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PROGRAMA DE PÓS-GRADUAÇÃO EM GEOQUÍMICA: PETRÓLEO E MEIO AMBIENTE - POSPETRO

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AVALIAÇÃO DA OCORRÊNCIA DE COMPOSTOS ORGANOCLORADOS EM ORGANISMOS MARINHOS DA BAÍA DE TODOS OS SANTOS, BAHIA, BRASIL

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RESUMO

Com objetivo de avaliar a contaminação por PCBs em uma baía tropical exposta a diferentes pressões antrópicas foram analisadas amostras de bivalves (ostras, sururu e chumbinho) coletadas em diferentes partes da Baía de Todos os Santos (BTS), Bahia, Brasil. Adicionalmente, amostras de bivalves e peixes adquiridos em um mercado da cidade de Salvador foram analisadas para estudar a exposição humana a PCBs através da ingestão. A identificação e quantificação das PCBs de interesse foram feitas por GC/MS após extração por microondas e purificação com ácido sulfúrico. Em amostras de bivalves, as concentrações variaram entre < 0,08 e 50,13 ng g^{-1} (peso seco), sendo que os maiores valores foram detectados nas de ostras, seguidos por chumbinho e sururu das regiões do Estuário do Subaé e Madre de Deus/Mataripe; ambas as regiões conhecidamente impactadas por atividades antrópicas. Com relação aos peixes, das doze espécies analisadas, apenas cinco apresentaram níveis de PCBs acima dos limites de detecção, variando de 0,23 a 4,55 ng g^{-1} e 0,51 a 26,05 ng $g^{-1,}$ em peso seco e peso lipídico, respectivamente. De maneira geral, as concentrações de PCBs na BTS são mais baixas que na maioria das regiões ao redor do mundo, sobretudo aquelas localizadas no Hemisfério Norte. Os índices TEL e PEL mostram que a biota local não deve sentir efeitos adversos relacionados à presença desses contaminantes, assim como o consumo do pescado comercializado na cidade de Salvador aparentemente não representa riscos claros à saúde humana.

Palavras-chave: PCBs, bivalves, peixes, BTS.

ABSTRACT

In order to evaluate contamination by PCBs in a tropical bay exposed to different anthropic pressures, samples of bivalves (mangrove oyster, mangrove mussel and clams) were collected in different parts of Todos os Santos Bay, Bahia, Brazil. In addition, samples of bivalves and fish, purchased in a seafood market in the city of Salvador were analyzed to study human exposure to PCBs through ingestion. Identification and quantification of PCBs were done by GC/MS after microwave extraction and purification with sulfuric acid. In samples of bivalves, concentrations ranged from <0.08 to 50.13 ng g^{-1} (dry weight), with the highest values being detected in mangrove oyster, followed by clams and mangrove mussel of the Subaé estuary and Madre de Deus/Mataripe; both regions known to be impacted by anthropic activities. Regarding fish samples, froma all 12 species analyzed, only 5 presented levels of PCBs above the detection limit, ranging from 0.23 to 4.55 ng g^{-1} and 0.51 to 26.05 ng g^{-1} by dry weight and lipid weight, respectively. In general, concentrations of PCBs in BTS are lower than in most regions around the world, especially those located in the Northern Hemisphere. TEL and PEL indexes showed that local biota should not feel adverse effects related to the presence of these contaminants, just as the consumption of the fish marketed in the city of Salvador apparently does not represent a clear risk to human health.

Keywords: PCBs, bivalves, fish, BTS.

LISTA DE SIGLAS

BTS – Baía de Todos os Santos

DDD – Dicloro-difenil-dicloroetano

DDE – Dicloro-difenil-dicloroetileno

DDT – Dicloro-difenil-tricloroetano

DOU – Diário Oficial da União

EFSA – European Food Safety Authority (Autoridade Européia para a Segurança Alimentar)

GC-ED – Cromatografia gasosa acoplada a detector de captura de elétrons

GC-MS – Cromatografia gasosa acoplada a espectrômetro de massas

HCB – Hexaclorobenzeno

HCH – Hexaclorociclohexano

Kow – Coeficiente de partição octanol-água

MMA – Ministério do Meio Ambiente

MRC – Material de Referência Certificado

OCPs – Pesticidas Organoclorados

PCBs – Bifenilas Policloradas

PEL – Probable Effect Level (Nível Provável de Efeito)

PNUMA – Programa das Nações Unidas para o Meio Ambiente

SIM – Monitoramento Seletivo de Íons

TCDD – Tetraclorodibenzodioxina

TEL – Treshold Effect Level (Nível Limiar de Efeito)

UNEP – Programa Ambiental das Nações Unidas

SUMÁRIO

1 INTRODUÇÃO

A necessidade do aumento na produção de alimentos para suprir a demanda de um progressivo crescimento populacional, aliada ao desenvolvimento científico e tecnológico, teve como consequência a criação de uma série de substâncias tóxicas, oriundas dos mais diversos processos, tais como: produção de papel e plástico, geração e composição de produtos agrícolas, incineração de lixo e uma variedade de processos industriais (QUINETE, 2011).

Nesse contexto, as atividades antrópicas são responsáveis por um aumento substancial de impactos negativos ao meio ambiente (HALPERN et al., 2013). As regiões costeiras, locais de concentração de bens e serviços para a população e uma variedade de habitats para muitos organismos, é especialmente afetada por esse desenvolvimento tecnológico, que se traduz em fluxos antropogênicos de elementos traços, e outros contaminantes como os compostos organoclorados, para corpos d'água (MARTIN; MEYBECK, 1979; NRIAGU, 1993; JENNERJAHN, 2012; BATANG et al., 2016).

Os POPS são um grupo de compostos que devido a suas propriedades físico-químicas tem um longo tempo de permanência no ambiente, bioacumulam, apresentam toxicidade e podem ser transportados para longe de suas fontes através do transporte atmosférico e oceânico (STOCKHOLM CONVENTION, http://chm.pops.int/). Em 2001, foi assinada na Suécia, por 92 países, a Convenção de Estocolmo, que estabeleceu o compromisso de seus signatários em desenvolver métodos de redução e/ou eliminação da emissão dos POPs (STOCKHOLM CONVENTION, http://chm.pops.int/), além de realizar monitoramento constante de seus níveis ambientais. Atualmente, existe a adesão de 151 países, incluindo o Brasil, que através da Portaria Interministerial 19, de 2 de janeiro de 1981 estabeleceu, entre outras coisas, a proibição de fabricação, comercialização e uso de PCBs em todo território nacional (BRASIL, 1981). No ano de 2004, o texto da Convenção foi aprovado por meio do Decreto Legislativo nº 204, de 7 de maio de 2004, e promulgado via Decreto nº 5.472, de 20 de junho de 2005, assumindo assim o compromisso de banimento total de PCBs até o ano de 2025 (BRASIL, 2005).

Inicialmente, o texto da Convenção estabeleceu o impedimento da produção, utilização, importação e exportação dos chamados "dirty dozen", que são doze poluentes considerados críticos, todos organoclorados e entre eles as PCBs. Posteriormente novos compostos foram introduzidos nesse texto, que hoje também é composto por compostos organobromados e perfluorados (UNEP, 2015).

Muitos POPs foram amplamente utilizados ao redor do mundo, sobretudo nas décadas de 70 e 80, tendo como principais finalidades a agricultura; sendo usados no combate à pragas agrícolas, a saúde pública; através do combate a vetores de doenças, e processos industriais; sobretudo o uso em equipamentos fabris (UNEP, 2008). Apesar da regulamentação pela Convenção de Estocolmo, eles ainda são amplamente detectados no ambiente marinho do Brasil e do mundo (MIRANDA; YOGUI, 2016, LEE et al., 2015).

1.1. PCBs

PCBs são hidrocarbonetos sintéticos formados por dois anéis aromáticos que possuem um ou mais átomos de cloro ligados a sua molécula, o que lhes confere uma variedade de 209 diferentes congêneros, sendo que apenas 130 deles ocorrem no meio ambiente (Figura 1). O número e posição dos átomos de cloro no grupo bifenila vão definir a conformação espacial da molécula e a toxicidade dos congêneres (ATSDR, 2000).

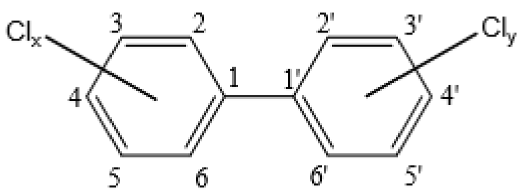

Figura 1 – Estrutura química das PCBs. Extraída de ATSDR, 2000.

As posições 2, 2’, 6 e 6’ são denominadas posições *orto*, ao passo que 3, 3’, 5 e 5’ correspondem às posições *para*. Os anéis de benzeno têm a capacidade de rotacionar em torno da ligação que os une, assim, quando estão no mesmo plano, tem-se a configuração planar e quando formam um ângulo de 90º entre si, tem-se a configuração não planar (ATSDR, 2000). A conformação planar é considerada a mais tóxica, por possuir ação bioquímica semelhante a da tetraclorodibenzodioxina (TCDD), poluente clorado altamente tóxico (MCCONNELL et al., 1978).

As propriedades físicas e químicas das PCBs (Quadro 1) são resultado e dependem da posição e do número de átomos de cloro presentes em cada molécula. De um modo geral, pressão de vapor, solubilidade na água e biodegradabilidade decrescem com o aumento no número de cloros. No entanto, lipofilicidade e capacidade de adsorção se comportam de maneira inversa (LOGANATHAN; KANNAN, 1994).

Quadro 1 – Propriedades físico-químicas das PCBs, de acordo com o número de átomos de cloro. Fonte: ATSDR, 2000.

PCB (Congêneres)	Fórmula	Log Kow	Solubilidade em água (mg L^{-1}; 20 – 25°C)	Pressão de vapor (Pa; 25ºC)
Monoclorado	$C_{12}H9Cl$	4,5 – 4,7	1,3 – 7,0	2200 – 920
Diclorado	$C_{12}H_8Cl_2$	5,0 - 5,6	0,054 – 0,79	370 – 75
Triclorado	$C_{12}H_7Cl_3$	5,6 – 6,1	0,015 – 0,64	110 – 13
Tetraclorado	$C_{12}H_6Cl_4$	5,9 – 6,7	0,019 – 0,17	18 – 4,4
Pentaclorado	$C_{12}H_5Cl_5$	6,4 – 7,5	0,0045 – 0,012	5,3 – 0,88
Hexaclorado	$C_{12}H_4Cl_6$	7,1 – 8,3	0,00044 – 0,00091	1,9 – 0,2
Heptaclorado	$C_{12}H_3Cl_7$	7,9	0, 00047	0,53 – 0,05
Octaclorado	$C_{12}H_2Cl_8$	8,4 – 8,6	0,00018 – 0,00027	0,08 – 0,009
Nonaclorado	$C_{12}H_1Cl_9$	9,1	0,00011	0,032 – 0,011
Decaclorado	$C_{12}Cl_{10}$	9,6	0,000016	0,0056

O uso das PCBs teve início em 1929 na forma de misturas técnicas apresentando diferentes percentagens de cloro. Essas misturas foram sintetizadas por diversos países e receberam nomes como: Phenoclor® na França; Kanechlor® no Japão; Clophen® na Alemanha; Fenclor® na Itália e Aroclor® nos Estados Unidos (EUA). No Brasil não se tem registros da produção de PCBs, sendo que eles foram importados da Alemanha e principalmente dos EUA, que comercializou PCBs no Brasil com o nome de Ascarel® (WHO, 1990). A baixa inflamabilidade e ponto de fusão elevado permitem que sejam muito resistentes a altas tensões elétricas, apresentando também maior durabilidade em relação a outros óleos isolantes. Por esse motivo, foram amplamente utilizados em transformadores elétricos, resistores, disjuntores, capacitores, unidades de correção de potência (UCP) e outros equipamentos (MMA, 2015).

Em decorrência da alta resistência a degradação e por possuírem alta volatilidade, as PCBs podem ser transportadas, através da atmosfera, a partir de zonas de baixa latitude para zonas de alta latitude, em um padrão conhecido como destilação global (WANIA; MACKAY, 1996). A ocorrência desses compostos em locais como o Ártico (BRAUNE et al., 2001), a Antártida (MONTONE et al., 2001) e outras áreas remotas como o Monte Everest (LI et al., 2006), evidencia esse padrão, uma vez que nessas regiões o aporte direto é baixo.

Durante o transporte entre os diversos compartimentos ambientais, esses compostos estão sujeitos a uma série de processos que envolvem: retenção (absorção/adsorção), transformação (biodegradação) e transporte (deriva, volatilização, lixiviação, escoamento superficial), assim como a interação desses processos (MELO et al., 2010). Drenagem superficial, descarga fluvial e transporte atmosférico são as principais vias de aporte de poluentes para o ambiente marinho (GORNI; WEBER, 2004).

Após o processo de lixiviação, uma vez no ambiente marinho, a tendência é que os compostos semi-voláteis se associem ao material particulado em suspensão, tendo o sedimento como destino final (FISK et al., 2005; DUBUS et al., 2000). Processos hidrodinâmicos que causam erosão e remobilização de sedimentos ou até mesmo a ação da fauna bentônica são responsáveis por disponibilizar esses compostos novamente para a coluna d’água, onde podem ser absorvidos por organismos (MUIR et al., 1988).

Os efeitos negativos dessas substâncias atingem os diferentes compartimentos ambientais, além de representarem um significativo risco à saúde humana. PCBs são responsáveis, entre outras coisas, por uma série de efeitos danosos aos sistemas imunológico (supressão da ação imunológica em animais e humanos), reprodutivo (falhas reprodutivas em vários animais selvagens) além de potencial efeito cancerígeno em humanos (SERDAR et al., 2014; ATSDR, 2010), o que impulsiona a investigação de suas concentrações e possíveis efeitos em diferentes locais ao redor do mundo.

Os organismos marinhos são usados de maneira recorrente como objeto de estudo da contaminação por compostos organoclorados. Em um nível global, uma série de estudos avaliou a ocorrência de PCBs em peixes (CIBRIAN et al., 2015; KAFILZADEH et al., 2015; WANG et al., 2015; BETTINETTI et al., 2016; DESHPANDE et al., 2016; ENDO et al., 2016; PAN et al., 2016; ROBINSON et al., 2016; LU et al., 2017; MUZYED et al., 2017; MWAKALAPA et al., 2017; PEDRO et al., 2017;

STROBEL et al., 2017; VERHAERT et al., 2017), em bivalves (ACOSTA et al., 2015; ALI et al., 2015; CARRO et al., 2015; KASIOTIS et al., 2015; MILUN et al., 2016; SMALLING et al., 2016; SZCZYBELSKI et al., 2016; CAMPILLO et al., 2017) e até em ambos, além de crustáceos (HERNANDEZ et al., 2017; LI et al., 2017; VAROL; SUNBUL, 2017).

No Brasil, o número de trabalhos ainda é incipiente e direcionado principalmente para as regiões sul e sudeste. A grande maioria dos estudos de PCBs em espécies marinhas acontece em mamíferos (por exemplo, DORNELES et al., 2015; QUINETE et al., 2011; SANTOS-NETO et al., 2014; LEONEL et al., 2014; LAVANDIER et al., 2019; MÉNDEZ-FERNANDEZ et al., 2018; BARBOSA et al., 2018), mas também há, em menor número, trabalhos realizados em peixes (AZEVEDO-SILVA et al., 2009; QUINETE et al., 2011; LAVANDIER et al., 2013; CASCAES et al., 2014; MIRANDA; YOGUI, 2016; DA SILVA et al., 2016; MENDES et al., 2016; VIEIRA et al., 2016; MAGALHÃES et al., 2017) e bivalves (TAVARES et al., 1988; TAVARES et al., 1999; NASCIMENTO et al., 1986; SILVA et al., 2003). Dessa forma, existe ainda uma carência de estudos em peixes e bivalves, principalmente os de interesse comercial.

2 HIPÓTESES DO ESTUDO

- A Baía de Todos os Santos apresenta contaminação por PCBs, que foi mais pronunciada nos pontos de amostragem mais próximos às possíveis fontes, como as unidades fabris em Madre de Deus;
- A população da cidade de Salvador está sujeita à exposição de PCBs através da ingestão de peixes vendidos nos mercados populares.

3 OBJETIVOS GERAL E ESPECÍFICOS

3.1 OBJETIVO GERAL

Avaliar o grau de contaminação por PCBs em algumas áreas da Baía de Todos os Santos e no pescado consumido na cidade de Salvador.

3.2 OBJETIVOS ESPECÍFICOS

a) Avaliar a ocorrência e distribuição de PCBs na biota da Baía de Todos os Santos;

b) Avaliar o grau de contaminação por PCBs em peixes e bivalves comercializados na cidade de Salvador;

c) Comparar as concentrações atuais com valores pretéritos.

d) Avaliar possíveis riscos à saúde humana, associados ao consumo de pescado.

4 MATERIAIS E MÉTODOS

4.1 ÁREA DE ESTUDO

Segunda maior baía do país, ocupando uma área de 1.233 km^2 e 184 km de perímetro de costa, a Baía de Todos os Santos (BTS) localiza-se entre as coordenadas 08º30'e 18º30' S e 37º30' e 46º30' W (Figura 2). Seu entorno compreende uma extensa área urbana, com mais de 3 milhões de habitantes, além de uma zona industrial variada. No seu perímetro localizam-se ainda a Base Naval de Aratu, o Polo Petroquímico de Camaçari (maior do hemisfério Sul), além de atividades de exploração refino de óleo e gás (CRA, 2004).

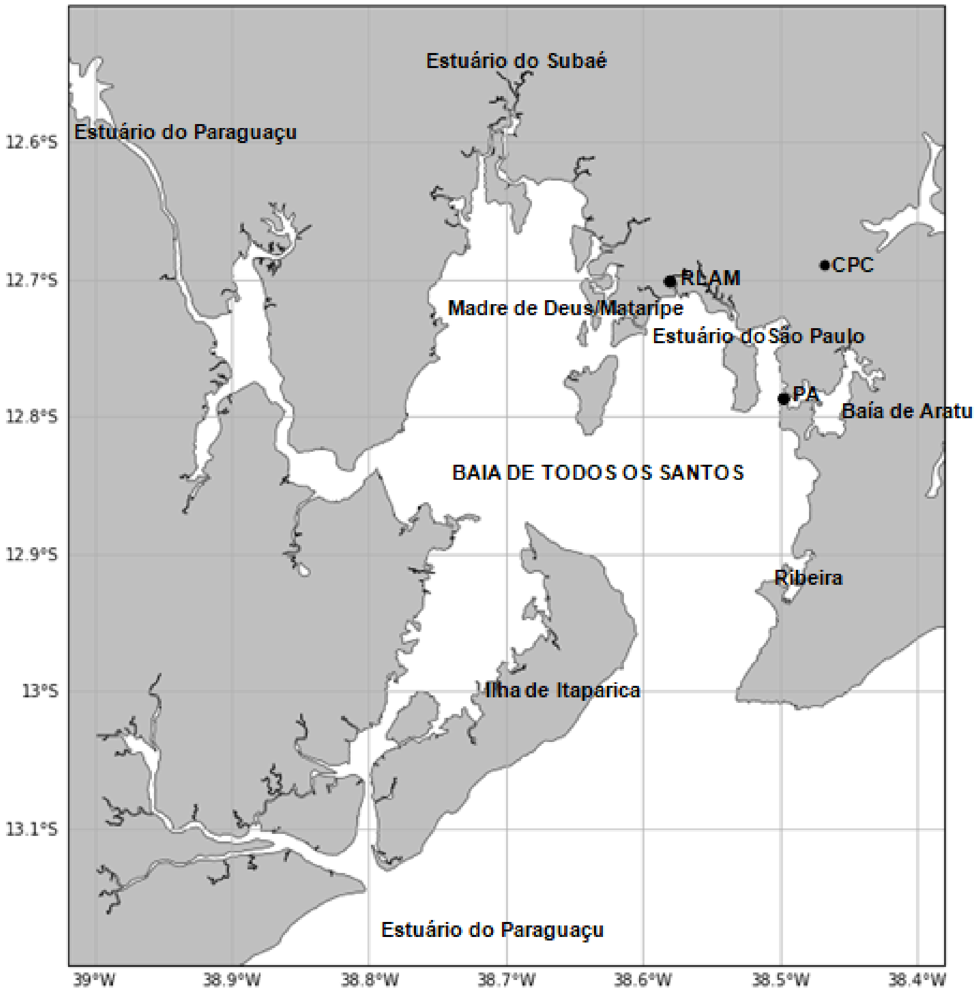

Figura 2 – Mapa da área de estudo (CPC= Complexo Petroquímico de Camaçari; PA= Porto de Aratu; RLAM= Refinaria Landulfo Alves de Mataripe).

Entre as atividades industriais que são desenvolvidas destacam-se as químicas, petroquímicas, metalúrgicas, de produtos alimentícios e fertilizantes. O desenvolvimento dessas atividades envolve o uso de uma variedade de produtos químicos, que inclui, entre outros, o cloro (HATJE et al., 2009).

4.2 AMOSTRAGEM E PREPARAÇÃO DAS AMOSTRAS

Este trabalho utilizou amostras pertencentes ao repositório do Laboratório de Oceanografia Química – UFBA de responsabilidade da Profª. Dra. Vanessa Hatje. As amostras também foram utilizadas em teses de doutorado previamente desenvolvidas por Eça (2013) e Fahning (2016). A esse laboratório couberam as etapas de coleta e pré-tratamento das amostras.

A coleta se deu em oito diferentes setores da BTS, além da região da baía de Camamu (externa à BTS, usada como área controle). Foram utilizadas 3 espécies de bivalves (*Crassostrea rhizophorae*, *Mytella guyanensis* e *Anomalocardia brasiliana*), a fim de observar a contaminação da baía, e 12 espécies de peixes comprados em mercados populares, no sentido de avaliar a qualidade do pescado que é consumido na cidade de Salvador (*Dasyatis americana, Mycteroperca Bonaci, Caranx crysos, Micropogonia furnieri, Scomberomorus brasiliensis, Thunnus atlanticus, Sardinella brasiliensis, Salminus maxillosus, Ocyurus chrysurus, Seriolla dumerili, Cynoscion leiarchus, Lutjanus synagris*).

Após a coleta manual dos bivalves, as amostras foram refrigeradas até a chegada em laboratório, onde foi feita a lavagem dos bivalves com água ultrapura, além da abertura dos mesmos, a retirada dos tecidos e a formação de amostras compostas com vinte indivíduos cada, e então, congeladas. Para as amostras de peixes, foram adquiridos três indivíduos de cada espécie. Em laboratório, uma fração do músculo da região abdominal de cada indivíduo foi retirada. Esse material foi lavado com água ultrapura e posteriormente congelado. Antes da realização das análises, todas as amostras foram liofilizadas, moídas em um moinho de bolas e armazenadas em um dessecador.

Os procedimentos analíticos podem ser observados com maior detalhamento nas teses de doutorado supracitadas (EÇA, 2013; FAHNING, 2016).

4.3 PROCEDIMENTOS ANALÍTICOS

A extração, baseada no método de Dias (2013), foi realizada através de microondas, e consistiu no uso de 2 g de amostra de tecido macerado que foram distribuídos nos diferentes frascos do microondas. Foram então adicionadas, em cada amostra, 100 uL de solução (1 ng uL^{-1}) de cada padrão surrogado (PCB 103 e PCB 198). A temperatura de extração foi de 115 °C durante 15 minutos com 20 mL da mistura n-hexano:diclorometano (1:1 v/v). Os extratos foram então concentrados a 2 mL, dos quais foram retirados 0,2 mL para determinação de percentual lipídico pelo método gravimétrico. Esse método consiste na pesagem de um vial vazio em balança analítica e a posterior introdução dos 0,2 mL de extrato da amostra nesse vial. Após a secagem, uma nova pesagem é executada e a diferença entre os dois valores fornece o percentual de lipídios da amostra.

Posteriormente, os extratos foram purificados por três vezes com 1 mL de ácido sulfúrico e lavados com água ultrapura, também por três vezes, para retirada do ácido. Por fim, os extratos foram concentrados a 0,9 mL e foram adicionados 0,1 mL do padrão de recuperação (TCMX).

Os processos de identificação e quantificação se deram através de um cromatógrafo de gás acoplado a um espectrômetro de massas (GC/MS) com impacto de elétrons. Os extratos foram injetados no modo sem divisão de fluxo (*splitless*), tendo o gás hélio como gás de arraste. As temperaturas do injetor, da interface e da fonte de íons foram, respectivamente, 280 °C, 280 °C e 300 °C.

A análise de PCBs envolveu a investigação de 48 diferentes congêneres: 8, 18, 28, 31, 33, 44, 49, 52, 56/60, 66, 70, 74, 87, 95, 97, 99, 101, 105, 110, 114, 118, 123, 126, 128, 132, 138, 141, 149, 151, 153, 156, 157, 158, 167, 170, 174, 177, 180, 183, 187, 189, 194, 195, 199, 203, 206, 209.

Para controlar a qualidade dos dados gerados, três recursos foram utilizados: os brancos do método (3x desvio padrão dos valores detectados em amostras fortificadas com os padrões de interesse), para avaliar possíveis contaminações e influência de impurezas; o uso de duplicatas (20% das amostras), para avaliar a precisão; e o uso de Material de Referência Certificado (MRC), que avalia a exatidão do procedimento analítico. Neste estudo, o MRC usado foi o IAEA 432, para mexilhões.

5. RESULTADOS E DISCUSSÃO

A estrutura da dissertação exigida pelo Programa de Pós-Graduação em Petróleo e Meio Ambiente (POSPETRO) contempla a apresentação do trabalho no formato de um artigo científico escrito em língua inglesa. Dessa forma, o item Resultados e Discussão consiste na apresentação do artigo.

APRESENTAÇÃO DO ARTIGO

EVALUATION OF ORGANOCHLORINE COMPOUNDS OCURRENCE IN MARINE ORGANISMS FROM TODOS OS SANTOS BAY, BAHIA, BRAZIL

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Abstract

In order to evaluate contamination by polychlorinated biphenyls (PCBs) in a tropical bay exposed to different anthropic pressures, samples of bivalves (*Crassotrea rhizophorae, Mytella guyanensis* and *Anomalocardia brasiliana*) were collected in different parts of Todos os Santos Bay, Bahia, Brazil. In addition, samples of bivalves and fish, purchased from a seafood market in the city of Salvador were analyzed to study human exposure to PCBs through ingestion. Identification and quantification of PCBs were done by GC/MS after microwave extraction and purification with sulfuric acid. In samples of bivalves, concentrations ranged from <0.08 to 50.13 ng g^{-1} (dry weight), with the highest values being detected in mangrove oyster, followed by clams and mangrove mussel of the Subaé estuary and Madre de Deus/Mataripe; both regions known to be impacted by anthropic activities. Regarding fish samples, froma all 12 species analyzed, only 5 presented levels of PCBs above the detection limit, ranging from 0.23 to 4.55 ng g^{-1} and 0.51 to 26.05 ng g^{-1} by dry weight and lipid weight, respectively. In general, concentrations of PCBs in BTS are lower than in most regions around the world, especially those located in the Northern Hemisphere. Indexes showed that local biota should not feel adverse effects related to the presence of these contaminants, just as the consumption of the fish marketed in the city of Salvador apparently does not represent a clear risk to human health.

Keywords: PCBs, bivalves, fish, contamination.

1 INTRODUCTION

Population growth, industrial and technological development, as well as the intense exploitation of natural resources over the years has resulted in a substantial increase in environmental degradation around the world (CRUTZEN; STOERMER, 2000; HALPERN ET AL., 2008). As a consequence, anthropogenic inputs of contaminants, especially for water bodies, have intensified and changed the global biogeochemical cycles and jeopardize the ecosystem health (NRIAGU, 1993; BOYLE et al., 2014). Among all the contaminants affecting marine environments, polychlorinated biphenyls (PCBs) have received attention over the decades due to their wide distribution and toxic effects to biota and humans (YANG et al, 2005: ZHOU et al., 2018).

PCBs are part of a broader group of substances known as Persistent Organic Pollutants (POPs) according to the Stockholm Convention. This denomination is related to their toxicity, resistance to degradation, bioaccumulation in biota and long-distance transport through atmospheric and oceanic currents (STOCKHOLM CONVENTION; http://chm.pops.int). The Stockholm Convention on POPs was signed in 2001 by 92 countries, which are compromised to develop methods for reducing and/or eliminating the emission of these substances. Currently, there are 152 signatories countries involved, including Brazil, which formally joined the convention in 2004 (STOCKHOLM CONVENTION; http://chm.pops.int). However, despite these regulations, these compounds are still widely detected in the marine environment worldwide (MIRANDA, YOGUI, 2016; LEE et al, 2015) even in considered pristine areas, such as the deep ocean (JAMIESON et al, 2017), poles (STROBEL et al, 2018), and high mountains (LI et al, 2018).

Marine organisms, such as fish and mussels, are widely used in studies of PCBs distribution for several reasons (CAMPILLO et al., 2017; COMMENDATORE et al., 2015; WANG et al., 2019; OZIOLOR et al., 2018; MAGALHÃES et al., 2017). Fish have the capacity to uptake PCBs, mainly through food, and are a key part of coastal populations diet as an important source of proteins, vitamins and minerals (WANG et al., 2015). Thus fish consumption is a potential source of human exposure to PCBs (BAPTISTA et al., 2013; DARNERUD et al., 2006; KIVIRANTA et al., 2004). Mussels, besides the great nutritional importance and wide distribution in coastal regions, are filtering organisms and have a high capacity to bioconcentrate contaminants (GOLDBERG et al., 1978). Also, since they are sessile organism, they reflect the contamination from the area where they were collected (BEYER et al., 2017). Thereupon, the combined use of these organisms allows observing the contamination issue from two perspectives: the potential threat that the consumption of these species may represent to the population and detection of hotspots of PCBs contamination.

Although PCBs represent an environmental problem around the world (LESLIE et al., 2013; TORRES et al., 2015; MILUN et al., 2016; RAGAB et al., 2016) there is still a lack of data from tropical environments, such as Brazil. Besides de low number of studies in Brazilian coast, most studies focus on POPs in marine mammals from the southern and southeastern regions (DORNELES et al., 2015; LAVANDIER et al., 2015; LEONEL et al., 2014; LAVANDIER et al., 2019; MÉNDEZ-FERNANDEZ et al., 2018).

Only few sparse studies evaluate POPs contamination in biota from northeastern states (SANTOS-NETO et al, 2014; MIRANDA; YOGUI, 2016).

Todos os Santos Bay (BTS), the second largest bay in Brazil (1233 km^2), is inserted in a context of high industrial development and exploitation of natural resources. The oldest oil refinery (Landulpho Alves Refinery - RLAM) in Brazil is located in the region as well as the largest petrochemical complex in South America (Camaçari Industrial Center) and the third largest metropolitan area in Brazil (Salvador with about 2.9 million of habitants) (CIRANO; LESSA, 2007; IBGE, http://www.ibge.gov.br). Although some studies investigated the occurrence of contaminants in biota from BTS (RIOS et al., 2017; BRITO et al., 2016; DE SOUZA et al., 2011; GILLJAM et al., 2016), most of them are related to trace elements (for example, BARBOSA et al., 2019; BRITO et al., 2016; SOUZA et al., 2011; EÇA et al., 2013) and all studies regarding POPs in biota were carried out prior to the year 2000 and reported the occurrence, in some areas, of PCBs and pesticides (such as, DDT, HCB, HCH, aldrin, dieldrin, endrin) in bivalves, fishes and crabs (NASCIMENTO et al., 1986; TAVARES et al., 1988; TAVARES; COSTA, 1999).

In this study, the occurrence and distribution of PCBs were investigated in mussel samples from BTS regions with distinct anthropogenic pressures. Moreover, fishes and bivalves, bought from an important market in the city of Salvador, were used to evaluate human exposition to PCBs through food consumption.

2 METHODOLOGY

2.1 Sampling

Samples included in this work represent the long-term regional data collection efforts promoted by the Todos os Santos Bay Multidisciplinary Project, which employed clean procedures with rigorous quality control protocols. This collection includes samples from eight different regions of BTS (Madre de Deus/Mataripe, Paraguaçu Estuary, Jaguaripe Estuary, Subaé Estuary, Aratu Bay, São Paulo Estuary, Itaparica and Ribeira) and also at Camamu Bay, used as a control site (Figure 1). Bivalve species – mangrove oyster (*Crassostrea rhizophorae*), mangrove mussel (*Mytella guyanensis*) and clams (*Anomalocardia brasiliana*) – were collected by hand, stored and transported to the laboratory in refrigerated containers. Due to the biogeographical differences in bivalves distribution, it was not possible to collect all species from every sampling region. Additionally, three individuals of twelve fish species and 20 individuals of each bivalve were purchased from a popular market of Salvador city, named Água

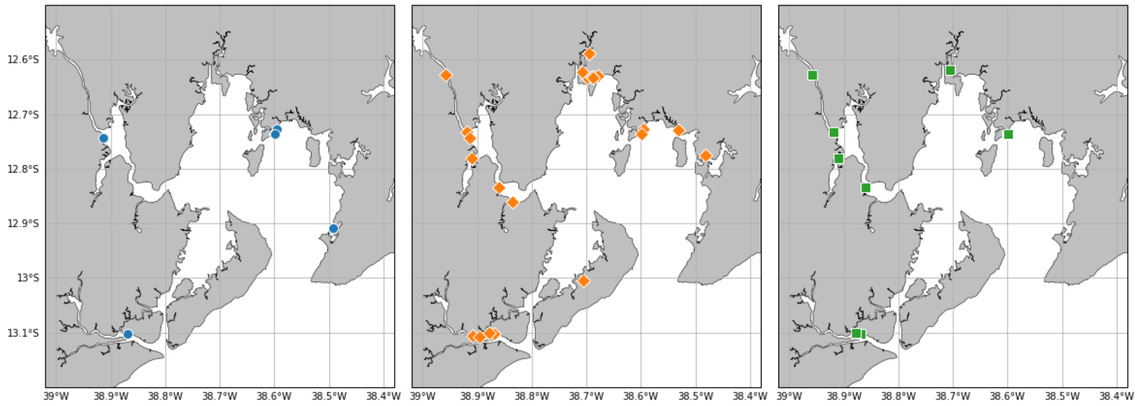


Figure 1 – Map of the study área. Samples of clams (blue), mangrove oyster (orange) and mangrove mussel (green).

de Meninos. Details of sample collection treatment and storage have been described elsewhere (EÇA, 2013; FAHNING, 2016).

In the laboratory, muscle samples were removed from the fish and bivalves removed from the shell and pooled; all samples were frozen. Prior analysis, all tissues were freeze-dried (Alpha 1-4 LD plus lyophilizer, Christ, Germany) and comminuted using a ball mill (8000 D, SP ex sample prep., USA).

2.2 Chemical analysis

Analysis followed the method described by Dias et al. (2013). Briefly, approximately 2 g of dry tissue mixed with sodium sulfate were extracted with 20 mL of *n*-hexane and dichloromethane (1:1) in a microwave (Multiwave PRO, Anton Paar) at 115 °C for 15 min. Prior extractions, to all samples and blanks, 2,2′,4,5′,6-pentachlorobiphenyl (PCB 103) (AccuStandard, USA) and 2,2′,3,3′,4,5,5′,6-octachlorobiphenyl (PCB 198) (AccuStandard, USA) were added as surrogate. Then, extracts were concentrated to 2 mL, from which 0.2 mL were removed for gravimetric determination of lipids. The remaining extracts were cleaned up with 1 mL of sulfuric acid (3 times) and subsequently washed with ultrapure water (3 times), to remove the acid. Finally, the purified extracts were concentrated to 0.9 mL, and 0.1 mL of a recovery standard (2,4,5,6-tetrachlorometaxylene - TCMX) was added.

2.3 Instrumental parameters

PCB analysis was performed on a gas chromatograph coupled to a mass spectrometer (GC/MS) with electron impact (Agilent Technologies, model 5973N). Extracts were injected in splitless mode in a HP-5MS capillary column (30 m x 0.25 mm x 0.25 µm). Helium was used as the carrier gas, with a constant flow of 1.1 mL min^{-1}. Injector, interface and ion source temperatures were, respectively, 280 °C, 280 °C and 300 °C. GC oven was programmed as follows: 75 °C for 3 min, ramped at 15 °C min^{-1} to 150 °C, ramped at 2 °C min^{-1} to 260 °C, and ramped at 20 °C min^{-1} to 300 °C (with a final hold of 1 min).

PCBs analyzed in this study including the sum of 48 isomers and congeners as follows: 8, 18, 28, 31, 33, 44, 49, 52, 56/60, 66, 70, 74, 87, 95, 97, 99, 101, 105, 110, 114, 118, 123, 126, 128, 132, 138, 141, 149, 151, 153, 156, 157, 158, 167, 170, 174, 177, 180, 183, 187, 189, 194, 195, 199, 203, 206, 209 (based on the numeration proposed by Ballschmiter and Zell, 1980).

2.4 Quality control

Quality control was based on Lauenstein and Cantillo (1998). For each extraction batch blanks were analyzed and, when target compounds were detected, their values were subtracted from the samples. For duplicate samples the mean relative percent difference was 14.5%. Surrogate recoveries ranged from 60% to 85%. Concentrations reported in the IAEA 432 were in good agreement with the acceptable limit of ± 30%.Quantification of target compounds was based on internal standards and a six-point linear calibration curve with correlation coefficient of at least 0.995. PCBs were identified by retention time, target ion, and confirmation ion ratios in comparison to external standards. Limits of quantification (LQ) were calculated by dividing the lowest calibration level of a target compound by the mass of the sample extracted.

2.5 Human Health Risk Assessment

To assess human health risk from consumption of fishes and bivalves from BTS the human estimated daily intake (EDI) was calculated, from WHO (1998), based in the total concentration of dioxin-like PCBs in fish (DL-PCBs , in pg of WHO-TEQ-PCB per gram of wet fish tissue), fish consumption habits of the local human population (C, in grams of ingested fish per day), and the average body weight of the local human population (BW, in kilogram):

EDI = DL-PCBs x C / BW

3 RESULTS & DISCUSSION

3.1 Bivalves

PCBs concentration in mangrove oysters, mangrove mussels and clams are presented at Table 1 and ranged from < 0.08 to 50.13 ng g^{-1} dw. Overall mangrove oysters showed the highest PCBs concentration followed by clams and mangrove mussels, it could be explained by differences in feeding guilds as well as habitat. Among mangrove oysters and mangrove mussels, the highest mean concentration was found in samples from Subaé Estuary whereas for clams the highest values were reported in Madre de Deus/Mataripe region; important to notice that for this species no samples were collected from Subaé Estuary. For all three species the lowest values were detected in samples from Jaguaripe Estuary. Subaé Estuary is an area historically subjected to high anthropogenic pressure (ANDRADE et al., 2017, GILLJAM et al., 2016, HATJE; BARROS, 2012), being one of the most contaminated areas in the BTS, where impacts to the benthic biota were already identified (HATJE et al., 2006). On the other hand, Jaguaripe Estuary has little anthropogenic influence and present relatively well preserved conditions (HATJE; BARROS, 2012).

For comparison purpose, mangrove oysters and mussels were also collected from Camamu Bay, a region well preserved and subject to low anthropogenic influences (HATJE et al., 2008). For both organisms, values in samples from Camamu Bay were the lowest, being even lower than those detected in Jaguaripe Estuary. Even though, the number of samples analyzed from Camamu Bay is small, it helps to confirm that the area is a well preserved site considering PCBs occurrence.

Table 1 – PCBs concentration (ng g^{-1} dry weight) for bivalves from BTS The (*) highlights places with only one sample and with no range of variation.

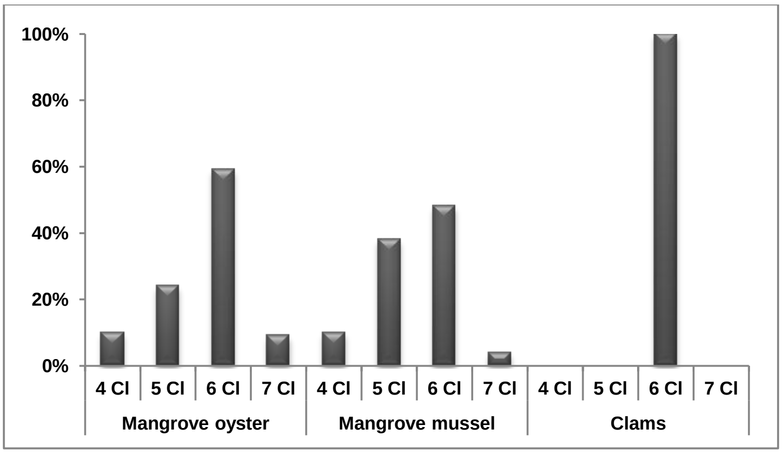
Species/Sites		Present Study		Tavares et al. 1988
Mangrove oyster	**N**	**Average**	**Range**	**Average**
M. de Deus/Mataripe	2	2.8	1.97 – 3.63	-
Paraguaçu Estuary	6	0.77	0.51 – 1.28	-
Jaguaripe Estuary	4	0.33	0.20 – 0.45	-
Subaé Estuary	6	17	9.36 – 50.13	-

Aratu Bay	2	8.57	8.44 - 8.71	-
São Paulo Estuary	1	7.75*	-	12.67
Itaparica	1	2.69*	-	-
Água de Meninos	1	1.00	-	-
Camamu Bay	2	0.12	<0.08 – 0.24	-
Mangrove mussel				
M. de Deus/Mataripe	1	0.56*	-	-
Paraguaçu Estuary	4	0.03	<0.08 – 0.13	-
Jaguaripe Estuary	2	0.08	<0.08 - 0.16	-
Subaé Estuary	1	3.42*	-	-
Água de Meninos	1	4.63*	-	-
Camamu Bay	1	<0.08	-	-
Clams				
M. de Deus/Mataripe	3	2.9	0.74 - 5.22	2.67
Paraguaçu Estuary	1	2.3*	-	0.4
Jaguaripe Estuary	1	1.28*	-	-
Ribeira	2	1.69	0.79 - 2.59	2.00
Água de Meninos	1	0.7*	-	-

From all the 48 PCBs analyzed, 29 congeners were detected in bivalve samples. Hexachlorobiphenyls accounted for the highest percentage (48-100 %) of PCBs, followed by pentachlorobiphenyls (0 - 38 %) and heptachlorobiphenyls (0 - 9 %) (Figure 2). This pattern of higher occurrence of hexachlorobiphenyls in samples of marine organisms has been observed in previous studies in Brazil (LAVANDIER et al., 2013, QUINETE et al., 2011, MAGALHÃES ET AL. 2017, MIRANDA; YOGUI, 2016) and in the world (BORDAJANDI et al. 2003; SAPOZHNIKOVA et al., 2004; KAMPIRE et al., 2015; CAMPILLO et al., 2017). According to DACHS et al. (2002), PCBs congeners are able to fractionate with latitudinal variation due to temperature differences. In tropical regions such as Brazil (higher temperatures), heavier congeners (penta to decachlorobiphenyls) tend to prevail, due to the relatively low vapor pressure. Lighter PCBs have higher vapor pressure and volatilize more easily (WANIA; SU, 2004). Thus, in regions of low temperatures, like temperate zones and poles, the lighter congeners (mono to tetrachlorobiphenyls) have higher ocurrence. Studies in these regions corroborate this behavior (KHAIRY et al., 2016; CABRERIZO et al., 2016; VECCHIATO et al., 2014; ZHU et al., 2015). In addition, the most found classes of PCBs in this study (mainly penta and hexachlorobiphenyls) were abundantly present in technical mixtures produced by the United States and imported by Brazil, such as Aroclor 1254. (LAVANDIER et al. al., 2013)

Among PCBs detected, PCBs 153 and 138 represented approximately 45%, 43% and 98% of the PCBs load for mangrove oysters, mangrove mussels, and clams, respectively. Both PCB 153 and 138 are hexachlorobiphenyls congeners highly persistent due to their chemical structure with 2 ≤ *ortho*-chlorines and no vicinal hydrogen atoms or with vicinal hydrogen atoms in the *ortho-* and *meta-* positions in combination with two to three *ortho*-chlorines. The reduced number amount of vicinal hydrogen prevents oxygen from entering the molecule hindering the metabolism of these PCBs (BRUHN et al., 1995); it explains its occurrence in higher concentrations in biota samples. In Brazil, a number of studies have shown that PCB 153 is the most commonly found in several matrices, followed by PCBs 138 and 180: cetaceans (LAILSON-BRITO et al., 2010; BARBOSA et al., 2018), marine birds (CUNHA et al., 2012) and crabs (SOUZA et al., 2008).

Figure 2 – Percentage of PCB concentration according to the number of chlorines in the molecule.



Tavares et al. (1988) measured concentrations of PCBs in several bivalves species from BTS sampled in 1985/1986. As for most studies, PCBs values in Tavares et al. (1988) were reported in wet weight base, so a mean value of 85% water content was used to compare values between both studies (Table 1).

Values reported by Tavares et al. (1988) in clams from Madre de Deus/Mataripe and Ribeira were similar to those reported in this study. However, concentrations for São Paulo Estuary back in 1980’s were almost twice those detected here (from 12.67 to 7.75 ng g^{-1} dw), whereas for Paraguaçu Estuary an increased was observed (from 0.4 to 2.3 ng g^{-1} dw). PCBs quantification in Tavares et al (1988) was accomplished by employing a standard PCB mixture instead of selected individual congeners, but the authors used a ratio of 3.17, from Porte et al., 1988, to estimate the sum of 7 individual congeners (PCBs 28, 52, 101, 118, 138, 153 and 180) for BTS samples. Besides all the limitations regarding quantification using a PCBs mixture, in the present study 48 congeners quantified were compared to 7 in the previous study (TAVARES et al., 1988). So, when comparing concentrations of same congeners reported in both studies is possible to notice that difference in PCBs levels in oysters from 1985/1986 to 2014 decreased even more (from 12.67 to 2.87 ng g^{-1} dw), for others species/regions they remained almost the same.

Although São Paulo Estuary is located middle way between Madre de Deus and Aratu Bay, it shows PCBs concentrations in mangrove oysters similar to those detected in the latter and higher than those detected in the former. Therefore, the proximity to Aratu Industrial Complex and to Camaçari Petrochemical Complex seem to be the main source of PCBs to the region. These activities often implied the use of transformers, electric capacitors, and hydraulic fluids which used to operate with technical mixtures of PCBs. Nevertheless, the substitution for PCB free oil/hydraulic fluids started in middle 1980’s and could explain the decrease values detected in mangrove oysters from São Paulo Estuary. On the other hand, the increase in PCBs values detected for clams from Paraguaçu Estuary could be related to the sampling location. While Tavares et al. (1988) collect samples near the Paraguaçu mouth where dilution play a important role, in the present studies sampling were carried out in region more inside the Estuary.

In terms of comparison at a broader level, it is possible to observe that the values reported in this study are two to three orders of magnitude lower than those reported in bivalves from regions with a high degree of urbanization and industrialization around the world (Table 2), such as Qingdao Bay (China), Boston Harbor (USA) and Sydney Estuary (Australia). Qingdao Bay, for example, sits on the shores of one of China's major cities which are highly industrialized mainly in the area of electronics and telecommunications (ZHANG; RASIAN, 2013; KIM; ZHANG, 2008). This information ratifies the association between industrial development environments and higher occurrence of PCBs.

Table 2 – Previous PCBs studies in bivalves samples. Values in dry weight (ng g^{-1})

Location	PCBs	References
Todos os Santos Bay, Brazil	0.1 – 17	Current study
Qingdao Bay, China	4622 - 7881	Pan et al., 2010
Boston Harbour, USA	338	Vorkamp et al., 2010
Sydney Estuary, Australia	147 - 282	Vorkamp et al., 2010
Arcachon Bay, France	38 - 60	Thompson et al., 1999
Mediterranean Coast, Spain	0.1 – 5.8	Campillo et al., 2017
Guanabara Bay, Brazil	48 - 61	Petrus et al., 2014

Aleutian Archipelag, Alaska	7 - 2800	Reese et al., 2012
Patagonia, Argentina	0.41 – 0.6	Commendatore et al., 2015
Sepetiba Bay, Brazil	6.7 – 9.1	Petrus et al., 2014

The general trend of higher values of contaminants at sites in the Northern Hemisphere when compared to those found in the Southern Hemisphere (JOHNSON-RESTREPO et al., 2005; YOGUI et al., 2003; TAO et al., 2006) is showed in Table 2. This is justified by the fact that there is greater industrialization to the north, since its development process preceded that of the south. In addition, there is a limitation of information regarding environmental contamination in the South compared to the North (LAILSON-BRITO et al., 2010).

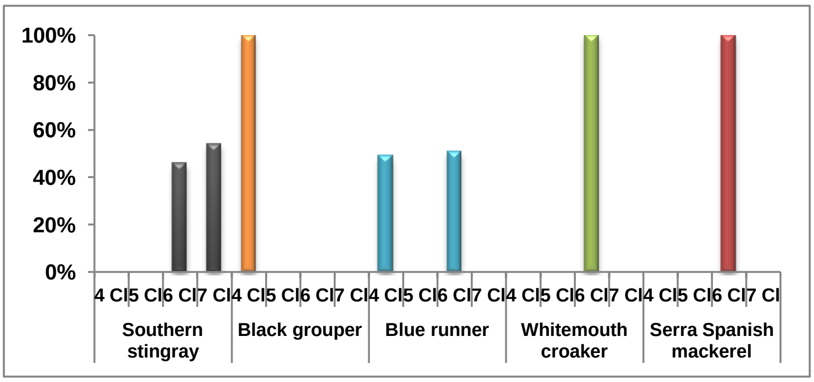
3.2 Fishes

A high variability in PCBs concentration was observed among individuals for each species analyzed which could be explained due to differences in the biological parameters as well as differences on sampling places. However, such information were not available since fishes were bought in seafood market. Thus, data here is only discussed regarding differences in concentrations, pattern of occurrence and their relationship with trophic position and habitats in general. Moreover, considering that lipid content have a great variation among species, PCBs levels were normalized to lipid weight before further discussions (Table 3).

Nine different PCB congeners were detected in five of the twelve edible species of fish analyzed. Average concentrations ranged from 0.51 to 26.06 ng g^{-1} lw (Table 3) with the highest mean concentration found in southern stingray (*Dasyatis americana*) samples (26.05 ng g^{-1} lw) followed by black grouper (*Mycteroperca Bonaci*) (2.25 ng g^{-1} lw), blue runner (*Caranx crysos*) (1.86 ng g^{-1} lw), whitemouth croaker (*Micropogonia furnieri*) (1.48 ng g^{-1} lw), and serra spanish mackerel (*Scomberomorus brasiliensis*) (0.51 ng g^{-1} dw). Other species did not present concentrations above the method detection limit (MDL).

The highest concentrations detected in southern stingray could be related to the fact that the species habits are associated to sediment, since this compartment is one of major sink of PCBs to aquatic environments (BORJA et al., 2005). Others species have pelagic habits, even though some could prey on benthic species, such as the whitemouth croaker.

Figure 3 – Percentage of PCB concentration according to the number of chlorines in the molecule, in fishes.



PCBs with six chlorines were the major contributors in edible fish samples from BTS (Figure 3) with PCB 153 as the predominant congener (35% of the total concentration). Similar results were found in others studies with fish from brazilian coast (CASCAES et al., 2014; MAGALHÃES et al., 2017; MIRANDA; YOGUI, 2016; AZEVEDO E SILVA et al., 2007).

Table 3 – Values of lipid percentage variation, mean concentration and range of PCB concentration in fishes (dw= dry weight, ww= wet weight, lw= lipid weight).

Species	Lipids (%)	Average (dw)	Range (dw)	Average (ww)	Average (lw)	Habitat and Trophic Categories
Southern stingray *(Dasyatis americana)*	2.31 - 2.98	4.55	<0.38 - 11.98	0.68	26.05	Sandy and muddy bottoms/carnivore
Black grouper *(Mycteroperca Bonaci)*	0.62 - 2.44	0.23	<0.38 - 0.68	0.03	2.25	Reefs/carnivore
Blue runner *(Caranx crysos)*	10.86 - 15.59	1.6	<0.38 - 4.24	0.24	1.86	Pelagic-Coastal/carnivore
Whitemouth croaker *(Micropogonia furnieri)*	3.24 - 14.76	0.83	<0.38 - 1.38	0.12	1.48	Over muddy and sandy bottoms/ carnivore
Serra Spanish mackerel *(Scomberomorus brasiliensis)*	4.32 - 28.50	0.5	<0.38 - 1.51	0.07	0.51	Pelagic/carnivore
Blackfin tuna *(Thunnus atlanticus)*	1.70 - 2.69	<0.38	<0.38	-	-	Pelagic/carnivore
Brazilian sardine *(Sardinella brasiliensis)*	5.37 - 10.35	<0.38	<0.38	-	-	Shallow coastal areas/Carnivore
Dorado *(Salminus maxillosus)*	1.03 - 1.50	<0.38	<0.38	-	-	Lagoons/carnivore
Yellowtail snapper *(Ocyurus chrysurus)*	2.03 - 16.04	<0.38	<0.38	-	-	Reef/Planktonic or carnivore
Greater amberjack *(Seriolla dumerili)*	1.59 - 3.02	<0.38	<0.38	-	-	Deep marine reefs/Carnivore
Smooth weakfish *(Cynoscion leiarchus)*	0.64 - 0.84	<0.38	<0.38	-	-	Muddy and sandy estuarine bottoms/carnivore
Lane snapper *(Lutjanus synagris)*	1.12 - 6.68	<0.38	<0.38	-	-	Reefs and vegetated sandy bottoms/Carnivore

The concentration values detected in fishes from the seafood market in Salvador are lower than those detected in species from other regions of Brazil, such as São Paulo and Pernambuco coast (Table 4). Similar results were found when compared with studies from others countries considered contaminated. From values like 199 ng g^{-1} in Bangladesh, to the extreme 16,500 ng g^{-1} reported for Galveston Bay in the United States. On the other hand, some works found concentrations that are more consonant with those observed in the BTS, such as the Sanzibar Islands in Tanzania (maximum of 1.22 ng g^{-1}) and the Western Mediterranean Sea, Spain, Tunisia and Egypt (between 0.2 and 1.8 ng g^{-1}).

Table 4 – Previous PCB studies in fishes samples. Values in lipid weight (ng g^{-1}).

Localização	PCBs	Referência
Todos os Santos Bay, Brazil	0.5 - 26	Current study
Cau Hai Lagoon, Vietnam	26 - 43	Tran et al., 2019
Western Mediterranean Sea	0.2 – 1.8	Junqué et al., 2018
Galveston Bay, USA	43.5 - 16,500	Oziolor et al., 2018
Bengala Bay, Bangladesh	32 - 199	Habibullah-Al-Mamun et al., 2019
Sanzibar Islands, Tanzania	0 – 1.22	Mwakalapa et al., 2018
São Paulo Coast, Brazil	691 - 1454	Cascaes et al., 2014
Santos Bay, Brazil	27 - 117.8	Magalhães et al., 2017
Ilha Grande Bay, Brazil*	46 - 552	Lavandier et al., 2013
Pernambuco Coast, Brazil	53.9 - 867	Miranda; Yogui, 2016

*Calculated considering a lipid weight of 5%

3.3 PCBs human intake and effects on biota

Since human estimated daily intake (EDI) is only calculated considering the most toxic PCBs (non-*ortho* and mono-*ortho* congeners) and none of these were detected in fish or clams from BTS above MDL, EDI was only calculated for mangrove oysters and mangrove mussels. Since there is no data available for bivalve consumption, Brazilian population average fish consumption was used instead (39.7 g day^{-1}, MAPA, 2014). Moreover, according to IBGE (2010) the average body weight related to age was used to determine EDI for different ages and genders.

EDI values for mangrove oyster and mangrove mussels from BTS are presented in Table 5. All values were lower than those presenting a potential risk to human health (4 pg kg^{-1} day^{-1}, WHO, 1998). Also, concentrations of the most toxic PCBs detected in this study (dioxin-like PCBs) were lower than the maximum acceptable value determined by Brazilian regulation of 6.5 pg g^{-1} WHO-TEQ-PCB (MAPA, 2015).

Table 5 – Mean EDI values (pg kg^{-1} day^{-1}) for bivalves.

	Age (years)	Average body weight (kg)	Subaé oyster	Aratu oyster	M. Deus oyster	São Paulo oyster	Subaé mussel	Á. Meninos mussel
Man	3 to 11	24,4	0,0127	0,0051	0,0180	0,0057	0,0200	0,0291
	12 to 17	51,3	0,0060	0,0024	0,0086	0,0027	0,0093	0,0138
	18 to 64	67,7	0,0046	0,0018	0,0065	0,0021	0,0071	0,0105
	>64	63,7	0,0049	0,0020	0,0069	0,0022	0,0075	0,0111
Woman	3 to 11	24,7	0,0126	0,0051	0,0178	0,0057	0,0194	0,0287
	12 to 17	48,1	0,0064	0,0026	0,0091	0,0029	0,0099	0,0148
	18 to 64	59,6	0,0052	0,0021	0,0074	0,0023	0,0080	0,0119
	>64	57,9	0,0054	0,0022	0,0076	0,0024	0,0082	0,0123

In order to evaluate the possible toxicity of levels detected in the present study and due to the absence of reference values at the national level, PCBs concentrations were compared to the Threshold Effect Level (TEL) and Probable Effect Level (PEL) indexes (BUCHMAN, 2008). Although this type of approach has limitations, it allows a comparison of data on a world scale. While the former represents the level below which adverse effects to the biological community are rarely expected, the latter designates a level above which there is likely to be an adverse effect on the biota. All concentrations measured in the present study are below the TEL (21.6 ng g^{-1}), suggesting that the concentrations of PCBs found should not pose a risk from the ecological point of view.

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4 CONCLUSIONS

Overall PCBs levels in bivalves and fishes from BTS were lower than those detected in species from most regions of the world, especially those highly contaminated in Northern Hemisphere. Values were also lower than PEL suggesting that no adverse effects should be observed in mangrove oysters and mangrove mussels. Regarding commercial fishes from the seafood market of Salvador city, PCBs levels are low and apparently do not present concentration values that pose a risk to human health regarding polychlorinated biphenyls.

Among the different region of BTS, higher concentrations were detected near industrial and harbor regions as expected and lower concentrations are reported in regions relatively well preserved. Also, the fact that PCBs were detected in very low levels in Camamu Bay and only in mangrove oysters corroborate to confirm the region as a more pristine site.

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6 CONCLUSÃO

Os resultados gerados por este estudo indicam as seguintes constatações:

- Os níveis de PCBs em bivalves e peixes na BTS foram mais baixos que na maior parte do mundo, sobretudo em relação ao Hemisfério Norte.
- Os valores se encontram abaixo do PEL, o que sugere que não devem ser observados efeitos adversos para os bivalves.
- O pescado comercializado na cidade de Salvador não apresenta concentrações de PCB que signifiquem risco ao consumo humano.
- Entre as regiões da BTS, como esperado, as maiores concentrações de PCBs foram encontradas em áreas industriais e portuárias, e as menores foram registradas em regiões relativamente bem preservadas.
- A Baía de Camamu, usada como região controle, apresentou valores muito baixos de PCBs apenas em sururu, confirmando a ideia de ser uma área mais prístina.

Diante do amplo alcance e alarmante risco apresentado pelo uso de PCBs, com uma série de impactos ambientais e humanos já discutidos neste trabalho, mostra-se fundamental a investigação e monitoramento dessas substâncias no ambiente, assim como a fiscalização do cumprimento das normas restritivas e acordos internacionais.

Segundo o texto da Convenção de Estocolmo, é prerrogativa dos países signatários estimular a produção científica, através do fomento a atividades de pesquisa, desenvolvimento, monitoramento e cooperação com relação aos poluentes orgânicos persistentes. Além disso, o texto também alerta para a necessidade de observar a efetivação das metas propostas, a fim de verificar se os níveis estão de fato sendo reduzidos (UNEP, 2010). Para isso, é necessário gerar continuamente dados a respeito de ocorrência, fontes e distribuição desses compostos no tempo e no espaço, através da realização de estudos que envolvam uma quantidade ainda maior de amostras, assim como a análise de outros compostos clorados, também listados pelo texto da Convenção e, portanto, potencialmente prejudiciais.

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