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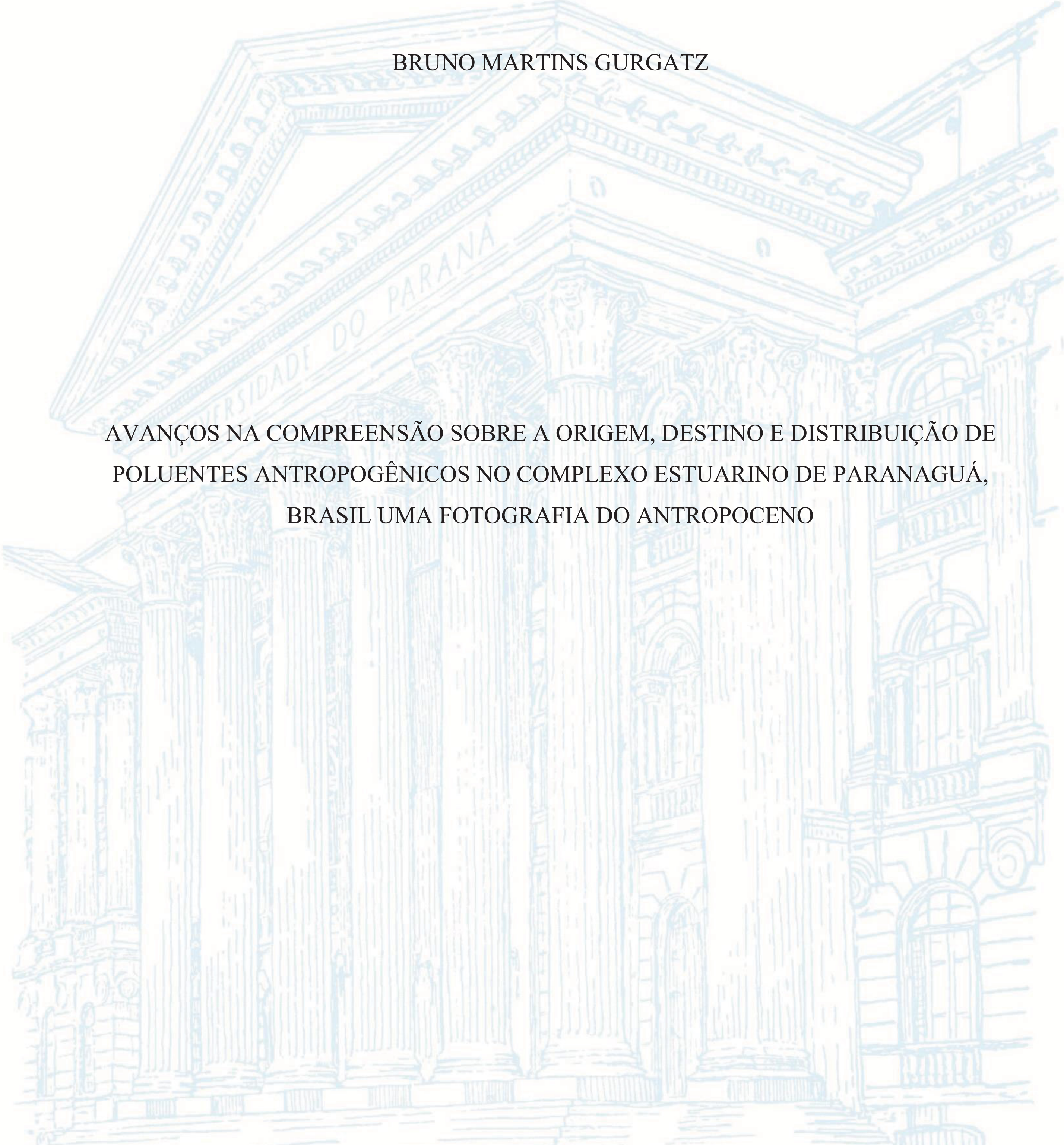

BRUNO MARTINS GURGATZ

AVANÇOS NA COMPREENSÃO SOBRE A ORIGEM, DESTINO E DISTRIBUIÇÃO DE POLUENTES ANTROPOGÊNICOS NO COMPLEXO ESTUARINO DE PARANAGUÁ, BRASIL UMA FOTOGRAFIA DO ANTROPOCENO

PONTAL DO PARANÁ
2023

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

Orientador: Prof. Dr. César de Castro Martins

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Os membros da Banca Examinadora designada pelo Colegiado do Programa de Pós-Graduação SISTEMAS COSTEIROS E OCEÂNICOS da Universidade Federal do Paraná foram convocados para realizar a arguição da tese de Doutorado de **BRUNO MARTINS GURGATZ** intitulada: **AVANÇOS NA COMPREENSÃO SOBRE A ORIGEM, DESTINO E DISTRIBUIÇÃO DE POLUENTES ANTROPOGÊNICOS NO COMPLEXO ESTUARINO DE PARANAGUÁ, BRASIL UMA FOTOGRAFIA DO ANTROPOCENO.**, sob orientação do Prof. Dr. CÉSAR DE CASTRO MARTINS, que após terem inquirido o aluno e realizada a avaliação do trabalho, são de parecer pela sua APROVAÇÃO no rito de defesa.

A outorga do título de doutor está sujeita à homologação pelo colegiado, ao atendimento de todas as indicações e correções solicitadas pela banca e ao pleno atendimento das demandas regimentais do Programa de Pós-Graduação.

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Aos trabalhadores do mundo.

Uni-vos.

AGRADECIMENTOS

Quando pequeno, lembro de meus pais me dizendo que meu único trabalho era estudar. Eu levei isso um pouco a sério demais.

Em 2023, completo 15 anos de UFPR, orgulhosamente cursados integralmente em setores no litoral do Paraná, criados ou que receberam aportes estruturais significativos durante o governo do Partido dos Trabalhadores, do Presidente Lula e da Presidenta Dilma. É impossível não reconhecer a importância da luta dos trabalhadores para o acesso universal à educação pública popular de qualidade. Isso mostra como é possível fazer ciência de ponta e trazer desenvolvimento real (não meramente econômico), onde quer que haja vontade política e um povo soberano.

Iniciei no extinto e controverso Curso Técnico em Orientação Comunitária, que me proveu uma ampla e profunda base de consciência de classe e crítica social. Agradeço a todos os professores e amigos desta época, que proveram desde cedo todo aporte necessário para uma formação decolonial, popular e revolucionária.

Na graduação, cursei bacharelado em Gestão Ambiental, guiado por um medo da época de criança em relação ao "aquecimento global". Mal sabia eu que isso levaria à uma completa mudança em relação à minha compreensão da problemática ambiental. Agradeço assim a todos os companheiros ambientalistas, professores, pesquisadores e amigos, os quais hoje encontro por todo o país, trabalhando de maneira incansável e crítica para a preservação da biodiversidade no planeta terra.

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Por fim, agradeço a você que está lendo.

Muito obrigado.

O nosso futuro será lindo como um arco-íris
Que se forma na poça de uma água suja de óleo

Plástico - Novíssimo Edgar

RESUMO

Marcadores orgânicos geoquímicos em sedimentos constituem uma ferramenta para se compreender a acumulação de substâncias no ambiente ao longo do tempo. Elas podem indicar as atividades antrópicas em uma região, pois estão associados a fontes de poluição previamente estudadas e caracterizadas. Considerando que a análise de um testemunho sedimentar pode prover um “filme” da história ambiental e desenvolvimento industrial de uma região, a análise dos sedimentos superficiais pode prover uma “fotografia” do período geológico atual. Este trabalho avaliou o estado de conservação recente do Complexo Estuarino de Paranaguá (CEP) pela perspectiva da Química Ambiental, caracterizando as concentrações, a distribuição espacial e as fontes de emissão de diferentes contaminantes. Para tal, foram desenvolvidas três diferentes investigações. 1 – Uma avaliação das concentrações e fontes de hidrocarbonetos policíclicos aromáticos (HPAs) nos sedimentos superficiais no CEP; 2 – Uma avaliação das concentrações de alquilbenzeno lineares (LABs) nos sedimentos superficiais do CEP, como forma de traçar a contaminação por efluentes (esgoto) no estuário; e 3 – o monitoramento de um ano das concentrações de $PM_{2.5}$ na atmosfera do município de Paranaguá. Sedimentos finos e matéria orgânica foram os principais fatores que controlaram as concentrações de HPAs no CEP. Porém as contribuições de fontes antropogênicas também foram identificadas. A queima de biomassa e de combustíveis fósseis predominaram. Há a contribuição de uma bacia hidrográfica adjacente, resultante da construção de interconexões entre grandes rios e de anos de desmatamento intensivo na Mata Atlântica local. A fonte primária de esgoto no CEP foram os rios do entorno do município de Paranaguá, que transportam efluentes das estações de tratamento da cidade ou drenam o esgoto direto lançado nas fossas na região de Valadares, sem tratamento na época do estudo. Quanto ao $PM_{2.5}$ em Paranaguá, as concentrações encontradas estão próximas aos limites médios sugeridos pela Organização Mundial da Saúde, com casos de altas concentrações diárias. A atividade rodoviária e a estrutura de abastecimento de navios foram identificadas como principais fontes. As informações apresentadas fundamentam um alerta: regiões prioritárias para a conservação da biodiversidade global já apresentam evidências químicas de alterações antropogênicas, apresentando concentrações de substâncias em seus compartimentos ambientais não compatíveis com o enquadramento de uma região prístina.

Palavras-chave: Antropoceno. Marcadores orgânicos geoquímicos. Poluição. Meio Ambiente. Sedimentos estuarinos.

ABSTRACT

Sedimentary geochemical organic markers constitute a tool for understanding of the accumulation of susbtances in the environment over time and can indicate the anthropogenic activities in a region, as they are directly associated with previously characterized sources of pollution. Considering that the analysis of a sediment core can provide a "movie" of the environmental history and industrial development of a region, the analysis of surface sediments can provide a "photograph" of the current geological period. This study assessed the recent conservation status of the Paranaguá Estuarine System (PES) from an environmental chemistry perspective, characterizing the concentrations, spatial distribution, and emission sources of different pollutants or chemical markers of anthropogenic activities. Three different investigations were conducted: 1 - An assessment of the concentrations and sources of polycyclic aromatic hydrocarbons (PAHs) in surface sediments in the PES; 2 - An assessment of linear alkylbenzenes (LAB) concentrations in surface sediments of the PES to effluent (sewage) input tracing in the estuary; and 3 - A one-year monitoring of $PM_{2.5}$ concentrations in Paranaguá city atmosphere. Fine sediments and organic matter were the main PAH controlling factors, but anthropogenic sources were also identified. Biomass burning and fossil fuel combustion predominated. We identified a contribution from an adjacent watershed resulting from the construction of interconnections between large rivers and years of intensive deforestation in the local Atlantic Forest. The primary source of sewage in the PES was the Paranaguá surrounding rivers, which carries effluents from the city's treatment plants or untreated sewage directly discharged by Valadares region. $PM_{2.5}$ annual mean concentrations were close to the average limits suggested by the World Health Organization, with high short-term (daily) concentrations. Road traffic and ship refueling infrastructure were identified as the main sources. The results presented an alert: priority regions for global biodiversity conservation exhibit chemical evidence of anthropogenic influence, with concentrations of molecular markers and susbtances in their environmental compartments that are not compatible with the classification of a pristine area.

Keywords: Anthropocene. Organic geochemical markers. Pollution. Environment. Estuarine sediments.

SUMÁRIO

1 INTRODUÇÃO

A poluição química tem potencial para causar danos ecossistêmicos e para a saúde humana em diferentes escalas. Devido a sua importância, é considerada uma das nove barreiras planetárias para a segura operação da vida humana na Terra (Rockström *et al.*, 2009). Em 2022, foi classificada como uma das barreiras já ultrapassadas, devido às emissões de diversas substâncias estarem aumentando em um ritmo que supera a capacidade global de avaliação e monitoramento, ou seja, estão fora de controle (Persson *et al.*, 2022).

O oceano é erroneamente tratado como sumidouro viável de diferentes poluentes, devido à propensão humana a usar a diluição como solução para a poluição (Hatje *et al.*, 2021). Neste sentido, os ecossistemas estuarinos são especialmente ameaçados, visto que o desenvolvimento humano e consequente degradação dos ambientes marinhos tendem a ocorrer em áreas próximas à costa, e que as condições hidrodinâmicas limitadas (i.e., a circulação restrita de água e baixa profundidade), dificultando a diluição, dispersão e degradação dos resíduos e poluentes descartados no meio ambiente (Muniz *et al.*, 2013; Weber, 1992).

Compreender os impactos das atividades humanas e identificar os agentes químicos que atuam sobre os ambientes estuarinos é vital para um futuro sustentável que considere a vulnerabilidade destes ecossistemas frente à pressão dos interesses econômicos (Visbeck, 2018; Zijp *et al.*, 2017). Devido à emergência do tema, a Década da Ciência Oceânica para o Desenvolvimento Sustentável da Organização das Nações Unidas elencou como um de seus desafios “entender e vencer a poluição marinha” (ONU, 2022).

O avanço instrumental da Química Ambiental possibilitou o desenvolvimento de uma ciência que busca a identificação e atribuição das fontes de poluentes para a natureza. Utilizando-se da proporção entre diferentes substâncias no ambiente (os poluentes ou indicadores) e de sua interação com parâmetros ambientais, estima-se a contribuição das diferentes fontes de emissão, provendo importantes informações para o desenvolvimento de programas de gestão ambiental (Thunis *et al.*, 2019).

A análise de marcadores orgânicos geoquímicos em sedimentos provê uma ferramenta para se compreender a acumulação de compostos no ambiente ao longo do tempo. Ela pode indicar as atividades antrópicas em uma região pois estão associados a fontes de poluição previamente estudadas e caracterizadas (Martins, 2005). Considerando que a análise de um testemunho sedimentar pode prover um “filme” da história ambiental e desenvolvimento industrial de uma região (como em Martins *et al.*, 2010a; Chang *et al.*, 2018), a análise dos sedimentos superficiais pode prover uma “fotografia” do período geológico atual, principalmente na última década (Cowie, 2005).

Apesar da comunidade científica ainda não ter definido um “*golden spike*”, ou seja, ponto de referência preciso para marcar o início da época, já é reconhecido que o Antropoceno é o intervalo geológico no qual muitos processos da Terra são profundamente alterados pelo impacto humano (Crutzen, 2006; SQS, 2023).

Considerando que na ciência da sustentabilidade a produção de conhecimento deriva de uma concepção não restrita a disciplinas, mas transcende barreiras acadêmicas e pressupõe a interação com a sociedade (Fernandes; Philippi Jr., 2017; Klein, 2010), este trabalho apresenta uma investigação integrada das fontes de diferentes poluentes nos sedimentos e na atmosfera do Complexo Estuarino de Paranaguá, uma região que devido ao seu contexto único apresenta conflitos entre a conservação ambiental e projetos de infraestrutura logística de grande impacto, proporcionando obter uma fotografia inicial do Antropoceno através das ferramentas de Química Analítica disponíveis no Laboratório de Geoquímica e Poluição Marinha da Universidade Federal do Paraná (LaGPoM).

A seguir, são apresentadas as três problemáticas ambientais relacionadas à poluição de ecossistemas costeiros, marcadores geoquímicos orgânicos e a determinação de suas fontes, como forma de apresentar conceitos e termos necessários à compreensão dos três capítulos seguintes.

2 FUNDAMENTAÇÃO TEÓRICA

2.1 ÁGUAS RESIDUAIS E OS MARCADORES DE ESGOTO

O século XX foi caracterizado pela expansão dos processos de urbanização por todo o planeta. Políticas neoliberais pautadas em interesses privados trouxeram processos de rápida e descontrolada urbanização para países em desenvolvimento, que historicamente possuem frágeis políticas ambientais e de acesso à saúde (Harvey, 1996). O processo de gentrificação dos centros urbanos, ou seja, de alocar a classe trabalhadora em redutos de interesse econômico, resultou em regiões periféricas com alta densidade demográfica, baixa renda, e frequente incidência de problemas de saúde ambiental (Harvey, 1996; Zukin, 1987). Neste sentido, o lançamento irregular de esgotos sanitários em águas marinhas ou estuarinas se tornou um dos principais problemas relacionados à urbanização da zona costeira brasileira (Hatje *et al.*, 2021; Martins *et al.*, 2008).

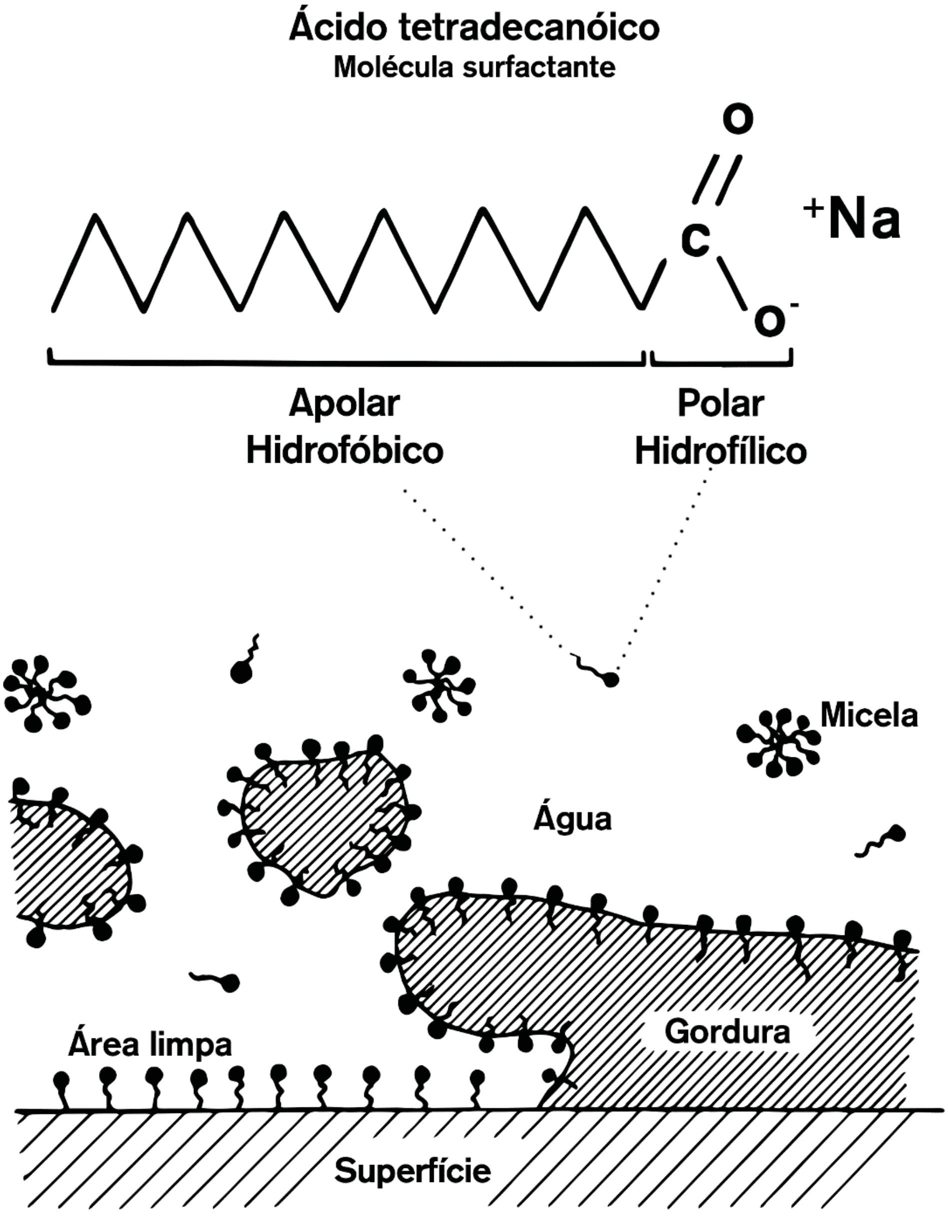
Dentre as diversas fontes de contaminação para os ambientes costeiros, o esgoto representa uma das mais preocupantes devido ao aporte de elevado volume de material biológico nocivo à saúde ambiental. A introdução de esgoto não tratado no meio ambiente pode influenciar diretamente os ciclos biogeoquímicos, causar desequilíbrios ecossistêmicos, e provocar efeitos deletérios diretos na saúde de organismos expostos (Breitburg *et al.*, 2018; Iwamoto *et al.*, 2010; Nilsen *et al.*, 2019).

O contexto brasileiro apresenta apenas 51,2% de sua população coberta por serviços de tratamento dos esgoto (Ministério das Cidades, 2023). Devido à complexidade e escala do problema, a Oficina de Planejamento Regional do Atlântico Sul para a Década da Ciência Oceânica no Brasil definiu a falta de sistemas de esgoto adequados e estações de tratamento de águas residuais como principal fonte de poluentes no Atlântico Sul (Hatje *et al.*, 2021).

2.1.1 Surfactantes

Os surfactantes (do inglês *surface-active agents*) consistem em uma classe de compostos químicos que agem na interface entre fases distintas, através de sua polaridade. Em geral, consistem em moléculas com duas partes: uma “cauda” apolar hidrofóbica formada por uma cadeia de hidrocarbonetos, e uma “cabeça” polar hidrofílica formada por um ácido carboxílico. Esta estrutura possibilita a redução da tensão superficial entre as fases e a quebra de partículas de gordura, que por fim, acabam dispersas num tipo de emulsão (Connell, 2013). A Figura 1 apresenta a estrutura de um exemplo de surfactante e ilustra o mecanismo utilizado em processos de limpeza, no qual a cabeça polar se liga à água e a cauda apolar se liga à gordura, tendendo a formação de micelas, ou seja, agregados globulares de moléculas.

FIGURA 1: EXEMPLO DE MOLÉCULA SURFACTANTE (ÁCIDO TETRADECANÓICO) E ILUSTRAÇÃO DE SEU FUNCIONAMENTO EM UM PROCESSO DE LIMPEZA.



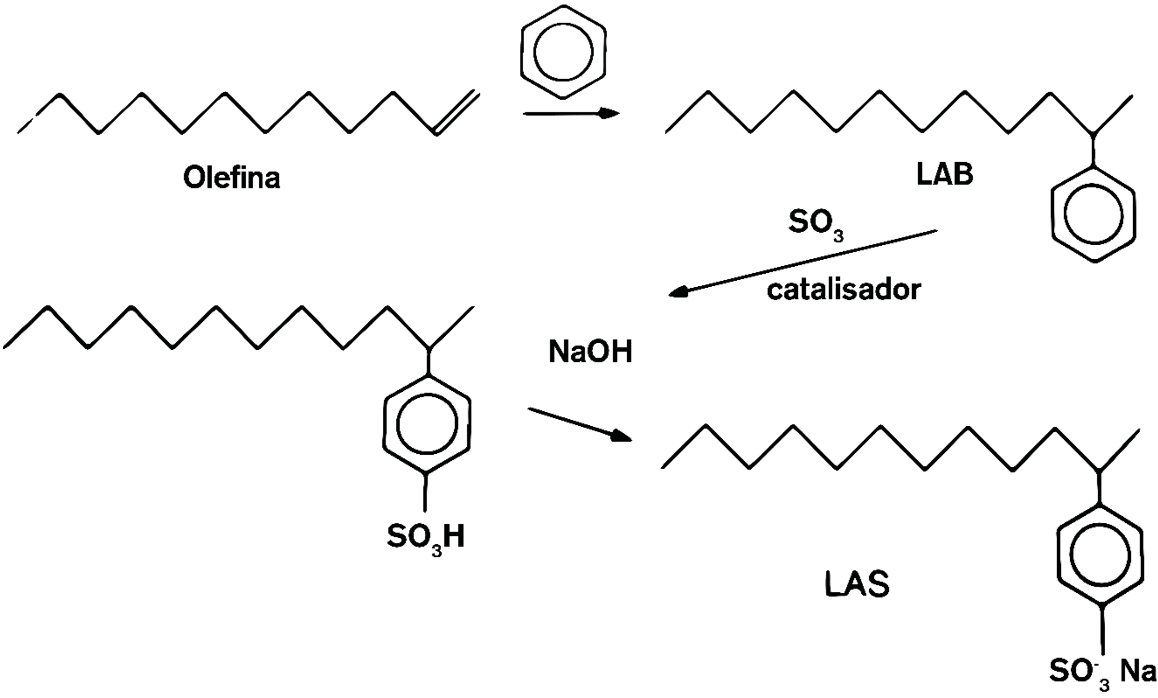
FONTE: ADAPTADO E TRADUZIDO DE CONNELL (2013)

2.1.2 Alquilbenzenos lineares como marcadores de contaminação por esgotos

Durante a década de 1950, houve uma progressiva substituição dos sabões produzidos com óleo vegetal por alquilbenzenos sulfonados (ABSs) produzidos a partir do refino do petróleo. Com o passar do tempo, tais moléculas se mostraram resistentes à biodegradação, e sua acumulação em estações de tratamento de esgoto causaram diversos episódios de acúmulo de espuma na água tratada ao final do processo. Isso levou à adoção dos alquilbenzeno sulfonados lineares (LAS, do inglês *linear alkylbenzene sulfonates*) como matéria prima e é ainda a mais adotada nos dias de hoje para fabricação de detergentes (Connell, 2013).

O querosene é a matéria prima para obtenção de parafinas lineares (um hidrocarboneto linear acíclico saturado) com alta pureza, que são convertidas para olefinas (hidrocarbonetos que possuem cadeia aberta e ligações duplas) por eliminação de hidrogênio (desidrogenação). Estas olefinas reagem com benzeno com o uso de um catalisador, para assim produzir alquilbenzenos lineares (LABs). Os LABs são hidrocarbonetos aromáticos utilizados como matéria-prima para fabricação de LAS (Connell, 2013; Shokri; Karimi, 2021). A Figura 2 apresenta a síntese de LAS a partir de olefinas, passando pela formação dos LABs no processo.

FIGURA 2: PROCESSO DE SÍNTESE DE LAS A PARTIR DE OLEFINAS.



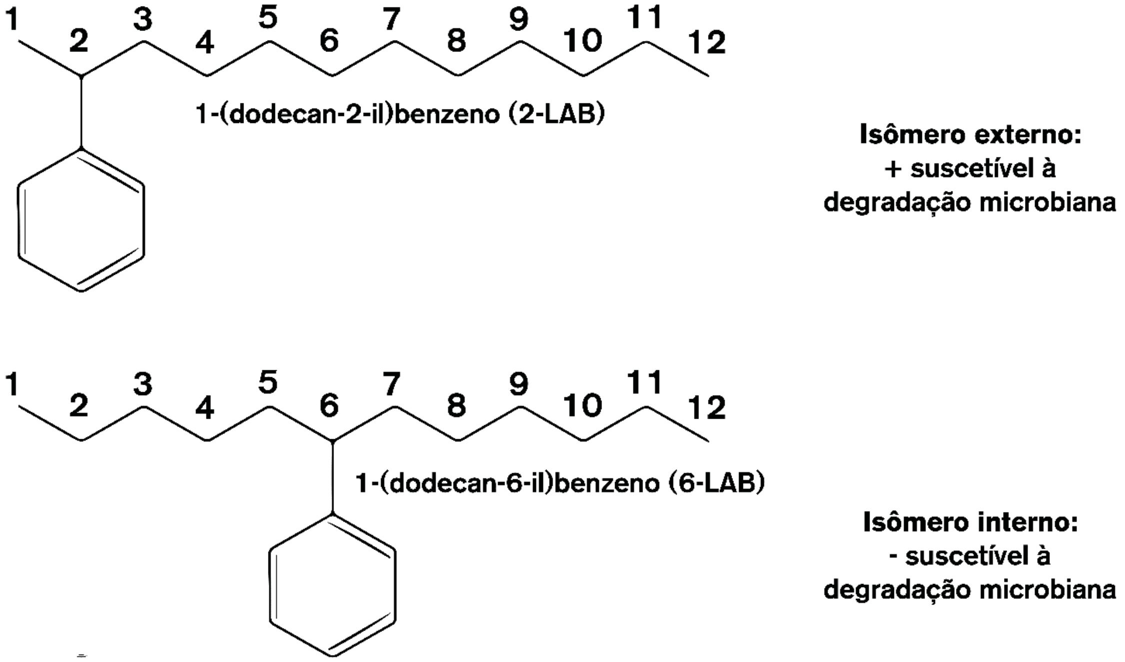
FONTE: TRADUZIDO DE CONNELL (2013).

Aproximadamente 13% dos LABs se mantém intactos durante o processo de sulfonação, permanecendo como resíduo passível de ser rastreado no produto final ou em amostras ambientais, devido sua relação com a fonte antropogênica e persistência a degradação . Desta forma, eles podem ser caracterizados como marcadores de contaminação por resíduos de esgoto, e prover informações importantes sobre tais fontes (Alkhadher *et al.*, 2020a; Eganhouse; Blumfield; Kaplan, 2002; Takada; Eganhouse, 1998).

2.1.3 Degradação e atribuição de fontes

Os diferentes padrões de concentração dos isômeros dos LABs podem nos prover importantes informações relativas à capacidade de degradação das moléculas no meio aquático. Um método comum está na avaliação da proporção entre isômeros internos e externos (*I/E ratio*) como forma de se estimar a degradação dos LABs, considerando que os externos são degradados com maior facilidade (Alkhadher *et al.*, 2020b; Cabral; Martins, 2018; Martins *et al.*, 2008). A Figura 3 apresenta a comparação entre uma molécula de LAB com isômero interno e externo.

FIGURA 3: ISÔMEROS DE LABS EM COMPARAÇÃO RELATIVA À SUA SUSCEPTIBILIDADE À DEGRADAÇÃO MICROBIANA.



FONTE: O AUTOR (2023).

O cálculo do *I/E ratio* se dá através da razão ([6-C_{12} LAB] +[5-C_{12} LAB])/([4-C_{12} LAB] + [3-C_{12} LAB] + [2-C_{12} LAB]), sendo que valores baixos (I/E ∼1.0) estão relacionados à aporte de efluente recente e tratado (Takada; Ishiwatari, 1990). Outras razões incluem C_{13}/C_{12} ([Σ-6, 5, 4, 3, 2-C_{13} LAB]/[Σ-6, 5, 4, 3, 2-C_{12} LAB]), baseada na maior susceptibilidade à degradação dos homólogos C_{12} (Luo *et al.*, 2008), e a proporção entre moléculas de cadeia longa ou curta (L/S do inglês *long/short*), calculada como (5-C_{13} LAB + 5-C_{12} LAB)/(5-C_{11} LAB + 5-C_{10} LAB) (Gustafsson *et al.*, 2001).

2.2 HIDROCARBONETOS POLICÍCLICOS AROMÁTICOS

A crise climática global é fomentada principalmente pelo uso massivo de combustíveis fósseis e o desmatamento de áreas florestadas. Tais atividades, ao modificar os fluxos naturais de carbono, desencadeiam alterações climáticas que ameaçam o suporte à vida na Terra (Carrington; Taylor, 2022; Ripple *et al.*, 2020). Tanto a queima de material vegetal, quanto o derramamento ou queima de óleos combustíveis, constituem-se como atividades que, ao transformar a matéria orgânica, geram diferentes compostos orgânicos poluidores ou indicadores de atividade antropogênica (Abdel-Shafy; Mansour, 2016).

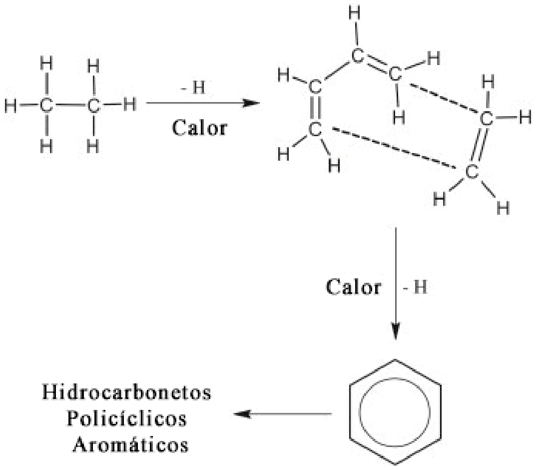
Os hidrocarbonetos policíclicos aromáticos (HPA, ou PAH, do inglês *polycyclic aromatic hydrocarbons*) correspondem a uma classe de moléculas orgânicas constituídas por no mínimo dois anéis aromáticos condensados, dispostos em diferentes arranjos estruturais. São formados somente por átomos de carbono e hidrogênio, podendo estes últimos estarem substituídos por grupos alquilados (Jalili; Barkhordari; Ghiasvand, 2020; Kang; Lee; Kwon, 2016). A estrutura composta por seis átomos de carbono em forma de anéis (policíclico) e insaturações (ligações π) gera ângulos de ligação de 120º entre os átomos, que junto à ressonância em suas ligações (aromático), possibilita uma relativa estabilidade química, em comparação com outros hidrocarbonetos cíclicos com menor número de átomos de carbono (Ucko, 1992).

Os HPAs estão listados entre os poluentes ambientais regulados de grande preocupação na atualidade devido a sua elevada toxicidade, com determinadas moléculas possuindo ação mutagênica, carcinogênica e/ou teratogênica (Kim *et al.*, 2013; Simão *et al.*, 2020). A maior parte dos HPAs emitidos globalmente resultam de atividades humanas, com maiores contribuições vindo de países em desenvolvimento como China, Índia, Indonésia e Brasil, devido ao uso extensivo de combustíveis vegetais em países asiáticos e por desmatamento na América do Sul (Shen *et al.*, 2013). Em regiões desenvolvidas, como Ásia Central, América do Norte e Europa, o setor de transportes é a principal fonte de HPAs (Han *et al.*, 2020; Shen *et al.*, 2013). Por fim, existem ainda fontes naturais, como exudações de petróleo, incêndios florestais naturais, erupções vulcânicas e transformações diagenéticas da matéria orgânica que inserem esses compostos no ambiente (Abdel-Shafy; Mansour, 2016; Lin *et al.*, 2020).

2.2.1 Fontes e métodos de diferenciação

A formação dos HPAs inicia-se a partir de moléculas de hidrocarbonetos saturados (ou seja, somente com ligações σ), em condições com baixos teores de oxigênio. Em temperaturas elevadas, as ligações são quebradas formando radicais livres, que irão se combinar em estruturas aromáticas, resistentes à degradação térmica (Ravindra et al., 2008). Um exemplo de formação de um HPA é mostrado na Figura 4.

FIGURA 4: PIROSSÍNTESE DOS HPAS INICIANDO COM O ETANO.



FONTE: TRADUZIDO DE RAVINDRA *et al.* (2008).

Os HPAs são comumente diferenciados entre petrogênicos e pirogênicos, o que reflete em sua massa molecular, sua permanência no ambiente e até mesmo em sua toxicidade. Ainda, há HPAs de fontes biológicas, provenientes da síntese de bactérias e algas, além da formação através de transformações diagenéticas da matéria orgânica. Porém, tais processos não são bem descritos até o presente momento (Abdel-Shafy; Mansour, 2016), sendo que as duas primeiras fontes citadas predominam sobre esta última.

Os HPAs "**petrogênicos**" constituem predominantemente por um grupo de compostos de baixa massa molecular (2 ou 3 anéis aromáticos), assim como homólogos alquilados C_1 a C_4 (Alquil-HPAs), que são encontrados em maior proporção a partir de óleos brutos de petróleo ou de seus derivados. As principais fontes de emissão estão em falhas nos processos de extração, transporte e armazenamento de petróleo, assim como em vazamentos de combustíveis e óleos de motores. São formados a partir da transformação da matéria orgânica durante a formação do óleo bruto, em temperaturas inferiores a 150º C, em um processo que pode durar milhões de anos para ocorrer (Kang; Lee; Kwon, 2016; Yang *et al.*, 2018).

Os HPAs "**pirolíticos**" ou "**pirogênicos**" são formados majoritariamente por compostos de maior massa molecular (4 a 6 anéis aromáticos). Sua formação se dá na pirólise, um processo em que a matéria orgânica é exposta à altas temperaturas (> 350 ºC) com pouco ou nenhum oxigênio. Os principais exemplos desta formação são a queima incompleta de combustíveis em motores, queima de biomassa vegetal para aquecimento doméstico ou em termoelétricas, ou mesmo na queima de florestas e vegetações rasteiras (Abdel-Shafy; Mansour, 2016; Manzetti, 2013).

A partir da compreensão da diferença estrutural entre os HPAs e as variadas fontes de emissão, diversas estratégias foram desenvolvidas para se estabelecer as possíveis origens destes compostos em matrizes ambientais. A seguir, um detalhamento dos métodos de diferenciação entre fontes de HPAs.

2.2.2 Razões entre diferentes isômeros de HPAs

Uma das principais maneiras de se diferenciar as distintas fontes de emissão de HPAs está na avaliação das razões entre isômeros, ou seja, moléculas de mesma fórmula molecular, mas com estrutura química diferente. Yunker *et al*. (2002) apresentam uma revisão sistemática, onde diversas razões foram aplicadas possibilitando investigar se as emissões são provenientes de fontes petrogênicas ou pirogênicas. Foram elencadas sete razões principais entre HPAs para se utilizar em estudos de grande abrangência territorial e com ampla diversidade de prováveis fontes. No mesmo sentido, Tobiszewski e Namieśnik (2012) listam ainda razões que se baseiam na soma dos HPAs de maior e menor massa molecular e da combinação de grupos de moléculas que estejam mais relacionadas à combustão como fonte de emissão.

2.2.3 Distribuição de homólogos alquilados

Determinados HPAs podem apresentar grupos alquil, sendo assim chamados de homólogos alquilados C_1 a C_4, dependendo do número de ramificações presentes na molécula. Os HPAs formados em altas temperaturas tendem a apresentar menos ramificações que os formados em menores temperaturas. Tais radicais estão relacionados com a transformação da matéria orgânica nos hidrocarbonetos presentes na composição do petróleo ao longo de milhões de anos (Abdel-Shafy; Mansour, 2016; Wang; Fingas; Page, 1999). Essa regra é particularmente funcional para as séries do naftaleno, dibenzotiofeno, fluoreno, fenantreno e criseno (Yang *et al.*, 2018). Desta maneira, convencionou-se identificar a emissão dos HPAs petrogênicos a partir da observação da distribuição/abundância em forma de sino dos grupos homólogos. Para identificação de emissões pirogênicas, a distribuição/abundância segue o formato de curva decrescente (Overton *et al.*, 2016; Wang; Fingas; Page, 1999).

Um exemplo da utilização desta técnica está na identificação das fontes de HPAs no desastre de vazamento de petróleo ocorrido no Golfo do México, em 2010. A avaliação apontou uma distribuição em "forma de sino" para os grupos de menor massa molecular, e valores baixos para os hidrocarbonetos de maior massa molecular, com 5 ou 6 anéis. O perfil apresentado é claramente identificado como "petrogênico", o que provavelmente está relacionado aos vazamentos ocorridos (Overton *et al.*, 2016).

2.2.4 Os 16 HPAs prioritários

Em 1976, a Agência Ambiental Americana (EPA, do inglês *Environmental Protection Agency*) publicou uma lista de 129 poluentes prioritários para monitoramento em matrizes ambientais, para fins de regulação (Keith; Telliard, 1979). O contexto da época remontava à consolidação da consciência ambiental, ocorrendo cerca de uma década após a publicação de "Primavera Silenciosa", de Rachel Carson, que pela primeira vez, identificou os efeitos deletérios do uso de pesticidas no ambiente (Carson, 1962).

Uma das investigações que deu início à formulação da lista dos 129 poluentes prioritários em estudos ambientais ocorreu a partir de uma avaliação realizada pela EPA em corpos d'água próximos à uma usina petroquímica estabelecida no estado americano da Louisiana. Os pesquisadores esperavam encontrar altos níveis das substâncias químicas utilizadas como matérias primas na indústria (etano, propano, nitrogênio, etc.) ou seus produtos (amônia, propileno, octano, etc.). Por outro lado, o que detectaram foi uma série de compostos orgânicos como xilenos, naftaleno e seus isômeros alquilados, indenos e seus isômeros alquilados, entre outros (Keith, 2015). Investigações como essas suscitaram na primeira lista de poluentes, conhecida como os "65 poluentes tóxicos" do decreto norte-americano de 1976. Apesar disso, essa lista apresentava algumas imprecisões, como a falta de objetividade (alguns nomes listados na verdade eram grupos de compostos), de valores mínimos para regulação, e de especificação dos métodos de análise (Keith; Telliard, 1979; Keith, 2015).

Nos anos 1970, a cromatografia gasosa acoplada a espectrometria de massas (GC-MS) já estava consolidada como método mais versátil para identificação de diversos compostos orgânicos no ambiente, mesmo ainda não sendo computadorizada. Assim, foi estabelecida como técnica instrumental padrão para determinação, assim como os limites mínimos para detecção. Quanto ao problema dos grupos de compostos, a solução encontrada se deu em selecionar analitos representativos para cada classe. No ano de 1979, os laboratórios da EPA já haviam encontrado cerca de 1259 compostos, que foram estudados para compor a lista final de 129 poluentes prioritários, conforme critérios como frequência de ocorrência, quantidade produzida pelas indústrias, toxicidade e disponibilidade de métodos de análise (Andersson; Achten, 2015; Keith, 2015).

Desta lista final com 129 poluentes, 16 eram HPAs, que ficaram conhecidos como os "16 HPAs prioritários da EPA". Os três primeiros, oriundos das primeiras listas foram acenafteno, naftaleno e fluoranteno. Sete HPAs foram selecionados conforme os critérios ditos anteriormente: (benz[*a*]antraceno, benzo[*a*]pireno, benzo[*b*]fluoranteno, benzo[*k*]fluoranteno, criseno, dibenz[*a,h*]antraceno, e indeno[1,2,3-*c,d*]pireno). Três foram selecionados devido ao seu potêncial carcinogênio em recursos aquíferos: acenafteno, fluoreno e fenantreno. Por fim, antraceno foi selecionado por ser proveniente do alcatrão e intermediário de outras substâncias químicas; o benzo[*g,h,i*]perileno, por representar o grupo dos HPAs de 6 anéis; e o pireno, por ser proveniente de uma série de processos de combustão. Os HPAs ramificados não foram incluídos devido a dificuldades analíticas da época (Keith, 2015).

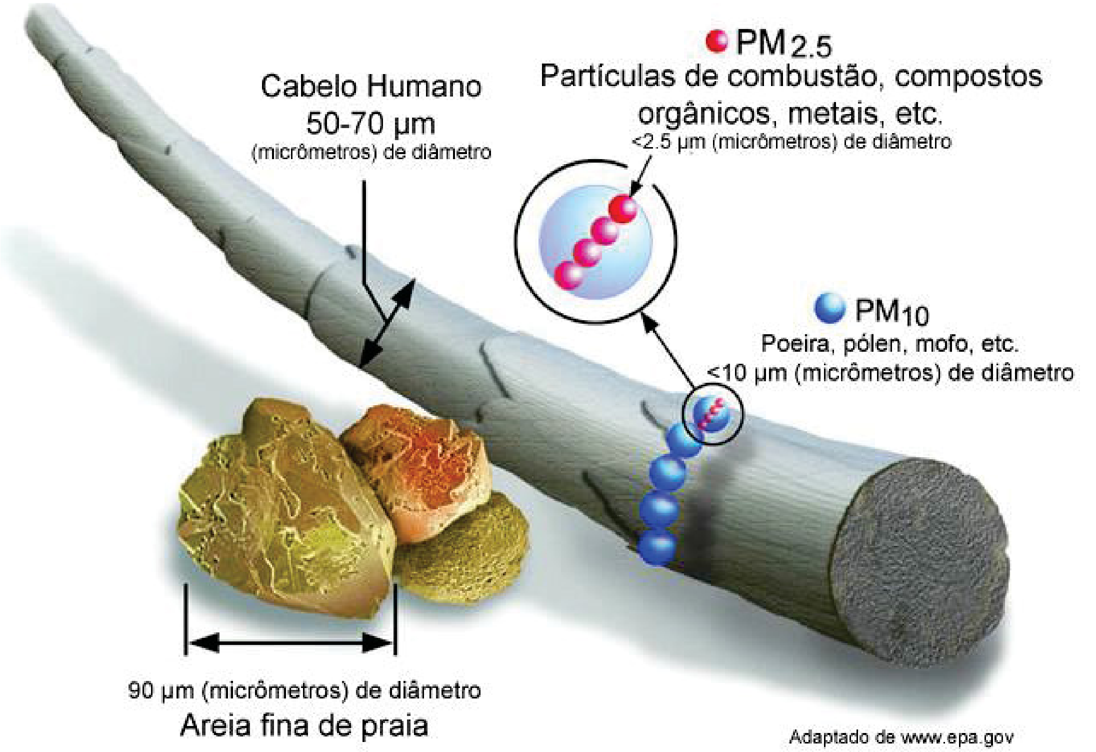
Apesar dessa lista ter sido desenvolvida por um corpo técnico altamente capacitado, sendo representativa e útil nos anos seguintes ao seu desenvolvimento e possuir um peso histórico inegável, a determinação de HPAs em amostras ambientais com ênfase apenas nestes compostos pode acarretar interpretações limitadas. Ao não considerar outros HPAs que estão fora da lista, ela pode representar resultados subestimados. Além disso, alguns HPAs tóxicos não estão inclusos, como os compostos alquilados que podem trazer tantos riscos quanto os seus homólogos não substituídos (Andersson; Achten, 2015; Keith, 2015). Por fim, Andersson e Achten (2015) sugerem uma lista de 40 HPAs relacionados à toxicidade ambiental, além de listas referentes aos Nitro-HPAs e aos compostos heterocíclicos.

2.3 MATERIAIS PARTICULADOS ATMOSFÉRICOS

Reconhecida mundialmente como um dos maiores problemas de saúde pública, a poluição do ar é responsável por diversos efeitos na saúde, desde doenças cardiorrespiratórias, até interferências neurológicas crônicas e mortes (Chen *et al.*, 2015; Marcantonio *et al.*, 2021). Somente no ano de 2012, estimou-se que a poluição do ar foi responsável por 7 milhões de óbitos (WHO, 2014). Além disso, a poluição atmosférica está distribuída de maneira desigual entre a população mundial, sendo que 7,3 bilhões de pessoas estão diretamente expostas a concentrações inseguras. Dessas, 80% vivem em países de baixa e média renda (Rentschler; Leonova, 2023). Na América Latina, a tendência se repete, com riscos para a saúde associados à poluição atmosférica afetando de maneira desigual populações com algum tipo de privação socioeconômica (Gouveia *et al.*, 2022).

O material particulado (PM, do inglês, *Particulate Matter*) é uma mistura de partículas sólidas e/ou líquidas presentes na atmosfera, com tamanho e densidade suficientemente pequenas para que permaneça por determinado tempo em suspensão. Também conhecido como aerossóis, consistem em uma classificação física de partículas encontradas no ar, como poeira, fuligem, fumaça e gotículas líquidas. Sendo assim, não são substâncias, mas uma mistura de vários componentes. Quanto menor o tamanho de uma partícula, maior possibilidade de deposição em áreas mais internas do sistema respiratório e, consequente, o desenvolvimento de efeitos deletérios à saúde (Braga *et al.*, 2001). Devido a isso, para fins metodológicos, são comumente divididas em PTS (Partículas Totais em Suspensão), PM_{10} ou “inaláveis” (menor ou igual a 10 µm de diâmetro) e $PM_{2.5}$ ou “finas” (menor ou igual a 2,5 µm de diâmetro) (Braga *et al.*, 2001; Guarnieri; Balmes, 2014), como apresentado na Figura 5.

FIGURA 5: FRAÇÕES DO MATERIAL PARTICULADO EM COMPAÇÃO AO TAMANHO DE GRÃOS DE AREIA E FIO DE CABELO.



Adaptado de www.epa.gov
(Agência de Proteção Ambiental dos Estados Unidos)

FONTE: TRADUZIDO DE US ENVIRONMENTAL PROTECTION AGENCY, DISPONÍVEL EM HTTP://WWW.EPA.GOV.

A exposição crônica ao $PM_{2.5}$ contribuiu para mais de 4 milhões de mortes em estimativa para 2019, o que o tornou um dos mais consistentes e robustos preditores de mortalidade, relacionado principalmente as causas respiratórias e cardiovasculares (HEI, 2020). Estudos encontraram que o aumento de 10 $\mu g\ m^{-3}$ na concentração atmosférica deste poluente resulta em acréscimo de 6% de mortalidade geral e 11% para mortalidade por problemas cardiovasculares (Hoek *et al.*, 2013; Lim *et al.*, 2012).

As emissões de $PM_{2.5}$ têm como principal fonte a queima de combustíveis fósseis para atividades como geração de energia, processos industriais, aquecimento residencial e transporte urbano. Isto resulta em um contexto onde os padrões geográficos de distribuição das emissões de $PM_{2.5}$ estão relacionados ao crescimento econômico dos países (HEI, 2020; Ma *et al.*, 2022). Estas partículas, em geral, são compostas por uma mistura de moléculas orgânicas, metais traços, além de íons como nitrato e sulfato. A variação na sua composição química e características físicas pode prover informações relativas à fonte, condições climáticas e geográficas, a partir do uso de ferramentas estatísticas e de modelagem que relacionem os dados físico-químicos à padrões de emissão (Albuquerque *et al.*, 2019; Ma *et al.*, 2022).

O $PM_{2.5}$ foi incluído nos Padrões Nacionais de Qualidade do Ar do Brasil somente em 2018 (Resolução CONAMA 491/2018), implementando padrões intermediários progressivos, e estabelecendo os valores sugeridos pelos *guidelines* de 2005 da Organização Mundial da Saúde como padrões finais para implementação no futuro (Albuquerque *et al.*, 2019; CONAMA, 2018). Apesar desta demanda, o país possui uma rede de monitoramento da qualidade do ar com cobertura limitada, centrada quase exclusivamente em grandes metrópoles (Marcilio; Gouveia, 2007).

2.4 ATRIBUIÇÃO DE FONTES

O avanço da Química Analítica e dos métodos estatísticos computacionais proporcionou o desenvolvimento de uma ciência que visa quantificar e determinar as diferentes contribuições das fontes de poluição para uma determinada amostra ambiental. A atribuição de fontes pode proporcionar informações importantes para estratégias de controle e emissão de poluentes e a compreensão de fluxos biogeoquímicos (Andersson, 2011; Keith, 2015).

Inicialmente aplicados no estudo do PM atmosférico, os métodos de atribuição de fontes baseados em modelos de receptores são atualmente utilizados para se investigar qualquer amostra ambiental na qual possa se pressupor que as concentrações medidas são o resultado da soma das contribuições de massa de várias fontes independentes ou tipos de fontes (Hopke, 2009). A análise de PMF (do inglês "*Positive Matrix Factorization*") e PCA (do inglês *Principal Component Analysis*) são métodos estatísticos multivariados que proporcionam a determinação de fontes desconhecidas, partindo da interpretação dos padrões de poluentes encontrados (Andersson, 2011; Hopke, 2009). Outros modelos buscam comparar a razão isomérica entre compostos como apresentado para o caso dos HPAs e o apontamento de fontes petrogênicas *vs* pirogênicas (Yunker *et al.*, 2002). Determinadas moléculas, como os LABs, podem ser consideradas traçadoras de fontes. Conhecidas como marcadores moleculares, eles são utilizados devido à sua relativa estabilidade e sua associação direta com fontes antropogênicas conhecidas, como os efluentes domésticos (Takada; Eganhouse, 1998).

Como complemento, a utilização de outras variáveis ambientais pode prover informações importantes para a compreensão das fontes de poluentes. Um exemplo prático está na análise de gráficos polares bivariados, que combinam as concentrações de diferentes poluentes com informações de direção e velocidade do vento, apontando as direções que concentram fontes mais expressivas de emissão (Uria-Tellaetxe; Carslaw, 2014).

Por fim, os métodos possuem particularidades e condições específicas para serem utilizados, além de fragilidades inerentes ao método (Hopke, 2009). Neste sentido, este trabalho buscou explorar as diferentes ferramentas de atribuição de fontes aplicáveis às matrizes ambientais que estavam à disposição.

2.5 ÁREA DE ESTUDO

O litoral paranaense é um território que compreende sete municípios localizados na planície litorânea do estado do Paraná, na região sul do Brasil, banhados pelas águas da proção Sul do Oceano Atlântico (Bigarella, 2001). Sua geomorfologia acidentada e a distância dos centros agrícolas fez com que somente no século XX fosse possível que a região se inserisse dentro do contexto econômico internacional, a partir da consolidação de um complexo portuário voltado à exportação da produção brasileira de soja. Desta forma, a região é considerada uma fronteira na expansão do modo de produção capitalista sobre os territórios, pois se insere no contexto econômico global, mas ainda preservando características naturais e culturais distintas (Tiepolo, 2016; Tiepolo; Denardin, 2017).

Este atraso na exploração econômica, aliado à presença de unidades de conservação proporcionou para a região uma vasta área com alguns dos últimos remanescentes contínuos de Mata Atlântica (Claudino-Sales, 2019). A megadiversidade deste bioma não se expressa somente através da alta taxa de endemismo que ele mantém (Myers *et al.*, 2000; Tabarelli *et al.*, 2005), mas também pela sociodiversidade que abriga, com destaque para a presença de grupos indígenas como os Guarani Mbya ou comunidades pesqueiras tradicionais, como a do "Maciel" (Góes; Parrili; Foppa, 2020; Onofre; Antiquera; Quadros, 2018). Este contexto sociobiodiverso proporcionou à inclusão da área na lista de Patrimônio Mundial Natural e Reserva da Biosfera da UNESCO (Claudino-Sales, 2019; UNESCO, 1999).

A região abriga dois estuários: a baía de Guaratuba em sua parte sul (Marone *et al.*, 2006) e o Complexo Estuarino de Paranaguá (CEP) (Lana *et al.*, 2001), que constitui o cenário desta pesquisa, em sua parte norte.

2.5.1 O Complexo Estuarino de Paranaguá

O Complexo Estuarino de Paranaguá (CEP) (também encontrado na literatura como Sistema Estuarino de Paranaguá - PES) é um sistema estuarino sub-tropical formado por dois corpos d'água, conhecidos historicamente como Baía de Paranaguá e Antonina (Eixo Leste-Oeste), e Baía de Laranjeiras e Pinheiros (Eixo Norte-Sul), que ocupam uma área de aproximadamente 612 km² no litoral norte paranaense (Angeli *et al.*, 2020a; Lana *et al.*, 2001). Ele possui um volume de água de aproximadamente 2×10^9 m^3, sendo dominado por forçantes de maré e descargas fluviais das montanhas da Serra do Mar (Angeli et al., 2020a; Lana et al., 2001; Martins et al., 2010).

Paladino et al. (2022) dividem o CEP em três áreas distintas com base nos processos deposicionais: (i) Baía de Antonina, onde os rios Nhudiaquara e Cachoeira desempenham um papel fundamental na entrada e transporte de sedimentos provenientes da Serra do Mar; (ii) Zona de Máxima de Turbidez (TMZ, do inglês "*Turbidity Maximum Zone*"), onde o equilíbrio hidrodinâmico entre a drenagem fluvial de água doce e a intrusão de água marinha no estuário favorece a deposição de sedimentos mais finos; e (iii) Plataforma Continental, que é a área onde a influência da água marinha nos padrões hidrodinâmicos e nas fontes de sedimentos é predominante. De maneira similar, Wilhelm et al. (2023) demonstraram que a Baía de Antonina está sob influência fluvial significativa, recebendo matéria orgânica terrestre, enquanto o restante do Eixo Leste-Oeste apresenta contribuições mistas (ou seja, matéria orgânica terrestre e oceânica).

2.5.2 História ambiental recente

Ao norte das margens do CEP predominam regiões florestadas provenientes do processo de implementação de unidades de conservação ocorrido a partir da década de 1980. Neste período, empresas como *American Electric Power*, *General Motors* e *Chevron Texaco* financiaram a implementação de projetos de crédito de carbono baseados na recuperação de 19.000 ha de áreas degradadas na região, anteriormente impactadas por práticas agrícolas e pecuárias incipientes (Ferretti; de Britez, 2006). Ao mesmo tempo, o poder público também criou unidades de conservação, resultando nos atuais 756.069 ha protegidos, dos quais somente 24% se encontram no enquadramento de proteção integral (Carlucci; Marcilio-Silva; Torezan, 2021; Tiepolo, 2016). Neste sentido, Tiepolo (2016) relata que as unidades de conservação apresentam "*baixo nível de consolidação devido a equívocos conceituais, problemas fundiários, erros na demarcação dos limites e ausência de políticas públicas voltadas à conservação da natureza e a participação social*".

A bacia do Rio Cachoeira, também localizada na margem norte do CEP, provê uma descarga de 21,13 $m^3 s^{-1}$ de água, sendo o principal contribuinte ao sistema. Seu fluxo aumentou em 50% a partir da interconexão com a bacia do rio Capivari, na década de 1970, voltada à construção de uma central hidroelétrica (Cattani; Lamour, 2016; Odreski *et al.*, 2003).

Ao sul de suas margens, o CEP abriga os terminais portuários de Paranaguá e Antonina. Recebendo investimentos, desde os anos 1970, devido à demanda na exportação da produção brasileira da soja, o porto de Paranaguá é considerado o maior porto do sul do Brasil, líder latino-americano no transporte de granéis. A atividade portuária na região trouxe consigo o surgimento de um polo industrial de fertilizantes e de um terminal petroquímico, bem como a intensificação dos processos de urbanização (Campos Neto *et al.*, 2009; de Lima *et al.*, 2018). Conflitos ambientais são frequentes e tendem a se intensificar devido à existência de pelo menos 10 projetos de infraestrutura portuária já com licenciamento ambiental prévio para implementação no CEP, focados em subsidiar a exportação dos produtos do agronegócio e a exploração das reservas de petróleo da camada pré-sal do litoral brasileiro (Góes *et al.*, 2020; Pigosso & de Paula, 2021).

Há décadas o sistema fiscal brasileiro privilegia a cadeia da produção de soja com desonerações e incentivos fiscais baseados na estrutura tributária promulgada na Emenda Constitucional nº 18, de 1965, em detrimento de outras alternativas necessárias à segurança alimentar da população brasileira (Campos, 2023). Este modelo de produção também apresenta uma série de externalidades ambientais como emissão de gases estufa, contaminação por agroquímicos e desmatamento (Ortega *et al.*, 2005). A China é o maior importador individual da soja brasileira, com a maior parte de suas importações provenientes dos estados de Mato Grosso, Paraná e Rio Grande do Sul (Escobar *et al.*, 2020).

Castro (2013) mostra que o Brasil adotou uma política voltada ao transporte rodoviário, o que fez com que a frota de veículos automotores aumentasse de 18 para 64 milhões entre 1990 e 2010, com estimativas que preveem que em 2030 a frota brasileira se aproximará a 230 milhões de veículos. As externalidades envolvidas no transporte rodoviário brasileiro são congestionamento, acidentes, poluição do ar e poluição sonora. O transporte rodoviário é o principal meio de transporte da produção brasileira de soja para os portos responsáveis por sua exportação, e Paranaguá, o maior município nas margens do CEP.

2.6 JUSTIFICATIVA

Os diferentes usos da terra ao longo do gradiente estuarino e os distintos níveis de conservação nos dois eixos do CEP o tornaram um estudo de caso para a compreensão de impactos antropogênicos em estuários. A intensificação da ocupação humana e do uso da terra na região é representada pelas concentrações de marcadores moleculares como HPAs, coprostanol e *n*-alcanos em testemunhos sedimentares, com aumento nas concentrações desde as camadas que caracterizam os anos 1950 (Cabral *et al.,* 2019, Martins *et al.,* 2015, Wilhelm *et al.,* 2023). Estes marcadores moleculares e outros poluentes preocupantes têm sido reportados na literatura como presentes no CEP. Microplásticos foram encontrados em ostras destinadas ao consumo humano (Vieira *et al.,* 2021), e nos sedimentos de todas as praias amostradas, mesmo aquelas localizadas em áreas de proteção ambiental (Mengatto; Nagai, 2022). Concentrações de metais (Angeli *et al.,* 2020a) e HPAs (Cardoso; Dauner; Martins, 2016; Gurgatz *et al.*, 2023) nos sedimentos do CEP estão abaixo do observado dentre os estuários antropizados. Em contraste, as concentrações de HPAs em peixes e plâncton foram 15 vezes maiores que nos sedimentos (Froehner et al., 2018), indicando uma possível via de transporte entre compartimentos ambientais.

A introdução de esgoto no CEP foi avaliada através de esteróis fecais em sedimentos (Martins *et al.*, 2010), bactérias indicadoras em água (Kolm *et al.*, 2018), e material particulado em suspensão e sedimentos superficiais através de marcadores como coprostanol e LABs (Cabral *et al.*, 2018; Cabral and Martins, 2018). Em geral, os maiores valores encontrados estão na região próxima à cidade de Paranaguá. Além disso, testemunhos sedimentares mostraram aumento nas concentrações de coprostanol nas camadas superiores acompanhando o desenvolvimento desta cidade (Cabral *et al.*, 2019). Apesar disso, a baixa resolução espacial das amostras disponíveis nesses estudos não fornece informações suficientes para uma compreensão clara de suas fontes e dispersão, além de ignorar pequenas fontes urbanas pontuais.

Em relação à qualidade do ar estudos com o uso de biomonitores como liquens (Falcão *et al.*, 2020; Gurgatz *et al.*, 2017) e cascas de árvore (Gurgatz *et al.*, 2016, 2018) foram realizados no município de Paranaguá, identificando uma diferenças significativas na qualidade ambiental entre áreas residenciais e portuárias. Identificou-se também um contexto de injustiça ambiental, na qual os locais onde habitam indivíduos de baixa renda apresentaram os piores indicadores de contaminação (Gurgatz *et al.*, 2016).

Concentrações de dióxido de nitrogênio, amônia e PTS similares aos de localidades mais populosas ou com intensas atividades antrópicas foram identificados em Paranaguá (Souza *et al.*, 2020). As concentrações de benzeno, tolueno, etilbenzeno e xileno (BTEX) foram similares aos do porto de Nápoles, Itália, e ambos foram superiores aos do porto de Long Beach, Estados Unidos, o qual possui uma de redução de poluentes atmosféricos focada no uso de energia não proveniente de combustíveis fósseis (Sarmiento *et al.*, 2023).

Quanto aos materiais particulados, um trabalho identificou que a concentração de PM_{10} ultrapassou o seu padrão de qualidade do ar em vigência no Brasil em 12% dos dias monitorados (Santana; Moreira; Armani, 2020). Apesar disso, não se encontra na bibliografia científica até o momento, estudos que avaliem o $PM_{2.5}$ em Paranaguá.

3 OBJETIVOS

Este trabalho visa avaliar o estado de conservação recente do Complexo Estuarino de Paranaguá pela perspectiva da Química Ambiental, caracterizando as concentrações, a distribuição espacial e as fontes de emissão de diferentes poluentes ou marcadores químicos de introdução antropogênica.

Espera-se contribuir para o conhecimento relativo à identificação de fontes de contaminação química em áreas costeiras, zonas protegidas e territórios prioritários para a conservação da biodiversidade, constantemente sujeitos ao impacto ambiental proveniente do avanço de grandes projetos de desenvolvimento em seus arredores.

3.1 OBJETIVOS ESPECÍFICOS

Os objetivos específicos, bem como os respectivos itens desta Tese, são:

- Caracterizar a pressão antropogênica sobre o CEP utilizando HPAs como indicadores de qualidade ambiental (Capítulo I);
- Apontar as principais fontes de HPAs para o estuário (Capítulo I);
- Investigar possíveis focos e dinâmicas de contaminação por esgoto e suas fontes de emissão no CEP através de marcadores moleculares como os LABs (Capítulo II);
- Investigar o risco ambiental relacionado à poluição atmosférica na região, determinando as concentrações e as fontes de $PM_{2.5}$ no município de Paranaguá, Brasil (Capítulo III).

4 POLYCYCLIC AROMATIC HYDROCARBONS IN A NATURAL HERITAGE ESTUARY INFLUENCED BY ANTHROPOGENIC ACTIVITIES IN THE SOUTH ATLANTIC: INTEGRATING MULTIPLE SOURCE APPORTIONMENT APPROACHES

Este capítulo consiste no manuscrito intitulado "*Polycyclic aromatic hydrocarbons in a Natural Heritage Estuary influenced by anthropogenic activities in the South Atlantic: Integrating multiple source apportionment approaches*", produzido a partir da avaliação das concentrações de HPAs nos sedimentos do CEP.

A avaliação de HPAs em sedimentos é uma boa ferramenta para avaliar impactos antropogênicos em ecossistemas pois eles são traçáveis em relação a suas fontes, e o ambiente sedimentar provê uma relativa conservação das propriedades químicas das substâncias aderidas ao sedimento (Martins, 2005). Para isso podem ser empregadas diferentes técnicas de atribuição de fontes, em geral baseadas na diferença de massa molecular entre substâncias emitidas (como as razões isoméricas), ou na avaliação estatística da distribuição de substâncias em comum (como PCA ou PMF).

Considerando que o CEP está sob pressão de diferentes forças econômicas e políticas, ao mesmo tempo que abriga uma rica sociobiodiversidade em seu território, este trabalho buscou integrar as diferentes técnicas de atribuição de fontes de HPAs e a maior malha amostral já coletada na área de estudo, para caracterizar o impacto antropogênico sobre o estuário a partir de um indicador direto do avanço dos meios de produção, que é o consumo de combustíveis fósseis e biomassa.

Além dos HPAs, parâmetros sedimentares foram avaliados em 84 pontos distribuídos por todo o estuário. Os resultados apontam para baixas concentrações, que não apresentam risco ecológico até então, e mostram como projetos de conservação florestal refletem em uma boa qualidade ambiental para o estuário próximo.

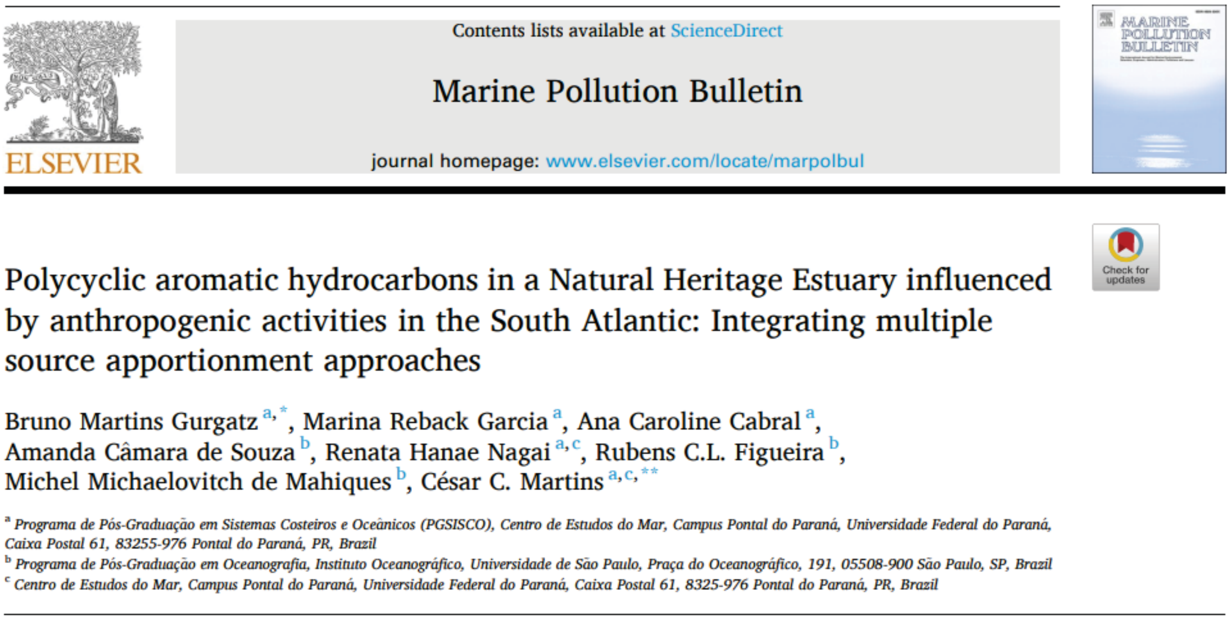
Apesar disso, a localização das concentrações mais elevadas se deu na desembocadura do rio Cachoeira, que é alimentado por uma bacia impactada por obras de conexão nos anos 1970, e explorada por atividades de agricultura intensiva antes do período de reflorestamento.

As fontes predominantes foram a queima de biomassa e de combustíveis fósseis, com uma contribuição pequena de fontes petrogênicas e da indústria do papel. Neste sentido, a fotografia que esta investigação nos dá é de um CEP pouco impactado neste Antropoceno inicial, mas que já apresenta indícios de que a atividade humana se tornou evidente na Geologia da Terra.

Este trabalho foi publicado no periódico "*Marine Pollution Bulletin*" (Fonte: Gurgatz et al. (2023).

) (Gurgatz *et al.*, 2023), com colaboração com pesquisadores do LabPaleo² e do Instituto Oceanográfico da Universidade de São Paulo, e pode ser acessado pelo link https://doi.org/10.1016/j.marpolbul.2023.114678.

FIGURA 6: CABEÇALHO DO ARTIGO PUBLICADO NO PERIÓDICO *MARINE POLLUTION BULLETIN*.



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Polycyclic aromatic hydrocarbons in a Natural Heritage Estuary influenced by anthropogenic activities in the South Atlantic: Integrating multiple source apportionment approaches

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FONTE: GURGATZ ET AL. (2023).

4.1 ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) were analysed in the sediments of one of the most well-preserved estuaries in South Brazil, the Paranaguá Estuarine System (PES), using several source apportionment tools. The ∑PAH ranged from < DL to 125.6 ng g^{-1} dw (dry weight) (average 29.9 ± 26.1 ng g^{-1} dw), and the lowest levels detected were similar to those found in other protected areas of the world. In general, the PAH concentrations indicated excellent environmental quality for the entire estuary. Principal component analysis indicated that fine sediments and total organic carbon were the main factors controlling PAH concentrations in the PES. Multiple PAH sources were identified in the study area; biomass burning and fossil fuel combustion predominated but considerable amounts of petrogenic residues were also observed. We identified evidence of a contribution from an adjacent watershed resulting from the construction of interconnections between large rivers and from years of intense deforestation in the local Atlantic Forest.

Keywords: anthropogenic impacts, sediment, protected areas, principal component analysis, chemical stressors.

4.2 INTRODUCTION

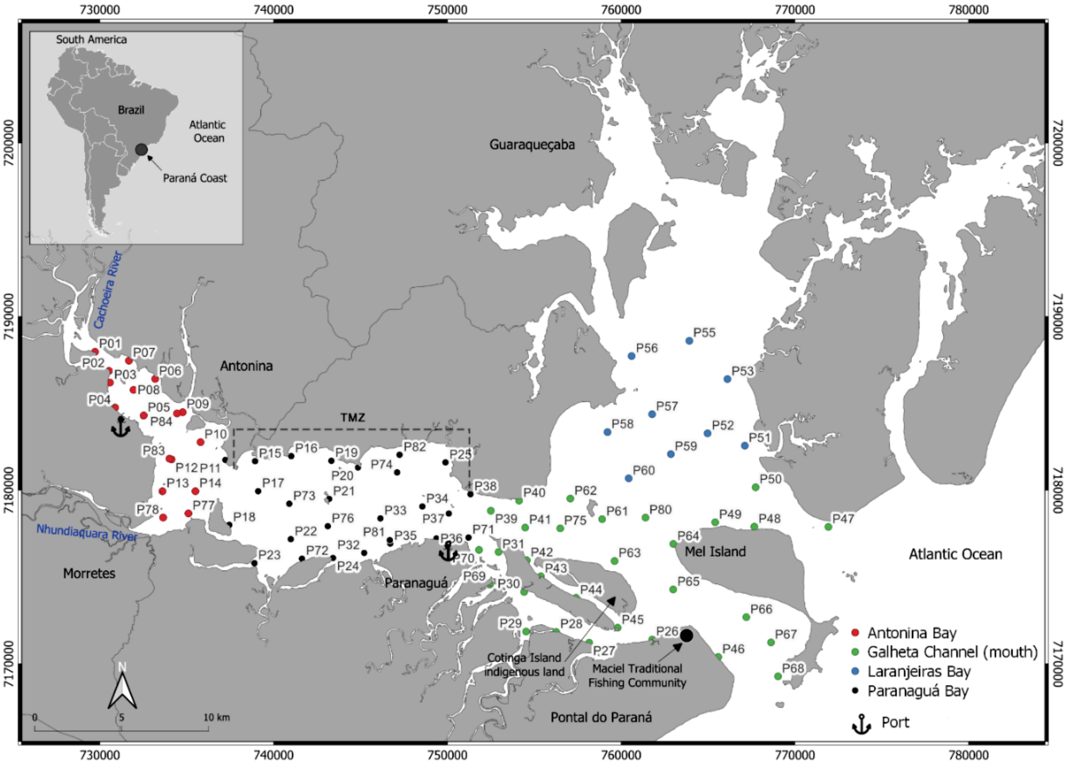
Chemical stressors are exogenous environmental compounds that can adversely affect ecological components (Norton et al., 1992; Lichtveld et al., 2018). The occurrence and deposition of chemical stressors in sediments can adversely affect public health and ecology and have profound socioeconomical implications (Botwe et al., 2017). Among environmental contaminants, polycyclic aromatic hydrocarbons (PAHs) are compounds of significant concern due to their toxicity and mutagenic, carcinogenic, and teratogenic effects on biota (Kim et al., 2013; Simão et al., 2020; Garcia and Martins, 2021). They can persist in the environment and have the potential to bioaccumulate and be transferred into the food web (Ukalska-Jaruga et al., 2019; Turja et al., 2020; Wang et al., 2021). Their hydrophobic properties and low degradation rates allow them to persist in aquatic environments, including sediments (Zhang et al., 2015). Not surprisingly, the occurrence of PAHs in estuarine sediments has been widely reported in various studies (as presented in the following sections).

Currently, the most significant fraction of PAHs emitted globally are derived from human activities. The largest contributions come from developing countries such as China, India, Indonesia, and Brazil due to the extensive use of coal and biomass fuels in Asian countries and due to deforestation fires in South America (Shen et al., 2013). In developed regions, such as Central Asia, North America, and Europe, the transportation sector (e.g., trucking, railroads, shipping) has been the main PAH source (Shen et al., 2013; Han et al., 2020b). Natural PAH sources include natural oil seepage and forest burning, volcanic eruptions, and diagenetic transformations of organic matter (Abdel-Shafy and Mansour, 2016; Lin et al., 2020).

Sediment PAH concentration assessment is an excellent tool for tracing anthropogenic impacts on ecosystems due to the various traceable sources of PAHs, such as fossil fuel combustion, plant biomass incineration, petroleum and related spillage (Abdel-Shafy and Mansour, 2016), and due to the specific characteristics of sediments, which are strongly related to sorption properties (Jesus et al., 2022). The main techniques used to perform source apportionment for PAHs in sediments are based on diagnostic ratios of selected PAH isomers, which allows researchers to form general distinctions between compounds of pyrolytic and petrogenic origins (Yunker et al., 2002; Chang et al., 2018; Garcia et al., 2019), and based on the use of sediment source fingerprinting through multivariate analysis, such as principal component analysis (PCA) (Stanimirova et al., 2005; Angeli et al., 2020a; Collins et al., 2020). Additionally, positive matrix factorization (PMF), a multivariate statistical method, is widely used to estimate pollutant sources in groups of samples (Paatero and Tapper, 1994; Norris et al., 2014; Pichler et al., 2021). Integration of isomer molecular ratios and multivariate analysis with good spatial resolution are the best methods for PAH source apportionment evaluations, especially in environments under increased human pressure. The coupling of these techniques is even more relevant in low-impact environments (e.g., Sutilli et al., 2019; Rose et al., 2020) since low PAH concentrations can make diagnostic ratios less effective (Dudhagara et al., 2016; Ranjbar Jafarabadi et al., 2017).

The Paranaguá Estuarine System (PES, Fig. 1) (48°25'W, 25°30'S), located in the South Atlantic, Brazil, is an extensive subtropical estuarine system formed by two major water bodies under distinct anthropogenic activity levels (Lana et al., 2001; Angeli et al., 2020b). Its estuarine margins are in direct contact with some of the last preserved areas of the Atlantic Forest, one of the richest biomes in terms of biodiversity in the world (Rezende et al., 2018; Claudino-Sales, 2019); this area is considered a World Heritage Site and Biosphere Reserve (UNESCO 1999, Claudino-Sales, 2019). On the other hand, port and industrial activities and the fast urbanization processes occurring in the region can threaten the conservation of these ecosystems and the environmental health of the estuary (Campos Neto et al., 2009; Beuren et al., 2018; Angeli et al., 2020b).

FIG. 1: MAP OF THE STUDIED AREA ON THE PARANÁ COAST, SOUTH ATLANTIC, BRAZIL. SURFICIAL SEDIMENT SAMPLING SITES COLOURED ACCORDING TO THE SECTOR TO WHICH THEY BELONG IN THE PARANAGUÁ ESTUARINE SYSTEM. PORTS, TMZ (TURBIDITY MAXIMUM ZONE), CITIES, TRADITIONAL COMMUNITIES AND MAIN RIVER NAMES ARE ALSO PRESENTED.



SOURCE: THE AUTHOR (2023)

The environmental quality of the PES has been investigated using chemical stressors such as trace elements (e.g., Angeli et al., 2020b), microplastics (e.g., Mengatto and Nagai, 2022), bioaccumulation features (Froehner et al., 2011), sewage (e.g., Cabral et al. 2018), and sediment transport (Mayerle et al., 2015; Cruz and Noernberg, 2020; Paladino et al., 2022). Petroleum hydrocarbons, including PAHs and aliphatic compounds, have been previously analysed (e.g., Martins et al., 2015; Cardoso et al., 2016). However, these studies had low sample sizes and did not use different approaches to PAH source apportionment; they mainly focuses on diagnostic ratios.

The region, known as the 'Paraná coast', is under pressure from economic and political forces to install a series of port infrastructure projects. Of these, at least 18 projects are already environmentally licenced; the aims of these projects are to expand agricultural production exports and provide spaces to support the exploration of Brazilian presalt oil reserves (Tiepolo, 2016, Góes et al., 2021). However, the advancement of infrastructure projects in territories of traditional communities may result in few economic and political advances (Haesbaert, 2015). In the study area, examples of these communities are the Guarani Mbya indigenous people and the ancient fishing community of Maciel, both threatened by port projects in Pontal do Paraná city (Onofre et al., 2018; Góes et al.; 2020).

The PES currently has a high conservation level. Therefore, the planned infrastructure projects and rapid urbanization of the surrounding territory provide opportunities to study how environmental impacts and ecosystem changes arising from different human activities result in complex chemical contamination. Additionally, the ecological, social, and economic importance of the PES make this a priority site for environmental research.

The aim of this study was to identify the human impact on a natural heritage estuary by integrating PAH diagnostic ratios and multivariate analysis using the most extensive sampling of surface sediments carried out in the PES to date. The objectives of the study were to (1) investigate the spatial distribution of sedimentary PAHs from a nonimpacted subtropical estuarine system; (2) identify whether PAH sources are directly linked to port activities, biomass and petroleum by-product burning and oil spills; and (3) provide an example of the use of diagnostic ratios in estuarine regions with low PAH concentrations.

4.3 MATERIAL AND METHODS

4.3.1 Study area

The PES (Fig. 1) is a South American subtropical estuarine environment that covers an area of 612 km² and hosts a water volume of approximately 2×10^9 m^3 (Lana et al., 2001). The system is classified as a wave-dominated estuary, with river-dominated bays and residual circulation vortices in the estuary mouth (Cruz and Noernberg, 2020; Paladino et al., 2022).

The salinity gradient is mainly controlled by tides and fluvial influence, with a gradual increase from the inner section to the mouth of the estuary. The residence time is approximately 3.49 days (Lana et al., 2001; Marone et al., 2005). Surface sediment grain size presents an increasing trend in fine sediment towards the inner portions of the PES, with a mean grain-size (in ϕ units) of 5.35 in Antonina Bay, 3.51 in Paranaguá Bay, 3.81 in the Galheta channel, and 5.07 in Laranjeiras Bay (Angeli et al., 2020b). The turbidity maximum zone (TMZ) is present in Paranaguá Bay. The mixture of continental and marine waters is responsible for several depositional processes, erosion, and the resuspension of particulate matter (Angeli et al., 2020b).

The northern (N–S) axis, which hosts Laranjeiras Bay, is surrounded by the main ecological corridor of the Atlantic Rainforest. The region is considered one of two Brazilian 'hotspots' for biodiversity conservation priorities because many endemic species are present and exceptional loss of habitat has occurred (Rezende et al., 2018). The diversity of mammals, endemic microfauna, birds, and woody plants per hectare potentially exceeds the values of the Amazon biome (Myers et al., 2000; Colombo and Joly, 2010, Claudino-Sales, 2019). The Atlantic Rainforest has less than 7% of its original area and has become one of the world's most threatened biomes, mainly due to the fragmentation of its habitats. Due to these characteristics, a system of conservation units was established with 29 areas divided between the states of São Paulo and Paraná, including a mountain chain, peaks, hills, valleys, and coastal areas (Claudino-Sales, 2019).

A large part of the margin of the western (E–W) axis, which hosts Paranaguá and Antonina Bays, is also occupied by these forest remnants; however, it is characterized mainly by two port terminals: Paranaguá and Antonina. The Paranaguá Port is the largest in South Brazil and is of great economic importance due to its role in the transport of Brazilian soybeans to China (de Lima et al., 2018). Since 1970, Paranaguá port has received massive investments due to the importance of Brazilian soybean production; the port has emerged as a leader in this sector, leading to the emergence of an urban agglomerate, an industrial fertilizer complex, and a petrochemical terminal in its surrounding areas (Campos Neto et al., 2009; Beuren et al., 2018).

4.3.2 Sampling and preliminary procedures

The sampling of superficial sediments (0-3 cm) was performed in March 2018 using a stainless steel Van Veen grab. A total of 84 samples were collected, which were distributed between the two axes of the PES, as shown in Fig. 1. The sediments were frozen (−20 °C) after sampling, freeze-dried, carefully homogenized with a mortar and pestle, and stored in clean glass jars until PAH analysis.

4.3.3 Bulk parameters

The grain size of the sediment samples, as presented by Angeli et al. (2020b) and Paladino et al. (2022), was determined for the total dried sediment by a Malvern Hydro 2000 instrument. Two grams of each sample sediment was used, and it was predecarbonated with hydrochloric acid 10% and 25% sodium hexametaphosphate. The organic matter was removed with 30% hydrogen peroxide. The results are presented as fine sediments, calculated as the percentage (%) of the sum of silt (3.9 to 62.5 μm) and clay (0.24 to 3.9 μm) fractions. Bulk organic matter (total organic carbon: TOC, and total nitrogen: TN) was determined using a Costech elemental analyser.

4.3.4 Laboratory and instrumental analyses of PAHs

The analytical procedure for PAH analysis was based on the United Nations Environment Program method (UNEP, 1992) with the adaptations described in Wisnieski et al. (2016). Approximately 20 g of dry sediment was Soxhlet extracted over 8 h using 80 mL of a mixture of dichloromethane (DCM) and *n*-hexane (1:1, v/v). Activated copper was added to remove elemental sulfur. A standard surrogate mixture of deuterated compounds (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) was added before each blank and sample extraction. The DCM/*n*-hexane extract was purified by liquid adsorption column chromatography using 5% deactivated alumina (1.8 g) and silica (3.2 g). Elution was performed with 10 mL of *n*-hexane to obtain fraction 1 (containing aliphatic hydrocarbons and petroleum biomarkers, not discussed in this study) and 15 mL of a mixture of DCM and *n*-

hexane (3:7, v/v) to obtain fraction 2, which contained the PAHs. The concentrated extract (500 μL) was stored in glass vials. Before gas chromatographic analysis, an internal standard (benzo[*b*]fluoranthene-d_{12}) was added.

Instrumental analyses of PAHs were performed with a gas chromatograph (Agilent Model 7890A) coupled to a mass spectrometer (Agilent 5973 N inert MSD with Triple-Axis Detector) using a fused silica capillary column (30 m, 0.25 mm internal diameter, 0.25 μm film thickness) coated with 5% diphenyl/dimethyl siloxane. A 2 μL aliquot of PAH extracts was injected in splitless mode at an injector temperature of 280 °C. The oven temperature was programmed to ramp up 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 and the ion source were conditioned at 300 °C and 230 °C, respectively. Data acquisition was performed in selected ion monitoring (SIM) mode.

Individual PAHs and their abbreviations (listed in Table S1, 'S' denotes Supplementary Information) were identified by matching their ion mass fragments (m/z) and retention times with those from a standard mixture (Z-014G-FL, AccuStandard, USA). The calibration range used in the quantification was 0.10 to 2.00 ng μL^{-1}.

The analysed compounds, as well as their specific groups categorized as low molecular weight (LMW, N = 8 compounds), high molecular weight (HMW, N = 14), alkyl PAHs (N = 32), and natural (N = 2) compounds, are also summarized in Table S1. $\sum_{16}$PAH refers to the 16 priority pollutant PAHs listed by the US EPA (Wang et al. 2008), and ∑PAH refers to the sum of 22 parental and 32 alkylated PAH molecules, excluding perylene and retene. The PAH concentrations are expressed as ng g^{-1} of sediment dry weight (ng g^{-1} dw).

4.3.5 Quality assurance procedures

The instrumental detection limit (DL) was 0.50 ng g^{-1} dw for PAHs, defined based on the lowest concentration of PAHs (0.02 ng μL^{-1}), multiplied by the final extraction volume (500 μL), divided by the dry sediment mass (20 g) weighed prior to extraction. Blanks were performed for each extraction batch of 11 samples and did not show interferences in the analyses of the target compounds (i.e., detected levels higher than 3 x DL). The recovery of surrogate standards was acceptable (Table S2). Naphthalene-d_8 presented low recovery (31.0 ± 7.9%), as reported in previous studies (e.g., Zhang et al., 2008; Pichler et al., 2021), due to the volatility of this low molecular weight surrogate. Repeatability was assessed by triplicate analysis of the sediments, and the relative standard deviation ranged between 2.7 and 10.5%

for the analysed compounds. The mean individual recoveries between the different PAHs from the standard mixture were 91 ± 13% and 91 ± 9% in the spiked sediments and blanks, respectively (Table S3). The sediment reference material (IAEA-417; International Atomic Energy Agency) analyses displayed at least 80% of the 16 pollutant priority PAHs listed by the US EPA within acceptable concentration ranges (Table S4).

4.3.6 Data analysis and source apportionment

Statistical analysis was carried out and graphing was performed using the software R (R Core Team 2021) and JASP (JASP Team 2021). Interpolation and spatial analysis were developed using QGIS Development Team 2022. Due to a lack of normality, data were subjected to Spearman's correlation test.

The three diagnostic tools were applied to estimate sedimentary PAH source apportionment as follows:

(1) Diagnostic ratios presented by Yunker et al. (2002) and Tobiszewski and Namieśnik (2012) involving individual isomers and grouped compounds were applied to verify the prevalence of specific pyrolytic or petrogenic sources in the PES samples. Since PAHs are emitted as a complex mixture containing different structural isomers, the relative concentration ratios of PAH molecular isomers provide a qualitative approach for distinguishing a given emission source due to their environmental fate processes. Table S5 presents the diagnostic ratios investigated in this study as well as the corresponding sources. The results were investigated for source predominance as well as geographic distribution.

(2) Principal component analysis (PCA) (e.g., Johnson et al., 2007) was used for source apportionment and determination of potential factors affecting PAH distribution. It included individual PAH molecules (Aceph and DBT were removed due to < LD in all samples) to rationalize PAH occurrence in each sector and suggest source apportionment patterns. Sediment bulk parameters (TOC, TN, and fine sediments) were included in this analysis to elucidate the environmental factors related to PAH distribution.

(3) The positive matrix factorization mathematical receptor model (PMF) (Paatero and Tapper, 1994; Norris et al., 2014) serves as an environmental forensics tool, and it was used to quantify the contribution of various sources to the total PAH concentrations; the variables in the datasets were reduced to source types and source contributions. The model was explored for 3 to 5 factors. The run containing 4 factors exhibited the best fit and the most suitable solution to elucidate the sources of PAHs and was chosen to explain the results of this work.

The parameters used were a non-random start (seed: 1, for replicability) and a running number of 20 (Sun et al., 2020; Yuan et al., 2021), and S/N <1 was classified as weak (BbC, BcA, Ant, DBA, Flr, Ace, BP). Acenaphthene and dibenzothiophene were removed because it was < DL in all samples.

Each of the methods was explored independently. Then, an interpretation was carried out based on the potential sources of the area, the profiles generated by the apportionment models and the environmental history of the basins that form the PES.

Sediment quality thresholds, which are defined for $\sum_{16}$PAH, were assessed considering the threshold effect levels (TELs) and probable effect levels (PELs), which were based on the probability of deleterious effects on the biota (Long, 2006; Buchman, 2008; Pichler et al., 2021). In addition, US NOAA's ERM (Effect Range-Median) and ERL (Effect Range-Low) Sediment Quality Guidelines (Long et al., 1995) were also considered, which were based on the toxicological responses of benthic organisms.

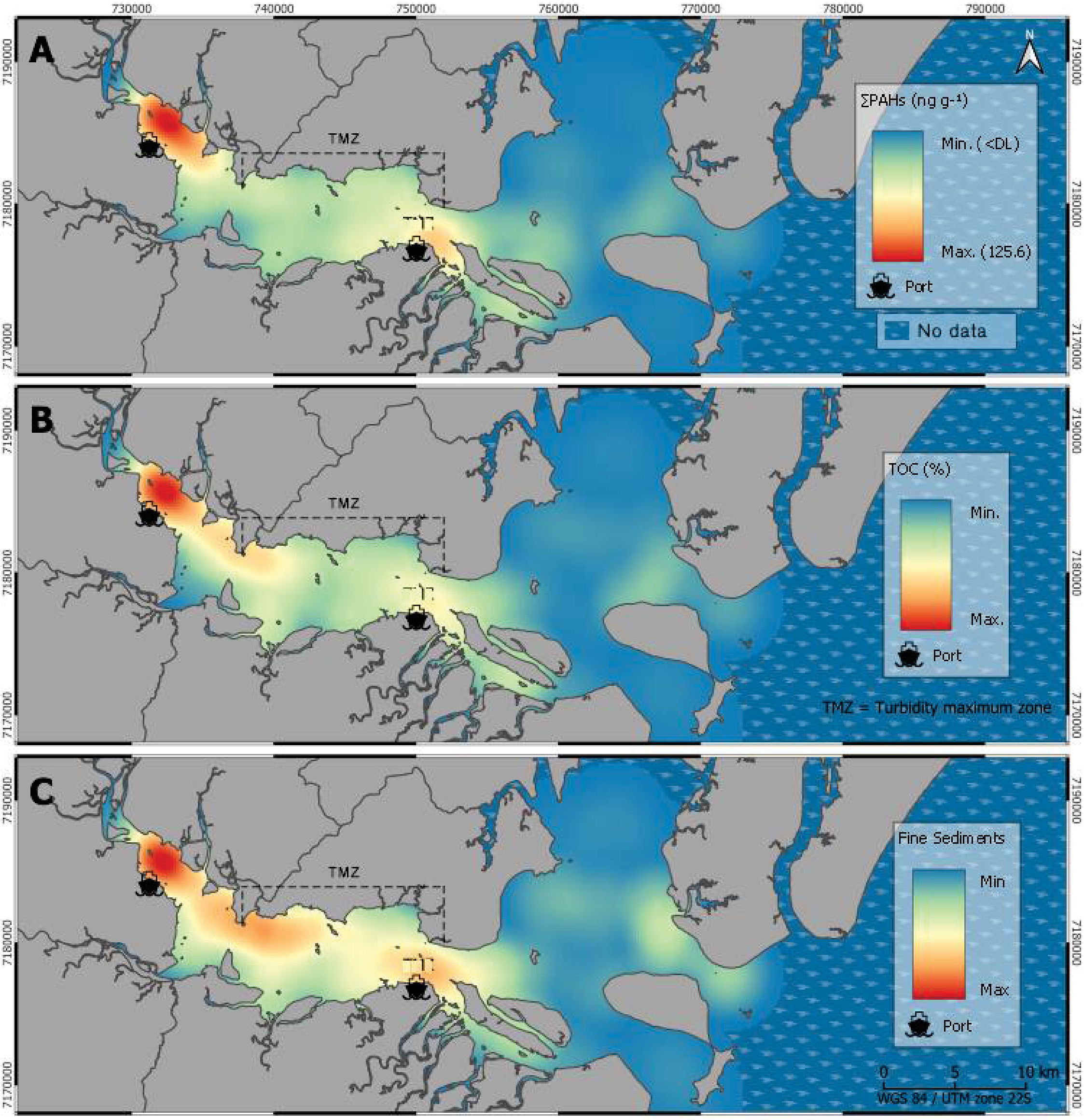
4.4 RESULTS

4.4.1 PAH concentrations, spatial distribution, diagnostic ratios and ecological risk assessment

The concentration of $\sum$PAH in the PES ranged from < DL to 125.6 ng g^{-1} dw, with an average of 29.9 ± 26.1 ng g^{-1} dw, almost double the value found for $\sum_{16}$PAH (15.7 ± 15.5 ng g^{-1} dw, with a maximum of 83.1 ng g^{-1} dw).

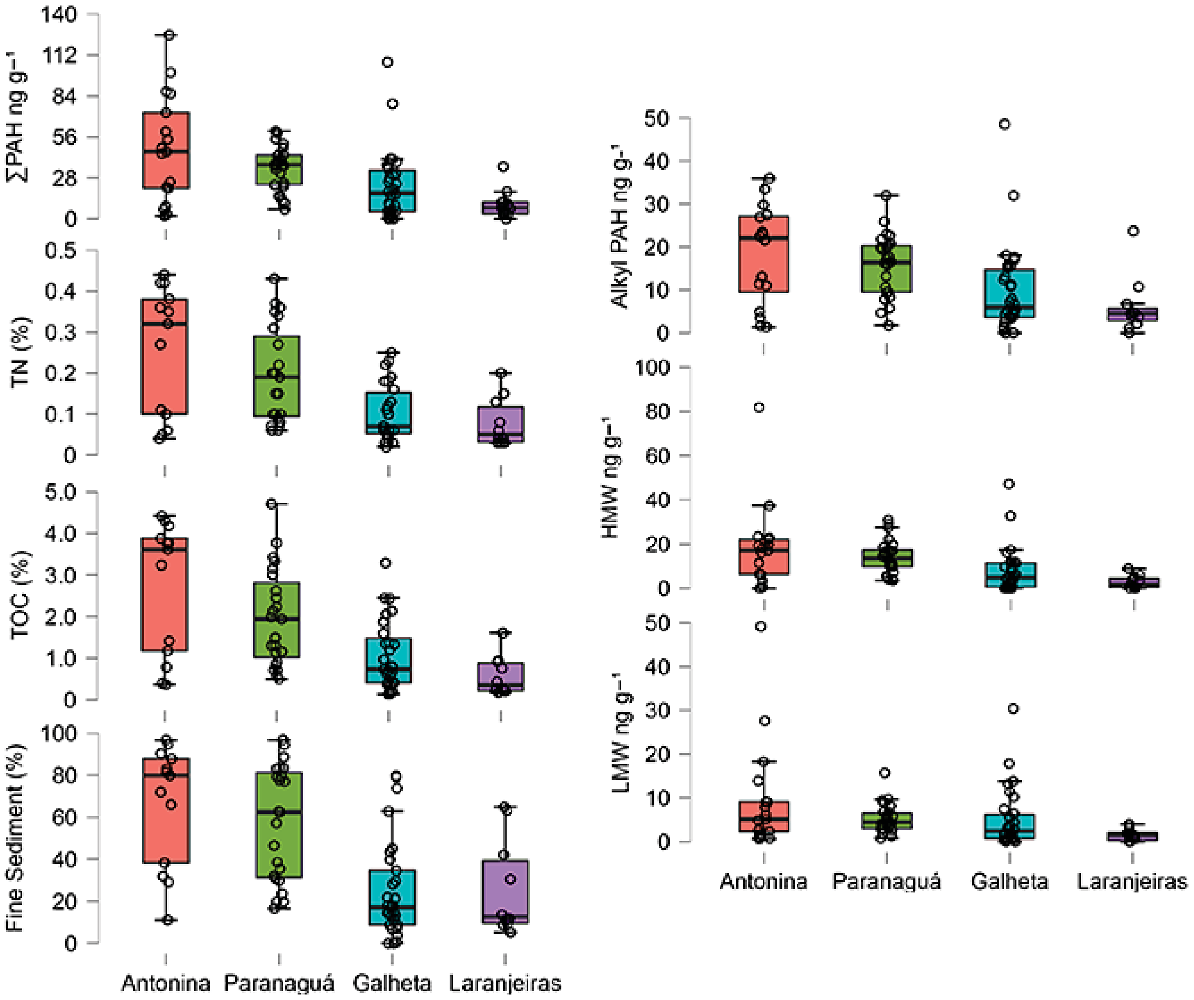
The grouped PAH distribution presented similar concentrations of alkylated (13.2 ± 10.8 ng g^{-1} dw) and HMW (4–6 ring PAHs) (11.2 ± 12.4 ng g^{-1} dw) PAHs, while LMW (2-3 ring PAHs) compounds presented the lowest average concentration (5.5 ± 7.4 ng g^{-1} dw). The highest concentrations of $\sum$PAH and selected groups (LMW, HMW, and alkyl PAHs) were recorded in Antonina Bay on the western side of the PES (Fig. 2; Fig. S1), followed by the Paranaguá Bay, Galheta channel, and Laranjeiras Bay sectors (Fig. 3). The same pattern was also observed in TOC, TN, and grain size (referred to in this work as fine sediments, which is the sum of silt+clay fractions), and a high positive correlation ($\rho > 0.70$, *p value* < 0.001) between these variables was obtained (Table S6 and Fig. S2). In addition, there was a slight spatial difference in the distribution of LMW (Fig. S1); it was slightly higher in the area near the Cotinga Island margins.

FIG. 2: COMPARISON OF INTERPOLATED SPATIAL DISTRIBUTION OF A: ∑PAH (ng g^{-1}), B: TOC (%) AND C: FINE SEDIMENTS (%) IN THE PARANAGUÁ ESTUARINE SYSTEM SURFICIAL SEDIMENTS.



SOURCE: THE AUTHOR (2023)

FIG. 3: BOXPLOT DISTRIBUTION OF $\sum$PAH, TN, TOC, FINE SEDIMENT, ALKYL, LMW AND HMW PAHS IN SEDIMENT SAMPLES OF THE PARANAGUÁ ESTUARINE SYSTEM SECTORS (ANTONINA BAY, PARANAGUÁ BAY, GALHETA CHANNEL AND LARANJEIRAS BAY).

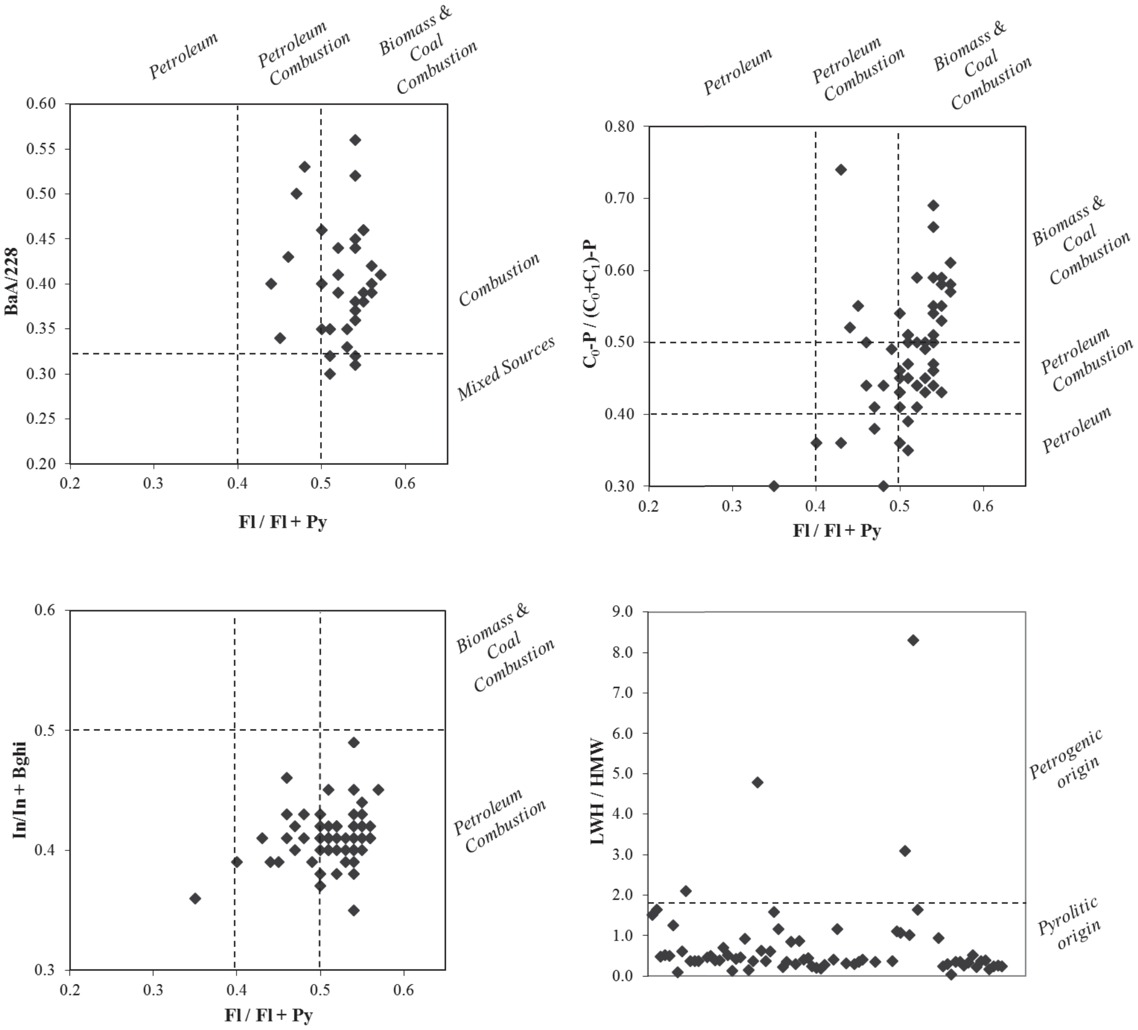


SOURCE: THE AUTHOR (2023)

The diagnostic ratios (Fig. 4 and Table S5) of individual PAHs were calculated. Fig. S3 presents the distribution of the ratios by sample site. The results indicate a predominance of PAHs from pyrolytic sources but differ with respect to the source material (predominantly from oil combustion for In/(In+Bghi); mixed combustion sources for C_0/C_0+C_1-P/A; and biomass burning for BaA/228 and Fl/Fl+Py).

Sediment quality thresholds established for $\sum_{16}$PAH based on the toxicological responses of benthic organisms are presented in Table S7. Except for Naph, which exceeded the TEL at site P9, all PES levels were below the thresholds.

FIG. 4: PAH DIAGNOSTIC RATIOS USED TO INFER THE SOURCES OF PAHS IN THE SURFICIAL SEDIMENT SAMPLES FROM THE PARANAGUÁ ESTUARINE SYSTEM. MORE INFORMATION ON EACH DIAGNOSTIC RATIO IS AVAILABLE IN TABLE S3.

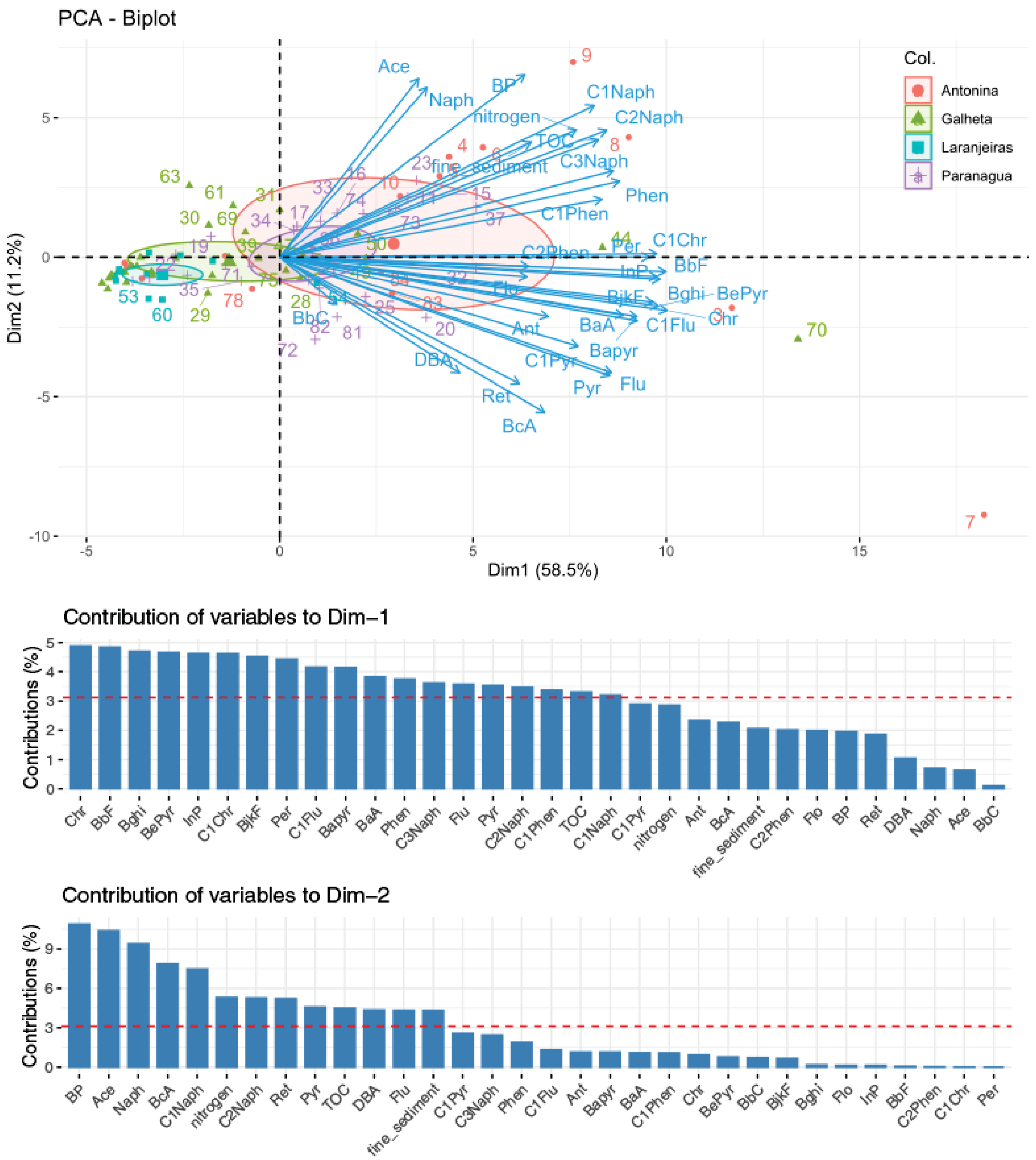


SOURCE: THE AUTHOR (2023)

4.4.2 Source apportionment based on principal component analysis and positive matrix factorization

The PCA biplot for the two dimensions with the highest explained variance (69.7%) of the compounds in the PES samples is presented in Fig. 5.

FIG. 5: PRINCIPAL COMPONENT ANALYSIS BIPLOT BASED ON TOTAL ORGANIC CARBON (TOC), TOTAL NITROGEN (TN), FINE SEDIMENTS AND THE RELATIVE ABUNDANCE (%) OF EACH INDIVIDUAL PAH DETECTED AT THE SAMPLED SITES OF THE PARANAGUÁ ESTUARINE SYSTEM SEDIMENTS AND INDIVIDUAL CONTRIBUTIONS FOR DIMENSION 1 AND 2. A LIST OF PAH ABBREVIATIONS IS AVAILABLE IN TABLE S1.



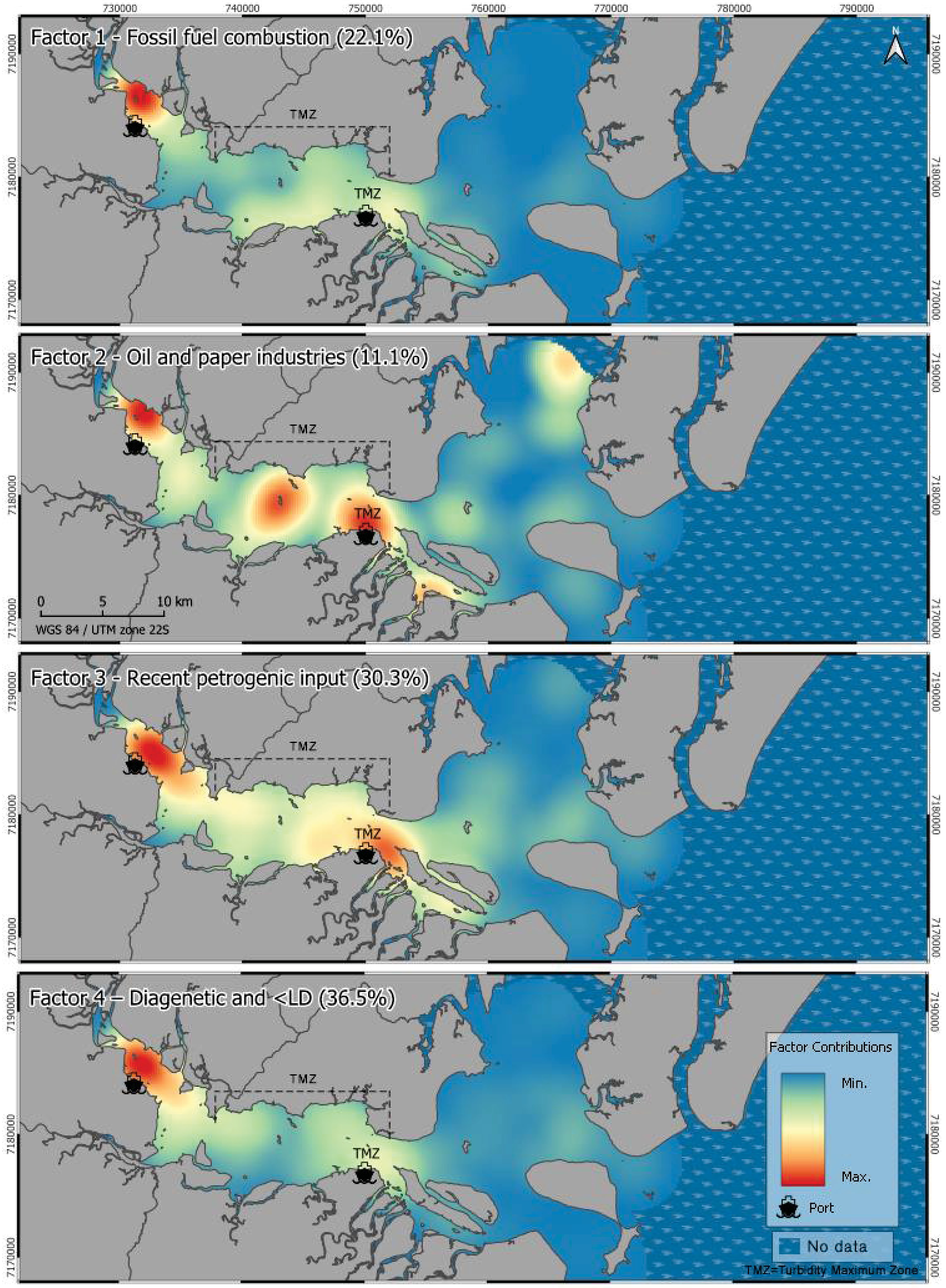
SOURCE: THE AUTHOR (2023)

Dimension 1 (58.5% of explained variance) elucidates the environmental factors affecting PAH distribution. This result corresponds to the overall levels of individual PAH concentrations, following TOC and fine sediments, confirming these as main factors affecting PAH distribution in the PES. The highest values of these variables (PAHs and bulk data) are directly related to sampling sites from Antonina Bay. The PCA also reveals that the clusters of samples located in Laranjeiras Bay and at the mouth of the estuary (Galheta channel) are on the negative side of the scale and are negatively related to all variables; the sediments are coarser and have lower TOC, and consequently, lower PAH concentrations.

Dimension 2 (11.2% of explained variance) corresponds to two different groups from different sources (pyrolytic/biogenic *vs.* petrogenic compounds). The positive Axis 2 shows the group characterized by LMW PAHs, such as naphthalene and its alkylated homologues, which are related to samples located in the innermost part of Antonina Bay (i.e., P4, P6, P8, and P9). Thus, the region with the highest average concentration of PAHs in the PES (Antonina Bay) has a predominance of compounds related to oil (LMW PAHs) (Yunker et al., 2002). The Ret and C_2Phen distribution in the PCA in Dimension 2 followed compounds from anthropogenic sources, and we can assume that the occurrence of this compound in the PES sediments may be related to the paper cutting sector of industries and to pulp mill effluents. HMW PAHs such as Flu, BcA, Pyr, and DBA are prevalent in the negative quadrant of Dimension 2. Most of the representative samples in the negative axis of Dimension 2 are located close to the urban area of Paranaguá, such as sites P20, P70, P72, and P81, which are in the Galheta channel category but are close to the Itiberê River, the main urban river crossing Paranaguá city. This result suggests the presence of PAHs from pyrolytic sources originating from the urban areas and port activities of Paranaguá city. Site P7, located in Antonina Bay, can be considered an outlier, as shown in Fig. 3, for the LMW and HMW PAH box plots.

The PMF model source types and contributions were defined by the interpretation of the four generated factors presented below. The factors (Fig. S4) and their distributions (Fig. 6) were interpreted as follows:

FIG. 6: COMPARISON OF THE INTERPOLATED SPATIAL DISTRIBUTION OF FACTOR CONTRIBUTIONS EVALUATED IN THE POSITIVE MATRIX FACTORIZATION MODEL FOR THE PAH CONCENTRATIONS IN THE PES.



SOURCE: THE AUTHOR (2023)

- Factor 1 (Fossil fuel combustion): related to the negative quadrant of the PCA (Fig. 5). Flu, Pyr, DBA, and BcA influenced this factor, and it represented pyrolytic sources from the combustion of fossil fuels in urban and port areas (Yunker et al., 2002; Du and Jing, 2018, Pichler et al., 2021). These compounds were grouped similarly, as they were found in the negative quadrant of Dimension 2 of the PCA. Their distribution extends along Paranaguá Bay, reaffirming the role of fossil fuel combustion in the urban area.
- Factor 2 (Oil and Paper industries): presents a significant contribution of Alkyl-PAHs such as C_1Phen, C_1Pyr, and C_1Flu, which indicate petrogenic sources from runoff or oil spills (Pedrete et al., 2017).
- Factor 3 (Recent petrogenic input): the residual compounds are LMW PAHs (Naph, BP, Aceph) related to petrogenic input (Yunker et al., 2002, Yuan et al., 2021).
- Factor 4 – Diagenetic and <LD: characterized as diagenetic by the substantial contribution of Per (as confirmed by the % perylene/∑(5 ring PAHs) ratio shown in Fig. S3F) (Neff et al., 2005; Pichler et al., 2021), and <LD the due the high contribution of Flr, Ant, and BbC, which are compounds that presented multiple <LD levels, which led to a grouping of these variables in this factor.

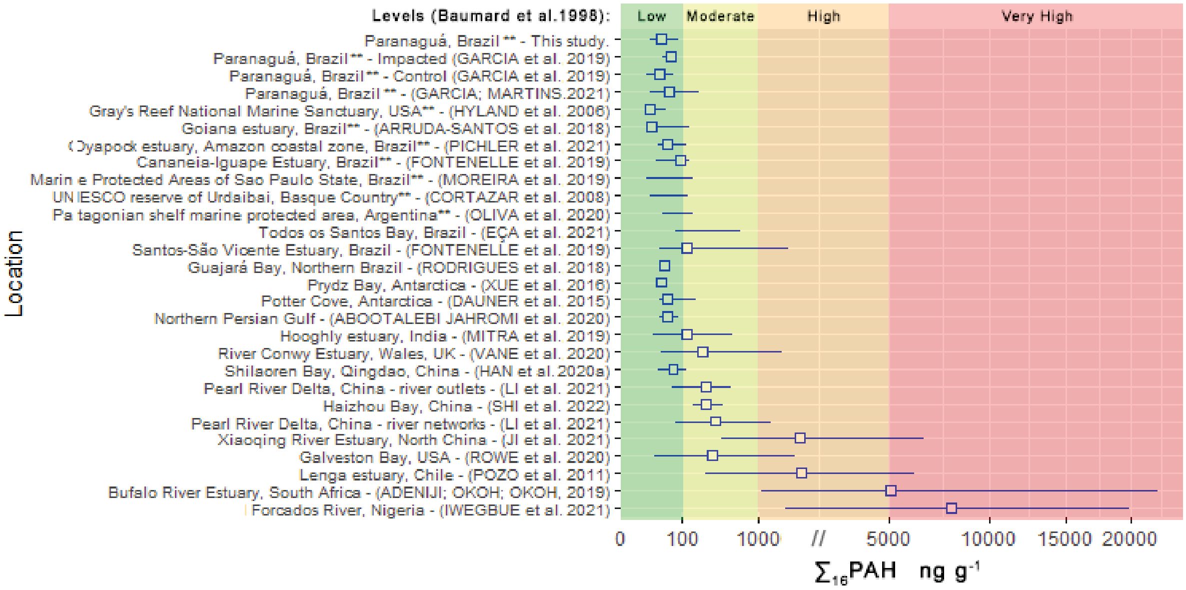
The diagenetic process is the factor that contributes most to the total variance (36.5%), and it is characterized by the widespread presence of Per throughout the estuary. Recent petrogenic inputs (30.3%) are probably related to the use of fuels for navigation, which results in chronic contamination from small oil spills. Fossil fuel combustion (22.1%) and petrol and paper industries (11.1%) were also identified as source factor profiles, and this demonstrates model accuracy at identifying even smaller sources, such as the paper industries.

4.5 DISCUSSION

4.5.1 PAH concentrations and spatial distribution and ecological risk assessment

The $\sum_{16}$PAH concentrations are similar to those detected in the Oyapock estuary on the Amazon coast, a preserved ecosystem with several conservation units in the region (Pichler et al., 2021), and in other environmental protected areas, such as Grey's Reef National Marine Sanctuary in the USA (Hyland et al., 2006), the Cananeia-Iguape estuary in Brazil (Fontenelle et al., 2019) or the Patagonian Shelf in Argentina (Oliva et al., 2020). In addition, the $\sum_{16}$PAH mean levels were also similar (Garcia et al., 2019) or lower (Garcia and Martins, 2021) than those found in the pristine mangrove areas of the PES, suggesting that, in general, PES surface sediments present low levels of hydrocarbon contamination. More examples of $\sum_{16}$PAH concentration ranges in estuarine environments, in addition to those with environmental protection (highlighted with **), are presented in Fig. 7, and these emphasize the low levels of $\sum_{16}$PAH recorded in the present study. Therefore, most $\sum$PAH concentrations recorded in the PES can be classified as 'Low' based on surface sediment PAH pollution levels, as proposed by Baumard et al. (1998), except for three sampling points (P7 = 125 ng g^{-1} dw; P70 = 107 ng g^{-1} dw and P9 = 100 ng g^{-1} dw), which barely exceeded the maximum value for this classification (100 ng g^{-1} dw).

FIG. 7: CONCENTRATION RANGES FOR $\sum_{16}$PAH (ng g^{-1} dw) IN SEVERAL ESTUARINE ENVIRONMENTS WORLDWIDE AND THEIR RESPECTIVE CONTAMINATION LEVELS AS PROPOSED BY BAUMARD ET AL. (1998): LOW = 0-100 ng g^{-1} dw, MODERATE = 100-1000 ng g^{-1} dw, HIGH = 1000-5000 ng g^{-1} dw, AND VERY HIGH = > 5000 ng g^{-1} dw. LOCATIONS NAMES AS DESCRIBED IN THE STUDIES. **FULLY PROTECTED OR SURROUNDED BY PROTECTED AREAS.



SOURCE: THE AUTHOR (2023).

Some examples of estuarine environments with $\sum_{16}$PAH concentrations above those found in this study are the Buffalo River Estuary in South Africa (Adeniji et al., 2019) and the Forcados River in Nigeria (Iwegbue et al., 2021), and both have pyrogenic PAH sources from runoff and industrial effluents. Additionally, the Xiaoqing River Estuary in China (Ji et al., 2021) and Galveston Bay in the USA (Rowe et al., 2020) are characterized by oil spillages from the wharf, and the River Conwy Estuary in the United Kingdom (Vane et al., 2020) and the Lenga Estuary in Chile (Pozo et al., 2011) have PAHs with pyrolytic origins. Moreover, the levels of $\sum_{16}$PAH found in the PES were considerably lower than those found in the Santos-São Vicente Estuary, Southeast Brazil, which hosts the largest port and petrochemical industrial complex in Brazil (Fontenelle et al., 2019), and in the Todos os Santos Bay, Northeast Brazil (Venturini et al. 2004).

TOC is often recognized as a variable that most influences PAH distribution in estuarine environments (e.g., Ranjbar Jafarabadi et al., 2017), and this was confirmed in the present study as a high positive and significant correlation was observed between TOC and $\sum$PAH (Fig. S2, Table S6) and they had similar spatial distributions (Fig. 2). Thus, the relatively low PAH levels in the PES may be partially explained by the low mean sedimentary TOC content. Regarding Antonina Bay, in addition to high TOC levels, the presence of high percentages of fine sediments at the inner sector of the PES may also contribute to the high concentrations of PAHs in these areas.

The sediment transport dynamics in the estuary are the result of the interactions between sediment sources (river discharge input from Serra do Mar sediments) and hydrodynamic patterns (deposition of finer sediments in the TMZ, resuspension and mixing due to vortices in the estuary mouth) (Cruz and Noernberg, 2020; Paladino et al., 2022). The riverine sediment transport direction is towards the centre of the estuary, and marine sediment influence from oceanic forcings also occurs in the direction of the centre of the estuary (Paladino et al., 2022). The preferential sediment depositional area located in Antonina Bay is related to contributions from the Cachoeira River, the main regional waterway that discharges water and sediments into the E–W axis of the PES (average water discharge of 21.13 $m^3 s^{-1}$) (Lana et al., 2001; Cattani and Lamour, 2016). Moreover, Cabral and Martins (2018) suggested that the TMZ in the mixture zone (between Antonina and Paranaguá Bays) can act as a sediment deposition trap and may promote the accumulation of PAHs in this sector. Angeli et al. (2020a) and Combi et al. (2013) identified the region on the opposite margin of Paranaguá Port as a potential area of pollutant accumulation. Our study confirms these trends but identifies Antonina Bay as the first 'hotspot' for PAH accumulation, followed by the region on the opposite margin of Paranaguá Port, similar to the distribution of trace and major metals from terrigenous sources (Angeli et al., 2020b).

Therefore, the results reaffirm the role of sedimentary variables related to organic matter (represented by TOC and TN) and grain size as major factors that determine the distribution of PAHs in the PES, and these are controlled by fluvial input and the geomorphology of the estuary (Cardoso et al., 2016; Garcia and Martins, 2021). The similar distribution of the different groups of compounds (alkyl, LMW, and HMW PAHs) also suggests similar sources in all bays inside the PES, but the intensities were different. The Games-Howell post hoc comparison test (for nonparametric data) revealed that the mean value of ∑PAH was significantly different between the Antonina and Laranjeiras Bays samples and between Paranaguá and Laranjeiras, showing a decreasing gradient of concentrations following the order: Laranjeiras Bay ≈ Galheta channel < Paranaguá Bay ≈ Antonina Bay (Fig. 3).

The sedimentation characteristics of Antonina Bay were historically influenced by two different processes: 1) the interconnection of the Capivari River Basin to the Cachoeira River for the construction of a hydroelectric plant in the 1970s, which increased river flow by 50%; and 2) the high rates of deforestation in the region between the 1960s and 1980s, which promoted an increase in terrestrial material and, consequently, in the sedimentary input

(Odreski et al., 2003; Wilhelm et al., 2023). It is suggested that such transformations resulted in the high rate of sedimentation in Antonina Bay (2.6 cm y^{-1}, Odreski et al., 2003) and were fundamental to shaping the spatial distribution of PAHs in the PES.

The $\sum_{16}$PAH concentrations in the PES probably do not induce deleterious effects and toxicological responses on benthic organisms. Nevertheless, continuous monitoring is strongly recommended, especially in areas of high PAH deposition, because PAH mixtures can cause adverse biological effects on organisms even at low concentrations (Li et al., 2021).

4.5.2 Source apportionment based on multiple approaches

Diagnostic ratios of individual PAHs indicate a predominance of PAHs from pyrolytic sources but indicate differences in the source materials (essentially oil combustion sources and biomass burning). Mixed sources are also reported because alkylated PAHs are frequently related to petrogenic sources and HMW PAHs are related to pyrolytic sources (Overton et al., 2016; Yang et al., 2018). The low concentrations of LMW can be explained by the fact that these molecules are less hydrophobic and more bioavailable than HMW. Cardoso et al. (2016) found that LMW PAHs in the PES are more dominant in the suspended particulate material. A matrix that provides a short period of time between emission and analysis allows for less degradation or assimilation by organisms; thus, the compounds present on these matrices consist of recently emitted compounds. The ‘bell’ shaped distribution of the relative distribution of Alkyl-naphthalenes (Fig. S5) also suggests recent petrogenic input (Neff et al., 2005; Pedrete et al., 2017), and this type of profile is widely observed in Paranaguá and Antonina Bays, suggesting navigation-related inputs. The significant contribution of alkyl-PAHs is evident in the region of Laranjeiras Bay and may represent inputs coming from small fishing communities in Guaraqueçaba city. The contribution of these compounds is similar to that of Ret (Oikari et al., 2002; Peixoto et al., 2019) and C_2Phen (Chalbot et al., 2006), which suggests industrial sources since these compounds indicate contamination from paper industries, which are present in the area of the Paranaguá port.

HMW PAHs such as Flu, BcA, Pyr, and DBA are associated with emissions from the incomplete pyrolysis of fuels and biomass (Yunker et al., 2002). The inputs of HMW PAHs in the Cachoeira River watershed are associated with agricultural activities such as biomass burning during deforestation processes combined with fossil fuel combustion by agricultural and transportation machinery. These compounds began to be introduced to the system when watercourse changes and deforestation were carried out in the 1960s to 1980s (Odreski et al., 2003). After these compounds are emitted to the atmosphere, they can be deposited in soils and carried to water bodies through drainage during heavy storms; this phenomenon was also found in two Brazilian estuarine systems impacted by sugarcane production (Maioli et al. 2010).

Pyrolytic inputs from vehicle traffic in urban centres and from port activities in the PES are also expected, mainly from the cities of Paranaguá and Antonina. Paranaguá has pyrolytic emissions from different sources. Gurgatz (2018) identified road transport as the primary source of atmospheric soft particulate matter, and the highest concentrations were observed on days when the wind blew from the port area. In addition, marine transport and solid waste incineration are also possible sources of PAH emissions in the region. This information, combined with the direction and intensity of the prevailing wind (up to 2.15 m s^{-1}) from the port area to the middle estuary (Terassi et al., 2019), suggests the possibility of contaminant inputs into the Antonina watershed from Paranaguá port activities via atmospheric routes.

Retene, a 3-ring PAH commonly associated with natural or diagenetic sources (Kong et al., 2021), has also been associated with surface sediments contaminated by resin acids from pulp mill effluents (Oikari et al., 2002; Peixoto et al., 2019). Its distribution in the PCA was consistent with compounds from anthropogenic sources, and we can assume that the occurrence of this compound in the PES sediments may be related to pulp and paper industries in the Paranaguá port complex. Similarly, C_2Phen compounds are associated with the paper cutting sector in industries (Chalbot et al., 2006) and are related to the Ret distribution in this analysis. Finally, Perylene was confirmed to originated from a natural (diagenetic) source at all sites based on the ratio between Per and the sum of 5-ring PAHs (Fig. S3F).

Three different approaches were used to estimate the sources of PAHs for the surface sediments of the PES. These approaches were shown to be complementary because of the way they treated the data from the PAH analysis. The diagnostic ratios are helpful for differentiating between pyrolytic and petrogenic sources and, in the first case, differentiating between biomass burning or oil combustion. In our study, the PCA and PMF techniques showed a slightly larger influence of petrogenic sources than that identified with the diagnostic ratios. The occurrence of low individual PAH concentrations in the PES and the probable processes of degradation and transformation of these compounds may affect the evaluation (Dudhagara et al., 2016; Ranjbar Jafarabadi et al., 2017). In addition, the diagnostic ratios do not consider sedimentary variables such as TOC or grain size, which can cause misinterpretation in low PAHs concentration areas, in which physicochemical variables may play an important role in the distribution of organic pollutants.

PCA was indicated to be useful for understanding the variables have similar or inverse trends (including sedimentary variables) and for identifying the predominance of certain groups of molecules in different bays. Due to its exploratory nature, PCA does not provide the tools to quantify contributions by source. In this sense, using PMF allowed quantification of the source contributions to the PAH levels found in the PES.

Based on these findings, the use of additional statistical methods to complement the diagnostic ratios is necessary to provide information beyond pyrolytic/petrogenic source identification. The results of our study indicated that paper industry activities may have a significant contribution to the PAH levels in the PES. Similarly, the diagenetic component provided by the input of organic matter in Antonina Bay and the strong influence of sedimentary characteristics were only elucidated due to coupling among different multivariate statistical analyses.

The PAHs detected in the PES originate from multiple sources but their presence is mainly controlled by sedimentary factors such as TOC and grain size. Most of the variance in concentration is determined by TOC and fine sediments; LMW PAHs and HMW PAHs are related to fine sediments and TOC in Antonina and Paranaguá, respectively. The Galheta channel and Laranjeiras present low levels for all variables, indicating excellent environmental quality for both regions based on the PAH evaluation. The results agree with the multivariate analysis performed by Garcia and Martins (2021), who found similar clusters of compounds and similar spatial distributions in a study carried out in the mangroves of the same estuary.

The integration of several source apportionment methods made identification of estuarine ecosystem dynamics based on impacts to the watersheds that supply water to it possible. Understanding the pressures caused by different anthropic activities is essential for sustainable estuarine management, and scientifically, it presents a way to understand how these environments are affected in the context of the Anthropocene.

4.5.3 Challenges in an increased anthropogenic activity scenario

Determination of environmental variables can provide a baseline for current environmental health conditions, and it is necessary to support future studies that evaluate the impacts of food and oil production chains in vulnerable environments. Such information is also important to support territorial planning, such as the Long-Term Strategic Plan for the Paraná Coastal Biodiversity Conservation Program, which is in the development phase (FUNBIO 2021). In addition, a broad sampling network meets the growing demand to reduce map uncertainty for biodiversity sciences and conservation policies and to improve economic and environmental efficiency in decision-making (Jansen et al., 2022).

The current literature confirms that PAH concentrations in sediments can be used to identify and measure human impacts on the Earth and can be applied as a valuable tool to record and define temporal and spatial landmarks in the Anthropocene (Corlett, 2015; Waters et al., 2016; Subramanian, 2019). Despite the low concentration of PAHs in the PES, this area cannot be considered a pristine environment in its entirety due to the probable occurrence of several other chemical stressors. For instance, microplastics, which have been shown to be notable markers of the current human influence on earth systems, have already been found throughout the PES sandy beaches, including in Laranjeiras Bay (Mengatto and Nagai, 2022), and high concentrations of PAHs have been found adsorbed to plastic pellets near the sand beaches of the PES mouth (Gorman et al., 2019).

These results suggest that in the future, the PES, even in its less inhabited areas, may no longer be considered an environment that is isolated from human actions. Due to the global implementation of ‘carbon bombs’, which are being planned independently of the agreements to reduce the emission of greenhouse gases (Carrington and Taylor, 2022), vulnerable regions such as the Paraná coast need socioenvironmental schemes that monitor, prevent and mitigate chemical stressor contamination and other environmental issues related to large oil infrastructure projects.

4.6 CONCLUSIONS

This study provides the most extensive assessment of PAHs in the PES, a World Heritage Site and Biosphere Reserve, covering 84 samples in 612 km^2. Valuable information was obtained on the concentration, spatial distribution, source apportionment, and potential risks associated with PAHs in the surface sediments of the PES, one of Brazil's most well-preserved estuaries.

As expected, the PAH concentrations recorded were low and presented no ecological risk under current conditions. The highest concentrations of PAHs were observed in Antonina Bay, and this provided evidence of anthropogenic impacts on the Rio Cachoeira watershed resulting from the construction of an interconnection between large rivers and from years of intense deforestation in the Atlantic Forest.

Multiple sources were identified in the PES, and the predominant sources were related to biomass burning and fossil fuel combustion, as indicated by the analysis of PAH groups and diagnostic ratios. However, a considerable presence of petrogenic influences was also identified by PCA and PMF analysis.

The Galheta channel and Laranjeiras Bay sediments showed few contributions from sedimentary variables to the accumulation of PAHs, indicating excellent environmental quality in both regions with respect to PAH sedimentary contamination. This environmental quality resulted not only from conservation measures but was also due to favourable sedimentary features related to organic matter and grain size. Both methods (PCA and PMF) identified an important source of anthropogenic Ret and C_2Phen, indicating contamination from industrial paper waste. Despite its small contribution to the overall models, this is an issue of concern and suggests that this source should be closely monitored by local authorities.

In this study, the status of PAH pollution was assessed using a large dataset and robust source apportionment methods. The difference between the pollutant levels in the PES bays showed how nature conservation promotes the maintenance of healthy environmental conditions and demonstrated how environmental impacts generated upstream can influence the pollutant levels of downstream ecosystems.

4.7 ACKNOWLEDGMENTS

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at: https://doi.org/10.1016/j.marpolbul.2023.114678.

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5 TRACING SEWAGE CONTAMINATION IN A SOUTH ATLANTIC NATURAL HERITAGE ESTUARY USING SEDIMENTARY LINEAR ALKYLBENZENES AND THEIR DIAGNOSTIC RATIOS

Este capítulo apresenta o manuscrito "*Tracing sewage contamination in a South Atlantic Natural Heritage estuary using sedimentary linear alkylbenzenes and their diagnostic ratios*", que avaliou o aporte de esgoto no CEP através da análise de LABs.

A análise de LABs nos sedimentos dos mesmos 84 pontos nos quais os HPAs foram analisados mostrou que o esgoto não é a principal fonte de matéria orgânica para o estuário, e que as concentrações encontradas foram baixas em comparação com estuários mais densamente habitados.

A principal fonte de esgoto está nos dois rios próximos às áreas urbanizadas do município de Paranaguá, que apresentaram maiores concentrações deste marcador e diferenças nos níveis de degradação, refletindo a presença ou ausência de sistemas de tratamento nas comunidades próximas à eles.

Por fim, conclui-se que o CEP apresenta um panorama de elevada conservação de seus compartimentos ambientais sedimentares relativo ao lançamento de efluentes, mas que a proteção florestal de margens estuarinas e a sanitização de rios com a implementação de sistemas eficientes de coleta e tratamento de esgoto são essenciais para a contínua manutenção de tais níveis.

Este trabalho está em revisão pelos demais autores, e será posteriormente submetido para publicação.

Highlights

- Sewage input on a Natural Heritage estuary were estimated using linear alkylbenzenes
- Sewage is not the main organic carbon source to Paranaguá Estuarine System sediments
- Primary source of linear alkylbenzenes is sewage input from highly urbanized rivers
- Linear alkylbenzenes degradation are related to absence or wastewater treatment level
- Low concentrations in the environment protected sites reflects conservation efforts

5.1 ABSTRACT

Paranaguá Estuarine System (PES) is an extensive subtropical estuarine system located in South Atlantic Ocean, Brazil, that present one of the last preserved areas of Atlantic Forest and is recognized by UNESCO as a Natural Heritage. Human impact derived by a fast and non-planed urbanization process and two port complexes, was evaluated using linear alkylbenzenes (LABs), a molecular marker related to sewage input. The concentrations of the ∑LABs in PES dry weight sediments ranged from <DL to 42.7 ng g^{-1} dw, with an average of 6.5 ± 7.8 ng g^{-1} dw. The primary source of LABs are the rivers surrounding Paranaguá city, whereas the input of allochthonous organic carbon and fine sediments are mainly associated with discharges from Antonina rivers watershed. The recent unplanned occupation of estuarine margins, with untreated sewage being discharged directly into the environment or into local septic tanks explains the low degradation levels of LABs founded in some sectors of PES. Despite the current low LAB concentrations reflecting low changes in the PES environmental quality, modelling in a context of climate change predict a decrease in the river discharge from Antonina rivers, which could lead to a sewage accumulation issue by reducing dilution and water renewal rates within the PES.

Keywords: wastewater; marine protected area; estuarine environment; anthropogenic influence; sediment.

5.2 INTRODUCTION

The ocean is mistakenly treated as a sink for several pollutants, due to the human propensity to use dilution as a solution to remeadiate pollution scenarios (Hatje et al., 2021; Knowlton, 2004). The input of untreated sewage into the environment can directly influence biogeochemical cycles, due to rising nutrient loads that lead to oxygen decline (Breitburg et al., 2018). In addition, this complex pollutant is able to cause serious human and animal health problems, since several pathogens and chemicals can be available through this route, being incorporated by diffent levels of trophic web (Iwamoto et al., 2010; Nilsen et al., 2019).

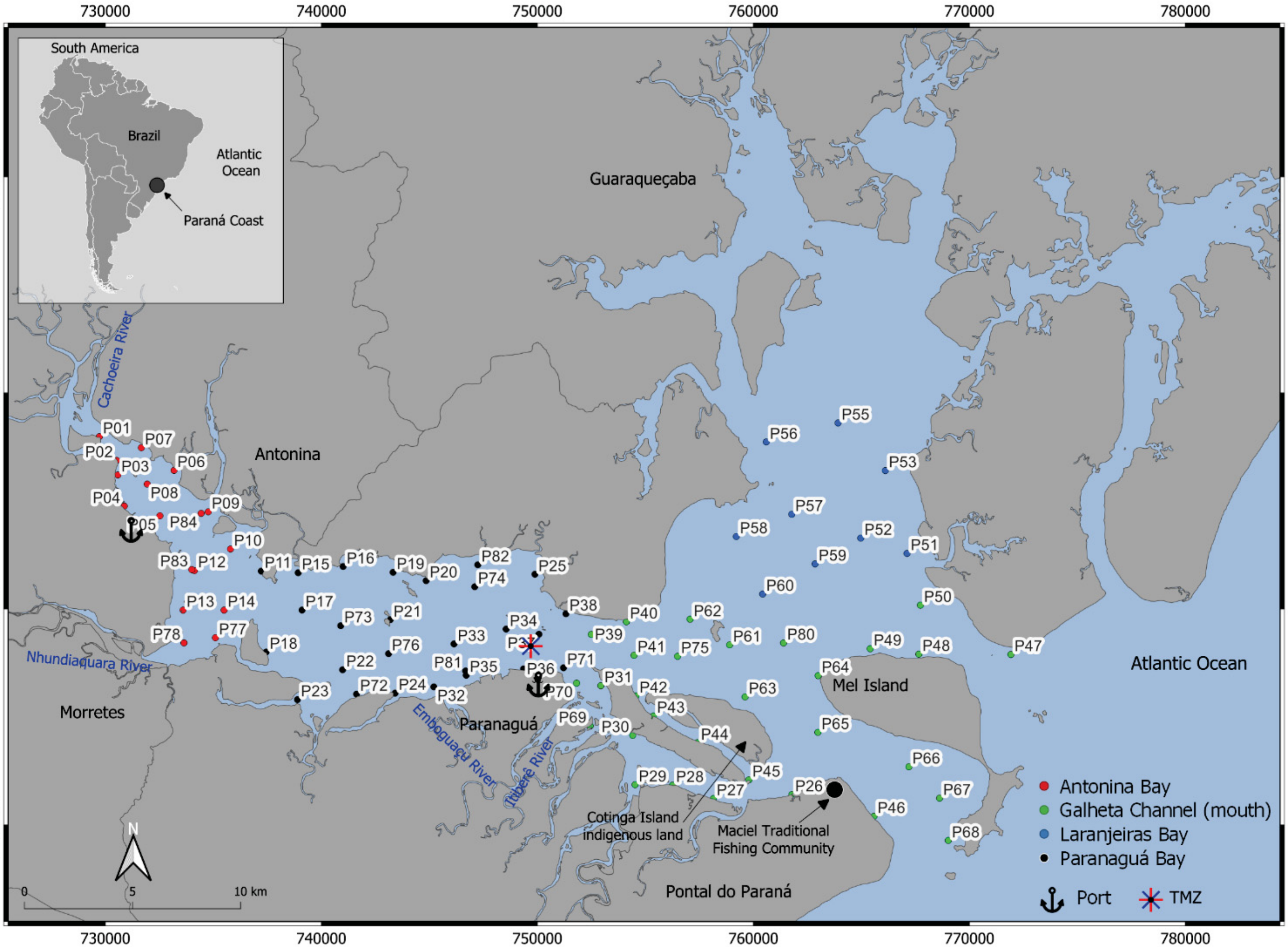
Urban settlements established in coastal areas of developing countries produce a critical environmental quality alarming, once it is estimated only 8% of the municipal and industrial wastewater has been properly trated before discharge in marine/estuarine (UNEP, 2017). The Regional South Atlantic Planning Workshop for the UN Decade of Ocean Science defined the lack of adequate sewage and wastewater treatment plants as main source of pollutants in the South Atlantic (Hatje et al., 2021). The management and monitoring of sewage pollution in estuarine regions tends to be essential, due to the social and ecological value of this ecosystem, which provides food and economic resources not only to urban centers, but also for traditional and vulnerable fishing communities (Hoang et al. 2020; Taylor and Suthers, 2021).

Linear alkylbenzenes (LABs) are aromatic hydrocarbons utilized as raw materials for the production of linear alkylbenzene sulfonates (LAS), which constitute the majority of domestic detergents in use today (Connell, 2013; Shokri and Karimi, 2021). A small amount of LABs persist after the sulfonation process, remaining as traceable residues in the final product or in the environment (Alkhadher et al., 2020b). They are used as molecular markers of sewage and anthropogenic waste due their association with anthropogenic sources and resistance to degradation (Alkhadher et al. 2020a; Eganhouse et al., 2002; Takada and Eganhouse, 1998). The concentration patterns of LAB isomers (n-C_{11} to n-C_{14}; $n = 2–7$) provide information about the degradation rates of these molecules in aquatic environments, supporting indirect evaluations of LAB aerobic degradation during wasterwater treatment or water column processes (Eganhouse et al. 1983; Takada and Eganhouse 1998). A commom approach involves the ratio between internal and external isomers (I/E ratio) as a means of discerning linear alkylbenzene degradation, given that external isomers are more susceptible to biodegradation (Alkhadher et al., 2020b; Takada and Ishiwatari, 1990).

The Paranaguá Estuarine System (PES, Fig. 1), located in South Atlantic, Brazil, is an extensive subtropical estuarine system formed by the drowning of fluvial valleys and Holocene sea level. Its drainage area of 4,078 km² promotes a large sediment input from Serra do Mar, a mountain range formed with a rocky and crystalline complex (Lana et al., 2001; de Paula et al., 2021; Wilhelm et al., 2023). Its northern margins are in direct contact with some of the last preserved areas of Atlantic Forest, including coastal environments with high biodiversity rates, but severely degraded along the last centuries of South America colonization process (Carlucci et al., 2021).

The region is considered a World Natural Heritage Site and Biosphere Reserve (Claudino-Sales, 2019; UNESCO, 1999) and a hotspot for global conservation (Myers et al., 2000). In the southern margins, PES presents two port complexes that contributed to a fast and non-planed urbanization process. The city of Paranaguá hosts ‘Porto Dom Pedro II’ since 1872. It is the largest South American port facility specialized in soybean export, which accounts for a significant portion of the region's economic activity (Angeli et al., 2020b; Beuren et al., 2018; Campos Neto et al., 2009). The coastal land use and occupation, driven by the growth of the Brazilian agribusiness since the 1970s, resulted in a city with a port area, a fertilizer industrial complex and a petrochemical terminal in its surroundings, and a large urban agglomeration in an underprivileged residential zone with the highest population density among the seven cities of the Paraná state coast, with a context of environmental injustice (Estades 2003; Gurgatz et al., 2016; Tiepolo, 2016). Furthermore, there are at least 10 infrastructure projects in the environmental licensing process (Pigosso and De Paula, 2021).

FIG. 1. MAP OF STUDIED AREA IN PARANÁ STATE COAST, SOUTH ATLANTIC, BRAZIL. SURFICIAL SEDIMENT SAMPLING SITES COLORED ACCORDING TO THE SECTOR TO WHICH THEY BELONG IN THE PARANAGUÁ ESTUARINE SYSTEM. PORTS, TMZ (TURBIDITY MAXIMUM ZONE), CITIES, TRADITIONAL COMMUNITIES AND MAIN RIVERS NAMES ARE ALSO PRESENTED.



SOURCE: THE AUTHOR (2023)

The diverse land uses along the estuarine gradient, coupled with the distinct forest conservation levels between the two axes become PES a worldwide case study for the comprehension of anthropogenic impacts on estuaries. Levels of metals (Angeli et al., 2020a) and polycyclic aromatic hydrocarbons (PAH) (e.g., Cardoso et al., 2016, Gurgatz et al., 2023) in PES are comparatively lower than those observed in other anthropized estuaries. In contrast, the concentrations of PAHs in fish and plankton were 15 times more than in sediments (Froehner et al., 2018). Microplastics were found in almost all sampled beaches, including those located within environmental protection areas (Mengatto and Nagai 2022) and in oysters destined for human consumption (Vieira et al., 2021).

The environmental quality of PES regarding to sewage input has been assessed by faecal sterols in sediments (Martins et al., 2010), faecal indicator bacteria in water (Kolm et al., 2018), and suspended particulate matter and surface sediments using chemical markers such coprostanol and LABs (Cabral et al., 2018; Cabral and Martins, 2018) commonly finding the highest values close to the region of the city of Paranaguá. Sedimentary cores showed that the increase in coprostanol values in the upper layers of the core follow the urban development of Paranaguá city (Cabral et al., 2019). Despite these scientific effords to understand the environmental quality status of the regions, the low sample resolution available in these studies does not provide enough information for a clear understanding of its sources and dispersion and ignore small urban punctual sources.

A recent study demonstrated that the hydrodynamics systems present on Southwestern Atlantic Ocean region are effective in the dispersion of residues from sewage outfalls, and that the local currents avoid pollution being carried back towards the coastline and beaches (Harari et al. 2019). However, the assessment of sewage dispersion within the PES is crucial once it is an estuarine environment with lower mixing rates than the open sea, being in direct contact with major urban settlements such Paranaguá city. In addition, the modelling of sewage dispersion requires the source identification and the level of sewage input in a spatial perspective, what can be obtained by the analysis of molecular markers as LABs.

Following the recent endeavor to establish the future perspectives related to the occurrence of the chemical stressor in the PES, we assessed the sewage as a source of organic matter (OM) and pollutants, describing the dynamics of input and distribution of LABs in sediments, and relating to the human impact on an UNESCO Natural Heritage estuary, through the most extensive sampling of surface sediments carried out in the subtropical estuary to date.

5.3 STUDY AREA

The PES (Fig. 1) is a subtropical estuarine environment composed by two main water bodies subdivided into Antonina Bay and Paranaguá Bay (East-West Axis), Laranjeiras Bay (North-South Axis) and Galheta Channel (mouth), covering an area of approximately 612 km² and a water volume of approximately 2×10^9 m^3 along the northern coast of Paraná state (Brazil) (Angeli et al., 2020a; Lana et al., 2001; Paladino et al., 2022). It is dominated by tidal forcing and river runoff hydrodynamics from “Serra do Mar” mountains (Angeli et al., 2020a; Lana et al., 2001; Martins et al., 2010).

Paladino et al. (2022) subdivided the PES into three distinct areas, based on the depositional processes: (i) Antonina Bay, where the Nhudiaquara and Cachoeira rivers discharge plays a key role in the input and transport of sediments from the Serra do Mar; (ii) the Turbidity Maximum Zone (TMZ), where the hydrodynamic balance of freshwater river drainage and marine water intrusion within the estuary favor the deposition of finer sediments; and, (iii) the area downstream of the estuary, where the marine water influence on hydrodynamic patterns and sediment sources is predominant. Similarly, Wilhelm et al. (2023) demonstrated that Antonina Bay is under significant fluvial influence, receiving terrestrial OM, whereas Paranaguá bay is under mixed contributions (i.e., terrestrial and oceanic OM). The intensification of human occupation and land use in the region were identified by the increase of molecular markers as PAHs, coprostanol and *n*-alkanes in sediment cores, with an increase since the 1950s (Cabral et al., 2019, Martins et al., 2015, Wilhelm et al., 2023).

The primary contribution of freshwater is the Cachoeira river wathersed, on its northern margin, with an input of 21.13 m^3 s^{-1}. Its flow increased by 50% with the interconnection with the Capivari River Basin, in the 1970s, to the construction of a hydroelectric power plant (Odreski et al., 2003; Polli et al., 2021).

The estuarine system is surrounded by five cities (inhabitants in 2022 national census): Pontal do Paraná (30,425), Paranaguá (145,829), Morretes (18,309), Antonina (18,091) and Guaraqueçaba (7,430) (IBGE 2023a). Paranaguá have an economy based on port activities, while beach tourism is widely explored in Pontal do Paraná from December to February, when Paraná coast exceeds one million visitors, contributing to the loss of environmental quality (Grimm et al. 2012).

A large Atlantic Forest reforestation area predominate in cities, such Guaraqueçaba and Antonina, resulting from the process of implementation of conservation actions from the 1980s onwards. Together with Morretes, these cities share a context of low population density, traditional fishing communities and ecotourism (Estades, 2003; Ferretti and de Britez, 2006). The region is considered one of two Brazilian biodiversity conservation priority hotspots due its large number of endemic species and exceptional loss of habitat (Rezende et al., 2018).

5.4 MATERIAL AND METHODS

5.4.1 Sampling and preliminary procedures

The sampling of the superficial sediment (0-3 cm) was performed in March 2018, using a stainless steel Van Veen grab. A total of 84 samples were collected, distributed between the two axes of the PES, as shown in Fig. 1. Sediments were frozen (−20 ˚C) after sampling, freeze-dried, carefully homogenized with a mortar, and stored in clean glass jars until analysis.

5.4.2 Bulk parameters

The grain size of the sediment samples (referred here as fine sediments, which is the sum of silt+clay fractions) was determined for the total dried sediment by a Malvern Hydro 2000 instrument. The results are presented as fine sediments, calculated as the percentage (%) of the sum of silt (3.9 to 62.5 µm) and clay (0.24 to 3.9 µm) fractions. Bulk organic matter (total organic carbon: TOC, and total nitrogen: TN) was determined using a Costech elemental analyser. Bulk parameters data was presented by Angeli et al. (2020b) and Paladino et al. (2022).

5.4.3 Laboratory and instrumental analyses of LABs

The analytical procedure for LAB analysis was based on the United Nations Environment Program method (UNEP 1992) with the adaptations described in Wisnieski et al. (2016). Approximately 20 g of dry sediment was Soxhlet extracted over 8 h using 80 mL of a mixture of dichloromethane (DCM) and *n*-hexane (1:1, v/v). Activated copper was added to remove elemental sulfur. A standard surrogate (1-C_{12}LAB, 0.5 µg) was added before each blank and sample extraction. The DCM/*n*-hexane extract was purified by liquid adsorption column chromatography using 5% deactivated alumina (1.8 g) and silica (3.2 g). Elution was performed with 10 mL of *n*-hexane to obtain the LABs fraction and 15 mL of a mixture of DCM and *n*-hexane (3:7, v/v) to obtain the fraction 2, which contained the PAHs (presented in Gurgatz et al. (2023). The concentrated extract was spiked with an internal standard (1-C_{19}LAB, 0.5 μg) and stored in glass vials.

Instrumental analyses of LABs were performed with a gas chromatograph (Agilent Model 7890A) coupled to a mass spectrometer (Agilent 5973 N inert MSD with Triple-Axis Detector) using a fused silica capillary column (30 m, 0.25 mm internal diameter, 0.25 μm film thickness) coated with 5% diphenyl/dimethyl siloxane. A 2 μL aliquot of LABs extracts was injected in splitless mode at an injector temperature of 280 °C. The oven temperature was programmed to ramp up 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 and the ion source were conditioned at 300 °C and 230 °C, respectively. Data acquisition was performed in selected ion monitoring (SIM) mode and identified by matching their ion mass fragments (m/z) and retention times with those from a standard mixture. Calibration was performed based on an external standard solution containing 1-CmLABs (m = 10, 11, 13 and 14) (Supelco, 99% purity) at concentrations ranging from 0.25 to 2.0 ng μL^{-1}. LABs were identified by ion mass fragments (m/z 91, 92 and 105) and by matching the retention times with a mixture of all the n-C_m-LABs (m = 10–13; n = 2–7) provided by Deten Química S.A. (LABs Mix Lot LPS 0025/08). ∑LABs refer to the sum of the 26 LAB congeners and LAB concentrations are expressed as ng g^{-1} of sediment dry weight (ng g^{-1}).

5.4.4 Quality assurance procedures

The instrumental detection limit (DL) was 0.50 ng g^{-1} dw for LABs, defined based on the lowest concentration of LABs (0.02 ng μL^{-1}), multiplied by the final extraction volume (500 μL), divided by the dry sediment mass (20 g) weighed prior to extraction. Blanks were performed for each extraction batch of 11 samples and did not show interferences in the analyses of the target compounds (i.e., detected levels higher than 3 x DL). The recovery of surrogate standard was acceptable (50 – 99%, mean = 76 ± 16%). Repeatability was assessed by triplicate analysis of the sediments, and the relative standard deviation ranged between 3.2 and 12.6% (mean = 6.0 ± 2.3%) for the analyzed compounds. The mean individual recoveries between the different LABs from the standard mixture were 85.0 ± 0.3% and 84.6 ± 0.6% in the spiked sediments and blanks, respectively.

5.4.5 Data analysis

Statistical analysis was carried out and graphing was performed using the software R (R Core Team 2021) and JASP (JASP Team 2021). Interpolation and spatial analysis were developed using QGIS (QGIS Development Team 2022). Due to a lack of normality, data were subjected to Spearman's correlation test.

LAB degradation was assessed by molecular isomers ratios. The main LAB degradation indicator are the I/E isomers ratios, as follow, that allow evaluate the sewage treatment level found in the sediment (Takada and Ishiwatari, 1990):

$I/E\ (C_mLABs) = [6\text{-}C_mLAB + 5\text{-}C_mLAB] / [4\text{-}C_mLAB + 3\text{-}C_mLAB + 2\text{-}C_mLAB] \quad (m = 11\text{–}13)$

Lower values (I/E ~1.0) are related to recent and treated sewage input (Alkhadher et al., 2023a; Takada and Ishiwatari, 1990).

The I/E (C_{12}LAB) ratio can be used to estimate the % LAB degradation through the equation (Arruda-Santos et al., 2023; Takada and Eganhouse, 1998):

$\text{LAB degradation } (\%) = 81 * \log (I/E) + 15.$

Other diagnostic ratios proposed in literature are:

$C_{13}/C_{12} = [\Sigma\ n\text{-}C_{13}LAB] / [\Sigma\ n\text{-}C_{12}LAB] \quad (n = 2\text{–}6)$

$L/S = 5\text{-}(C_{13} + C_{12})\ LABs / 5\text{-}(C_{11} + C_{10})\ LABs$

These ratios are based on the increased degradation for the n-C_{12} LAB homolog group in the environment (Luo et al., 2008), as difference biodegradation rates considering long (C_{13} and C_{12}, L) and short (C_{11} and C_{10}, S) alkyl side chain in water column and during sedimentation (Gustafsson et al., 2001).

5.5 RESULTS AND DISCUSSION

5.5.1 LAB concentrations and spatial distribution

The concentrations of the ∑LABs in the PES sediments ranged from <DL to 42.7 ng g^{-1}, with an average of 6.5 ± 7.8 ng g^{-1}, being classified as 'low' LABs pollution levels (<DL–200 ng g^{-1}), as proposed by Arruda-Santos et al. (2023). Nevertheless, the findings reveal a upward trend compared to samples collected in Feb, 2012 and reported by Cabral and Martins (2018) (< DL to 21.0 ng g^{-1}, average of 4.44 ± 5.86), that may reflect the sewage input increase as response by the population increase in the region. In fact, Paranaguá city, the most populous settlement of this region, experienced a population growth of 3.2% between both sampling campaings (PNUD, 2017).

The average concentration was found to be lower than those reported in other locations along the Brazilian coast, such as Tubarão riverbed (Cabral et al., 2020), Babitonga Bay (Martins et al., 2014) and Capibaribe Estuary (Arruda-Santos et al., 2023) (42.3 ± 35.5 ng g^{-1}, 62.1 ± 109.5 ng g^{-1} and 749 ng g^{-1}, respectively). Similarly, our results indicate lower concentrations compared to several studies in countries with high population density, such as Malaysia and China, where LABs have been extensively investigated (Fig. 2). The LAB levels detected in this study are comparable to those found in highly conserved regions such as Antarctica (Dauner et al., 2015; Martins et al., 2012, 2002). Additional examples of ∑LAB concentration ranges in estuarine and coastal environments are presented in Fig. 2.

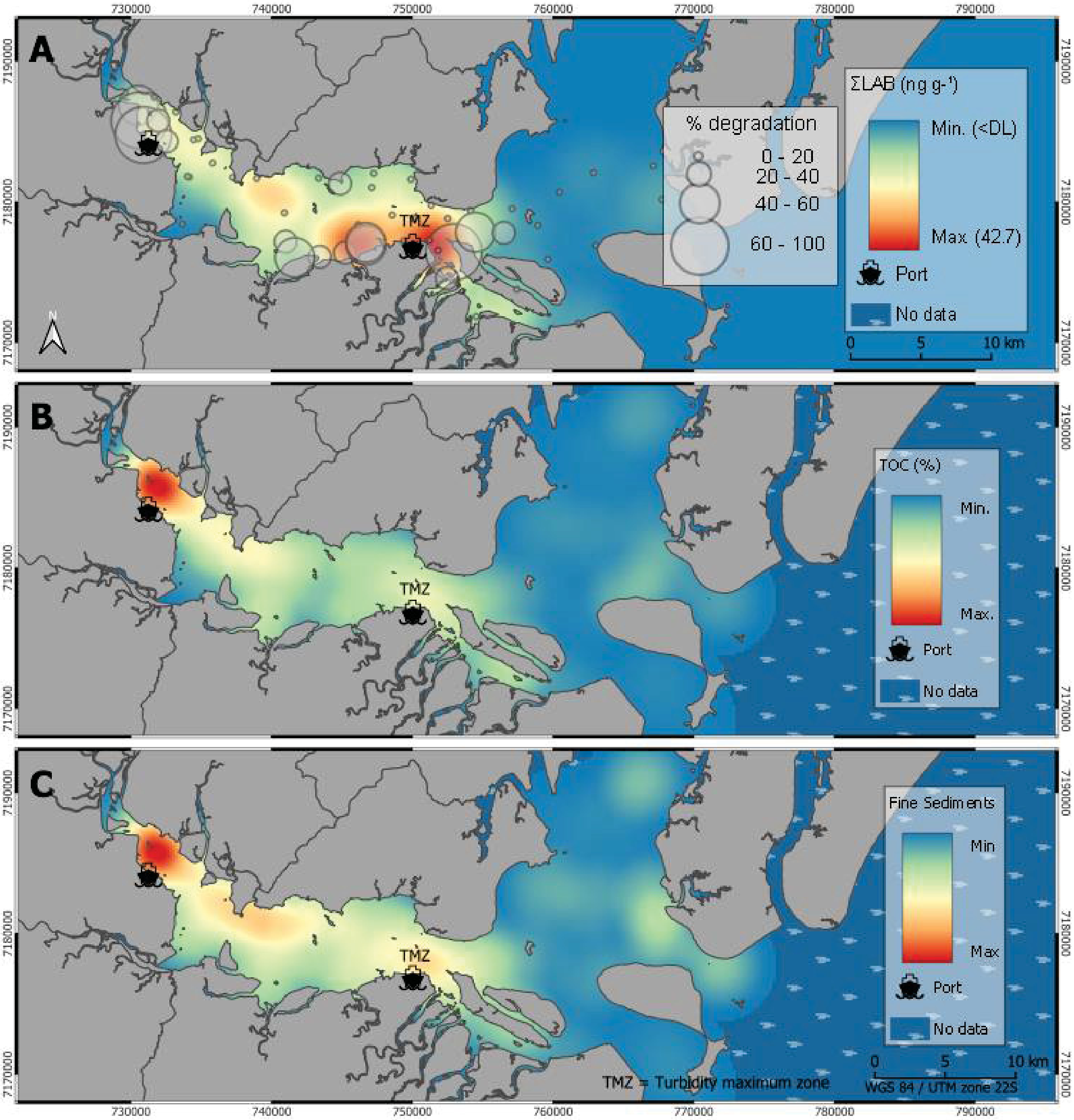
The areas with the relative highest concentration of LABs are close to the city of Paranaguá (two red spots in Fig. 3A). According to the classification by Paladino et al. (2022), those samples are near the TMZ, where wave and tidal processes promote approximately equal influence on the sediment's deposition. In this way, the distribution of LABs is strongly related to sources from the runoff of the Paranaguá rivers, that the compounds trend to be deposited in the low energy zones of TMZ. Further information about these primary sources and details about the rivers are discussed in the following sections.

Considering the main historical impact area of PES, that correspond to Paranaguá Bay, ∑LAB average goes up to 11.3 ng g^{-1}, which is almost twice the PES ∑LAB total average. The highest concentrations of ∑LABs were identified in Paranaguá Bay, followed by the Antonina Bay or Galheta channel (similar concentrations), and Laranjeiras Bay sectors, respectively (Fig. 4). Laranjeiras Bay sediments resulted in the lowest ∑LAB average (0.61 ± 1.20 ng g^{-1}), concentrations similar to those found at sites with near pristine conditions, as the South Polar environment (e.g., Dauner et al., 2015).

FIG. 2. CONCENTRATION RANGES FOR ∑LABS (NG G-1) IN SEVERAL ESTUARINE ENVIRONMENTS WORLDWIDE. ∑LABS REFER TO THE SUM OF THE 26 LAB CONGENERS RANGING FROM N-C10 TO N-C14 (N = 2–7). THE THRESHOLD COLORS REPRESENT DIFFERENT ∑LAB CONCENTRATION RANGES AND POLLUTION AS FOLLOWS: GREEN (0-200) REPRESENTS LOW, YELLOW (200-2000) DENOTES MODERATE, AND RED (2000-6000) HIGH CONCENTRATIONS AND POLLUTION LEVEL, AS PROPOSED BY ARRUDA-SANTOS ET AL. (2023).

SOURCE: THE AUTHOR (2023). FIGURE REFERENCES: (CABRAL ET AL., 2020), (DAUNER ET AL., 2015), (MAGAM ET AL., 2016) ,(WANG ET AL., 2014), (CABRAL AND MARTINS, 2018), (MARTINS ET AL., 2014), (ARRUDA-SANTOS ET AL., 2023), (ZHANG ET AL., 2021), (HARDOIM ET AL., 2021), (MACÍAS-ZAMORA AND RAMÍREZ-ALVAREZ, 2004), (MOREIRA ET AL., 2021), (ALKHADHER ET AL., 2020A), (BURUAEM ET AL., 2013), (ALKHADHER ET AL., 2023B), (ALKHADHER ET AL., 2016), (ALKHADHER ET AL. 2016), (ALKHADHER ET AL., 2023A), (MASOOD ET AL., 2022), (WEI ET AL., 2014). (MARTINS ET AL., 2012), (MASOOD ET AL., 2016), (MARTINS ET AL., 2002), (MARTINS ET AL., 2008), (HE ET AL., 2018), (HUANG ET AL., 2021).

FIG. 3. INTERPOLATED SPATIAL DISTRIBUTION OF A -∑LABS (NG G-1), B - TOC (%) AND C - FINE SEDIMENTS IN THE PARANAGUÁ ESTUARINE SYSTEM SURFICIAL SEDIMENTS.



SOURCE: THE AUTHOR (2023).

The predominant isomers were n-C_{13}, n-C_{12} and n-C_{11}LABs (2.8 ± 3.1, 2.2 ± 2.6 and 1.3 ± 2.0 ng $g^{-1,}$ respectively), with very similar spatial distribution (Fig. S2). The n-C_{10} and n-C_{14} presented very low average concentrations (close to <DL). The DETEN company, a subsidiary of CEPSA (Compañia Española de Petróleos, S.A.) supplies approximately 95% of the Brazilian detergent industry's, with an annual production capacity of 220,000 tons of LABs (DETEN, 2023). The DetenLAB® 240, main commercial product, exhibits the approximately following percentages of each group of LAB congeners and isomers: n-$C_{<10}$ = 0.7 %, n-C_{10} =

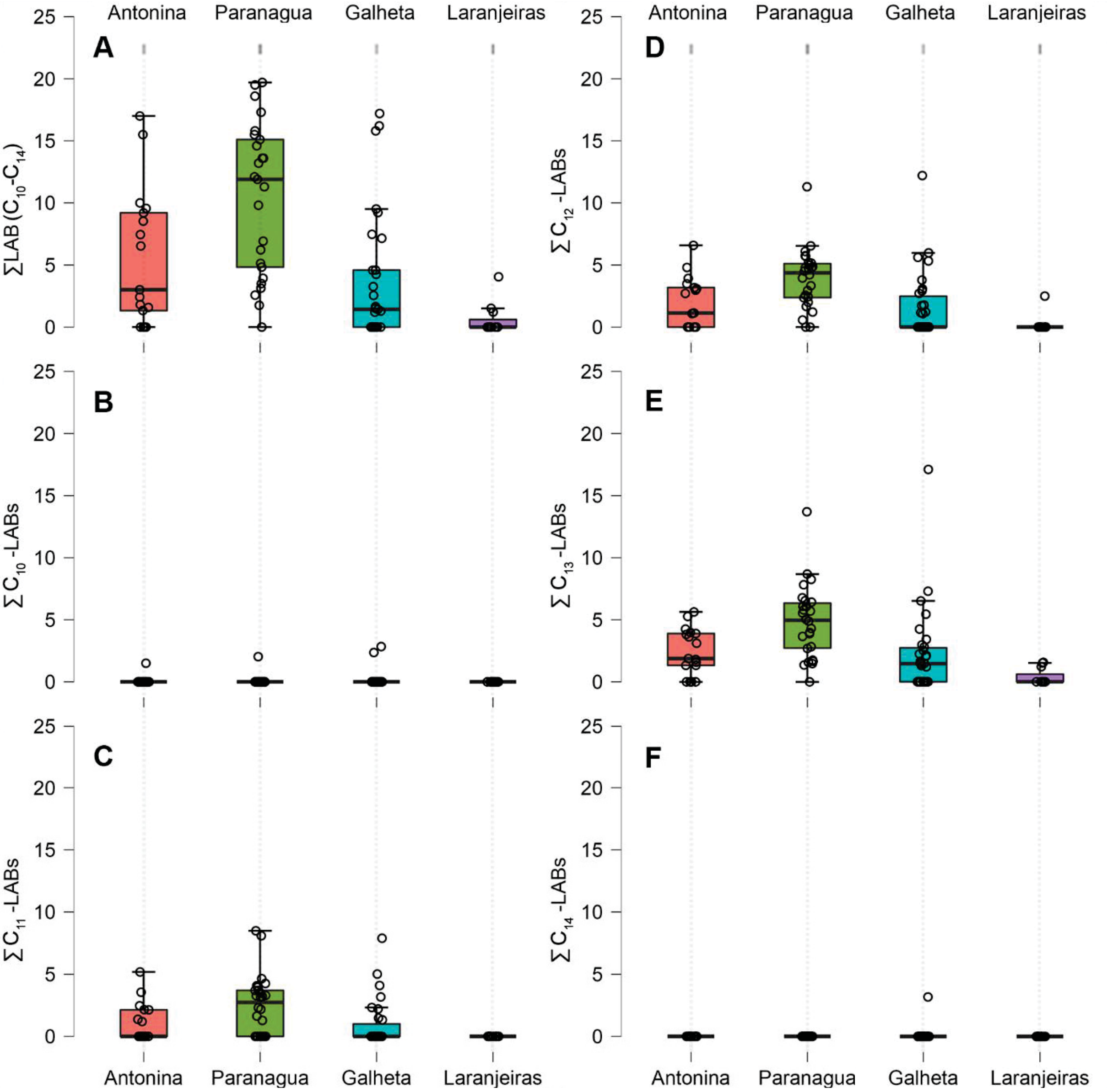
14%, n-C_{11} = 34%, n-C_{12} = 30%, n-C_{13} = 30%, n-C_{14} = 0.8% (CEPSA, 2019). Despite a lower proportion of n-C_{11}LABs found in PES, due selective losses (by biodegradation) of high solubility n-C_{11} homologs while effluent particles trend to settle down (Alkhadher et al., 2020a), the LABs found in PES study corroborate the LABs profile from to Deten product. The occurrence of this similar 'fingerprint' suggests recent input of domestic detergent from local sources (Cabral et al., 2020; Martins et al., 2014) agreeing with previous studies in the region (Cabral and Martins, 2018).

Polli et al. (2021) demonstrated that Antonina Bay presented consistently lower discharges than the baseline for its two main tributaries, Cachoeira and Nhundiaquara rivers, under climate change scenarios, warning that the decrease in river discharge may impact the hydrodynamics features of PES, decreasing potentially the dilution of sewage loads in the area.

5.5.2 Correlation between bulk parameters and LABs

Spatially, ∑LAB exhibits a spatial distinct distribution compared to TOC and fine sediments (Fig. 3A, 3B, and 3C, respectively), suggesting the sources of LABs may be different than main sources of TOC and TN. The correlation of ∑LABs with TOC, TN and grain size was found to be statistically significant, but in a moderate level ($\rho > 0.5$, p-value < 0.001) (Table 1). Spatial and statistical analysis shows us that the characteristics of the sediment play a secondary role in the distribution of LABs in PES. This fact is corroborated by the low concentrations found in Antonina Bay, despite its higher concentration of fine sediments and TOC (Fig. S1, "S" denotes Supplementary Information).

FIG. 4. BOXPLOT DISTRIBUTION OF ΣLABS (A) AND EACH GROUP OF ΣLABS ISOMERS CONCENTRATIONS (B, C, D, E AND F) (IN ng g-1) IN SEDIMENT SAMPLES OF PARANAGUÁ ESTUARINE SYSTEM SECTORS (ANTONINA BAY, PARANAGUÁ BAY, GALHETA CHANNEL AND LARANJEIRAS BAY).



SOURCE: THE AUTHOR (2023).

TABLE 1. SPEARMAN CORRELATION (□) MATRIX FOR TOTAL ORGANIC CARBON (TOC), FINE SEDIMENTS (SUM OF SILT AND CLAY FRACTIONS) AND ∑LABS.

Variable		**Fine sediment**	**TOC**	**∑LABs**
TOC	Spearman's (ρ)	0.851*	-	-
∑LABs	Spearman's (ρ)	0.541*	0.664*	-
TN	Spearman's (ρ)	0.856*	0.975*	0.645*

* p <0.001

Shapiro-Wilk test for multivariate normality: 0.804, p<0.001.

SOURCE: THE AUTHOR (2023).

This correlation results are consistent with findings from different worldwide estuaries (e.g., Alkhadher et al., 2023b, 2020b; Bakhtiari et al., 2018; Huang et al., 2021; Macías-Zamora and Ramírez-Alvarez, 2004; Zhang et al., 2012, locations in Fig. 2), where moderate correlations of LABs with TOC and TN indicate that domestic sewage does not constitute the primary source of OM for estuarine sediments. The primary source of ∑LAB are the wastewater input in the rivers from Paranaguá city, whereas the discharge of TOC and fine sediments is associated with natural (terrestrial OM) discharges from Antonina rivers watershed, as a result of the contribution of the Rio Cachoeira watershed, as the build of an interconnection between large rivers and years of intense deforestation in the Atlantic Forest (Gurgatz et al., 2023; Odreski et al., 2003).

Other contaminants to PES, as PAHs, exhibited a more diffuse distribution and were correlated with TOC in PES (Gurgatz et al., 2023), suggesting a different source from LABs (sewage) and PAHs (petroleum and by-products input and pyrolytic process, fossil fuels and biomass combustion). In the other hand, both PAHs and LABs were linked to a same primary source (sewage) and presented similar spatial distributions in South China Sea and Peninsular Malaysia (Alkhadher et al., 2020a; Luo et al., 2008)

4.3. Assessment of degradation using LABs as indicators

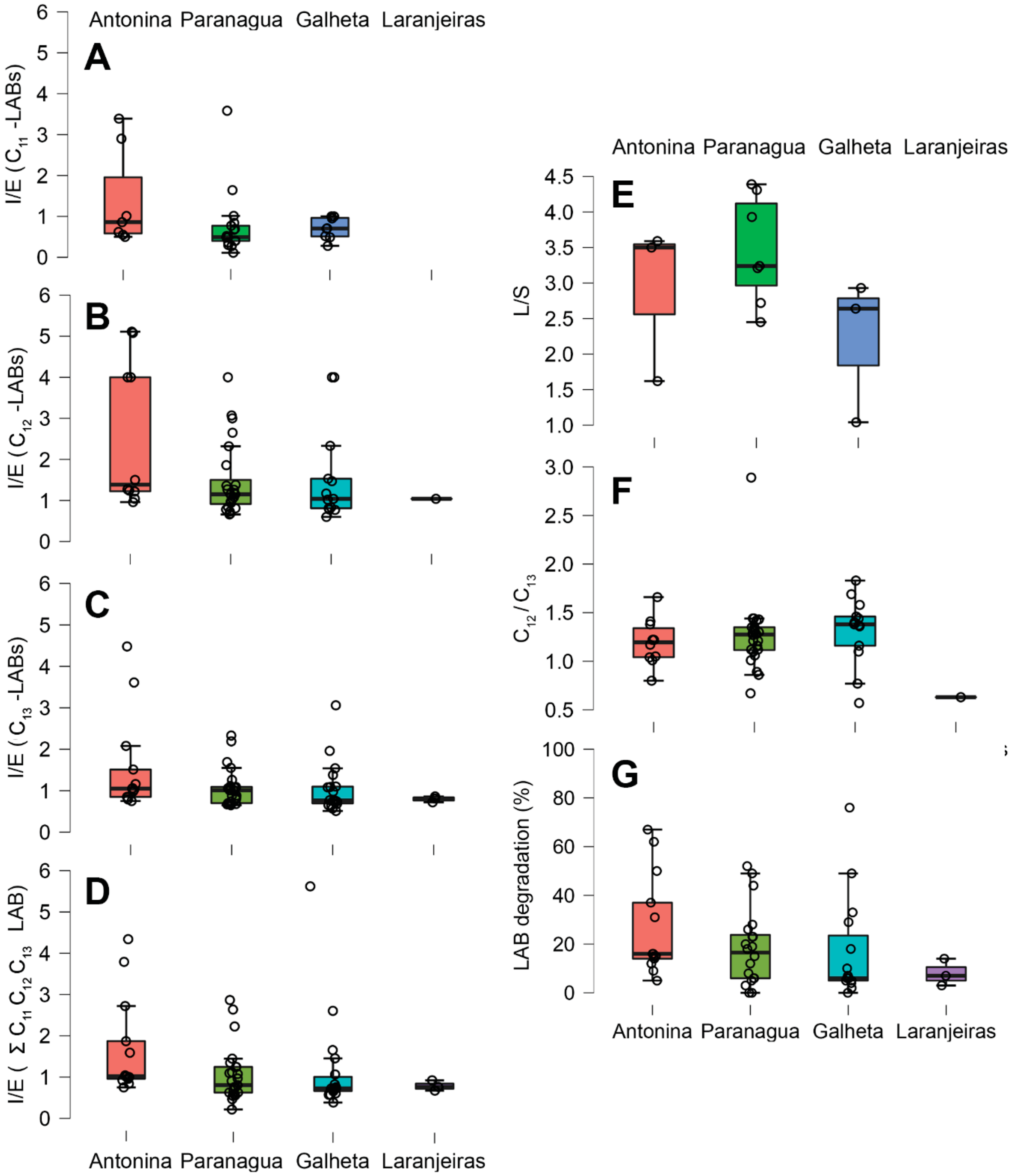
In general, the PES exhibited low I/E values (I/E ~1.0) across its compartments, with slightly higher values in Antonina Bay (Fig. 5). This suggests chronic untreated or primary treated sewage presence throughout the PES, with the exception of Laranjeiras Bay, which displayed low values of LABs as a whole.

The L/S ratio presented similar results than I/E ratio, with higher average degradation rates in Antonina and Paranaguá sectors, but with distinct distributions. However, it is not possible to use this ratio with a high degree of confidence due to the not detected (< DL) or extremely low values of 5-C_{10}LAB found. As for the C_{13}/C_{12} ratio, there were differences in the order of the mean degradation rates, following the order by sector: Antonina < Paranaguá < Galheta, but with discreet differences between the values, which does not allow for robust inferences.

The southern side of the E-W axis of the estuary exhibited higher degradation rates, as shown in the % LAB degradation map (Fig. 6A), and this is attributed to extensive urban development, particularly in the areas surrounding the ports of Paranaguá and Antonina. The presence of primary sewage treatment facilities with discharges into urban rivers contributes to this trend. The northern side presented low overall values of this parameter due to its forest conservation landscape. However, its lower degradation values likely indicate punctual direct discharges, which may be due traditional communities with limited wastewater treatment practices.

The general LAB degradation rates found in PES in this study was quite similar to Cabral and Martins (2018) estimated to samples collected in Feb, 2012 and demonstrate that despite the overall increase in LABs concentration over the 6-year period between the studies, the dynamics of sewage input in the PES remained unchanged, with few evidence of improvement on the wasterwater treatment facilities.

FIG. 5. EVALUATION OF LAB DEGRADATION USING SELECTED DIAGNOSTIC RATIOS IN SEDIMENT SAMPLES OF PARANAGUÁ ESTUARINE SYSTEM SECTORS (ANTONINA BAY, PARANAGUÁ BAY, GALHETA CHANNEL AND LARANJEIRAS BAY). THE I/E (CMLABS) (M = 11–13) RATIOS ARE PRESENTED IN A, B, C AND D. THE LONG (L) AND SHORT (S) ALKYL SIDE CHAIN RATIO (L/S) IS PRESENTED IN E. THE SUM OF N-C13 LAB VS N-C12 LAB HOMOLOG GROUP (C13/C12) ARE IN F AND PERCENTAGE OF LAB DEGRADATION IS IN G.



SOURCE: THE AUTHOR (2023).

5.5.2.1 The Paranaguá rivers as main driver of LABs input

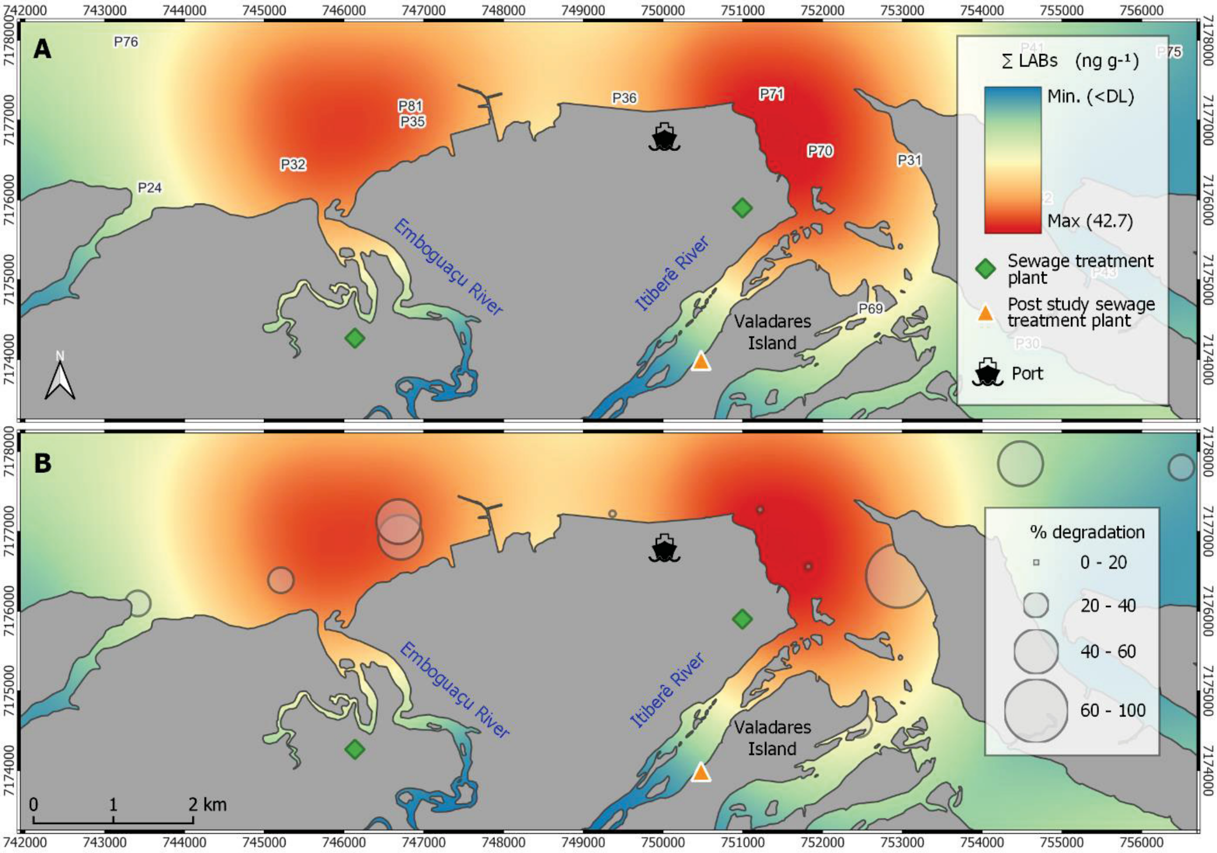
Paranaguá has the highest population density among PES cities, with an economy based on port activities. The mainland portion of the municipality is geographically divided by two rivers: the Emboguaçu to the west and the Itiberê to the east (Fig. 1).

The Paranaguá Bay, where the Emboguaçu and Itiberê rivers discharge (Fig. 1), exhibited the highest average ∑LAB values in this study (11.3 ng g^{-1} dw). The highest concentrations (Fig. 6A) were identified at the mouths of the both rivers, reflecting the impact of urbanization surrounding these water bodies.

The occupation experienced rapid growth since late 1800s, with the establishment of a port on the Itiberê River. Since 1935, the Dom Pedro II port was relocated to the north, in direct contact to PES (IBGE 2023b). Today, the Itiberê River has mixed uses, including tourism, fishing, shipyards instalations, among others. Its margins are highly urbanized. Furthermore, one of its margin's interfaces with Valadares Island, a residential area with high population density, low economic indicators, and unplanned settlements. On the other side of the city, the Emboguaçu River experienced a late occupation compared to Itiberê, but is also characterized by unplanned urbanization and working-class port-related housing (Caneparo 2000).

The Emboguaçu and Itiberê rivers are the final destination of the treated effluent from sewage treatment plants (green diamonds in Fig. 06B) and presented the current highest levels of LABs in their mouths, e.g., P81 (17.3 ng g^{-1}) and P35 (15.1 ng g^{-1}) for Emboguaçu, and P71 (15.8 ng g^{-1}) and P70 (42.7 ng g^{-1}) for Itiberê river mouths. However, the sites associated with the mouth of the Itiberê River exhibited lower LAB degradation compared to those of the Emboguaçu River (Fig. 6B).

FIG. 6: ZOOM VIEW OF SPATIAL DISTRIBUTION OF ∑LABS CONCENTRATION (A) AND % LAB DEGRADATION (B) IN THE SURROUNDING OF PARANAGUÁ CITY AND THEIR RIVERS MOUTHS. THE SPATIAL ∑LABS CONCENTRATION FOR THE WHOLE SYSTEM WAS PRESENTED IN FIG. 3A.



SOURCE: THE AUTHOR (2023).

This trend can be explained by the unplanned occupation of Valadares Island, where until the year 2019, sewage was discharged directly into the environment or into septic tanks (B&F Dias 2019). The use of septic tanks in sandy coastal plains increases the risks of water contamination and health hazards to the population (Scandura and Sobsey 1997).

The distinct LAB degradation pattern between the two rivers in agreement with field observations related to the human occupation, land use and sewage treatment facilities show the feasibility of LABs as temporal molecular markers of the Anthropocene, as discussed in a global perspective for PAHs (e.g., Bao et al., 2020; Chang et al., 2018) and ^{137}Cs (Ferreira et al., 2016).

5.6 CONCLUSION

This study tracked the human impact in an UNESCO World Natural Heritage estuary located in South Atlantic using linear alkylbenzenes (LABs) as sewage molecular markers. The spatial distribution of sedimentary LABs in Paranaguá Estuarine System (PES) is not driven by bulk properties such as TOC or grain size; instead, it is associated with the distance and magnitude from the potential emission source.

The primary LAB sources in PES are the rivers surrounding the Paranaguá city, which transport eflluents from the city's treatment plants, as well as the wastewaters from the population of Valadares Island, which, until the study date, was lacked sewage treatment.

The low concentrations found in sites far from the hotspots, particularly, the Laranjeiras Bay, can be attributed to its adjacent watersheds safeguarded by an extensive system of conservation units. This findings highlights the importance of two environmental policies for Brazil's achievement of the Sustainable Development Goals (SDGs): emphasizing forest conservation to ensure environmental services and focus on sewage and rivers sanitation to ensure ocean health.

Complementary, LABs can provide a geochemical tool for describing the impact of population density on environments, the extent of sewage treatment in contemporary societies, to promote the health of one of the largest areas of preserved subtropical estuarine areas of South Hemisphere. This study show the significance of integrating approaches in environmental sciences to provide precise and pertinent information for decision-making.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Bruno Martins Gurgatz: Data acquisition, Formal analysis, Methodology, Writing - original draft, review & editing. Vinícius Rogel Paulino de Oliveira: Data acquisition, Formal analysis, Writing – review. Michel Michaelovitch de Mahiques: conceptualization, Writing – review. Funding acquisition, Project administration. César C. Martins: Formal supervision, Conceptualization, Writing – review & editing.

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6 ASSESSING PM2.5 IN A PROTECTED ECOSYSTEM IN THE SOUTH ATLANTIC UNDER MASSIVE PORT ACTIVITIES: EVIDENCE OF HIGH CONCENTRATIONS AND MULTIPLE SOURCES

Este capítulo apresenta o manuscrito "*Assessing $PM_{2.5}$ in a protected ecosystem in the South Atlantic under massive port activities: evidence of high concentrations and multiple sources*", resultado do monitoramento de um ano de $PM_{2.5}$ no município de Paranaguá.

Esta pesquisa iniciou-se durante o processo de Mestrado do autor, no qual os dados foram coletados e processados, finalizando neste processo de Doutorado, com o desenvolvimento das análises de atribuição de fontes.

Este trabalho realizou o primeiro monitoramento de $PM_{2.5}$ em Paranaguá, em um período no qual este poluente, considerado uma das principais causas de mortalidade, ainda não estava incluso nos Padrões Nacionais de Qualidade do Ar.

Os resultados apontam para altos níveis de $PM_{2.5}$, com uma concentração anual média no limite do que é sugerido como seguro pela Organização Mundial da Saúde, e diversos casos de altas concentrações diárias. A atividade rodoviária e a estrutura de abastecimento de navios foram identificadas como principais fontes.

Este trabalho aponta para a atividade industrial portuária como principal risco ambiental localizado às margens do CEP, e sugere um panorama no qual a conservação ambiental, localizada à margem oposta do porto, não se traduz como bem estar para a maior parte da população da região.

Este trabalho está em fase de revisão por pares no periódico "*Environmental Geochemistry and Health*".

6.1 ABSTRACT

Long-term exposure to atmospheric fine particulate matter ($PM_{2.5}$) is a major human health concern. Respiratory and cardiovascular diseases are the main consequences. In this study, we present the source apportionment of $PM_{2.5}$ in a large port region in the South Atlantic, located in a Natural Heritage Estuary, which is a particularly sensitive ecosystem and a marine protected area. The $PM_{2.5}$ mean concentration was 15.3 ± 7.5 µg m^{-3}, with a range from 0.7 to 41.0 µg m^{-3}, exceeding both World Health Organization target thresholds 3 and 4, as well as the Air Quality Guideline level. Notably, 10% ($n = 34$) of the samples exceeded the Brazilian environmental quality threshold for $PM_{2.5}$ 24-hour mean (25 µg m^{-3}), which is significant since the guidelines recommend a maximum of 3 to 4 exceedance days per year. Bivariate plots with meteorological data and positive matrix factorization (PMF) were employed to estimate the sources of $PM_{2.5}$ from soluble ions and trace and major metal compositions. The findings suggest that truck activity in a nearby parking lot is the primary source of $PM_{2.5}$, and the presence of a transportation structure linked to grain transportation was identified as a secondary source. Additionally, the findings of this study demonstrate an urgent need to address the impact of the Brazilian soybean export industry on human health and biodiversity in the region, given the context of excessive $PM_{2.5}$ concentrations and the risks they presumably pose.

Keywords: air quality, port pollution, marine protected areas, emission sources, positive matrix factorization.

6.2 INTRODUCTION

Long-term exposure to fine particulate matter ($PM_{2.5}$, particles with a diameter < 2.5 μm) dispersed in the atmosphere from human activities contributed to more than 4 million deaths in 2019, making this one of the most relevant groups of pollutants and the most consistent and robust predictor of mortality from several diseases, mostly due to cardiovascular and respiratory causes (HEI, 2020).

$PM_{2.5}$ is typically a mixture of carbon, organic molecules, trace and major metals, sulphate, and nitrate. The variation in their composition and physical properties can provide valuable information about sources, meteorological conditions, geographic location, and environmental quality when statistical and modelling tools and related physical-chemical data to known emission patterns are associated (Albuquerque et al., 2019; Ma et al., 2022).

$PM_{2.5}$ emissions are primarily caused by the burning of fossil fuels during several activities, such as power generation, industrial processes, residential heating, and urban transportation. As a result, the geographic patterns of $PM_{2.5}$ emissions are closely related to socioeconomic development (HEI, 2020; Ma et al., 2022).

The Paraná coast, located in the Brazilian South Atlantic sector, is known for its native communities, such as the Guarani Mbya indigenous people and the traditional fishing community of Maciel (Góes et al., 2020; Onofre et al., 2018). It has one of the largest continuous areas of preserved Atlantic Forest, which is classified as one of the richest biomes in biodiversity in the world. This local sociobiodiversity context led to the area being listed as a World Heritage Site and Biosphere Reserve (Claudino-Sales, 2019; UNESCO, 1999).

The region has at least 18 port infrastructure projects with approved environmental permission to promote the exportation of agricultural production and to support the exploration of the Brazilian presalt oil reserves, threatening the conservation of local sociobiodiversity and the health of surrounding communities (Góes et al., 2021; Tiepolo, 2016). Paranaguá city, the economic centre of the Paraná coast, hosts the largest port in South Brazil, named Paranaguá port, and is the leader in bulk transport of soybean production in Latin America (de Lima et al., 2018). Additionally, the Paranaguá port is surrounded by urban settlements, an industrial fertilizer complex and a petrochemical terminal (Angeli et al., 2020; Beuren et al., 2018; Campos Neto et al., 2009). The combination of these factors puts the local environment and population at risk, highlighting the urgent need for environmental monitoring and management to ensure the protection of local communities and ecosystems.

The limited coverage of air quality monitoring stations in South America, which are typically focused on major urban centres, presents a significant challenge to the effective enforcement of air quality standards. In smaller cities and towns, air quality data are often nonexistent or limited to isolated studies (Andrade et al., 2012; Polezer et al., 2022). This situation is particularly concerning for estuarine and coastal areas that host industrial and port complexes, which are typically located far from urban centres and are subject to monitoring requirements set out in their own operating licences. As a result, the effectiveness of air quality monitoring in these areas is largely dependent on self-reporting by the companies themselves. On the other hand, air quality has been the top environmental priority, since 2013, for European ports (Puig et al., 2021).

The handling of goods and port activities at Paranaguá port in Brazil might result in atmospheric pollution, leading to negative impacts on air quality in the surrounding area. Previous studies have shown that exposure to high levels of air pollution in port locations is associated with negative health consequences (Chen and Hoek, 2020). Therefore, estimating the sources and concentrations of fine aerosols is essential for investigating the effects of air pollution from port activities on the environment and public health in Paranaguá and related ecosystems.

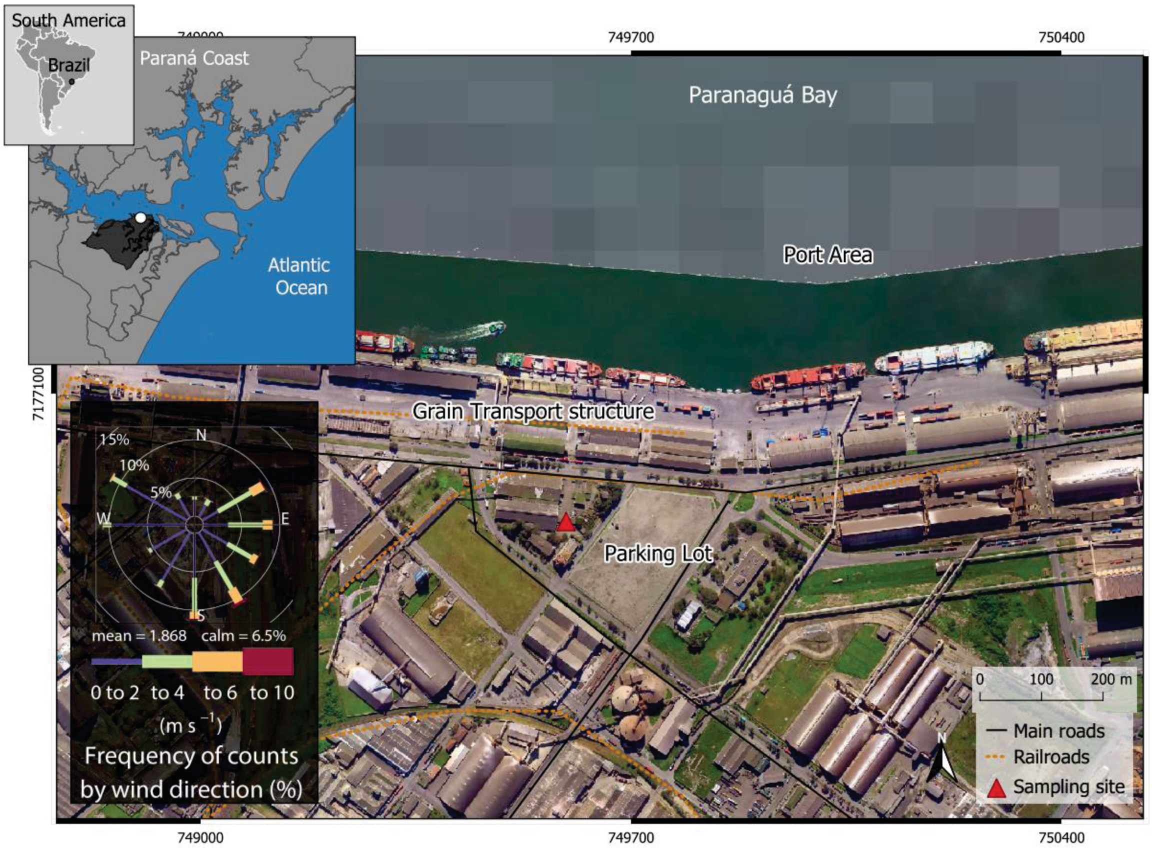
The purpose of this study was to examine the concentrations and sources of $PM_{2.5}$ in an important port region in the South Atlantic by conducting the most extensive and rigorous $PM_{2.5}$ sampling to date in Paranaguá city. The study's primary objectives were as follows: (i) identifying the primary sources of $PM_{2.5}$ based on positive matrix factorization analysis, (ii) assessing and contrasting the $PM_{2.5}$ concentrations found in other port regions with the World Health Organization's (WHO) threshold values, and (iii) examining plausible mechanisms and dynamics of $PM_{2.5}$ transport. In addition, we aimed to establish a robust baseline for future investigations on atmospheric pollution in the study region and make a significant contribution to the global inventory of air quality in port regions.

6.3 MATERIAL AND METHODS

6.3.1 Study area

The study was conducted in the city of Paranaguá, located in the coastal zone of the state of Paraná, Brazil. The air samples were collected on the rooftop of the Brazilian federal revenue building, situated in the port area of the city (25°30’17”S, 48°31'01"W, Fig. 1). The docks are situated to the north of the sampling site. At the same time, a grain transport structure for ships can be found to the northwest. Additionally, there is a large unpaved truck parking lot east of the collection site.

FIG. 1. MAP OF THE STUDIED AREA IN PARANAGUÁ CITY, PARANÁ COAST, SOUTH ATLANTIC, SHOWING THE SAMPLING SITE AND POTENTIAL SOURCES.



SOURCE: THE AUTHOR (2023).

Paranaguá is surrounded by the Serra do Mar mountain range, and it has a subtropical climate. Prevailing winds are from the south and southeast, while light breezes are identified in the west. During the study period, the average temperature in Paranaguá was 22 °C, and the relative humidity of the air was 83%.

6.3.2 Sampling and gravimetric analysis

Samples were collected approximately 3 m above ground level. Daily samples (24 ± 2 h) of $PM_{2.5}$ were collected with 37 mm polycarbonate filters (Nuclepore$^{®}$) using a low volume sampler (Harvard Impactor) operated at 10 L min^{-1}. Samples were taken between December 15th, 2016, and December 16th, 2017. The mass concentration was determined by weighing the filter before and after sampling using an analytical microbalance with a sensitivity of 0.1 µg. Standard protocols (NIOSH 0500) were followed, with filters conditioned at an appropriate temperature (20 °C) and relative humidity (50%).

In addition to gravimetric analysis, each filter was analysed to determine the mass concentration of black carbon (BC, related to fossil fuel burning) and brown carbon (BrC, related to biomass burning) (Malmborg et al., 2021) using a SootScan OT21 optical transmissometer (Magge Scientific) at both infrared (880 nm) and ultraviolet (370 nm) wavelengths. The destructive nature of the analyses required the samples to be randomly divided for soluble ion and metal analyses, with a sample size that reached the standard requirements of the laboratory equipment.

6.3.3 Soluble ion determination

Soluble ion determination was carried out in $PM_{2.5}$ samples (n = 105) using ion chromatography (ICS 5000, Dionex). Anions (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) were determined with an IonPac AS19 column with potassium hydroxide as the eluent (gradient from 1 to 45 mmol L^{-1}, 0.33 mL min^{-1}). Cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were determined with an Ion Pac CS12A column and a CG12A precolumn with methane sulfonic acid as the eluent under isocratic conditions (20 mmol L^{-1}, 0.33 mL min^{-1}). Laboratory reagent blanks were used in each batch, and analyses were performed in triplicate.

Detection limits, calculated according to USEPA (1997), in brackets, in ng m^{-3}, were Cl^- (0.96), NO_3^- (11.0), SO_4^{2-} (14.1), PO_4^{3-} (0.79), Na^+ (5.04), NH_4^+ (18.4), K^+ (7.72), Mg^{2+} (0.28), and Ca^{2+} (15.3).

6.3.4 Determination of major and trace metals

Determination of major and trace metals was carried out in $PM_{2.5}$ samples (n = 78) using an EDXRF MiniPal 4 spectrometer (PANalytical, Almelo) equipped with a silicon drift detector (SDD). The determination of the optimum tube voltage and the current was based on reference standards (Micromatter Seattle, USA) and was validated by measuring several thin layer standards for each element, as well as a reference material from the National Institute of Standards and Technology (NIST 2783 - air particulate on filter media). The best spectra and calibration curves were obtained in a He atmosphere with 600 s of acquisition time under two conditions: a tube voltage of 30 kV and a current of 0.3 mA, with detection limits, in brackets, for Cr (0.39), Cu (0.32), Fe (0.69), Mn (0.35), Pb (0.81), Se (0.40), Ti (0.35), and Zn (0.50); and a tube voltage of 9 kV and a current of 1.0 mA for Al (0.53), Sr (0.30) and Si (2.30). Further details of the analytical method are described by Polezer et al. (2018).

6.3.5 Data analysis

Maps were developed using QGIS (QGIS Development Team, 2022). Statistical analysis and generating graphs were performed using the software JASP (JASP Team, 2021) and R (R Core Team, 2021). The R package openair (Carslaw and Ropkins, 2012) was used to generate bivariate graphs to understand the place of the local sources using meteorological data, mapping the pollutant concentrations by wind variables as a continuous surface (Carslaw and Ropkins, 2012; Masiol et al., 2016).

The Spearman nonparametric test was applied to examine the correlation of $PM_{2.5}$ with meteorological parameters, number of ships and trucks and BC fraction (Table S1, 'S" denotes Supplementary Information, in Appendix 1).

Meteorological data (wind direction and speed, relative humidity, precipitation and temperature) were provided by the Paraná Environmental Technology and Monitoring System (SIMEPAR) through a meteorological station located in the Paranaguá aeroclub (25°32'07"S, 48°31'38"W).

The results of this study were compared with both the World Health Organization's (WHO) 2021 guidelines (WHO, 2021) and the Brazilian national standards proposed by the National Council for the Environment (CONAMA) (Resolução n°. 491, de 19 de Novembro de 2018, 2018). The WHO guidelines were used to assess the levels of fine particulate matter in terms of potential harm to human health. The national standards established by CONAMA, on the other hand, were based on earlier WHO guidelines from 2005. We also calculated the increase in the risk of general mortality associated with $PM_{2.5}$ levels in the study area based on the approach proposed by Chen and Hoek (2020), which stated the combined risk ratio (RR) for $PM_{2.5}$ and natural-cause mortality as 1.08 (95% CI 1.06, 1.09) per 10 $\mu g\ m^{-3}$ assuming a linear relationship.

Enrichment factors (EFs) are geochemical tools used to assess an element's enrichment or depletion relative to a reference value. The calculation of EF values involves dividing the concentration of the element of interest by the concentration of the reference element in the same sample and then dividing this ratio by the corresponding ratio in a reference material (Shafie et al., 2013). In this study, EF values were applied to the trace and major metal concentrations, and Al was used as the reference element because this metal is related to a natural source, derived from parental rocks and linked to clay minerals to the studied area (Angeli et al., 2020). Crustal reference concentrations were provided by Mason and Moore (1982). EF values are classified into the following categories: EF ≤ 1 – no enrichment; 2< EF< 5 – minimal enrichment; 5<EF<20 – significant enrichment; 20<EF<40 – very high enrichment; EF>40 – extremely high enrichment (Akoto & Anning, 2021; Birch, 2023).

Statistical analyses were performed by applying positive matrix factorization (PMF) (Norris et al., 2014; Paatero and Tapper, 1994) to quantify the contribution of sources to total $PM_{2.5}$ concentrations. As the chemical analyses were performed on different filters, two PMF analyses were performed to identify the sources of pollution. The PMF for ion analysis used the following parameters: $PM_{2.5}$ (as total variable), BC (black carbon), Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}. PMF analysis of elemental composition used: $PM_{2.5}$ (as total variable), BC, Al, Si, Cr, Pb, Fe, Ti, Mn, Se, Sr, and Zn. Cu was removed from the PMF analysis due to the limited amount of valid data. BC was classified as “weak” in both analyses due to the low signal-to-noise value in both cases. The number of factors was determined by the lowest factor number possible when over 80% of mapping was achieved, suggesting that the number of factors may be appropriate (Norris et al., 2014).

6.4 RESULTS AND DISCUSSION

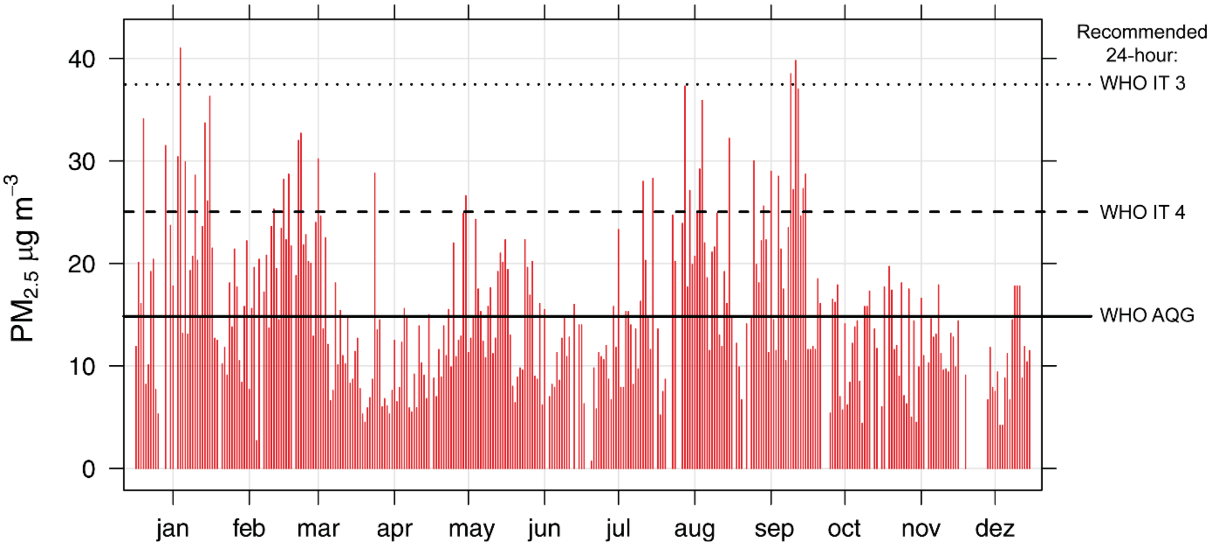
6.4.1 $PM_{2.5}$ concentration

A total of 326 valid was sampled in Paranaguá. $PM_{2.5}$ mean concentration was 15.2 ± 7.5 $\mu g\ m^{-3}$, ranging from 0.7 to 41.0 $\mu g\ m^{-3}$. The $PM_{2.5}$ annual mean concentration in Paranaguá exceeded WHO 2021 interim target nº 3 (15 $\mu g\ m^{-3}$), nº 4 (10 $\mu g\ m^{-3}$) and the Air Quality Guideline (AQG) level (5 $\mu g\ m^{-3}$). Regarding local outdoor atmospheric legislation, Brazilian National Environmental Council (CONAMA) intermediate standard nº 3 and final standards (15 and 10 $\mu g\ m^{-3}$) were exceeded.

The mean concentration (15 $\mu g\ m^{-3}$) represents an 8% increase in the risk of general mortality in the port region of Paranaguá due to $PM_{2.5}$ levels, to 2017, according to the combined risk ratio (RR) for $PM_{2.5}$ and natural-cause mortality (1.08, to 95% CI 1.06, 1.09) per 10 $\mu g\ m^{-3}$ $PM_{2.5}$, assuming a linear relationship (Chen and Hoek, 2020; WHO, 2021).

For short-term (24-hour), the results showed that 10% (n = 34) of the samples in this study exceeded both the final threshold for $PM_{2.5}$ 24-hour mean (25 µg m^{-3}) established by the Brazilian CONAMA and the interim target n° 4 (25 µg m^{-3}) established by WHO guidelines. Additionally, 42% (n = 137) of the samples exceeded the WHO Air Quality Guideline (AQG) for the 24-hour mean $PM_{2.5}$ (15 µg m^{-3}). These findings are significant when compared to the WHO's recommendation of a maximum of 3 to 4 exceedance days per year (99th percentile of the dataset), highlighting the urgent need for effective measures to control and reduce $PM_{2.5}$ pollution in the study area, given the significant proportion of samples that exceeded the air quality guidelines established by the WHO and the CONAMA, both for annual mean values and short-term concentrations.

FIGURE 2. DAILY $PM_{2.5}$ CONCENTRATIONS IN 2017. THE BLACK DASHED LINES REPRESENT THE 24-HOUR MEAN WHO INTERIM TARGET N° 3 AND N° 4, AND THE SOLID BLACK LINE SHOWS THE 24-HOUR MEAN AIR QUALITY GUIDELINE (AQG), BOTH BASED ON THE WHO (2021) GUIDELINES.



SOURCE: THE AUTHOR (2023).

The annual mean concentrations of $PM_{2.5}$ in Paranaguá port were comparatively lower than those in Bushehr in the Persian Gulf (52.8 µg m^{-3}) (Akhbarizadeh et al., 2021), Rio Grande, Brazil (31. 9 ± 17.8 µg m^{-3} in industrial areas and 26.8 ± 9.4 µg m^{-3} in urban areas) (Gutierrez et al., 2020); Xiamen Bay, Southeast China (32.8 ± 18.9 µg m^{-3}) (Wu et al., 2020); Bangkok, Thailand (77.0 ± 21.2 µg m^{-3}) (ChooChuay et al., 2020) and Gdynia, Northern Poland coast (24.3 ± 22.5 µg m^{-3}) (Siudek, 2022). The $PM_{2.5}$ annual means in Paranaguá were similar to those observed in Porto Alegre, South Brazil (urban area: 15.4 µg m^{-3}, rural area: 7.0 µg m^{-3})

(Dallarosa et al., 2008), Barranquilla, Colombia (15.1 - 18.1 µg m^{-3}) (Duarte et al., 2022) and Buenos Aires, Argentina (15 µg m^{-3}) (Arkouli et al., 2010).

BC and BrC concentrations ranged from 0.3 to 4.8 µg m^{-3} (mean = 2.3 ± 0.7) and from 0.3 to 2.7 µg m^{-3} (mean = 1.3 ± 0.4), respectively. BC emissions are suggestive of fossil fuel sources (Malmborg et al., 2021) and account for approximately 15% of the average mass of $PM_{2.5}$ in the atmosphere of Paranaguá. Moreover, Gurgatz et al. (2023) and Garcia and Martins (2021) found that high molecular weight polycyclic aromatic hydrocarbons, which are known to be produced from the combustion of fossil fuels, are present in the superficial sediments of the Paranaguá estuary. Therefore, there is evidence that the burning of fossil fuels represents a significant source of hydrocarbon inputs to the local environment.

The concentration of $PM_{2.5}$ revealed a positive Spearman nonparametric correlation with temperature (0.183, $p = 0.001$) as well as a negative correlation with relative humidity (-0.236, $p \leq .001$), probably due to the contribution of high temperatures to reduce humidity and consequently to concentrate suspended particles in the air (Table S1). A very similar scenario was described for Rio Grande, South Brazil, which hosts a large port city with usually high humidity levels due to frequent cold fronts (Gutierrez et al., 2020), as the optimal humidity for a rapid increase in $PM_{2.5}$ is between 45 and 84% (Zhang et al., 2017). Since the average humidity in Paranaguá is close to the upper boundary of this range (80%), even small decreases in relative humidity could lead to an increase in $PM_{2.5}$ concentrations.

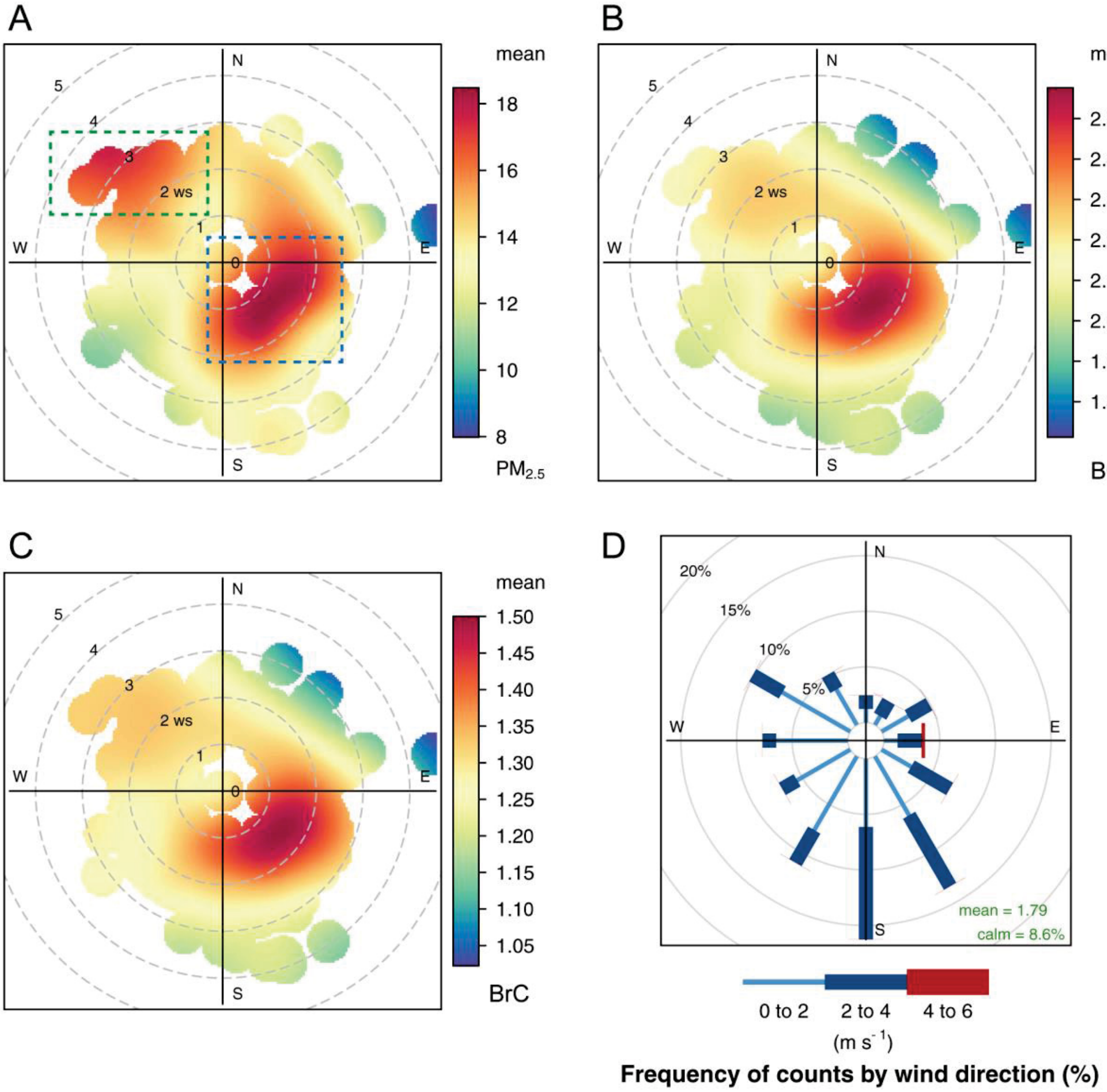
Precipitation and humidity were shown to be important factors in the removal of $PM_{2.5}$ from the air (-0.238, $p < 0.001$ and -0.236, $p < 0.001$, respectively). However, humidity had no effect on BC and BrC ($p \geq 0.005$), which is probably explained by the hydrophobicity of these particles (McMeeking et al., 2011).

Similarly, significant relationships were found for PM_{25} with trucks and ships numbers (0.160, $p = 0.004$ and 0.166, $p = 0.003$, respectively). However, trucks were shown to play an important role in soot formation, with higher and more significant values for BC and BrC (0.250, $p = < 0.001$ and 0.242, $p =< 0.001$, respectively) than ships (0.168, $p = 0.003$ and 0.159, $p = 0.005$, respectively). Diesel combustion for road transportation is a well-established source of BC emissions (Kholod et al., 2016). Previous studies on the occurrence of PAHs in Paranaguá Bay sediments pointed to fossil fuel burning as an important source in the area (Garcia et al., 2019; Garcia and Martins, 2021; Gurgatz et al., 2023). Those findings suggest that both trucks and ships contribute significantly to $PM_{2.5}$ levels, but trucks, with their higher levels of BC emissions, are particularly important for soot formation.

6.4.2 Source apportionment based on bivariate plots

Bivariate plots were used to analyse the monitored $PM_{2.5}$ concentrations under different wind conditions. The daily average in meteorological data (due to $PM_{2.5}$ being analysed in this sample cut) can bring a smoothing bias in the results and lower resolution of possible sources (Carslaw and Ropkins, 2012). However, the results were useful for performing a preliminary investigation of the possible directions from which the studied pollutants are being emitted. This can be seen in Fig. 3, which shows the bivariate plotting of pollutants and wind conditions for the analysed period.

FIG. 3. BIVARIATE PLOTS OF A) $PM_{2.5}$, B) BC AND C) BRC FOR PARANAGUÁ PORT IN 2017. D) FREQUENCY COUNTS BY WIND DIRECTION FOR PARANAGUÁ PORT IN 2017. THE CENTRE OF THE PLOT CORRESPONDS TO A WIND SPEED OF 0 m s^{-1}.

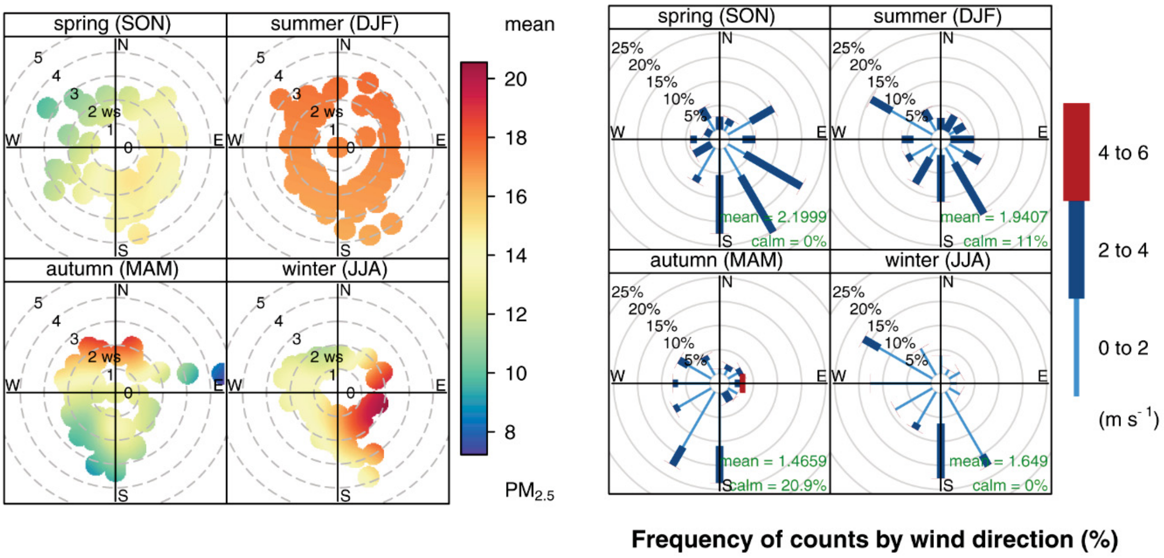


SOURCE: THE AUTHOR (2023).

A primary source of aerosols, marked by a blue dashed square in Fig. 3A, was identified due to higher average concentrations observed for winds blowing from the southeast at speeds up to 3 m s^{-1}. The presence of the same red mark in the BC plot (Fig. 3B) indicates that the source is likely associated with fossil fuel combustion. In Fig. 4, this source is primarily detected in the winter season, as can be observed from the red spot located to the southeast in the graph depicting winter, as shown in Fig. 4. The location and direction of the source suggest that it may be linked to the presence of an access road to the port and a large truck parking area near the sampling station, which at the time of the study was unpaved (Fig. 4). The findings suggest that aerosols are locally sourced, and their concentration increases during periods with low wind speeds.

A secondary source (green dashed square in Fig. 3A) was identified by increasing average concentrations for winds blowing from the NW direction at speeds up to 4 m s^{-1}. In contrast to the previous source, it does not appear in the BC plot (Fig. 3B), indicating that it is not associated with fossil fuel combustion. The presence of a grain transport structure in this direction, which moves grains between warehouses and ships, may be responsible for the emissions. This secondary source is primarily detected during the autumn season (red spots in autumn, as shown in Fig. 4).

FIG. 4. BIVARIATE PLOTS FOR $PM_{2.5}$ AND FREQUENCY OF COUNTS BY WIND DIRECTION SEPARATED BY SEASON FOR PARANAGUÁ PORT IN 2017.



SOURCE: THE AUTHOR (2023).

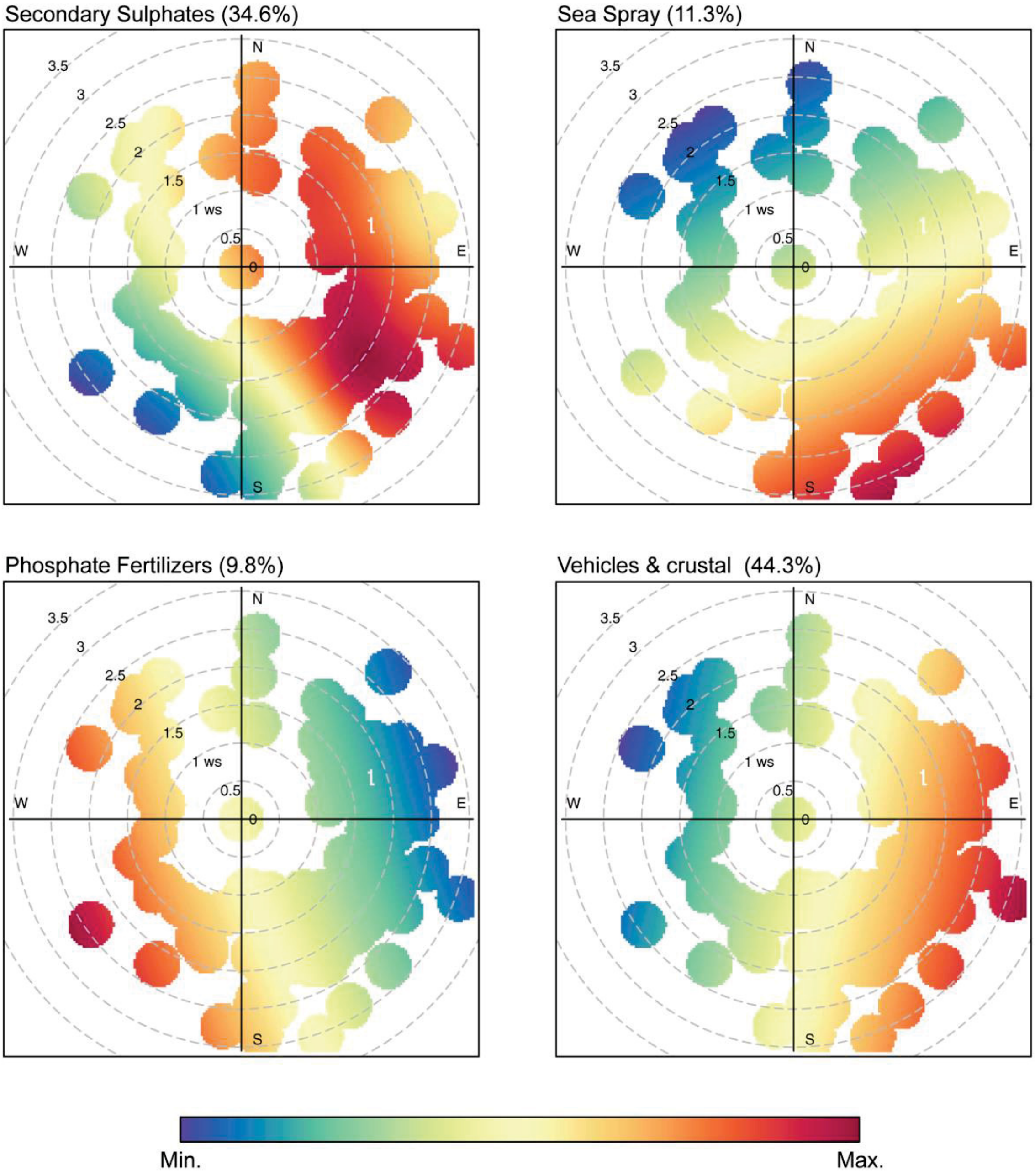
According to Machado et al. (2016), the primary wind directions in the studied region are E, SE, and S. The frequency of counts by wind direction indicates that wind speed decreases during autumn and winter (Fig. 4), with winds typically not exceeding 2 m s^{-1}. This observation may account for nearby sources, as higher wind speeds are necessary for the effective dispersion of particles.

6.4.3 Soluble ion concentrations and source apportionment

The soluble ionic compounds concentrations were ranked in the following order: SO_4^{-2} > NH_4^+ > PO_4^{3-} > Na^+ > NO_3^- > Ca^{2+} > K^+ (Table S2). SO_4^{2-} and NH_4^+ were identified as dominant in similar studies in port areas (Pérez et al., 2016; Tolis et al., 2015) and are related to secondary sulphate formation, generated by the combination of SO_2 air masses from road traffic with NH_3 from industrial fertilizer activity, once SO_2 is oxidized in the atmosphere to form H_2SO_4, which reacts with NH_3 to produce secondary sulphates (Dahari et al., 2021; Gutierrez et al., 2020; Reche et al., 2012).

Four factors were defined as the best fit for soluble ions based on PMF (Fig. S1 for profiles and Fig. 5 for bivariate plots):

FIG. 5. BIVARIATE PLOTTING GRAPHS FOR PMF-RESOLVED SOURCE PROFILES FOR SOLUBLE ION ANALYSES.



Secondary Sulphates (34.6%)

Sea Spray (11.3%)

Phosphate Fertilizers (9.8%)

Vehicles & crustal (44.3%)

SOURCE: THE AUTHOR (2023).

(1) Secondary sulphates (34.6%): This profile is primarily attributed to the presence of SO_42- and NH_4^+ ions and BC, which is consistent with findings from previous studies conducted in Barcelona port, Spain (Pérez et al., 2016) and Southeast Asia (Dahari et al., 2021). This factor is associated with the formation of secondary sulphates (Gutierrez et al., 2020; Reche et al., 2012). The BC in this factor corroborates the fossil fuel burning contribution from trucks and ships. A similar profile has also been observed in an urban area of São Paulo, Brazil, as a result of the conversion of vehicular SO2 (Castanho and Artaxo, 2001; Pereira et al., 2017). The source location east of the sampling site (Fig. 5) is due to the intense port activity in this direction, including a large truck parking lot.

(2) Sea spray (11.3%): Explained by Cl-, Na+ and NO3- ions that indicate a sea salt source (Dahari et al., 2021; Pérez et al., 2016) originating from the coastal area to the southeast. The presence of NO3- is due to the interaction of saline spray with NOx, as already described for the port area of Barcelona, Spain (Pérez et al., 2016), Algeciras bay, Lecce city, Italy (Cesari et al., 2016).

(3) Phosphate fertilizers (9.8%): As explained by PO_4^{3-}, this factor suggests fertilizer sources (Papastefanou, 2001), which is also supported by previous findings in the Brazilian port city of Rio Grande (Gutierrez et al., 2020). There are several industries in the study area that process phosphatic rocks, and the Port of Paranaguá imported 479.424 tons of this material. In addition, it imported 1.106.659 tons of NPK fertilizers, 198.845 tons of diammonium hydrogen phosphate, and 1.107.016 tons of ammonium dihydrogen phosphate, among other fertilizer mixtures with phosphate in their composition (SINDIADUBOS, 2017). The direction of emissions is consistent with the location of the industrial complex in the region.

(4) Vehicles and crustal contributions (44.3%): NO3-, Na+, K+, Mg2+, Ca2+ and BC. This factor results from the combination of soil resuspension and atmospheric emissions from vehicle exhaust, similar to that described by Lodhi et al. (2009) and Pereira et al. (2017). For Southeast Asia, K+ and BC are associated with vehicle emissions, and Mg2+ and Ca2+ are related to mineral dust (Dahari et al., 2021). The direction of the emissions suggests that they originate from the nearby unpaved parking lot and the urbanized region of the city.

The two dominant profiles contributing to the concentrations of soluble ions in $PM_{2.5}$ in Paranaguá were vehicles and crustal (44.3%) and secondary sulphates (34.6%). The latter, formed by the reaction between SO_2 and NH_3, is linked to traffic and fertilizer industries, suggesting that these are the primary sources of soluble ions in this region. Notably, traffic appears to significantly contribute to atmospheric pollutants in Paranaguá, which differs from the major sources of ionic species found in the port city of Rio Grande, South Brazil, where industries play a predominant role (Gutierrez et al., 2020).

6.4.4 Trace and major metal concentrations and source apportionment

Table 1 presents the results of the analysis of trace and major metals and their enrichment factors (EFs) to verify whether the source of each element is natural or anthropogenic.

TABLE 1: CONCENTRATION AVERAGES, MAXIMUM VALUES (MAX.), NUMBER OF SAMPLES DETECTED (N), AND ENRICHMENT FACTOR (EF) OF TRACE AND MAJOR METALS FROM $PM_{2.5}$ SAMPLES.

	Average [ng g^{-3}]	**Max. [ng g^{-3}]**	**Min. [ng g^{-3}]**	**N**	**EF* Average**
Al	70 ± 35	178	18	76	Reference element
Se	3.8 ± 1.3	8.1	1.3	76	58852
Sr	1.7 ± 1.0	5.2	0.4	68	5
Si	256 ± 125	602	52	76	1
Fe	124 ± 58	291	43	76	3
Ti	10 ± 5	29	2.7	76	3
Mn	4.9 ± 3.2	18	0.45	56	6
Cr	2.3 ± 1.2	5.6	0.39	76	32
Cu	1.8 ± 1.3	5.7	0.39	21	45
Zn	9.6 ± 4.3	30	2.7	76	188
Pb	3.7 ± 2.5	14	0.40	70	430

EF: ≤ 1 – no enrichment; 2< EF< 5 – minimal enrichment; 5<EF<20 – significant enrichment; 20<EF<40 – very high enrichment; EF>40 – extremely high enrichment.

SOURCE: THE AUTHOR (2023).

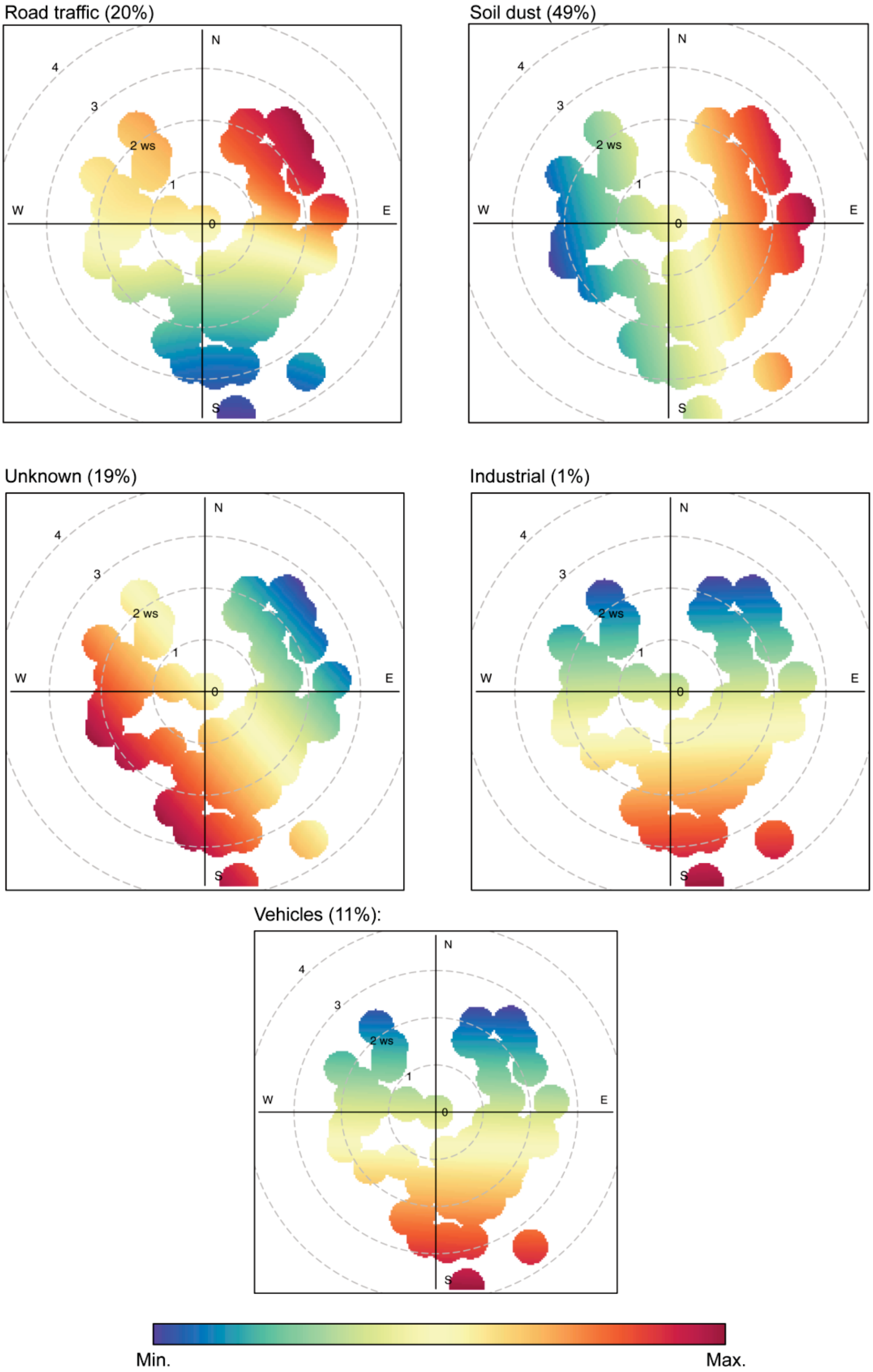
The elements Cr, Cu, Zn, and Pb exhibited EF averages exceeding 20, indicating significant enrichment and suggesting a potential anthropogenic source. Notably, Se displayed an extremely high EF value; however, this result is likely attributed to methodological issues due to the low reference value used. Further investigations and caution are necessary to accurately interpret the enrichment of Se in the analysed samples.

The elements Sr, Si, Fe, Ti, and Mn exhibited average EF values lower than 20, with Ti and Si specifically not exceeding a value of 10 in any individual sample (Appendix 2. Research data). These results are comparable to their background levels or relatively unaffected by anthropogenic sources, as they are usually associated with the Earth's crust (Viana et al., 2008).

The EFs obtained are similar to those found by Machado et al. (2016) in Paranaguá for atmospheric deposition. Both studies revealed enriched levels of Cu and Zn, while Mn was also identified as an enriched element but only in the previous study. Both studies concurred that Fe was not enriched, implying that its concentrations were relatively consistent with background levels.

For PMF analysis on trace and major metals, five factors were determined (Fig. S2 for profiles and Fig. 6 for bivariate plots):

FIG. 6. BIVARIATE PLOTTING GRAPHS FOR PMF-RESOLVED SOURCE PROfiLES FOR MAJOR AND TRACE METALS ANALYSIS.


Road traffic (20%)

Soil dust (49%)

Unknown (19%)

Industrial (1%)

Vehicles (11%):

SOURCE: THE AUTHOR (2023).

(1) Road traffic (20%): Cr and Zn with BC explain this profile. This profile is related to vehicular emissions, particulate resuspension, and the detritus of automotive parts. Similar profiles have been observed on highways in Hong Kong (Cheng et al., 2015), Beijing (Yu et al., 2013) and all of Southeast Asia (Dahari et al., 2021). The wind direction points to the port region, which suggests a relationship with heavy vehicles.

(2) Soil dust (49%) is characterized by Al, Si, Fe, Ti, Se and BC, related to crustal elements (Dahari et al., 2021) from soils (Cheng et al., 2015; Pérez et al., 2016; Yu et al., 2013), which is consistent with the result of the EF analysis. The emission direction graph points to the east, where there was a large unpaved truck parking lot, which contributes to the resuspension of soil elements and justifies the presence of BC in this profile.

(3) Unknown (19%): Si and Sr were the main components. Although these elements are found in resuspended road dust (Cheng et al., 2015; López et al., 2011), this factor was attributed to unknown sources because it is not compatible with other elements, or they are not important elements in these profiles.

(4) Industrial (1%): Pb and Mn. Although this profile is usually related to the metallurgical industries (Cesari et al., 2016; Cheng et al., 2015; Pérez et al., 2016), the low contribution observed in the study area may be related to emissions from secondary industrial activity, such as boilers or welding operations. This profile could also be related to traffic (Lodhi et al., 2009), but the absence of BC suggests a nonvehicular source. The direction of the emission sources agrees with the location of large fertilizer and alcohol industries.

(5) Vehicles (11%): Pb, Zn and BC. Profile characterized as vehicle exhaust emission, detritus of its components (Cesari et al., 2016; Lodhi et al., 2009; Moreira et al., 2018; Yu et al., 2013) and oil combustion (Polezer et al., 2018). The wind direction points to the urban area pointed to a source location.

Similar to the analysis of soluble ions, the main source identified for the trace and major metals is from traffic, but in this case, it is related to soil resuspension. Additionally, the industrial source presented little contribution to these results.

6.5 SUMMARY AND CONCLUSIONS

In this study, we identified several cases of high short-term and a high annual mean for $PM_{2.5}$ in the Paranaguá port region, one of the largest Brazilian ports and the leader in grain exports. Based on the WHO guidelines, the observed levels are alarming and may cause several health problems. The levels are not well monitored in Brazil. These findings highlight the urgent need for effective measures to mitigate the negative impacts of port activities on air quality and public health in Brazil. Ensuring compliance with air quality standards and protecting public health is a challenge, highlighting the need for an urgent expansion of air quality monitoring infrastructure across the country, including in nonurban areas.

Two different approaches were used to estimate the sources of $PM_{2.5}$ in the Paranaguá port area. The results indicated that truck activity in a nearby parking lot was the main source, and the presence of a transportation structure was probably related to fertilizer and grain transportation as a secondary source of fine particulate matter. Due to the global implementation of ‘carbon bombs’, which are being planned independently of the agreements to reduce the emission of greenhouse gases, there is no reason to believe that there will be a reduction in the use of fossil fuels and road transportation, especially in the context of a developing country such as Brazil. The case of Paranaguá serves as a reminder of how international economic interests can lead to the exploitation of a territory, its inhabitants, and its biodiversity. Additionally, the results demonstrated that fine aerosol particulate matter is a potential environmental quality indicator for estuarine human impact areas, especially when pollutant levels are lower in sediments and the water column.

The port of Paranaguá achieved first place in environmental performance according to the Environmental Performance Index of the Brazilian National Waterway Transport Agency established by Paraná Ports Administration in 2017. This study raises questions about the effectiveness of the index applied to evaluate Brazilian ports, which does not ensure the real measurement of the environmental risk provided by current port institutions and the nearby port and urban infrastructure. As previously shown, this index is not compatible with the international model of port environmental management, which prioritizes atmospheric pollution in the structure of its indices, considering it as an environmental priority since 2013.

Decision-makers must also consider that the impacts described in this study can synergistically and unpredictably combine with the impact of all the infrastructure projects planned for a region. These impacts are the result of a policy aimed at exploiting the last remaining conserved areas in Brazil for the production and export of soybeans and other commodities. The profitability of Brazilian soybean is questionable when considering the social and environmental costs of production.

We recommend conducting additional research on the organic compounds present in $PM_{2.5}$ within the Paranaguá Estuarine System to gain a better understanding of the influence of fossil fuel combustion and grain transportation on environmental conditions. Previous investigations have already been conducted on sediments in Paranaguá Bay, which have identified fossil fuel burning as a significant contributor to the region's pollution. As a result, an evaluation of the atmospheric sources of these compounds could provide valuable insights into the input and distribution of pollutants from the atmosphere to the ocean, as well as the specific role of fossil fuels in this process, making a significant contribution to the global inventory of air quality in port regions.

6.6 STATEMENTS AND DECLARATIONS

6.6.1 Authorship contributions

Bruno Martins Gurgatz: Conceptualization, Data acquisition, Formal analysis, Methodology, Writing - original draft, review & editing. Luiza Natalino: Methodology, Writing - review & editing. Julia Stefany Chagas Albrecht: Data acquisition, Formal analysis, Writing - review & editing. Camila Arielle Bufato Moreira: Formal analysis, Writing - review & editing. Marina Reback Garcia: Formal analysis, Writing - review & editing. Emerson Joucoski: Formal analysis, Writing - review & editing. Ricardo Henrique Moreton Godoi: Supervision, Funding acquisition, Project administration, Writing – review. César C. Martins: Formal analysis, Supervision, Writing – review & editing. Rodrigo Arantes Reis: Conceptualization, Funding acquisition, Project administration, Writing – review.

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6.6.4 Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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7 CONCLUSÕES

As três investigações apresentadas caracterizam o CEP a partir do impacto proveniente das atividades produtivas (HPAs), lançamento de efluentes (LABs) e transporte de mercadorias (PM2.5).

Sedimentos finos e matéria orgânica foram os principais fatores que controlaram as concentrações de HPAs no CEP. Entretanto, fontes antropogênicas também foram identificadas. A queima de biomassa e de combustíveis fósseis predominaram, mas quantidades residuais de fontes petrogênicas foram observadas. Identificamos evidências da contribuição de uma bacia hidrográfica adjacente resultante da construção de interconexões entre grandes rios e de anos de desmatamento intensivo na Mata Atlântica local.

A fonte primária de LABs no CEP foram os rios do entorno do município de Paranaguá, que transportam efluentes das estações de tratamento da cidade ou drenam o esgoto direto lançado nas fossas na região de Valadares, sem tratamento na época do estudo.

Quanto ao PM2.5 em Paranaguá, as concentrações encontradas estão próximas aos limites médios sugeridos pela Organização Mundial da Saúde, com casos de altas concentrações diárias. A atividade rodoviária e a estrutura de abastecimento de navios foram identificadas como principais fontes.

O "retrato do Antropoceno" apresentado aqui mostra um CEP já explorado pela agricultura e pecuária extensiva, pela ocupação desordenada de seu território, e pelo uso portuário-industrial de suas margens estuarinas. Apesar de preservado em grande parte do território, o CEP não pode ser considerado um ambiente prístino devido às concentrações de marcadores antropogênicos identificadas ao longo do gradiente estuarino. Além disso, o risco ambiental relacionado à poluição atmosférica é evidente para as grandes populações de trabalhadores submetidos ao trabalho portuário na região de Paranaguá.

8 CONSIDERAÇÕES FINAIS

Saltavore (2008) diz que a externalidade é a divergência entre custos privados e custos sociais. Eles surgem pois a economia baseada na livre iniciativa e concentração econômica raramente incorpora os impactos sociais, ambientais e sanitários consequentes das atividades produtivas que geram produtos e serviços, o que representa um importante entrave para a sustentabilidade (Soares; Porto, 2007).

Este trabalho apresentou, a partir de três abordagens, a concentração de poluentes e marcadores ambientais como uma ferramenta para caracterizar as pressões e impactos antrópicos presentes em um ecossistema. Considerando a natureza dos problemas ambientais como interdisciplinares, onde os sistemas sociais, econômicos, ecológicos e climáticos estão normalmente relacionados (MacLeod; Nagatsu, 2018), os resultados obtidos evidenciam a importância da história ambiental para a compreensão dos fenômenos observados nos depósitos sedimentares, e como eles refletem as principais externalidades que incidem sobre o CEP.

A identificação de fontes, abordada em todos os capítulos apresentados, dá suporte a noção de que a poluição química no contexto contemporâneo é um fenômeno relacionado à expansão de um modo de produção insustentável que vem causando mudanças ambientais ao ponto de caracterizar uma nova época geológica (Subramanian, 2019). Em geral, os resultados apontam que os principais processos produtivos da região (como a antiga agricultura extensiva na margem norte do CEP ou a atividade portuária na margem sul) ou processos decorrentes destes como desmatamento ou urbanização são as principais fontes de interferência antrópica neste ecossistema. Apresenta-se aqui na forma de mapas de calor, a invisível cicatriz deixada pelo impacto da exploração econômica de um território.

As informações apresentadas fundamentam um alerta: regiões prioritárias para a conservação da biodiversidade global já apresentam evidências químicas de alterações antropogênicas, apresentando concentrações de compostos em seus compartimentos ambientais não compatíveis com o enquadramento de uma região prístina.

Recentes mudanças no contexto político brasileiro apontam para avanços de pautas ambientais e relacionadas à ciência e tecnologia, após desmonte de tais áreas durante o período do governo deposto nas eleições de 2022 (Tollefson, 2022). Apesar disso, o foco na preservação da Amazônia e a aposta na falácia de um agronegócio sustentável de modelo neoliberal sugerem que a problemática da poluição ambiental dos ecossistemas ainda será tratada de maneira secundária no contexto nacional (Corcioli; Medina; Arrais, 2022; Oliveira; de Souza e Silva, 2021). Globalmente, a expansão em curto prazo da indústria de combustíveis fósseis está ocorrendo independentemente dos acordos para reduzir a emissão de gases de efeito estufa através de mais de 195 grandes projetos de exploração de petróleo e gás (as “Bombas de Carbono”, como denunciado pelo jornal britânico The Guardian) (Carrington; Taylor, 2022). Neste sentido, tanto no contexto nacional quanto global, as economias de mercado continuam conduzindo os estados às políticas ambientais insuficientes para a proteção de seus ecossistemas e manutenção dos serviços ambientais.

Assumir o Antropoceno como época geológica é assumir uma relação intrínseca entre ser humano e meio ambiente. Assumir essa relação é considerar que a história humana possui um conflito ético entre a sustentabilidade e o desenvolvimento econômico, que só pode ser resolvido a partir de uma mudança de perspectiva que vai além da compreensão dos impactos, mas na própria constituição da sociedade que almejamos.

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ANEXOS (SUPPLEMENTARY INFORMATION)

Supplementary Information - Polycyclic aromatic hydrocarbons in a Natural Heritage Estuary influenced by anthropogenic activities in the South Atlantic: Integrating multiple source apportionment approaches

TABLE S1. PAHS ANALYZED IN THE PRESENT STUDY, THEIR ABBREVIATIONS, GROUPS, AND THE INDICATION OF OCCURRENCE TO THE LIST OF THE 16 PRIORITY PAHS OF THE EPA AND THE EXPANDED 40 PAHS LIST ACCORDING TO ANDERSSON E ACHTEN (2015).

	Compound	**Abbreviation**	**16 EPA PAHs**	**40 PAHs**
PAHs (2-3 rings) Low Molecular Weight (LMW) (N = 8)	naphthalene	Naph	X	X
	biphenyl	BP		
	acenaphthylene	Ace	X	X
	acenaphthene	Aceph	X	X
	fluorene	Flr	X	X
	dibenzothiophene	DBT		
	phenanthrene	Phen	X	X
	anthracene	Ant	X	X
PAHs (4-6 rings) Molecular Weight (HMW) (N = 14)	fluoranthene	Flu	X	X
	pyrene	Pyr	X	X
	benz[*c*]anthracene	BcA		
	benz[*a*]anthracene	BaA	X	X
	chrysene	Chr	X	X
	benzo[*b*]fluoranthene	BbF	X	X
	benzo[*j*+*k*]fluoranthene	BjkF	X	X
	benzo[*e*]pyrene	BePyr		
	benzo[*a*]pyrene	BaPyr	X	X
	indene[1,2,3-*c,d*]pyrene	InP	X	X
	dibenzo[*a,h*]anthracene	DBA	X	X
	benzo[*b*]chrysene	BbC		
	benzo[*g,h,i*]perylene	Bghi	X	X
Alkyl PAHs (8 subgroups, N = 32)	C_1- naphthalenes (N = 2)	C1Naph		X
	C_2- naphthalenes (N = 7)	C2Naph		X
	C_3- naphthalenes (N = 5)	C3Naph		
	C_1- phenanthrenes (N = 5)	C1Phen		X
	C_2- phenanthrenes (N = 3)	C2Phen		
	C_1- fluoranthenes (N = 3)	C1Flu		
	C_1-pyrenes (N = 2)	C1Pyr		X
	C_1-chrysenes (N = 5)	C1Chr		X
Naturals (N = 2)	retene	Ret		X
	perylene	Per		

Reference

Andersson, J.T., Achten, C., 2015. Time to say goodbye to the 16 EPA PAHs? Toward an up-to-date use of PACs for Environmental Purposes. Polycyclic Aromatic Compounds 35, 330–354. https://doi.org/10.1080/10406638.2014.991042

TABLE S2. SURROGATE RECOVERY FOR DEUTERATED STANDARDS USED IN THE SEDIMENT ANALYSES.

	Sediment (n = 84)	**Blanks (n = 12)**
naphthalene-d_8	31.0 ± 7.9%	35.8 ± 7.8%
acenaphthene-d_{10}	46.7 ± 8.8%	50.4 ± 5.4%
phenanthrene-d_{10}	61.5 ± 8.8%	61.4 ± 5.2%
chrysene-d_{12}	73.4 ± 7.2%	74.9 ± 5.9%
perylene-d_{12}	74.4 ± 10.7%	69.2 ± 5.4%

TABLE S3. INDIVIDUAL PAH RECOVERY FOR BLANK AND SEDIMENT SPIKE. SD: STANDARD DEVIATION

* DENOTES % RECOVERY OUT OF THE RECOMMENDABLE RANGE (50 – 110 %, DENOUX ET AL. 1998).

Compounds (16 EPA PAHs)	**% recovery ± SD**	
	Blank Spike (N = 3)	**Sediment Spike (N = 3)**
naphthalene *	94 ± 2	102 ± 9
acenaphthylene	98 ± 10	92 ± 12
acenaphthene	88 ± 2	90 ± 4
fluorene	96 ± 3	106 ± 2
phenanthrene	98 ± 2	100 ± 2
anthracene	70 ± 2	64 ± 1
fluoranthene	102 ± 2	100 ± 1
pyrene	92 ± 2	88 ± 1
benz[*a*]anthracene	80 ± 1	80 ± 1
chrysene	92 ± 2	86 ± 3
benzo[*b*]fluoranthene	90 ± 3	86 ± 2
benzo[*j*+*k*]fluoranthene	82 ± 1	82 ± 1
benzo[*a*]pyrene	74 ± 1	66 ± 1
indene[1,2,3-	102 ± 2	98 ± 2
dibenzo[*a,h*]anthracene	98 ± 2	108 ± 2
benzo[*g,h,i*]perylene	94 ± 2	106 ± 2
Mean	91 ± 9	91 ± 13
Minimum	70	64
Maximum	102	108

Reference

Denoux, G.J., Gardinali, P., Wade, T.L., 1998. Quantitative determination of polynuclear aromatic hydrocarbons by gas chromatography/mass spectrometry - selected ion monitoring (SIM) mode. NOAA Technical Memorandum NOS ORCA 130. 129-139.

TABLE S4. RESULTS FROM ANALYSIS OF SEDIMENT REFERENCE MATERIAL (IAEA-417; INTERNATIONAL ATOMIC ENERGY AGENCY). MEAN AND REFERENCE INTERVAL OBTAINED FROM IAEA-417 REFERENCE SHEET. * DENOTES VALUES OUT OF THE RECOMMENDABLE RANGE (UPPER AND LOWER ± 35% OF 95% CONFIDENCE REFERENCE INTERVAL AS PROPOSED BY WADE AND CANTILLO, 1994).

Compounds (16 EPA PAHs)	IAEA-417 (N = 3)	Mean Value	Reference interval	Interval ± 35 %
	ng g^{-1} dw			
naphthalene	78	150	100 - 200	65 - 270
acenaphthylene	NA	NA	NA	NA
acenaphthene	89	230	130 - 230	85 - 311
fluorene *	86	3900	160 -300	104 - 405
phenanthrene	2424	630	3400 - 4400	2210 - 5940
anthracene *	252	7700	520 -740	338 - 999
fluoranthene	4473	6000	6800 - 8600	4420 – 11,610
pyrene	3619	3200	5300 - 6700	3445 - 9045
benz[*a*]anthracene	2363	3600	2800 - 3600	1820 - 4860
chrysene	2318	4100	3100 - 4100	2015 - 5535
benzo[*b*]fluoranthene	2333	2000	3100 - 5100	2015 - 6885
benzo[*j*+*k*]fluoranthene	1337	2800	1800 - 2200	1170 - 2970
benzo[*a*]pyrene	1645	2700	2400 - 3200	1560 - 4320
indene[1,2,3-*c,d*]pyrene *	1108	1100	2500 - 2900	1625 - 3915
dibenzo[*a,h*]anthracene	367	2300	510 - 1700	332 - 2295
benzo[*g,h,i*]perylene	1314	150	1900 - 2700	1235 - 3645

Reference

Wade, T.l., Cantillo, Y.A., 1994. Use of standards and reference materials in the measurement of hydrocarbons residues. Chemistry Workbook. NOAA Tech. Mem. NOS ORCA 77, Silver Spring, Maryland, 59p.

TABLE S5. PAH DIAGNOSTIC RATIOS FOR SOURCE APPORTIONMENT EVALUATED IN THIS STUDY.

Ratio	Description	Petrogenic	Pyrogenic	Biomass Burn	Ref.
Fl/Fl+Py	fluoranthene / fluoranthene + pyrene	< 0.40	0.40 – 0.50	> 0.50*	Yunker et al. (2002)
BaA/228	benz[*a*]anthracene / benz[*a*]anthracene / + chrysene	< 0.20	> 0.35		
In/(In+Bghi)	indene[1,2,3-*c,d*]pyrene / indene[1,2,3-*c,d*]pyrene + benzo[*g,h,i*]perylene	< 0.20	0.20 – 0.50	> 0.50	
C_0/C_0+C_1 P	not alkylated / not alkylated +alkylated phenanthrenes	< 0.40	> 0.40	>0.50	
∑LMW/∑HMW	Low Molecular Weight PAHs/High Molecular Weight PAHs	> 1	< 1		Tobiszewski e Namieśnik (2012)
%perylene/∑(5 ring PAHs)		antropic <10% = >10% = natural			Tobiszewski e Namieśnik (2012)

*SEWAGE SOURCE.

TABLE S6. SPEARMAN CORRELATION (ρ) MATRIX FOR TOTAL NITROGEN (TN), TOTAL ORGANIC CARBON (TOC), FINE SEDIMENTS (SUM OF SILT AND CLAY FRACTIONS) AND ∑PAHS.

Spearman's correlations

Variable		**TN**	**TOC**	**fine sediment**	**∑PAHs**
1. TN	Spearman's (ρ)	—			
	p-value	—			
2. TOC	Spearman's (ρ)	0.975	—		
	p-value	<0.001	—		
3. fine sediment	Spearman's (ρ)	0.856	0.851	—	
	p-value	<0.001	<0.001	—	
4. ∑PAHs	Spearman's (ρ)	0.822	0.836	0.706	—
	p-value	<0.001	<0.001	<0.001	—

Shapiro-Wilk test for multivariate normality: 0.855 *p*-value < 0.001

TABLE S7. SEDIMENT QUALITY THRESHOLDS FOR $\sum_{16}$PAH BASED ON TOXICOLOGICAL RESPONSES OF BENTHIC ORGANISMS COMPARED TO THIS STUDY.

PAH	**ERL**	**ERM**	**TEL**	**PEL**	**This study**	
					Average	**Maximum**
naphthalene	160	2100	34.6	391	3.51	38.2
acenaphthylene	44	640	6.7	88.9	0.23	3.86
acenaphthene	16	500	5.9	128	< DL	< DL
fluorene	19	540	21.2	144	0.06	2.12
phenanthrene	240	1500	86.7	544	1.42	7.98
anthracene	853	1000	46.9	245	0.05	1.02
fluoranthene	600	5100	113	1494	1.91	19.5
pyrene	665	2600	153	1398	1.79	18.6
benz[*a*]anthracene	261	1600	74.8	693	0.48	3.26
chrysene	384	2800	108	846	0.83	5.41
benzo[*b*]fluoranthene	na	na	na	na	1.21	5.63
benzo[*j+k*]fluoranthene	na	na	na	na	0.57	3.73
benzo[*a*]pyrene	430	1600	89	763	0.62	3.84
indeno[1,2,3-*c,d*]pyrene	na	na	na	na	1.19	6.27
dibenz[*a,h*]anthracene	63.4	260	6.22	135	0.04	0.86
benzo[*g,h,i*]perylene	na	na	na	na	1.76	9.19
$\sum_{16}$PAH	4000	44,792	619	5672	15.7	83.1

FIG. S1. INTERPOLATED SPATIAL DISTRIBUTION OF PAHS GROUPS IN PES. TMZ = TURBIDITY MAXIMUM ZONE. EACH SQUARE REPRESENTS THE DISTRIBUTION OF: A: ∑PAH, B: LMW PAHS, C: HMW PAHS, D: ALKYL PAHS.

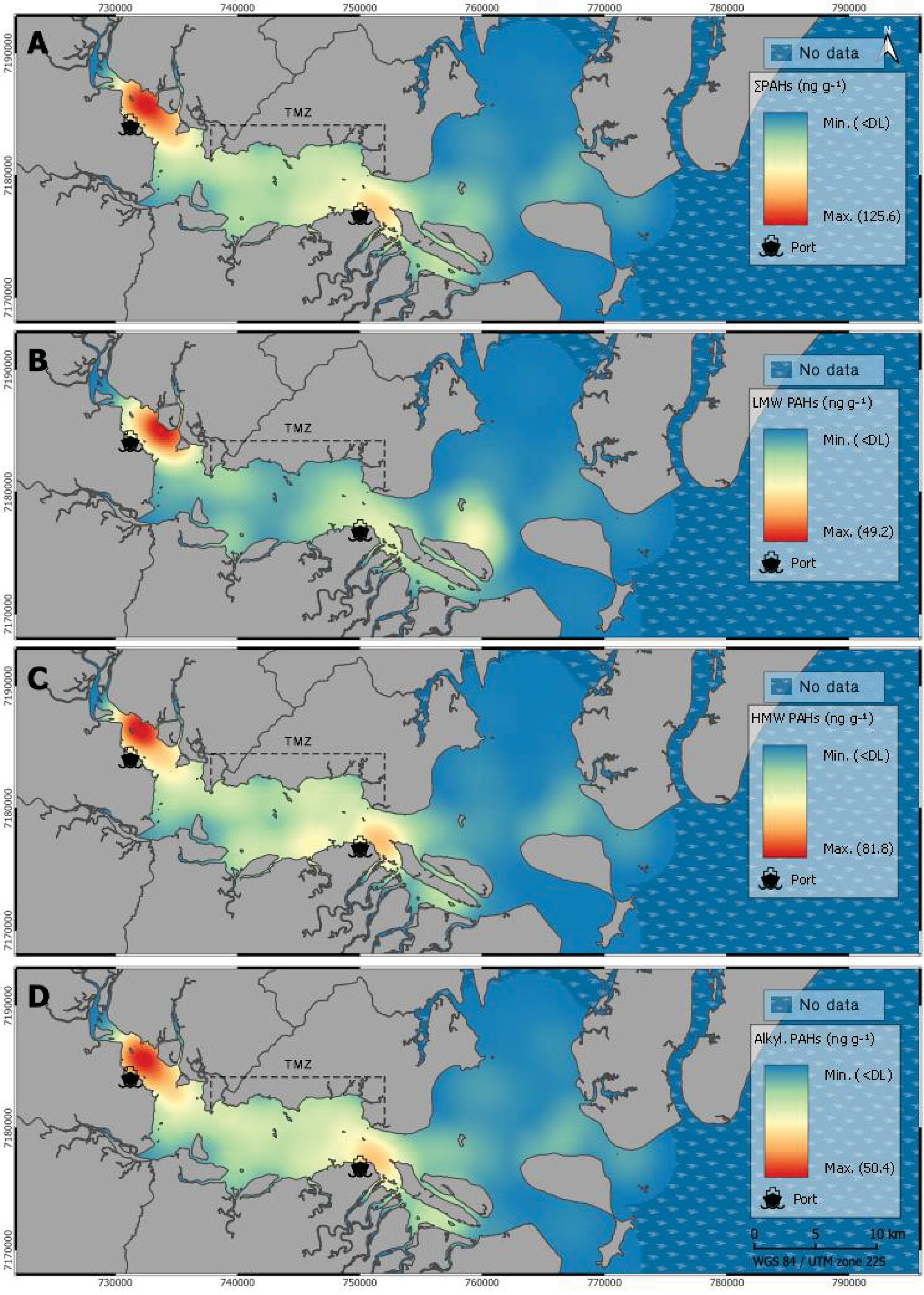


FIG. S2. SPEARMAN CORRELATION CROSS PLOTS FOR ∑PAH (REFERRED TO AS SUM_PAHS), TOC, TN AND FINE SEDIMENT IN PES.

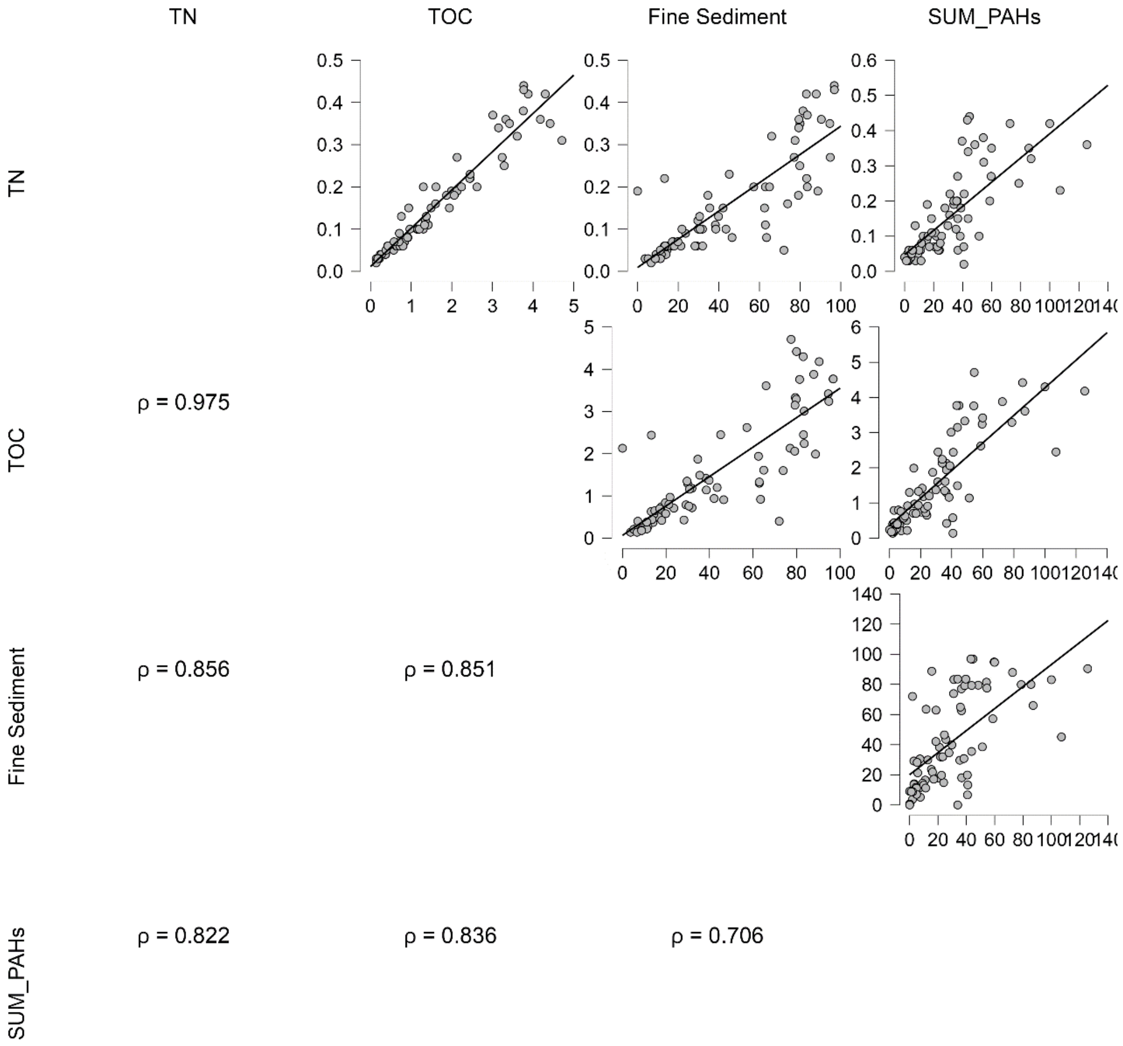


FIG. S3. SPATIAL DISTRIBUTION OF PAH DIAGNOSTIC RATIOS FOR SOURCE APPORTIONMENT IN PES. MORE INFORMATION ABOUT EACH DIAGNOSTIC RATIO IS AVAILABLE IN TABLE S3.

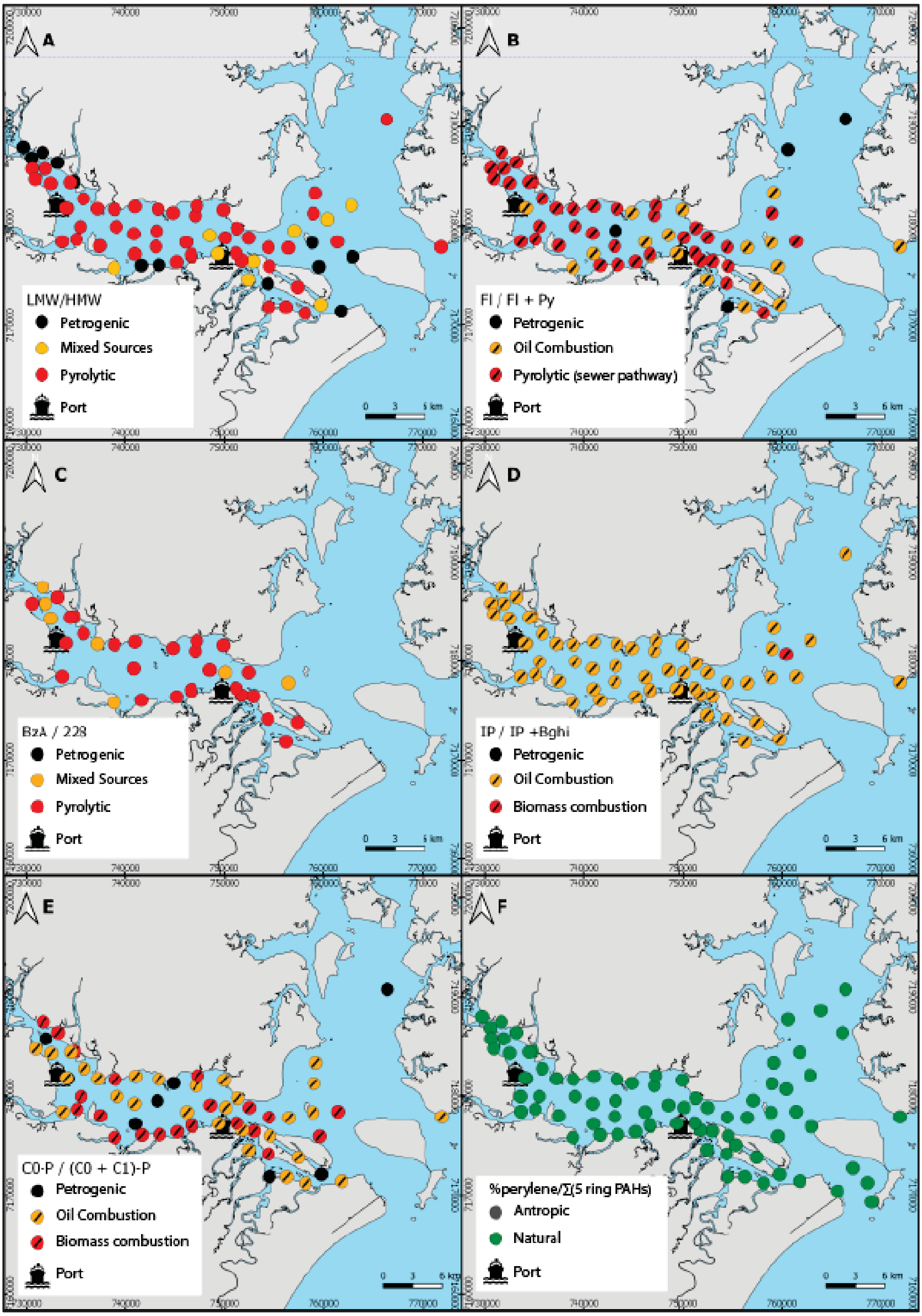


Fig. S4. Source profiles identified for surface sediments in PES, obtained from the PMF model using parental and alkyl PAHs. The variable "total" was created specifically for the PMF analysis to represent the totality of PAH emissions in PES, and is based on the sum of all compounds evaluated, unlike ∑PAH, which does not include the natural compounds retene and perylene.

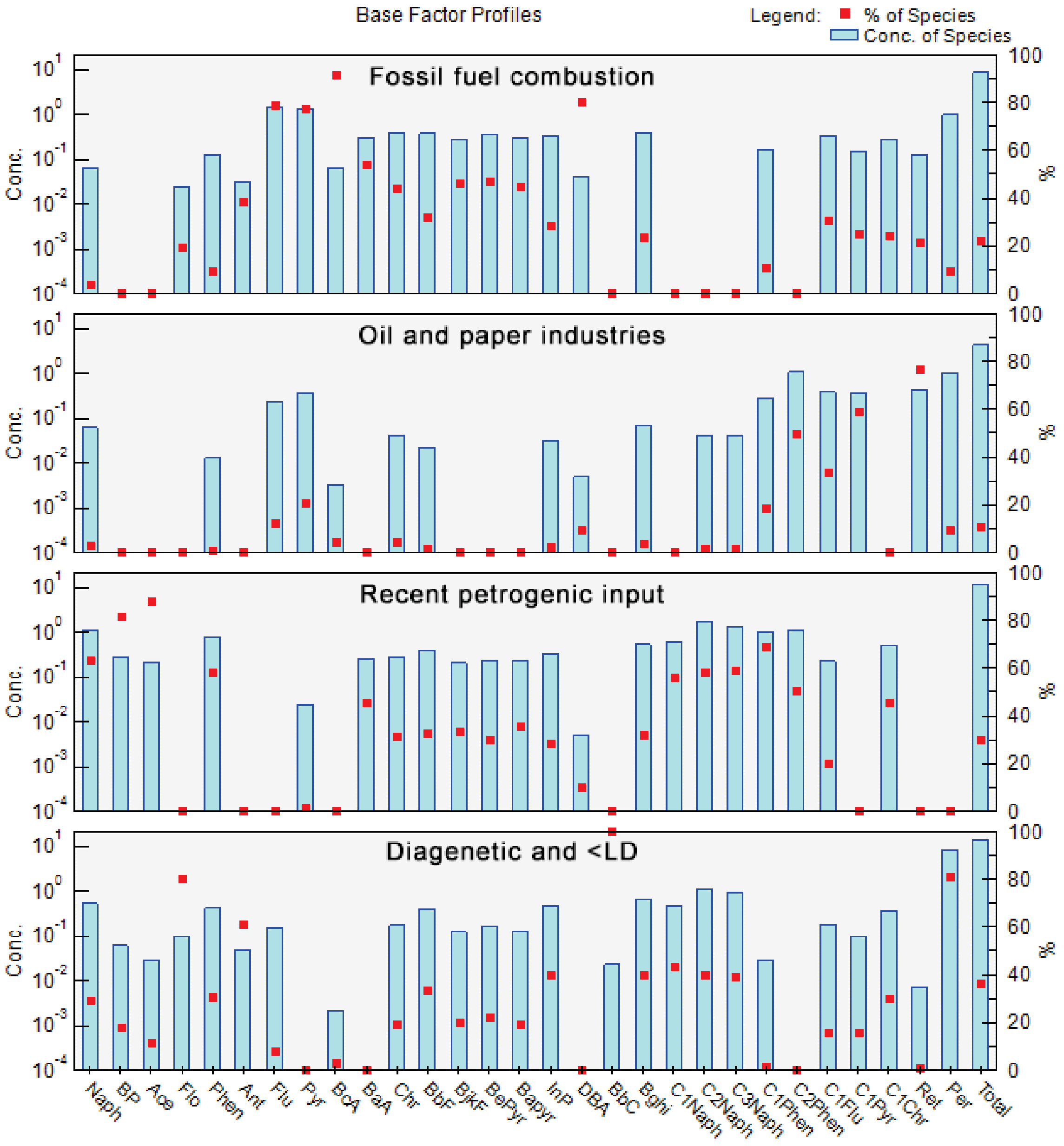
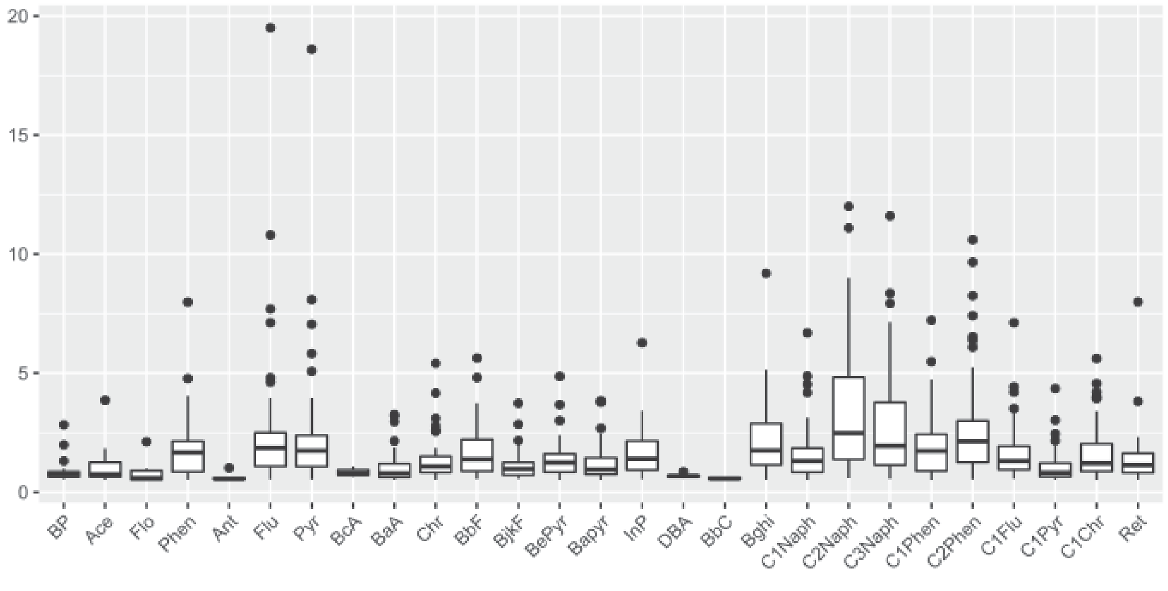


Fig. S5. Boxplot of individual PAH concentrations in PES. Perylene and naphthalene were removed due visualization issues. Acenaphthene and dibenzothiophene were removed due <LD in all samples.



Supplementary Information - Tracing sewage contamination in a South Atlantic Natural Heritage estuary using sedimentary linear alkylbenzenes and their diagnostic ratios

FIG. S1. DISTRIBUTION OF TOTAL NITROGEN (TN), TOTAL ORGANIC CARBON (TOC) AND FINE SEDIMENTS IN PARANAGUÁ ESTUARINE SYSTEM SECTORS (ANTONINA BAY, PARANAGUÁ BAY, GALHETA CHANNEL AND LARANJEIRAS BAY).

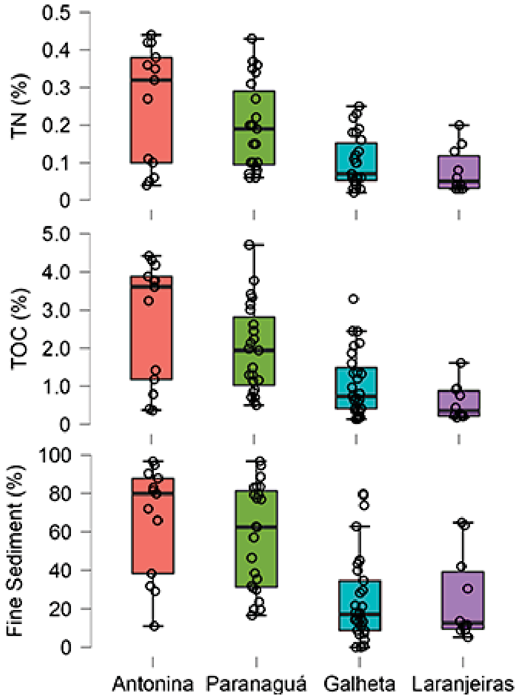
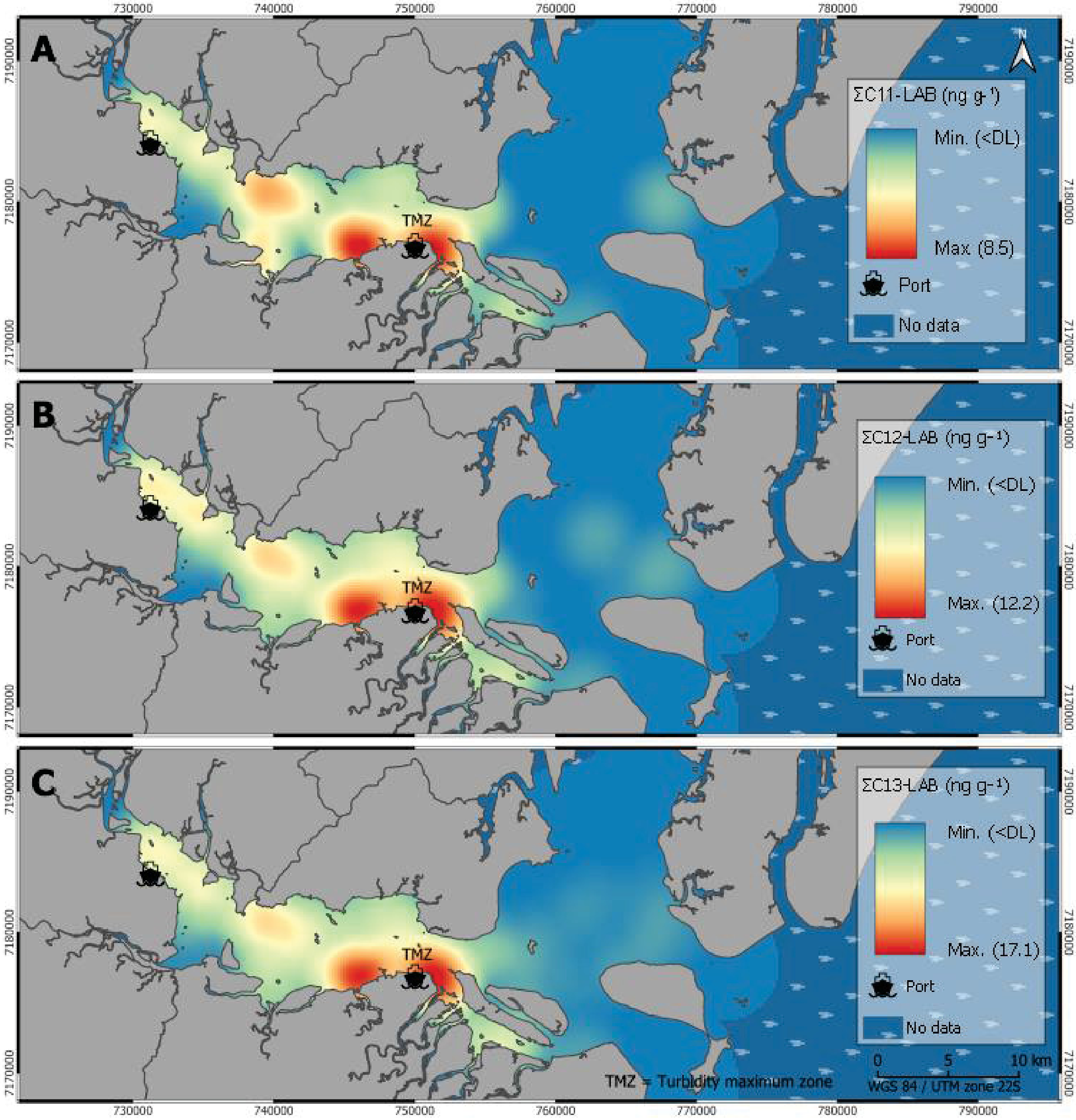


FIG. S2. INTERPOLATED SPATIAL DISTRIBUTION OF LABS GROUPS IN PES.



Supplementary Information - ASSESSING PM2.5 IN A PROTECTED ECOSYSTEM IN THE SOUTH ATLANTIC UNDER MASSIVE PORT ACTIVITIES: EVIDENCE OF HIGH CONCENTRATIONS AND MULTIPLE SOURCES

TABLE S1. SPEARMAN CORRELATION MATRIX FOR DAILY FINE PARTICULATE MATTER ($PM_{2.5}$), BLACK CARBON (BC), BROWN CARBON (BRC), PRECIPITATION (PRECIP), TEMPERATURE (TEMP.), RELATIVE HUMIDITY (RH), WIND SPEED (WS), SHIPS AND TRUCKS.

Spearman's Correlations

Variable		$PM_{2.5}$	BC	BrC	Precip.	Temp.	RH	WS	Ships	Trucks
$PM_{2.5}$	Spearman's (ρ)	—								
	p-value	—								
BC	Spearman's (ρ)	0.534 ***	—							
	p-value	<0.001	—							
BrC	Spearman's (ρ)	0.544 ***	0.988 ***	—						
	p-value	<0.001	<0.001	—						
Precip.	Spearman's (ρ)	-0.238 ***	-0.220 ***	-0.213 ***	—					
	p-value	<0.001	<0.001	<0.001	—					
Temp.	Spearman's (ρ)	0.183 **	-0.122 *	-0.104	0.166 **	—				
	p-value	0.001	0.032	0.070	0.003	—				
RH	Spearman's (ρ)	-0.236 ***	-0.010	-0.047	0.379 ***	-0.349 ***	—			
	p-value	<0.001	0.864	0.416	<0.001	<0.001	—			
WS	Spearman's (ρ)	-0.016	-0.068	-0.055	0.171 **	0.240 ***	-0.265 ***	—		
	p-value	0.779	0.219	0.319	0.002	<0.001	<0.001	—		
Ships	Spearman's (ρ)	0.166 **	0.168 **	0.159 **	-0.261 ***	-0.053	-0.162 **	-0.075	—	
	p-value	0.003	0.003	0.005	<0.001	0.367	0.005	0.187	—	
Trucks	Spearman's (ρ)	0.160 **	0.257 ***	0.242 ***	-0.160 **	-0.185 **	0.031	-0.171 **	0.090	—
	p-value	0.004	<0.001	<0.001	0.004	0.001	0.597	0.002	0.111	—

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

Shapiro-Wilk Test for Multivariate Normality: 0.332, $p < 0.001$ (non-parametric)

TABLE S2. AVERAGED CONCENTRATION OF IONIZABLE SPECIES EXTRACTED FROM $PM_{2.5}$ SAMPLES AND ANALYZED BY ION CHROMATOGRAPHY.

	Average [ng g^{-3}]	**Max. [ng g^{-3}]**	**N**
Cl^-	96 ± 13	1272	94
NO_3^-	137 ± 12	475	84
SO_4^{2-}	2292 ± 275	7489	105
PO_4^{3-}	245 ± 26	3151	104
Na^+	207 ± 16	952	104
NH_4^+	418 ± 16	2042	88
K^+	128 ± 8.9	739	104
Mg^{2+}	29 ± 2.3	251	105
Ca^{2+}	138 ± 15	834	104

FIGURE S1: POSITIVE MATRIX FACTORIZATION (PMF) PROFILES FOR SOLUBLE IONS.

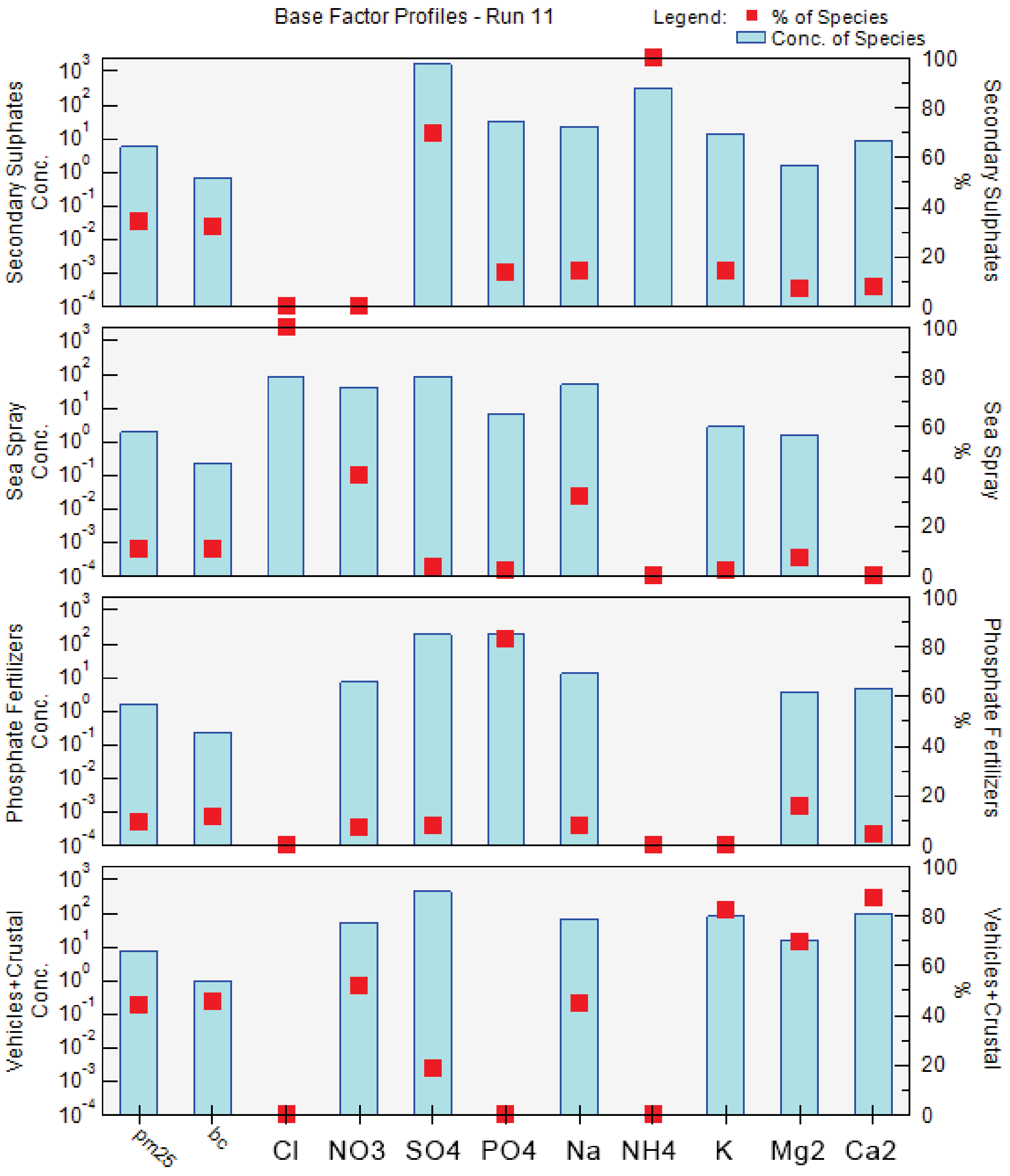


FIGURE S2. POSITIVE MATRIX FACTORIZATION (PMF) PROFILES FOR TRACE AND MAJOR METALS.