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**Panorama da contaminação por poluentes orgânicos persistentes em mamíferos
marinhos da costa brasileira**

Florianópolis
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Orientador: Prof. Dra. Juliana Leonel

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Andressa Elias de Matos

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O presente trabalho em nível de mestrado foi avaliado e aprovado por banca
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Certificamos que esta é a **versão original e final** do trabalho de conclusão que foi
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Florianópolis, 2023.

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RESUMO

Organoclorados compreendem uma classe de compostos amplamente utilizados pela indústria e agricultura, principalmente entre as décadas de 1940 e 1970, e são caracterizados por sua alta estabilidade química, resistência à degradação, capacidade de bioacumulação na biota e potenciais efeitos toxicológicos. Em 2001, foram reconhecidos pela Convenção de Estocolmo como poluentes orgânicos persistentes que devem ter seu uso restrito ou proibido. Apesar das restrições, ainda são comumente encontrados no ambiente marinho, principalmente em animais do topo da cadeia alimentar. Os mamíferos marinhos têm sido utilizados no estudo da contaminação do ambiente marinho por organoclorados, graças ao potencial de bioacumulação que apresentam para estes contaminantes. No Brasil, vários estudos têm buscado determinar a contaminação de mamíferos marinhos por organoclorados, mas não há uma revisão abrangente com o panorama da contaminação dessas espécies ao longo da costa brasileira. Nesta revisão, buscamos avaliar os padrões de ocorrência e distribuição de organoclorados em mamíferos marinhos ao longo da costa brasileira, bem como identificar lacunas existentes neste campo de estudo para o Brasil. A busca e seleção dos artigos foi dividida em duas triagens nas bases de dados Science Direct (1^a triagem) e Scopus (2^a triagem), além de uma busca complementar no Google Scholar e na lista de referências dos artigos selecionados nas duas primeiras triagens. Para a seleção dos estudos foram considerados 3 critérios: ter sido realizado na costa brasileira; ter avaliado a contaminação de mamíferos marinhos por organoclorados; apresentar o valor das concentrações para os POPs analisados. Ao todo, foram selecionados e avaliados 25 artigos publicados entre 2002 e janeiro de 2023, com o maior número de estudos concentrado na região Sudeste (20), seguida das regiões Sul (8) e Nordeste (2). Não foram encontrados estudos na região norte. As espécies mais estudadas foram *Sotalia guianensis*, *Pontoporia blainvillei* e *Stenella frontalis*, respectivamente. Os organoclorados mais estudados foram PCBs e DDTs, com maiores concentrações em indivíduos coletados na região sudeste. Apenas quatro estudos analisaram tendências temporais de organoclorados em mamíferos marinhos.

Palavras-chave: POPs; Cetáceos; Odontocetes; Organoclorados.

ABSTRACT

Organochlorines comprise a class of compounds widely used by industry and agriculture, mainly between the 1940s and 1970s, and are characterized by their high chemical stability, resistance to degradation, ability to bioaccumulate in biota and toxicological effects. In 2001, they were recognized by the Stockholm Convention as persistent organic pollutants that must have their use restricted or prohibited. Despite the restrictions, they are still commonly found in the marine environment, especially in animals at the top of the food chain. Marine mammals have been used in the study of contamination of the marine environment by organochlorines, thanks to the bioaccumulation potential they present for these contaminants. In Brazil, several studies have sought to determine the contamination of marine mammals by organochlorines, but there is no comprehensive review with the panorama of contamination of these species along the Brazilian coast. In this review, we sought to assess the patterns of occurrence and distribution of organochlorines in marine mammals along the Brazilian coast, as well as to identify existing gaps in this field of study for Brazil. The search and selection of articles was divided into two screenings in the Science Direct (1^a screening) and Scopus (2^a screening) databases, in addition to a complementary search on Google Scholar and in the reference list of the articles selected in the first two screenings. For the selection of studies, 3 criteria were respected: having been carried out on the Brazilian coast; evaluate the contamination of marine mammals by organochlorines; present the value of the concentrations for the analyzed POPs. In all, 25 articles published between 2002 and January 2023 were selected and evaluated, with the largest number of studies concentrated in the Southeast region (20), followed by the South (8) and Northeast (2) regions. No studies were found in the northern region. The most studied species were *Sotalia guianensis*, *Pontoporia blainvilliei* and *Stenella frontalis*, respectively. The most studied organochlorines were PCBs and DDTs, with higher concentrations in individuals collected in the southeast region. Only four studies analyzed temporal trends of organochlorines in marine mammals.

Keywords: POPs; Cetaceans; Odontocetes; Organochlorines.

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LISTA DE ABREVIATURAS E SIGLAS

CAPES - Coordenação de Aperfeiçoamento de Pessoal de Nível Superior
CHLs – Clordanos
CNPq - Conselho Nacional de Desenvolvimento Científico e Tecnológico
DDD – Diclorodifenildicloroetano
DDE - Diclorodifenildicloroetileno
DDT– Diclorodifeniltricloroetano
FAPESC – Fundação de Amparo à Pesquisa e Inovação do Estado de Santa Catarina
FMAs - Franciscana Management Areas
HCB – Hexaclorobenzeno
HCH – Hexaclorociclohexano
IBGE - Instituto Brasileiro de Geografia e Estatística
LD – Limite de detecção
N.D – Não detectado
ONU – Organização das Nações Unidas
PBDEs – Éteres Difenil Polibromados
PCB – Bifenilas Policloradas
POPs – Poluentes orgânicos persistentes
TEQ - Equivalência Tóxica (Toxic Equivalency)
UNEP – Programa das Nações Unidas para o Meio Ambiente
WHO - World Health Organization

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1 INTRODUÇÃO

O Brasil é um país rico em biodiversidade marinha, a qual constitui importante fonte de renda para as populações costeiras, em especial pescadores, maricultores, comerciantes e comunidades locais. Sendo assim, a qualidade e saúde ambiental dessas regiões assume elevada importância econômica e sobre a saúde daqueles que consomem e dependem dos produtos e serviços providos pelo mar. Estima-se que só no ano de 2015 a economia marinha e costeira no Brasil tenha sido responsável por cerca de 19% do PIB (produto interno bruto) (Carvalho & Moraes, 2021). Em contrapartida, as últimas décadas têm sido marcadas pelos impactos antrópicos sobre as regiões costeiras de todo o mundo, principalmente devido a ocupação humana nessas regiões, resultando na degradação de habitats pelos processos de urbanização e industrialização (Diegues, 1999). Uma das consequências disso é a poluição, resultante principalmente da descarga de efluentes de origem doméstica, industrial e agrícola e o descarte inadequado de resíduos que adentram os mares e oceanos todos os dias. Os efluentes e resíduos muitas vezes são lançados no ambiente marinho sem qualquer tipo de tratamento prévio, sendo comumente carregados dos mais diversos tipos de contaminantes, afetando negativamente a vida marinha, a economia e as comunidades costeiras (Garbossa *et al.*, 2017; Braga *et al*, 2000; Beiras, 2018).

Como forma de tentar reverter, minimizar e mitigar esses impactos, em 2015, a Organização das Nações Unidas (ONU) estabeleceu a Agenda 2030, com 17 objetivos a serem alcançados até o ano de 2030 para um desenvolvimento mais sustentável, entre os quais podemos destacar o objetivo 14 que visa a promoção de um uso mais sustentável dos oceanos e de seus recursos. Já em 2017, a primeira avaliação mundial dos oceanos da Nações Unidas, indicou que estaríamos ficando sem tempo para gerir o oceano de maneira sustentável. Desde a década de 1950, tem se observado uma tendência de crescimento populacional muito expressivo. De acordo com a projeção da ONU para a população mundial, a estimativa para o ano de 2020 era de aproximadamente 8 bilhões de pessoas no mundo, com a tendência de aumento para aproximadamente 10 bilhões em 2050 (United Nations, 2019). Com isso, as preocupações relacionadas às pressões antrópicas sobre os oceanos tornam-se ainda mais evidentes. Em 2017, foi proclamada pela Assembleia Geral das Nações Unidas a década da ciência oceânica (2021-2030), visando desenvolver projetos e ações de apoio para a implementação da Agenda 2030 no uso mais sustentável dos oceanos. Considerando a importância dos mares e oceanos para a manutenção da biodiversidade marinha e o

desenvolvimento humano, estudos que avaliem os níveis de contaminação dos oceanos por compostos oriundos de atividades humanas são de extrema relevância e podem contribuir para o desenvolvimento de políticas públicas que reduzam os impactos antrópicos sobre as regiões mais afetadas pela poluição (United Nations, 2019; United Nations, 2015; UNESCO-IOC, 2021).

Entre os contaminantes mais comumente encontrados no ambiente marinho estão os organoclorados. Os organoclorados foram amplamente utilizados em atividades agrícolas e industriais, principalmente entre as décadas de 1940 e 1970, quando teve início um processo de restrição e banimento de seus usos em diversos países devido aos seus efeitos adversos sobre o meio ambiente, a biodiversidade e a saúde humana (WHO, 1979; Erickson & Kaley II). Os efeitos adversos dos organoclorados incluem potencial carcinogênico, desregulação endócrina, efeitos tóxicos, transferência dos contaminantes via leite materno e placenta e persistência ambiental (Witczak, *et al.*, 2021; Li *et al.*, 2008). Entre os organoclorados mais comuns destacam-se os DDTs e os PCBs. O DDT (Diclorodifeniltricloroetano) é um praguicida que foi amplamente utilizado durante a segunda guerra mundial no combate a epidemias de tifo em áreas militares, tendo seu uso expandido, posteriormente, para a agricultura e o combate a outros vetores, como os mosquitos transmissores da malária. Já as Bifenilas policloradas (PCBs), foram utilizadas em misturas comerciais com diversas aplicações, tais como em fluídos dielétricos de transformadores e capacitores, fluídos hidráulicos, fluídos de transferência de calor, aditivos em tintas, óleos lubrificantes, entre outras (Jensen, 1972; UNEP, 2017; WHO, 1979; Erickson & Kaley II).

Uma das primeiras restrições quanto ao uso de organoclorados no Brasil foi a Portaria do Ministério da Agricultura, Pecuária e Abastecimento (MAPA) Nº 329/85. Entre os compostos listados estão o aldrin, o clordano, o DDT, o endrin, o toxafeno, o mirex e o heptacloro. Mas apesar da proibição de uso, distribuição e comercialização desses compostos, a Portaria impôs exceções quanto ao uso de iscas formicidas à base de aldrin e mirex, uso de cupinicidas à base de aldrin para florestamento, uso emergencial dos compostos na agricultura e uso em campanhas de saúde pública (BRASIL, 1985). Posteriormente outras restrições foram feitas, como:

- a) Em 1998, o Ministério da Saúde excluiu aldrin, endrin, DDT e heptacloro da lista de substâncias autorizadas para emprego agrícola e domissanitário (BRASIL, 1998);
- b) O princípio ativo clordano foi listado em 2005, pela ANVISA, como não permitido em inseticidas domissanitários (BRASIL, 2005).

c) O DDT, apesar de contemplado na Portaria do MAPA de 1985, entrou nas exceções estabelecidas pela portaria, e teve seu uso continuado na agricultura e em campanhas de saúde pública. Seu uso, fabricação, importação, exportação e manutenção em estoque, só foram proibidos definitivamente em 2009, através da Lei Nº 11.936/09 (BRASIL, 2009).

No caso dos PCBs seu uso, fabricação e comercialização foram proibidos, a partir de 1981, através da Portaria interministerial Nº 19/81. Adicionalmente foram estabelecidas posteriormente, resoluções e instruções normativas para o controle de sua eliminação em território nacional, como a Lei Nº 12.288/06, do estado de São Paulo, que trata da eliminação controlada de PCBs e seus resíduos, bem como, a descontaminação de equipamentos que contenham PCBs no estado (SÃO PAULO, 2006). Em âmbito federal, existe a resolução CONAMA Nº 09/93, que trata do destino adequado, transporte e armazenamento de óleos lubrificantes que contenham PCBs, em todo o território nacional, e ainda, um projeto de lei da câmara dos deputados (Nº 128 de 2018) em tramitação, que trata da eliminação controlada de PCBs e seus resíduos no país (BRASIL, 1993; BRASIL, 2018).

Em 2001, os organoclorados foram reconhecidos pela Convenção de Estocolmo como poluentes orgânicos persistentes (POPs), que deveriam ter seu uso banido ou restrito nos países signatários da Convenção, incluindo o Brasil (UNEP, 2017). Os POPs compartilham algumas características como resistência a degradação, capacidade de bioacumular na biota e biomagnificar através da cadeia trófica e o transporte marítimo e atmosférico de longo alcance, permitindo que cheguem a regiões afastadas de suas fontes de origem e atinjam os mais diversos compartimentos ambientais. No ambiente marinho, devido às suas propriedades físico-químicas como lipofilicidade e a capacidade de bioacumular e biomagnificar na biota, atingem principalmente as espécies de topo da cadeia trófica, como os mamíferos. Tendo isso em vista, os mamíferos marinhos costumam ser ótimos indicadores da contaminação ambiental por organoclorados e são utilizados com frequência nesse tipo de análise (Ross, 2000). No Brasil, há diversos estudos investigando a contaminação dos mamíferos marinhos por POPs (Alonso *et al.*, 2012; Dorneles *et al.*, 2010, Leonel *et al.*, 2008; Quinete *et al.*, 2011), porém não existe uma revisão abrangente sobre o ocorrência e monitoramento de organoclorados. Aguilar *et al.* (2002), apontou a existência de algumas lacunas que ainda precisavam ser preenchidas com o desenvolvimento de outros estudos, entre elas, a ausência de métodos de amostragem padrão para comparações entre os níveis de contaminação e a ausência de estudos desse tipo no hemisfério sul. Uma revisão mais atual

(Law, 2014) buscou determinar o panorama de contaminação dos mamíferos marinhos por POPs com o propósito de avaliar as tendências temporais, incluindo estudos no hemisfério sul, constatando um decréscimo nas concentrações de POPs em países cuja legislação já está há mais tempo em vigor, além de uma variabilidade nas concentrações de outros POPs.

Revisões sistemáticas da literatura podem auxiliar nos rumos de outras pesquisas que precisam ser desenvolvidas, além de fornecer um conjunto de dados de extrema relevância, tanto científica, quanto legal, quando avaliamos o cumprimento de legislações vigentes. Tendo isso em vista, o presente trabalho consiste na primeira revisão sobre a ocorrência de organoclorados em mamíferos marinhos da costa brasileira.

2 HIPÓTESES

As concentrações e o padrão de ocorrência dos compostos organoclorados em mamíferos marinhos da costa brasileira variam de acordo com os hábitos alimentares e habitat das espécies, bem como em função do tipo e intensidade das pressões antrópicas próximas às áreas de estudo.

3 OBJETIVOS

3.1.1 Objetivo Geral

Identificar padrões de ocorrência e distribuição espacial, temporal e entre espécies dos compostos organoclorados em mamíferos da costa brasileira, bem como, as principais lacunas e necessidades de estudos futuros.

3.1.2 Objetivos Específicos

- Apontar os locais que apresentam uma lacuna maior em relação ao desenvolvimento desse tipo de estudo;
- Determinar os níveis de concentração de poluentes orgânicos persistentes por região e por espécie;
- Comparar o estado de contaminação das quais espécies mais estudadas, bem como, indicar as que necessitam de um maior número de estudos;
- Avaliar as concentrações reportadas em função das características da área adjacente (agrícola, urbana e industrial);

4 METODOLOGIA

A busca dos artigos foi dividida em três etapas: Primeira triagem, segunda triagem e busca complementar. O intervalo de tempo das publicações incluídas na revisão é entre 2002, ano do primeiro estudo publicado e revisado por pares sobre o tema, e janeiro de 2023. Para que um o artigo fosse selecionado, deveria cumprir 3 critérios: ter sido realizado na costa brasileira; ter avaliado a contaminação de mamíferos marinhos por organoclorados; apresentar o valor das concentrações para os POPs analisados.

A primeira triagem foi feita na base *Science Direct*, em maio de 2021, utilizando a seguinte combinação de palavras-chave: POPs; marine mammals, organochlorine e Brazil. A base *Science Direct* é limitada na combinação de palavras-chave, por isso quando combinados muitos termos, ainda que similares, a busca retorna um volume muito pequeno de artigos, nesse sentido, optou-se por utilizar apenas os termos mais importantes para a pesquisa, com um retorno de 250 documentos. Após a pesquisa inicial, foi feita uma pré-seleção de artigos com a utilização da ferramenta de filtragem por tipo de documento da própria *Science Direct*. A pré-seleção teve como intuito filtrar apenas artigos de pesquisa e descartar previamente qualquer outro tipo de documento, como resumos, capítulos de livro e artigos de revisão. Na pré-seleção, apenas as caixas contendo “Research articles” e “Short communications” mantiveram-se marcadas, com um retorno de 87 documentos que tiveram seus resumos analisados. Destes, apenas 9 cumpriram os critérios de seleção para compor a revisão.

A segunda triagem de artigos foi feita em junho de 2021 na base *Scopus*, a qual permite uma combinação de palavras-chave de várias formas, fazendo com que o resultado da busca seja mais específico. Tendo isso em vista, utilizamos a seguinte combinação de palavras-chave: “POPs” OR “persistent organic persistent” OR “organochlorine” OR “DDT” OR “PCB” OR “CHL” AND *Brazil AND “marine mammal” OR “pinnipedia” OR “dolphin” OR “cetacea” OR “sirenia”. Ao todo, a busca retornou 31 documentos, dos quais 21 cumpriam todos os critérios de seleção, mas 8 deles já haviam sido selecionados na primeira triagem, portanto, foram selecionados da segunda triagem apenas 13 artigos.

A terceira triagem de artigos consistiu em uma busca complementar no *Google Scholar* e na lista de referências de outros artigos, entre maio de 2021 e janeiro de 2023. A busca complementar permitiu a seleção de mais 3 artigos para compor a revisão, totalizando 25.

5 RESULTADOS

Os resultados da presente dissertação serão apresentados na forma de artigo científico, conforme permitido pelo regulamento interno do PPGOCEANO.

Polychlorinated biphenyl and chlorinated pesticides concentrations and profiles in marine mammals from Brazilian waters: a review

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5.1 ABSTRACT

Marine mammals have been used in the study of contamination of the marine environment by organochlorines, thanks to the bioaccumulation potential they present for these contaminants. In Brazil, several studies have sought to determine the contamination of marine mammals by organochlorines, but there is no comprehensive review on the contamination of these species along the coast. In this review, we assessed the patterns of occurrence and distribution of organochlorines in marine mammals along the Brazilian coast. The search and selection of articles was divided into two screenings in the Science Direct (1^a screening) and Scopus (2^a screening) databases, in addition to a complementary search on Google Scholar and in the reference list of the articles selected in the first two screenings. 25 articles were evaluated, with the largest number of studies concentrated in the Southeast region, followed by the South and Northeast regions. No studies were found in the northern region. The most studied species were *Sotalia guianensis*, *Pontoporia blainvilie* and *Stenella frontalis*, respectively. The most studied organochlorines were PCBs and DDTs, with higher concentrations in individuals collected in the southeast region, which may be related to the fact that this region is one of the most impacted by industrial activities, urbanization and

agricultural development.. Only four studies analyzed temporal trends of organochlorines in marine mammals. The results of this study provide a comprehensive database that can help in the development of public policies in Brazil related to the control and monitoring of organochlorines, as well as the development of conservation strategies for marine mammal species that occur on the coast.

Key words

POPs; marine pollution; cetaceans;

5.2 INTRODUCTION

Organochlorine contaminants comprise a family of several groups of compounds, such as PCBs, DDTs, HCB, HCHs, Mirex and CHLs, with application in the industry, agriculture and disease vector control (Barra *et al.*, 2002). These compounds present high toxicity, resistant to degradation, tendency to bioaccumulation and biomagnification (Tanabe, 2002). Moreover, they became widely distributed geographically due to volatility and transport through atmospheric circulation (Wania and Mackay, 1996). Therefore, since 2001, several organochlorines were recognized by the Stockholm Convention as persistent organic pollutants (POPs), which should have their use banned or restricted by the signatory countries (UNEP, 2017).

Even though manufacturing and use of organochlorine compounds were both banned or limited to specific applications in several nations by 1970s - 1980s, they are still widely reported in the marine environment with heavy burden, especially in high trophic level species (Dorneles *et al.* 2013; Oliveira-Ferreira *et al.*, 2021; Megson *et al.*, 2022). The reasons are the organochlorine high persistence together with the slow and continuous release from old equipment, stockpiles, waste dumps/landfills and e-waste handling as well as unintentional production, such as those emitted as by-products of industrial thermal processes (e.g. cement, iron and steel industry) (Qi *et al.*, 2013; Debela *et al.*, 2020; Mao *et al.*, 2021;). Actually, for PCBs occurrence in China, the last appears to be as important as intentional production (Cui *et al.* 2015); however, such data are scarce for other countries.

Additionally, recent studies have called attention to the impact of climate change on the fate and behavior of POPs since they are influenced by temperature, wind speed, precipitation, and solar radiation. While the increase in temperature has the potential to enhance long-range transport of POPs to the Poles as well as to remobilize compounds

trapped in the ice, it also can cause a faster degradation of these chemicals. Thus, climate change-driven processes on POPs cycling and distribution could have serious, but not yet well understood, consequences on exposure and accumulation on living organisms (Valle *et al.*, 2007; Nadal *et al.*, 2015; Borga *et al.*, 2022).

One of the groups more vulnerable to organochlorine contamination, regarding both exposure and toxicity, are marine mammals, especially toothed whales (Odontoceti) (Tanabe *et al.* 1994). They are long-lived organisms, predators that occupy a high level in the trophic web and have low capacity to metabolize organochlorine compounds (Tanabe *et al.*, 1988). On the other hand, they are very useful to assess the occurrence and bioavailability of organochlorine in the marine environment serving as a model for human exposure contamination from seafood consumption. From a toxicological perspective, they are an important tool to study long-term effects of pollution by POPs (Aguilar, 1987). Studies have reported that organochlorines can contribute to immunosuppression, reproductive system implications, and act as endocrine disruptors (Sormo *et al.*, 2009, Tanabe *et al.*, 2002; Murphy *et al.*, 2018; Kannan *et al.*, 1989). However, the lack of a more comprehensive understanding of toxicological consequences makes it difficult to establish threshold values for different groups of cetaceans.

Brazil has a rich and diverse marine environment that is home to many species; only among marine mammals are approximately 54 species (Abreu *et al.*, 2020). Unfortunately, this environment also suffers several anthropogenic pressures resulting from the high loads of pollutants released to the ocean, especially near urban centers, industrial complexes and agricultural areas. In this context, of organochlorine compounds, specially PCBs and DDTs, are one of the main groups of contaminants detected in the Brazilian marine environment (Yogui *et al.*, 2010; Souza *et al.*, 2008; Taniguchi *et al.*, 2016; Lailson-Brito *et al.*, 2012; Sánchez-Sarmiento *et al.*, 2017; Combi *et al.*, 2013).

Despite the well-established threat these compounds pose to marine mammals there is no comprehensive review on the patterns of organochlorine monitoring in marine mammals from Brazil. Therefore, this review aimed: a) systematically summarize the spatial distributions of organochlorine contaminants in marine mammals species occurring in Brazilian waters by screening existing publications; b) assess differences in POPs concentrations among species considering habitat and ecology; c) investigating temporal trends; and d) discuss the existing gaps in organochlorine monitoring. This review will

provide a scientific basis for disentangling environmental contamination to organochlorine in Brazil and help to better implement the actions of the Stockholm Convention on POPs.

5.3 MATERIALS AND METHODS

5.3.1 Article selection

Data were obtained exclusively from peer-reviewed articles published up to January 2023 and found in two online publication databases Science Direct (First screening) and Scopus (Second screening). To test the most relevant keywords in the selected articles related to the theme, we used the bibliometrix tool together with the R software (Figure 1). In addition, a complementary search was performed using Google Scholar and the reference list of selected articles in the Science Direct and Scopus databases. Grey literature (theses, dissertations, book chapters), review articles and other documents were discarded (Figure 2). More details regarding the article selection and the list of compiled articles can be found in the Supplementary Information section (SI).



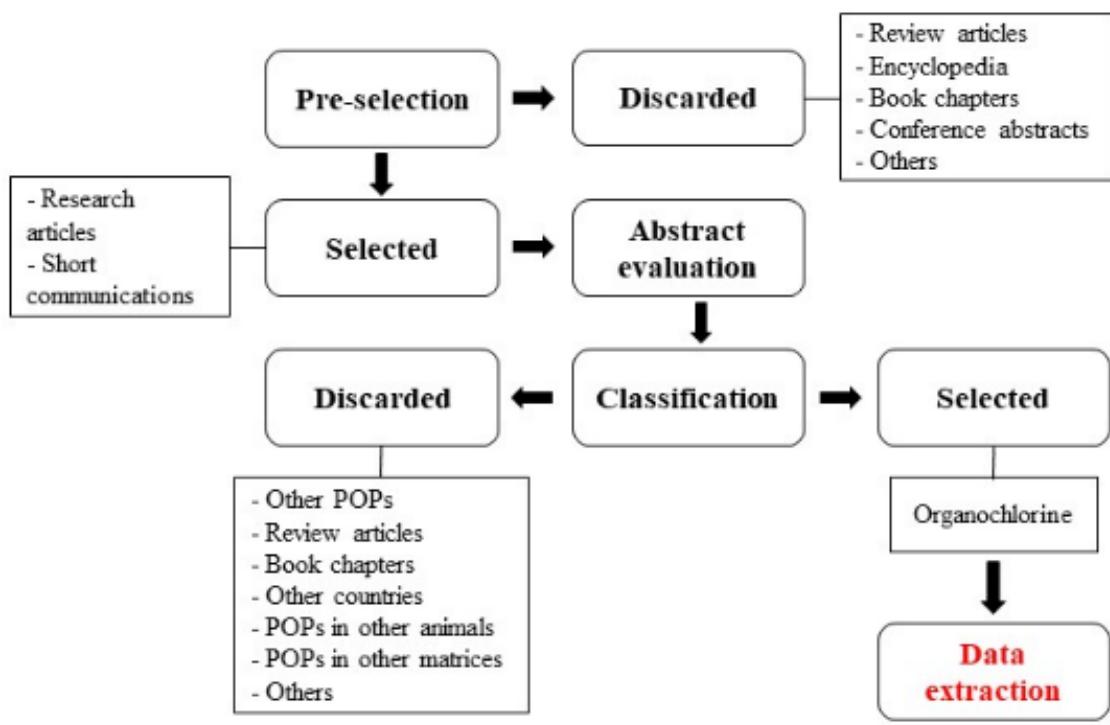
Figure 1: Word cloud on studies of contamination of marine mammals by organochlorines in Brazil. Bibliometrix (Scopus and Science Direct).

(A)

First screening

(Science Direct)

Keywords: POPs; Marine mammals; Organochlorine; Brazil;



(B)

Second screening

(Scopus)

Keywords: “POPs” OR “persistent organic persistent” OR “organochlorine” OR “DDT” OR “PCB” OR “CHL” AND *Brazil AND “marine mammal” OR “pinnipedia” OR “dolphin” OR “cetacea” OR “sirenia”

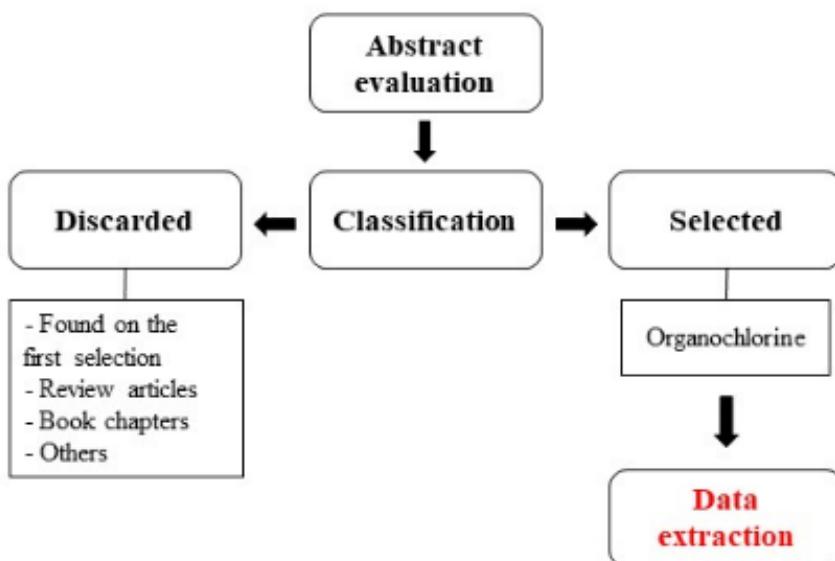


Figure 2: Methodology of search and selection of articles. (A) First screening. (B) Second screening.

5.3.2 Analytical Considerations and Data Quality

Even though the protocols for organochlorine analysis were well established and certified standard materials were available for several matrices, a global interlaboratory assessment showed that many laboratories still have problems to obtain a good reproducibility (standard deviations <25%), specially for organochlorine pesticides (de Boer *et al.* 2022). Therefore, all data included here are from articles that reported some sort of quality control (blanks, replicates, use of certified standard materials, etc).

From the selected publications, the following data were collected: study area, species, year of collection, number of samples, sex, and organochlorine concentrations. Several available data consisted mainly of mean concentrations, but, whenever it was available, minimum and maximum values were also extracted and used in the discussion.

Organochlorine concentrations were all expressed in lipid basis to minimize the heterogeneity due to distinct nutritive conditions and laboratory methods used for lipid extraction. Although most of the samples presented the concentrations in lipid weight, some authors presented the concentrations of organochlorines in wet weight. In these cases, to standardize the concentrations, we converted the values in wet weight to lipid weight using the lipid content of the sample. If the value was not available, the mean value of 70% (lipid content) was used as suggested by Aguilar *et al.* (2002).

5.4 RESULTS AND DISCUSSION

5.4.1 General overview

A total of 25 articles, published from 2003 to 2023, reported concentrations of PCBs and organochlorine pesticides in 13 different species and one sub species from the southern to northeast coast of Brazil (Table 1, Table S1). The majority ($n = 23$) of articles focussed on cetaceans (odontocetes), one in pinnipeds (otariids) and one in sirenians; no studies on mysticeti were identified (Table S1). The most studied species, according to the number of publications in which they appear, were: *Sotalia guianensis*, *Pontoporia blainvilliei* and *Stenella frontalis* (Table 1, Figura S1); thus a more detailed discussion was presented for these species. Almost all studies ($n = 23$) were carried out with samples collected from the Southern and Southeastern region (Figure 3) which covers less than 50% of the total Brazilian coastal extension (~ 8000 km). It reflects the lack of an even distribution of research facilities prepared to conduct such analysis around the country, as well as a greater concentration of research groups in the Southeast and South regions of Brazil.

Table 1: PCBs and chlorinated pesticides concentrations and PCBs/DDTs ratio in marine mammals of Brazil.

Specie	Location	Survey Years	Tissue	n/sex	PCBs	DDTs	HCHs	HCB	Mirex	CHLs	PCBs/DDTs	Reference
<i>Sotalia guianensis</i>	Guanabara Bay, Rio de Janeiro	1996	blubber	1M	12 843	-	-	-	-	-	-	Da Silva <i>et al.</i> (2003)
				1F	3 740	-	-	-	-	-	-	
<i>Sotalia guianensis</i>	Cananeia Estuary, São Paulo	1996 - 2001	blubber	4M	5 700 (1 610 - 7 600)	72 300 (7 240 - 125 000)	28 <td>18 (9 - 22)</td> <td>149 (129 - 178)</td> <td>33 (21 - 47)</td> <td>12,7</td> <td data-kind="parent" data-rs="2">Yogui <i>et al.</i> (2003)</td>	18 (9 - 22)	149 (129 - 178)	33 (21 - 47)	12,7	Yogui <i>et al.</i> (2003)
				5F	3 740 (200 - 9 220)	6 810 (541 - 9 900)	6 <td>13<br (<1="" -="" 24)<="" td=""/><td>153 (14 - 312)</td><td>16 (1 - 22)</td><td>1,8</td><td data-kind="ghost"></td></td>	13 <td>153 (14 - 312)</td> <td>16 (1 - 22)</td> <td>1,8</td> <td data-kind="ghost"></td>	153 (14 - 312)	16 (1 - 22)	1,8	
<i>Sotalia guianensis</i>	South Coast São Paulo and Paraná	1997 - 1999	blubber	9M(i)	9 700 (2 800 - 22 000)	22 000 (3 900 - 64 000)	15 (4 - 61)	16 (4 - 28)	-	150 (50 - 500)	2,3	Kajiwara <i>et al.</i> (2004)
				8M(m)	34 000 (10 000 - 79 000)	52 000 (12 000 - 150 000)	19 (8 - 38)	68 (7 - 400)	-	420 (150 - 1 100)	1,5	
				4F(i)	12 000 (6 000 - 20 000)	14 000 (1 400 - 25 000)	12 <td>25 (2 - 57)</td> <td>-</td> <td>180 (6 - 310)</td> <td>1,16</td> <td data-kind="ghost"></td>	25 (2 - 57)	-	180 (6 - 310)	1,16	
				5F(m)	11 000 (1 300 - 49 000)	7 600 (1 000 - 29 000)	2 <td>19 (2 - 79)</td> <td>-</td> <td>150 (15 - 680)</td> <td>0,7</td> <td data-kind="ghost"></td>	19 (2 - 79)	-	150 (15 - 680)	0,7	
<i>Sotalia guianensis</i>	Guanabara Bay, Rio de Janeiro	2000 - 2004	blubber	7M/4F/1IN	34 810 (6 663 - 99 175)	7 953 (2075 - 21 504)	-	46 <td>-</td> <td>-</td> <td>0,2</td> <td data-kind="parent" data-rs="3">Lailson- Brito <i>et al.</i> (2009)</td>	-	-	0,2	Lailson- Brito <i>et al.</i> (2009)
	Sepetiba/Illa Grande Bays, Rio de Janeiro	1997 - 2005		3M/2F	12 294 (1745 - 25 482)	3 863 (652 - 9 998)	-	29 (13 - 78)	-	-	0,3	
	Paranaguá Bay, Paraná	1995 - 2002		13M/2F	4 564 (765 - 14 333)	5 757 (980 - 23 555)	-	41 <td>-</td> <td>-</td> <td>1,3</td> <td data-kind="ghost"></td>	-	-	1,3	
<i>Sotalia guianensis</i>	Santos, São Paulo	2004 - 2005	blubber	2M	45 610	43 190	120	120	1 010	300	0,9	Alonso <i>et al.</i> (2010)
	North Coast, São Paulo			1F	27 860	24 570	40	130	240	290	0,9	
<i>Sotalia guianensis</i>	South Coast, São Paulo	2003	blubber	1M	1 970	5 870	11	67	46	14	3	Yogui <i>et al.</i> (2010)
<i>Sotalia guianensis</i>	North Coast, Rio de Janeiro		liver	10	24 312	-	-	-	-	-	-	Quinete <i>et al.</i> (2011)
<i>Sotalia guianensis</i>	Rio de Janeiro		blubber	7M	100 290 (56 096 - 160 355)	-	-	-	-	-	-	Dorneles <i>et al.</i> (2013)
				4F	107 865 (34 662 - 279)	-	-	-	-	-	-	

					407)							
<i>Sotalia guianensis</i>	North Coast, Ceará	2005 - 2011	blubber	1M/2F/IN	2 230 (20 - 3 850)	330 (6 - 630)	<3	20 (<3 - 40)	80 (20 - 120)	-	0,1	Santos-Neto et al. (2014)
	Metropolitan region, Ceará			4M/4F	7 350 (40 - 17 300)	1 110 (60 - 1 910)	40 (<2.6 - 50)	7 (<3 - 10)	90 (40 - 150)	-	0,1	
	South Coast, Ceará			7M/6F	1 120 (30 - 3 640)	300 (3 - 820)	30 (<3 - 80)	6 (<3 - 8)	70 (20 - 160)	-	0,3	
<i>Sotalia guianensis</i>	Central-North Coast, Rio de Janeiro	2003 - 2012	muscle	5M	5 584 (3 880 - 8 740)	-	-	-	-	-	-	Lavandier et al. (2015)
				3F	7 590 (3 269 - 7 010)	-	-	-	-	-	-	
			liver	5M	7222 (5 370 - 9 990)	-	-	-	-	-	-	
				3F	13073 (1 520 - 11 400)	-	-	-	-	-	-	
<i>Pontoporia blainvillei</i>	South Coast, São Paulo and Paraná	1997 - 1999	blubber	11M(i)	2 100 (320 - 4 900)	1 700 (580 - 3 600)	2 (<1 - 4)	11 1 - 21)	-	40 (5 - 94)	0,8	Kajiwara et al. (2004)
				5M(m)	5 300 (1 800 - 12 000)	9 900 (1 800 - 35 000)	4 (3 - 5)	11 (9 - 13)	-	64 (38 - 110)	1,9	
				8F(i)	2 200 (970 - 5 000)	2 800 (670 - 3 200)	7 (1 - 5)	10 (6 - 18)	-	38 (17 - 74)	1,3	
				5F(m)	2 300 (1 500 - 3 000)	1 200 (950 - 1 400)	5 (2 - 7)	9 (6 - 12)	-	39 (31 - 47)	0,5	
<i>Pontoporia blainvillei</i>	South Coast, São Paulo	1999 - 2001	blubber	4M	5 590	3 080	3	54	-	3		Yogui et al. (2010)
				4F	2 350	1 100	<2	13	-	24 900		
<i>Pontoporia blainvillei</i>	South Coast, Rio Grande do Sul	1994 - 2004	blubber	73	5 120 (1 270 - 10 555)	1 037 (230 - 3 447)	-	30 (5 - 47)	62 (34 - 106)	82 (11 - 261)		Leonel et al. (2010)
<i>Pontoporia blainvillei</i>	South Coast, São Paulo		blubber	7M/1F	3184 (909 - 5849)	1501 (445 - 5811)	-	52 (10 - 61)	-	-		Lailson-Brito et al. (2011)
	North Coast, São Paulo			1M	3709	1554	-	48	-	-		
	Paraná			1F	996	1890	-	16	-	-		
<i>Pontoporia blainvillei</i>	North Coast, Rio de Janeiro	2011 - 2012	liver	4M/5F	12 125 (6 107 - 26 199)	-	-	-	-	-	-	Lavandier et al. (2016)
<i>Pontoporia blainvillei</i>	South Coast, São Paulo	2013 - 2015	blubber	4F (pregnant)	742 (208 - 1 596)	347 (130 - 635)	3 (<0.9 - 8)	9 (3 - 13)	12 (8 - 20)	<1		Barbosa et al. (2018)

				4 fetuses	480 (107 - 1 021)	263 (138 - 327)	< 0.9	7 (<1 - 16)	4 (<0.6 - 8)	5 (<1 - 16)				
<i>Pontoporia blainvillei</i>	Espírito Santo Coast	2003 - 2015	blubber	23	24 900 (312 - 66 000)	1 080 (117 - 29 900)	-	25 (0.6 - 60)	235 (36 - 865)	-		Oliveira-Ferreira et al. (2022)		
		2016 - 2019		10	23 600 (266 - 12 800)	1 520 (205 - 5 360)	-	27 (7 - 65)	189 (34 - 1 060)	-				
<i>Pontoporia blainvillei</i>	North Coast, São Paulo	2000 - 2018	blubber	5M(i)	2 268 (1 043 - 2 873)	427 (276 - 516)	3 (<nd - 8)	18 (6 - 19)	12 (<nd - 31)	<nd		Montone et al. (2023)		
	Central Coast, São Paulo			1M (m)	18 903	7114	<nd	21	259	36				
				3F(i)	2 627 (494 - 3 208)	461 (94 - 670)	0.1 (<nd - 3)	13 (6 - 19)	16 (<nd - 19)	0.1 (<nd - 19)				
				3F(m)	2 326 (1 842 - 2 809)	430 (351 - 509)	0.6 (<nd - 1.1)	8 (7 - 9)	35 (15 - 55)	<nd				
				23M(i)	4 418 (308 - 14 745)	1 013 (79 - 3 189)	0.05 (<nd - 21)	17 (3 - 57)	15 (<nd - 65)	11 (<nd - 48)				
				5M(m)	19 177 (2 833 - 42 192)	3 634 (561 - 7 186)	5 (<nd - 13)	31 (20 - 66)	69 (11 - 250)	36 (4 - 98)				
				16F(i)	2 608 (434 - 22 181)	382 (95 - 1 517)	0.05 (<nd - 25)	13 (9 - 134)	17 (<nd - 49)	5 (<nd - 123)				
				7F(m)	3 068 (326 - 8 594)	573 (150 - 2 405)	0.1 (<nd - 27)	12 (<nd - 69)	34 (4 - 67)	6 (<nd - 27)				
				34M(i)	1 003 (113 - 4 281)	409 (36 - 2 663)	0.05 (<nd - 86)	11 (<nd - 52)	20 (<nd - 52)	33 (<nd - 116)				
				18M(m)	3 070 (1 239 - 12 059)	898 (252 - 4 048)	3 (<nd - 343)	13 (9 - 24)	48 (21 - 317)	52 (<nd - 343)				
				17F(i)	1 057 (81 - 11 971)	370 (192 - 2 791)	0.05 (<nd - 66)	15 (<nd - 54)	18 (<nd - 54)	32 (<nd - 548)				
				5F(m)	797 (207 - 2 923)	155 (107 - 951)	8 (<nd - 9)	4 (<nd - 24)	20 (8 - 10)	<nd				
<i>Steno bredanensis</i>	South Coast, São Paulo	2000	blubber	1M	26 800	118 000	14	18	-	13		Yogui et al. (2010)		
<i>Steno bredanensis</i>	Rio de Janeiro	2000 - 2005	blubber	1M/2F	86 400 (790 - 139 000)	26 400 (1 560 - 50 000)	-	290 (80 - 490)	-	-		Lailson-Brito et al. (2012)		
<i>Steno bredanensis</i>	Rio de Janeiro		blubber	1M	74 705	-	-					Dorneles et al. (2013)		
				2F	84 794 (2510 - 167 079)	-	-	-	-	-				
<i>Steno bredanensis</i>	Central-North Rio de Janeiro	2003 - 2012	muscle	1M	17 4700	-	-	-	-	-		Lavandier et al. (2015)		
				4F	45 320 (3 630 - 152 600)	-	-	-	-	-				

				liver	1M	192 200	-	-	-	-	-	-	
					4F	101 657 (7 830 - 353 200)	-	-	-	-	-	-	
<i>Steno bredanensis</i>	Southeastern Brazil	2013 - 2019	blubber	19	212 900 (5 600 - 647 900)	38 400 (400 - 108 800)	-	200 (<10 - 50)	2 000 (100 - 7 200)	-			Oliveira- Ferreira et al (2021)
	Southern Brazil			4	70 300 (21 700 - 241 800)	23 500 (14 300 - 177 800)	-	200 (100 - 200)	2 700 (1 200 - 7 600)	-			
	Outer continental shelf, Southern Brazil			5	188 500 (64 000 - 293 600)	16 300 (10 500 - 106 400)	-		1 600 (1 300 - 18 800)	-			
<i>Stenella frontalis</i>	South Coast, São Paulo and Paraná	1997 - 1999	blubber	1M(i)	58 000	25 000	50	71	-	660			Kajiwara et al. (2004)
				1M(m)	60 000	48 000	27	84	-	690			
<i>Stenella frontalis</i>	South Coast, São Paulo	2001	blubber	1M	19 300	31 700	22	113	-	5			Yogui et al. (2010)
<i>Stenella frontalis</i>	South Coast, São Paulo	2004 - 2007	blubber	3M	12 730 (5 922 - 23 659)	4 187 (1882 - 6854)	14 (<2 - 20)	33 (5- 59.)	393 (252 - 673)	9 (4 - 15)			Leonel et al. (2012)
				3M/6F	7 701 (774 - 20 789)	2 084 (79 - 4934)	8 (<2 - 14)	10 (<2 - 21.8)	198 (74.3 - 413)	9 (<2 - 29)			
<i>Stenella frontalis</i>	Ceará	2006	blubber	1M	1 890	2 880	110	60	2 380				Santos-Neto et al. (2014)
<i>Stenella frontalis</i>	South Coast, São Paulo	2005 - 2014	blubber	4M	18 800	6 830	72	57	320	17			Méndez- Fernandes et al. (2016)
				6F	48 600	15 800	100	101	1 400	<1			
<i>Stenella frontalis</i>	São Paulo	2005 - 2015	blubber	25M	16 600	2 850	-	20	180				Méndez- Fernandes et al. (2018)
				21 F	6 500	1 400	-	10	100				
<i>Stenella frontalis</i>	Rio de Janeiro	2007 - 2012	muscle	4M/2F	9 030 (2 514 - 23 748)	-	-	-	-	-	-	-	Lavandier et al. (2019)
					12 621 (6 091 - 29 138)	-	-	-	-	-	-	-	
<i>Stenella coeruleoalba</i>	Ceará	2007	blubber	1F	960	1 070	60	100	100	-			Santos-Neto et al. (2014)
<i>Stenella longirostris</i>	Ceará	2008-2010	blubber	1M/1F	6 035	685	70	25	315	-			Santos-Neto et al. (2014)
<i>Tursiops truncatus</i>	South Coast, São Paulo	1997	blubber	1M	5 910	2 420	8	80	-	38			Yogui et al. (2010)
<i>Tursiops truncatus</i>	Rio de Janeiro	2000 - 2005	blubber	2M	11 800 (10 100 - 13 500)	5 000 (4 550 - 5 470)	-	50 (40 - 70)	-	-			Lailson- Brito et al. (2012)

<i>Tursiops truncatus</i>	Rio de Janeiro	2007 - 2012	muscle	3M/1F	⁴ 131 (1 598 - 7 783)	-	-	-	-	-	-	-	Lavandier et al. (2019)
			liver	3M/1F	6 734 (3 078 - 15 306)	-	-	-	-	-	-	-	Righetti et al. (2019)
<i>Tursiops truncatus gephyreus</i>	Laguna Estuarine System, Santa Catarina	2015 - 2016	blubber	7	9 285 (696 - 19 337)	5 304 (294 - 17 267)	-	50 (0.3 - 182)	158 (0.24 - 283)	50 (0.21 - 258)			Righetti et al. (2019)
	Patos Lagoon Estuary, Rio Grande do Sul			10	21 460 (5 444 - 51 491)	2 228 (99 - 5260)	-	28 (0.24 - 56)	308 (76 - 568)	46 (0.35 - 233)			
<i>Delphinus delphis</i>	South Coast, São Paulo and Paraná	1997 - 1999	blubber	1M	17 000	200	24	32	-	200			Kajiwara et al. (2004)
<i>Delphinus capensis</i>	Rio de Janeiro	2000 - 2005	blubber	2M/2M	8 400 (1 770 - 25 500)	2 400 (150 - 75 600)	-	40 <td>-</td> <td></td> <td></td> <td></td> <td data-kind="parent" data-rs="4">Lailson-Brito et al. (2012)</td>	-				Lailson-Brito et al. (2012)
<i>Orcinus orca</i>	Rio de Janeiro	2000 - 2005	blubber	1F	257 200	125 600	-	2 910	-	-			
<i>Pseudorca crassidens</i>	Rio de Janeiro	2000 - 2005	blubber	1F	63 700	17 900	-	280		-			
<i>Lagenodelphis hosei</i>	Rio de Janeiro	2000 - 2005	blubber	1M/3F	1 600 (600 - 4 370)	990 (410 - 1 680)	-	110 <td>-</td> <td>-</td> <td></td> <td></td> <td data-kind="ghost"></td>	-	-			
<i>Lagenodelphis hosei</i>	Ceará	2009 - 2010	blubber	2F	1 775	4 285	145	80	530	-			Santos-Neto et al. (2014)
<i>Trichechus manatus</i>	Pernambuco		blood	3M/5F	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10		Anzolin et al. (2012)
<i>Trichechus manatus</i>	Alagoas		blood	3M/1F	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10		Anzolin et al. (2012)
<i>Trichechus manatus</i>	Parafíba		blood	3M/1F	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10		Anzolin et al. (2012)
<i>Artocephalus australis</i>	Southern Brazil	1999	blubber	3M/5F	8 064	2 129	7	3	-	613			Fillmann et al. (2007)

*Concentrations are expressed in ng/g⁻¹ lw. Mean (min - max).

*ND – Not detected

*DL - Detection limited

Regarding a size, age and sexual maturation there is no consensus on how to classify the animals (juvenile vs adult or mature vs immature). Reproductive status would be preferred for this rating, since maternal transfer (via placenta and lactation) is a known detoxification process for females and plays an important role in organochlorine concentration (Borrell *et al.*, 1995; Aguilar & Borrell, 1994; Barbosa *et al.*, 2018). However, reproductive status determination implies sampling and processing the gonads which is time and money consuming and not always feasible. Consequently, several studies classify the animals just as juvenile or adult even though they did not explain what are the practical differences between the two groups. Most of these based such separation (juvenile vs adult) on the growth curve or age estimation from teeth layer analysis, implying that adults are mature individuals, even though it is not recommended to use size/age to assess sexual maturity due to the high plasticity in mammal sizes (Conversani *et al.*, 2020; Silva *et al.*, 2020). For studies that classify individuals between mature and immature, although it is not possible to state that there is a significant difference in concentrations due to the low number of samples, it is possible to observe that the highest concentrations of contaminants are generally found in mature individuals (for example Kajiwara *et al.*, 2004; Montone *et al.*, 2023).

As well as sexual maturation, sex is also an important parameter for OCs concentration and composition. However, due to the small number of samples, most studies did not report OCs data separating male and females or did not detect differences among sex.

Another reason for concern is the interference of the state of decomposition on compounds concentrations and patterns of distribution (Borrell & Aguilar, 1990). Most samples used for OCs analysis are from dead animals found stranded on the coast or incidentally caught during fishing operations. Even though there is a system that classifies the carcasses according to their decomposition state (for example, Geraci and Lounsbury, 1993), only few publications describe it.

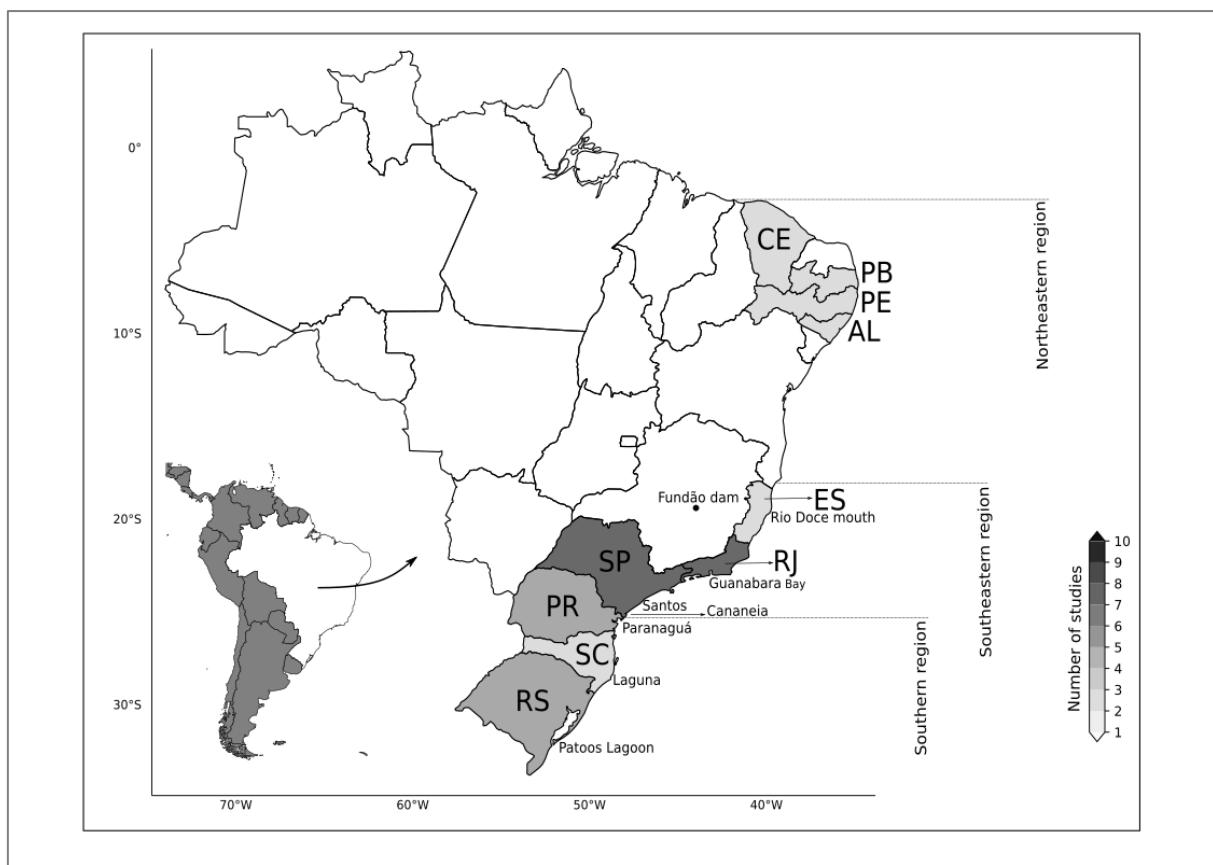


Figure 3: Map showing the Brazilian regions and state where studies were conducted as well as the main features described in the discussion section. RS: Rio Grande do Sul; SC: Santa Catarina; PR: Paraná; SP: São Paulo; RJ: Rio de Janeiro; ES: Espírito Santo, AL: Alagoas, PE: Pernambuco; PB: Paraíba; CE: Ceará.

5.4.2 *Sotalia guianensis*

S. guianensis (Guiana dolphin) has already been recorded in shallow waters (up to 50 m) from Southern Brazil (Florianópolis, SC) to Honduras (Da Silva *et al.*, 2010). They consume both marine and estuarine species such as demersal and pelagic fishes, neritic cephalopods, shrimps and crabs (Table S2) (Secchi *et al.*, 2018). Due to their coastal habits, the species is exposed to several threats including environmental degradation from the input of contaminants and, therefore, is on the red list (IUCN) with near threatened status (Lailson-Brito *et al.*, 2010; Yogui *et al.*, 2010; Santos-Neto *et al.*, 2014). They can exhibit residence patterns, such as those from Santos Estuary, Cananeia Estuary, Sepetiba Bay and Guanabara Bay (Nery *et al.*, 2008; Azevedo *et al.*, 2007; Santos *et al.*, 2001;).

The lowest PCBs average concentrations in *S. guianensis* are detected in samples from Ceará State (1 120 - 7350 ng g⁻¹ lw), Paranagua Bay (4 564 ng g⁻¹ lw) and Cananeia Estuary (3 740 - 5 700 ng g⁻¹ lw), whereas the highest values were detected in Santos (27 860 - 45 610 ng g⁻¹ lw) and Guanabara Bay (100 290 - 107 865 ng g⁻¹ lw) (Figure 4) (Santos-Neto

et al. 2014, Yogui *et al.* 2003, Dorneles *et al.* 2013, Lailson-Brito *et al.* 2010). Both Santos and Guanabara Bay are some of the most industrialized and urbanized areas along the Brazilian coast and well known for the occurrence of high levels of distinct classes of contaminants (Olivatto *et al.*, 2019; Baptista Neto *et al.*, 2006; Fontana *et al.*, 2012; Medeiros & Bícego, 2004; Nishigima *et al.*, 2001; Luiz-Silva *et al.*, 2001). Actually, Souza *et al.* (2018) showed the PCBs levels in Santos are related to the urban and industrial development of the region and even nowadays values can be a threat to the marine biota. On the other hand, Cananéia is historically an agricultural region and Ceará State, specially in the non-metropolitan area, is less industrialized and centered in other economic activities, such as fishing and tourism (Santos-Neto *et al.* 2014).

According to the authors, the high PCBs concentrations reported in species from the Guanabara Bay ($> 100\,000 \text{ ng g}^{-1} \text{ lw}$) - and also some of the highest reported for small coastal cetaceans in the world - is explained by the high anthropogenic status of the area (Dorneles *et al.* 2013). Other studies found lower PCBs values in *S. guianensis* from the same area: 13 000 $\text{ng g}^{-1} \text{ lw}$ in samples from 1996 and 35 000 $\text{ng g}^{-1} \text{ lw}$ in samples from 2000 - 2004 (Silva *et al.* 2003, Lailson-Brito *et al.* 2010). It suggests an increase in PCBs levels over the last two decades, possibly related to remaining stocks of PCBs-containing equipment. Azevedo *et al.* (2017) observed a decline of approximately 37% in the population of *S. guianensis* from Guanabara Bay in the last two decades and suggested it may be strongly associated with environmental degradation, including exposure to contaminants. Therefore, these high concentrations claim for further investigation on the potential deleterious effects of PCBs on the *S. guianensis* resident population from Guanabara Bay.

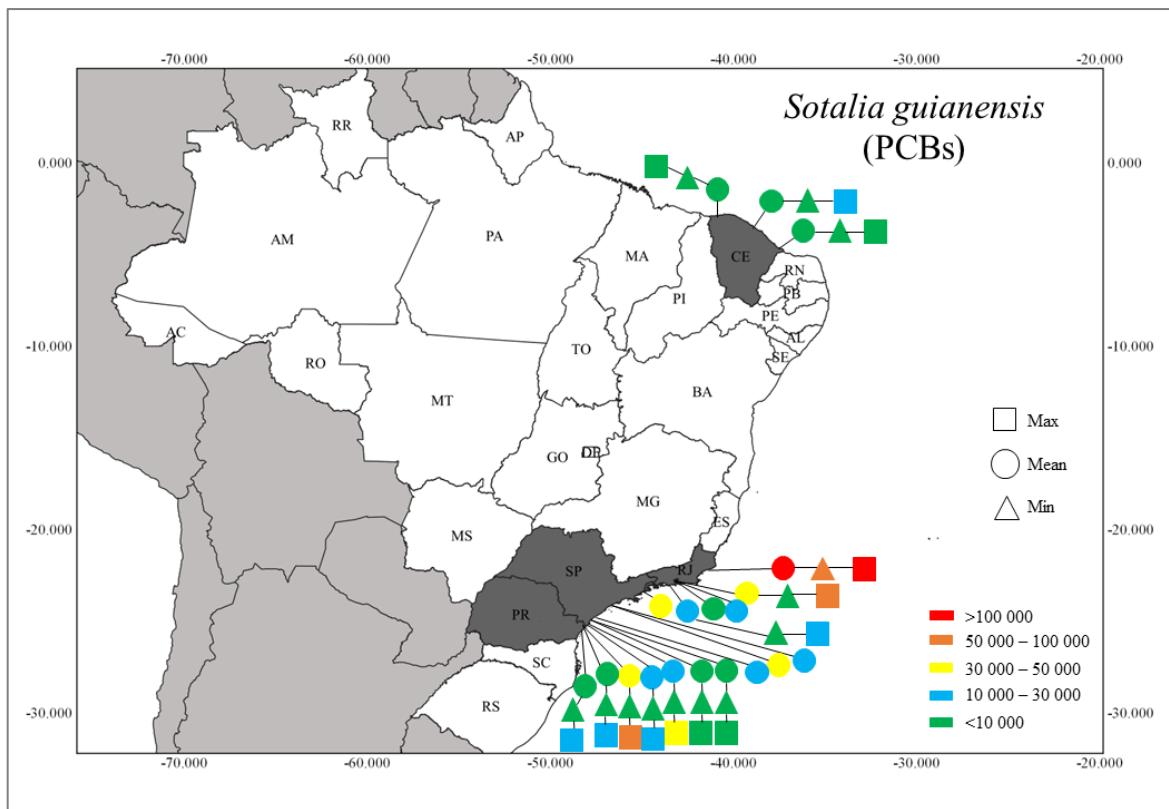


Figure 4: Mean, maximum and minimum concentrations of PCBs in *Sotalia guianensis* collected along the Brazilian coast. Only blubber samples are considered. Concentrations are expressed in ng g⁻¹ lw.

DDTs average concentrations in *S. guianensis* ranged from 300 ng g⁻¹ lw (South Coast, Ceará) to 72 300 ng g⁻¹ lw (Cananeia Estuary, São Paulo) (Figure 5) (Yogui *et al.* 2003, Santos-Neto *et al.* 2014). Cananeia is a well known area for DDT intensely used in the past (1970s - 1980s) and it explains the highest values detected in samples from South São Paulo and Paraná Coast. Actually, the DDT/PCBs ratios in these regions ranged from 1.3 (Paranaguá Bay, Paraná) to 12.3 (Cananéia Estuary, São Paulo). Male specimens always showed higher values for the ratio (12.8 vs 1.8 for Cananeia, 1.5 vs 0.7 for South São Paulo and Paraná Coast), even among young individuals (2.3 vs 1.16 South São Paulo and Paraná Coast). It seems to result from the differences among compounds detoxification through placenta and lactation transfers; Barbosa *et al.* (2018) reported that DDTs are easier than PCBs to transfer via placenta.

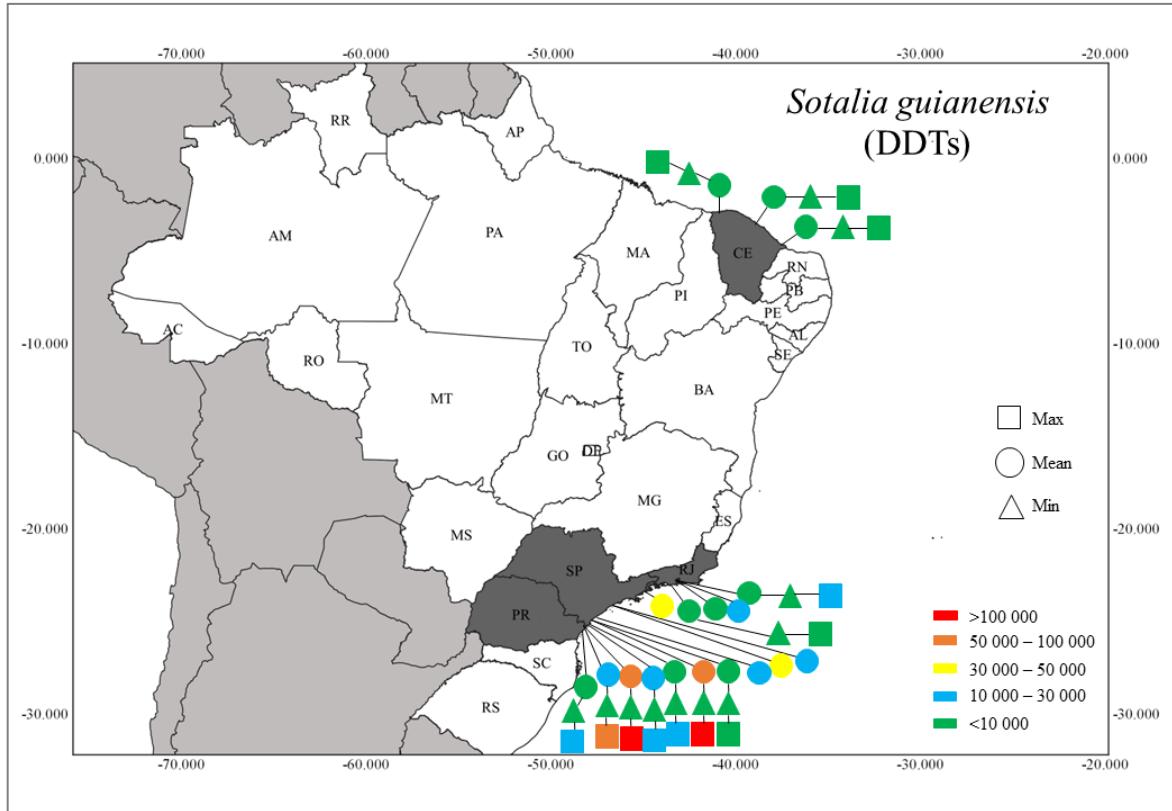


Figure 5: Mean, maximum and minimum concentrations of DDTs in *Sotalia guianensis* collected along the Brazilian coast. Only blubber samples are considered. Concentrations are expressed in ng g^{-1} lw.

5.4.3 *Pontoporia blainvilliei*

Pontoporia blainvilliei, also known as Franciscana, is a dolphin endemic to the Southwest Atlantic, distributed between the state of Espírito Santo, Brazil, and the Golfo San Matías, Argentina (Zerbini *et al.*, 2017). Franciscana dolphins have predominantly coastal and have occasionally estuarine habits, occur in shallow water, and feed on several species of demersal fish, cephalopods and crustaceans (Table S2) (Zerbini *et al.*, 2017;). *P. blainvilliei* is among the most endangered dolphin species in the South Atlantic, being classified as globally vulnerable and critically endangered in Brazil (ICMBIO, 2018; Zerbini *et al.*, 2017). According to Cunha *et al.* (2014), *P. blainvilliei* distribution is divided in eight Franciscana Management Areas (FMA), being five of them in the Brazilian territory (Figure S3). Nowadays, there is organochlorine data for only four of them (FMA Ia, FMA IIa, FMA IIb and FMA IIIa).

The highest PCBs mean concentrations in *P. blainvilliei* - considering only blubber samples - were reported in the Central Coast of São Paulo ($19\ 177\ \text{ng g}^{-1}$ lw) (Figure 6). The region is home of Cubatao Industrial complex and the largest harbor in South America, the

Port of Santos. On the other hand the lowest values were detected in the South Coast of São Paulo and Paraná (from 797 to 5590 ng g⁻¹ lw) (Montone *et al.*, 2023; Lailson-Brito *et al.*, 2011). Such high variation on PCBs values from these two regions appears to be related to age, sexual maturation and year of sampling.

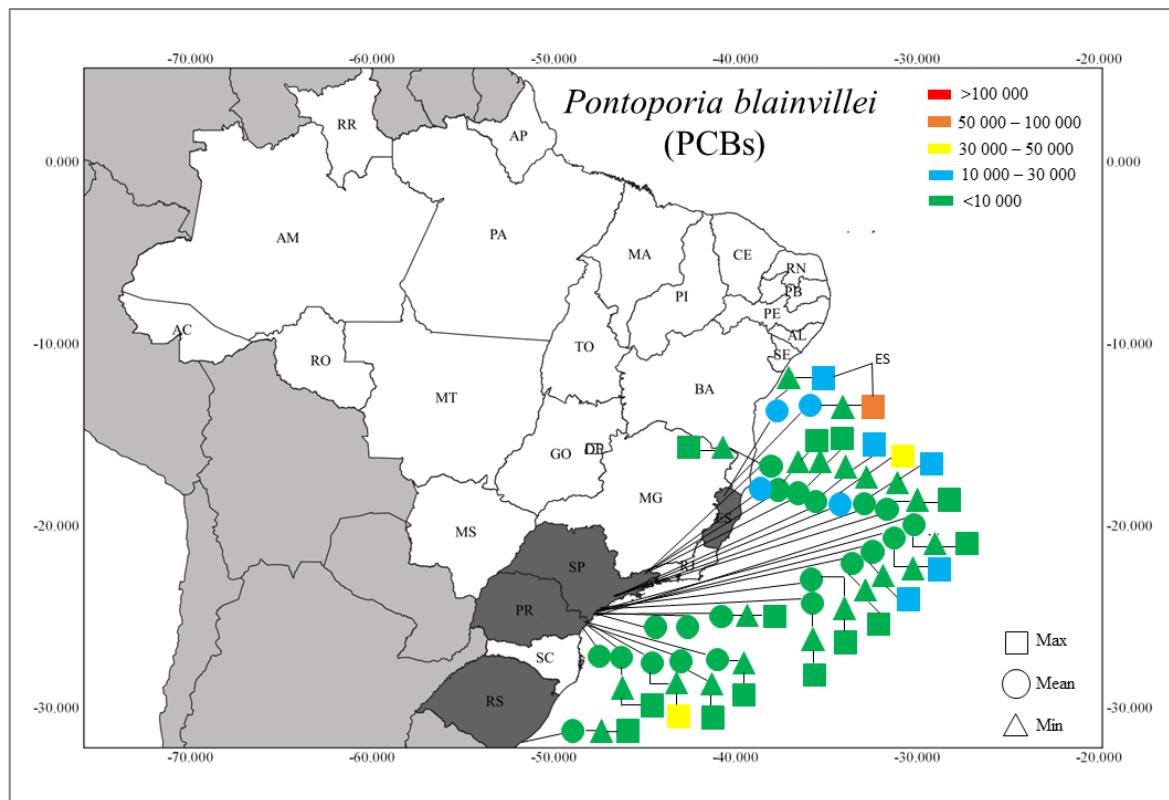


Figure 6: Mean, maximum and minimum concentrations of PCBs in *Pontoporia blainvilliei* collected along the Brazilian coast. Only blubber samples are considered. Concentrations are expressed in ng g⁻¹ lw.

For DDTs, both the highest as well as some of the lowest mean concentrations occurred in samples from the South Coast of São Paulo and Paraná (9 900 and 155-898 ng g⁻¹ lw) (Figure 7) (Kajiwara *et al.*, 2004; Montone *et al.*, 2023). It was probably caused due to the difference in the year of sampling; while the highest concentrations were detected in samples from 1997 - 1999, the lowest were from a more recent sampling (Montone *et al.* 2023, Kajiwara *et al.* 2004). When analyzing the pair mother-fetus, Barbosa *et al.* (2018) also reported low values for both PCBs and DDTs in Cananéia, São Paulo (mother: PCBs = 742 ng g⁻¹ lw, DDTs = 347 ng g⁻¹ lw and fetuses: PCBs = 480 ng g⁻¹ lw, DDTs = 263 ng g⁻¹ lw). It is a good example of transplacental transfer, where animals already exhibited pollutants levels even before they are born.

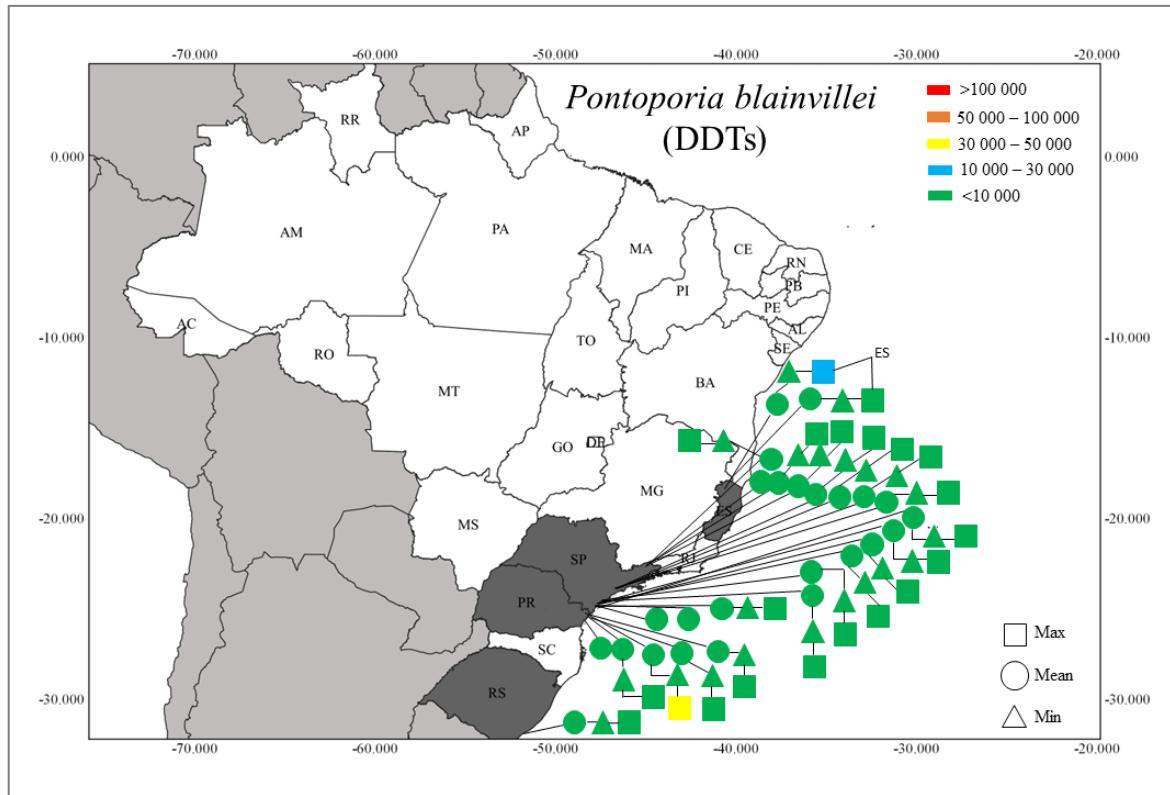


Figure 7: Mean, maximum and minimum concentrations of DDTs in *Pontoporia blainvilliei* collected along the Brazilian coast. Only blubber samples are considered. Concentrations are expressed in ng g⁻¹ lw.

Oliveira- Ferreira *et al.* (2022) assess POPs contamination in *P. blainvilliei* from FMA Ia, the smallest and more isolated population of the species, before and after Fundão dam collapsed in Minas Gerais. This accident released millions of cubic meters of mud containing mining residue through the Rio Doce to the marine environment with the potential to influence the dynamics of organic compounds in the environment with severe consequences to all species, but mostly to endangered populations. More than differences in POPs levels, the authors reported a shift from a predominance of PCBs in the species before the accident toward a predominance of DDTs after the accident. However, such results should be interpreted with caution, since data from before the dam collapse resulted from a group of individuals sampled over a 12 years span, and such differences between the two groups could be a temporal trend due to other causes. For example, Alava *et al.* (2011) detected an increase in DDT levels for *Zalophus wollebaeki* (Galapagos sea lion) in 2005-2008 due to a rise in their use.

5.4.4 *Stenella frontalis*

The Atlantic spotted dolphin (*Stenella frontalis*) is an endemic species of the Atlantic Ocean that occurs from tropical to warm temperate waters. They occur from the continental shelf (20 - 200 m) to the continental shelf slope (~1000 m), (Braulik *et al.*, 2018; Moreno *et al.*, 2005). In the Southwest Atlantic (SWA), especially off the coast of Brazil, the species tends to prefer more coastal habitats and feeds on a variety of pelagic and benthic fish, cephalopods and benthic invertebrates (Table S2) (Braulik *et al.*, 2018. Moreno *et al.*, 2005). *S. frontalis* is on the IUCN Red List of Threatened Species with the status of Least Concern, with incidental fishing being the main threat to the species (Braulik *et al.*, 2018). However, as a species with predominantly coastal habits in Brazil, pollution cannot be ruled out as an important source of threat to these individuals. Even though some population separations are already known, especially in the USA, there is still a lack of information about their population structure for most parts of the Atlantic Ocean. Moreno *et al.* (2004) identified the occurrence of *S. frontalis* in two distinct regions, one north of 6°S and other between 21°S and 33°S, suggesting that there are at least two distinct populations along the Brazilian coast.

The oldest article regarding PCBs and DDTs in *S. frontalis* reported values of 59 000 and 36 500 ng g⁻¹ lw, respectively, in two males from the South Coast of São Paulo and Paraná States sampled in 1997-1998 (Figures 8 and 9) (Kajiwara *et al.* 2004). The following studies reported, in general, decreasing values of both groups of compounds suggesting a temporal trend (Yogui *et al.* 2010, Leonel *et al.* 2012, Mendez-Fernandez *et al.* 2018). However, most of them analyzed a limited number of samples making it difficult to affirm any temporal trend. More recently, Mendez-Fernandez *et al.* (2018) investigated POPs occurrence and trends in *S. frontalis* from São Paulo coast and reported a decrease in PCBs and DDTs concentrations from 2005 to 2015. Even though these studies used samples mostly from the South coast of São Paulo - an agriculture where DDTs were commonly used in the 1970s, they reported a PCBs/DDTs ratio higher than one. According to Leonel *et al.* (2014), the higher concentrations of PCBs than DDTs imply a larger influence from an industrialized region, such as Santos Harbour and Cubatão Industrial Complex located in the central coast of São Paulo. Actually, the former is the largest commercial harbor in South America and the latter is one of the most important petrochemical and metallurgical centers in Brazil (Bícego *et al.* 2006).

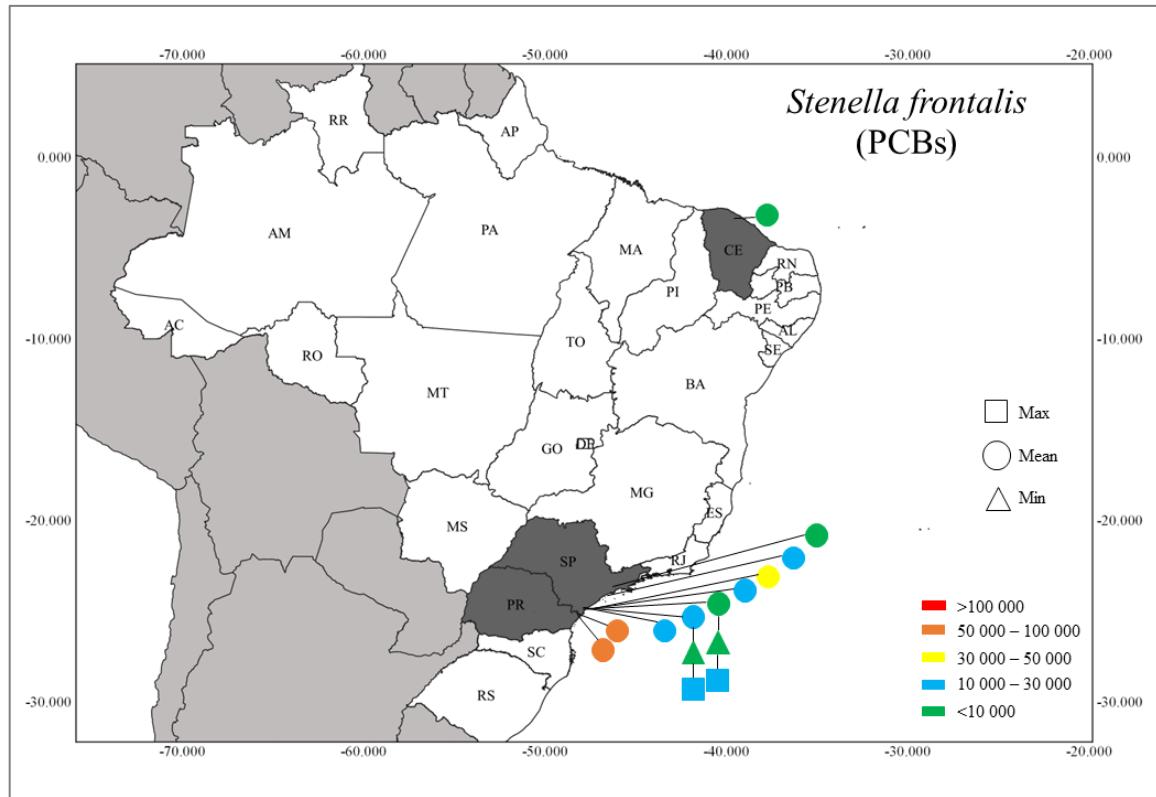


Figure 8: Mean, maximum and minimum concentrations of PCBs in *Stenella frontalis* collected along the Brazilian coast. Only blubber samples are considered. Concentrations are expressed in ng g^{-1} lw.

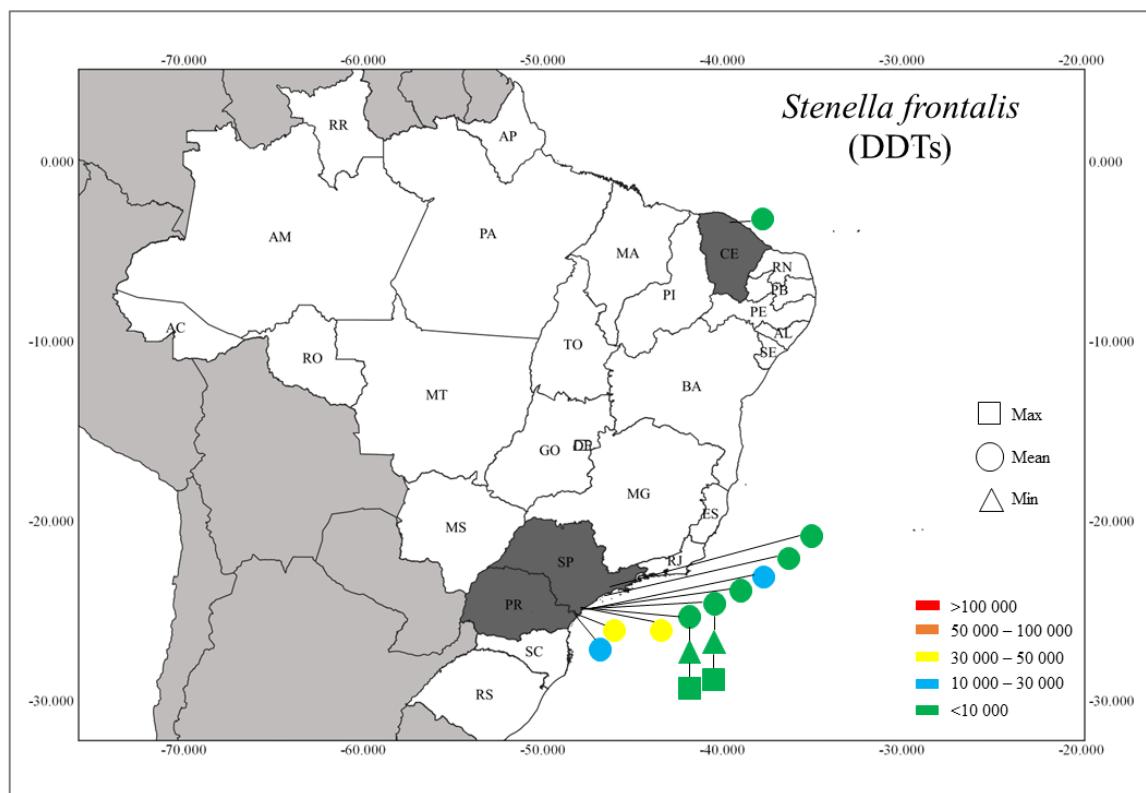


Figure 5: Mean, maximum and minimum concentrations of DDTs in *Sotalia guianensis* collected along the Brazilian coast. Only blubber samples are considered. Concentrations are expressed in ng g⁻¹ lw.

PCBs values in *S. frontalis* from the Rio de Janeiro coast are similar to those detected in São Paulo (Lavandier *et al.* 2019), suggesting that they comprise the same population. On the other hand, Santos-Neto *et al.* (2014) reported lower PCB and DDTs concentrations in *S. frontalis* from Ceará (northeast coast of Brazil) and a PCBs/DDTs ratio lower than one. Both results signal a separation between the populations as proposed by Moreno *et al.* (2004). However, due to the small number of samples, more studies should be conducted to test this hypothesis.

5.4.5 Other species

In addition to the three species described above, eight other species and one subspecies of cetaceans sampled off the Brazilian coast were reported in the article selected in the present study. Most of them ($n = 7$) occur in the continental shelf (*O. orca*, *P. crassidens*, *T. truncatus*, *S. bredanensis*, *D. delphis*, *S. coeruleoalba*, and *S. longirostris*), a sub species in coast waters (*T. truncatus gephycrus*) and one specie in open ocean (*L. hosei*) (Table 1 and Table S2).

Overall, for continental shelf species, the highest POPs concentrations were reported for *O. orca* followed by *S. bredanensis* > *P. crassidens* > *D. delphis* > *T. truncatus* > *S. longirostris* > *S. coeruleoalba* (Table 1). According to Lailson-Brito *et al.* (2012) the highest concentration in *O. orca* and *P. crassidens* are due to the trophic levels of both species that prey on other large vertebrates while the high concentrations in *S. bredanensis* are due to their habitat in brazilian waters, in the inner continental shelf. Although *S. bredanensis* habits oceanic waters deeper than 1000 m, in the Southern Atlantic Ocean they can also be found in shallower waters, over the continental shelf (Kiszka *et al.*, 2019; De Carvalho Flores & Ximenez, 1997). Oliveira- Ferreira *et al.* (2021) used POPs concentrations to distinguish three populations of *S. bredanensis* from Brazilian waters, two coastal (southeastern Brazil and southern Brazil) and one offshore (outer continental shelf of southern Brazil). For males PCBs values reached 647 900 ng g⁻¹ lw in the southeastern population, the highest level detected in marine mammals from Brazilian waters and also the highest for the species globally.

Besides studies in cetaceans, POPs levels were reported in two other groups of marine mammals from the Brazilian coast: one in pinnipeds (otariids) and one in sirenians. Anzolin *et al.* (2012) reported POPs concentrations below detection level for all blood

samples in West Indian manatees (*Trichechus manatus*) from Pernambuco, Paraíba and Alagoas States, Northeastern Brazil. Fillmann *et al.* (2007) analyzed POPs in eight tissues of juvenile Southern American fur seals and reported the highest values of PCBs and DDTs in blubber (7.8 ng g⁻¹ lw and 2.1 ng g⁻¹ lw, respectively).

Due to the variability of species and tissues analyzed, it is difficult to establish a comparison between the concentrations of contaminants for different regions sampled. In addition, the low number of samples from the 10 species and 1 subspecies reported here makes it difficult to establish comparisons even between individuals from different studies that belong to the same species. The low number of samples for different species is justifiable, since the organisms analyzed in this type of study are collected according to the opportunity. However, in order to be able to establish future comparisons, it is recommended to analyze a larger sample of the species reported here.

5.4.6 Temporal Trends

Only four studies assessed temporal trends for POPs in marine mammals from Brazilian waters, three of them for *P. blainvilliei* and one for *S. frontalis* (Leonel *et al.*, 2010; Oliveira-Ferreira *et al.*, 2022; Montone *et al.*, 2023; Mendéz-Fernandez *et al.*, 2018). Unlike studies from Northern Hemisphere that identified a decrease for POPs levels already before 2000 (Borrell & Aguilar, 2007; Aguilar & Borrell, 2005), no temporal trend was detected for PCBs and Mirex in *P. blainvilliei* from FMA IIIa over a 10 year period (1994 - 2004), while DDTs, CHLs and HCB concentrations showed only a modest decrease (Leonel *et al.* 2010). The lack of decrease in Mirex and PCBs concentrations could be a result of they high stability as well as the fact that Mirex importation was allowed until 1992 and its use probably continued for a few more years, and that PCBs continues to be release from remaining PCBs-containing equipments. Actually, according to Breivik *et al.* (2007), PCBs levels will not decline before 2010-2030.

On the other hand, more recent studies that include samples from a period after the Stockholm Conventions banned/regulated use and production of several organochlorinated compounds, detected more pronounced trends. Oliveira-Ferreira *et al.* (2022) analyzed *P. blainvilliei* from FMA Ia from 2003 to 2019 and reported a downward trend for DDTs, Mirex and HCB concentrations until 2015 when an increase was observed until 2019. This rise does not appear to be related to a more recent use of such compounds, but it suggests that the Fundão dam collapsed that happened in 2015 and dragged the riverbed made pesticides used

in agricultural activities in the area and stocked in the sediment available again (Soares *et al.*, 2013; Soares *et al.*, 2017). The fact that the levels of PCBs kept steady during the same period reinforce such hypotheses. In *P. blainvilleanus* from FMA IIa and FMA IIb a decrease in concentrations was observed from 2000 to 2018 for PCBs, DDTs, Mirex, CHLs, HCHs, but not for HCB (Montone, *et al.*, 2023). Additionally, Mendez-Fernandez *et al.* (2018) reported a decrease in both PCBs and DDTs concentrations for *S. frontalis* from 2005 to 2015.

Despite the fact that temporal trends show some decrease in POPs levels, it is worth to note that there are gaps regarding how much of each compound was produced/imported and how much is still stocked or being used in old equipment. Several countries do not present the historical and current record of the production and use of these products, while others keep this information confidential, making it difficult to quantify (Voldner & Li, 1995). Even though part of the total stock of PCBs in Brazil (~130,000 tons) was incinerated, pure PCBs and equipment with PCBs can still reach about 10,000 tons since after the prohibition, in 1981, equipment containing PCBs were still allowed to remain in use up to the end of their operational life (Fillmann and Leonel, 2011). Moreover, there are no data/studies about non-intentional production, e.g. as by-products of industrial thermal processes. Concerning DDTs, it was prohibited for agricultural purposes in 1985, but allowed for pest control of epidemic diseases (such as malaria) until 2009 (Brasil, 2009); the last registration of DDT importation was in 2001 (7000 kg) (Brasil, 2023). Such uncertainties could explain the lack of more pronounced temporal trends in POPs concentration in marine mammals from Brazilian waters.

5.4.7 Comparison of PCBs Levels to Effects Thresholds

Despite the known toxicity of organochlorine compounds in marine mammals, it is a challenge to link an observable effect in individuals to a specific compound exposure, because of the ethical and logistical constraints involving laboratory and field exposure studies as well as the potential synergistic and antagonistic interactions among substances make it difficult to evaluate their individual effects. However, comparisons with the existing threshold values are important to assess whether PCBs levels pose toxicological risks to the studied species.

One of the most used threshold values (PCBs = 17 000 ng g⁻¹ lw, for blubber) resulted from semi-field and field toxicity studies conducted with seals, otters and mink (Kannan *et al.* 2000) and is based on the sum of PCBs. Therefore, it must be used with caution here since seals, otters and cetaceans differ in their capacity to metabolize distinct

PCBs as a result of the difference in the families of cytochrome P450 presented in each of them. For example, cetaceans ability to metabolize PCBs are higher than otter for those with vicinal H-atoms only in the ortho- and meta-positions, but lower to those with vicinal H-atoms in the meta- and para-positions and with two ortho-chlorines (Boon *et al.* 1997). Others PCBs threshold values were calculated, such as those described by Desforges *et al.* (2016) for lymphocyte proliferation ($5\ 420\ \text{ng g}^{-1}\ \text{lw}$) and phagocytosis suppression in neutrophils ($1\ 100\ \text{ng g}^{-1}\ \text{lw}$) in cetaceans.

In Brazil, there are no parameters that define toxicity limits of organochlorines in mammals, therefore, here we consider the values proposed by Kannan *et al.* (2000) and Deforges *et al.* (2016), which are widely used. Even though most studies reported values lower than those detected in species from the Northern Hemisphere, some of them surpassed the threshold value described by Kannan *et al.* (2000) and most of them surpassed the values described by Desforges *et al.* (2016) (Figure 10). Such results reinforce the concern raised by Azevedo *et al.* (2017) regarding the decline in the population of *S. guianensis* from Guanabará Bay being related to the high concentrations of PCBs detected in the species. Additionally, they corroborate the hypothesis that the population of *S. bredanensis*, in southeastern Brazil, is at risk of decline in the coming decades, as projected in the study by Oliveira-Ferreira *et al.* (2021).

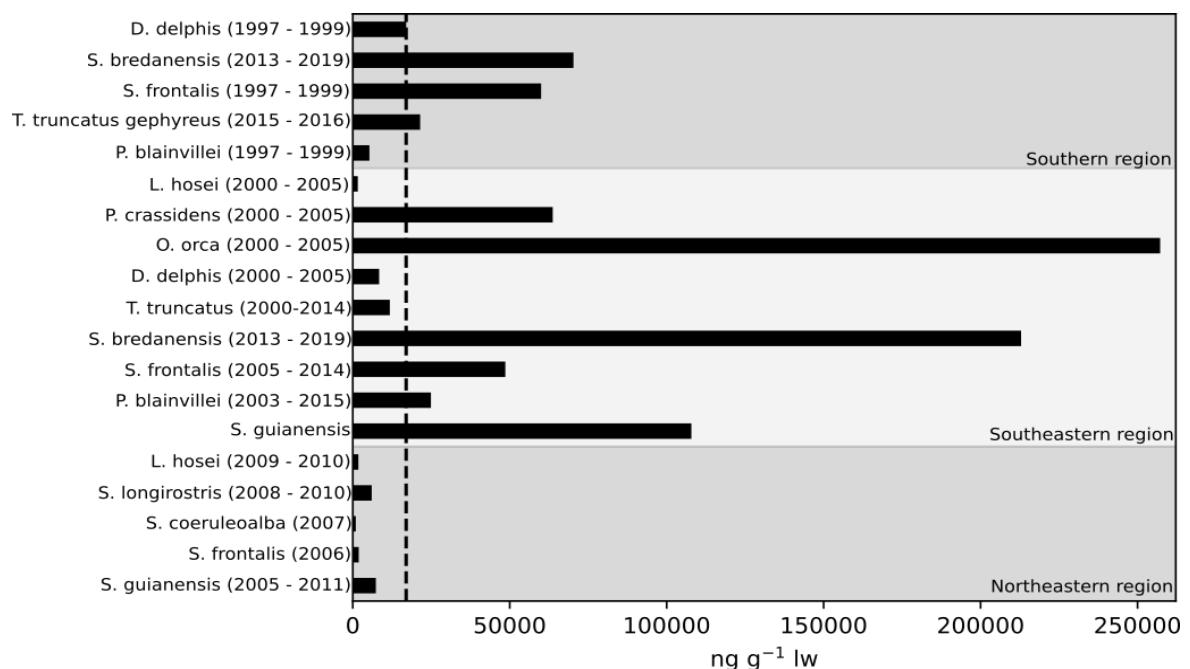


Figure 10: Highest values detected for each species according to the geographical region where they were sampled in the Brazilian waters. Dotted line represents the threshold value (Kannan *et al.* 2000).

5.5 FINAL REMARKS

There is no homogeneous distribution of studies along the Brazilian coast, with the majority concentrated in the south and southeast regions. This may be a reflection of the large concentration of research centers and universities in these regions, as well as the lack of equity in the distribution of research-oriented resources among the different regions of the country. The most studied species have predominantly coastal habits, which may justify their use as a sample, since this type of study usually uses organisms as the opportunity arises, such as accidental capture and strandings. The habitat of the three most studied species seems to be related to the levels of contamination of the individuals, as the highest concentrations of PCBs and DDTs were found in individuals collected in highly industrialized and urbanized regions or with a history of agricultural activities. This reinforces the hypothesis that the analyzed species can be sentinels of local contamination, however, a larger sample of individuals of the same species and from different regions would be necessary to test it, since the variability of collected species and analysis methods of the studies evaluated, makes it difficult to establish statistical tests that identify significant differences between the samples. Most studies do not report concentrations of contaminants separating individuals by sex or sexual maturation, which can make comparisons between individuals from different studies difficult, since the sex and maturity of individuals directly influence the contamination load, thus, in future studies it is recommended that this distinction be made, if the sampled individual presents sufficient conditions to make it. The tissue also seems to influence the concentrations of contaminants, with blubber being the most recommended due to its tendency to accumulate organochlorine contaminants. Thus, considering the importance of standardization in conducting studies and presenting data, it is recommended that in future studies, whenever possible, priority be given to the analysis of blubber to the detriment of other tissues. Studies on the temporal trend of organochlorines are scarce, but those that exist show a downward trend in the level of contamination of organisms. However, due to the low number of studies, continuous monitoring of marine mammals is recommended. Despite the heterogeneity of the data, it is possible to see that the implementation of organochlorine restriction and prohibition policies in the country were really effective, as there is a tendency for these contaminants to decrease in the marine environment. With that in mind, the present study provides a consistent base of data that can help in the development and implementation of future public policies aimed at the control and monitoring of organochlorines in Brazil, as well as the fulfillment of the commitments assumed by the country in the Stockholm Convention.

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Supplementary Information

Polychlorinated biphenyl and chlorinated pesticides concentrations and profiles in marine mammals from Brazilian waters

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1. Article Selection

Literature search was carried out in three-step processes: a) article searching on Science direct web page; b) article searching on Scopus web page; and c) complementary search on Google Scholar and references from other articles. In all stages inclusion criteria are: a) studies carried out on the Brazilian waters; b) studies assessing organochlorine occurrence in marine mammals; and c) studies with data (present in the article) regarding organochlorine contamination.

The first stage, carried in the Science Direct database, used the following keywords: POPs, marine mammals, organochlorine, Brazil; this phase was called pre-selection (Figure S1A). Additionally, in the selection phase, a filter tool was also used to select only "Research Articles" and "Short Communications". Further, articles selected passed through the abstract analysis stage to assure that only the target studies (organochlorine in marine mammals from Brazilian coast) were included; all others studies were excluded.

The second step, carried in the Scopus database, used the combination of the following keywords: "POPs" OR "persistent organic pollutants" OR "Organochlorine" OR "DDT" OR "PCBs" OR "CHL" AND *Brazil AND "marine mammal" OR "Pinnipedia" OR "cetaceans" OR "Sirenia" (Figure S2B). During the abstract analysis, articles already found in the first step as well as review articles, theses, dissertations, book chapters, and other documents were discarded.

On the third step, a complimentary search was carried out on Google Scholar and from the references of other articles. At this stage, only articles that met the selection criteria and did not appear in previous screenings were included in the review.

2. Species identification

Individuals were identified at the species or sub species level. Additionally, two corrections were made to the species name; a) two articles used “*Sotalia fluviatilis*” where it should be *Sotalia guianensis* as explained by Monteiro-Filho *et al.*, 2002; Cunha *et al.*, 2005; Caballero *et al.*, 2007; Fettuccia *et al.*, 2009; and checked on the IUCN List of Threatened Species (Secchi *et al.*, 2018); b) two articles used "Delphinus capensis", but in 2016 the Society for Marine Mammalogy removed Delphinus capensis from its list of marine mammal species, recognizing all common dolphins as a single species, *Delphinus delphis*. This change has also been checked against the IUCN endangered species list (Bräulik *et al.*, 2021).

3. Results and Discussion

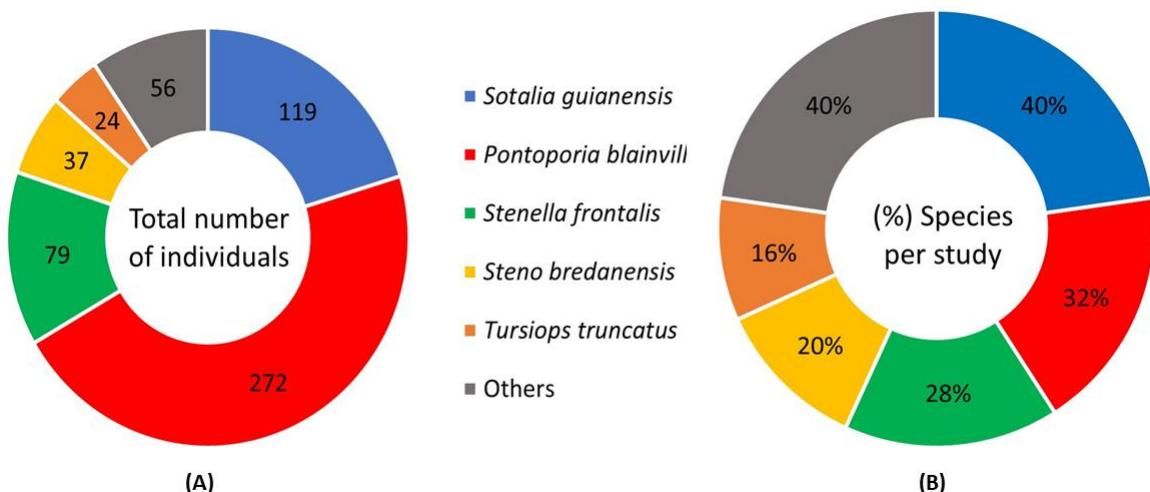


Figure S1: (A) total number of individuals of each species used in the studies; (B) most studied species in relation to the total number of publications, according to the number of studies in which each one appears (percentage values exceed 100% because some studies evaluated more than one species). “Others” category encompasses 8 distinct species.

Table S1: list of compiled articles regarding organochlorine compounds in marine mammals from the Brazilian waters (2003-2023).

	Title	Study area	Region	Species	Study
1	Polychlorinated Biphenyls and Organochlorine Pesticides in Edible Fish Species and Dolphins from Guanabara Bay, Rio de Janeiro, Brazil	RJ	SE	<i>Sotalia fluviatilis</i>	Silva <i>et al.</i> (2003)
2	Chlorinated pesticides and polychlorinated biphenyls in marine tucuxi dolphins (<i>Sotalia fluviatilis</i>) from the Cananéia estuary, southeastern Brazil	SP	SE	<i>Sotalia fluviatilis</i>	Yogui <i>et al.</i> (2003)
3	Contamination by Persistent Organochlorines in Cetaceans Incidentally Caught Along Brazilian Coastal Waters	SP PR	SE S	<i>Sotalia guianensis</i> <i>Pontoporia blainvilliei</i> <i>Stenella frontalis</i> <i>Delphinus capensis</i>	Kajiwara <i>et al.</i> (2004)
4	Accumulation patterns of organochlorines in juveniles of <i>Arctocephalus australis</i> found stranded along the coast of Southern Brazil	RS	S	<i>Arctocephalus australis</i>	Fillmann <i>et al.</i> (2007)
5	Long-term trends of polychlorinated biphenyls and chlorinated pesticides in franciscana dolphin (<i>Pontoporia blainvilliei</i>) from Southern Brazil	RS	S	<i>Pontoporia blainvilliei</i>	Leonel <i>et al.</i> (2010)
6	High organochlorine accumulation in blubber of Guiana dolphin, <i>Sotalia guianensis</i> , from Brazilian coast and its use to establish geographical differences among populations	RJ PR	SE S	<i>Sotalia guianensis</i>	Lailson-Brito <i>et al.</i> (2010)
7	Levels of persistent organic pollutants and residual pattern of DDTs in small cetaceans from the coast of São Paulo, Brazil	SP	SE	<i>Pontoporia blainvilliei</i> <i>Stenella frontalis</i> <i>Sotalia guianensis</i> <i>Tursiops truncatus</i> <i>Steno bredanensis</i>	Yogui <i>et al.</i> (2010)
8	Occurrence of chlorinated pesticides and polychlorinated biphenyls (PCBs) in guiana dolphins (<i>Sotalia guianensis</i>) from Ubatuba and Baixada Santista, São Paulo, Brazil	SP	SE	<i>Sotalia guianensis</i>	Alonso <i>et al.</i> (2010)
9	Specific profiles of polybrominated diphenylethers (PBDEs) and polychlorinated biphenyls (PCBs) in fish and tucuxi dolphins from the estuary of Paraíba do Sul River, Southeastern Brazil	RJ	SE	<i>Sotalia guianensis</i>	Quinete <i>et al.</i> (2011)
10	Organochlorine concentrations in franciscana dolphins, <i>Pontoporia blainvilliei</i> , from Brazilian waters	SP PR	SE S	<i>Pontoporia blainvilliei</i>	Lailson-Brito <i>et al.</i> (2011)

11	Contamination by chlorinated pesticides, PCBs and PBDEs in Atlantic spotted dolphin (<i>Stenella frontalis</i>) in western South Atlantic	SP PR SC	SE S	<i>Stenella frontalis</i>	Leonel <i>et al.</i> (2012)
12	Organochlorine compound accumulation in delphinids from Rio de Janeiro State, southeastern Brazilian coast	RJ	SE	<i>Orcinus orca</i> <i>Pseudorca crassidens</i> <i>Tursiops truncatus</i> <i>Steno bredanensis</i> <i>Delphinus capensis</i> <i>Lagenodelphis hosei</i>	Lailson-Brito <i>et al.</i> (2012)
13	Contaminant concentrations, biochemical and hematological biomarkers in blood of West Indian manatees <i>Trichechus manatus</i> from Brazil	PE AL PB	NE	<i>Trichechus manatus</i>	Anzolin <i>et al.</i> (2012)
14	High accumulation of PCDD, PCDF, and PCB congeners in marine mammals from Brazil: A serious PCB problem	RJ	SE	<i>Sotalia guianensis</i> <i>Steno bredanensis</i>	Dorneles <i>et al.</i> (2013)
15	Organochlorine concentrations (PCBs, DDTs, HCHs, HCB and MIREX) in delphinids stranded at the northeastern Brazil	CE	NE	<i>Sotalia guianensis</i> <i>Lagenodelphis hosei</i> <i>Stenella longirostris</i> <i>Stenella frontalis</i> <i>Stenella coeruleoalba</i>	Santos-Neto <i>et al.</i> (2014)
16	An assessment of PCB and PBDE contamination in two tropical dolphin species from the Southeastern Brazilian coast	RJ	SE	<i>Sotalia guianensis</i> <i>Steno bredanensis</i>	Lavandier <i>et al.</i> (2015)
17	PCB and PBDE levels in a highly threatened dolphin species from the Southeastern Brazilian coast	RJ	SE	<i>Pontoporia blainvilliei</i>	Lavandier <i>et al.</i> (2016)
18	Validating the use of biopsy sampling in contamination assessment studies of small cetaceans		SE	<i>Stenella frontalis</i>	Méndez-Fernandez <i>et al.</i> (2016)
19	Contamination status by persistent organic pollutants of the Atlantic spotted dolphin (<i>Stenella frontalis</i>) at the metapopulation level	SP	SE	<i>Stenella frontalis</i>	Méndez-Fernandez <i>et al.</i> (2018)
20	Transplacental transfer of persistent organic pollutants in La Plata dolphins (<i>Pontoporia blainvilliei</i> ; Cetartiodactyla, Pontoporiidae)	SP	SE	<i>Pontoporia blainvilliei</i>	Barbosa <i>et al.</i> (2018)
21	PCB and PBDE contamination in <i>Tursiops truncatus</i> and <i>Stenella frontalis</i> , two data-deficient threatened dolphin species from the Brazilian coast	RJ	SE	<i>Tursiops truncatus</i> <i>Stenella frontalis</i>	Lavandier <i>et al.</i> (2019)

22	Biochemical and molecular biomarkers in integument biopsies of freeranging coastal bottlenose dolphins from southern Brazil	SC	S	<i>Tursiops truncatus gephyreus</i>	Riguetti <i>et al.</i> (2019)
23	Long-Term Consequences of High Polychlorinated Biphenyl Exposure: Projected Decline of Delphinid Populations in a Hotspot for Chemical Pollution	RJ PR RS	S SE	<i>Steno bredanensis</i>	Oliveira -Ferreira <i>et al.</i> (2021)
24	Franciscana dolphins, <i>Pontoporia blainvillei</i> , as environmental sentinels of the world's largest mining disaster: Temporal trends for organohalogen compounds and their consequences for an endangered population	ES	SE	<i>Pontoporia blainvillei</i>	Oliveira-Ferreira <i>et al.</i> (2022)
25	Temporal trends of persistent organic pollutant contamination in Franciscana dolphins from the Southwestern Atlantic	SP	SE	<i>Pontoporia blainvillei</i>	Montone <i>et al.</i> (2023)

Table S2: Habitat, preys, geographical distribution, assessment, and common names of species included in this review.

Species	Assessment	Habitat	Preys	Distribution	Reference (IUCN)
<i>Sotalia guianensis</i>	Near threatened	Wetlands (inland) Marine Neritic Marine Coastal/Supratidal	Demersal and pelagic fishes (Sciaenidae, Clupeidae, Mugilidae, Trichiuridae, and Batrachoididae), neritic cephalopods (Loliginidae), and penaeid shrimps	Santa Catarina (Brazil) to Honduras	Secchi et al. (2018)
<i>Pontoporia blainvilliei</i>	Vulnerable	Marine Neritic Marine Oceanic	Its prey includes a variety of shallow-water fish (e.g., sciaenids, engraulids, gadids, batrachoids, trichiurids and carangids) cephalopods, and crustaceans	Northern Golfo San Matias (Argentina) to Espírito Santo (Brazil)	Zerbini et al. (2017)
<i>Delphinus delphis</i>	Least concern	Marine Neritic Marine Oceanic	Their prey includes epipelagic and mesopelagic fishes and a smaller proportion of squids	They occur in tropical to cold temperate waters in the Indian, Atlantic and Pacific oceans	Braulik et al. (2021)
<i>Arctocephalus australis</i>	Least concern	Marine Neritic Marine Oceanic Marine Intertidal Marine Coastal/Supratidal	A generalist species, it feeds according to the availability of prey, with pelagic and demersal fish and cephalopods being the most common in its diet	West coast of the South Atlantic and East of the South Pacific, stretching from Rio Grande do Sul (Brazil) to the southern tip of South America	Cárdenas-Alayza et al. (2016)
<i>Stenella frontalis</i>	Least concern	Marine Neritic Marine Oceanic	Its prey includes a wide variety of epipelagic and mesopelagic fish, squid and benthic invertebrates.	They only occur in the Atlantic Ocean between 50°N and 25-30°S and in the western Atlantic, they have a distribution from southern Brazil to New England (USA)	Braulik & Jefferson (2018)
<i>Tursiops truncatus</i>	Least concern	Wetlands (inland) Marine Neritic Marine Oceanic Marine Coastal/Supratidal	Variety of prey species, including fish, squid, shrimp and crustaceans	Occur worldwide through tropical and temperate inshore, coastal, shelf, and oceanic waters	IUCN (2019)
<i>Steno bredanensis</i>	Least concern	Marine Neritic Marine Oceanic	Oceanic and coastal fish, cephalopods and large pelagic fishes	Pacific, Atlantic and Indian Oceans between 40°N and 35°S	Kiszka et al. (2019)
<i>Orcinus orca</i>	Data deficientes	Marine Neritic	Variety of species of marine mammals,	Cosmopolitan, the species has a	Reeves et al.

		Marine Oceanic	seabirds, sea turtles, many species of fish and cephalopods	wide distribution, occurring in most marine habitats, but prefers cold waters and areas with high productivity	(2017)
<i>Pseudorca crassidens</i>	Near threatened	Marine Neritic Marine Oceanic	Large fish, cephalopods and according to the opportunity, they can feed on small dolphins	Regions far from the coast in the three main oceans, not exceeding latitudes greater than 50°	IUCN (2018)
<i>Lagenodelphis hosei</i>	Least concern	Marine Neritic Marine Oceanic	Mesopelagic fishes (myctophids), cephalopods, and crustaceans	Pacific, Atlantic and Indian Oceans between 30°N and 30°S	Kiszka & Braulik (2018)
<i>Stenella longirostris</i>	Least concern	Marine Neritic Marine Oceanic	Variety of small fish, squids, prawns and invertebrates of benthic reefs	Pacific, Atlantic and Indian Oceans between 40°N and 40°S	Braulik & Reeves (2018)
<i>Stenella coeruleoalba</i>	Least concern	Marine Neritic Marine Oceanic	Variety of small, midwater and pelagic or benthopelagic organisms	Between 50°N and 40°S, although there are records outside these limits, such as the Kamchatka Peninsula, southern Greenland, Iceland, Faroe Islands and Prince Edward Island	Braulik (2019)
<i>Trichechus manatus</i>	Vulnerable	Wetlands (inland) Marine Neritic Marine Intertidal Marine Coastal/Supratidal Artificial/Aquatic & Marine	Seagrasses and a variety of submerged vegetation, floating and emerging	Bahamas to north of Bahia (Brazil)	Deutsch et al. (2008)
<i>Tursiops truncatus gephyreus</i>	Vulnerable	Wetlands (inland) Marine Neritic Marine Oceanic Marine Coastal/Supratidal	Fish and cephalopod species	Paraná (Brazil) to province of Chubut (Argentina)	Vermeulen et al. (2019)

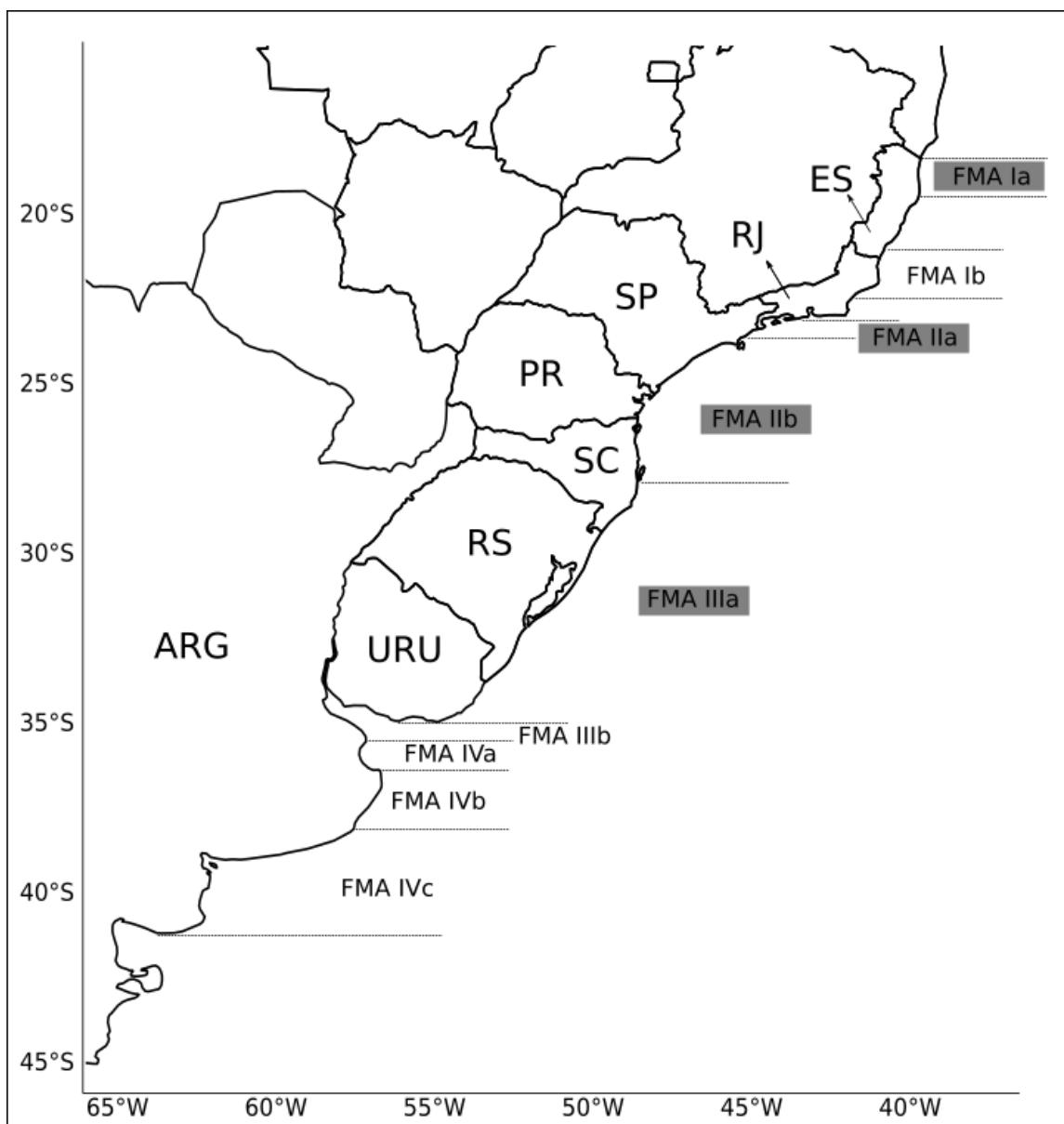


Figure S2: Franciscana Management Areas (FMAs); the gray box indicated those from which there is POPs data (considering Brazilian waters). ARG: Argentina; URU: Uruguai; RS: Rio Grande do Sul; SC: Santa Catarina; PR: Paraná; SP: São Paulo; RJ: Rio de Janeiro; ES: Espírito Santo.

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6 CONCLUSÃO

Na presente revisão organizamos os estudos sobre a ocorrência de organoclorados em mamíferos marinhos da costa brasileira. Identificamos que os estudos não são distribuídos de maneira homogênea ao longo da costa, sendo a maior parte desenvolvida nas regiões sudeste e sul. Não existe uma padronização nos métodos de coleta, análise e apresentação dos dados, o que dificulta o estabelecimento de comparações entre estudos diferentes, assim como já verificado em outras revisões. Recomendamos que o máximo de dados extraíveis das espécies trabalhadas em estudos futuros de ocorrência de organoclorados em mamíferos marinhos, sejam organizados e divulgados. Apesar de diversas espécies de mamíferos terem sido avaliadas, a maior parte dos estudos se concentra em três espécies costeiras: *Sotalia guianensis*, *Pontoporia blainvilliei* e *Stenella frontalis*. As maiores concentrações de organoclorados foram encontradas em indivíduos coletados em regiões de alto impacto por atividades antrópicas (agricultura, indústrias, urbanização), o que reforça nossa hipótese da relação entre os níveis de contaminação e a área de coleta. O habitat e a dieta das espécies também parecem influenciar nos níveis de contaminação dos indivíduos, uma vez que os mais contaminados costumam se alimentar de presas que ocupam níveis tróficos mais altos, reforçando o potencial de bioacumulação e biomagnificação desses compostos ao longo da teia trófica. O tecido também influencia nas concentrações dos contaminantes, sendo a gordura (blubber) o mais comumente estudado e com as maiores concentrações devido a afinidade dos organoclorados por lipídeos. Nos próximos estudos recomendamos que sempre que as condições do indivíduo permitem, seja feita a análise de blubber para a análise de contaminação de mamíferos por organoclorados, pois possibilita uma padronização de dados e comparações. Apesar da heterogeneidade dos dados, é possível perceber que a implementação de políticas de restrição e banimento de organoclorados no país foram realmente eficazes, pois há uma tendência de diminuição desses contaminantes no ambiente marinho. Pensando nisso, o presente estudo fornece uma base consistente de dados que podem auxiliar no desenvolvimento e implementação de futuras políticas públicas voltadas para a conservação dos mamíferos marinhos da costa brasileira, o controle e monitoramento de organoclorados no Brasil e o cumprimento dos compromissos assumidos pelo país na Convenção de Estocolmo.

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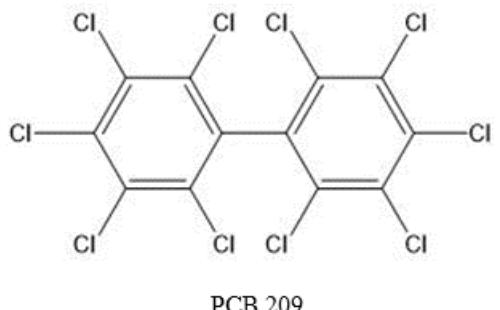
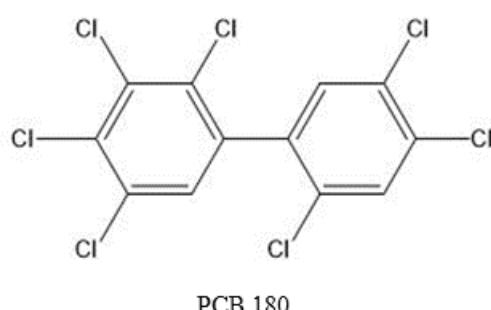
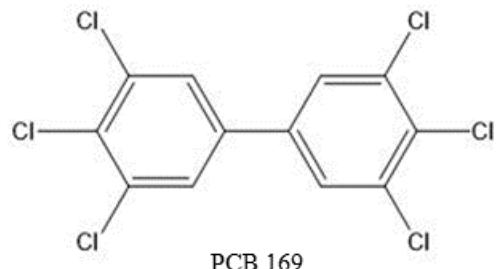
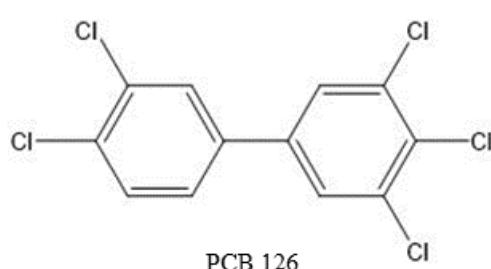
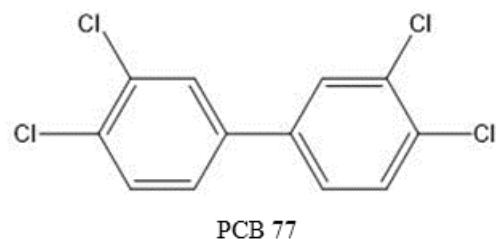
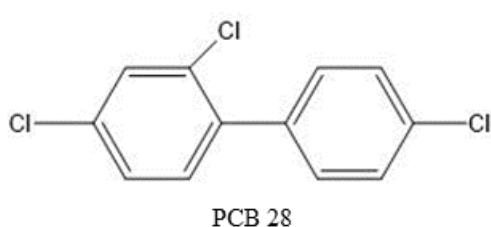
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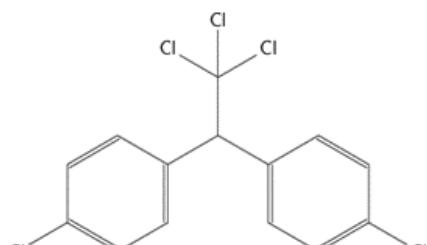
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APÊNDICE A – Estruturas moleculares dos POPs

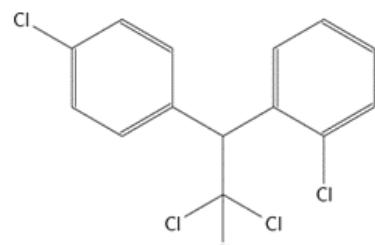
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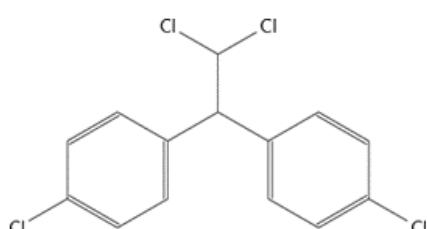
Praguicidas Organoclorados e metabólitos



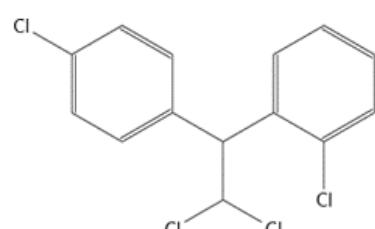
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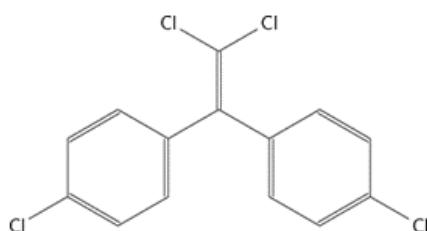
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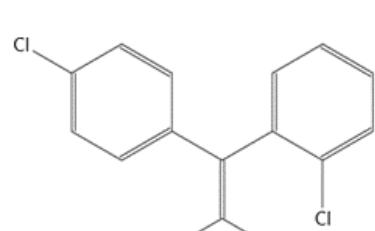
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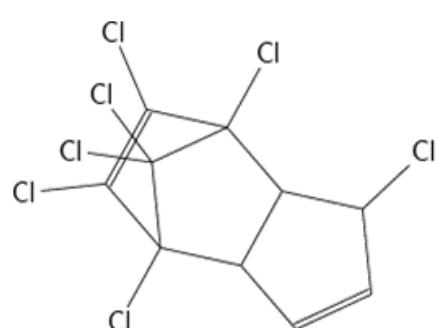
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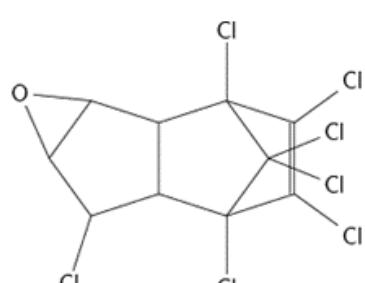
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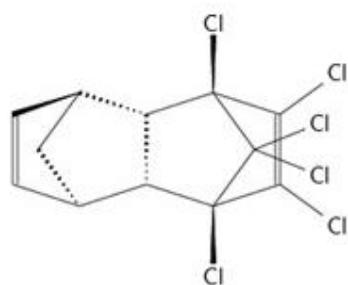
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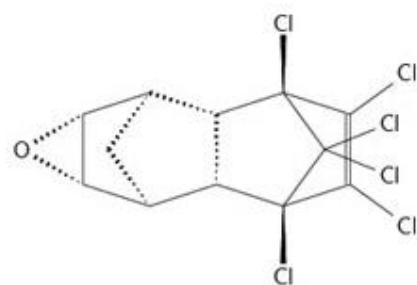
Heptacloro



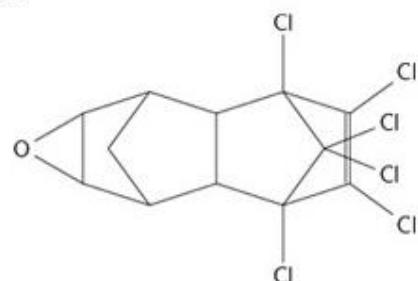
Heptacloro
Epoxide



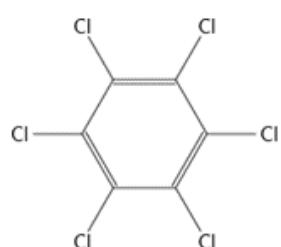
Aldrin



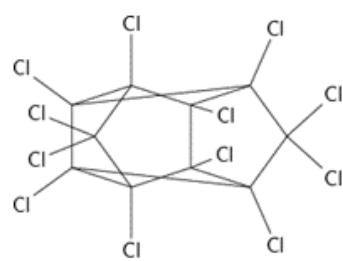
Dieldrin



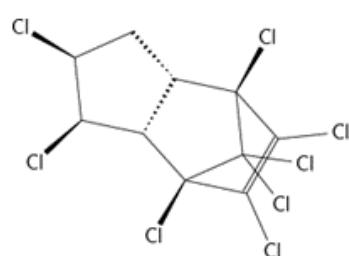
Endrin



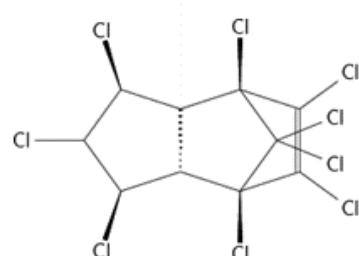
HCB



Mirex



Cis Clordano

Trans
Nonacloro

APÊNDICE B- Propriedades físico-químicas dos organoclorados

Nome comum	Fórmula molecular	Solubilidade em água	Pressão de vapor	log Kow
Aldrin	C ₁₂ H ₈ Cl ₆	27 µg/L ⁻¹ (25°C)	2.3 x 10 ⁻⁵ mm Hg (20°C)	5.17-7.4
Bifenilas policloradas	C ₁₂ H _(10-n) Cl _n	0.01 a 0.0001 µg/L ⁻¹ (25°C)	1.6-0.003 x 10 ⁻⁶ mm Hg (20°C)	4.3-8.26
Clordano	C ₁₀ H ₆ Cl ₈	56 µg/L ⁻¹ (25°C)	0.98 x 10 ⁻⁵ mm Hg (25°C)	6.00
DDT	C ₁₄ H ₉ Cl ₅	1.2-5.5 µg/L ⁻¹ (25°C)	0.2 x 10 ⁻⁶ mm Hg (20°C)	6.19
Dieldrin	C ₁₂ H ₈ Cl ₆ O	140 µg/L ⁻¹ (20°C)	1.78 x 10 ⁻⁷ mm Hg (20°C)	3.69-6.2
Endrin	C ₁₂ H ₈ Cl ₆ O	220-260 µg/L ⁻¹ (25°C)	2.7 x 10 ⁻⁷ mm Hg (25°C)	3.21-5.34
Heptacloro	C ₁₀ H ₅ Cl ₇	180 µg/L ⁻¹ (25°C)	0.3 x 10 ⁻⁵ mm Hg (20°C)	4.4-5.5
Hexaclorobenzeno	C ₆ H ₆	50 µg/L ⁻¹ (20°C)	1.09 x 10 ⁻⁵ mm Hg (20°C)	3.93-6.42
Mirex	C ₁₀ Cl ₁₂	0.07 µg/L ⁻¹ (25°C)	3 x 10 ⁻⁷ mm Hg (25°C)	5.28
Toxafeno	C ₁₀ H ₁₀ Cl ₈	550 µg/L ⁻¹ (20°C)	3.3 x 10 ⁻⁵ mm Hg (25°C)	3.23-5.50

Fonte: Elaborado pelo autor com base em Barra *et al.* (2002).