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ADRIELLE BEATRICE DO Ó MARTINS

DETERMINAÇÃO DE CONTAMINANTES EMERGENTES E HIDROCARBONETOS POLICÍCLICOS AROMÁTICOS: DISPOSITIVOS DE AMOSTRAGEM PASSIVA EM ÁGUA

Salvador
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Orientadoras:
Prof.ª Dr.ª Ana Cecília Rizzatti de Albergaria Barbosa
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Ao meu pai;
minhas irmãs, mães.
Ao amor da minha vida.

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“Sonhar mais um sonho impossível,
Lutar quando é fácil ceder,
Vencer o inimigo invencível.”

Buarque de Hollanda et. al (1972) interpretado por Maria Bethânia

RESUMO

Ambientes costeiros localizados próximo a centros urbanos e industriais são usualmente contaminados por compostos de origem antropogênica, como os hidrocarbonetos policíclicos aromáticos (HPAs) e os contaminantes emergentes (CECs). Nos sistemas marinhos, as concentrações desses compostos geralmente são baixas devido a processos como diluição e degradação. No entanto, a presença desses contaminantes é preocupante mesmo em concentrações relativamente baixas, conforme evidenciado pela detecção de efeitos biológicos em níveis ambientais. Dentre as diferentes formas para monitoramento destes ambientes costeiros, dispositivos de amostragem passiva (*passive sampler devices*, PSDs) têm sido amplamente estudados para avaliar a presença de compostos orgânicos antropogênicos em ambientes aquáticos. Com isto, diversos modelos estão sendo testados, como o caso das tiras de silicone da J-Flex®, utilizadas neste trabalho. O presente estudo avaliou a aplicabilidade deste material para monitoramento simultâneo de compostos emergentes e históricos em coluna d'água. Para isso, foi desenvolvido um método analítico para uso dos PSDs em estudos de contaminação por CECs, empregando-o posteriormente em estudos ambientais. Foram realizados testes de recuperação dos analitos, procedimentos de validação do método analítico e experimentos baseados no método co-solvente para estimar o coeficiente de partição dos analitos (K_{PW}) de interesse. Este estudo determinou os K_{PW} para seis fragrâncias (tetrametil acetiloctahidronaftaleno - OTNE, fantolida - AHMI, tonalide - AHTN, celestolide - DPMI, galaxolide - HHCB, traseolida - ATII) e oito filtros UV (benzofenona-3 – BP3, avobenzona - ABZ, octocrileno - OCT, 2-hidroxibenzofenona – 2OHBP, 4-metilbenzilideno cânfora – 4MBC, homosalato - HMS, salicilato de 2-etil-hexila – EHS e metoxicinamato de 2-etil-hexila – EHMC). Os valores de log K_{PW} obtidos variaram de 4,46 (BP3) a 6,47 (EHMC). Após aplicação em campo, a adequação da borracha de silicone como PSD foi comprovada, observando-se o alcance mais lento e mais preciso do equilíbrio. Após a validação de todas as etapas do método analítico, os PSDs foram expostos em uma região da Baía de Todos os Santos (Bahia – Brasil), região turística, com forte presença de atividades aquáticas, náuticas e incluída em parque ambiental marinho durante um ano. As concentrações livremente dissolvidas variaram de 1,16 (DPMI) a 303 (HHCB) pg L^{-1} para as fragrâncias e de 3.55 (2OHBP) a 4051 (HMS) pg L^{-1} para os filtros UV. Para contaminantes legados, a soma da concentração livremente dissolvida variou de 9,39 a 1197 pg L^{-1} para PCBs, de <MDL (limite de detecção do método) a 7,05 pg L^{-1} para pesticidas organoclorados e de 3.759 a 21.975 pg L^{-1} para HPAs. De acordo com as razões diagnósticas os HPAs apontam origem em fontes mistas (pirolíticas e petrogênicas). Foi realizada uma avaliação de risco ambiental para as substâncias químicas para as quais havia dados ecotoxicológicos disponíveis, indicando que os filtros UV e os contaminantes históricos representam o maior risco potencial para os organismos. De forma complementar, um levantamento bibliográfico através de uma revisão sistemática foi realizado a fim de investigar as respostas dos biomarcadores em organismos bivalves aos CECs, visto que na literatura há uma forte comparação entre a avaliação de contaminação através dos amostradores passivos e esta classe de organismos. Em geral, o estudo revelou que os efeitos dos contaminantes nestes organismos ainda não é claro, porém há alteração nas atividades e níveis da maiores os biomarcadores na presença destes compostos.

Palavras – chave: contaminantes orgânicos; borracha de silicone; HPAs, produtos de cuidado pessoal.

ABSTRACT

Coastal environments located near urban and industrial centers are usually contaminated by compounds of anthropogenic origin, such as polycyclic aromatic hydrocarbons (PAHs) and emerging contaminants (CECs). In marine systems, the concentrations of these compounds are generally low due to processes such as dilution and degradation. However, the presence of these contaminants is of concern even at relatively low concentrations, as evidenced by the detection of biological effects at environmental levels. Among the different ways of monitoring these coastal environments, passive sampler devices (PSDs) have been widely studied to assess the presence of anthropogenic organic compounds in aquatic environments. Various models are being tested, such as the J-Flex® silicone strips used in this study. This study evaluated the applicability of this material for simultaneous monitoring of emerging and legacy compounds in the water column. To this end, an analytical method was developed for the use of PSDs in CEC contamination studies, and subsequently used in environmental studies. Analyte recovery tests, analytical method validation procedures and experiments based on the co-solvent method were carried out to estimate the analyte partition coefficient (K_{PW}) of interest. This study determined the K_{PW} for six fragrances (tetramethyl acetyloctahydronaphthalene - OTNE, phantolide - AHMI, tonalide - AHTN, celestolide - DPMI, galaxolide - HHCB, traseolide - ATII) and eight UV filters (benzophenone-3 - BP3, avobenzone - ABZ, octocrylene - OCT, 2-hydroxybenzophenone - 2OHBP, 4-methylbenzylidene camphor - 4MBC, homosalate - HMS, 2-ethylhexyl salicylate - EHS and 2-ethylhexyl methoxycinnamate - EHMC). The log K_{PW} values obtained ranged from 4.46 (BP3) to 6.47 (EHMC). After a field test, the suitability of silicone rubber as a PSD was proven, with slower and more accurate balance being achieved. After all the stages of the analytical method had been validated, the PSDs were exposed in a region of Todos os Santos Bay (Bahia - Brazil), a tourist region with a strong presence of aquatic and nautical activities and included in a marine environmental park during one year. Freely dissolved concentrations ranged from 1.16 (DPMI) to 303 (HHCB) pg L^{-1} for fragrances and from 3.55 (2OHBP) to 4051 (HMS) pg L^{-1} for UV filters. For legacy contaminants, the sum of the freely dissolved concentration ranged from 9.39 to 1197 pg L^{-1} for PCBs, from <MDL (method detection limit) to 7.05 pg L^{-1} for organochlorine pesticides and from 3,759 to 21,975 pg L^{-1} for PAHs. According to the diagnostic ratios, the PAHs originate from mixed sources (pyrolytic and petrogenic). An environmental risk assessment was carried out for the chemical substances for which ecotoxicological data was available, indicating that UV filters and legacy contaminants represent the greatest potential risk to organisms. To complement this, a bibliographic survey using meta-analysis was carried out in order to investigate the responses of biomarkers in bivalve organisms to CECs, since in the literature there is a strong comparison between the assessment of contamination through passive samplers and this class of organisms. In general, the study revealed that the effects of the contaminants on these organisms is still unclear, but there are changes in the activities and levels of the major biomarkers in the presence of these compounds.

Key-words: organic contaminants; silicone rubber; PAHs, personal care products.

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APRESENTAÇÃO E ESTRUTURA

O presente documento consiste na tese de doutorado intitulada "Determinação de contaminantes emergentes e hidrocarbonetos policíclicos aromáticos: dispositivos de amostragem passiva" apresentada ao Programa de Pós-Graduação e Energia e Ambiente, executada pela discente Adrielle Beatrice do Ó Martins sob orientação das professoras Ana Cecília Rizzatti de Albergaria Barbosa e Tatiane Combi.

Este documento é composto por uma sessão estrutural e três artigos científicos. Na primeira sessão, há a introdução ao tema, abordando o referencial teórico base para interpretação dos resultados obtidos. Os resultados desta tese estão apresentados na forma de três artigos científicos completos, incluindo introdução, metodologia, resultados e material suplementar, com vista a responder o seguinte objetivo geral: Implementar uma metodologia analítica referente a utilização de dispositivos de amostragem passiva, com foco na determinação de hidrocarbonetos policíclicos aromáticos e grupos selecionados de contaminantes emergentes em água, validando esta metodologia em campo. Este objetivo geral foi dividido nos seguintes objetivos específicos: 1) Implementar uma metodologia analítica para análise simultânea dos HPAs e CECs em amostradores passivos; 2) Determinar a ocorrência dos HPAs e CECs em região costeira usando-se como matriz os amostradores passivos; 3) Comparar respostas de biomarcadores de estresse oxidativo e detoxificação dos organismos bivalves frente a exposição por CECs.

O primeiro artigo "*Determining silicone-water partition coefficients for monitoring personal care products in waters*" apresenta os resultados geradis através do experimento de co-solvente e a metodologia desenvolvida para o uso eficaz das tiras de silicone como amostradores passivos em estudos de contaminação marinha. O segundo artigo, intitulado "*One-year passive monitoring hydrophobic organic contaminants in coastal waters: legacy contaminants vs. contaminants of emerging concern*", utiliza-se dos dados gerados no primeiro artigo e traz os resultados de uma avaliação temporal de um ano em uma região costeira (Baía de Todos os Santos, Bahia, Brasil) no que se refere aos compostos históricos e emergentes. O último artigo, intitulado "*Personal care products and biomarkers of detoxification and oxidative stress in bivalves: a systematic review of laboratory studies*", é uma revisão sistemática e meta-análise de dados. Ele apresenta uma revisão sobre estudos laboratoriais para avaliação e identificação de biomarcadores de estresse oxidativo em ostras através da indução da contaminação por produtos de cuidado pessoal, e este produto auxiliará em futuras interpretações na comparação entre os dados obtidos por dispositivos de amostragem passiva e aqueles obtidos através de organismos bivalves.

Capítulo 1

1 INTRODUÇÃO

A determinação dos contaminantes e avaliação dos seus comportamentos no ambiente marinho são importantes para o cumprimento do item 14 dos Objetivos de Desenvolvimento Sustentável (ODS) - a conservação e o uso sustentável dos oceanos, dos mares e dos recursos marinhos (United Nations, 2017). Para concretização dos objetivos fixados nas diretivas ambientais, programas de monitoramento e avaliação ambiental se fazem necessários. Um projeto estratégico de longo prazo é fundamental para rastrear tendências e identificar pontos críticos (Atkins *et al.*, 2011). Eles também asseguram que a informação sobre o estado atual do ambiente entendida, além de permitir avaliar se os esforços regulatórios de prevenção e mitigação estão sendo eficazes (Boye *et al.*, 2019).

Uma vez no ambiente aquático, o destino de diferentes grupos de contaminantes pode não ser claro, visto os distintos processos e mecanismos de transporte aos quais estes compostos estão sujeitos nos corpos d’água. Eles podem, por exemplo, sofrer processos de bioacumulação, permanecer na fração dissolvida, associados ao material particulado suspenso, sedimentar, entre outros. A distribuição entre as diferentes frações vai depender das características físico-químicas dos compostos e do meio em que se encontram (Schmidt; Jochmann, 2012). Enquanto compostos mais hidrofóbicos tendem a se associar ao material particulado em suspensão e sedimentar, aqueles mais hidrofílicos acabam permanecendo mais tempo dissolvidos na água. Já a assimilação biológica de diferentes compostos pode acontecer por via dérmica, pela alimentação e através da respiração. Contudo, a dinâmica de absorção de alguns grupos de contaminantes ainda vem sendo estudada (Loh *et al.*, 2018).

Dentre os compostos que podem contaminar os ambientes aquáticos, os hidrocarbonetos policíclicos aromáticos (HPAs) ocupam uma posição importante em estudos ambientais. HPAs são um grupo de compostos persistentes e semivoláteis, formados por dois ou mais anéis benzênicos condensados. Eles podem induzir efeitos nocivos aos organismos e seres humanos, visto que a maior parte destes compostos aromáticos possuem propriedades carcinogênicas, teratogênicas e mutagênicas (Alegbeleye; Opeolu; Jackson, 2017). Assim, a presença de HPAs no ambiente é de preocupação para ecossistemas e à saúde humana. Suas principais fontes para os sistemas costeiros são antropogênicas, como derrames de óleos e seus derivados, a deposição de compostos provindos da queima parcial de material orgânico e combustíveis fósseis e a descarga de efluentes domésticos e industriais (Kasiotis; Emmanouil, 2015). De maneira geral, os HPAs podem ser divididos em dois principais grupos: petrogênicos (presentes na composição do petróleo e de seus subprodutos) ou pirogênicos (formados a partir da queima incompleta da matéria orgânica) (Wild; Jones, 1995). Ainda é possível listar outras origens, como a diagenética, que ocorre através de transformações naturais da matéria orgânica mediante processos de descarboxilação e aromatização (Tissot; Welte, 1978), e a biogênica, na qual os HPAs são sintetizados por organismos como bactérias, plantas e fungos (Law; Biscaya, 1994).

Outra classe de compostos que têm recebido recente atenção em estudos ambientais são os contaminantes de preocupação emergente (*contaminants of emerging concern* – CECs). Os CECs compreendem diferentes grupos de compostos químicos sintéticos que não são comumente monitorados, mas têm o potencial de entrar e acumular no ambiente, podendo causar efeitos ecotoxicológicos adversos (Barber, 2014). Este termo abrange diversos grupos de substâncias que, embora possam estar presentes no ambiente há anos, não eram detectáveis com as metodologias analíticas disponíveis anteriormente (Maruya *et al.*, 2014). Os CECs incluem os produtos de cuidado pessoal (PCPs), como as fragrâncias, filtros solares, repelentes de insetos e produtos antimicrobianos, compostos organofosforados, produtos farmacêuticos, entre outros (Combi *et al.*, 2016; Pintado-Herrera *et al.*, 2016). Devido a sua ampla utilização no dia a dia em produtos de consumo, atividades domésticas, indústria e agricultura, os CECs são continuamente introduzidos no ambiente principalmente através do aporte de efluentes urbanos e industriais, sejam eles tratados ou não tratados (Terzić *et al.*, 2008).

Em geral, estudos que buscam avaliar a presença, concentrações e fontes de contaminantes hidrofóbicos no ambiente aquático utilizam principalmente os sedimentos e/ou organismos biomonitores como matrizes de avaliação (Borja *et al.*, 2004). Na água, este tipo de avaliação é mais complexo devido às baixas concentrações normalmente encontradas destes contaminantes. A análise de HPAs e CECs nessa matriz pode demandar a utilização de grandes volumes para uma indicação precisa da concentração do composto, dificultando a realização dos procedimentos amostrais e analíticos, além de gerar interferências que podem reduzir ou prejudicar a análise (Liu *et al.*, 2006; Yates *et al.*, 2013). Visando reduzir as incertezas analíticas, facilitar os procedimentos de amostragem de contaminantes apolares em água e a capacidade de integração temporal dos dados, os dispositivos de amostragem passiva (*passive sampler devices* - PSDs) vêm sendo utilizados nas últimas décadas, promovendo importantes avanços (Booij; Smedes, 2010; Booij; Smedes; Van Weerlee, 2002). A otimização de metodologias para análise de contaminantes alinha-se com o objetivo já citado da ODS, visto que as vantagens do uso destes dispositivos podem resultar em uma interpretação mais robusta e eficiente dos dados, o que auxiliará nas tomadas de decisão em relação à contaminação dos corpos hídricos.

Neste contexto, o presente trabalho pretende implementar uma metodologia analítica referente à utilização de dispositivos de amostragem passiva, com foco na determinação de hidrocarbonetos policíclicos aromáticos e grupos selecionados de contaminantes emergentes em água, aplicando esta metodologia em campo em monitoramento ambiental de longo-prazo.

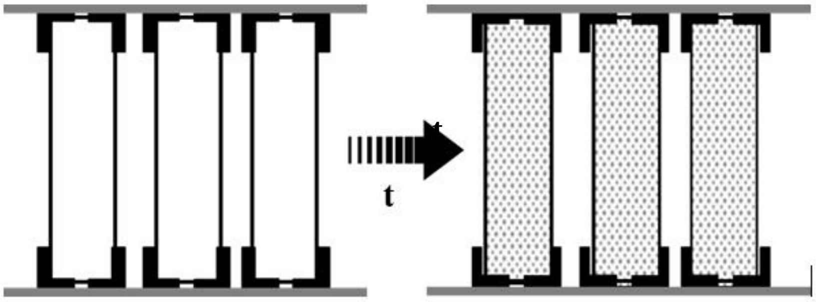
1.1. Amostragem passiva aquática: Dispositivos de amostragem

Amostradores passivos são projetados para permanecer durante dias ou semanas no ambiente, podendo assim acumular concentrações médias dos compostos orgânicos presentes no ambiente aquático ao longo de um período (Miège *et al.*, 2009; Tiedeken *et al.*, 2017; Wille *et al.*, 2012). O seu princípio de operação baseia-se na adsorção de um contaminante presente no ambiente por difusão passiva. Isso ocorre porque há, nos amostradores passivos, uma fase receptora que acumula os contaminantes, uma vez que estes possuem maior afinidade com as moléculas do amostrador em relação àquelas presentes na água (Greenwood; Mills; Vrana, 2009).

Nos últimos 20 anos, a amostragem passiva tem sido proposta como uma ferramenta promissora para superar potenciais limitações relacionadas a métodos tradicionais de análise de água (Lissalde *et al.*, 2016). Dentre as limitações da amostragem de contaminantes na matriz aquática pode-se citar a representatividade da amostra, tanto nas variáveis temporais quanto espaciais. Para se obter dados de um longo período, é necessário realizar diversas amostragens, com grande frequência coletas, despendendo de mais tempo e recursos (Torres *et al.*, 2022). Outro fator que pode ser limitante neste tipo de análise diz respeito às concentrações de contaminantes em corpos aquáticos, especialmente marinhos e costeiros. De modo geral, as concentrações encontradas nestes ambientes são relativamente baixas (na ordem de partes por bilhão – ppb), sendo necessários processos de pré-concentração das amostras e/ou amostragens de grandes volumes de água (Novák *et al.*, 2018). Neste sentido, a utilização de PSDs apresenta algumas vantagens, como a possibilidade de obtenção de um limite de quantificação mais baixo e a avaliação do nível geral de contaminação, incluindo episódios esporádicos de poluição de curto prazo (Lissalde *et al.*, 2016).

Existe uma gama de amostradores passivos utilizados em ambiente aquático, tais como o POCIS (sorvente fixado entre duas membranas) e o *Chemcatcher* (membrana limitadora de difusão e um adsorvente de fase sólida - disco Empore C18). Dispositivos de amostragem feitos de um material de fase única, como polietileno, polioximetileno e polidimetilsiloxano (Figura 1.1), apresentam vantagens, uma vez que são reutilizáveis e relativamente mais baratos (Sun *et al.*, 2019). Assim, eles têm sido cada vez mais desenvolvidos, tendo seus usos aumentados ao longo dos últimos tempos (Vrana *et al.*, 2005). A Figura 1.1, demostra o princípio de funcionamento deste amostrador, o qual, quando inserido no meio a ser amostrado, torna-se enriquecido em relação aos analitos presentes na coluna d’água.

Figura 1.1. Representação de um amostrador passivo de material em fase única em ambiente aquoso. Primeiramente, livre de qualquer contaminante, o amostrador é inserido no ambiente e durante o período de amostragem, este concentra os analitos presentes no meio (Autor, 2021). t = tempo que o amostrador deverá ser exposto no meio. Esse é determinado conforme o grupo de contaminantes de interesse, bem como o objetivo do trabalho.



Estudos têm descrito o comportamento e o uso de borrachas de silicone como amostrador passivo para acessar a contaminação na coluna d’água por pesticidas organoclorados (Prokeš; Vrana; Klánová, 2012), bifenilas policloradas (PCBs; Silva-Barni *et al.*, 2019), hidrocarbonetos policíclicos aromáticos (HPAs; Vrana *et al.*, 2018) e contaminantes de preocupação emergente (CECs; Pintado-Herrera *et al.*, 2020). Estes estudos indicam que esta é uma ferramenta promissora para a determinação de contaminantes orgânicos no ambiente aquático. Entretanto, com a descontinuação na produção da borracha sintética da marca

Altesil®, que foi utilizada nestes estudos, novos modelos estão sendo testados, como o caso das tiras de silicone da J-Flex®.

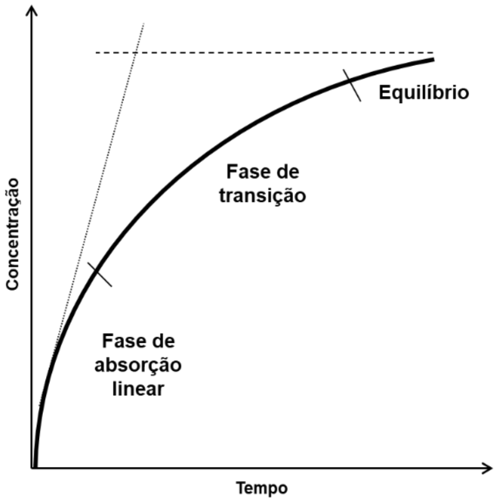
1.1.1. Princípios da amostragem passiva

Existem dois tipos de amostradores passivos: os de partição e os de adsorção. O primeiro é aquele utilizado para contaminantes hidrofóbicos (por exemplo, tiras de silicone), nos quais os compostos-alvo são absorvidos e há a possibilidade de entrarem na fase de equilíbrio. O segundo tipo de amostrador é aquele utilizado para contaminantes polares (por exemplo, POCIS). Nestes, os compostos adsorvem ao material (i.e. ligação de superfície), nunca alcançando a fase de equilíbrio (Smedes; Booij, 2012; Vrana *et al.*, 2018). Nos dois tipos de amostradores, a amostragem ocorre de acordo com a 1ª lei de Fick, considerando que o fluxo de partículas em um sistema unidimensional é causado por um gradiente de concentração. Ou seja, a concentração é resultado da diferença de potencial químico existente entre os analitos no meio amostrado e no PSD (Kot-Wasik *et al.*, 2007; Paul *et al.*, 2014).

As variáveis que afetam o processo de absorção para amostradores de partição são bem conhecidas (resistência na camada limite da água, na membrana e entre as partes do próprio material de adsorção). Assim, a quantidade de contaminantes absorvida pelos PSDs pode ser utilizada para calcular a concentração livremente dissolvida na fase aquosa. Por outro lado, há uma série de fatores inconstantes no processo de absorção em amostradores de adsorção e, portanto, também há mais incertezas envolvidas no cálculo da concentração livremente dissolvida nestes amostradores (Smedes; Bakker; de Weert, 2010). Fatores como a temperatura do ambiente, hidrodinâmica local, bioincrustação no amostrador, sorção dos compostos em carbono orgânico dissolvido, fotodegradação dos compostos e até mesmo a geometria das estruturas são relevantes quando se realiza este tipo de amostragem (Vrana *et al.*, 2019).

O processo de difusão nos PSDs de partição acontece em três estágios (Figura 1.2). Primeiramente, ocorre a fase de absorção linear, onde os contaminantes são absorvidos a uma taxa diretamente proporcional à sua concentração na água. Com a continuidade da amostragem, é iniciada a fase de transição, onde a concentração do contaminante se aproxima gradualmente do estágio de equilíbrio no amostrador. Na terceira e última fase, o equilíbrio entre a fase aquosa e o amostrador é atingido. Esta cinética de absorção dos contaminantes vai depender de fatores como a temperatura e a taxa de amostragem (quantidade de contaminante absorvido/adsorvido em um determinado período). Quanto mais elevadas forem estas taxas de amostragem, mais rápido será atingido o equilíbrio (Booij; Smedes; Van Weerlee, 2002)

Figura 1.2. Perfil de particionamento dos analitos pelo amostrador de partição. Adaptado de BOOIJ; SMEDES; VAN WEERLEE (2002).

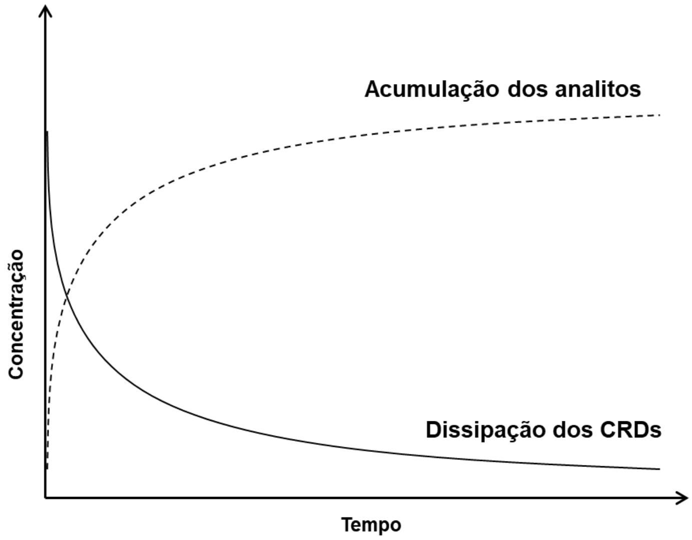


1.1.2. Taxa de amostragem e concentração livremente dissolvida em água

As taxas de amostragem (R_S) de analitos específicos por amostradores passivos dependem de um conjunto complexo de variáveis ambientais em interação, incluindo temperatura, hidrodinâmica do local (fluxo de água/velocidade/turbulência), bioincrustação, sorção dos compostos em carbono orgânico dissolvido, fotodegradação e geometria das estruturas (Allan; Jenssen, 2019; Jonker *et al.*, 2015; Rusina *et al.*, 2010; Sun *et al.*, 2019). Os efeitos potenciais dessas variáveis ambientais devem ser melhor definidos a fim de estimar com maior precisão os dados relativos à concentração de substâncias químicas no ambiente (O'Hara, 2009).

Para compreender a influência destes fatores ambientais nos amostradores, são utilizados compostos de referência de desempenho (CRDs). Os CRDs são compostos químicos que não são encontrados no ambiente, sendo então adicionados aos amostradores antes da exposição em campo para que seja observada a sua taxa de dissipação durante a exposição. Por conta da troca de compostos que ocorre entre o silicone e o meio aquoso, a cinética de dissipação destes compostos pode ser utilizada para avaliar as taxas de amostragem e indicar o fluxo de acumulação dos analitos (Figura 1.3, Pintado-Herrera *et al.*, 2016).

Figura 1.3. Comparação entre a amostragem dos analitos e a dissipação dos CRDs, demostrando que à medida que os CRDs são dissipados, os analitos são acumulados no silicone. Adaptado de (Prokeš; Vrana; Klánová, 2012).



Para o cálculo da taxa de amostragem (R_S), considera-se que a captação é controlada apenas pela camada limítrofe da água, ou seja, avaliando a dissipação de CRDs, deve-se seguir a Equação (1.1):

$$R_S = B \; x \; A \; x \; M^{-0,47} \qquad \text{Equação (1.1)}$$

Onde:

B = fator de proporcionalidade (ou fator de fluxo) estimado a partir da dissipação dos compostos de referência de desempenho (CRDs);

A = área da superfície do amostrador (m^2);

M = massa molecular do analito (g mol^{-1}), esta variável é elevada a -0,47 para ajustes de incertezas no modelo.

Para calcular a massa de um contaminante acumulado no amostrador, deve-se considerar o tempo de exposição (t), a R_S e coeficiente de partição amostrador-água (K_{PW}) (Greenwood; Mills; Vrana, 2009; Söderström; Lindberg; Fick, 2009). Os cálculos da concentração livremente dissolvida do analito no meio (C_W), devem ser realizados após a confirmação do estágio de particionamento em que os analitos se encontram através da Equação (1.2):

$$E_P = \frac{[R_S \; x \; t]}{K_{PW} \; x \; m}$$ Equação (1.2)

Onde:

E_P = estágio de particionamento;

R_S = taxa de amostragem (L dia^{-1});

t = tempo de exposição (dias);

K_{PW} =coeficiente de partição amostrador-água;

m = massa do amostrador.

Caso o resultado da Equação (1.2) seja < 1, os analitos ainda estão na fase linear de particionamento com o amostrador, indicando pouco tempo de exposição, baixa taxa de amostragem ou uma elevada hidrofobicidade do composto. Caso o resultado seja > 1, a amostragem está no estágio de equilíbrio ou próximo ao equilíbrio, indicando analito pouco hidrofóbico, exposição longa ou alta taxa de amostragem (Smedes; Booij, 2012). No primeiro caso, a concentração dissolvida (C_W) é calculada de acordo com a Equação (1.3) e no segundo caso, de acordo com a Equação (1.4):

$$C_W \approx \frac{N_t}{R_S \; x \; m}$$ Equação (1.3)

$$C_W = \frac{N_t}{K_{PW} \; x \; m}$$ Equação (1.4)

Onde:

C_W = concentração livremente dissolvida;

N_t = quantidade de analito no amostrador no final da exposição;

R_S = taxa de amostragem (L dia^{-1})

K_{PW} =coeficiente de partição amostrador-água;

m = massa do amostrador.

Como compostos hidrofóbicos possuem um elevado valor de coeficiente de partição amostrador-água (K_{PW}), a capacidade de amostragem para esses compostos é considerada alta. No caso dos compostos menos hidrofóbicos, com coeficiente de partição octanol-água (log K_{OW}) < 4, o equilíbrio é atingido com mais facilidade (Smedes; Bakker; de Weert, 2010).

1.1.3. Amostragem biótica: bioacumulação e biomarcadores

Existem diversos métodos de monitoramento que podem ser utilizados para avaliar a contaminação de uma área. Dentre essas, podemos citar: o monitoramento químico, através da avaliação da concentração em matrizes abióticas, como em água, sedimentos, solos, ou o material particulado em suspensão; monitoramento da bioacumulação, através da medida dos contaminantes em tecidos da biota presentes na região estudada; e o monitoramento de efeitos biológicos, através da avaliação da exposição e efeitos através da determinação de alterações adversas (Pampanin; Sydnes, 2013).

A biodisponibilidade de contaminantes geralmente é estimada através da análise da presença dos contaminantes nos organismos e da análise dos efeitos biológicos. Através desses métodos, pode-se também verificar o potencial tóxico e o risco que esses compostos podem gerar aos ecossistemas (Schuijt *et al.*, 2021). Organismos marinhos podem incorporar os contaminantes presentes em um meio através de seu contato com o sedimento, material particulado em suspensão, coluna d'água, através da respiração, ou do suprimento alimentar (Laffon *et al.*, 2006). A bioacumulação é definida como o processo de absorção e acúmulo de substâncias químicas do meio ambiente pelos organismos (Mackay *et al.*, 2013; Sanganyado; Rajput; Liu, 2018). Estudos de biomonitoramento considerando os processos de bioacumulação são boas alternativas para compreensão do estado ambiental de uma região, uma vez que esse processo tende a aumentar a concentração dos contaminantes na matriz biótica em relação à abiótica, facilitando a detecção dos compostos (Joyce *et al.*, 2015). Entretanto, a razão de incorporação depende não somente da disponibilidade dos contaminantes, mas também de fatores bióticos e abióticos, como razão de filtração/alimentação, metabolismo, temperatura, salinidade, entre outros (Fernández-Tajes *et al.*, 2011).

Dentre os organismos usados em estudos de biomonitoramento, os bivalves têm recebido destaque, devido às suas características como organismos sentinela. Estes organismos são filtradores, sésseis, de fácil amostragem e apresentam grande distribuição geográfica (Cortez *et al.*, 2018; Joyce; Burgess, 2018; Lopes *et al.*, 2020). Além disso, diversas espécies representam uma potencial fonte de contaminação aos seres humanos, uma vez que servem de alimento. Dessa forma, muitos programas e agências de monitoramento têm usado moluscos bivalves para avaliar a biodisponibilidade de contaminantes em sistemas costeiros. Um exemplo é a *International Mussel Watch*, que atua desde 1995 monitorando contaminantes em águas costeiras usando como sentinelas espécies bivalves (Farrington *et al.*, 2020).

A distribuição dos compostos orgânicos no tecido dos bivalves condiciona-se a fatores externos, como a disponibilidade desses compostos e proximidade de fontes de contaminação. A fisiologia desses animais, como o metabolismo e a excreção, determina a extensão da acumulação dos compostos assimilados (Prest *et al.*, 1995). Trabalhos recentes demostram a afinidade de contaminantes orgânicos com estes organismos. Aguirre-Rubí et al. (2018) concluíram que uma variedade de compostos orgânicos persistentes, como os HPAs e fragrâncias sintéticas de almíscar, em combinação com diferentes níveis de matéria orgânica e fatores ambientais, provocam perturbação na condição de saúde de ostras de mangue. Estudos realizados em um manguezal do arquipélago de Guadalupe, mostraram uma alta concentração de benzo[a]pireno em ostra (65,4 ng g^{-1} dw), nível excedente do limiar fixado pela Comunidade Europeia (n. o CE 2065/2003) (Ramdine *et al.*, 2012). Na costa da Galícia, em 2019, elevados níveis de contaminação por HPAs (6,8 a 317 ng g^{-1} em peso seco) e octocrileno (141 ng g^{-1} em peso seco) foram encontrados em amostras de berbigão (Rodil *et al.*, 2019).

Além disso, a avaliação dos biomarcadores de efeito e exposição nos seres vivos pode evidenciar a ligação entre a exposição às substâncias químicas e os impactos na saúde dos indivíduos expostos (Baussant *et al.*, 2011; Munari *et al.*, 2018). Com o intuito de assegurar sua sobrevivência, os organismos evoluíram mecanismos de defesa celular contra a presença de compostos desconhecidos, como a biotransformação e a eliminação de xenobióticos (Trevisan *et al.*, 2016). Estes mecanismos podem ser utilizados para avaliar a biodisponibilidade dos contaminantes para os bivalves. Os biomarcadores de exposição são uma resposta biológica a um ou mais extressores que proporcionam uma medida de exposição e, por vezes, também de efeito tóxico (Depledge; Fossi, 1994). O uso desses sinais se faz importante, pois eles promovem um alerta, podendo indicar um possível impacto ambiental antes que este possa ser observado em níveis biológicos mais complexos (Santana *et al.*, 2018).

1.2. Contaminantes orgânicos no ambiente aquático

1.2.1. Hidrocarbonetos Policíclicos Aromáticos

Os HPAs são compostos orgânicos formados por dois ou mais anéis benzênicos condensados em configurações lineares, angulares ou agrupadas (Figura 1.4; Yu *et al.*, 2016; Alegbeleye; Opeolu; Jackson, 2017; Fang *et al.*, 2020). Eles podem ocorrer naturalmente como produto formado por microrganismos, por degradação térmica da matéria orgânica ou exsudação natural do petróleo. Porém, as fontes predominantes de HPAs para o ambiente marinho são as antrópicas, como a queima de combustíveis fósseis, derrames acidentais ou crônicos de petróleo e seus derivados, e descarte de efluentes industriais e domésticos (Alegbeleye; Opeolu; Jackson, 2017).

Existem mais de 100 moléculas distintas de HPAs espalhadas em regiões marinhas ou continentais (Guo, Yongyong *et al.*, 2011). Para propósito de monitoramento ambiental, a Agência de Proteção Ambiental dos Estados Unidos (USEPA) classificou 16 compostos considerados como prioritários em estudos de contaminação, baseados em suas distribuições, fontes e toxicidades (Figura 1.4; Tabela 1.1). Trabalhos que estudam a distribuição dos HPAs no ambiente, provindos tanto de fonte petrogênica quanto de pirogênicas, avaliam principalmente esses 16 compostos (Keshavarzifard; Zakaria; Hwai, 2017).

A maioria das moléculas de HPAs possuem elevada toxicidade, tendo, alguns de seus exemplares, propriedades carcinogênicas, mutagênicas, genotóxicas e imunotóxicas (Tabela 1.1; Guo *et al.*, 2011; Vajani; Gnansounou; Pandey, 2017; Sun *et al.*, 2021). Muitas ainda atuam como disruptores endócrinos, afetando as características reprodutivas e de desenvolvimento (Honda; Suzuki, 2020). Uma vez que a ocorrência de HPAs nos ambientes naturais representa um risco aos seres humanos e aos organismos expostos, há uma necessidade constante de se estudar a distribuição desses compostos em sistemas aquáticos (Alegbeleye; Opeolu; Jackson, 2017).

Devido ao caráter apolar das estruturas moleculares dos HPAs (Tabela 1.1), estes compostos apresentam baixa solubilidade na água (Neff, 1979). Elas ainda se caracterizam por terem, em sua maioria, alto ponto de ebulição, sendo encontrados de maneira ubíqua no ambiente. Assim, uma vez lançados no ambiente, os HPAs podem ter diversas rotas. Os compostos podem agregar-se ao MPS (permanecendo na coluna d'água ou depositando-se nos sedimentos), serem ingeridos por organismos, solubilizar na água ou até serem bio/fotodegradados (Varanasi; Usha, 1989).

Figura 1.4. Estrutura química dos 16 Hidrocarbonetos Policíclicos Aromáticos considerados prioritários pela Agência de Proteção Ambiental dos Estados Unidos. (Adaptado de PAMPANIN; SYDNES, 2013)

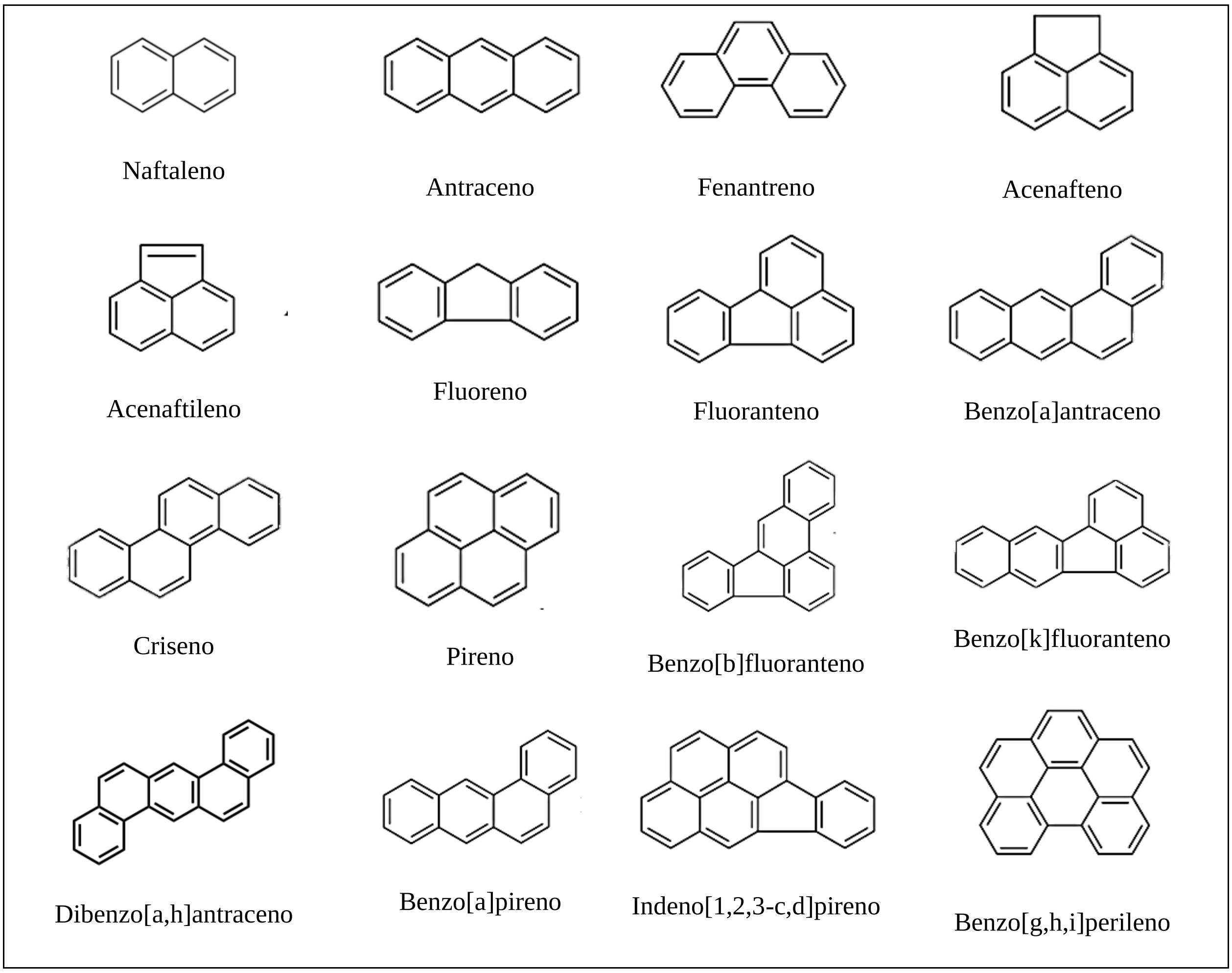


Tabela 1.1 – Propriedades físico-químicas e tóxicas dos 16 Hidrocarbonetos Policíclicos Aromáticos considerados como prioritários em estudos de contaminação pela Agência de Proteção Ambiental dos Estados Unidos (autoria própria).

Composto	SA	Log K_{OW}	PE	Propriedades tóxicas
Naftaleno	32	3,36	217,9	n.e.
Acenaftaleno	3,93	4,08	280,0	n.e.
Acenafteno	3,40	4,32	297,0	n.e.
Fluoreno	1,90	4,18	295,0	Carcinogênico
Fenantreno	1,00-1,30	4,46	340,0	Carcinogênico
Antraceno	0,05-0,07	4,45	339,9	Carcinogênico
Fluoranteno	0,26	5,53	384,0	Genotóxico, Carcinogênico
Pireno	0,14	5,30	404,0	Tóxico, Carcinogênico
Benzo[a]antraceno	0,01	5,60	437,6	Tóxico, Genotóxico, Carcinogênico
Criseno	0,002	5,60	448,0	Tóxico, Genotóxico, Carcinogênico
Benzo[b]fluoranteno	0,0014	6,60	n.e.	Tóxico, Genotóxico, Carcinogênico
Benzo[k]fluoranteno	0,0008	6,85	480,0	Tóxico, Genotóxico, Carcinogênico
Benzo[a]pireno	0,0038	6,00	311,0	Tóxico, Genotóxico, Carcinogênico
Dibenzo[a,h]antraceno	0,0005	6,00	524,0	Tóxico, Genotóxico, Carcinogênico
Indeno[1,2,3-c,d]pireno	0,00053	7,70	536,0	Tóxico, Genotóxico, Carcinogênico
Benzo[ghi]perileno	0,00026	7,00	>500	Tóxico, Genotóxico, Carcinogênico

*Solubilidade na água - SA, mg L^{-1}; Coeficiente de partição octanol-água – Log K_{OW}; Ponto de Ebulição – PE, º C; n.e. - não encontrado. Fonte das informações: Centre for Food Safety Food, 2004; Richardson, (2018).

1.2.2. Produtos de cuidado pessoal (PCPs)

Uma das classes de contaminantes emergentes atualmente estudada são as fragrâncias sintéticas e filtros ultravioleta (UV). Esses compostos são lançados no ambiente com frequência, a uma taxa ligeiramente crescente. Persistentes ou não, eles podem induzir efeitos negativos nos ecossistemas devido a sua ação e presença crônica (Taheran *et al.*, 2018).

A abordagem principal no campo de estudos de contaminantes emergentes, pincipalmente produtos de cuidado pessoal, são os possíveis efeitos adversos em organismos e ecossistemas.

Estes compostos têm sido investigados e efeitos bioacumulativos têm sido observados em mamíferos, de forma similar aos contaminantes históricos (Gago-Ferrero *et al.*, 2013). Também tem sido reportada a bioacumulação, alterações no metabolismo e estresse oxidativo em organismos bivalves, onde notou-se altas taxas de absorção ao filtro UV octocrileno (Pintado-Herrera *et al.*, 2024).

De modo geral, estudos recentes indicam que a crescente presença destes compostos no ambiente aquático pode induzir potenciais efeito em organismos. A possibilidade destes causarem danos através da interferência nos transportadores de efluxo de resistência multixenobiótica (MXR), considerada a primeira linha de defesa dos organismos a xenobióticos, tem sido estudada e divulgada (Chen; Gong; Kelly, 2017; Cunha *et al.*, 2017; Daughton; Ternes, 1999). Mesmo que estes contaminantes não apresentem riscos severos aos organismos, a atuação na resistência de MXR gera fragilidades as barreiras de defesa contra xenobióticos mais fragilizadas, permitindo uma via de acumulação de contaminantes no organismo (Amberger, 2014; Cunha *et al.*, 2017).

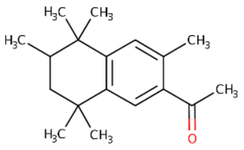
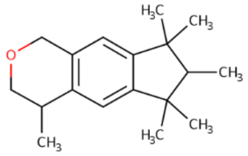
1.2.2.1. Fragrâncias sintéticas: almíscares policíclicos

As fragrâncias de almíscar sintético são compostos aromáticos que são utilizados na indústria para mimetizar odores (Hong *et al.*, 2021). Comumente usados como aditivos de fragrâncias, substituindo os raros e caros almíscares naturais (Li *et al.*, 2020; Wang *et al.*, 2015). Podem ser divididos em quatro grupos: derivados de nitrobenzeno (NM), fragrâncias alicíclicas (FA), fragrâncias policíclicas (FP) e fragrâncias macrocíclicas (FM). Como exemplo de cada grupo, tem-se as fragrâncias cetona, o *cyclomusk*, a galaxolida e o *ambrettolide*, respectivamente. Nos dias de hoje, a categoria dos FP domina a produção global de fragrâncias, visto que alguns NM, FM e FA foram banidos, tiveram o seu uso restrito devido ao potencial tóxico ao ambiente ou possuem alto custo de produção (IFRA, 2021).

De acordo com Montes-Grajales *et al*. (2017), as fragrâncias galaxolida (HHCB) e tonalida (AHTN) são as mais reportadas em estudos ambientais, principalmente devido a sua ampla utilização nos mais variados produtos ao redor do mundo. Estas substâncias têm características similares de alta persistência, bioatividade, bioacumulação em organismos, além de serem potenciais disruptores endócrinos (Gadelha *et al.*, 2019). As fontes destes compostos para o ambiente estão relacionadas ao uso de cosméticos, produtos de higiene pessoal, e produtos de limpeza (Wong *et al.*, 2019).

A HHCB e AHTN foram incluídas no “Registro, Avaliação, Autorização e Restrição de Produtos Químicos” (REACH), uma lista de substâncias que suscitam elevada preocupação em estudos ambientais. A HHCB é classificada como muito persistente e bioacumulativa de acordo com a *European Chemicals Agency* (2021). As suas propriedades físico-químicas (Tabela 1.2) comprovam que estes compostos podem não ser facilmente removidos por processos convencionais de tratamento de água, representando um risco potencial para organismos aquáticos e a saúde pública (Ebele; Abou-Elwafa Abdallah; Harrad, 2017; Hong *et al.*, 2021).

Tabela 1.2. Estrutura química e propriedades físico-químicas dos compostos Tonalida (AHTN) e Galaxolida (HHCB) (autoria própria). Fonte das informações: (PubChem, 2021; 2021)

	AHNT	**HHCB**
Fórmula molecular	$C_{18}H_{26}O$	$C_{18}H_{26}O$
Nomenclatura da IUPAC	*1-(3,5,5,6,8,8- hexamethyl-6,7-dihydronaphthale n-2-yl)ethanone*	*4,6,6,7,8,8- hexamethyl-1,3,4,7- tetrahydrocyclopent a[g]isochromene*
Fórmula estrutural		
Massa molar (g mol^{-1})	258.4	258.4
Solubilidade em água (mg L^{-1})	1.25	1.75
Coeficiente de partição octanol/água (log K_{OW})	5.7	5.9
Pressão de vapor	5.12 x 10^{-4}	5.45 x 10^{-4}

Estudos recentes mostram que os FP podem induzir efeitos nocivos à saúde. Ehiguese *et al.* (2021), por exemplo, comprovaram que a AHTN e a HHCB podem induzir danos neuroendócrinos em *Ruditapes philippinarum*. Parolini *et al.* (2015) indicaram que a AHTN causa múltiplos tipos de toxicidades em organismos aquáticos, incluindo genotoxicidade. Ehiguese *et al.* (2021a) avaliaram o risco ambiental estimado de HHCB e AHTN, sendo estes caracterizados como alto para as espécies *Phaeodactylum tricornutum, Isochrysis galbana* (em crescimento), *Paracentrotus lividus* e *Mytillus. galloprovincialis* (larvas em desenvolvimento).

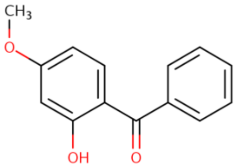
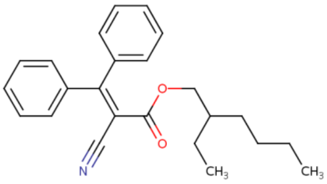
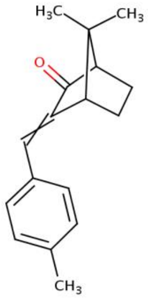
1.2.2.2. Filtros ultravioleta (UV)

Os filtros UV orgânicos são compostos químicos que absorvem os raios ultravioletas, protegendo a área onde são aplicados contra a ação da radiação. Em geral, eles podem divididos em duas categorias: filtros UV utilizados em PCPs para proteger o cabelo e pele de danos causados pelo sol; e estabilizadores UV utilizados em produtos como plásticos e tintas para proteger os polímeros e pigmentos contra a fotodegradação e evitar a descoloração (Brausch; Rand, 2011; Langford *et al.*, 2015; Lopes *et al.*, 2020). No entanto, estes compostos foram reconhecidos nas últimas décadas como contaminantes orgânicos de relevante importância no ambiente aquático (European Commission, 2003). Devido aos seus elevados coeficientes de partição e baixa solubilidade em água (Tabela 1.3), essas substâncias podem apresentar um alto potencial de bioacumulação (Gago-Ferrero *et al.*, 2013; Pintado-Herrera *et al.*, 2024). Como exemplos de compostos usados em filtros UVs que são comumente detectados em ambientes marinhos têm-se a benzofenona-3 (BP3), o octocrileno (OC) e o 4-metilbenzilideno cânfora (4-MBC) (Picot Groz *et al.*, 2014).

Fontes de compostos utilizados em filtros UV para o ambiente incluem unidades de tratamento de água residuária e atividades recreativas na água. Balmer *et al.*, (2005) encontraram a presença de EHMC, 4-MBC, BP3 e OC em plantas de tratamento de água da Suíça. Os autores estimaram que 118, 49, 69 e 28 g destes compostos sejam produzidos por dia, respectivamente, a cada 10.000 habitantes, em períodos de grande utilização, como no verão.

Estudos recentes sugerem que filtros UV são potencialmente tóxicos em várias espécies (Boyd *et al.*, 2021). Downs *et al.*, (2016) afirmaram que o BP3 provocou efeitos foto-tóxicos e induziu a ossificação do coral *Stylophora pistillata* (plânulas). Blüthgen *et al* (2014) sugerem que OC pode ter um impacto na hematopoiese, fluxo sanguíneo, formação de vasos sanguíneos e desenvolvimento de órgãos (ex. coração) em peixe-zebra. Os autores ainda sugerem que este composto poderia estar agindo como um disruptor endócrino nestes organismos.

Tabela 1.3 – Estrutura química e propriedades físico-químicas dos compostos benzofenona-3 (BP3), o octocrileno (OC) e o 4-metilbenzilideno cânfora (4-MBC) (autoria própria). Fonte das informações: (OctocrylenePubChem, 2021; Oxybenzone2021; 4-Methylbenzylidene camphor2021).

	BP3	**OC**	**4-MBC**
Fórmula molecular	$C_{14}H_{12}O_3$	$C_{24}H_{27}NO_2$	$C_{18}H_{22}O$
Nomenclatura da IUPAC	*(2-hydroxy-4-methoxyphenyl)-phenylmethanone*	*2-ethylhexyl 2-cyano-3,3-diphenylprop-2-enoate*	*(3Z)-1,7,7-trimethyl-3-[(4-methylphenyl)methylidene] bicyclo[2.2.1]heptan-2-one*
Fórmula estrutural			
Massa molar (g mol^{-1})	228.2	361.5	254.4
Coeficiente de partição octanol/água (log K_{OW})	3.70	6.10	5.14

Dessa forma, estudos que avaliam a presença destes compostos em ambientes aquáticos são importantes, uma vez que a introdução no ambiente tem sido constante (Kroon *et al.*, 2020) e ainda não se sabe quais efeitos podem gerar a longo prazo em organismos vivos.

Capítulo 2

ARTIGO 1

DETERMINING SILICONE-WATER PARTITION COEFFICIENTS FOR MONITORING PERSONAL CARE PRODUCTS IN WATERS

Abstract

Globally, there has been an escalation in the production and utilization of substances categorized as contaminants of emerging concern (CECs), including personal care products (PCPs) as synthetic fragrances and UV filters. In marine systems, the concentrations of these compounds are usually low due to processes as dilution and degradation. However, the presence of these contaminants in aquatic ecosystems is concerning even at relatively low concentrations, as evidenced by the detection of biological effects at environmental levels. Thus, the development of more efficient sampling methods, such as passive sampling, is necessary for analyzing these compounds in marine systems. To address this, this study determined the partition coefficients (log K_{PW}) for six fragrances (tetramethyl acetyloctahydronaphthalene, phantolide, tonalide, celestolide, galaxolide, traseolide) and eight UV filters (benzophenone-3, avobenzone, octocrylene, 2-hydroxybenzophenone, 4-methylbenzylidene camphor, homosalate, 2-ethylhexyl salicylate, and, 2-ethylhexyl methoxycinnamate) on the J-Flex silicone strip through the co-solvent method in a rotating experiment conducted over the period of 2 months. The log K_{PW} values obtained ranged from 4.46 to 6.47. Values obtained in this study were correlated with previous findings and strong positive correlations were observed for UV filters and fragrances, even when they were from different silicone suppliers. A field application test was performed, demonstrating the suitability of the J-Flex silicone rubber for sorbing these compounds over a 2-months exposure period. This suitability was attributed to the slower and more accurate attainment of equilibrium by the J-Flex silicone rubber.

Keywords: Passive sampler, Personal Care Products, UV filters, Fragrances.

2.1. INTRODUCTION

The number of new organic synthetic compounds entering the market has been increasing over the years (Wang *et al.*, 2023). This trend is attributed to factors such as crescent demand for specialized materials in various sectors (e.g., pharmaceutical and cosmetic markets, industrial applications, agriculture), advancements in chemical synthesis methodologies, and continuous research and development efforts aiming to create novel compounds (Nikolenko *et al.*, 2023; Sandoval *et al.*, 2024). Thus, these compounds, including pesticides, pharmaceuticals, flame retardants, plasticizers, personal care products (PCPs), among others, have been extensively used globally in recent decades and can potentially reach natural environments (Mamy *et al.*, 2015). Their main sources to aquatic systems include wastewater treatment facilities, untreated effluents, and, in some cases, direct inputs (Manetti; Tomei, 2024).

Personal care products (PCPs), such as fragrances, UV filters, and antimicrobials, have emerged as contaminants of emerging concern (CECs) in recent years. These substances are extensively utilized in health and cosmetic products, resulting in continuous environmental inputs (Mabitla; Chiwaye; Daramola, 2023). They have been detected in various environmental matrices, such as soil (Yager *et al.*, 2014), water (Tiedeken *et al.*, 2017), biota (Gadelha *et al.*, 2019) and groundwater (Dodgen *et al.*, 2017). Some PCPs have been associated with suspected adverse effects on both ecological and human health, as well as the potential for bioaccumulation, highlighting the importance of studying these compounds in aquatic ecosystems (Geissen *et al.*, 2015; Mojiri *et al.*, 2019; Zambianchi *et al.*, 2017). Therefore, developing sampling strategies for the determination of PCPs in aquatic systems is important in terms of understanding these compounds and assessing their environmental behavior and potential impacts on ecosystems.

Accessing the freely dissolved concentrations of PCPs in water has been a limiting factor in environmental chemistry. The use of natural waters as a matrix reduces the representativeness of the sample, both in temporal and spatial variables (Pintado-Herrera *et al.*, 2016). Considering that the concentrations of contaminants tend to change over a period (Coes *et al.*, 2014), or a time evaluation, that sampling must be done in short periods of time, spending a lot of time and resources. Another associated factor is that the concentration of contaminants found in these environments is relatively low, requiring pre-concentration processes of the samples (Novák *et al.*, 2018).

Passive sampling devices (PSDs) are a simple and efficient approach that have been demonstrated as a robust tool in assessments of occurrence and levels of hydrophobic organic contaminants in water (Bajagain *et al.*, 2023; Yates *et al.*, 2013). Due to their sorption capability, PSDs can be employed to assess time-weighted average concentrations of chemicals over a period, avoiding the overestimation of freely dissolved target contaminants in environment (Alvarez, 2013; Smedes; Booij, 2012). Semipermeable membrane devices, polyethylene strips, polar chemical integrative sampler (POCIS), and silicone strips are very common passive samplers for monitoring organic contaminants in aquatic systems (Kanwischer *et al.*, 2021; Lima; Pacheco; Cassella, 2019; Pintado-Herrera *et al.*, 2020; Vrana *et al.*, 2018; Zendong *et al.*, 2014). Among them, silicone strips (i.e., silicone rubber - SR) present some advantages, such as low cost, reusability, and simple construction (Rusina *et al.*, 2007). Silicone strips have affinity for hydrophobic organic contaminants and present uncomplicated sample processing (Vrana *et al.*, 2005). As a result, SR has been used in monitoring studies, of CECs (Pintado-Herrera *et al.*, 2020), polycyclic aromatic hydrocarbons (PAHs; Schäfer et al., 2010), polychlorinated biphenyls (PCBs; Allan et al., 2009), organochlorine pesticides (OCP; NOVÁK et al., 2018), chlorinated paraffins (Godere *et al.*, 2021), and others.

AlteSil™ SR has been employed to evaluate different nonpolar organic compound groups, such as PAHs, polychlorinated biphenyls, pesticides, and some CECs in environmental studies (Booij; Smedes, 2010; Novák *et al.*, 2018; Pintado-Herrera *et al.*, 2020; Silva-Barni *et al.*, 2019; Vrana *et al.*, 2018). But, this brand of silicone sheet has been discontinued and new types of SR are being studied and calibrated for environmental applications, such as the J-Flex™ silicone, which have already been validated for contaminants as PCBs, PAHs (Smedes *et al.*, 2009), and a few UV filters (Verhagen *et al.*, 2019).

However, there is still a gap regarding the partition coefficient between J-Flex™ silicone rubber and water for specific PCPs, such as the fragrances and the UV filters. K_{PW} data becomes fundamental in the study of passive samplers because by using the silicone rubber, which equilibrates with the surrounding medium, the K_{PW} must be used together with the concentration found in the sampler to estimate the sampling scenario of the analytes (kinetic or in equilibrium) and determine the concentration freely dissolved in water (Yates *et al.*, 2007).

The aim of this study was to determine the silicone/water partition coefficients (K_{PW}) of selected PCPs for J-Flex™ silicone rubber to validate this device as a passive sampler in studies of aquatic contamination by PCPs.

2.1.1. Theory

In order to convert the PSD uptake into freely dissolved aqueous concentrations (C_w), the polymer-water partition coefficient (K_{PW}) must be considered (Verhagen *et al.*, 2019). K_{PW} is a crucial parameter that describes the polymer's capacity to absorb the compound relative to the water phase, and the C_W can be calculated according to the equation 2.1:

$$C_W = \frac{N^t}{K_{PW}\, m_S\left[1-exp\left(-\frac{R_S t}{K_{pw} m_S}\right)\right]} \qquad \text{Equation (2.1)}$$

where C_W (g kg^{-1}) is the freely dissolved concentration in the water, N (g kg^{-1}) represents the concentration in the polymer, K_{OW} is the polymer-water partition coefficient, m_S (kg) the mass of the sampler, R_S (L day^{-1}) the sampling rate (volume of water that is cleared through uptake of the sampler per unit of time), and t is the time of exposure. The R_S is calculated as a function of the dissipation of the performance reference compounds (PRCs), through the equation 2.2:

$$R_S = F\ x\ A\ x\ M^{-0,47} \qquad \text{Equation (2.2)}$$

where F is the proportionality factor (or flow factor) estimated from the dissipation of the PRCs (F=Nt/N0; where N0 is the dosed amount measured in a reference sampler, Nt is the amount in the sampler after exposure); A represents the surface area of the sampler (m^2) and M is the molecular mass of the analyte (g mol^{-1}).

Whether utilizing equilibrium or kinetic sampling in SR passive sampling, the results show the quality of the measured C_w depends significantly on the precise calculation of the K_{PW} (Smedes *et al.*, 2009; Sun *et al.*, 2019), which is defined as (equation 2.3):

$$K_{PW} = {C_{polymer}}\big/{C_{water}} \qquad \text{Equation (2.3)}$$

where $C_{polymer}$ is the concentration in SR and C_{water} is the concentration in water.

It is important to observe that the SR is more effectively used for chemicals with octanol-water partition coefficient (Log K_{OW}) above 3 (hydrophobic compounds) to reach the equilibrium phase (Pintado-Herrera *et al.*, 2016; Smedes, 2012). Otherwise, the equilibrium phase may not be achieved for some hydrophobic chemicals due to their high diffusive transport trough the water boundary layer and limited PSD exposure time.

The measurement of K_{PW} was undertaken using a cosolvent method (Smedes *et al.*, 2009). Partition coefficients were measured in pure water and water-methanol mixtures up to a methanol mole fraction of 50% (v/v). Subsequently, log K_{PW} in pure water was determined as the intercept of linear regression of the coefficients found in the different methanol:water ratios with the corresponding methanol mole fractions (Smedes, 2018).

2.2. METHODOLOGY

2.2.1. Materials, reagents, and chemicals

Commercial silicone rubber (0.3 ± 0.2 mm thick, translucent) was purchased from J-Flex Rubber Products (London, England). Chromatography-grade methanol and ethyl acetate were purchased from Sigma–Aldrich (J.T. Baker, The Netherlands). Galaxolide and the deuterated PAH mixture (d_8-naphthalene, d_{10}-acenaphthene, d_{12}-phenanthrene- and d_{12}-perylene), Triphenyl phosphate-d_{15} (TPP-d_{15}) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Benzophenone-3 (BP3), octocrylene (OC), 2-hydroxybenzophenone (2OHBP), homosalate (HMS), 2-ethylhexyl salicylate (EHS), 2-ethylhexyl-4-methoxycinnamate (EHMC), and 4-methylbenzylidene camphor (4MBC) were purchased from Sigma–Aldrich (Madrid, Spain). Phantolide (AHMI), tonalide (AHTN) celestolide (ADBI), galaxolide (HHCB), traseolide (ATII) avobenzone (ABZ) and cashmeran (DPMI) were purchased from LGC Standards (Barcelona, Spain). OTNE fragrance was purchased from Bordas Chinchurreta Destilaciones (Seville, Spain). Stock solutions of these analytes were prepared in methanol and stored at −20 °C in tightly closed amber vials.

2.2.2. Silicone sheet preparation

The J-Flex silicone rubber (SR) strips (4.5 x 2.75 cm) underwent a cleaning process following the methodology described by Smedes and Booij (2012), with modifications. Briefly, the SR were mechanically shaken in hot water to remove excess powder. The next step involved extracting the SR in Soxhlet for 100 h with ethyl acetate to eliminate oligomers. Subsequently, SR has undergone a solvent exchange process being immersed in Methanol (MeOH) for 48 h with two solvent changes. The sheets were cleaned using a lint-free tissue and left to air-dry under a fume hood until the solvent had completely evaporated.

The spike method, based on Booij et al. (2002) with modifications, was used to load the target contaminants (fragrances and UV filters) into the spiked sheets. The sampling sheets (SRs) were soaked in amber bottles containing 100 mL of methanol with the chemicals of interest to achieve a nominal concentration of 50 ng of each chemical per SR. After soaking in methanol, ultrapure water was added according to the specific conditions outlined in Table S1. The bottles were then placed on an orbital shaker set to 100 rpm for 7 days to ensure thorough loading of the contaminants.

After this step, the polymer sheets were taken out of the water/methanol solution, gently cleaned using a lint-free tissue, and left to air-dry overnight under a fume hood to ensure the complete removal of any remaining solvent. Subsequently, the sheets were carefully stored in sterile amber containers at -20 °C until they were required for future applications. The variances in the chemical masses among the spiked sheets was below 5 %.

2.2.3. Silicone-water partition coefficient (K_{PW}) measurement

The cosolvent method was used to determine the K_{PW} for emerging contaminants (Smedes, 2018; Smedes; Booij, 2012). Briefly, the acquired K_{PW} values in pure water (0 % methanol) were validated using a simple linear regression between ultrapure water results and data obtained through the cosolvent method. The selection of polymer masses and analyte quantities depends on the specific fraction of methanol within the water-methanol mixture utilized for K_{PW} measurement. In this experiment, each silicone strips were fortified with 50 ng of each compound.

Amber bottles with volumes ranging from 0.2 L to 2.5 L were utilized to prevent potential analyte photodegradation. The methanol content in the methanol-water solution varied from 0 to 50 % (v/v) as detailed in the Supplemental Data (Table S2). For the smaller volumes, experiments were conducted in duplicate, while duplicates of larger volumes were not feasible due to limitations in the rotation equipment. All bottles underwent two months of agitation in orbital shakers operating at 100 rpm while maintained at room temperature (25 °C). At the conclusion of the experiment, water, methanol-water solutions, and polymer sheets were individually extracted and analyzed to determine the K_{PW} values.

The final K_{PW} values were determined from the concentrations found in the polymer and in the water or water/methanol mixture, both at ng Kg^{-1}. Subsequently, the partition coefficients of the polymer/aqueous mixture ($K_{P,M}$) were calculated as the ratio of $C_{polymer}$ to C_{water} (Equation 2.3). The $logK_{PW}$ (pure water, 0% MeOH) was determined as the intercept from the linear regression of the values obtained for $logK_{P,M}$ in relation to the molar fraction of methanol (MF).

2.2.4. Extraction, analysis, and QA/QC

Silicone sheets were extracted according to Allan et al. (2013) and Pintado-Herrera et al. (2016) with modifications. The SR was soaked in *n*-pentane at 50 rpm during 8h (1 g:60 mL; sampler:solvent). The extraction tests with the main analytes under same conditions presented recoveries between 45 and 154 % for all substances of interest (Supplemental Material A, Table S3).

Water samples were extracted according Pintado-Herrera et al. (2013) with modifications. The samplers were transferred to larger amber bottles and then diluted with ultrapure water to achieve a minimum 10 % of methanol (Supplemental Material A, Table S2). Sodium chloride (NaCl) was added to the samples to enhance ionization (1 g:100 mL; NaCl:water/methanol sample), and surrogate standards were added (100 ng PAHs-d). The mixtures were then processed through stir bar sorptive extraction (SBSE) (700 rpm; overnight). After deployment, stir bars were ultrasound-extracted in a vial with 2 mL of ethyl acetate. The extractions tests presented recoveries ranging from 43.5 to 157 %, excepting for 2-OHBP (35.6 %), for all substances of interest (Supplemental Material A, Table S3). All the extracts were evaporated under a gentle stream of N_2 to 250 µL or 500 µL and then 100 ug L^{-1} of triphenyl phosphate-d15 (TPP-d_{15}) was added as internal standard.

Finally, separation of analytes was performed on a Bruker 456-GC (EUA) using a Rxi-5Sil MS column (30 m × 0.25 mm i.d. × 0.25 µm film thickness consisting of 5% diphenyl and 95% polydimethylsiloxane), keeping the helium carrier gas flow at 1 mL min^{-1} and the injection port temperature at 320 °C. The column temperature ramp was as follows: 70 °C for 3.5 min, increased by 25 °C min^{-1} to 180 °C, then by 5 °C min^{-1} to 320 °C, and held for 5 min.

Atmospheric pressure gas chromatography time-of-flight mass spectrometry (APGC-Tof-MS) Bruker IMPACT II (EUA) was used for the identification and quantification of analytes.

Data was processed using Bruker TASQ 2.0 software. Identification and quantification of target compounds were based on retention times and exact mass for each analyte to those for commercially available standards. Quantification of target compounds was performed using calibration curves (from 1 to 400 µg L^{-1}), prepared in ethyl acetate. Only calibration curves with r^2 greater than 0.99 were accepted. Procedural blanks, which consisted of extracting clean strip of silicone rubber with the same procedure as that for the rest of the samples, were also analyzed. In general, the blank samples showed no contamination and when target analytes were found, they were subtracted from the sample results.

Internal standard recovery ranged between 83 and 130 % for water and between 91.6 and 110 % for SR. Instrument limit of detection and method limit of detection (mLOD) were calculated according to signal to noise (S/N; Table S4 of Supplemental Material A). iLOD was calculated based on the S/N of the lowest value of the calibration curve, adjusting this value to when the S/N was equal to 3. The mLOD was obtained from the value found for the iLOD adjusted by the pre-concentration of the sample and its recovery for silicone rubber or water. iLOD ranged between 0.0160 (HHCB) to 0.7515 (ABZ) µg L^{-1}, water mLOD ranged between 0.0002 (OC) to 0.0125 (HMS) µg L^{-1} and silicone mLOD ranged between 0.0001 (OC) to 0.0022 (OTNE) µg L^{-1}.

In addition, Origin was the data analysis and graphing software used in this work.

2.2.5. Field study

In addition to the laboratory experiments a passive sampler was deployed for 71 days (May to July 2023) at 1 site (-12.999462N, -38.530946S) at a pier in Todos os Santos Bay (2nd largest coastal bay, Brazil), being 2 meters deep at low tide and up to 8 meters deep at high tide, located in the northeast part of Brazil, near the city of Salvador. J-Flex (5.5 x 9 x 0.03 cm) SR sheets were used. The exposure time chosen was determined on the basis of Smedes (2018)' equilibrium studies. Triplicate strips were deployed below the water surface using stainless steel in parallel with the water flow, attached to a cement pit structure, and subsequently submerged (Figure 4). During deployment, information on salinity, water temperature, and air temperature was collected using a multiparameter sensor (AKSO 0320).

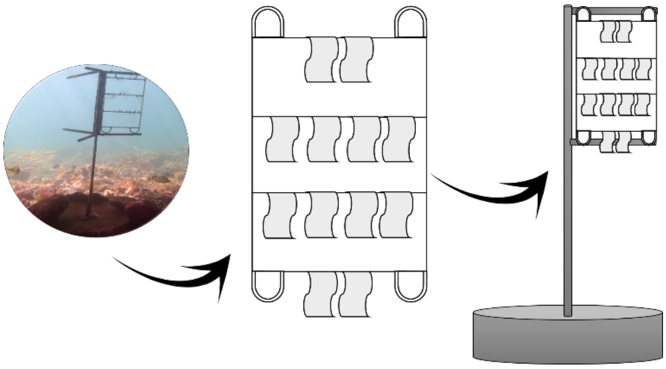


Figure 4. Passive Sampler Device structure.

Samples were retrieved and its surfaces was cleaned on site with local water. Samples were packed into sealed glass containers shielded from sunlight and transported back to the laboratory where they were stored at –20 °C until samples extraction and analysis. Sampling preparation and extraction methods were similar to those described above. Deuterated PAHs such as d_8-naphthalene, d_{10}-acenaphthene, d_{12}-phenanthrene- and d_{12}-perylene were used as the PRCs. The fortifying method described in Booij et al. (2002) and with the aforementioned explanation was used to load the PRC into the spiked sheets. PRCs are used to calculate the F value (proportionality factor or flow factor) estimated from its dissipation. Preparation controls included the initial concentration of the PRCs in the sample prior to exposure and the possible contamination during preparation.

2.3. RESULTS AND DISCUSSION

2.3.1. Silicone K_{PW} measurements

The estimated K_{PW} of the tested fragrances and UV filters are listed in Table 2.1 along with their chemical properties. Two types of linear regression were used to compare the K_{PW} results. The molar fraction (MF) model was determined using the results of the co-solvent method as a function of the moles of MeOH in each experiment. For the liquid/liquid (LL) volume model, the K_{PW} results were plotted against the percentage of the volume of methanol used in each experiment.

The standard deviation (SD) of the log K_{PW} among the experiment replicates ranged from 0.0002 (tonalide) to 0.07 (octocrylene) log units for the MF model and between 0.002 (tonalide) and 0.08 (avobenzone) log units for the LL model. Considering the low SD reported for these compounds and the mass balance obtained between the water/methanol mixture and polymer equilibrium was confirmed.

Table 2.1. Molecular weights, octanol-water partition coefficients (K$_{OW}$), measured silicone-water partition coefficients for fragrances and UV filters in this study and silicone data obtained in literature for the same compounds. n.e. = not evaluated. J-Flex, Altesil and, Powell are silicone rubber suppliers.

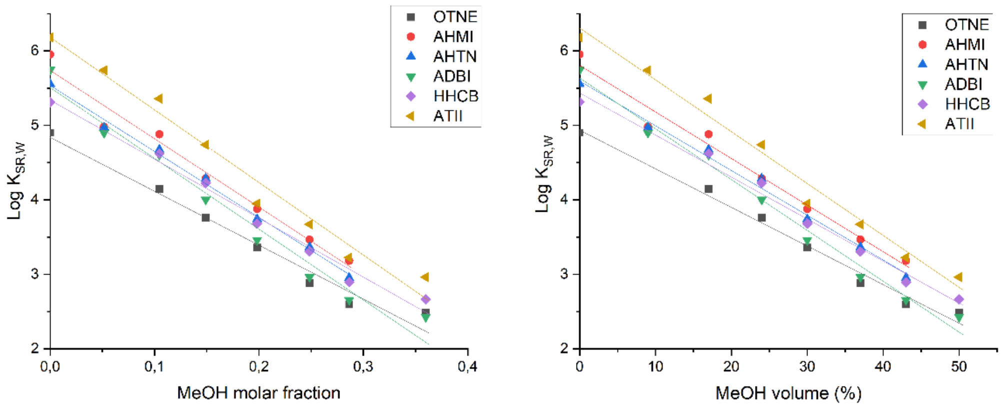
Compounds	Molecular Weight	Log K$_{OW}$	Log K$_{PW}$ J-Flex measured (L kg^{-1})	Log K$_{PW}$ Altesil (L kg^{-1}) [1]	Log K$_{PW}$ Powell (L kg^{-1}) [2]	Log K$_{PW}$ Altesil (L kg^{-1}) [3]
Fragrances						
Tetramethyl acetyloctahydronaphthalene (OTNE)	234.30	5.60	4.86 (± 0.03)	3.63 (± 0.20)	n.e.	n.e.
Phantolide (AHMI)	244.30	5.90	5.63 (± 0.001)	3.78 (± 0.002)	n.e.	5.08
Tonalide (AHTN)	258.40	5.70	5.46 (± 0.005)	4.01 (± 0.03)	n.e.	5.29
Celestolide (ADBI)	244.30	5.90	5.51 (± 0.02)	3.96 (±0.008)	n.e.	5.26
Galaxolide (HHCB)	258.40	5.90	5.70 (± 0.03)	3.97 (± 0.00)	n.e.	5.32
Traseolide (ATII)	244.30	6.30	6.18 (± 0.01)	4.36 (± 0.01)	n.e.	n.e.
UV Filters						
Benzophenone-3 (BP3)	198.20	3.79	4.47	3.08 (± 0.02)	3.69 (± 0.11)	n.e
Avobenzone (ABZ)	228.20	6.10	4.96 (± 0.08)	n.e.	n.e.	n.e.
Octocrylene (OC)	254.30	7.53	4.96 (± 0.05)	4.96 (± 0.11)	6.32 (± 0.06)	n.e.
2-Hydroxybenzophenone (2OHBP)	290.40	3.47	4.65 (± 0.01)	3.04 (± 0.09)	n.e.	n.e.
4-Methylbenzylidene camphor (4MBC)	250.30	4.95	5.08 (± 0.01)	3.39 (± 0.03)	5.05 (± 0.08)	n.e.
Homosalate (HMS)	262.36	5.82	5.85 (± 0.001)	4.55 (± 0.09)	5.41 (± 0.05)	n.e.
2-Ethylhexyl salicylate (EHS)	310.40	5.77	5.80 (± 0.03)	4.70 (± 0.09)	n.e.	n.e.
2-Ethylhexyl methoxycinnamate (EHMC)	361.40	5.77	6.47 (± 0.02)	4.77 (± 0.00)	6.40 (± 0.07)	n.e.

[1](Pintado-Herrera *et al.*, 2016) [2](Verhagen *et al.*, 2019) [3](Smedes, 2018)

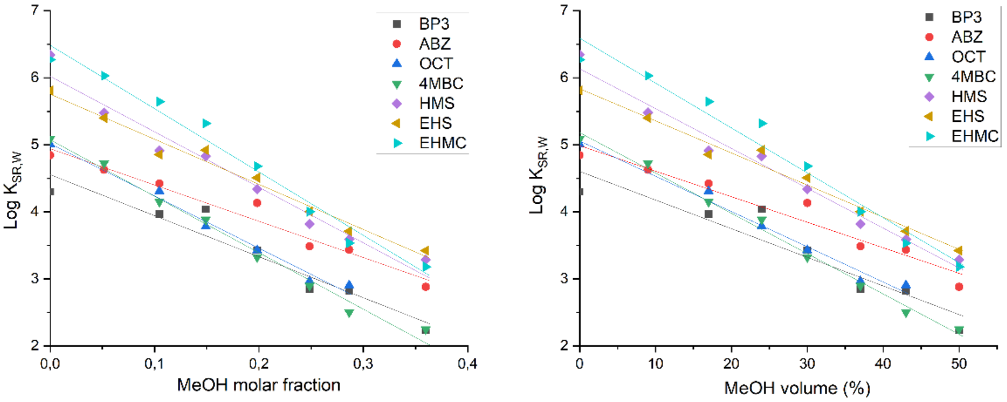
Comparing the MF and LL models, the difference between the two ranged from 0.02 to 0.28 log units, demonstrating consistency in the results obtained. In this study, the results obtained through the MF model were considered as a reference, as this model consistently proved to be more appropriate according to previous studies (Smedes et al., 2009; Verhagen et al., 2019; Figure 2.1; Table 2.1). All the coefficients of determination for both the LL model and the MF model are shown in the Supplementary Material A, Table S5.

Figure 2.1. Comparison between polymer/water partition coefficients (log K_{PW}) determined using the cosolvent method as a function of the molar fraction model and liquid/liquid volume model plotted against the molar fraction and volume of methanol.

Fragrances

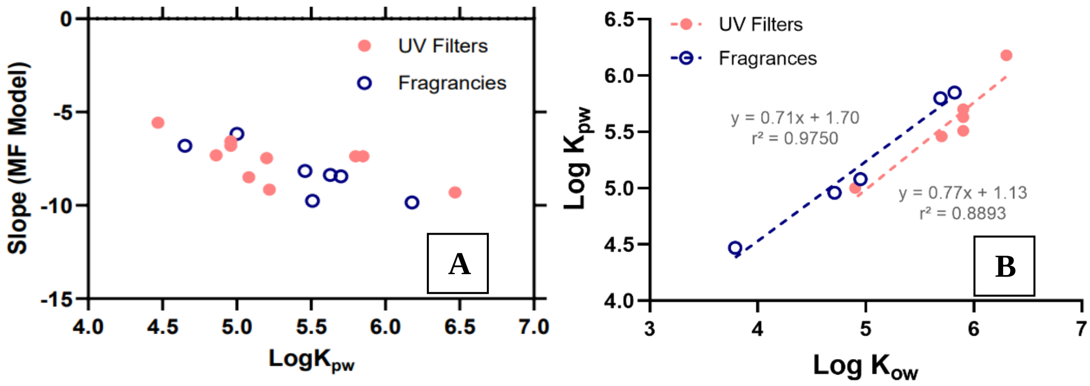


UV Filters



Although hydrophobic organic compounds tend to exhibit similar behavior, the intrinsic characteristics of these compounds (e.g., complexes structures, solubility) may lead to distinct behaviors and unusual relationships between slope-hydrophobicity (Smedes, 2018). The slope can be interpreted as the molecule's sensitivity to variation based on the hydrophobicity of the environment, as demonstrated in Smedes (2018) where seven groups of organic compounds were compared. However, when analyzing only two groups of personal care products (fragrances and UV filters), significant similarity was found between them (Figure 2.2). Based on the literature and the slope-hydrophobicity results obtained in this study, they exhibit similar behavior, indicating that their properties, beyond their similar organic nature, are expressed similarly when compared to the hydrophobicity of the molecules (K_{PW}).

Figure 2.2. (A) Slopes of log K_{PW} measured in various methanol/water mixtures versus the mole fractions of methanol in that mixture (MF) and the final log silicone/water partition coefficients (logK_{PW}). (B) Log K_{PW} plotted versus the log octanol/water partition coefficient (log K_{OW}) as listed in Table 2.1.

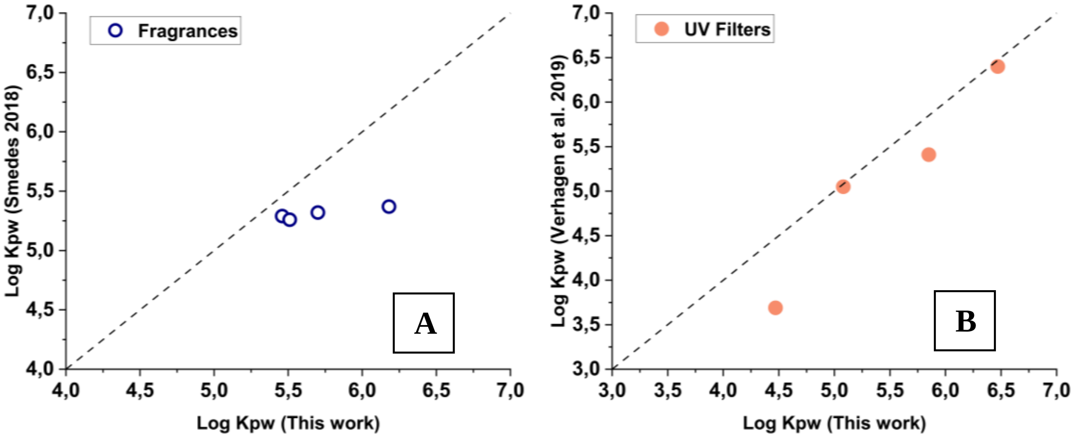


The relationship between log K_{OW} and log K_{PW} was also explored using simple linear regression. The determination coefficient (r^2) results indicated a strong correlation, both for fragrances ($r^2 = 0.9750$, $p = 0.0017$) and for UV filters ($r^2 = 0.8893$, $p = 0.0048$). Similar relationships were found for fragrances ($r^2 = 0.8130$) and PCBs ($r^2 = 0.8140$) by Smedes (2018). Verhagen et al. (2019) identified a relationship with $r^2 = 0.90$ for UV filters using the Altesil silicone rubber, which is consistent with the correlation detected in this study.

When compared to the data previously presented by Pintado-Herrera et al. (2016) for the Altesil® silicone rubber, the values of K_{PW} reported in this study can differ by 0.68 log units (BP3), consistently showing higher values. This indicates that J-Flex® has higher K_{PW} values and may take longer to reach equilibrium. The results reported by Verhagen et al. (2019) for the red silicone rubber from Powell® were more similar to those proposed in this study, with a difference of 0.78 log units also for BP3. This suggests that these two silicone rubbers have similar properties, exhibiting similar log K_{PW} values for these compounds.

Pearson's correlation (significance level alpha = 0.05) was used to compare the data in this study with the data reported by Smedes (2018) and Verhagen et al. (2019) (Figure 2.3). A strong positive correlation was observed for UV filters ($r = 0.9677$ and p-value < 0.05) and fragrances ($r = 0.93279$, p-value $= 0.0672$), suggesting that, even with different types of silicone rubber, the behavior of log K_{PW} for UV filters and fragrances tends to be similar.

Figure 2.3. (A) Comparison of the estimated K_{PW} from Smedes (2018) and this work, the dashed line represents a 1:1 ratio. (B) Comparison of the estimated K_{PW} from Verhagen at al. (2019) and this study, the dashed line represents a 1:1 ratio.



The K_{PW} values found for J-Flex® SR are higher than those previously reported in the literature for Altesil® silicone strip (Pintado-Herrera *et al.*, 2016; Smedes, 2018), but similar to those found for Powell® silicone strip (Verhagen *et al.*, 2019). This suggests that J-Flex and Powell polymers are more suitable for passive sampling of fragrances and UV filters, as equilibrium will be reached more slowly and accurately (Rusina *et al.*, 2007).

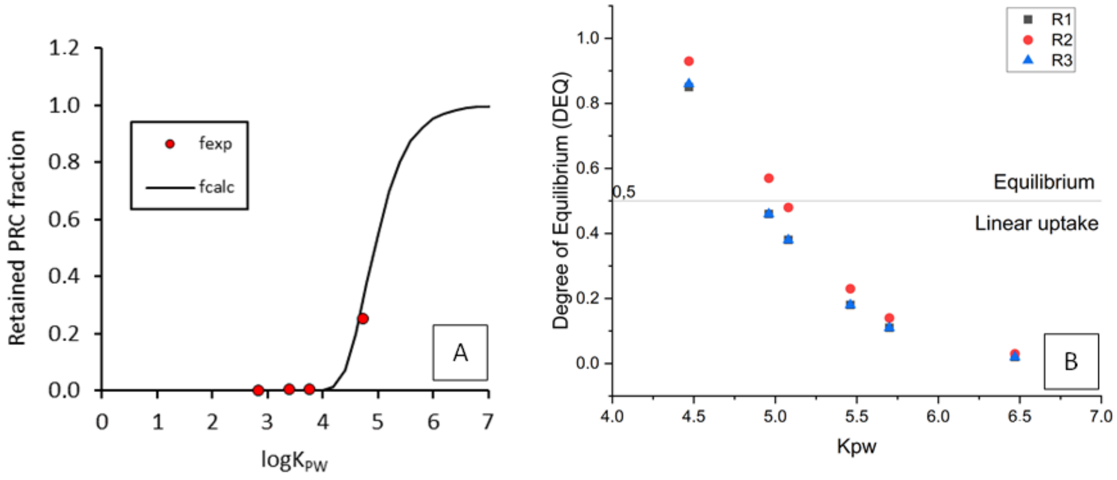
As observed in other studies, K_{PW} values are generally lower than K_{OW} values (Booij; Smedes; Van Weerlee, 2002; Pintado-Herrera *et al.*, 2016; Smedes, 2018; Yates *et al.*, 2007). In this work, the K_{PW} values for BP3 were higher, which suggests that this compound prefers the polymer phase more than the aqueous phase. Even though Verhagen et al. (2019) also found higher K_{PW} values for some compounds (4MBC, EHMC), these results can still be indicated as anomalous when compared to the others and requires further investigation.

2.3.2. Field application

J-Flex silicone rubber was evaluated as a passive sampler during a 71-day exposure period at a nautical club located in Todos os Santos Bay, NE Brazil. This area was selected for the field validation due to its multiple use (including leisure and water activities) coupled with its proximity to an underwater effluent outfall. Six compounds, including two fragrances (tonalide and galaxolide) and four UV filters (4MBC, BP3, EHMC and OC) were evaluated at this stage.

The sampling rate (R_S) and the freely dissolved concentration (C_W) were calculated according to Rusina et al. (2010) and Smedes et al. (2009), respectively (Equations 2.1 and 2.2 in theory section). The deuterated PAHs – d_8-naphthalene, d_{10}-acenaphthene, d_{12}-phenanthrene- and d_{12}-perylene – were used as performance reference compounds (PRCs) and their dissipation rates (f_{exp}) were used to estimate the R_S for the sampling period (5.8 L d^{-1}; Figure 2.4 A). The degree of equilibrium (DEQ) was used to obtain the final C_W results (Vrana et al.,2018). When DEQ ≤ 0.5, the compound concentration is considered to be in a linear uptake stage, and when DEQ ≥ 0.5, its in equilibrium (Figure 2.4 B).

Figure 2.4. A – Retained fraction of performance reference compounds according to the model by Rusina et al. (2010), where f_{exp} is the retained fraction obtained from PRCs dissipation in samples and f_{calc} is the adjusted model. B – Degree of equilibrium for all the analyzed compounds in three replicates (R1, R2 and R3) according to the silicone-water partition coefficients for fragrances and UV filters estimated in this study.



Galaxolide, tonalide, 4MBC, and EHMC exhibited DEQ below 0.5, indicating a linear uptake for these compounds. Equilibrium stage (DEQ > 0.5) was observed for BP3, which presented the lowest K_{PW} value (4.47) among the analyzed compounds. For OC, while one replicate presented DEQ < 0.5, the other two replicates presented DEQ > 0.5. The other compounds analyzed (OTNE, AHMI, ADBI, ATII, ABZ, 2OHBP, HMS, and EHS) had concentrations lower than the mLOD. The final C_W obtained for each compound according to their respective uptake stages are presented in Table 2.2.

The concentrations observed for fragrances (Table 2.2, 3.38 and 0.09 ng L^{-1} for galaxolide and tonalide, respectively) in this study are similar to those found in Calzoa, Spain (2.3 ng L^{-1} for galaxolide; Romero et al., 2022) and in Vellar River, India (1.00 ng L^{-1}, for tonalide; Vimalkumar et al., 2021). Regarding UV filters, BP3 and octocrylene presented the highest concentrations (6.97 and 1.99 ng L^{-1}, respectively), which is similar to results previously reported in Southern China (12.9 and 2.15 ng L^{-1}, respectively; Tsui et al., 2019). Overall, the concentrations detected in this study were relatively low. Despite galaxolide being recognized as one of the most common synthetic compounds in surface waters (Lange; Kuch; Metzger, 2015), fragrances in seawater from tropical regions are expected to exhibit relatively low concentrations due to the elevated evaporation rates of these volatile compounds and high rates of photodegradation (Buerge *et al.*, 2003; Lin; Apell; Mcneill, 2019). Additionally, the low concentrations of UV filters could be attributed to the timing of the exposure, which occurred during the winter period in the southern hemisphere. Thus, further studies are warranted to improve the understanding of seasonal variations and current levels of these compounds in coastal regions.

Table 2.2. Freely dissolved concentrations (C_W) and its respect standard deviations of galaxolide, tonalide, 4MBC, BP3, EHMC and OC in field after 71-days of exposure.

Compounds	C_W (ng L^{-1})
Fragrances	
Tetramethyl acetyloctahydronaphthalene (OTNE)	<mLOD
Phantolide (AHMI)	<mLOD
Tonalide (AHTN)	0.09 ± 0.01
Celestolide (ADBI)	<mLOD
Galaxolide (HHCB)	3.38 ± 0.44
Traseolide (ATII)	<mLOD
UV Filters	
Benzophenone-3 (BP3)	6.97 ± 0.11
Avobenzone (ABZ)	<mLOD
Octocrylene (OC)	1.99 ± 0.43
2-Hydroxybenzophenone (2OHBP)	<mLOD
4-Methylbenzylidene camphor (4MBC)	0.18 ± 0.03
Homosalate (HMS)	<mLOD
2-Ethylhexyl salicylate (EHS)	<mLOD
2-Ethylhexyl methoxycinnamate (EHMC)	0.11 ± 0.01

2.4. CONCLUSION

This study presented partition coefficients for six fragrances and eight UV filters on the J-Flex silicone strip, with log K_{PW} values ranging from 4.46 to 6.47. The results proved to be consistent with low variations between replicates and demonstrated significant correlations even when compared to studies that employed silicone from different manufacturers. The J-Flex polymer has proven to be suitable for environmental analysis of CECs in seawater. Environmental application confirmed the suitability of J-Flex silicone rubber for the detection and quantification of UV filters and fragrances in surface waters.

Capítulo 3

ARTIGO 2

ONE-YEAR PASSIVE MONITORING HYDROPHOBIC ORGANIC CONTAMINANTS IN COASTAL WATERS: LEGACY CONTAMINANTS VS. CONTAMINANTS OF EMERGING CONCERN

Abstract

Contamination of aquatic systems by legacy contaminants (e.g., polycyclic aromatic hydrocarbons - PAHs, persistent organic pollutants - POPs) and contaminants of emerging concern (CECs) represents a growing concern in modern societies, especially due to the possibility of toxic effects to organisms. Since most of these organic compounds are nonpolar (log $K_{OW} > 4$), measuring their freely dissolved concentrations (i.e., bioavailable fraction) can be challenging. In this study, the applicability of silicone rubber passive sampling devices (PSD) for the analysis of PAHs, POPs, and CECs was assessed through a one-year field deployment of samplers in an urbanized coastal region in NE Brazil. Results revealed the presence of all target analytes in the water column. Freely dissolved concentrations (C_W) ranged from 1.16 (celestolide) to 303 (galaxolide) pg L^{-1} for the fragrances (tonalide, celestolide, galaxolide, and cashmeran) and from 3.55 (2-hydroxybenzophenone) to 4051 (homosalate) pg L^{-1} for UV filters (benzophenone-3, octocrylene, homosalate, 2-ethylhexyl salicylate, 2-ethylhexyl-4-methoxycinnamate, 2-hydroxybenzophenone and 4-methylbenzylidene camphor). For legacy contaminants, C_W ranged from 9.39 to 1197 pg L^{-1} for PCBs ($\sum_5$PCBs), from <LOD (limit of detection) to 7.05 pg L^{-1} for organochlorine pesticides, and from 3,759 to 21,975 pg L^{-1} for PAHs. According to diagnostic ratios, PAHs seems to originate from mixed sources (pyrolytic and petrogenic) for most of the year. CECs and pesticides may be introduced by wastewater discharge and PCBs owing to the presence of a shipyard in the region. An environmental risk assessment was conducted for the chemical substances for which ecotoxicological data were available, indicating that UV filters and legacy contaminants pose the greatest potential risk to organisms. As this area is recognized as a marine park and considering the presence of corals and the region biodiversity, the results of the effects of the risks on the environment demand attention.

Keywords: Personal Care Products, UV filters, Fragrances, Polycyclic Aromatic Hydrocarbon, PCBs, pesticides, Todos os Santos Bay, passive samplers.

3.1. INTRODUCTION

Coastal marine ecosystems are the main receptors for anthropogenic contaminants (Cuevas; Martins; Costa, 2018; Hatje *et al.*, 2022). Wastewater discharge, traffic, industries, tourism, and fishery activities contribute to the increasing presence of a mixture of organic pollutants in coastal waters (Caballero-Gallardo *et al.*, 2021; Rodil *et al.*, 2019). As new chemical substances are constantly produced and detected in the environment, new categories are proposed to classify contaminants based on aspects such a present or past use and the existence or absence of regulations for their use. Legacy contaminants refer to groups of contaminants that have been monitored and regulated across most regions of the world, such as polycyclic aromatic hydrocarbons (PAHs) and POPs (persistent organic pollutants, including polychlorinated biphenyls - PCBs and organochlorine pesticides - OCPs). Regarding POPs, although their use has been banned internationally for decades through the Stockholm Convention (UNEP, 2019), they are still a cause for concern due to their high environmental persistence and toxic effects (Miniero; Iamiceli, 2008). As for PAHs, although their maximum permissible concentrations in the environment are also subject to specific regulations, their toxicity and multiplicity of sources (e.g. burning biomass and fossil fuels) means that their constant monitoring is necessary to guarantee the health of the environment (Burgess; Ahrens; Hickey, 2003).

Conversely, contaminants of emerging concern (CECs) refer to different groups of compounds that are not usually included in monitoring programs and not yet fully regulated (Pintado-Herrera; González-Mazo; Lara-Martín, 2013). The effects and presence of these compounds in natural environments began to be investigated only a few years ago, following improvements in analytical techniques and equipment (Taheran *et al.*, 2018). CECs include personal care products (PCPs), such as synthetic fragrances and UV filters, pharmaceuticals, organophosphate flame retardants (OFPRs), among others. Even though no significant acute effects have been reported in experiments due to CECs exposure, studies suggest that even at low concentrations there are adverse effects, such as the UV filter octocrylene which can cause sublethal toxic effects in *Mytilus edulis* (Falfushynska *et al.*, 2021) and the fragrance galaxolide which can cause alterations at a cellular level in *Ruditapes philippinarum* (Rilievo *et al.*, 2021).Thus, evaluating this compounds in different environments is important for understanding their environmental fate, distribution, and potential risks (Pintado-Herrera; González-Mazo; Lara-Martín, 2013).

To understand the dynamics of the levels and trends of inherited contaminants and CECs, it is important to access the functioning of the ecosystem by monitoring it. It is critical to choose a good sampling approach to comprehend the behavior of inputs in an ecosystem (Söderström; Lindberg; Fick, 2009). Even though water evaluation is toxicologically relevant, the loss of compounds in the extraction process (glass-bottle assimilation, filtration) and the extremely low concentration of some groups compounds found in a collected water bottle, such as PCBs, make it unreliable (Prokeš; Vrana; Klánová, 2012). Thus, the use of passive sampler devices (PSDs) is increasing because of these temporal evaluation characteristics. These devices are cost-effective, reliable, and can detect lower compound concentrations during water monitoring campaigns (Namieśnik *et al.*, 2005). Studies have shown the potential of silicone rubbers as PSDs in the evaluation of the water environment, assessing time-averaged legacy contaminants (Yates et al. 2011; Okay et al. 2017; Aminot et al. 2017; Xue et al. 2020; Ramírez et al. 2023) and CECs (Gallen et al. 2019; Pintado-Herrera et al. 2020).

Regarding to environments where passive sampling has been used, most of the studies has been carried out in the northern hemisphere, mainly in Europe, focusing on regions such as the River Alna, Oslo (Allan *et al.*, 2013; Pintado-Herrera *et al.*, 2016); Loch Shiel, Scotland (Yates *et al.*, 2013), German Bight and Baltic Sea, (Brockmeyer; Kraus; Theobald, 2015), Bay of Cádiz, Spain (Pintado-Herrera *et al.*, 2020), Danube River, Hungary (Vrana *et al.*, 2018), River Meuse, the Netherlands (de Weert *et al.*, 2020). Few studies have been carried out in the southern hemisphere, such as the study on the Quenquén Grande River in Argentina (Silva-Barni *et al.*, 2019), but none have looked at tropical environment.

To obtain new data for coastal tropical waters with a J-Flex silicone rubber, one-year passive monitoring was carried out at a yacht club in Todos os Santos Bay (Salvador, Brazil) to assess and evaluate selected groups of legacy and CEC compounds.

3.2. METHODOLOGY

3.2.1. Theory

To convert PSD uptake into freely dissolved aqueous concentrations (C_W), the polymer-water partition coefficient (K_{PW}) must be considered (Verhagen *et al.*, 2019). This is a crucial parameter that describes the capacity of the polymer relative to the water phase and can be calculated according to Equation 3.1:

$$C_W = \frac{N^t}{K_{PW}\, m_s\left[1-exp\left(-\frac{R_S t}{K_{pw} m_S}\right)\right]} \qquad \text{Equation (3.1)}$$

where C_W (g kg^{-1}) is the freely dissolved concentration in the water, N (g kg^{-1}) represents the concentration in the polymer, K_{PW} is the polymer-water partition coefficient, m_S (kg) the mass of the sampler, R_S (L day^{-1}) the sampling rate (volume of water that is cleared through uptake of the sampler per unit of time), and t is the time of exposure.

SRs is properly used for hydrophobic compounds, with an octanol-water partition coefficient (Log K_{OW}) greater than 3, to reach the equilibrium phase (Pintado-Herrera *et al.*, 2016; Smedes; Booij, 2012). However, for some hydrophobic chemicals, the equilibrium phase may not be reached due to their high diffusive transport through the water boundary layer and limited PSD exposure time. In such cases, to calculate the sampling rate (R_s), where the uptake is solely controlled by the water boundary layer (i.e. assessing the dissipation of performance reference compounds, PRCs), Equation 3.2 is used:

$$R_S = F\ x\ A\ x\ M^{-0,47} \qquad \text{Equation (3.2)}$$

where F is the proportionality factor (or flow factor) estimated from the dissipation of the PRCs ($F=N_t/N_0$; where N_0 is the dosed amount measured in a reference sampler, N_t is the amount in the sampler after exposure); A represents the surface area of the sampler (m²) and M is the molecular mass of the evaluated chemical with $M^{-0.47}$ accounting for the influence of chemical aqueous passive diffusion (g mol^{-1}).

Whether equilibrium or kinetic sampling is used in silicone rubber (SR) passive sampling, the results show the quality of the measured C_w depends significantly on the precise calculation of the sampler-water partition coefficient (K_{PW}; Smedes et al. 2009; Sun et al. 2019), and is defined as Equation 3.3:

$$K_{PW} = {C_{polymer}}/{C_{water}} \qquad \text{Equation (3.3)}$$

The polymer–water partition coefficient (K_{PW}) values used in this work were obtained from Martins at al. (*in prep.*) for CECs and Smedes (2018) for PAHs, PRCs and OCs.

The mass of a contaminant accumulated in the sampler is determined by exposure time, sampling rate (R_S), and sampler-water partition coefficient (Greenwood; Mills; Vrana, 2009; Söderström; Lindberg; Fick, 2009). However, to calculate the freely dissolved concentration of the analyte in the medium (C_W), it is necessary to identify the partitioning stage of the analytes using Equation 3.4:

$$DEQ = \left[1 - exp\left(-\frac{R_s t}{K_{pw}\, m_s}\right)\right] \quad \text{Equation (3.4)}$$

where DEQ represents the degree of equilibrium achieved by the chemical during sampler exposure. If the result of Equation 3.4 is < 0.5, the analytes are still in the linear phase of partitioning with the sampler, indicating either little exposure time, low sampling rate, or a high hydrophobicity of the compound. Conversely, if the result is > 0.5, sampling is at or near the equilibrium stage, indicating low hydrophobic analyte, long exposure or high sampling rate (Smedes; Booij, 2012). In the first case, the dissolved concentration (C_W) is calculated according to Equation 3.5; and in the second case, according to Equation 3.6:

$$C_W \approx \frac{C_p}{R_s\, x\, m} \quad \text{Equation (3.5)} \qquad C_W = \frac{C_p}{K_{pw}\, x\, m} \quad \text{Equation (3.6)}$$

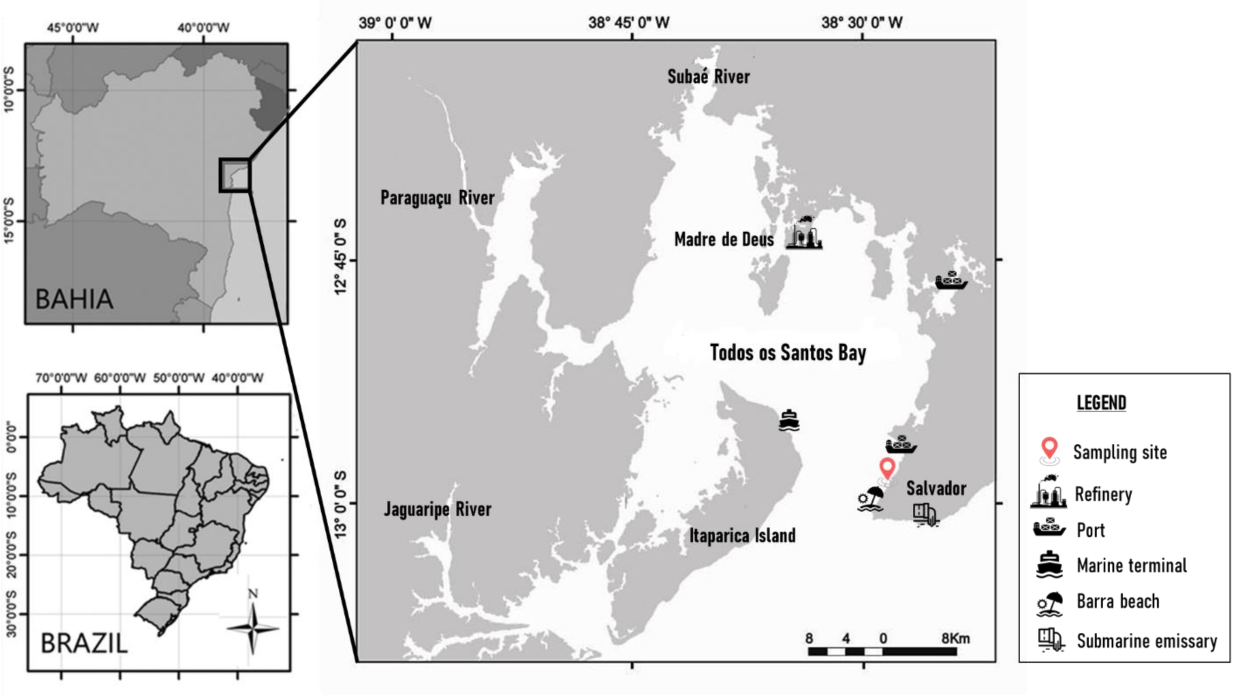
3.2.2. Materials

Commercial silicone rubber (0.3 ± 0.2 mm thick, translucent) was purchased from J-Flex Rubber Products (London, England). Chromatography-grade methanol, acetonitrile, and ethyl acetate were purchased from Sigma–Aldrich (J.T. Baker, The Netherlands). Galaxolide, deuterated PAH mixture (d_{12}-chrysene, d_{10}-phenanthrene, and d_{12}-perylene), and triphenyl phosphate-d_{15} (TPP-d_{15}) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Benzophenone-3 (BP3), octocrylene (OCT), homosalate (HMS), 2-ethylhexyl salicylate (EHS), 2-ethylhexyl-4-methoxycinnamate (EHMC), and 4-methylbenzylidene camphor (4-MBC) were purchased from Sigma–Aldrich (Madrid, Spain). Tonalide (AHTN), celestolide (ADBI), and cashmeran (DPMI) were purchased from LGC Standards (Barcelona, Spain). Stock solutions of these analytes were prepared in methanol and stored at −20 °C in tightly closed amber vials.

3.2.3. Study area

Todos os Santos Bay (TSB) (Figure 3.1) is the second largest bay in Brazil, with an area of 1200 Km^2. The bay is surrounded by the third largest metropolitan area in the country, Salvador, with over 2.9 million inhabitants (IBGE, 2021). The urbanization and industrial developments in the area, which includes the largest petrochemical complex in the Southern Hemisphere and two important ports, have led to contamination in ecologically sensitive areas of TSB (Beretta *et al.*, 2014; Celino *et al.*, 2010; de Almeida *et al.*, 2018; do Ó Martins *et al.*, 2020; Sotão Neto *et al.*, 2020). The sampling site, near the Marine Natural Park of Barra, features coral reef ecosystems and rich biodiversity. PSDs were deployed at a pier located in a yacht club in the region, with high circulation of boats and aquatic activities (e.g., diving).

Figure 3.1. Location of PSDs deployment.

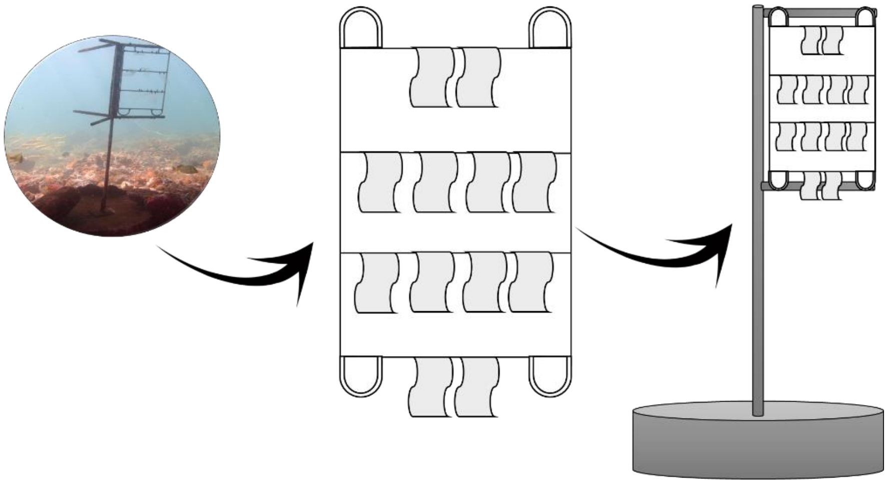


3.2.4. Preparation and deployment of PSDs

The cleaning and calibration processes of the silicone strips (J-Flex®, England) used in the present study followed the methodology described by Smedes and Booij (2012), with modifications. Briefly, SRs were mechanically shaken in hot water to remove excess powder. Next, for oligomer removal, the SRs was cleaned in Soxhlet for 100 h with acetonitrile. Then, the SRs was passed through a solvent change and immersed in methanol (MeOH) for 48 h, with two solvent changes during this period. This process is important for the next spike process, which occurs in methanol.

The cleaned SRs were spiked with performance reference compounds (PRCs; d_8-Naphtalene, d_{10}-Acenaphtene-, d_{10}-Phenanthrene and d_{12}-Perylene), according to Booij et al. (2002), to determine sampler-water exchange kinetics and sampling rates of compounds of interest. After enrichment, PSDs were deployed on-site in a stainless-steel grid containing 12 passive samplers, attached to a cement pit structure, and subsequently submerged (Figure 3.2). A set of 12 passive samplers (SR) were replaced approximately every 60 days throughout one year, during the following periods: C1 - December 2021 to February 2022; C2 - February to April 2022; C3 - April to July 2022; C4 – July to September 2022; C5 - September to November 2022; C6 – November 2022 to February 2023. During deployment, information on salinity, water temperature, and air temperature was collected using a multiparameter sensor (AKSO 0320). These data are presented in Table S1, Supplementary Material.

Figure 3.2. Passive Sampler Device structure.



3.2.5. Extraction and analysis

The analytical procedure was conducted using high-purity organic solvents (ethyl acetate - EtAc, MeOH, hexane - HEX, dichloromethane - DCM). Glassware was washed in a 1% Extran bath and decontaminated by calcination at 400 °C, except for volumetric materials, which were dried at room temperature and cleaned with organic solvents.

SRs (N= 4; 3 replicates) were extracted with 30 mL of a DCM:HEX mixture (2:1; v:v) using ultrasound-assisted extraction (Elmasonic®, Germany) in three 20-min extraction cycles. The resulting solution was transferred to round bottom flasks, concentrated in a rotary vacuum evaporator (Büchi®, Switzerland), and transferred to vials. The extracts were evaporated under a gentle stream of nitrogen to 500 µL and TPP-d_{15} was added as intern standard (final concentration: 100 ng mL^{-1}). SRs extraction tests recovery rates for all target substances ranged from 45.1% to 149%. To assess possible laboratory contamination, procedural blanks (clean SR) were analyzed using the same analytical procedure as the real samples. In the blank samples values lower than the method limit of detection (MDL) were detected except for OTNE for which up to 12.2 ng g^{-1} was measured.

Capillary gas chromatography separation of analytes was performed on a Bruker 456-GC (EUA) using a Rxi-5Sil MS column (30 m × 0.25 mm i.d. × 0.25 µm film thickness consisting of 5% diphenyl and 95% polydimethylsiloxane), keeping the helium carrier gas flow at 1 mL min^{-1} and the injection port temperature at 320 °C. The column temperature ramp was as follows: 70 °C for 3.5 min, increased by 25 °C min^{-1} to 180 °C, then by 5 °C min^{-1} to 320 °C, and held for 5 min. Atmospheric Pressure Gas Chromatography Time-of-flight mass spectrometry (APGC-Tof-MS) Bruker IMPACT II (EUA) was used for the identification and quantification of analytes. Data were processed using Bruker's TASQ 2.0 software. Identification and quantification of target compounds were based on comparing retention times, transitions, and ion ratios for each analyte to those of commercially available standards. Quantification was performed using calibration curves (from 1 to 400 ng mL^{-1}, 7 curve points, $r^2 > 0.99$), prepared in acetonitrile.

The recovery of internal standard (IS) ranged from 78.3 to 108 %. Instrument limit of detection and method limit of detection (mLOD) were calculated according to signal to noise (S/N; Table S2 of Supplemental Material B). iLOD was calculated based on the S/N of the lowest value of the calibration curve, adjusting this value to when the S/N was equal to 3. The mLOD was obtained from the value found for the iLOD adjusted by the pre-concentration of the sample and its recovery for silicone rubber or water. iLOD ranged between 0.001 (HHCB) to 4,41 (benz[b+k]Fluoranthene) µg L^{-1} and mLOD ranged between 0.0001 (HHCB) to 0.0031 (benz[g,h,i]perylene) µg L^{-1}.

3.2.6. Data analysis and risk assessment

Principal component analysis (PCA) was used to assess similarities between the total concentrations of different classes of contaminants (e.g., PAHs, PCBs, pesticides, UV filters, fragrances) and the physicochemical properties (air and water temperature, rainfall, etc). The software OriginPro 2024 was used for the PCA.

Additionally, a risk assessment was performed for target compounds with available ecotoxicological data on marine species. Measured environmental concentrations (MEC) were derived from the data presented in this study, whereas the predicted no-effect concentrations (PNEC) were obtained from the literature (Table S3, Supplemental Material). In cases where PNEC values were unavailable, they were estimated by adjusting toxicity data from acute and chronic experiments using an assessment factor (Pintado-Herrera *et al.*, 2017). An assessment factor of 1000 was applied for acute toxicity data, such as median effective concentration (EC50) or the concentration lethal to half of the test animals (LC_{50}), while a factor of 100 was used for chronic toxicity data, like the no observed effect concentration (NOEC). Hazard quotients (HQ) were calculated based on both MEC and PNEC values, according to equation 3.7.

$$HQ = {}^{MEC}/_{PNEC} \qquad \text{Equation (3.7)}$$

HQ values were then used for risk assessment followed an established framework (Kroon *et al.*, 2020; Pintado-Herrera *et al.*, 2017; Sánchez-Avila *et al.*, 2009): $HQ < 1$ = no significant risk, $1 \leq HQ < 10$ = small potential effects, $10 \leq HQ < 100$ = significant potential adverse effects, and $HQ \geq 100$ = adverse effects.

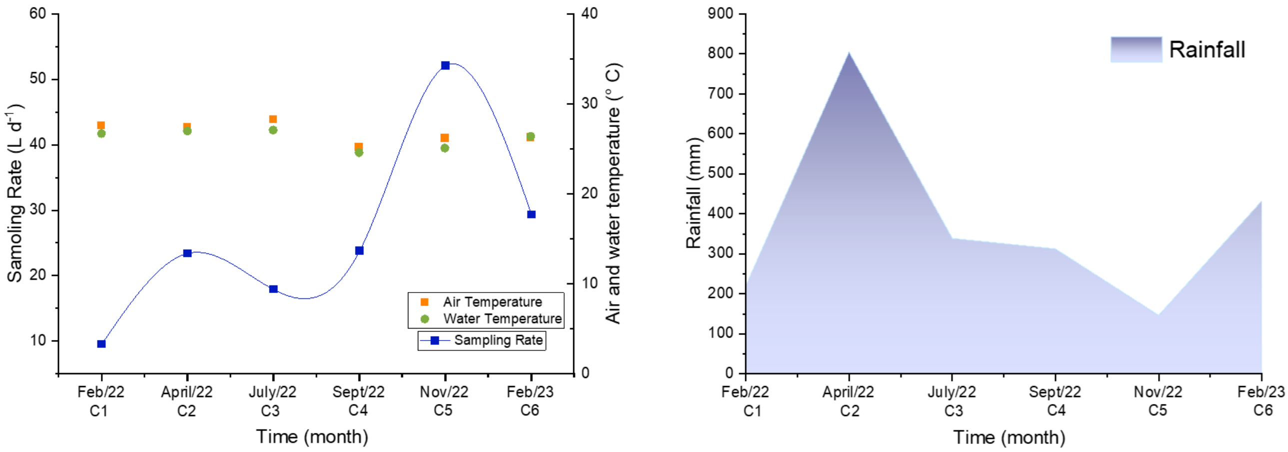
3.3. RESULTS AND DISCUSSION

3.3.1. Sampling rates of emerging and legacy contaminants for silicone rubber exposures

The dissipation of PRCs (Figure S1 of Supplemental Material B) with log K_{PW} values between 2.85 and 5.03 was observed over six sampling periods during one year of exposure. These values were taken into account when calculating the freely dissolved concentrations of all analyzed compounds. Dissipation of d_8-naphtalene was complete, leaving no traces in the samplers after the entire exposure period. The remaining masses of d_{10}-acenaphtene ranged from 0.04 to 1.07 % for periods C2 and C6, respectively. Similarly, d_{10}-phenantrene dissipate entirely during period C2, with residual compound contents varying from 0.23 to 0.75 % in extracted samples during periods C1 and C4, respectively. The compound d_{12}-perylene exhibited the highest preservation in silicone rubber, with residual compound contents ranging between 1.28 and 41.1 %, during periods C5 and C1, respectively.

Based on the dissipation of PRCs, R_S for all campaigns were calculated (Figure 3.3). The first sampling period (C1) presented the lowest R_S value (9.50 L d^{-1}), followed by C3, which was nearly twice as high (17.9 L d^{-1}). The highest R_S values were observed during periods C5 and C6 (29.3 and 52.1 L d^{-1}, respectively), despite these periods having the lowest rainfall accumulation (Figure 3.3). The difference between the campaigns may be attributed to variations in water turbulence during the sampling periods. In stagnant water conditions, the water boundary layer tends to be thicker, resulting in slower uptake and consequently lower sampling rate. Conversely, increased water movement results in a thinner water boundary layer, facilitating faster uptake and higher sampling rates (Smedes; Bakker; de Weert, 2010).

Figure 3.3. Estimated sampling rate (R_S), air temperature, water temperature, and rainfall in deployment of silicone rubbers, and in a year of passive sampling monitoring.



3.3.2. Compounds of Emerging Concern environmental behavior: Fragrances and UV Filters

Analyzed fragrances (tonalide, celestolide, galaxolide, and cashmeran) ranged from 1.09 (ADBI) to 303 (HHCB) pg L^{-1}, while UV filters (BP3, OCT, 2OHBP, 4MBC, EHS, HMS, EHMC) varied from 3.55 (2OHBP) to 4,051 (EHS) pg L^{-1} (Table 3.1). Individual concentrations of CECs can be found in Table S4, Supplementary Material B. Results obtained for fragrances and UV filters were relatively low when compared to those found in other bays. For instance, dissolved concentrations of fragrances in Todos os Santos Bay (TSB) were approximately a thousand times lower in comparison to Coombe Bay, United Kingdom (2,000 pg L^{-1}; Sumner et al. 2010) and Cadiz Bay, Spain (7,450 pg L^{-1}; Pintado-Herrera et al. 2020). A similar trend is observed for UV filters. Dissolved concentrations of BP3 were up to 30 times lower in this study (1,31 pg L^{-1}, mean) when compared to Chesapeake Bay, USA (31,100 pg L^{-1}; He et al. 2019). To the best of our knowledge, no other studies have reported dissolved concentrations of CECs in tropical coastal waters so far, thereby complicating comparisons under similar environmental conditions. Factors as high water recirculation dynamics in TSB (Lessa *et al.*, 2001), lower inputs of contaminants, and potential higher rates of evaporation and/or degradation in tropical conditions could contribute to the low concentrations of CECs observed in this study (Guo *et al.*, 2023; Wania; Mackay, 1996). However, further investigation is warranted to fully understand the influence of these factors.

Table 3.1. Minimum, maximum, mean, and standard deviation of freely dissolved concentration in a year of sampling (pg L^{-1}) for fragrances and UV filters.

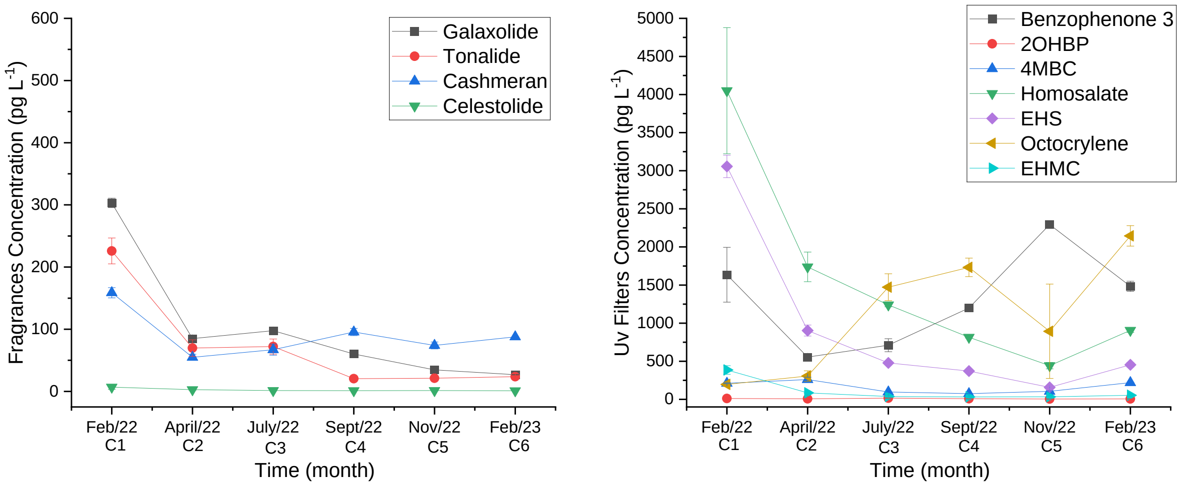
Compounds freely concentrations (pg L^{-1})

Fragrances	**AHTN**	**ADBI**	**HHCB**	**DPMI**
min	20.6	1.09	26.8	54.9
max	226	6.90	303	159
mean	72.2	2.43	101	89.7
SD	72.2	2.07	93.7	33.6

UV Filters	**BP3**	**OCT**	**2OHBP**	**4MBC**	**HMS**	**EHS**	**EHMC**
min	554	197	3.55	74.4	442	157	31.4
max	2294	2145	15.4	260	4051	3057	386
mean	1313	1124	8.35	161	1532	903	104
SD	584.0	721	3.94	71.3	1195	988	127

Figure 3.4 illustrates the variations in concentrations of fragrances and UV filters across different sampling periods. Both groups exhibit higher concentrations in the first sampling period (C1), covering December 2021 to February 2022. This trend could be attributed to the lower R_S during this period (9.5 L d^{-1}), resulting in reduced turbulence in the environment and slower dissipation of the compounds. Additionally, this observation may be associated to the first summer in the southern hemisphere following the end of the restraining measures related to the SARS-CoV-2 pandemic, followed by the increase in the number of bathers in coastal regions (Ferreira, 2021).

Figure 3.4. Freely dissolved concentrations of fragrances and UV filters variation in pg L^{-1}.



Among the fragrances, galaxolide consistently shows higher concentrations throughout the year, ranging from 26.8 to 303 pg L^{-1}, closely followed by tonalide and cashmeran, which ranged from 20.6 to 226 and 54.9 to 159 pg L^{-1}, respectively. Galaxolide and tonalide are among the most widely used fragrances in cosmetics and household cleaning products (Sommer, 2004) due to its strong fixation and stability. Their widespread use has led to increased production globally, with the European Union estimating production volumes between 1,000 and 10,000 tons for per year galaxolide (REACH, 2011) and 358 tons per year for tonalide (First evidences of the occurrence of polycyclic synthetic musk fragrances in surface water systems in Italy: Spatial and temporal trends in the Molgora River (Lombardia Region, Northern Italy)Villa *et al.*, 2012a). In the United States, the estimated volumes of galaxolide were between 450 and 4,500 tons per year (US EPA, 2016). However, tonalide photochemical degradation in surface waters appears to be much faster (half-life ≈4 h) than galaxolide degradation (half-life ≈135; Buerge *et al.*, 2003), which could explain the higher concentrations of HHCB in the environment. Conversely, celestolide exhibits lower concentrations ranging between 1.09 and 6.90 pg L^{-1} throughout the year. This observation may be attributed to the low K_{PW} of this compound, which gives it a greater preference for the aqueous phase comparing to the other fragrances.

The UV filters exhibited a similar pattern to the fragrances, with some compounds, notably HMS, EHS, and BP3, showing higher concentrations in the first and second sampling periods (C1 and C2, Figure 4). EHS and HMS are compounds with high K_{PW} values (5.80 and 5.85 respectively), unlike BP3 (4.47), but the results suggest a similar persistence behavior in the environment. Over the course of the year, BP3 and OCT were the predominant compounds, ranging from 554 to 2,294 pg L^{-1} and 197 to 2,145 pg L^{-1}, respectively. These compounds are widely used in personal care products, such as sunscreens and lotions, but also in applications such as paints, plastics to increase useful life, etc. OCT accounted for 35% of the Sweden market of sunscreen formulations in 2001 (Moeder *et al.*, 2010) and BP3 was present in 96.8 % of urine samples in the general U.S. population during 2003-2004 (Calafat *et al.*, 2008), showing the comprehensive way in which these compounds are highly available to the environment. Once in the environment, physical and chemical properties of each compound seem to have an influence on its environmental fate. These compounds have considerably different K_{OW}, (BP3 - 3.79 and OCT - 7.53) but similar K_{PW} for this silicone brand (4BP3 - 4.47 and OCT - 4.96; J-flex silicone rubber). This suggests that, despite differences in overall lipophilicity, both compounds have a relatively similar affinity for silicone compared to water, at least in the case of J-flex silicone.

Finally, the region where the PSDs were deployed is near a sewage treatment plant. Alongside recreational activities, such as bathing, swimming, and diving, these plants represent one of the main sources of CECs in aquatic systems (Blasco *et al.*, 2020; Burns *et al.*, 2021; Villa *et al.*, 2012b).

3.3.3. Environmental behavior and sources of PAHs, PCBs, and organochlorine pesticides

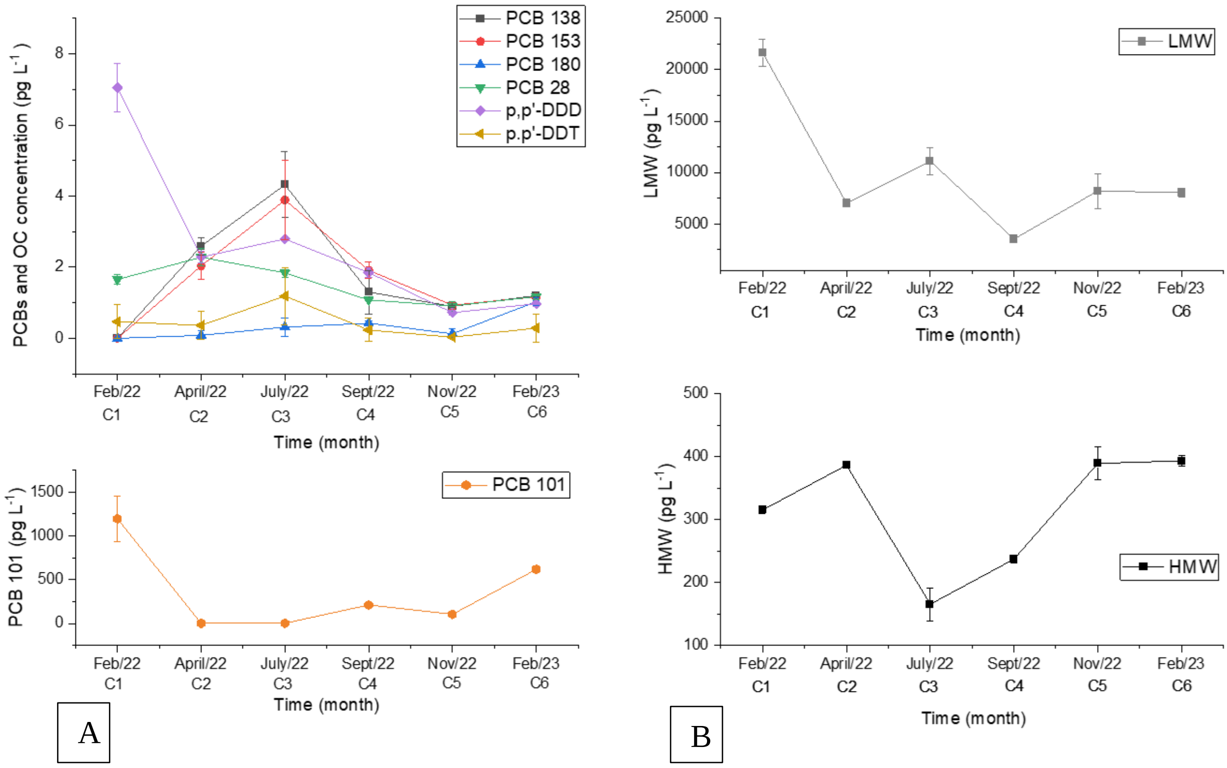
The total amount of quantified PCBs (PCB 28, PCB 101, PCB 138, PCB 153, and PCB 180) varied from 9.39 to 1197 pg L^{-1}. p,p'-DDD and p,p'DDT ranged between 0.72 to 7.05 and <MDL to 0.64 pg L^{-1}, respectively (Figure 3.2). Organochlorine compounds (PCBs and DDTs) were detected at relatively low concentrations, showing a similar range of concentrations across sampling periods.

Table 3.2. Minimum, maximum, mean, standard deviation and sum of freely dissolved concentration of 6 sampling campaigns (pg L^{-1}) for PAHs and OCs.

	Compounds freely concentrations (pg L^{-1})					
Campaigns	**1**	**2**	**3**	**4**	**5**	**6**
Polycyclic Aromatic Hydrocarbons						
min	10.5	1.99	1.63	2.77	1.62	4.32
max	12158	2412	4816	1176	3106	2867
mean	1690	569	868	289	661	647
sd	2260	607	1128	268	681	644
∑PAHs	21975	7393	11286	3759	8598	8410
∑HMW	21659	7005	11118	3524	8211	8034
∑LMW	315	386	165	237	389	393
ANT/(ANT+PHE)	0.06	0.18	0.09	0.38	0.14	0.40
FLU/(FLU+PYR)	0.52	0.60	0.69	0.66	0.66	0.59
BaA/(BaA+CHR)	0.16	0.12	0.15	0.10	0.13	0.13
IND/(IND+B[g,h,i]P)	0.44	0.49	0.43	0.68	0.59	0.59
∑LMW/∑HMW	0.01	0.06	0.01	0.07	0.05	0.05
Organochlorine compounds						
min	<MDL	0.08	0.32	<MDL	0.032	0.29
max	1195	2.59	4.32	211	106	618
mean	172	1.72	2.41	31.1	15.6	89.1
sd	292	0.85	1.269	51.5	25.7	151
∑OCs	1204	12.0	16.9	218	109	624

Higher concentrations were detected during the coldest period, specifically during C3 ($\sum_{OC}$=17.4 pg L^{-1}). The variation of OCs is presented in Figure 3.5 (A). As it has a boatyard, the nautical club carries out various repair and maintenance activities on watercraft. Among the PCB congeners, PCB 101 was the most prevalent, with concentrations up to 100 times higher than the others listed. Similar results were found in Daya Bay, China (Zhou *et al.*, 2001), where the probable sources included runoffs, wastewater, and sewage discharges. Important to note that, apart from PCB 28, this compound has the lowest K_{PW} value and has more marked hydrophobic characteristics than the other compounds.

Figure 3.5. (A) Variation of total dissolved concentrations of PCBs in pg L^{-1}. (B) Variation of low and high molecular weight polycyclic aromatic hydrocarbons year-variation in ng L^{-1}.



While p,p'-DDD was ubiquos throughout all sampling periods, p,p'-DDT was only detected in two campaings (C1 and C3). It's worth noting that production and use of p,p'-DDT has been banned around the world since the 1970s (Curtis; Lines, 2000), while DDD is a metabolite of DDT under anaerobic conditions (Connor *et al.*, 2007). Finding higher dissolved concentrations of this metabolite compared to the priority compound indicates that this substance is already entering the environment in its metabolized form.

The sum of the PAHs analyzed (acenaphthene, acenaphthylene, fluorene, anthracene, phenanthrene, pyrene, fluoranthene, perylene, chrysene, benz[a]anthracene, benzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene, and benz[b+k]fluoranthene; naphthalene data was excluded because it was a significant outlier; Grubb's test, $\alpha = 0.05$, $p < 0.05$) ranged from 3,759 (C4) to 21,975 (C1) pg L^{-1}, with the low molecular weight (LMW) and high molecular weight (HMW) PAHs ranged between 165 (C3) to 393 (C6) and 3,524 (C4) to 21,659 (C1) pg L^{-1}, respectively (Table 3.2). These results show an increase in the contamination of surface waters in the TSB, since the background concentrations of total PAHs in the region ranged from 3 to 110 pg L^{-1} (Celino *et al.*, 2010).

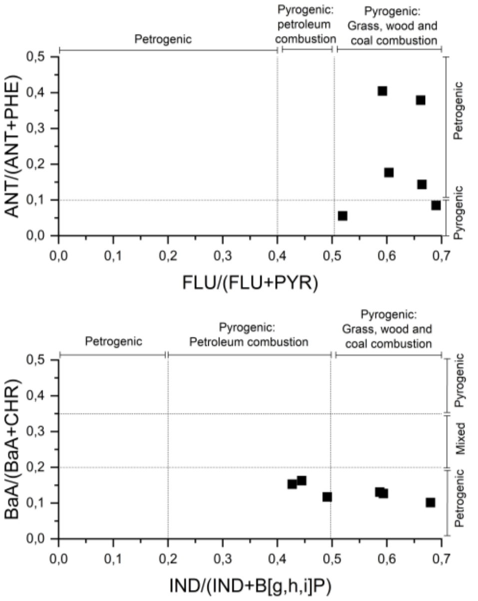
Among the compounds analyzed, PAHs consistently exhibited the highest values throughout the year, reinforcing their legacy and environmental concern. In contrast to organochlorines, PAHs are not produced intentionally by humans and their production has not been banned. These higher concentrations are largely related to the greater diversity of sources and the constant input of pollutants.

There is a higher dissolved concentration of low molecular weight (LMW) PAHs than high molecular weight (HMW) PAHs. It is important to emphasize that HMW PAHs are more resistant to microbial degradation and photo-oxidation in the water column, and there is a tendency for these compounds to adsorb into suspended particulate matter due to their similar physicochemical characteristics (Cardoso; Dauner; Martins, 2016).

Along with these characteristics, the higher concentrations of LMW PAHs may also be related to the presence of petrogenic sources (such as small and medium-sized boats and leaching from the mainland), and pyrogenic sources, such as the burning of fossil fuels, which also explain the predominance of this class of PAHs. This same behavior was already observed in TSB in 2010, indicating that surface water received anthropogenic PAHs from different sources and their occurrence cannot always be related to a particular source (Celino *et al.*, 2010). In the colder months of the year, when there is a reduction in the movement of boats and ships, there is also a drop in the C_W of HMW PAHs, but mainly LMW PAHs.

To infer the origin and better understand the sources of PAHs, diagnostic ratios using isomer PAHs pairs were calculated. Ratios using benzo[a]anthracene (BaA), chrysene (CHR), anthracene (ANT), phenanthrene (PHE), indeno[1,2,3-cd]pyrene (IND) and benzo[g,h,i]perylene (B[g,h,i]P) were calculated (Yunker et al. (2002) and Chen and Chen (2011)) and the results are presented in Figure 3.6.

Figure 3.6. PAH isomer ratios calculated in the present study. Phenanthrene (PHE), anthracene (ANT), benzo[a]anthracene (BaA), chrysene (CHR), indene[1,2,3cd]pyrene (IND), benzo[ghi]perylene (B[g,h,i]P). End-member values were used as reported in Yunker et al. (2002) and Chen and Chen (2011).

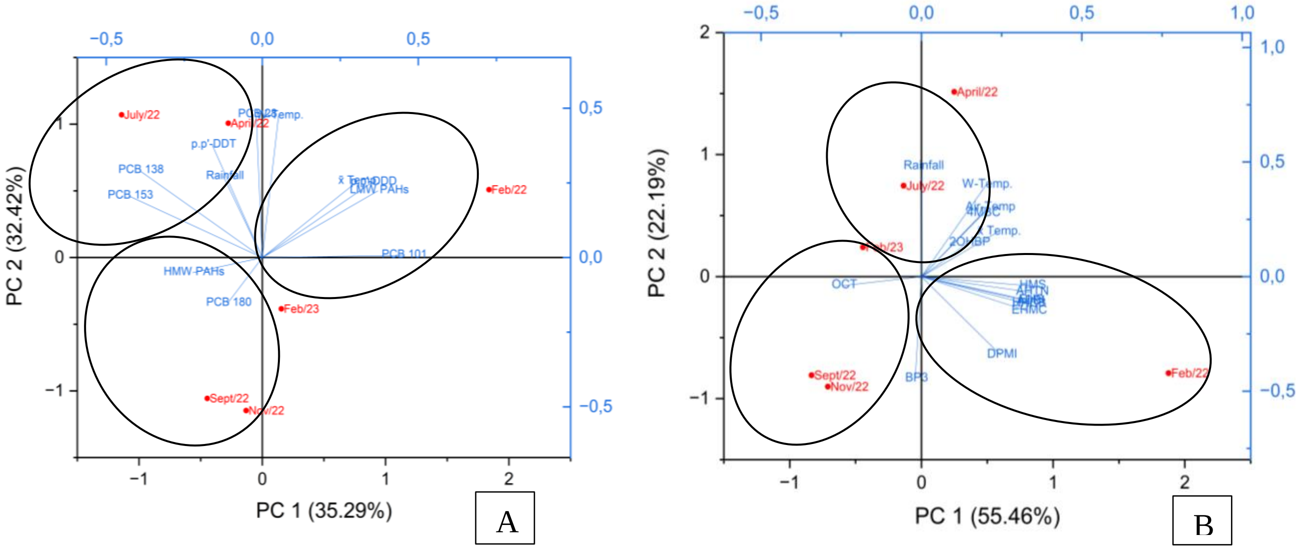


The ratios BaA/(BaA+CHR) and FLU/(FLU+PYR) point to single sources for these compounds, petrogenic and pyrogenic, respectively. The HMW/LMW ratio also indicates the pyrolytic origin for the PAH contaminants (Table 3.2). While the ANT/(ANT+PHE) and IND/(IND+B[g,h,i]P ratios point to mixed sources, which corroborates the various existing sources for that environment. So, given the flow of waterways in the region, the origin of the PAHs would be related to various sources, including the boat activities, burning of fuel, probable occasional oil spills, leaching and waste runoff.

3.3.4. Effect of seasonal variations, environmental variables, and correlations

Principal component analysis (PCA) was employed to identify relationships among the two groups of contaminants (legacy contaminants and CECs) and environmental variables (average air temperature, average water temperature and rainfall), allowing the recognition of similarities or differences among these variables. For legacy contaminants, PCA revealed two factors, explaining 67.71% (for PC1 and 32.42 % for PC2) of the total variation. Three distinct groups can be identified from the analysis. The first group shows a correlation between rainfall and average water temperature with the distribution of PCB 138, PCB 153, PCB 28, and p,p’-DDT, especially in April and July sampling (C2 and C3). Indeed, period C2 registered the highest rainfall accumulation of the year, which could potentially increase contaminant inputs through leaching processes. The second group is characterized by a correlation between HMW PAHs and PCB 180, a congener with a high degree of chlorination (seven chlorine atoms).

Figure 3.7 – Principal component analysis for rainfall, average air temperature, water temperature, legacy contaminants (A; low and high molecular weight polycyclic aromatic hydrocarbons, polychlororinated biphenyls 28, 101, 138, 153, 180 and p’,p-DDT and p’p-DDD) and those of emerging concern (B, Tonalide, Celestolide, Galaxolide, Cashmeran, Benzophenone 3, Octocrylene, 2OHBP, 4MBC, Homosalate, EHS, EHMC).



For CECs, two factors explained 77.65 % of the variation (55.46% for PC1 and 22.19 % for PC2; Figure 3.7 B), with three groups identified. The first group correlates rainfall and temperature with the UV filters 4-MBC and 2OHBP, particularly in April (C2) and July (C3). In contrast to PCBs, the lowest concentrations of these UV filters were detected during the period of higher rainfall accumulation, which can be partially explained by lower use of sunscreens in this period. Conversely, the second groups show correlations between the spring/summer campaigns (C4, C5, and C6) and the UV filters detected in higher concentrations in this study, namely OCT and BP3. The third group correlates all the fragrances and the UV filters, EHMC, and EHS in the first campaign (C1), exhibiting higher concentrations compared to the other campaigns. Commercial formulations (e.g., sunscreens, lotions, and cosmetics) usually comprise a blend of various active ingredients, including multiple UV filters combined with fragrances (Manová *et al.*, 2013). This combined use of these compounds might partially account for their correlation and elevated concentrations during the same period.

3.3.5. Potential risk of legacy and contaminants of emerging concern

The HQ values of individual compounds during all sampling campaigns ranged from 0.003 to 578,668 for the CECs and 0.003 to 119,504 for legacy contaminants (Table S6, Supplemental Material B). Nearly all UV filters presented a high potential risk of adverse effects (HQ > 100), except for 2OHBP. Conversely, the fragrances were associated with either non-significant risk (HQ < 1) or with minor potential effects (HQ < 10) except for cashmeran in C1, which posed a significant risk (10 ≤ HQ < 100).

Although concentrations of CECs in this study were not significantly high, certain UV filters have been linked to adverse effects on local ecosystems, particularly in tropical regions where UV filter consumption is higher (Downs *et al.*, 2014, 2016; He, Tangtian *et al.*, 2019). For instance, research by He *et al.*, (2023) has shown that a combination of the UV filters 4MBC, BP3, EHMC, EHS, OCT, among others, can negatively impact corals, fish, and sea snails, especially under elevated temperatures (30 ºC), resulting in coral bleaching and mortality. Similarly, environmental concentrations (2.28 to 228 µg L^{-1}) of BP3 have been associated with adverse effects on coral planulae mobility, mortality and coral bleaching rates (Downs *et al.*, 2016). Consequently, recent legislative actions have prohibited the use of compounds as BP3 and octinoxate in Hawaii, Key West and U.S. Virgin Islands due to their harmful effects on coral reefs (Bever, 2018; Fivenson *et al.*, 2021; Schneider; Lim, 2019). Given the potential risks associated with these compounds and the findings of this study, further research is necessary to comprehensively assess their impacts, particularly in tropical regions.

Regarding legacy contaminants, potential risk of adverse effects (HQ > 100) has been associated with ANT, B[a]P, and IND throughout the entire monitoring period and with PHE, PYR and FLT in C1. Overall, the remaining PAHs indicated potential risk of environmental impact (10 ≤ HQ < 100). PCBs 101, 128 and 153 demonstrated the potential to cause adverse effects (HQ > 100) in most of the sampling periods, while the other PCBs and DDTs presented low or insignificant risk (HQ < 1).

Compared to other studies, PAH freely concentrations reported by this study are similar to those detected in urbanized coastal regions (O’Hara, 2009; Schaanning; Harman; Staalstrøm, 2011). However, the dissolved fraction is an important indicator of what may be happening in the biotic and sedimentary fractions (Monteyne; Roose; Janssen, 2013). Significant freely concentrations will indicate higher ones in the compartments that contain greater physical and chemical similarities with lipophilic organic compounds. Owing to this behavior and the toxic characteristics of most PAHs, the concentrations found already indicate a significant effect on the biota. Studies have shown that negative effects were found in an exposure of the coral larvae *Acropora millepora* to six aromatic hydrocarbons individually (under high UV radiation, common in tropical regions), being more sensitive to anthracene and pyrene (Nordborg *et al.*, 2023). Therefore, even with a good knowledge of PAH behavior, it is important to emphasize the need to evaluate legacy compounds to assess environmental conditions and understand the risks associated with continuous inputs into the environment, especially in tropical regions.

3.4. Conclusion

The dissolved concentrations in the water were considered low, but this is worrying when associated with the low polarity of the contaminants analyzed. Legacy and emerging contaminants (PAHs, UV filters and fragrances) are influenced by temperature, with higher concentrations presents warmer months of the year. However, different sources of contamination were identified, depending on the chemical and the sampling site (e.g. boats and fuel burning for PAHs, recreational activities and wastewater discharges for fragrances, UV filters and pesticides). The results of a preliminary environmental risk assessment also indicated that specific compounds (mainly UV filters and PAHs) may pose a potential hazard to marine organisms, causing adverse biological effects. As this area is recognized as a marine park and considering the presence of corals and the region biodiversity, the results of the effects of the risks on the environment demand attention. It is therefore advisable to continue monitoring the region, with spatialization of sampling, in order to obtain robust data and come up with a strategy for mitigating contamination in the area.

Capítulo 4

ARTIGO 3

PERSONAL CARE PRODUCTS AND BIOMARKERS OF DETOXIFICATION AND OXIDATIVE STRESS IN BIVALVES: A SYSTEMATIC REVIEW OF LABORATORY STUDIES

Abstract

There is increasing concern about the presence and potential adverse effects of emerging contaminants, such as UV filters and synthetic musk fragrances, in aquatic ecosystems. However, there is a lack of information about the sublethal effects and ecological risks of these substances to non-target organisms. To better understand the mechanisms of these contaminants in bivalves, a systematic review of oxidative biomarkers was performed. Bivalves were chosen as the focus of this work because they can provide integrated information related to contamination by ecotoxicologically relevant substances over time. Bibliographic database searches resulted in 10 articles published between 2019 and 2022. The biomarkers superoxide dismutase, catalase, glutathione peroxidase, and glutathione reductase showed promising responses (increase or decrease) in the presence of the UV filters (oxybenzone, enzacamene, and octocrylene) and the fragrances (galaxolide and tonalide). Glutathione S-transferase showed the most significant increase in response to these compounds, making it the most promising biomarker. Our results indicate a limited number of studies on the toxicity of personal care products, highlighting the need for further research in this area.

Keywords: Personal care products, mollusks, oysters.

4.1. INTRODUCTION

4.1.1. Personal care products in the aquatic environment

Personal care products (PCPs), including disinfectants, fragrances, insect repellents, preservatives, and UV filters, are currently considered contaminants of emerging environmental concern or simply emerging contaminants (ECs) (EUROPEAN UNION, 2013; U.S. EPA, 2008). The daily use of these compounds results in their continuous introduction into aquatic systems. Thus, CECs have been increasingly detected in the environment, especially in rivers and groundwater, and wastewaters (Castiglioni *et al.*, 2018; Stuart *et al.*, 2012; Wilkinson *et al.*, 2017). Although the ecotoxicological response of most CECs are not yet fully known, recent studies indicate that even low environmental concentrations of some CECs can cause adverse on aquatic biota (Dodgen *et al.*, 2017; He, T. *et al.*, 2019; Jasinska *et al.*, 2015).

PCPs are synthetic chemical compounds that are widely used in everyday consumer goods such as cleaning products, cosmetics, hygiene products, lotions, and antiseptic products. Effluents discharges from residential and industrial wastewater treatment plants are the main sources of these compounds to the aquatic environment (Pintado-Herrera; González-Mazo; Lara-Martín, 2013; Xiao; Diaz-Rivera; Weavers, 2013). Additional sources of PCPs include agricultural application of contaminated biosolids and aquatic recreational activities, due to the leaching of substances applied to the skin (Boyd *et al.*, 2021; Picó; Barceló, 2015; Pintado-Herrera *et al.*, 2017).

The synthetic musk fragrances Galaxolide® (HHCB) and Tonalide® (AHNT) are commonly used in a wide range of hygienic and cosmetic products, such as perfumes, cleansing products, shampoos, moisturizing creams, and others (Clara *et al.*, 2011; Mu; Wen, 2013). Approximately 1,000 and 10,000 tons of HHCB and AHTN, respectively, are produced or imported per year in the European Union, representing about 95% of the market for all polycyclic musks (Aminot *et al.*, 2021; Santiago-Morales *et al.*, 2012). HHCB and AHTN are recognized as priority substances for environmental studies by the network of reference laboratories, research centers, and related organizations for monitoring emerging environmental substances (NORMAN-Network 2021). These contaminants are polycyclic, lipophilic compounds with octanol-water partition coefficients (log Kow) of 5.9 and 5.7, respectively (Ehiguese *et al.*, 2020). Additionally, HHCB is considered a high-priority contaminant due to its persistence and bioaccumulation potential (Howard; Muir, 2013; Mo *et al.*, 2019).

Organic UV filters are among the most widely used and produced PCPs in the world

(Santonocito *et al.*, 2020). UV filters are a heterogeneous group of organic compounds that are capable of absorbing UV radiation, such as oxybenzone (BP3), 4-methyl benzylidene camphor (4-MBC), octocrylene (OCR) and, octyl methoxycinnamate (EHMC). Due to their ability to protect the human skin against the harmful effects of exposure to UV radiation, these compounds are present in sunscreen formulations and various types of cosmetics such as hair sprays and lipsticks, being often used in tandem with fragrances (Brausch; Rand, 2011; Gago-Ferrero; Silvia Diaz-Cruz; Barcelo, 2013). Hygiene and cosmetic commercial products usually contain a mixture of different UV filters. A survey carried out in Switzerland showed that products such as sunscreens, lipsticks, makeup, and face creams could contain from 1 to 7 UV filters, with EHMC and OCR being the most frequently found (Manová *et al.*, 2013). Additionally, UV filters are also used in products materials as paints and plastics, providing protection against UV radiation and increased durability of the products.

Previous studies have reported potential adverse effects related to certain UV filters. For example, BP3 has been shown to affect the mobility of coral larvae and to increase the rate of coral bleaching (Downs *et al.*, 2016; He, T. *et al.*, 2019). Additionally, BP3 and 4-MBC have been found to have estrogenic effects, which can directly impact marine organisms and their reproduction (Brausch; Rand, 2011; Heneweer *et al.*, 2005; Sánchez Rodríguez; Rodrigo Sanz; Betancort Rodríguez, 2015). Furthermore, some UV filters, such as OCR, EHMC, and BP3, have demonstrated bioaccumulation and biomagnification potential (Brausch; Rand, 2011; Gago-Ferrero; Silvia Diaz-Cruz; Barcelo, 2013; Langford *et al.*, 2015; Picot Groz *et al.*, 2014).

Given the concern related to the fate of different groups of emerging contaminants in aquatic systems and their potential toxicity to non-target biota, it is important to evaluate the exposure of living organisms to these chemicals. In this sense, the use of biomarkers of exposure and effect can be a useful tool, since they can demonstrate the bioavailability of contaminants and potential adverse responses.

4.1.2. Oxidative stress biomarkers in bivalve organisms

Marine bivalves are considered sentinel organisms for monitoring pollutants in coastal environments due to their ability to bioaccumulate chemical contaminants in their soft tissues through both dermal and dietary routes. They are primarily filter-feeding organisms, which means that they ingest dissolved and particulate forms of different lipophilic contaminants (Cortez *et al.*, 2018). Additionally, they have low metabolic rates of xenobiotic products, which makes them more susceptible to bioaccumulation (Brooks *et al.*, 2009). As a result, bivalves can provide integrated information related to the contamination of ecotoxicologically relevant substances over time (Moschino; Delaney; Da Ros, 2012). Additionally, being sessile organisms, they can represent the contamination of the area where they were sampled (Earll; Evans, 1974).

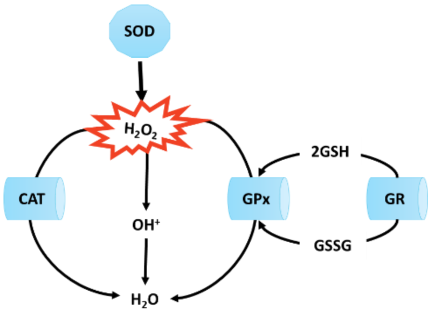
To assess contaminant bioavailability, bivalves have been used to analyze the concentrations of compounds in their tissues (Aguirre-Rubí *et al.*, 2019; Aminot *et al.*, 2021). Bioavailability can also be evaluated through the analysis of effect and exposure biomarkers, which allows for the establishment of a relationship between exposure to chemical agents and health effects in exposed individuals (Baussant *et al.*, 2011; Munari *et al.*, 2018). Although bioaccumulation of CECs by marine bivalves has been investigated in recent works (Aminot *et al.*, 2019, 2021; Di *et al.*, 2017; Gooding *et al.*, 2006; Maruya *et al.*, 2014; Picot Groz *et al.*, 2014).

To ensure survival, organisms have developed mechanisms to protect their cells in the presence of foreign compounds, such as excretion and biotransformation of xenobiotics (Trevisan *et al.*, 2016). These mechanisms can be used to assess the bioavailability of contaminants to bivalves and other organisms. Biomarkers of contamination are alterations at molecular, cellular, or physiological levels in response to the presence of a toxic compound (or a mixture of chemicals). Their response provides information about exposure and toxic effects of anthropogenic compounds (Depledge; Fossi, 1994), serving as an early warning and indicating the possibility of an environmental impact before it can be observed at more complex biological levels (Santana *et al.*, 2018).

One of the most significant biological responses in bivalves is oxidative stress, which can be experienced by all aerobic organisms when antioxidant defenses are overwhelmed by pro-oxidant forces (Di Giulio *et al.*, 1989). Hydroxyl radicals can react strongly with macromolecules, such as DNA and proteins, interfering with the lipids that make up the organism's cell membrane (Qian *et al.*, 2013). The production of these radicals occurs in electron transfer reactions during oxygen reduction metabolism, in the oxidative damage process (Hon-Wing; Vang; Mavis, 1981). To protect against this damage, there are several antioxidant enzymes present in the body, such as superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (GPx), and glutathione reductase (GR), as well as free radical scavengers (Cheung *et al.*, 2001). Changes and activities in these enzymes can result in biological responses of these organisms to the toxicity of bioavailable contaminants in the aquatic environment (Dalzochio *et al.*, 2016).

SOD, GPx, GR, and CAT converts superoxide radicals and hydrogen peroxide into less reactive species. SOD catalyzes the dismutation of superoxide radicals to hydrogen peroxide (H_2O_2) (Figure 1). Despite H2O2 is not a radical, it is quickly converted to a highly reactive OH+ radical by the Fenton reaction. GPx neutralizes hydrogen peroxide by extracting hydrogen from two GSH molecules, producing two H2Os and one GSSG. GR then regenerates GSH from GSSG and then, CAT neutralizes H_2O_2 into H_2O (Pandey; Rizvi, 2010).

Figure 4.1. Enzymatic antioxidant defense system. Superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (GPx), glutathione reductase (GR), oxidized glutathione (GSSG), and glutathione (GSH).



The dangerous effects of oxygen contain a lack of cellular functionality resulting from reactive species-triggered oxidation of macromolecules. Oxygen free radicals, which can be predominately, but not completely, derived from oxidative metabolism, are chargeable for this oxidation (Costantini *et al.*, 2010).

4.1.3. Systematic review motivation

Studies related to biomarkers of exposure to fragrances and UV filters in aquatic organisms date back to the early 2000s (Luckenbach; Epel, 2005). However, laboratory evaluations in controlled systems are needed to verify the behavior of organisms against these specific contaminants. Laboratory studies in controlled systems can bring important insights to the field of ecotoxicology (Binelli *et al.*, 2015; Bordalo *et al.*, 2020; Ehiguese *et al.*, 2020; Falfushynska *et al.*, 2021; Lopes *et al.*, 2020; O'Donovan *et al.*, 2020; Rilievo *et al.*, 2021; Santonocito *et al.*, 2020).

Different species can exhibit distinct biomarker response (Collins; Peck; Clark, 2021; Pérez; Blasco; Solé, 2004; Velki; Hackenberger, 2012). Similarly, different groups of CECs, such as UV filters and fragrances, may impact the biochemical structures of bivalve organisms in different ways, as observed in other groups of contaminants (Fonseca *et al.*, 2011). However, an overview conducted within the same taxonomic class can synthesize information and evaluate the behavior of these organisms in the face of this type of contamination. Thus, a systematic review could help answer basic questions about ecotoxicological studies of fragrances and UV filters, understand biomarker response patterns, and identify possible sources of variation, such as experimental approach types, exposure time, and analyte concentrations. In addition, these results may provide support for future experimental design protocols by giving a better understanding of the oxidative stress in these organisms caused by this class of contaminants. Therefore, it is important to report and compile observations on the bioavailability of pollutants and potential negative effects that exposure may have, and biomarkers of exposure and effect are excellent tools for obtaining this data.

4.2. Methodology

4.2.1. Research strategy and inclusion criteria

An extensive search was conducted in five online databases (ScienceDirect, Web of Science, Scopus, PubMed, and Springer) for papers regarding the evaluation of oxidative stress biomarkers in bivalve organisms, with no date limitations, until December 2023. The search was extended to all these databases in order to exclude most of the gaps that might exist in each database. Search strategies described below were applied to all databases, in an attempt to include all the compounds and biomarkers used by the researchers, and then cross-checked against each other, resulting in a final set of 289 publications. The used surveys were:

Survey 1: *(“biomarker*” or “oxidative stress”) and (“emerging contaminant” or “tonalide” or “galaxolide” or “EHMC” or “octocrylene” or “BP3” or “4MBC”) and (“oyster*” or “mollusk*” or “bivalve*” or “mussel”)*

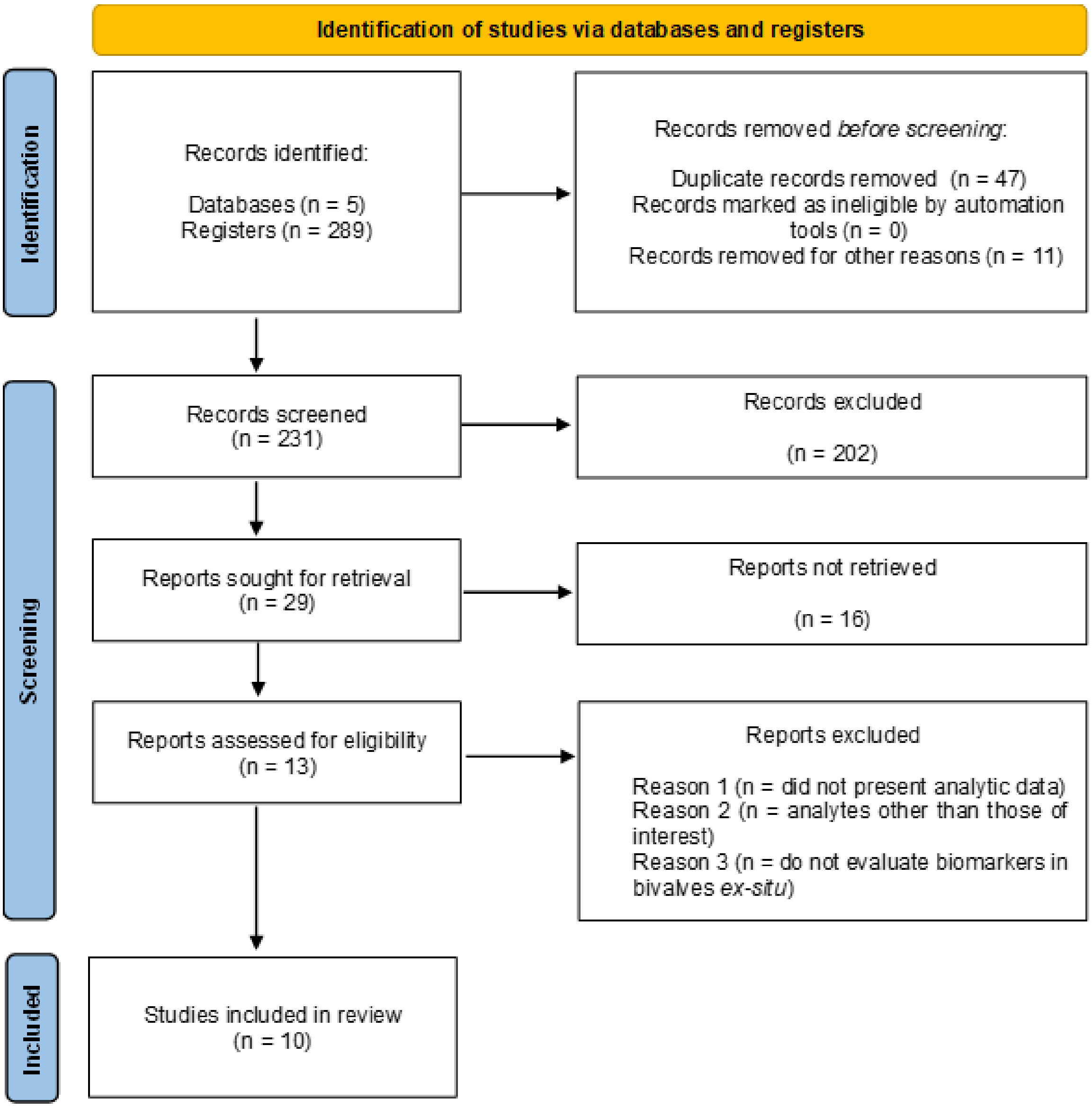
Survey 2: *(“biomarker” or “oxidative stress”) and (“emerging contaminant*” or “AHTN” or “HHCB” or “octyl methoxycinnamate” or “BP3” or “4MBC” or “benzophenone”) and (“oyster*” or “mollusk*” or “bivalve*” or “mussel”)*

Survey 3: *(“cellular damage”) and (“emerging contaminant” or “tonalide” or “galaxolide” or “EHMC” or “octocrylene” or “BP3”) and (“oyster*” or “mollusk*” or “bivalve*” or “mussel”)*

Survey 4: *("cellular damage") and ("emerging contaminant*" or "AHTN" or "HHCB" or "octyl methoxycinnamate" or "BP3" or "4-MBC" or "benzophenone") and ("oyster*" or "mollusk*" or "bivalve*" or "mussel")*

The references were analyzed using the StART® software, developed by the Software Engineering Research Laboratory (LaPES) of the Computer Department of the Federal University of São Carlos (DC/UFSCAR). In this software, the references were overlapped, and duplicates were identified. Then, references were evaluated regarding title, and abstract, and classified regarding inclusion status (accepted, rejected, or duplicate), priority (very high, high, low, very low), and score (delimited according to the frequency of the keywords in the title and abstract). In this evaluation, studies that did not contain the objects of study (bivalves, contaminants of interest, or subject of interest) were rejected. The references that obtained relevant keywords, presented data clearly, and worked with the predetermined analytes and phylum were chosen for further selection of pertinent studies. The following criteria were established for the inclusion of a study: (i) adherence to the research topic, (ii) availability of extractable data (*e.g.*, graphs, tables), and (iii) if the experiment was conducted under controlled conditions. These steps are summarized in Figure 4.2 (new PRISMA Flowchart, according to Page et al., 2021).

Figure 4.2 - The screening process used to reject or accept articles for meta-analysis; summarized and formatted as a PRISMA flow chart.



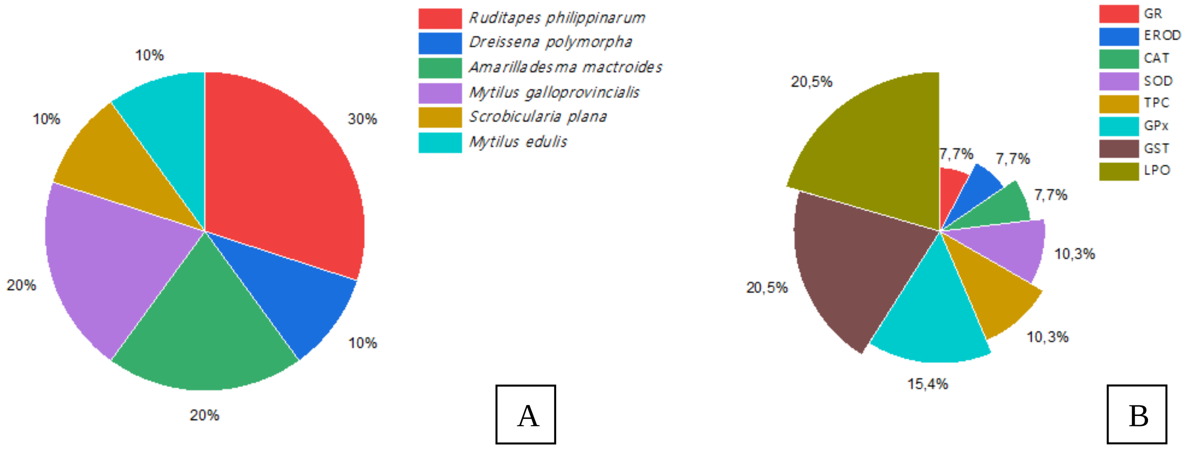
Finally, the selected articles (n = 10) were organized according to the authors, year of publication, country, continent, journal in which the paper was published, species, target compound, route of exposure, experimental conditions, compound dose, duration of the experiment, sample mass, pool of organisms used, tissue analyzed, and the biomarkers evaluated in each study. These data can be found in the Supplementary Material C (Table S1). The means, standard deviations, and sample size of each study were obtained from the texts, figures and tables provided in the articles. WebPlotDigitizer (version 4.5, 2022) was used to extract data from graphs.

4.3. Results and discussion

4.3.1. Database and general effects

The selected studies in this work that evaluate biomarkers in bivalves through the examination of selected PCPs were conducted as lab tests (as shown in Table 1). The species *Ruditapes philippinarum* was most commonly used as a biomonitor in these studies, with 3 studies utilizing it. This species has been recognized as a good biomonitor for coastal pollution assessments and environmental toxicology due to its widespread distribution, long life cycle, high tolerance to variations in salinity and temperature, ease of collection, and high capacity for bioaccumulation of contaminants (as cited in Park et al. 2006; Zhang et al. 2011). Other species that were also used in these studies include *Dreissena polymorpha* (1 study), *Amarilladesma mactroides* (2 studies), *Mytilus galloprovincialis* (2 studies), *Scrobicularia plana* (1 study), and *Mytilus edulis* (1 study). These species are also filter feeders and are widely used as sentinel organisms in contamination studies (Baussant *et al.*, 2001; Binelli; Riva; Provini, 2007; Fernández *et al.*, 2010; Joubert *et al.*, 2013; Lopes *et al.*, 2020) (Figure 4.3 A).

Figure 4.3. Distribution of species assayed (A) and biomarkers evaluated (B) in the selected studies.



The enzymatic biomarkers: ethoxyresorufin-O-deethylase (EROD, 3 studies) catalase (CAT, 3 studies), glutathione peroxidase (GPx, 6 studies), glutathione reductase (GR, 3 studies), superoxide dismutase (SOD, 4 studies) and glutathione-S-Transferase (GST, 8 studies); and oxidative damage biomarkers: lipid peroxidation (LPO, 8 studies) and protein carbonyl content (TPC 4 studies), were quantified and documented in the selected studies (Figure 4.3 B).

Table 4.1 - Identification of increased and decreased responses of oxidative stress biomarkers, induced by contamination by emerging contaminants (galaxolide, HHCB; tonalide, AHTN; oxybenzone - BP3, enzacamene - 4-MBC and, octocrylene - OCR), which obtained significant difference compared to the control experiment. NR = No response. SR (+) = with stimulation response. SR (-) = with suppression response. Lipid peroxidation – LPO; protein carbonyl content – TPC; Catalase – CAT; glutathione - GSH; glutathione peroxidase – GPx; glutathione reductase – GR; superoxide dismutase - SOD; glutathione-S-Transferase – GST; Ethoxyresorufin-O-deethylase - EROD. ^{1}Concentration at pH 8.1, ^{2}Concentration at pH 7.6, ^{3}Concentration adsorbed on microplastic (ng g^{-1}). ^{4} In 20º C condition. ^{5} In 24º C condition. ^{6} In bivalve's sperm.

					OXIDATIVE STRESS/DETOXIFICATION BIOMARKERS								
AUTHORS	**COMPOUND**	**SPECIES**	**EXPOSURE TIME**	**EXPOSURE CONCENTRATION ($\mu g\ L^{-1}$)**	**LPO**	**TPC**	**CAT**	**GSH**	**GPx**	**GST**	**GR**	**SOD**	**EROD**
(Parolini *et al.*, 2015)	HHCB	*Dreissena polymorpha*	18	0.1	NR	NR	-	-	-	-	-	-	-
				0.5	SR (+)	SR (+)	-	-	-	-	-	-	-
	AHTN			0.02	NR	NR	-	-	-	-	-	-	-
				0.08	NR	SR (+)	-	-	-	-	-	-	-
(Ehiguese *et al.*, 2020)	HHCB	*Ruditapes philippinarum*	21	0.005	SR (+)	-	-	-	SR (+)	SR (+)	SR (-)	-	SR (+)
				0.05	SR (+)	-	-	-	SR (+)	SR (+)	SR (-)	-	SR (+)
				0.5	SR (+)	-	-	-	SR (+)	SR (+)	SR (-)	-	SR (+)
				5	SR (+)	-	-	-	SR (+)	SR (+)	SR (-)	-	SR (+)
				50	SR (+)	-	-	-	SR (+)	SR (+)	SR (-)	-	SR (+)
	AHTN		21	0.005	SR (+)	-	-	-	NR	SR (+)	SR (-)	-	SR (+)
				0.05	SR (+)	-	-	-	SR (+)	SR (+)	SR (-)	-	SR (+)
				0.5	SR (+)	-	-	-	SR (+)	SR (+)	SR (-)	-	SR (+)
				5	SR (+)	-	-	-	NR	SR (+)	SR (-)	-	SR (+)
				50	SR (+)	-	-	-	NR	SR (+)	SR (-)	-	SR (+)
(Rilievo *et al.*, 2021)	HHCB	*Ruditapes philippinarum*	21	0.1	-	-	SR (+)	-	-	SR (+)	NR	SR (-)	-
				0.5	-	-	NR	-	-	SR (+)	NR	SR (-)	-
(Santonocito *et al.*, 2020)	4-MBC	*Ruditapes philippinarum*	7	1	-	-	NR	-	NR	SR (+)	-	NR	-
				10	-	-	NR	-	NR	SR (+)	-	NR	-

				100	-	-	SR (+)	-	NR	SR (+)	-	NR	-
(Lopes *et al.*, 2020)	BP3	*Amarilladesma mactroides*	4	1[1]	SR (-)	-	-	NR	-	SR (+)	-	-	-
				1[2]	NR	-	-	SR (+)	-	NR	-	-	-
(Bordalo *et al.*, 2020)	BP3	*Mytilus galloprovincialis*	4	0.01	SR (-)	NR	NR	-	NR	SR (-)	-	-	-
				0.1	NR	SR (+)	NR	-	NR	NR	-	-	-
				1	SR (+)	NR	NR	-	NR	NR	-	-	-
(O'Donovan *et al.*, 2020)	BP3	*Scrobicularia plana*	14	0.082[3]	SR (+)	-	-	-	SR (+)	-	-	SR (+)	-
(Falfushynska *et al.*, 2021)	OCR	*Mytilus edulis*	14	10	NR	NR	-	-	-	SR (+)	NR	-	NR
				100	NR	SR (+)	-	-	-	SR (+)	SR (-)	-	SR (-)
(Lopes *et al.*, 2022)	BP3	*Amarilladesma mactroides*	4	1[4]	SR (+)	-	-	SR (+)	SR (+)	NR	SR (+)	-	SR (-)
				1[5]	SR (+)	-	-	SR (-)	SR (-)	NR	SR (-)	-	SR (+)
(Cuccaro *et al.*, 2022)	4-MBC	*Mytilus galloprovincialis*	0.2[6]	100	SR (+)	-	-	-	-	-	-	-	-
				300	SR (+)	-	-	-	-	-	-	-	-
				600	SR (+)	-	-	-	-	-	-	-	-
			28	100	NR	SR (-)	-	-	NR	SR (+)	-	SR (-)	-
				300	NR	SR (-)	-	-	SR (+)	SR (+)	-	SR (-)	-
				600	NR	SR (-)	-	-	SR (+)	SR (+)	-	SR (-)	-

[1] Concentration at pH 8.1, [2] Concentration at pH 7.6, [3] Concentration adsorbed on microplastic (ng g^{-1}). [4] In 20º C condition. [5] In 24º C condition. [6] In bivalve's sperm.

7

4.3.2. Studies characteristics overview

Laboratory studies with bivalves have demonstrated that the selected CECs can significantly alter biomarker responses, particularly those related to biotransformation mechanisms in the organisms (Table 1). These studies have reported the responses on oxidative responses in the species *Dreissena polymorpha* and *Ruditapes philippinarum* following exposure to the fragrances HHCB and AHTN (Ehiguese *et al.*, 2020; Parolini *et al.*, 2015; Rilievo *et al.*, 2021). The biomarkers LPO, GPx, GST, and GR were found to respond significantly in these studies ($p < 0.01$), except for the lowest concentration of HHCB tested by Parolini et al., (2015) (0.1 µg L^{-1}). This exception contrasts with the results found by Ehiguese et al., (2020) for LPO, using *R. philippinarum*, where significant differences ($p < 0.01$) were detected when comparing a low concentration (5 ng L^{-1}) of HHCB to the control (absence of HHCB). This distinction may be related to the different habitats of the studied species, as *D. polymorpha* is a freshwater mollusk and *R. philippinarum* is a marine species.

The increase in GST response activity in *D. polymorpha* and *R. philippinarum* in all doses of HHCB tested are similar, making the behavior between these species comparable ($p < 0.05$). However, *R. philippinarum* exhibited a different behavior regarding GR activity in the studies by Rilievo et al., (2021) and did not show significant differences compared to the studies by Ehiguese et al., (2020) with the same species, despite testing similar concentrations of HHCB and the same exposure time (21 days). This distinct behavior (no significant response and activity suppression) may be associated with the different types of tissue analyzed in these studies (digestive glands and gills, respectively), as the potential of digestive gland analyses to access GR alterations has been previously reported (Choy *et al.*, 2007).

The influence of 4-MBC, BP3, and OCR on a cellular level was studied in a variety of bivalve species, including *Ruditapes philippinarum*, *Amarilladesma mactroides*, *Mytilus galloprovincialis*, *Scrobicularia plana*, and *Mytilus edulis* (Bordalo *et al.*, 2020; Cuccaro *et al.*, 2022; Falfushynska *et al.*, 2021; Lopes *et al.*, 2020, 2022; Santonocito *et al.*, 2020). The alterations mainly occurred in the biomarkers LPO, GST, and TPC, indicating that the specimens were experiencing oxidative stress and could suffer alterations in cellular membrane functions.

The biomarker responses presented variations among the species studied, indicating that they do not react in the same way to these bioavailable xenobiotics. For example, LPO activity was suppressed or unchanged for *Amarilladesma mactroides* and *Mytilus galloprovincialis* (except for 1 μg L^{-1} dose of BP-3), while it was stimulated for *Scrobicularia plana* following indirect exposure to BP-3 and *Mytilus edulis* following exposures of 10 to 100 μg L^{-1} of BP-3 and PBSA, respectively (as reported in Lopes et al., 2020; O'Donovan et al., 2020; Falfushynska et al., 2021). Another example is the reaction of GPx and SOD activities in *Ruditapes philippinarum* and *Mytilus galloprovincialis* when exposed to 4-MBC. *R. philippinarum* did not show any alterations in these activities, whereas *M. galloprovincialis* had these activities induced and suppressed, respectively (Cuccaro *et al.*, 2022; Santonocito *et al.*, 2020).

Another difference observed is in the type of tissue analyzed. Different approaches are used to determine biomarker responses in bivalves, using the digestive gland, gills, mantle, or whole soft tissue. Studies have reported that in bivalves, the most significant responses are found when analyzing the mantle and gills (Won et al. 2016; Abdou et al. 2020). In the aforementioned cases, only the analysis with *M. galloprovincialis* was performed using whole tissue. Comparing the results of exposure to 4-MBC between *R. philippinarum* and *M. galloprovincialis*, it is possible to assume they are similar at exposures of 100 μg L^{-1} (Bordalo *et al.*, 2020; Cuccaro *et al.*, 2022; Santonocito *et al.*, 2020).

Differences in pH, the presence of other substances, different temperatures, and distinct exposure approaches also influence the observed results. For example, low concentrations of BP-3 associated with microplastics allowed O'Donovan et al. (2020) to identify alterations in LPO, GPx, and SOD. Lopes et al., (2020) demonstrated that the alteration of biomarkers is influenced by acidification of the environment and may even decrease the biotransformation potential of bivalve organisms. Furthermore, Lopes et al. (2022) showed that higher temperatures allow for the suppression of the digestive gland's ability to react to the presence of BP-3.

Interactions between contaminants and environmental stressors can produce greater impacts than anticipated from either type of stress alone (Hooper *et al.*, 2013). The bioavailability of toxicants is affected by the physicochemical properties of the matrix, which means that different exposure scenarios might result in varied responses from the same overall environmental concentration of a toxicant (Holmstrup *et al.*, 2010). Therefore, changes in the environment, such as changes in pH, and associations with other substances, such as microplastics, directly influence the behavior of biomarkers, making it possible for substances, including emerging ones, to have a different impact on bivalves and potentially become more harmful to the organism.

4.3.3. Biomarkers behavior in bivalves exposed to fragrances and UV filters

Biomarkers showed different behaviors in response to CECs. In O'Donovan et al. (2020) and Rilievo et al. (2021), a significant increase in SOD activity was observed during the first exposure week, followed by a suppression of activity on the 14th day of exposure (when bivalves were exposed to BP-3 and HHCB, respectively). This indicates that the organisms began an oxidative stress process during the second week of exposure to the evaluated contaminants. This happens because the metalloenzyme SOD is the body's first defense against increased reactive oxygen species (ROS) by catalysing the superoxide radical reduction reaction, increasing H_2O_2 levels (Lushchak, 2011; Nayak *et al.*, 2022; Regoli; Benedetti; Giuliani, 2019). Thus, SOD activity levels can already present alterations after one week of exposure to BP-3.

In biomarker studies, CAT, when working in synergy with SOD, is one of the most sensitive antioxidant defenses against xenobiotics, increasing their activities significantly to contain ROS (Rilievo *et al.*, 2021). Although the response of CAT induction in bivalve mollusks is well described in the literature, in the selected studies, only Rilievo et al. (2021), Bordalo et al. (2020), and O'Donovan et al. (2020) have determined altered behavior of this antioxidant enzyme. Bordalo et al. (2020) found no change in activity during 96 hours of exposure to BP-3 at any dose (0.01, 0.1, and 1 µg L^{-1} of BP-3), as did Santonocito et al. (2020) for lower doses of 4-MBC (1 µg L^{-1}) over 10 days of exposure. On the other hand, Rilievo et al. (2021) identified a significant increase ($p < 0.001$) in CAT activity on the first 7 days of exposure to HHCB, showing that *Ruditapes philiphinarum* is sensitive to HHCB (0.1 and 0.5 µg L^{-1}) and 4-MBC (100 µg L^{-1}).

The GST, which can catalyze the glutathione reduced form (GSH) in xenobiotic substrates, play an important role in detoxifying the cell (Li *et al.*, 2021). Increased GST levels observed by Ehiguese et al. (2020) for HHCB and AHTN indicate the occurrence of biotransformation processes of these compounds in the cell through reduced GSH oxidation. Similarly, Falfushynska et al. (2021) detected a significant increase in GST activity for OCR (10 and 100 µg L^{-1}). This also happened in Cuccaro et al. (2022), wherein it was possible to observe the increase of GST activity (100, 300 and 600 µg L^{-1}). These findings suggest that these organisms (*Ruditapes philippinarum*, *Mytilus galloprovincialis*, and *Scrobicularia plana*) show relative sensitivity to GST activity for both fragrances and sunscreens.

The changes in the activity of GSH-related enzymes in bivalves exposed to BP-3 in Lopes et al. (2020), showed a significant increase in GSH activity during the exposure period of the contaminant ($p > 0.05$). Therefore, the increase or decrease of these enzymes can be considered a significant sign that the bivalve organism is under oxidative stress. Only Lopes et al. (2020)' study analyzed GSH activity, showing significant changes. This may represent the potential of the analysis of this biomarker in bivalves to analyze the response to contamination by UV filters and fragrances.

GPx, an antioxidant enzyme, produces hydrogen peroxide (H_2O_2) through the reaction of water (H_2O) and oxygen (O_2) when cells are under stress caused by contaminants (Ighodaro; Akinloye, 2018). This process causes GSH to be oxidized (Regoli; Benedetti; Giuliani, 2019). Changes in the activity of GSH-related enzymes in bivalves exposed to BP-3 suggested that the organisms were under oxidative stress (Lopes *et al.*, 2020).

Although it does not participate directly in neutralizing ROS, GR plays an important role in the organism's antioxidant defense. GR is considered an auxiliary oxidant enzyme, responsible for the GSH oxidized by GPx, maintaining the proper GSH concentrations in cells (van der Oost; Beyer; Vermeulen, 2003). The unexpected reduction in GR activity at all experimental doses in Ehiguese et al. (2020) for HHCB and AHTN, and in Lopes et al. (2020) in condition of 24º C for BP-3 may indicate that the altered response pattern of this biomarker may be a key mechanism for identifying damage caused by these compounds.

4.4 Conclusion

This review revealed that bivalves exhibit a significant cytotoxic reaction to synthetic musks AHTN (tonalide) and HHCB (galaxolide) and UV filters (oxybenzone - BP3, enzacamene - 4-MBC, and octocrylene - OCR). In general, the primary antioxidant defenses were recruited during the first week of the experiments. The biomarkers superoxide dismutase (SOD), catalase (CAT), and the glutathione group (peroxidase, reductase) show promising responses in alterations caused by the presence of fragrances and UV filters. The increase in GST activity at various contamination doses and exposure times for both UV filters and fragrances indicates that altered detoxifying enzyme activity is a common and sensitive response within this group of contaminants.

The available evidence suggests that the interactive effects of increased seawater temperatures and ocean acidification in combination with EC contamination can result in increased effects on aquatic biota. Despite this, the effects of predicted changes in environmental conditions on the toxicity and bioaccumulation of ECs in marine organisms are not fully understood. Given the increasing global consumption of chemical products and recent predictions of climate change, further research is needed to better understand the single and combined effects of widely used ECs and to identify appropriate biomarkers for these compounds.

Capítulo 5

CONCLUSÕES GERAIS

A tira de silicone J-Flex é um material eficaz para a análise ambiental de contaminantes em águas superficiais, demonstrando resultados consistentes e adequação para a detecção de compostos orgânicos com variação de K_{OW} entre 3,37 e 7,66.

A presença de contaminantes na água na Baía de Todos os Santos (Bahia, Brasil), mesmo em concentrações relativamente baixas, gera preocupações, especialmente em áreas com ecossistemas marinhos sensíveis, como parques marinhos. Recomenda-se o monitoramento contínuo, a espacialização da amostragem e o desenvolvimento de estratégias de mitigação para lidar com os possíveis riscos ambientais.

Os bivalves apresentam reações citotóxicas significativas a fragrâncias e filtros UV, com alterações nos mecanismos de defesa antioxidante e na atividade enzimática desintoxicante. Os efeitos interativos das mudanças ambientais, como o aumento da temperatura da água do mar e a acidificação dos oceanos, combinados com a exposição a contaminantes, destacam a necessidade de mais pesquisas para entender os efeitos dos contaminantes emergentes nos organismos e ecossistemas marinhos.

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MATERIAL SUPLEMENTAR A – ARTIGO 1

Table S1. Fortification scheme for silicone rubbers using methanol (Adapted from Booij et al., 2002).

Time	Volume MeOH	Added water volume	Total water volume	Water content	Step Time
(h)	(mL)	(mL)	(mL)	(% v/v)	(h)
0	100	0.00	0.00	0	0
24	100	12.3	12.3	11	24
48	100	12.7	25.0	20	24
72+	100	17.8	42.8	30	> 24
120+	100	23.8	66.7	40	> 48
168+	100	33.3	100	50	> 48

Table S2. Experimental setup for the determination of silicone rubber/water partition coefficient and dilution procedure for stir bar sorptive extraction (SBSE). w/w: percentage of methanol (MeOH) in the bottle.

	Experiment					**To extract with SBSE**		
No	**Volume (mL)**	**% w/w**	**MeOH Volume (L)**	**Water Volume (L)**	**Way of spike**	**Water add**	**Final Volume (L)**	**Final MeOH (%)**
1	2500	0	0	3	Aqueous Spike	0	2500	0
2	2000	0	0	2	Sheet Spike	0	2000	0
3	1700	9	153	1547	Sheet Spike	0	1700	9
4	1500	17	255	1245	Sheet Spike	1000	2500	10.2
5	800	24	192	608	Sheet Spike	1100	1900	10.1
6	350	30	105	245	Sheet Spike	700	1050	10
7	270	37	100	170	Sheet Spike	730	1000	10
8	360	43	155	205	Sheet Spike	1000	1360	10
9	200	50	100	100	Sheet Spike	1000	1200	10

Table S3. Recoveries (%) for the silicone rubber (SR) extraction and water extraction.

Compounds	SR extraction recovery (%)	Water extraction recovery (%)
Fragrancies		
Tetramethyl acetyloctahydronaphthalene (OTNE)	110	74.5
Phantolide (AHMI)	121	126
Tonalide (AHTN)	96.5	106
Celestolide (ADBI)	87.6	105
Galaxolide (HHCB)	103	106
Traseolide (ATII)	128	139
UV Filters		
Benzophenone-3 (BP3)	44.9	43.5
Avobenzone (ABZ)	64.8	76.7
Octocrylene (OC)	99.7	157
2-Hydroxybenzophenone (2-OHBP)	52.1	35.6
4-Methylbenzylidene camphor (4-MBC)	99.8	126
Homosalate (HMS)	154	102
2-Ethylhexyl salicylate (EHS)	121	104
2-Ethylhexyl methoxycinnamate (EHMC)	81.9	119

Table S4. Instrument limit of detection (iLOD), method limit of detection (mLOD), for silicone rubber (SR) and water in ppb.

Compounds		PSD extraction	Water extraction
	iLOD	**mLOD**	**mLOD**
Fragrances			
Tetramethyl acetyloctahydronaphthalene (OTNE)	0.1299	0.0022	0.0033
Phantholide (AHMI)	0.0160	0.0003	0.0003
Tonalide (AHTN)	0.0171	0.0003	0.0004
Celestolide (ADBI)	0.0235	0.0004	0.0003
Galaxolide (HHCB)	0.0160	0.0003	0.0004
Traseolide (ATII)	0.0313	0.0005	0.0008
UV Filters			
Benzophenone-3 (BP3)	0.0246	0.0004	0.0007
Avobenzone (ABZ)	0.7515	0.0125	0.0063
Octocrylene (OC)	0.0078	0.0001	0.0002
2-Hydroxybenzophenone (2OHBP)	0.0576	0.0010	0.0007
4-Methylbenzylidene camphor (4MBC)	0.0426	0.0007	0.0003
Homosalate (HMS)	0.0354	0.0006	0.0125
2-Ethylhexyl salicylate (EHS)	0.0142	0.0002	0.0003
2-Ethylhexyl methoxycinnamate (EHMC)	0.0476	0.0008	0.0007

Table S5. Coefficients of determination for both the LL model and the MF model.

	r² values			
Compounds	**LL model**		**MF model**	
	Replicate 1	**Replicate 2**	**Replicate 1**	**Replicate 2**
Fragrancies				
Tetramethyl acetyloctahydronaphthalene (OTNE)	0.9078	0.8999	0.9447	0.9459
Phantolide (AHMI)	0.9300	0.9684	0.9599	0.9764
Tonalide (AHTN)	0.9707	0.9870	0.9826	0.9911
Celestolide (ADBI)	0.9409	0.9266	0.9750	0.9678
Galaxolide (HHCB)	0.9409	0.9371	0.9542	0.9689
Traseolide (ATII)	0.9173	0.9250	0.9635	0.9679
UV Filters				
Benzophenone-3 (BP3)	0.9489	-	0.9310	-
Avobenzone (ABZ)	0.9714	0.9607	0.9655	0.9584
Octocrylene (OC)	0.9571	0.9560	0.9783	0.9675
2-Hydroxybenzophenone (2-OHBP)	0.9877	0.9127	0.9458	0.9662
4-Methylbenzylidene camphor (4-MBC)	0.9319	0.9463	0.9702	0.9817
Homosalate (HMS)	0.9482	0.9797	0.9879	0.9786
2-Ethylhexyl salicylate (EHS)	0.9571	0.9560	0.9783	0.9675
2-Ethylhexyl methoxycinnamate (EHMC)	0.9455	0.9657	0.9674	0.9802

MATERIAL SUPLEMENTAR B – ARTIGO 2

Table S1. Sampling day, air temperature, water temperature salinity, and conductivity of 6 sampling campaigns.

Campaign	Sampling day	Air temperature (º C)	Water temperature (º C)	Salinity (ppt)	Conductivity (mS/m)
	07/dec/21	27.6	26.7	39.4	62.4
C1	07/feb/22	27.4	27.0	35.3	57.5
C2	29/apr/22	28.3	27.1	34.1	56.1
C3	04/jul/22	25.2	24.6	35.7	58.1
C4	08/sept/22	26.2	25.1	36.4	59.4
C5	29/nov/22	26.3	26.4	36.5	59.1
C6	06/feb/23	27.9	27.9	36.1	59.0

Table S2. Method limit of detection (mLOD), instrument limit of detection (iLOD), and limit of quantification (LOQ) for quantified compounds.

Compounds	iLOD	mLOD	LOQ
UV Filters			
2OHBP	0.06	0.001	1.35
4MBC	0.10	0.001	0.82
Benzophenone 3	0.30	0.003	2.09
EHMC	0.20	0.002	1.04
EHS	1.00	0.008	1.06
Homosalate	0.06	0.001	0.88
OTNE	0.09	0.001	0.51
Octocrylene	0.02	0.000	1.29
Fragrances			
Cashmeran	0.40	0.003	1.04
Celestolide	1.00	0.008	0.84
Galaxolide	0.00	0.000	0.86
Tonalide	0.08	0.001	0.83
Polyciclic Aromatic Hydrocarbons			
Acenaphthene	0.25	0.002	0.91
Acenaphthylene	0.27	0.002	1.22
Anthracene	1.04	0.009	1.75
Benz[a]anthracene	1.78	0.015	2.46
Benz[b+k]Fluoranthene	4.41	0.037	1.69
Benzo(a)pyrene	0.14	0.001	1.02
Benzo[g,h,i]perylene	3.75	0.031	1.23
Chrysene	1.01	0.008	3.92
Fluoranthene	0.10	0.001	1.41
Fluorene	0.86	0.007	1.68
Indeno[1,2,3-cd]pyrene	3.37	0.028	1.01
Phenanthrene	0.20	0.002	1.46
Pyrene	0.16	0.001	1.76
Oganochlorine compounds			
PCB 101	1.79	0.015	1.20

PCB 138	1.94	0.016	1.09
PCB 153	1.10	0.009	1.11
PCB 180	0.64	0.005	0.96
PCB 28	0.11	0.001	0.94
PCB 52	0.12	0.001	1.04
p,p'-DDD	0.70	0.006	1.68
p,p'-DDE	1.02	0.009	1.12

Table S3. Ecotoxicological data used for Hazard Quotient calculation.

Compound	**Organism**	**Endpoint**	**Conc.**	**Unid.**	**Assessment Factor**	**PNEC (pg L^{-1})**	**References**
Acy	QSAR	PNEC	2129	pg L^{-1}	-	2129	(Liang *et al.*, 2023)
Ace	Fish	NOEC	2300	pg L^{-1}	100	23.0	(Cui *et al.*, 2016)
Flu		NOEC	1100	pg L^{-1}	100	11.0	
Phe		NOEC	3000	pg L^{-1}	100	30.0	
Ant		NOEC	30	pg L^{-1}	100	0.30	
Fla		NOEC	616	pg L^{-1}	100	6.16	
Pyr		NOEC	700	pg L^{-1}	100	7.00	
BaA		NOEC	3460	pg L^{-1}	100	34.6	
Chr		NOEC	700	pg L^{-1}	100	7.00	
BbkF	Fish	LC50	5000	pg L^{-1}	1000	5.00	(Jiang *et al.*, 2023)
BaP	Fish	NOEC	1.40	pg L^{-1}	100	0.01	(Cui *et al.*, 2016)
IcdP	*Raphidocelis subcapitata*	EC50	2.00	pg L^{-1}	1000	0.00	(Ministry of the Environment in Japan, 2015)
DahA	Fish	NOEC	500	pg L^{-1}	100	5.00	(Cui *et al.*, 2016)
BghiP	-	-	-	pg L^{-1}	-	-	-
p',p-DDD	Oncorhynchu smykiss	LC50	7000	pg L^{-1}	1000	7.00	ECOTOX Database*
p'p-DDT		NOEC	1000	pg L^{-1}	100	10.00	
Tonalide	-	PNEC	35.0	pg L^{-1}	-	35.0	(Swedish EPA, 2010)
Galaxolide	-	PNEC	44.0	pg L^{-1}	-	44.00	
Cashmeran	Medaka larvae	LC50	11600	pg L^{-1}	1000	11.60	(Yamauchi *et al.*, 2008)
Celestolide	Medaka larvae	LC50	1970	pg L^{-1}	1000	1.97	
Octocrylene	*Saltwater fish*	PNEC	0.08	pg L^{-1}	-	0.08	ECOSAR
EHS	*Daphnia magna*	NOEC	280	pg L^{-1}	10	28.0	(Nabholz, 1991)
HMS	Satwater fish	PNEC	0.01	pg L^{-1}	-	0.01	ECOSAR**
BP3		PNEC	0.94	pg L^{-1}	-	0.94	
4-MBC	*Ruditapes philippinarum*	LC50	77.1	pg L^{-1}	1000	0.08	(Santonocito *et al.*, 2020)
EHMC	*Potamopyrus antipodarum* (snail)	PNEC	0.28	pg L^{-1}	-	0.28	ECOSAR**
2OHBP	Organisms and strains/cells	PNEC	1229	pg L^{-1}	-	1229	(Guo *et al.*, 2020)
PCB 101	Fish	PNEC	0.01	pg L^{-1}		0.01	ECOTOX Database*
PCB 138	Fish	PNEC	0.003	pg L^{-1}		0.003	ECOTOX Database*
***PCB 153**	Fish	PNEC	0.001	pg L^{-1}		0.001	ECOTOX Database*
PCB 180	Fish	PNEC	0.025	pg L^{-1}		0.025	ECOTOX Database*

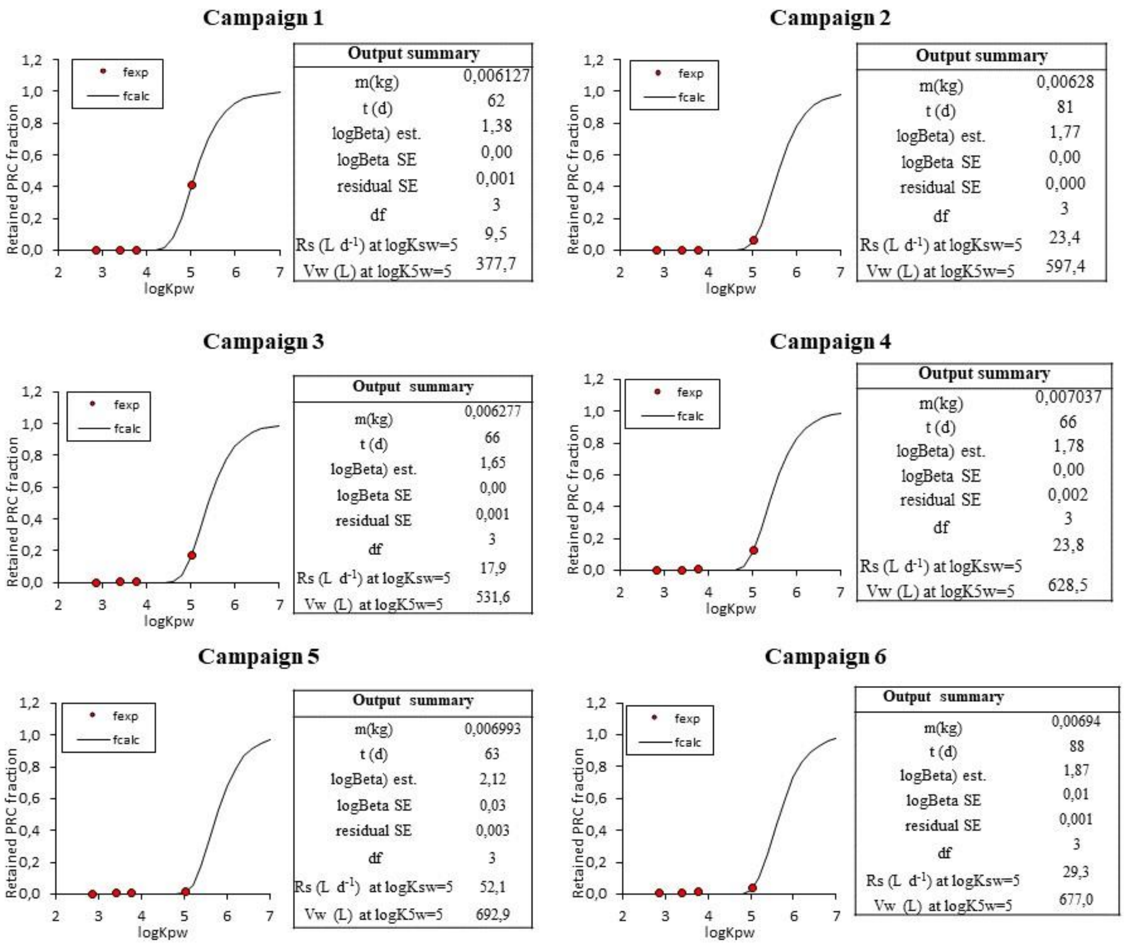
* *ECOTOX* database is a comprehensive Knowledgebase providing single chemical environmental toxicity data on aquatic and terrestrial species.

** ECOSAR (Ecological Structure Activity Relationships) predicts the potential toxicity of industrial chemicals to organisms living in the water body to which the chemicals are discharged.

Table S4 – Molecular Wright, octanol-water partition coefficient (log K_{OW}), polymer/silicone-water partition coefficient (logK_{PW}) and freely dissolved concentration of 6 sampling campaigns (pg L^{-1}) for fragrances, UV filters, polycyclic aromatic hydrocarbons, and organochlorine compounds.

Compounds	Molecular Weight (g mol $^{-1}$)	Log K_{OW}	logK_{PW} (L kg^{-1})	Compounds concentrations (pg L^{-1})					
				C1	C2	C3	C4	C5	C6
Fragrances									
AHTN	258	5,70	5,46	226 ± 20.8	69.6 ± 13.4	72.1 ± 12.1	20.6 ±1.53	21.2 ± 2.41	23.7 ± 0.45
ADBI	244	5,90	5,51	6.90 ± 3.57	2.72 ± 1.17	1.34 ± 0.71	1.16 ± 0.14	1.37 ± 0.59	1.09 ± 0.26
HHCB	258	5,90	5,70	303 ± 7.56	84.9 ± 3,05	97.7 ± 0.91	60.1 ± 0.08	34.7 ± 3.17	26.8 ± 0.50
DPMI	206	4,90	5,00	159 ± 8.28	54.9 ± 4.90	67.0 ±8.89	95.6 ± 5.79	73.9 ± 5.54	87.8 ± 0.27
UV Filters									
BP3	198	3,79	4,47	1635 ± 360	554 ± 5.65	710 ± 85.5	1199 ± 27.8	2294 ±36.2	1483 ± 66.4
OCT	254	7,53	4,96	197 ± 27.4	306 ± 68.7	1472 ± 176	1732 ± 122	893 ± 619	2145 ± 135
2OHBP	290	3,47	4,65	10.9 ± 0.43	7.47 ± 0.20	14.4 ± 2.39	7.86 ± 0.30	3.55 ± 0.52	4.85 ± 0.33
4MBC	250	4,95	5,08	211 ± 5.04	260 ± 29.5	95.9 ± 2.73	74.4 ± 3.95	105 ± 7.27	219 ± 6.62
HMS	262	5,82	5,85	4051 ± 827	1738 ± 194	1239 ± 25.0	814 ± 8.79	442 ± 42.2	906 ± 28.1
EHS	310	5,69	5,80	3057 ± 147	903 ± 72.8	478 ± 0.59	371 ± 6.02	157 ± 7.20	454 ± 30.8
EHMC	361	5,77	6,47	386 ± 56.3	84.5 ± 8.50	37.4 ± 3.01	31.4 ± 2.06	32.4 ± 1.44	53.7 ± 1.78
Polycyclic Aromatic Hydrocarbons									
ACE	154	3,92	3,45	323 ± 53.5	336 ± 188	199 ± 33.5	146 ± 17.9	289 ± 18.2	237 ± 29.4
ACN	152	4,00	3,07	12158 ± 2014	1922 ± 104	3557 ± 216	1176 ± 15.9	3106 ± 1712	2867 ± 66.1
FLU	166	4,18	3,58	907 ± 46.1	2412 ± 485	4816 ± 815	399 ± 3.50	677 ± 36.3	520 ± 19.7
ANT	178	4,54	3,91	350 ± 34.6	284 ± 96.1	145 ± 10.6	472 ± 175	406 ± 142	1295 ± 254
PHE	178	4,57	3,83	5916 ± 600	1321 ± 98.3	1561 ± 159	771 ± 11.7	2416 ± 108	1902 ± 49.2
PYR	202	5,18	4,38	964 ± 42.3	290 ± 21.1	260 ± 36.2	189 ± 5.08	443 ± 14.3	488 ± 48.1
FLT	202	5,22	4,29	1041 ± 126	441 ± 76.8	579 ± 53.6	370 ± 1.09	875 ± 9.46	708 ± 33.3
CHR	228	5,95	4,80	208 ± 8.01	295 ± 1.35	126 ± 25.6	143 ± 2.77	232 ± 15.2	262 ± 17.6
BaA	228	5,97	4,84	40.6 ± 0.30	39.4 ± 3.41	22.8 ± 5.81	16.2 ± 0.56	34.9 ± 7.17	38.1 ± 3.92
BaP	252	6,04	5,22	11.2 ± 0.88	2.82 ± 0.26	1.78 ± 0.23	43.9 ± 2.31	78.1 ± 1.87	72.0 ± 7.53
B[g,h,i]P	276	6,50	5,60	13.2 ± 1.06	1.99 ± 0.52	1.63 ± 0.44	2.77 ± 0.68	1.62 ± 1.47	4.32 ± 0.28
IND	276	6,58	5,59	10.5 ± 1.10	3.93 ± 2.91	4.65 ± 4.87	6.08 ± 1.19	2.30 ± 0.37	6.31 ± 0.33
B[b+k]F	252	6,84	5,26	31.6 ± 3.12	44.5 ± 9.27	11.8 ± 5.74	23.6 ± 1.22	38.2 ± 1.30	9.90 ± 1.52
Organochlorine compounds									
PCB 101	326	6,82	6,01	1195 ± 262	2.40 ± 0.28	3.09 ± 0.31	211 ± 4.15	106 ± 5.54	618 ± 37.0
PCB 138	361	7,34	6,46	<MDL	2.59 ± 0.24	4.32 ± 0.93	1.30 ± 0.61	0.90 ± 0.02	1.20 ± 0.04
PCB 153	361	7,34	6,45	<MDL	2.04 ± 0.38	3.89 ± 1.11	1.91 ± 0.23	0.93 ± 0.11	1.17 ± 0.07
PCB 180	395	7,66	6,72	<MDL	<MDL	0.32 ± 0.23	0.42 ± 0.05	<MDL	1.03 ± 0.10
PCB 28	391	5,77	5,23	1.66 ± 0.13	2.28 ± 0.24	1.84 ± 0.14	1.08 ± 0.02	0.91 ± 0.13	1.17 ± 0.08
p,p'-DDD	320	5,97	6,53	7.05 ± 0.68	2.28 ± 0.16	2.80 ± 0	1.85 ± 0.14	0.72 ± 0.07	0.98 ± 0.07
p.p'-DDT	354	6,76	7,85	0.47 ± 0.30	<MDL	0.64 ± 0.29	<MDL	<MDL	<MDL

Figure S1. Retained fraction of performance reference compounds according to the model by Rusina et al. (2010), where fexp is the retained fraction obtained from PRCs dissipation in samples and fcalc is the adjusted model. Information about sampler massa (m), exposition time (d), model variables (log B, logB SE, residuala SE, df), sampling rate (R_S), and volume (Vw).



Campaign 1

Output summary	
m(kg)	0,006127
t (d)	62
logBeta) est.	1,38
logBeta SE	0,00
residual SE	0,001
df	3
Rs (L d^{-1}) at logKsw=5	9,5
Vw (L) at logK5w=5	377,7

Campaign 2

Output summary	
m(kg)	0,00628
t (d)	81
logBeta) est.	1,77
logBeta SE	0,00
residual SE	0,000
df	3
Rs (L d^{-1}) at logKsw=5	23,4
Vw (L) at logK5w=5	597,4

Campaign 3

Output summary	
m(kg)	0,006277
t (d)	66
logBeta) est.	1,65
logBeta SE	0,00
residual SE	0,001
df	3
Rs (L d^{-1}) at logKsw=5	17,9
Vw (L) at logK5w=5	531,6

Campaign 4

Output summary	
m(kg)	0,007037
t (d)	66
logBeta) est.	1,78
logBeta SE	0,00
residual SE	0,002
df	3
Rs (L d^{-1}) at logKsw=5	23,8
Vw (L) at logK5w=5	628,5

Campaign 5

Output summary	
m(kg)	0,006993
t (d)	63
logBeta) est.	2,12
logBeta SE	0,03
residual SE	0,003
df	3
Rs (L d^{-1}) at logKsw=5	52,1
Vw (L) at logK5w=5	692,9

Campaign 6

Output summary	
m(kg)	0,00694
t (d)	88
logBeta) est.	1,87
logBeta SE	0,01
residual SE	0,001
df	3
Rs (L d^{-1}) at logKsw=5	29,3
Vw (L) at logK5w=5	677,0

Table S5. Pearson's correlation matrix between all paired variables investigated. In bold, significative correlations.

	Air-Temp	W-Temp.	Sal.	Cond.	pH	Rainfall	x̄ Temp.	HMW PAHs	LMW PAHs	PCB 101	PCB 138	PCB 153	PCB 180	PCB 28	p,p'-DDD	p.p'-DDT	AHTN	ADBI	HHCB	DPMI	BP3	OCT	2OHBP	4MBC	Homosalate	EHS	EHMC
Air-Temp	1.000																										
W-Temp.	**0.903**	1.000																									
Sal.	-0.060	-0.039	1.000																								
Cond.	-0.110	-0.103	**0.995**	1.000																							
pH	-0.042	0.193	-0.655	-0.665	1.000																						
Rainfall	0.218	0.490	-0.390	-0.442	**0.885**	1.000																					
x̄ Temp.	0.486	0.691	0.517	0.484	0.087	0.387	1.000																				
HMW PAHs	0.612	0.499	0.719	0.684	-0.694	-0.337	0.569	1.000																			
LMW PAHs	-0.260	-0.037	0.388	0.428	0.291	0.258	0.620	-0.053	1.000																		
PCB 101	0.068	0.153	**0.919**	**0.887**	-0.668	-0.345	0.525	**0.771**	0.184	1.000																	
PCB 138	0.518	0.457	-0.875	**-0.903**	0.494	0.414	-0.255	-0.306	-0.547	**-0.709**	1.000																
PCB 153	0.337	0.256	-0.916	**-0.939**	0.431	0.301	-0.475	-0.421	-0.669	**-0.740**	**0.968**	1.000															
PCB 180	-0.382	-0.084	-0.204	-0.201	0.212	0.061	-0.081	-0.405	0.095	0.039	0.028	0.100	1.000														
PCB 28	**0.772**	0.822	-0.198	-0.274	0.421	**0.722**	0.481	0.260	-0.129	-0.116	0.533	0.370	-0.402	1.000													
p,p'-DDD	0.520	0.421	0.663	0.600	-0.599	-0.169	0.422	**0.894**	-0.235	**0.724**	-0.268	-0.334	-0.512	0.407	1.000												
p.p'-DDT	**0.775**	0.655	-0.403	-0.460	-0.074	0.071	-0.062	0.301	-0.756	-0.129	0.766	0.725	-0.061	0.551	0.319	1.000											
Tonalide	0.578	0.492	**0.704**	0.648	-0.570	-0.141	0.553	**0.940**	-0.098	**0.739**	-0.296	-0.399	-0.529	0.431	**0.984**	0.275	1.000										
Celestolide	0.424	0.371	**0.809**	**0.762**	-0.527	-0.110	0.604	**0.885**	0.093	**0.774**	-0.473	-0.576	-0.557	0.359	**0.942**	0.042	**0.970**	1.000									
Galaxolide	0.498	0.388	**0.715**	0.660	-0.627	-0.209	0.448	**0.914**	-0.166	**0.744**	-0.333	-0.405	-0.545	0.364	**0.995**	0.251	**0.991**	0.964	1.000								
Cashmeran	0.006	-0.032	**0.895**	**0.866**	**-0.815**	-0.508	0.265	0.763	-0.048	0.934	**-0.701**	-0.677	-0.166	-0.172	**0.804**	-0.093	**0.776**	**0.802**	0.822	1.000							
Benzophenone 3	-0.439	-0.552	0.577	0.657	-0.593	**-0.756**	-0.011	0.200	0.431	0.377	**-0.745**	**-0.708**	0.001	**-0.794**	-0.065	-0.616	-0.004	0.104	0.019	0.389	1.000						
Octocrylene	-0.460	-0.319	-0.428	-0.411	0.101	-0.159	-0.513	-0.548	-0.254	-0.202	0.199	0.350	**0.889**	-0.537	-0.601	0.069	-0.672	**-0.743**	-0.643	-0.263	-0.004	1.000					
2OHBP	**0.719**	0.545	-0.196	-0.264	-0.258	-0.023	-0.101	0.441	**-0.835**	0.034	0.582	0.570	-0.281	0.558	0.568	**0.932**	0.493	0.287	0.503	0.162	-0.580	-0.117	1.000				
4MBC	0.328	0.628	0.369	0.324	0.357	0.647	**0.933**	0.312	0.644	0.389	-0.195	-0.389	0.024	0.552	0.283	-0.147	0.387	0.467	0.292	0.122	-0.221	-0.424	-0.183	1.000			
Homosalate	0.515	0.493	**0.725**	0.661	-0.476	-0.023	0.607	**0.887**	-0.023	**0.766**	-0.341	-0.444	-0.473	0.466	**0.972**	0.201	**0.985**	**0.978**	**0.975**	**0.778**	-0.063	-0.664	0.427	0.494	1.000		
EHS	0.425	0.401	**0.806**	**0.751**	-0.549	-0.113	0.594	**0.896**	0.030	**0.826**	-0.454	-0.545	-0.452	0.351	**0.962**	0.105	**0.978**	**0.989**	**0.974**	**0.842**	0.059	-0.645	0.342	0.466	**0.991**	1.000	
EHMC	0.378	0.342	**0.860**	**0.813**	-0.609	-0.197	0.590	**0.911**	0.077	**0.861**	-0.527	-0.614	-0.439	0.259	**0.943**	0.042	**0.966**	**0.987**	**0.964**	**0.875**	0.169	-0.632	0.277	0.438	**0.972**	**0.994**	1.000

Table S6. Hazard quotient calculated for all compounds analyzed during six campaigns. HQ < 1 = no significant risk in green, 1 ≤ HQ < 10 = small potential effects in orange, 10 ≤ HQ < 100 = significant potential adverse effects in dark orange, and HQ ≥ 100 = adverse effects in red.

	Hazard Quotients					
	C1	**C2**	**C3**	**C4**	**C5**	**C6**
Tonalide	6,45	1,99	2,06	0,59	0,61	0,68
Celestolide	3,50	1,38	0,68	0,59	0,70	0,55
Galaxolide	6,89	1,93	2,22	1,37	0,79	0,61
Cashmeran	13,68	4,74	5,78	8,24	6,37	7,57
Benzophenone 3	1748	593	760	1282	2453	1586
Octocrylene	2554	3971	19119	22490	11596	27862
2OHBP	0,01	0,006	0,013	0,006	0,003	0,004
4MBC	2736	3374	1244	966	1360	2837
Homosalate	578668	248338	177002	116265	63187	129456
EHS	109,18	32,23	17,06	13,24	5,61	16,21
EHMC	1369	300	133	111	115	190
Acenaphthene	0,15	0,16	0,09	0,07	0,14	0,12
Acenaphthylene	529	83,6	155	51,2	135	125
Fluorene	82,4	219	438	36,3	61,5	47,3
Anthracene	1167	948	484	1572	1352	4315
Phenanthrene	197	44,0	52,0	25,7	80,5	63,4
Pyrene	138	41,4	37,2	27,0	63,2	69,7
Fluoranthene	169	71,6	93,9	60,0	142	115
Chrysene	29,7	42,2	18,0	20,4	33	37
Benz[a]anthracene	1,17	1,14	0,66	0,47	1,01	1,10
Benzo(a)pyrene	802	201	127	3139	5578	5145
Benzo[g,h,i]perylene	-	-	-	-	-	-
Indeno[1,2,3-cd]pyrene	5273	961	607	3445	1723	3268
Benz[b+k]Fluoranthene	6,31	8,91	2,35	4,71	7,64	1,98
PCB 101	119504	239,6	309,2	21136	10571	61769
PCB 138		997	1662	500	346	463
PCB 153		1567	2993	1472	717	897
PCB 180		3,38	12,6	17,0	5,20	41,2
p,p'-DDD	1,01	0,33	0,40	0,26	0,10	0,14
p.p'-DDT	0,05	0,04	0,12	0,02	0,003	0,03

MATERIAL SUPLEMENTAR C – ARTIGO 3

Arquivo em excel anexo ao e-mail.

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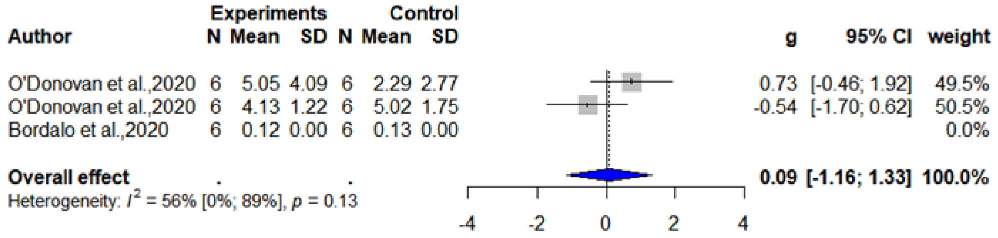
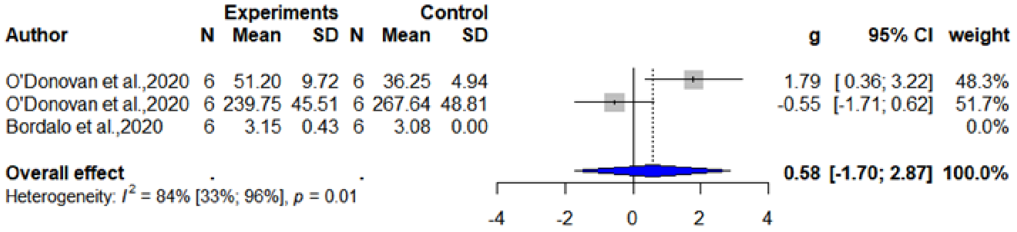


Author	Experiments			Control			g	95% CI	weight
	N	Mean	SD	N	Mean	SD			
O'Donovan et al.,2020	6	5.05	4.09	6	2.29	2.77	0.73	[-0.46; 1.92]	49.5%
O'Donovan et al.,2020	6	4.13	1.22	6	5.02	1.75	-0.54	[-1.70; 0.62]	50.5%
Bordalo et al.,2020	6	0.12	0.00	6	0.13	0.00			0.0%
Overall effect							**0.09**	**[-1.16; 1.33]**	**100.0%**

Heterogeneity: I^2 = 56% [0%; 89%], p = 0.13

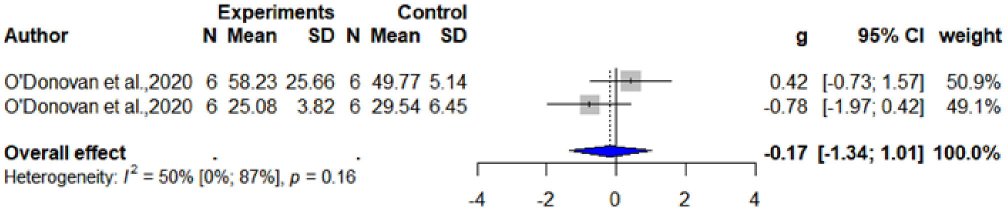
CAT



Author	Experiments			Control			g	95% CI	weight
	N	Mean	SD	N	Mean	SD			
O'Donovan et al.,2020	6	51.20	9.72	6	36.25	4.94	1.79	[0.36; 3.22]	48.3%
O'Donovan et al.,2020	6	239.75	45.51	6	267.64	48.81	-0.55	[-1.71; 0.62]	51.7%
Bordalo et al.,2020	6	3.15	0.43	6	3.08	0.00			0.0%
Overall effect							**0.58**	**[-1.70; 2.87]**	**100.0%**

Heterogeneity: I^2 = 84% [33%; 96%], p = 0.01

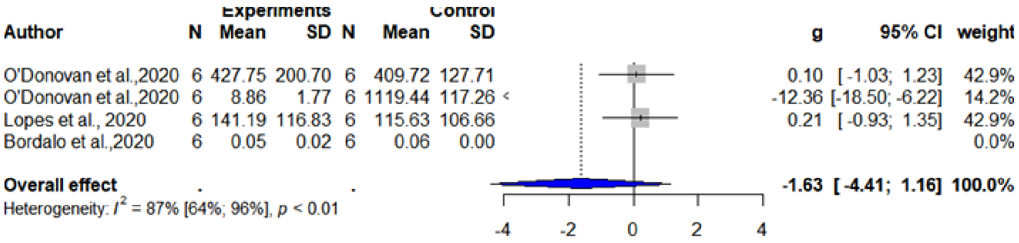
SOD



Author	Experiments			Control			g	95% CI	weight
	N	Mean	SD	N	Mean	SD			
O'Donovan et al.,2020	6	58.23	25.66	6	49.77	5.14	0.42	[-0.73; 1.57]	50.9%
O'Donovan et al.,2020	6	25.08	3.82	6	29.54	6.45	-0.78	[-1.97; 0.42]	49.1%
Overall effect							**-0.17**	**[-1.34; 1.01]**	**100.0%**

Heterogeneity: I^2 = 50% [0%; 87%], p = 0.16

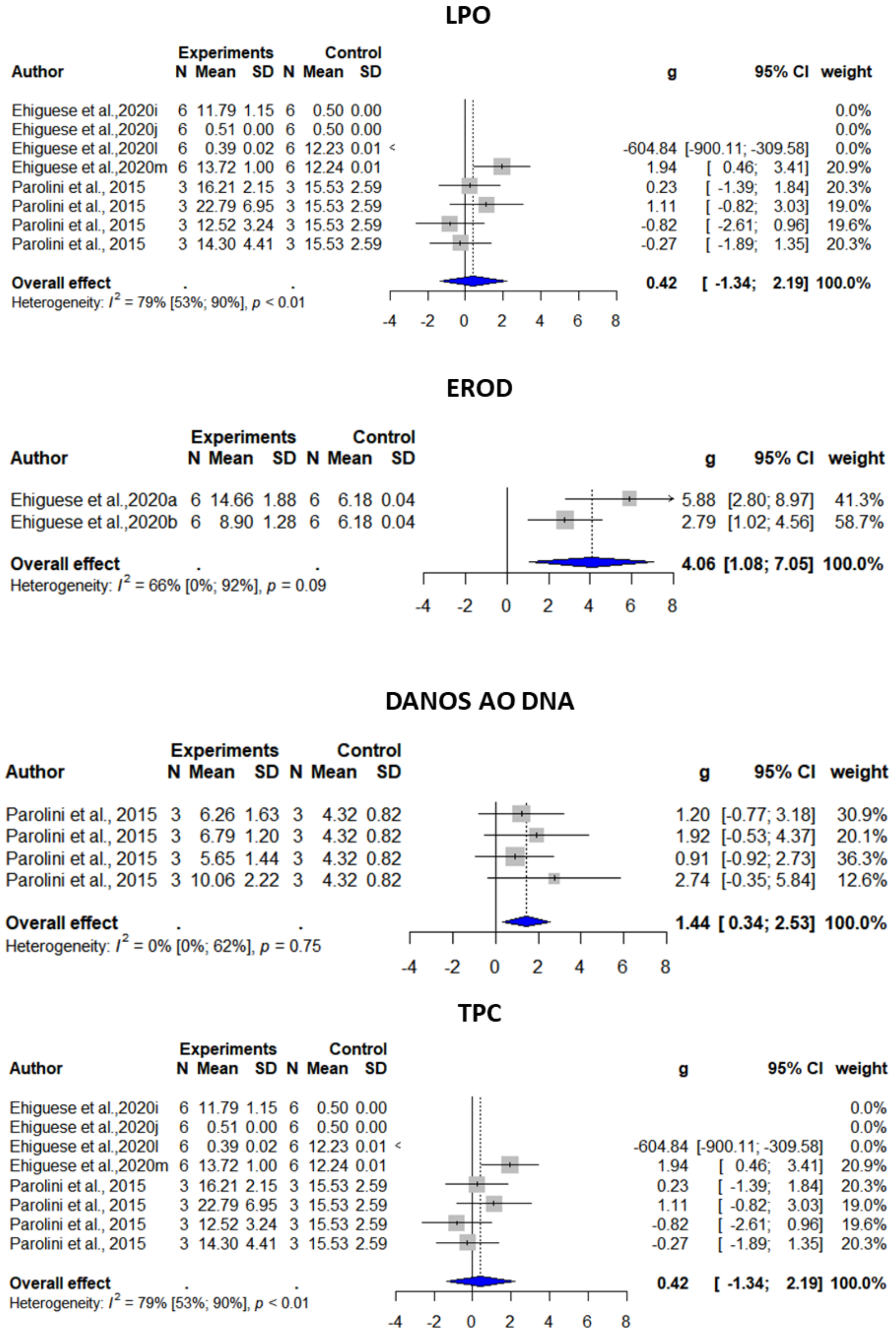
GST



Author	Experiments			Control			g	95% CI	weight
	N	Mean	SD	N	Mean	SD			
O'Donovan et al.,2020	6	427.75	200.70	6	409.72	127.71	0.10	[-1.03; 1.23]	42.9%
O'Donovan et al.,2020	6	8.86	1.77	6	1119.44	117.26	-12.36	[-18.50; -6.22]	14.2%
Lopes et al., 2020	6	141.19	116.83	6	115.63	106.66	0.21	[-0.93; 1.35]	42.9%
Bordalo et al.,2020	6	0.05	0.02	6	0.06	0.00			0.0%
Overall effect							**-1.63**	**[-4.41; 1.16]**	**100.0%**

Heterogeneity: I^2 = 87% [64%; 96%], p < 0.01

Figura S1. Forest-plots gerados pelos dados sumarizados na metanálise. Meta-análise de efeito global para etoxiresorufina-O-deetilase (EROD), superóxido dismutase (SOD) e glutationa S-transferase (GST), para Benzofenona-3 e 4-metil benzilideno cânfora. I² = Heterogeneidade, g = teste de heterogeneidade entre moderadores.



LPO

Author	Experiments N	Mean	SD	Control N	Mean	SD	g	95% CI	weight
Ehiguese et al.,2020i	6	11.79	1.15	6	0.50	0.00			0.0%
Ehiguese et al.,2020j	6	0.51	0.00	6	0.50	0.00			0.0%
Ehiguese et al.,2020l	6	0.39	0.02	6	12.23	0.01	-604.84	[-900.11; -309.58]	0.0%
Ehiguese et al.,2020m	6	13.72	1.00	6	12.24	0.01	1.94	[0.46; 3.41]	20.9%
Parolini et al., 2015	3	16.21	2.15	3	15.53	2.59	0.23	[-1.39; 1.84]	20.3%
Parolini et al., 2015	3	22.79	6.95	3	15.53	2.59	1.11	[-0.82; 3.03]	19.0%
Parolini et al., 2015	3	12.52	3.24	3	15.53	2.59	-0.82	[-2.61; 0.96]	19.6%
Parolini et al., 2015	3	14.30	4.41	3	15.53	2.59	-0.27	[-1.89; 1.35]	20.3%
Overall effect		.			.		**0.42**	**[-1.34; 2.19]**	**100.0%**

Heterogeneity: I^2 = 79% [53%; 90%], p < 0.01

EROD

Author	Experiments N	Mean	SD	Control N	Mean	SD	g	95% CI	weight
Ehiguese et al.,2020a	6	14.66	1.88	6	6.18	0.04	5.88	[2.80; 8.97]	41.3%
Ehiguese et al.,2020b	6	8.90	1.28	6	6.18	0.04	2.79	[1.02; 4.56]	58.7%
Overall effect		.			.		**4.06**	**[1.08; 7.05]**	**100.0%**

Heterogeneity: I^2 = 66% [0%; 92%], p = 0.09

DANOS AO DNA

Author	Experiments N	Mean	SD	Control N	Mean	SD	g	95% CI	weight
Parolini et al., 2015	3	6.26	1.63	3	4.32	0.82	1.20	[-0.77; 3.18]	30.9%
Parolini et al., 2015	3	6.79	1.20	3	4.32	0.82	1.92	[-0.53; 4.37]	20.1%
Parolini et al., 2015	3	5.65	1.44	3	4.32	0.82	0.91	[-0.92; 2.73]	36.3%
Parolini et al., 2015	3	10.06	2.22	3	4.32	0.82	2.74	[-0.35; 5.84]	12.6%
Overall effect		.			.		**1.44**	**[0.34; 2.53]**	**100.0%**

Heterogeneity: I^2 = 0% [0%; 62%], p = 0.75

TPC

Author	Experiments N	Mean	SD	Control N	Mean	SD	g	95% CI	weight
Ehiguese et al.,2020i	6	11.79	1.15	6	0.50	0.00			0.0%
Ehiguese et al.,2020j	6	0.51	0.00	6	0.50	0.00			0.0%
Ehiguese et al.,2020l	6	0.39	0.02	6	12.23	0.01	-604.84	[-900.11; -309.58]	0.0%
Ehiguese et al.,2020m	6	13.72	1.00	6	12.24	0.01	1.94	[0.46; 3.41]	20.9%
Parolini et al., 2015	3	16.21	2.15	3	15.53	2.59	0.23	[-1.39; 1.84]	20.3%
Parolini et al., 2015	3	22.79	6.95	3	15.53	2.59	1.11	[-0.82; 3.03]	19.0%
Parolini et al., 2015	3	12.52	3.24	3	15.53	2.59	-0.82	[-2.61; 0.96]	19.6%
Parolini et al., 2015	3	14.30	4.41	3	15.53	2.59	-0.27	[-1.89; 1.35]	20.3%
Overall effect		.			.		**0.42**	**[-1.34; 2.19]**	**100.0%**

Heterogeneity: I^2 = 79% [53%; 90%], p < 0.01

Figura S2. Forest-plots gerados pelos dados sumarizados na metanálise. Meta-análise de efeito global para peroxidação lipídica (LPO), etoxiresorufina-O-deetilase (EROD), danos ao DNA e teor de proteína carbonila (TPC), para Benzofenona-3 e 4-metil benzilideno cânfora. I² = Heterogeneidade, g = teste de heterogeneidade entre moderadores.