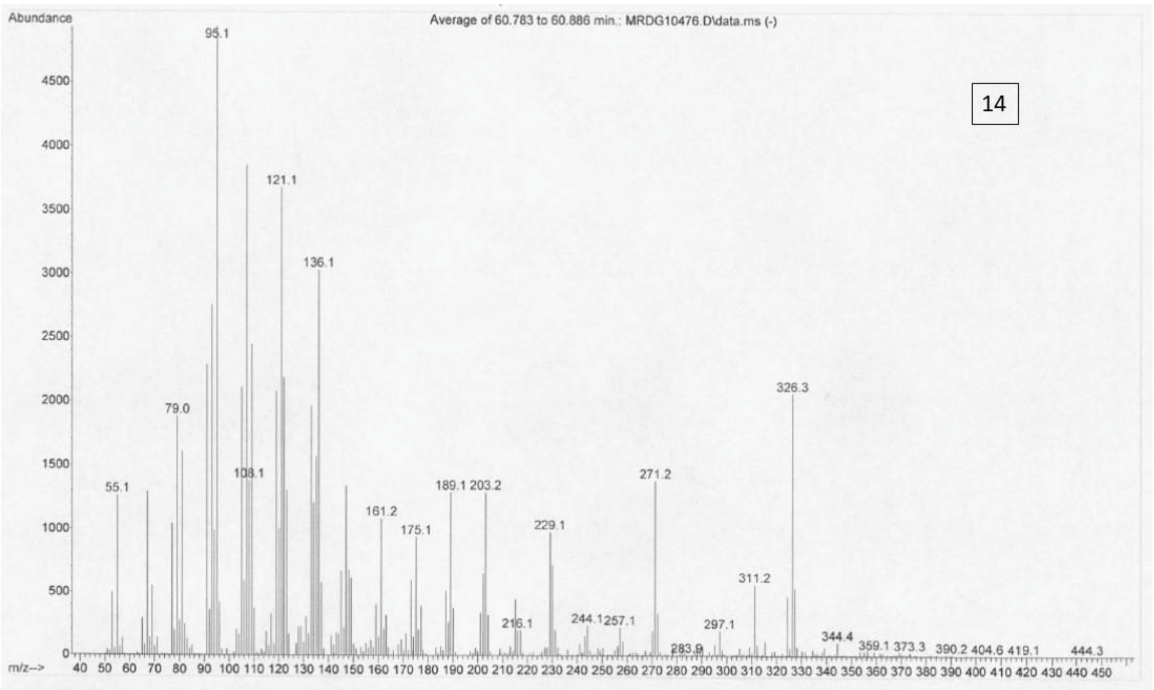

Abundance
Average of 59.731 to 59.815 min.: MRDG10476.D\data.ms (-)
11
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
136.1
95.1
123.1
81.1
109.1
149.1
273.2
55.1
328.3
205.2
163.1
191.2
177.2
231.1
313.2
299.2
259.2
68.1
218.1
245.2
286.3
345.4
358.4
374.4
388.5
401.9
414.7
429.6
447.5


Abundance
Average of 59.880 to 59.964 min.: MRDG10476.D\data.ms (-)
292.2
12
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
207.1
193.1
249.2
178.2
155.1
123.1
221.2
55.1
69.1
95.1
141.1
234.1
277.2
82.0
108.1
264.4
307.3
324.2
346.4
359.4
372.3
385.0
400.9
415.6
428.9
445.4



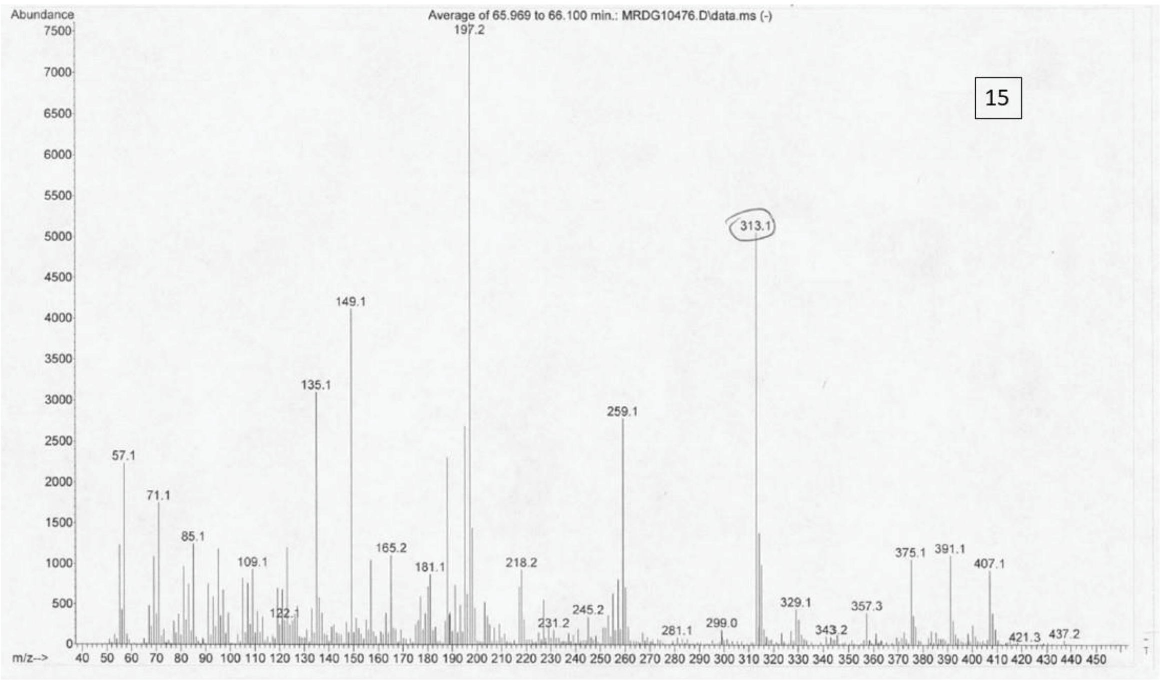
13

Abundance
Average of 60.406 to 60.508 min.: MRDG10476.D\data.ms (-)
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
275.2
290.2
195.1
181.1
155.1
215.1
247.2
260.1
229.1
81.1
95.1
114.1
133.1
55.1
68.0
168.1
305.3
319.4
337.2
358.4
374.4
387.2
400.6
414.3
431.2
445.5



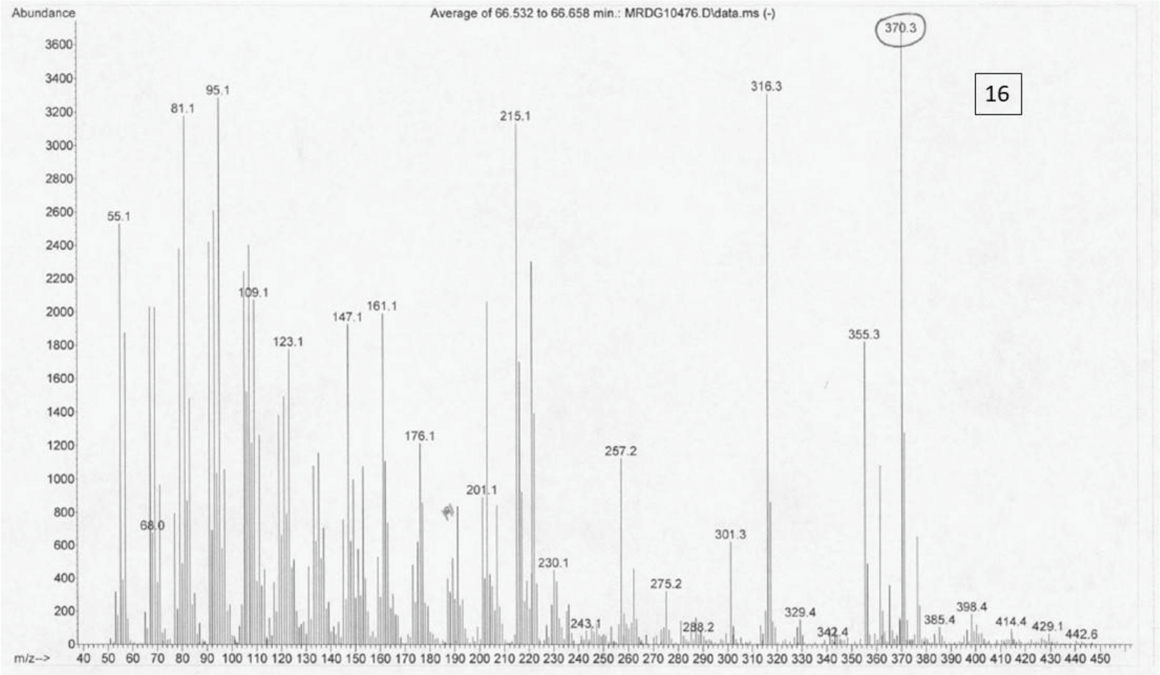
14

Abundance
Average of 60.783 to 60.886 min.: MRDG10476.D\data.ms (-)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
95.1
121.1
136.1
326.3
79.0
55.1
108.1
189.1
203.2
271.2
161.2
175.1
229.1
311.2
216.1
244.1
257.1
297.1
283.9
344.4
359.1
373.3
390.2
404.6
419.1
444.3



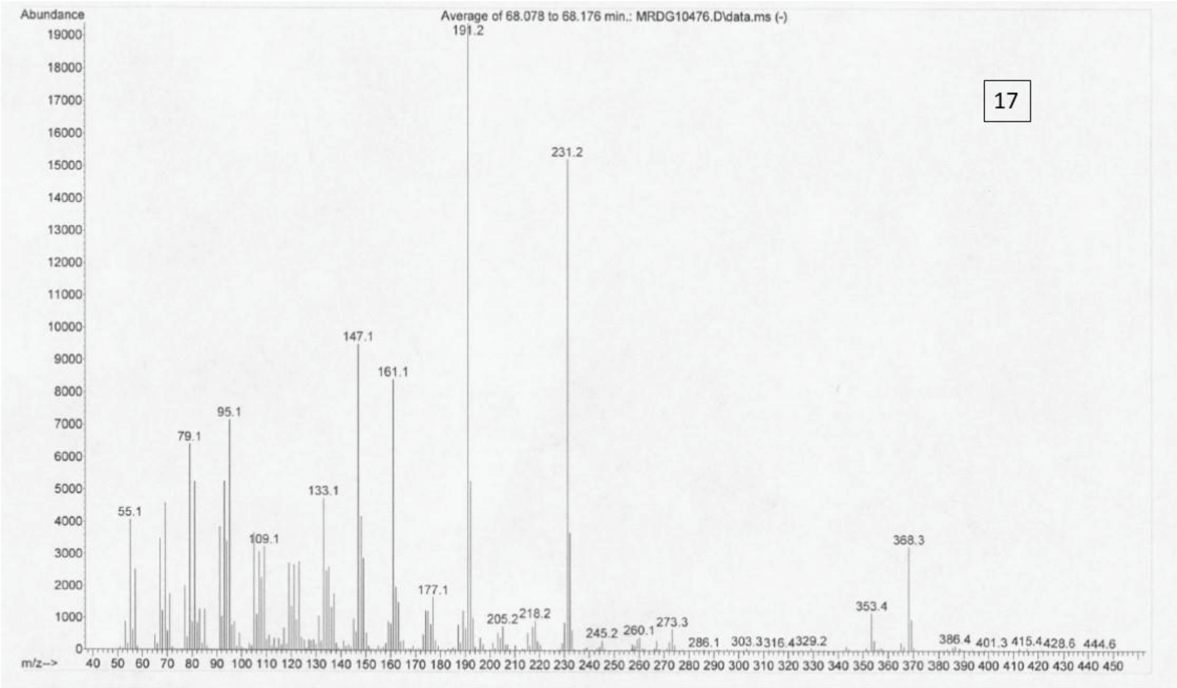
15

Average of 65.969 to 66.100 min.: MRDG10476.D\data.ms (-)
Abundance
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
197.2
313.1
149.1
135.1
259.1
57.1
71.1
85.1
109.1
122.1
165.2
181.1
218.2
231.2
245.2
281.1
299.0
329.1
343.2
357.3
375.1
391.1
407.1
421.3
437.2

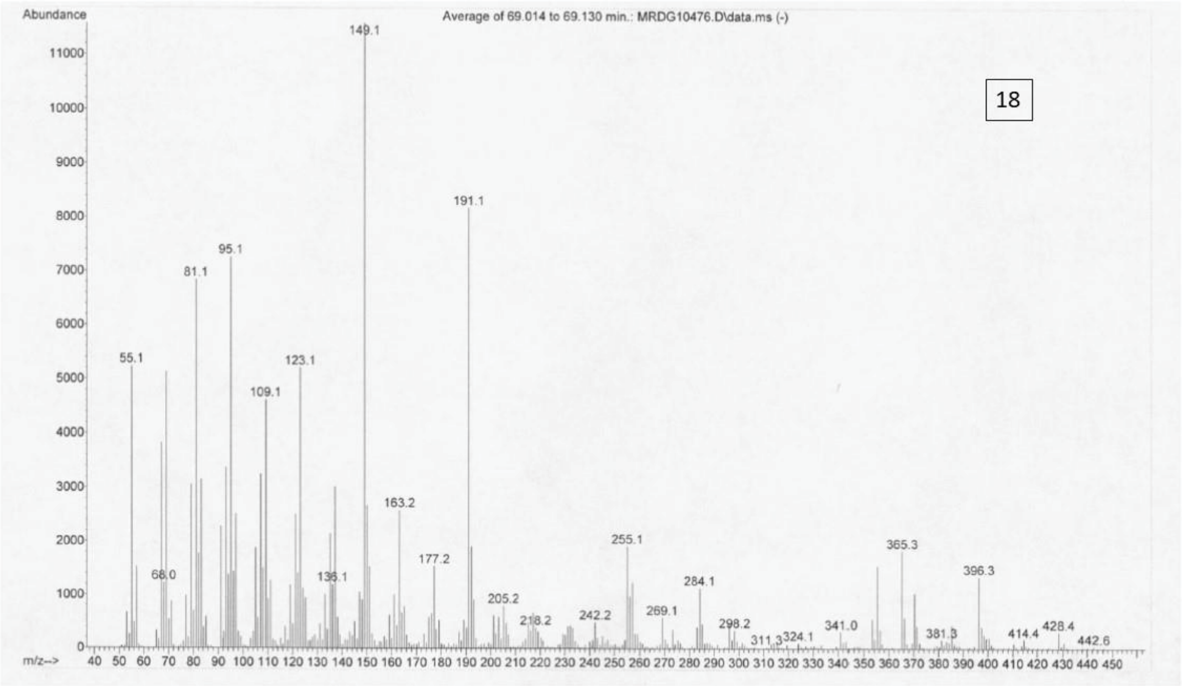


16

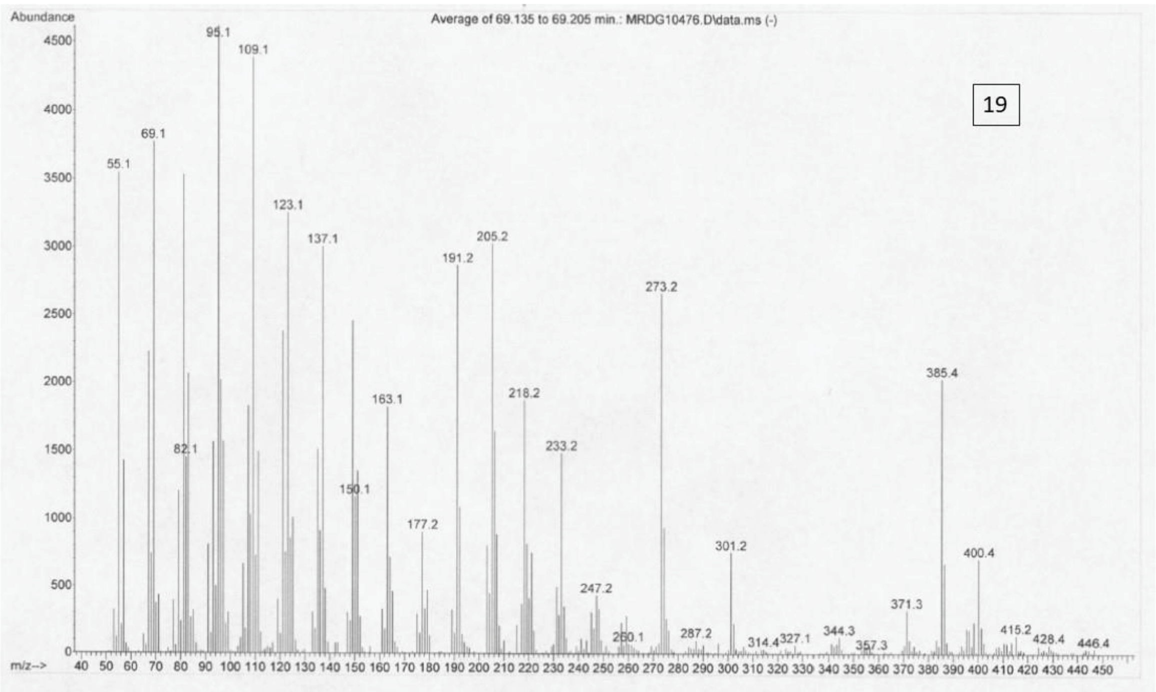
Average of 66.532 to 66.658 min.: MRDG10476.D\data.ms (-)
Abundance
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
370.3
316.3
95.1
81.1
215.1
55.1
109.1
161.1
147.1
123.1
355.3
176.1
257.2
201.1
68.0
301.3
230.1
275.2
243.1
288.2
329.4
342.4
385.4
398.4
414.4
429.1
442.6

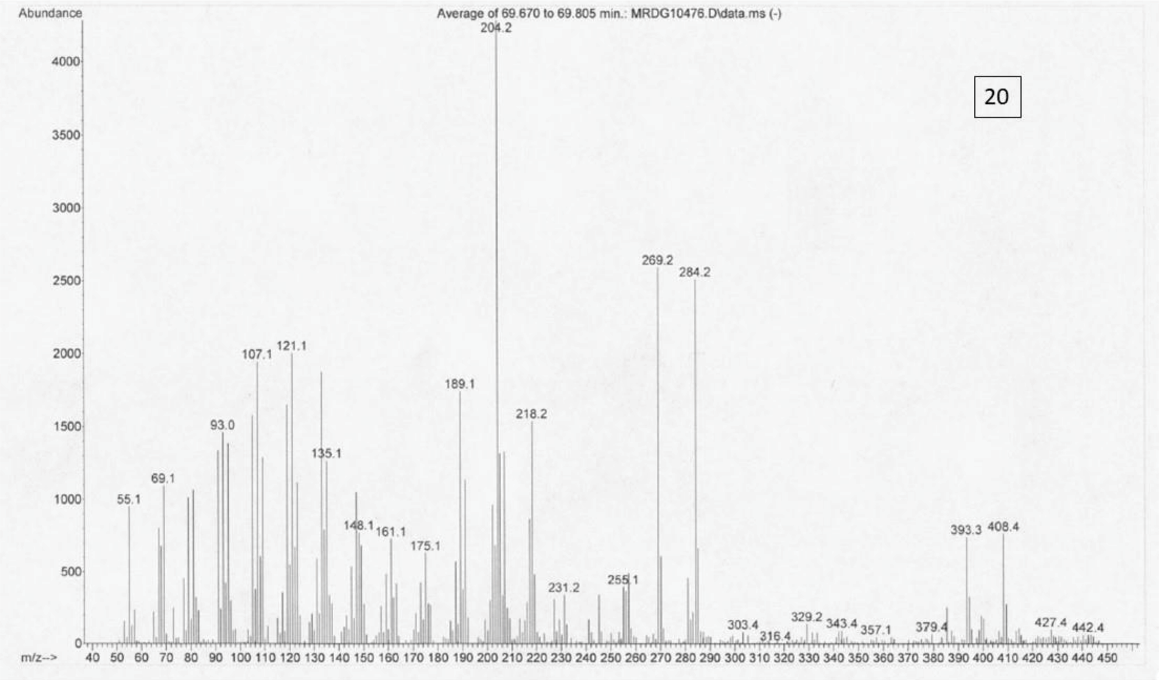

Average of 68.078 to 68.176 min.: MRDG10476.D\data.ms (-)
Abundance
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
191.2
231.2
147.1
161.1
95.1
79.1
133.1
55.1
109.1
368.3
177.1
353.4
205.2
218.2
273.3
245.2
260.1
286.1
303.3
316.4
329.2
386.4
401.3
415.4
428.6
444.6

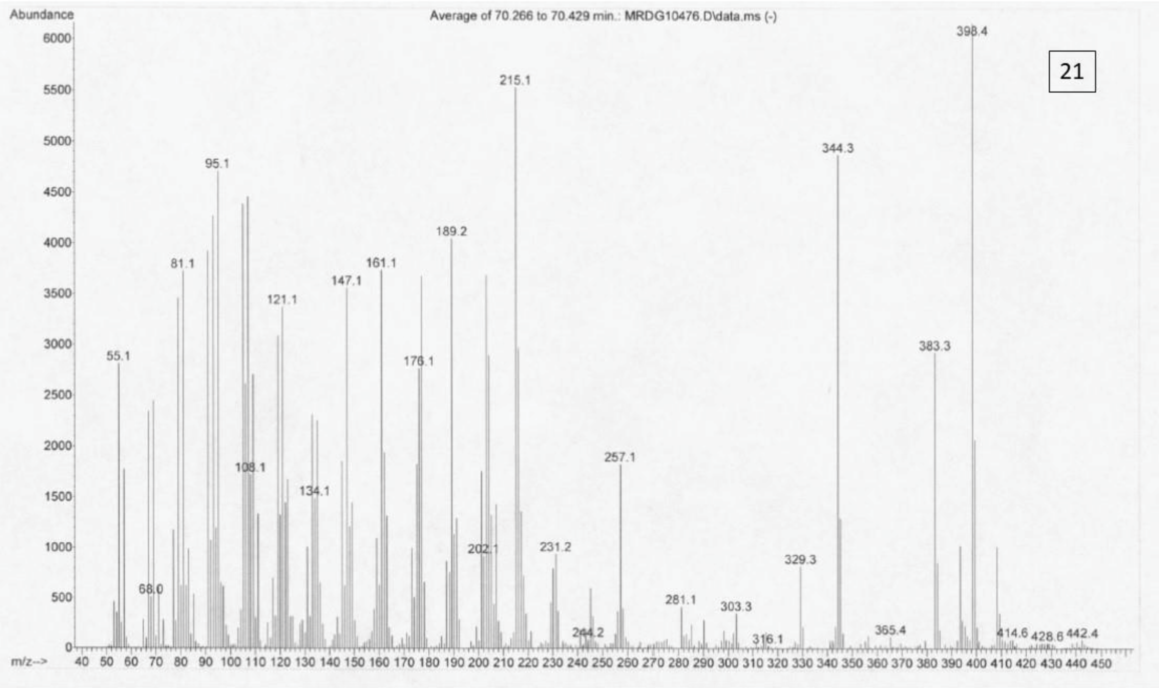
17

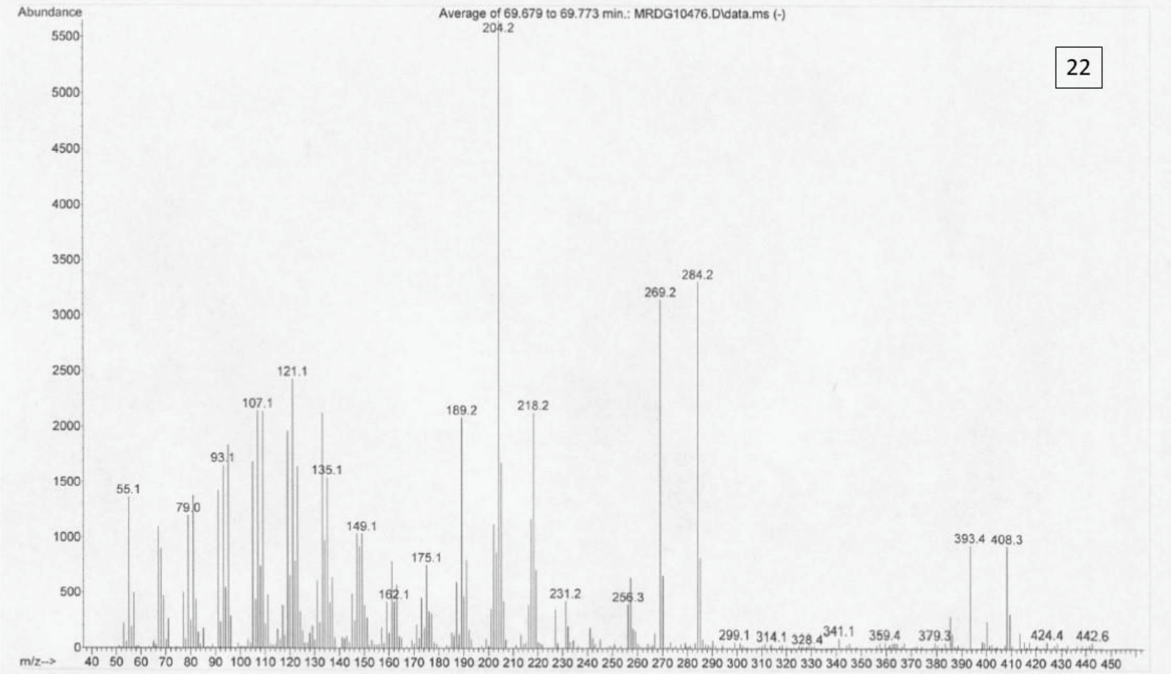

Average of 69.014 to 69.130 min.: MRDG10476.D\data.ms (-)
Abundance
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
149.1
191.1
95.1
81.1
55.1
123.1
109.1
163.2
177.2
255.1
365.3
396.3
68.0
136.1
205.2
218.2
242.2
269.1
284.1
298.2
311.3
324.1
341.0
381.3
414.4
428.4
442.6

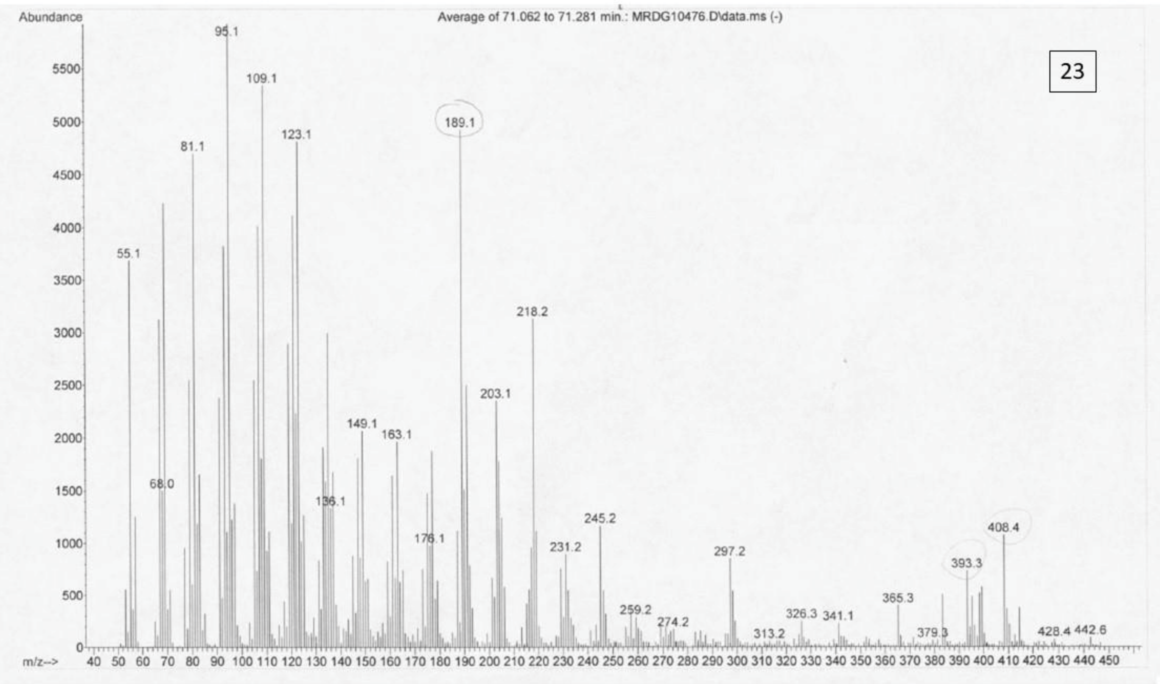
18


Abundance
Average of 69.135 to 69.205 min.: MRDG10476.D\data.ms (-)
19
4500
4000
3500
3000
2500
2000
1500
1000
500
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
95.1
109.1
69.1
55.1
123.1
137.1
205.2
191.2
273.2
385.4
163.1
218.2
82.1
233.2
150.1
177.2
301.2
400.4
247.2
371.3
260.1
287.2
314.4
327.1
344.3
357.3
415.2
428.4
446.4

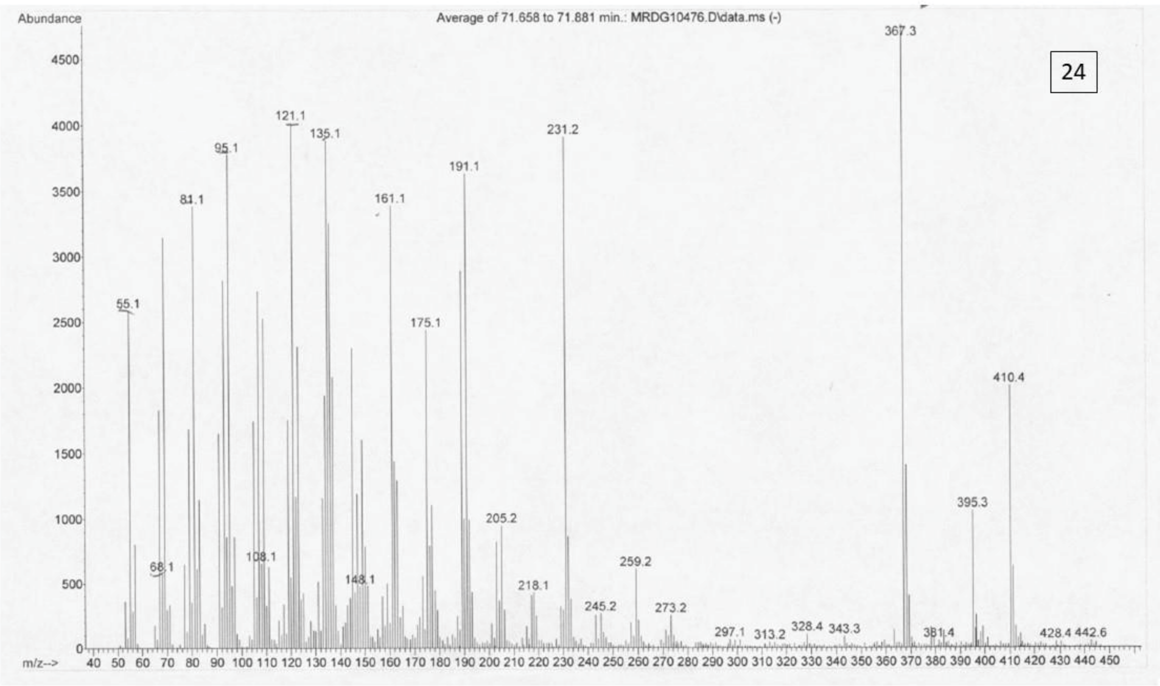

Abundance
Average of 69.670 to 69.805 min.: MRDG10476.D\data.ms (-)
20
4000
3500
3000
2500
2000
1500
1000
500
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
204.2
269.2
284.2
107.1
121.1
189.1
218.2
93.0
135.1
69.1
55.1
148.1
161.1
175.1
393.3
408.4
231.2
255.1
303.4
316.4
329.2
343.4
357.1
379.4
427.4
442.4


Abundance
Average of 70.266 to 70.429 min.: MRDG10476.D\data.ms (-)
21
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
398.4
215.1
344.3
95.1
189.2
81.1
161.1
147.1
121.1
383.3
55.1
176.1
257.1
108.1
134.1
202.1
231.2
329.3
68.0
281.1
303.3
244.2
316.1
365.4
414.6
428.6
442.4


Abundance
Average of 69.679 to 69.773 min.: MRDG10476.D\data.ms (-)
22
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450
204.2
284.2
269.2
121.1
107.1
189.2
218.2
93.1
135.1
55.1
79.0
149.1
175.1
393.4
408.3
162.1
231.2
256.3
299.1
314.1
328.4
341.1
359.4
379.3
424.4
442.6


Abundance
Average of 71.062 to 71.281 min.: MRDG10476.D\data.ms (-)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
95.1
109.1
189.1
81.1
123.1
55.1
218.2
203.1
149.1
163.1
68.0
136.1
245.2
176.1
231.2
297.2
408.4
393.3
365.3
259.2
326.3
341.1
274.2
313.2
379.3
428.4
442.6
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450

23


Abundance
Average of 71.658 to 71.881 min.: MRDG10476.D\data.ms (-)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
367.3
121.1
135.1
231.2
95.1
191.1
81.1
161.1
55.1
175.1
410.4
395.3
205.2
68.1
108.1
148.1
218.1
259.2
245.2
273.2
297.1
313.2
328.4
343.3
381.4
428.4
442.6
m/z-->
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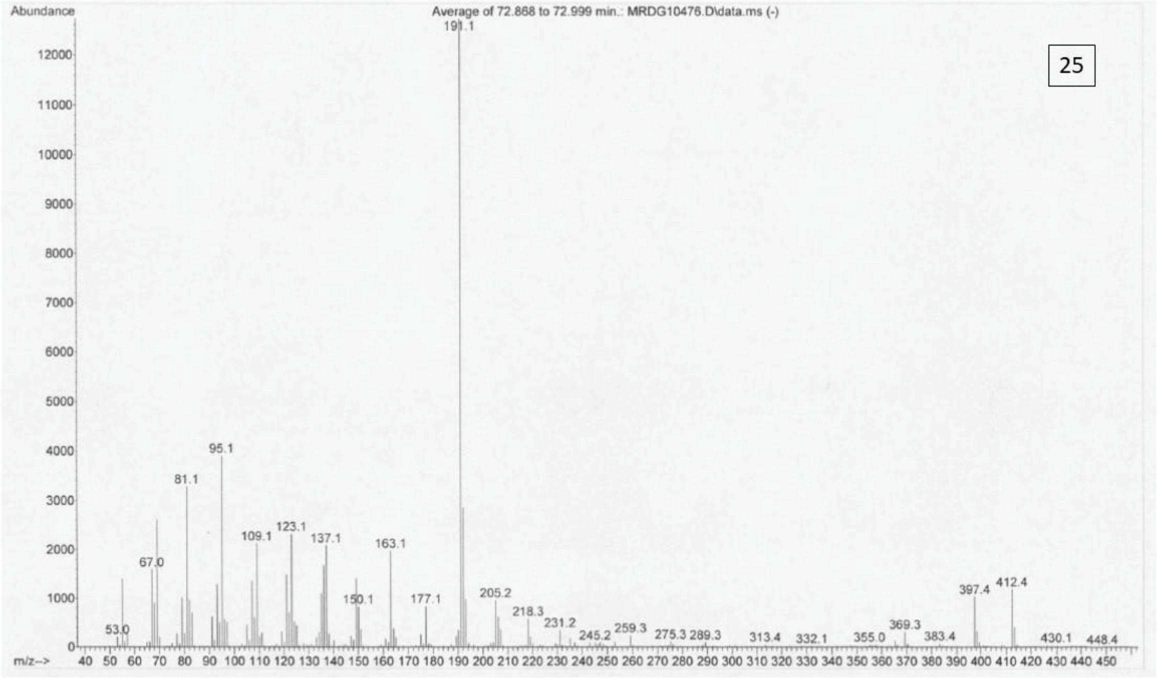
24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109.1
123.1
137.1
163.1
67.0
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177.1
205.2
218.3
231.2
245.2
259.3
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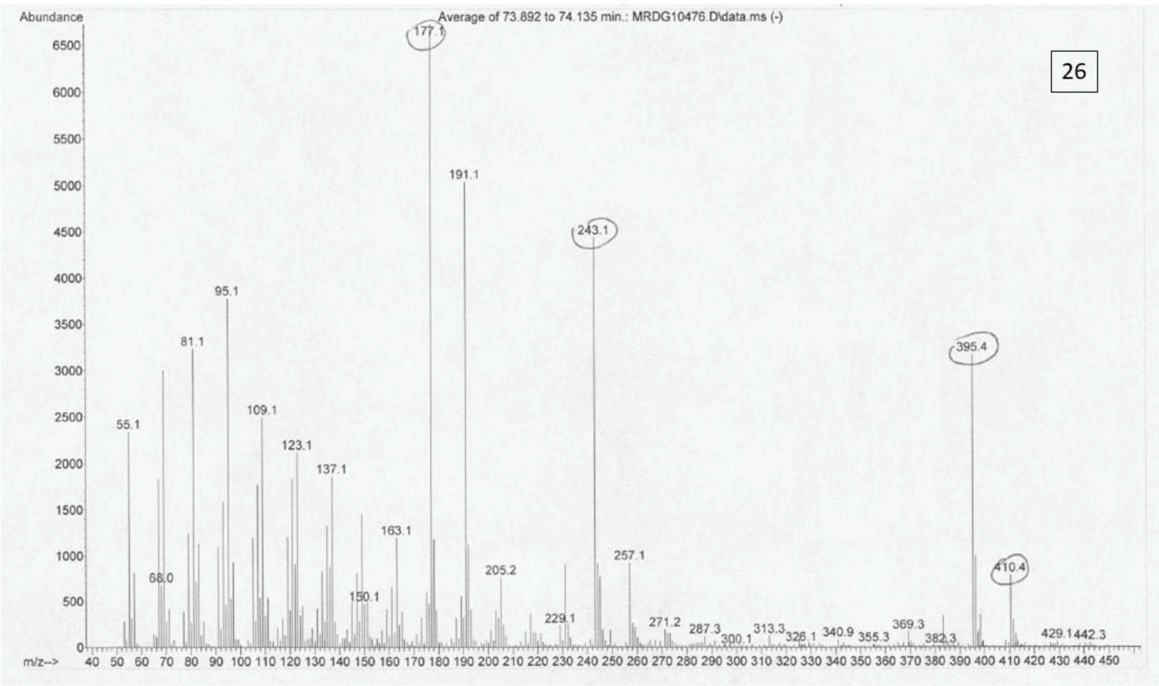
25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191.1
243.1
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81.1
395.4
55.1
109.1
123.1
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150.1
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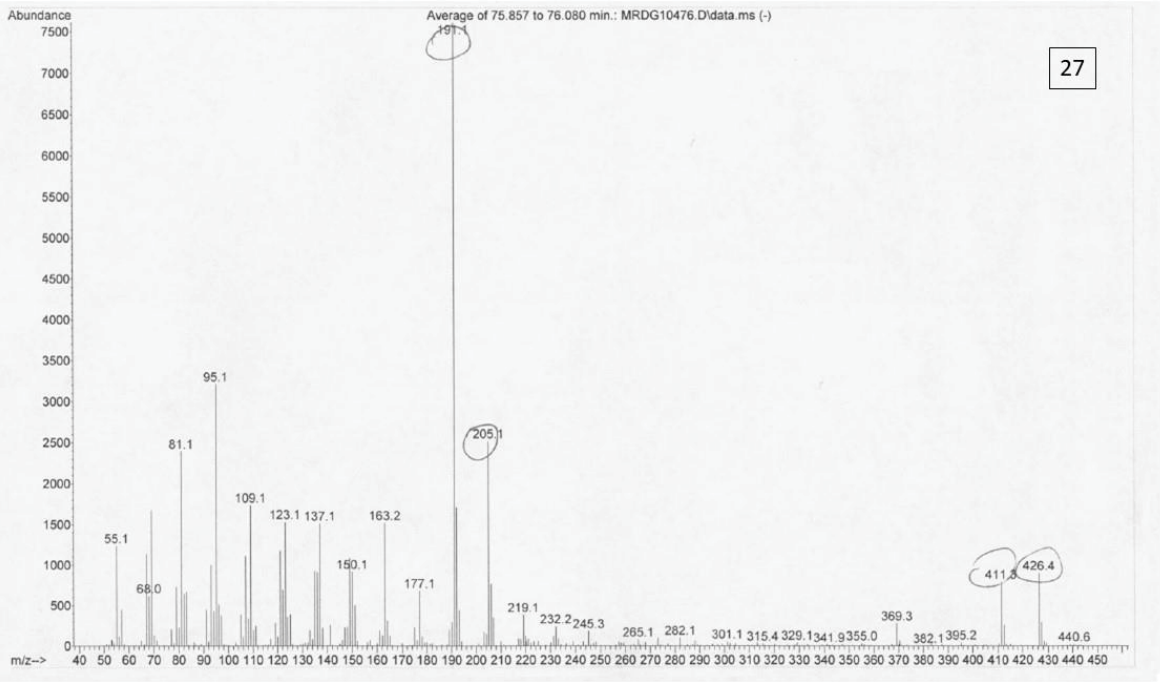
26

27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81.1
109.1
123.1
137.1
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150.1
68.0
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232.2
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265.1
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411.3
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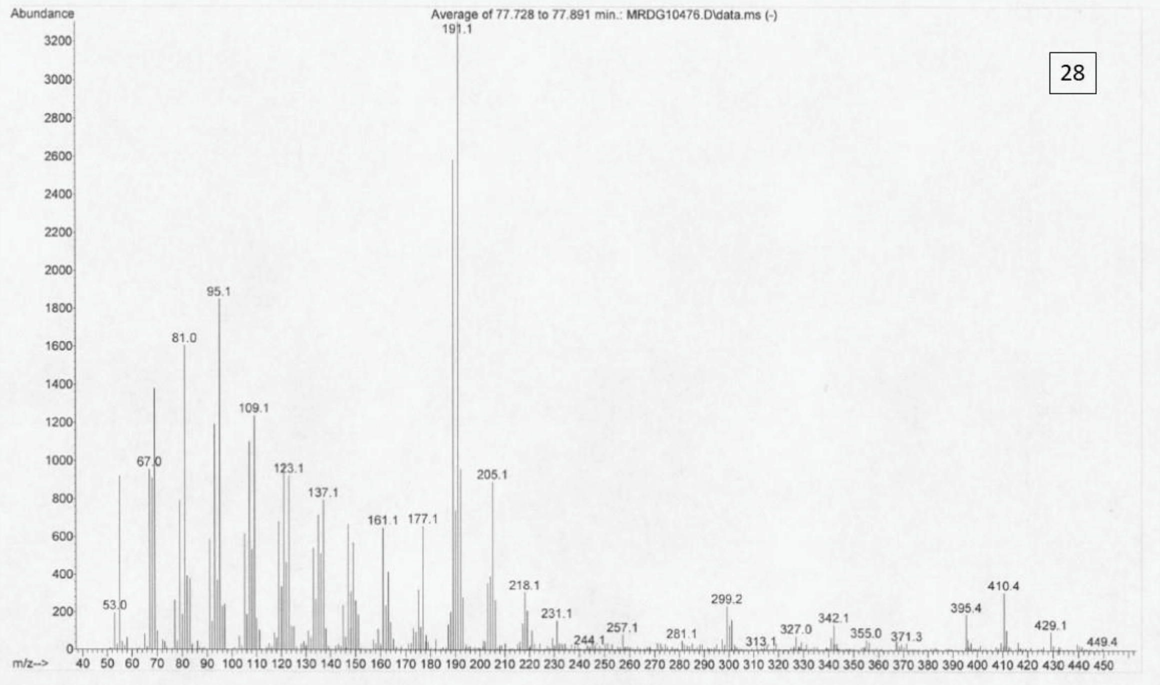
28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410.4
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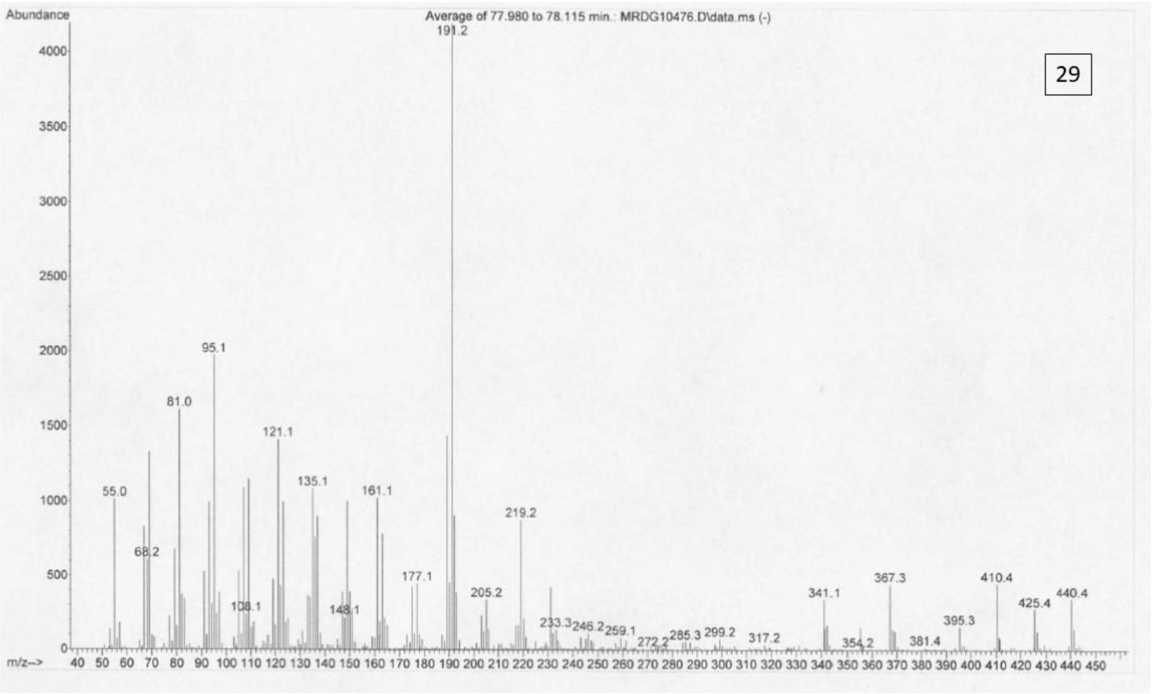
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81.0
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161.1
219.2
68.2
177.1
205.2
108.1
148.1
233.3
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259.1
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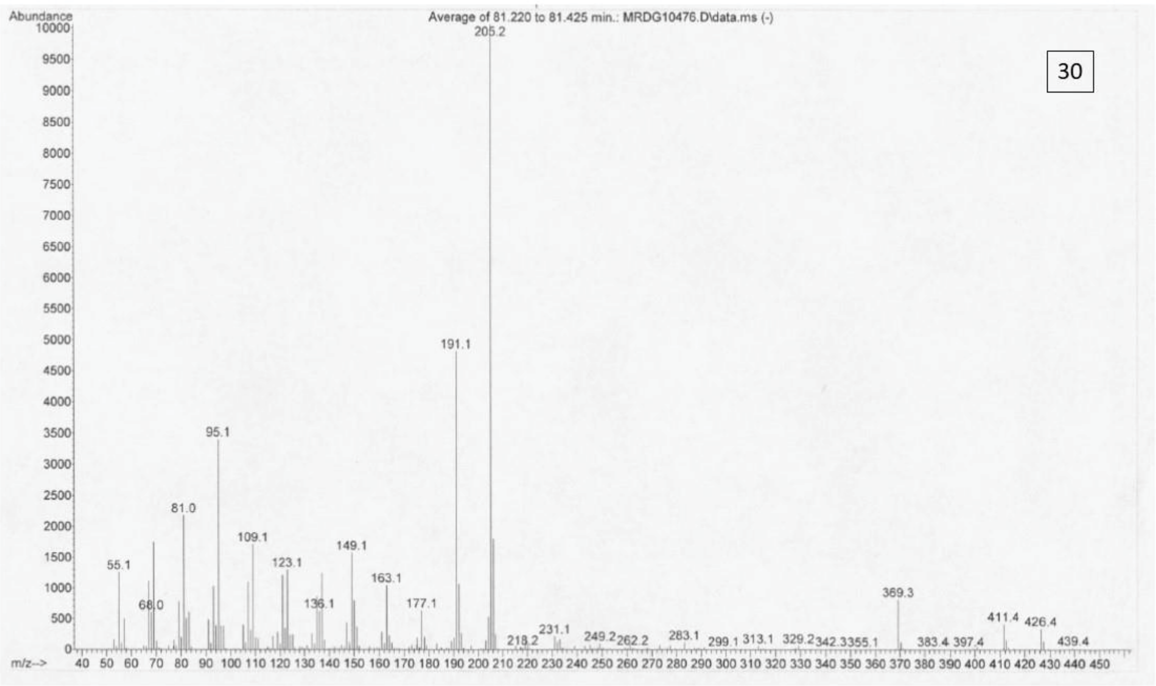
29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m/z-->
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205.2
191.1
95.1
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163.1
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249.2
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342.3
355.1
369.3
383.4
397.4
411.4
426.4
439.4

30

ANEXO 2 – RESULTADOS DAS ANALISES DO ITEM 3: TERPANOS E HOPANOS NOS SEDIMENTOS DE MANGUEZAL DO COMPLEXO ESTUARINO DA BAIA DE PARANAGUA

Compounds	Bio/Cat*	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Terpanes																					
C20 tricyclic terpane	Cat	7.7	14.2	16.6	3.7	13.4	3.8	4.9	5.7	5.3	20.0	1.3	1.1	1.3	2.4	3.9	2.0	1.3	3.4	1.2	1.2
C21 tricyclic terpane	Cat	14.1	15.1	27.0	6.5	35.1	11.5	17.7	15.8	10.8	15.8	1.1	1.9	0.9	3.1	4.5	2.3	3.7	11.1	2.9	2.9
Des-A-oleana-9,18-diene	Bio	6.8	10.4	48.4	27.1	7.1	0.8	6.6	6.8	1.5	19.0	1.3	0.5	6.5	11.5	3.5	0.2	1.7	27.0	2.2	2.2
Des-A-oleana-9,13(18)-diene	Bio	40.0	4.8	3.9	95.9	29.8	1.2	1.2	26.9	9.2	70.2	4.7	4.6	19.5	56.0	18.1	0.4	7.5	200.5	5.5	5.5
C22 tricyclic terpane	Cat	18.7	14.4	22.4	13.8	25.2	7.0	10.3	10.7	7.6	12.5	0.8	1.2	0.9	2.4	3.5	1.4	3.4	9.7	1.9	1.9
Des-A-lupana-5(10),22(29)-diene	Bio	2.7	8.3	7.2	6.0	6.6	0.2	2.6	4.9	1.4	7.0	0.5	0.3	1.4	5.4	2.2	0.2	1.4	20.2	1.2	1.2
Des-A-taraxera-5(10),14-diene	Bio	24.7	47.3	39.5	50.4	25.1	0.6	3.4	23.4	5.7	52.1	3.5	2.0	19.7	36.6	13.0	0.3	4.1	63.2	6.5	6.5
Des-A-oleana-5(10),13(18)-diene	Bio	8.2	12.5	9.8	11.9	8.1	2.4	1.4	4.7	2.2	14.6	1.0	0.9	5.5	10.4	6.6	<DL	<DL	26.8	<DL	<DL
10b(H)-Des-A-lupane	Bio	67.4	29.7	54.4	13.4	26.0	0.7	3.1	2.7	7.3	21.3	1.4	3.6	0.9	4.3	4.6	1.1	3.0	6.6	1.8	1.8
Des-A-26,27-bisnoroleana-5,7,9,11,13-pentaene	Bio	10.1	66.3	36.4	50.0	57.2	1.1	2.4	42.9	2.1	146.8	9.8	3.7	36.8	60.9	62.8	0.7	9.2	184.1	3.0	3.0
Des-A-26,27-bisnorursana-5,7,9,11,13-pentaene	Bio	10.2	39.4	31.6	20.5	35.6	2.6	13.1	15.4	7.0	36.2	2.4	2.4	5.1	22.9	11.7	1.1	10.2	60.6	2.4	2.4
C24 tetracyclic hopane	Cat	1.5	12.1	5.5	15.9	5.3	0.2	1.5	1.6	<DL	12.9	0.9	0.7	1.4	9.2	2.7	0.1	1.1	8.2	0.4	0.4
C25 tetracyclic hopane	Cat	5.2	4.5	8.0	1.5	9.0	2.2	3.9	3.4	3.9	4.2	0.3	0.4	<DL	0.9	1.0	0.5	1.1	12.5	0.5	0.5
Hopanes																					
Ts	Cat	10.8	6.6	9.8	1.9	11.0	0.8	4.7	2.9	6.8	13.0	0.9	0.6	0.4	3.5	2.8	0.5	0.7	5.1	0.5	0.5
1,2,3-Trisnortaraxera-5(10),14-diene	Bio	89.5	116.8	117.1	23.6	87.7	1.9	4.7	23.5	23.7	83.0	5.5	2.1	7.4	30.2	13.5	2.0	6.0	19.6	15.1	15.1
Tm	Cat	18.1	12.0	20.9	3.1	20.9	1.7	6.2	5.5	11.5	22.1	1.5	0.8	0.4	1.7	3.5	0.9	1.4	7.2	1.1	1.1
Monounsaturated triterpene (?)	Bio	48.7	46.4	65.7	8.9	48.6	1.8	2.6	14.5	17.3	47.7	3.2	3.2	3.0	15.9	16.5	0.0	2.3	12.0	5.8	5.8
17a(H), 21b(H)-30-Norhopane	Cat	72.0	43.3	73.0	15.2	89.8	3.8	25.1	4.0	47.5	79.5	5.3	3.2	1.3	16.0	11.0	1.4	4.8	2.2	5.5	5.5
Hop-17(21)-ene (diploptene)	Bio	45.9	7.7	19.5	8.3	18.4	0.6	2.3	5.7	5.3	12.3	0.8	0.3	1.4	8.0	2.0	0.3	2.1	5.5	1.6	1.6
Moretane C29?	Cat	21.8	9.6	21.5	3.5	20.4	0.6	2.6	5.8	10.2	23.5	1.6	0.9	1.1	3.2	3.5	0.4	0.8	5.4	1.8	1.8
17a(H), 21b(H)-Hopane	Cat	72.6	33.5	56.2	10.2	73.8	3.0	22.2	19.6	42.6	73.6	4.9	2.6	1.4	4.6	8.3	1.5	3.3	26.8	2.9	2.9
C29bb (or Moretane C30?)	Bio	50.6	21.8	40.2	7.9	39.9	1.4	4.3	11.8	17.3	41.6	2.8	1.6	2.1	7.5	7.2	0.9	2.3	2.6	0.3	0.3
C31 S extend hop	Cat	33.4	20.9	25.6	5.6	35.0	1.3	10.7	11.6	20.1	37.6	2.5	1.0	1.3	4.7	5.3	0.6	1.3	11.7	1.7	1.7
C31 R extend hop	Cat+Bio	67.1	25.8	47.6	8.4	52.2	1.8	10.0	18.5	31.1	65.6	4.4	2.1	1.4	5.7	9.6	1.5	3.4	16.6	4.3	4.3
C30 bb hopane (immature OM) (?)	Bio	16.3	2.0	9.6	1.7	14.9	0.5	4.1	3.7	7.3	15.7	1.0	0.3	<DL	0.9	1.7	0.5	2.9	4.9	0.4	0.4
C30 bb hopane (immature OM)	Bio	38.3	15.2	26.6	5.1	26.2	0.9	2.3	7.5	11.6	31.5	2.1	1.2	1.2	4.2	5.0	0.8	1.0	5.4	1.9	1.9
Oleanane	Bio	42.7	22.4	18.4	12.2	30.8	1.3	3.8	13.8	17.8	40.0	2.7	0.8	3.2	8.7	7.0	0.5	2.6	16.8	3.0	3.0
C32 S extend hop	Cat	19.8	12.4	12.5	3.8	19.3	0.6	5.8	6.1	12.2	20.6	1.4	0.7	0.8	2.1	3.3	0.4	0.9	7.7	1.0	1.0
C32 R extend hop	Cat	10.3	3.5	6.9	1.8	9.9	0.6	4.0	3.3	5.8	10.8	0.7	0.3	<DL	<DL	1.2	0.2	0.4	3.7	0.3	0.3
C31 methyl hopanoid (or C31 bb hopane)	Bio	34.2	12.3	2.6	4.7	21.2	0.7	1.2	5.3	9.3	28.3	1.9	1.1	<DL	<DL	2.8	0.4	0.5	4.3	1.4	1.4
C33 S extend hop	Cat	9.5	7.0	0.8	1.4	7.6	0.4	3.6	2.8	5.5	7.8	0.5	0.3	<DL	<DL	<DL	<DL	0.2	3.3	0.2	0.2
C33 R extend hop	Cat	6.2	2.5	3.0	1.0	4.2	0.1	2.0	1.6	2.9	4.5	0.3	0.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
∑Catagenic terpanes and hopanes**		321.80	211.85	309.72	88.88	380.10	37.45	125.23	100.46	192.64	358.38	23.89	15.88	11.30	53.83	54.58	12.03	24.49	118.19	22.02	22.02
∑Biogenic terpanes and hopanes**		536.11	463.43	530.92	347.52	483.22	18.90	59.11	213.43	145.98	667.04	44.47	28.59	113.67	283.45	178.28	9.48	56.90	660.02	52.25	52.25
Catagenic/Biogenic compounds		0.60	0.46	0.58	0.26	0.79	1.98	2.12	0.47	1.32	0.54	0.54	0.56	0.10	0.19	0.31	1.27	0.43	0.18	0.42	0.42

*** Catagenic or Biogenic** ****without C31 R extended hopane**

Compounds	Bio/Cat*	21	22	23	24	25	26	27	29	30	31	32	33	34	35	36
Terpanes																
C20 tricyclic terpane	Cat	2.7	2.4	9.5	3.1	2.4	0.4	2.4	6.2	9.4	12.5	4.5	5.5	2.6	0.9	3.4
C21 tricyclic terpane	Cat	3.9	8.0	10.0	5.3	9.4	15.2	4.7	12.8	10.1	6.3	6.2	3.7	1.5	1.7	5.2
Des-A-oleana-9,18-diene	Bio	2.1	2.4	10.1	5.5	5.7	1.4	18.2	10.1	2.8	3.1	1.4	2.0	2.8	0.6	2.1
Des-A-oleana-9,13(18)-diene	Bio	10.3	19.2	59.5	22.8	26.4	2.3	22.5	52.5	20.2	13.8	9.3	15.6	13.5	0.1	5.4
C22 tricyclic terpane	Cat	2.6	6.1	7.7	4.3	5.9	8.2	3.2	9.9	6.7	4.4	4.0	2.7	1.0	0.9	3.8
Des-A-lupana-5(10),22(29)-diene	Bio	1.4	0.0	5.8	2.4	2.7	0.7	2.3	6.1	3.1	1.7	1.5	2.2	0.9	0.2	1.2
Des-A-taraxera-5(10),14-diene	Bio	9.8	14.0	30.0	14.2	16.2	1.5	21.1	56.2	14.3	19.3	7.4	11.3	10.7	1.9	11.7
Des-A-oleana-5(10),13(18)-diene	Bio	<DL	5.4	8.7	4.0	4.1	<DL	2.4	<DL	4.7	5.0	2.1	3.7	2.9	0.5	<DL
10b(H)-Des-A-lupane	Bio	5.3	0.0	16.0	7.7	2.2	3.0	0.0	5.2	7.8	7.9	3.9	4.6	1.4	0.6	4.5
Des-A-26,27-bisnoroleana-5,7,9,11,13-pentaene	Bio	12.1	93.6	29.8	11.8	107.3	1.8	16.8	83.1	5.7	19.9	5.2	5.2	10.6	5.0	2.1
Des-A-26,27-bisnorursana-5,7,9,11,13-pentaene	Bio	4.5	14.7	16.2	7.5	12.1	9.9	5.9	22.4	8.4	7.4	4.4	3.0	3.2	1.2	3.7
C24 tetracyclic hopane	Cat	0.9	2.7	4.9	1.3	2.5	<DL	1.4	4.6	<DL	1.9	0.4	2.4	0.9	0.3	<DL
C25 tetracyclic hopane	Cat	1.1	2.3	2.4	1.2	1.6	2.2	1.3	3.1	2.5	1.8	1.4	0.9	0.5	0.3	1.6
Hopanes																
Ts	Cat	1.7	2.6	5.1	1.3	<DL	0.3	2.7	2.2	1.7	2.9	1.5	0.9	0.7	0.4	2.0
1,2,3-Trisnortaraxera-5(10),14-diene	Bio	25.7	8.9	63.7	13.9	9.4	1.0	18.6	33.6	45.6	46.9	14.9	24.0	9.6	3.0	27.0
Tm	Cat	3.7	4.3	9.0	2.2	1.8	0.4	3.9	3.8	6.4	6.0	3.0	2.8	1.7	0.7	4.5
Monounsaturated triterpene (?)	Bio	17.2	5.0	50.9	12.0	6.1	1.1	10.3	24.1	31.5	34.2	13.7	15.4	7.9	3.0	17.6
17a(H), 21b(H)-30-Norhopane	Cat	9.4	17.6	27.0	6.3	<DL	1.3	13.1	12.5	18.3	15.9	7.2	7.1	7.0	2.8	19.2
Hop-17(21)-ene (diploptene)	Bio	3.4	4.5	13.4	3.7	1.7	0.4	2.5	6.3	7.7	7.2	2.4	4.2	3.2	0.5	3.0
Moretane C29?	Cat	6.1	2.7	19.6	3.8	2.1	<DL	3.7	6.6	12.4	13.5	4.3	5.6	3.2	1.3	6.4
17a(H), 21b(H)-Hopane	Cat	7.9	12.7	23.0	5.0	4.2	<DL	10.6	7.5	17.0	14.3	5.2	5.1	7.0	2.5	16.0
C29bb (or Moretane C30?)	Bio	11.3	5.6	2.1	8.2	3.3	<DL	7.0	12.5	22.9	23.2	6.4	9.6	0.5	0.2	12.6
C31 S extend hop	Cat	4.8	6.3	15.6	1.8	2.9	<DL	6.6	3.2	10.6	11.8	2.8	5.0	4.5	1.6	11.7
C31 R extend hop	Cat+Bio	14.5	7.3	50.4	9.8	5.2	<DL	13.0	15.0	33.8	31.9	9.0	12.6	9.1	3.9	32.1
C30 bb hopane (immature OM) (?)	Bio	1.6	1.9	4.8	0.7	<DL	0.3	2.2	1.8	3.2	2.1	0.9	1.1	1.3	0.6	4.1
C30 bb hopane (immature OM)	Bio	7.6	3.0	29.2	5.8	2.5	0.4	5.2	9.0	15.7	15.7	4.2	6.9	5.3	2.3	12.6
Oleanane	Bio	7.2	12.8	24.9	7.4	2.3	0.7	7.2	9.7	17.3	15.5	2.0	5.1	11.5	5.5	25.5
C32 S extend hop	Cat	2.8	4.3	7.1	2.0	1.3	0.4	3.2	3.3	6.0	4.9	1.3	1.7	2.7	1.1	5.6
C32 R extend hop	Cat	1.0	1.7	3.3	0.7	<DL	<DL	1.7	1.2	2.3	1.9	0.6	0.6	1.4	0.4	3.4
C31 methyl hopanoid (or C31 bb hopane)	Bio	0.7	3.0	21.9	4.9	1.2	<DL	4.4	6.3	11.4	10.7	2.7	5.1	<DL	2.0	1.8
C33 S extend hop	Cat	0.2	1.7	5.5	1.3	<DL	<DL	1.7	1.2	2.3	1.0	0.7	0.7	<DL	0.5	0.5
C33 R extend hop	Cat	0.6	<DL	2.1	<DL	<DL	<DL	0.7	<DL	<DL	0.9	0.0	0.3	0.7	0.2	1.9
		21	**22**	**23**	**24**	**25**	**26**	**27**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**
∑Catagenic terpanes and hopanes**		49.21	75.47	151.82	39.63	34.11	28.57	61.02	78.18	105.64	100.04	42.99	44.81	35.22	15.82	85.21
∑Biogenic terpanes and hopanes**		120.16	194.11	387.03	132.66	203.17	24.58	146.67	339.09	222.25	233.43	82.61	118.91	85.03	27.16	134.84
Catagenic/Biogenic compounds		0.41	0.39	0.39	0.30	0.17	1.16	0.42	0.23	0.48	0.43	0.52	0.38	0.41	0.58	0.63

*** Catagenic or Biogenic** ****without C31 R extended hopane**

ANEXO 3 – RESULTADOS DAS ANALISES DO ITEM 4: HIDROCARBONETOS POLICICLICOS AROMATICOS NOS SEDIMENTOS DE MANGUEZAL DO COMPLEXO ESTUARINO DA BAIA DE PARANAGUA

Compostos	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**
HPAs (2-3 anéis)																																				
naftaleno	18.4	12.0	54.9	5.1	31.8	<DL	1.8	8.0	8.0	12.3	9.5	0.8	0.9	2.1	4.3	<DL	1.5	3.6	2.0	4.0	9.1	4.0	11.3	4.4	5.2	<DL	1.5	3.2	7.5	4.5	5.8	2.6	2.1	3.6	2.6	4.3
acenaftileno	<DL	<DL	8.4	<DL	2.7	<DL	<DL	<DL	<DL	4.9	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	2.0	2.1	2.6	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
acenafteno	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
fluoreno	1.3	1.2	1.6	0.6	1.7	<DL	<DL	0.6	0.7	1.9	1.1	<DL	<DL	<DL	0.5	<DL	<DL	0.5	<DL	<DL	1.2	0.8	1.3	<DL	<DL	<DL	<DL	0.6	<DL	0.6	0.5	<DL	<DL	<DL	<DL	<DL
fenantreno	14.2	21.3	13.7	5.1	24.6	1.2	2.3	4.4	6.6	8.4	12.8	0.6	0.8	1.3	5.8	0.5	1.0	2.4	2.7	1.9	18.7	4.1	5.2	2.9	3.0	4.8	1.5	4.1	5.6	5.3	5.1	1.8	1.3	2.4	<DL	3.9
antraceno	1.7	1.6	2.2	<DL	1.6	<DL	<DL	0.9	0.9	2.1	1.0	<DL	<DL	<DL	<DL	<DL	<DL	0.8	<DL	<DL	0.9	1.0	1.2	<DL	<DL	2.0	<DL	0.7	0.7	0.9	0.9	<DL	<DL	<DL	<DL	<DL
HPAs (4-6 anéis)																																				
fluoranteno	7.7	13.8	9.0	3.3	9.6	<DL	1.5	5.4	5.7	10.5	4.3	<DL	<DL	<DL	1.8	<DL	<DL	2.6	<DL	1.4	3.8	15.3	4.9	<DL	<DL	46.2	<DL	3.9	2.8	3.2	2.9	<DL	<DL	<DL	<DL	3.3
pireno	9.8	13.9	10.3	3.7	12.2	3.7	3.6	7.8	5.6	9.8	4.8	<DL	<DL	<DL	<DL	<DL	<DL	3.4	<DL	<DL	5.1	13.6	5.6	2.1	<DL	34.6	<DL	5.3	4.3	4.2	3.1	<DL	<DL	<DL	<DL	3.2
benzo(a)antraceno	5.8	8.6	1.6	0.6	3.8	<DL	<DL	<DL	2.6	4.2	0.8	<DL	<DL	<DL	0.6	<DL	1.4	2.4	<DL	0.5	1.4	8.9	3.0	<DL	<DL	21.0	1.5	1.9	1.3	<DL	<DL	<DL	1.3	<DL	<DL	0.6
criseno	3.4	5.2	2.7	0.7	4.7	<DL	0.7	0.9	2.1	3.0	1.7	<DL	<DL	<DL	0.6	<DL	0.6	1.4	<DL	0.7	1.5	8.0	1.9	0.5	<DL	18.3	1.2	1.1	3.3	1.3	1.1	<DL	<DL	<DL	<DL	1.2
benzo(b)fluoranteno	8.0	13.0	7.4	1.8	8.1	<DL	<DL	2.7	9.2	9.3	4.4	<DL	<DL	<DL	2.0	<DL	1.5	3.2	0.6	2.1	4.5	13.2	6.7	1.3	<DL	24.4	1.8	3.7	2.5	4.7	4.2	1.1	1.5	1.1	<DL	3.1
benzo(j+k)fluoranteno	3.0	4.9	3.5	<DL	3.3	<DL	<DL	<DL	2.1	3.0	1.7	<DL	<DL	<DL	<DL	<DL	<DL	1.6	<DL	<DL	1.6	8.1	3.0	<DL	<DL	16.7	<DL	1.5	0.0	1.6	1.6	<DL	<DL	<DL	<DL	1.4
benzo(e)pireno	10.0	13.6	9.3	2.3	9.4	<DL	1.0	2.6	10.7	11.3	5.1	<DL	<DL	1.0	2.4	<DL	2.1	5.1	<DL	1.8	4.3	18.3	6.0	1.3	0.8	34.1	3.0	3.9	2.6	4.6	4.5	1.2	1.4	1.1	0.9	3.5
benzo(a)pireno	5.6	11.8	5.8	1.6	6.6	<DL	<DL	1.8	7.9	7.3	3.5	<DL	<DL	<DL	1.7	<DL	1.3	3.5	<DL	1.1	2.9	21.0	4.2	<DL	<DL	39.1	1.7	2.3	1.7	2.8	2.8	<DL	<DL	<DL	<DL	2.5
indeno [1,2,3-c,d]pireno	8.4	7.0	6.9	0.9	6.5	<DL	<DL	1.6	7.0	7.8	3.4	<DL	<DL	<DL	1.5	<DL	<DL	2.3	<DL	1.5	3.5	8.5	5.8	1.1	0.6	11.6	1.0	3.5	2.0	3.4	3.4	0.9	1.1	0.8	<DL	2.4
dibenzo(a,h)antraceno	1.0	2.1	1.8	<DL	0.8	<DL	<DL	<DL	1.5	1.9	0.9	<DL	<DL	<DL	0.0	<DL	<DL	1.0	<DL	<DL	<DL	3.8	0.8	<DL	<DL	5.1	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
benzo(g,h,i)perileno	9.7	6.8	6.9	1.2	6.6	<DL	<DL	1.8	7.4	7.8	3.7	<DL	<DL	0.5	1.6	<DL	0.7	3.2	0.5	1.6	3.6	7.0	5.7	1.3	0.6	10.3	1.1	3.5	2.0	3.4	3.4	0.9	1.1	0.7	<DL	2.5
Alquil HPAs																																				
C_1-naftaleno	8.1	4.1	7.7	0.9	5.1	<DL	<DL	1.8	3.6	6.1	2.7	0.6	<DL	0.6	1.6	0.5	<DL	1.8	<DL	1.0	2.8	1.6	4.1	0.7	0.7	<DL	0.6	1.7	1.7	1.9	1.8	0.7	0.6	0.8	0.8	1.6
C_2-naftaleno	13.9	7.2	10.5	2.3	10.0	1.1	1.0	2.5	5.4	11.2	5.5	1.3	0.9	1.7	2.6	1.3	1.3	3.9	<DL	1.8	6.2	1.8	10.9	0.8	0.9	<DL	1.2	3.6	3.2	4.3	5.3	1.6	2.2	1.7	1.7	2.7
C_3-naftaleno	5.4	2.6	3.7	1.2	4.2	1.1	0.8	1.4	2.0	3.2	1.8	0.5	<DL	0.6	1.0	<DL	<DL	1.5	0.6	1.0	2.0	1.2	2.8	0.9	0.8	0.8	0.6	1.5	1.1	1.2	1.3	0.6	0.6	<DL	0.6	0.9
C_1-fenantreno	10.9	13.0	9.6	4.0	13.7	3.5	3.0	6.0	3.1	5.5	9.0	0.9	0.7	1.2	2.0	0.5	0.9	3.0	1.0	1.4	6.1	4.3	4.8	2.4	2.0	4.3	1.3	4.5	4.5	3.3	3.4	1.4	1.3	1.4	1.8	2.1
Naturais																																				
perileno	214.5	53.2	101.9	11.2	68.2	<DL	2.4	9.9	30.8	77.4	29.8	1.4	1.3	6.3	11.4	1.7	3.8	12.9	5.0	19.9	66.2	9.0	84.1	15.6	5.5	7.6	8.9	40.7	16.4	48.5	30.7	10.0	11.4	4.8	2.2	18.0

Compostos	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**
∑HPAs*	146.21	163.52	177.43	35.25	166.70	10.53	15.77	50.18	91.99	131.53	77.47	4.62	3.38	9.10	29.94	2.84	12.06	46.97	7.34	21.68	80.91	146.52	91.60	19.67	14.57	273.41	18.17	50.45	46.76	51.07	51.06	12.89	14.47	13.55	8.33	39.15
∑HPAs 16EPA	97.90	123.05	136.71	24.57	124.41	4.94	9.95	35.86	67.14	94.25	53.43	1.33	1.73	3.95	20.33	0.50	7.80	31.76	5.72	14.79	59.56	119.35	62.98	13.58	9.42	234.26	11.47	35.25	33.68	35.75	34.84	7.36	8.42	8.57	2.63	28.37
Alquil HPAs	38.31	26.89	31.45	8.40	32.93	5.59	4.86	11.68	14.11	25.95	18.97	3.29	1.65	4.13	7.21	2.34	2.12	10.11	1.62	5.14	17.06	8.91	22.67	4.77	4.37	5.08	3.75	11.29	10.47	10.77	11.72	4.33	4.70	3.85	4.85	7.29
HPAs (2-3 anéis)**	35.65	35.94	80.83	10.71	62.36	1.23	4.10	13.92	16.17	29.60	24.39	1.33	1.73	3.41	10.62	0.50	2.44	7.29	4.61	5.85	31.78	12.03	21.49	7.29	8.25	6.82	3.06	8.53	13.78	11.17	12.36	4.37	3.39	5.98	2.63	8.24
HPAs (4-6 anéis)*	72.25	100.69	65.15	16.14	71.41	3.71	6.81	24.58	61.71	75.98	34.11	<DL	<DL	1.56	12.11	<DL	7.50	29.57	1.11	10.69	32.07	125.58	47.44	7.61	1.95	261.51	11.36	30.63	22.51	29.13	26.98	4.19	6.38	3.72	0.85	23.62
%per/∑(HPAs 5 anéis)	86	48	77	62	66	nc^{a}	58	55	47	67	63	100	100	86	61	100	36	43	89	76	80	10	77	83	88	5	49	74	59	76	68	81	73	68	72	60
Σ(2-3)/Σ(4-6)	0.49	0.36	1.24	0.66	0.87	0.33	0.60	0.57	0.26	0.39	0.72	nc^{c}	nc^{c}	2.19	0.88	nc^{c}	0.33	0.25	4.15	0.55	0.99	0.10	0.45	0.96	4.23	0.03	0.27	0.28	0.61	0.38	0.46	1.04	0.53	1.61	3.09	0.35
Ant/ 178	0.11	0.07	0.14	nc^{2}	0.06	nc^{2}	nc^{2}	0.16	0.12	0.20	0.07	nc^{2}	nc^{2}	nc^{2}	nc^{2}	nc^{2}	nc^{2}	0.24	nc^{2}	nc^{2}	nc^{2}	0.20	0.18	nc^{2}	nc^{2}	0.30	nc^{2}	0.14	0.11	0.14	0.15	nc^{2}	nc^{2}	nc^{2}	nc^{1,2}	nc^{2}
Fl/ Fl + Py	0.44	0.50	0.47	0.47	0.44	nc^{3}	0.29	0.41	0.51	0.52	0.47	nc^{3,4}	nc^{3,4}	nc^{3,4}	nc^{4}	nc^{3,4}	nc^{3,4}	0.44	nc^{3,4}	nc^{4}	0.43	0.53	0.47	nc^{3}	nc^{3,4}	0.57	nc^{3,4}	0.42	0.40	0.44	0.48	nc^{3,4}	nc^{3,4}	nc^{3,4}	nc^{3,4}	0.50
BzA/ 228	0.63	0.62	0.37	0.46	0.45	nc^{5,6}	nc^{5}	nc^{5}	0.54	0.58	0.33	nc^{5,6}	nc^{5,6}	nc^{5,6}	0.48	nc^{5,6}	0.70	0.63	nc^{5,6}	0.45	0.48	0.53	0.61	nc^{5,6}	nc^{5,6}	0.53	0.56	0.63	0.28	nc^{5,6}	nc^{5,6}	nc^{5,6}	1.00	nc^{5,6}	nc^{5,6}	0.33
In / In + Bghi	0.46	0.51	0.50	0.45	0.50	nc^{7,8}	nc^{7,8}	0.47	0.49	0.50	0.48	nc^{7,8}	nc^{7,8}	nc^{8}	0.49	nc^{7,8}	nc^{8}	0.41	nc^{8}	0.49	0.49	0.55	0.51	0.46	0.47	0.53	0.48	0.50	0.49	0.50	0.50	0.49	0.50	0.50	nc^{7,8}	0.48
C_o-F/ Σ(C_o+C_1)-F	0.57	0.62	0.59	0.56	0.64	0.26	0.43	0.42	0.68	0.61	0.59	0.39	0.53	0.53	0.74	0.49	0.54	0.45	0.72	0.57	0.75	0.49	0.52	0.55	0.60	0.53	0.54	0.48	0.56	0.61	0.60	0.55	0.50	0.62	nc^{1}	0.65

*** = sem os naturais**
**** = sem os alquilados**
178 = fenantreno + antraceno
Fl + Py = fluoranteno + pireno

228 = benzo(a)antraceno + criseno
In + Bghi = indeno(1,2,3-c,d)pireno + benzo(g,h,i)perileno
(C_o+C_1)-F = fenantreno + C_1-fenantreno

nc^{a} : perileno < LDM
nc^{b} : HPAs (2-3 anéis) < LDM
nc^{c} : HPAs (4-6 anéis) < LDM

nc^{1} : fenantreno < LDM
nc^{2} : antraceno < LDM
nc^{3} : fluoranteno < LDM

nc^{4} : pireno < LDM
nc^{5} : benzo(a)antraceno < LDM
nc^{6} : criseno < LDM

nc^{7} : indeno < LDM
nc^{8} : benzo(ghi)perileno < LDM
nc^{9} : C_1-fenantreno < LDM

ANEXO 4 – LOCAIS DE AMOSTRAGEM DOS SEDIMENTOS DE MANGUEZAL DO COMPLEXO ESTUARINO DA BAIA DE PARANAGUA

Data	Pontos	Referência	Lat Long	Temp. (°C)	pH	Eh (mV)	% finos
11/12/2017	1	Rio Cachoeira	25˚ 24'55.8"S - 48˚ 43' 16.0"O	27,6	5,80	119	96
11/12/2017	2	Ilha das Rosas	25˚ 25'19.3"S - 48˚ 42' 05.8" O	32,1	6,64	-24	86
11/12/2017	3	Rio Faisquera	25˚ 25'52,8" S - 48˚ 39' 41,5"O	28,9	5,50	145	94
11/12/2017	4	Rio Nhudiaquara	25˚ 30'02,4"S - 48˚ 40' 24,9"O	28,3	6,15	37	15
11/12/2017	5	Ilha do Teixeira	25˚ 30'01,4"S - 48˚ 38' 44,6" O	27,3	6,36	35	92
11/12/2017	6	Ilha do Curral	25˚ 30'39,7"S - 48˚ 37' 14,3"O	24,4	7,13	52	2
11/12/2017	7	Porto de Paranaguá	25˚ 30'35,8"S - 48˚ 32' 51,5"O	26,6	7,33	141	2
11/12/2017	8	Ilha da Cotinga	25˚ 31'36,7" S - 48˚ 28' 08,3"O	26,8	6,45	-242	31
12/12/2017	9	Amparo (Rio das Ostras)	25˚ 28'29,4" S - 48˚ 30' 12,3"O	21,6	6,67	73	26
12/12/2017	10	Amparo (Rio Riozinho)	25˚ 27'25,1" S - 48˚ 30' 38,0"O	22,3	6,26	52	87
12/12/2017	11	Eufrazina	25˚ 27'21,6" S - 48˚ 35' 19,3"O	22,3	6,37	-192	37
12/12/2017	12	Saco do Tambarutaca	25˚ 26'57,8" S - 48˚ 27' 20,2"O	23,7	6,47	94	3
12/12/2017	13	Rio Retiro	25˚ 23'28,6" S - 48˚ 26' 07,1"O	23,7	6,32	-85	5
12/12/2017	14	Ilha Almeida	25˚ 19'17,5" S - 48˚ 25' 56,3"O	23,2	6,40	38	17
12/12/2017	15	Ilha Rasa	25˚ 21'45,2" S - 48˚ 25' 25,6"O	24,7	6,22	75	29
12/12/2017	16	Ponta do Hospital 1	25˚ 29'35,7" S - 48˚ 19' 47,5"O	29,3	6,92	144	1
12/12/2017	17	Ponta do Hospital 2	25˚ 29'33,6" S - 48˚ 21' 24,0"O	28,7	6,98	-296	2
12/12/2017	18	Ponta do Hospital 3	25˚ 29'40,0" S - 48˚ 22' 10,5"O	27,2	6,43	42	21
13/12/2017	19	Medeiros	25˚ 22'21,5" S - 48˚ 26' 50,4"O	27,1	6,06	100	6
13/12/2017	20	Itaqui	25˚ 20'44,6" S - 48˚ 27' 51,9"O	28,7	5,70	78	30
13/12/2017	21	Benito	25˚ 17'23.4"S - 48˚ 23' 48.0"O	25,8	5,81	124	49
13/12/2017	22	Gamela	25˚ 20'13.3"S - 48˚ 23' 37.2"O	29,1	6,25	-178	13
13/12/2017	23	Guaraquecaba (baía)	25˚ 16'09.9"S - 48˚ 19' 45.2"O	24,0	5,78	140	85
13/12/2017	24	Guaraqueçaba (cidade)	25˚ 18'49.8"S - 48˚ 19' 46.5"O	24,3	5,89	58	24
13/12/2017	25	Ilha das peças	25˚ 27'09.3"S - 48˚ 19' 48.3"O	24,3	6,05	148	8
13/12/2017	26	Encantadas	25˚ 33'34.0"S - 48˚ 18' 55.0"O	24,2	6,24	194	1
14/12/2017	27	Vila Superagui	25˚ 26'54.4"S - 48˚ 15' 44.1"O	26,5	6,30	66	13
14/12/2017	28	Rio das Pacas	25˚ 24'13.0"S - 48˚ 14' 07,7"O	26,7	6,46	-120	61
14/12/2017	29	Ilha Pinheiros	25˚ 21'14.5"S - 48˚ 14' 34.0"O	29,8	5,92	39	26
14/12/2017	30	Vila Sebuí (Canal do Varadouro)	25˚ 19'04.0"S - 48˚ 12' 12.1"O	26,3	6,32	110	61
14/12/2017	31	Barra do Poruquara	25˚ 19'30.5"S - 48˚ 15' 41.4"O	31,1	5,66	-127	73
14/12/2017	32	Vila Tibicanga	25˚ 20'30.4"S - 48˚ 16' 23.4"O	29,4	6,29	85	13
14/12/2017	33	Poço da Pescada	25˚ 21'10.5"S - 48˚ 17' 49.3"O	30,1	5,84	116	35
14/12/2017	34	Ilha em frente ao Guapicu	25˚ 22'07,8"S - 48˚ 19' 02.2"O	33,8	6,05	56	12
14/12/2017	35	Ao lado do Guapicu	25˚ 22'36,1"S - 48˚ 19' 09.9"O	28,1	6,80	150	3
14/12/2017	36	Rio Guaraguaçú	25˚ 32'46,8"S - 48˚ 27' 48.2"O	29,5	6,22	8	46