ORGANOHALOGEN COMPOUNDS IN YELLOWFIN TUNA (*Thunnus albacares*) FROM THE WESTERN INDIAN OCEAN

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Abstract
The concentration levels and distribution patterns of polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs) were investigated in the muscle and liver of yellowfin tuna (*Thunnus albacares*; YFT) from the western Indian Ocean. PCB and DDT concentrations were comparable in both tissues of YFT (108±74 and 25±14 ng.g^{-1} of lipid weight in muscle and 108±74 and 28±21 ng.g^{-1} lw in liver, respectively). YFT muscle exhibited higher HCB and lindane levels (297±195 and 25±17 ng g^{-1} lw) than liver (58±26 and 13±18 ng g^{-1} lw). Compared to previous works on worldwide POP contamination in tuna, YFT from the western Indian Ocean appeared moderately contaminated by PCBs and DDTs, whereas high concentrations of HCB and lindane were reported. As regards PBDEs, our preliminary results revealed levels below the analytical detection limits (4-6 pg.g^{-1} of dry weight). Finally, the specific analysis of PCB congeners revealed a profile dominated by hexa-, tetra- and pentachlorinated congeners, while among DDTs, the compound with the higher concentration was *p,p'*-DDE.

Introduction
Environmental pollution by persistent organic pollutants (POPs) is a hot topic around the world especially after the Stockholm Convention entered in force[1]. This is the first international instrument that aims to reduce the environmental contamination by POPs, and that can act as law enforcement among those countries who are signatories. Among POPs, some organohalogen compounds (e.g., polychlorinated biphenyls - PCBs) are of great concern because of their capacities to be bioaccumulated by aquatic organisms and biomagnified through the food chain. Because of the trophic transfer properties of these chemicals, species of high trophic levels and characterized by long lifespan, such as tuna fish, are susceptible to contain high POP body burdens. Studying POP contamination in top predators is thus essential as it serves as evidence for environmental exposure levels. Furthermore, POP concentrations in large predatory fish are of particular interest because fish is the main source of human exposure[2].
To our knowledge, there is very little information on POPs in tuna species, especially from the western Indian Ocean. Among tunas and associated exploited species, yellowfin tuna (YFT) constitutes the second largest tuna fishery worldwide[3]. In the Indian Ocean, YFT represents the second largest tuna catch encompassing 25% of the total catch of this region[4]. Unlike YFT fisheries in the Atlantic and Pacific Oceans, the Indian Ocean tuna fishery provides an important resource for East African and Asian developing countries and constitutes the major source of food proteins and omega-3 fatty acids for large populations in the region[5]. In addition to be a top marine predator, YFT is a high performance fish with very high metabolic rates and high food intake rates[6], factors which enhance POP exposure. Finally, this pelagic species presents a high migratory pattern that may expose it to different pollution pressures depending on its feeding areas. In this context, the main objective of this study was to obtain data on PCB, organochlorine pesticide (OCP) and polybrominated diphenyl ether (PBDE) contamination in YFT from the western Indian Ocean. Contaminant levels and profiles were studied in muscle and liver, and results were compared to literature data on worldwide POP contamination of tunas.

Material and Methods
Sampling
YFT (n=5) were caught by trolling line around anchored fishing aggregating devices (FADs) in December 2007 from the western Indian Ocean at locations near La Reunion Island (21°09'S / 55°30'E). White muscle tissues

from the dorsal region and liver were carefully dissected onboard and stored frozen at -20°C until processing. Table 1 displays all the biological characteristics of the samples.

Table 1. Biological characteristics of yellowfin tunas (YFT, n=5) collected from the western Indian Ocean.

	Sex	Fork length (cm)	Weight (kg)	Fat % Muscle	Fat % Liver
YFT1	Immature	53	2.93	1.1	9.1
YFT2	Immature	76	8.04	0.6	4.2
YFT3	Male	78	8.63	0.6	4.3
YFT4	Male	72	7.30	0.6	5.6
YFT5	Male	72	6.96	0.7	4.2

Chemical analysis

Samples were freeze-dried and ground up to a fine powder before their analysis for POPs at the Organic Contaminant Laboratory of IFREMER in Nantes, France. The Laboratory facilities include a clean, low dust atmosphere at positive pressure. Quality assurance / quality control procedures were included for every batch of five samples. The laboratory routinely participates in the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) intercomparison exercises for all analysed contaminants.

The fish tissue samples were analysed for PCBs, OCPs and PBDEs. The detailed analytical protocols for extraction and cleanup have been described previously[7]. Briefly, between 10 g (liver) and 20 g (muscle) of tissues were extracted using pressurized solvent extraction (ASE, Dionex Corp., CA) with dichloromethane, purified by gel permeation chromatography (Bio-Beads S-X3), treated with concentrated sulphuric acid in order to remove the remaining lipids, and fractionated on a silica and alumina open column. PCBs and OCPs were analysed by high resolution gas chromatography (HRGC) (GC3800, Varian) fitted with two electron capture detectors (ECD), using two columns of different polarities: a DB-5 (5% phenylmethylpolysiloxane) column of 60 m x 0.25 mm (film thickness 0.25 µm), and a HT8 (8% phenyl-polysiloxanecarborane) column of 50 m x 0.25 mm (film thickness 0.25 µm). Twenty-eight PCB congeners with 3–8 chlorine atoms (CB18, 28, 31, 44, 49, 52, 60, 66, 87, 101, 103, 105, 110, 112, 118, 123, 138, 143, 151, 153, 156, 167, 170, 174, 180, 183, 189, 194) were analysed including the dioxin-like mono-ortho and the 7 priority PCBs, as well as 17 organochlorine pesticides (α- and β-HCHs; lindane; DDTs,, DDDs and *pp'*-DDE; HCB; trans- and cis-chlordane; trans- and cis-nonachlor; heptachlor; heptachloroepoxide; pentachlorobenzene; aldrin). PBDEs (BDE-28, -47, -49, -66,-77, -85, -99, -100, -138, -153, -154, -183 and -209) were analysed using a gas chromatograph (Agilent 6890) coupled to a mass spectrometer (5973N) operated in negative chemical ionisation mode using methane as the reagent gas. Recovery surrogates including selected PCBs, OCPs and PBDEs were added to the samples before extraction. LODs were 10 and 100 $pg.g^{-1}$ of dry weight (dw) for PCBs and OCPs, and 4-6 $pg.g^{-1}$ dw for PBDEs.

Results and discussion

The studied YFT from the western Indian Ocean were immature or male specimen and presented very similar biological characteristics (Table 1), excepted for YFT1 which was smaller and exhibited higher muscle and liver fat contents.

PCB and organochlorine pesticide concentrations measured in YFT muscles and livers are reported in $ng.g^{-1}$ of lipid weight (lw) in tables 2 and 3. Only compounds presenting contamination levels above detection limits (LODs) in at least one sample were reported. As regards PBDEs, the different congeners were below LODs in YFT muscles and livers. These results were consistent with those observed in the muscle of skipjack tuna collected from Seychelles[8], and reinforce the hypothesis of the absence of significant PBDE pollution sources in this region.

The concentrations of the total analysed PCBs (sum of 28 PCBs) in YFT muscles ranged from 44 to 382 $ng.g^{-1}$ lw (Table 2). Levels in the same order of magnitude were observed in YFT livers when normalised to tissue fat content (52-621 $ng.g^{-1}$ lw). The 7 priority PCBs and dioxin-like mono-ortho PCBs accounted for approximately 50-65% and 15-35% in both tissues of YFT. The lowest concentrations of PCBs were recorded in the smallest individual (YFT1). In spite of similar biological characteristics, the other specimens exhibited very different contamination levels, suggesting a high inter-individual variability. Results from this study were generally higher than those from previous works on tuna contamination from different oceans worldwide. For instance,

Ueno et al.[9] reported PCB levels (sum of 117 congeners) of 1-130 ng.g^{-1} lw, 21-190 ng.g^{-1} lw and 350-590 ng.g^{-1} lw in the liver of skipjack tunas collected from the Indian Ocean, the northern Pacific Ocean and the southern Atlantic Ocean, respectively. As regards mono-ortho DL-PCBs (sum of 8 congeners), concentrations of 4-8 ng.g^{-1} lw, 6-20 ng.g^{-1} lw and 13 ng.g^{-1} lw were measured in the muscle of these same skipjack tuna samples[10]. Finally, PCB concentrations of 8-19 ng.g^{-1} lw were observed in the liver of bigeye tuna (*Thunnus obesus*) sampled in the northern Pacific Ocean[11]. Nevertheless, our results were lower than PCB levels observed in the liver of bluefin tuna (325-812 ng.g^{-1} lw) from the Mediterranean Sea[12].

Table 2. Polychlorinated biphenyls (ng.g^{-1} lw) in the muscle (M) and liver (L) of yellowfin tuna (YFT, n=5) from the western Indian Ocean.

	YFT1		YFT2		YFT3		YFT4		YFT5	
	M	L	M	L	M	L	M	L	M	L
CB 18	<LOD	<LOD	4.5	<LOD	6.4	<LOD	5.9	4.7	5.6	4.2
CB 31	0.8	2.0	5.3	4.6	9.2	7.9	6.7	6.1	8.2	4.0
CB 28	0.8	2.5	5.5	6.3	10.4	9.3	7.9	7.0	8.2	4.6
CB 52	5.4	11.1	26.4	29.7	58.5	43.4	22.3	29.2	33.6	12.9
CB 49	5.6	<LOD	8.2	<LOD	18.7	<LOD	8.3	15.9	9.5	5.7
CB 44	3.1	4.6	13.8	8.2	28.1	15.3	15.1	15.1	17.8	7.6
CB 101	3.8	3.8	11.6	11.8	38.2	10.7	16.3	44.3	12.8	6.4
CB 87	3.3	2.3	8.5	6.9	15.4	8.5	12.1	12.7	7.0	4.2
CB 110	5.5	5.8	19.4	13.9	44.3	15.7	23.2	56.5	14.9	9.4
CB 151	1.2	2.3	5.9	8.5	19.2	5.8	7.6	30.7	5.6	4.0
CB 118	5.3	2.9	15.8	10.1	26.8	11.0	20.2	54.7	12.2	8.8
CB 153	3.4	4.7	18.1	23.4	50.4	15.8	19.5	157.0	13.8	10.3
CB 105	2.7	2.4	5.2	4.1	10.7	5.2	8.3	11.5	4.1	2.1
CB 138	2.8	4.5	14.9	17.8	42.5	12.2	16.4	122.3	10.0	8.2
CB 183	<LOD	<LOD	<LOD	<LOD	3.0	<LOD	<LOD	9.7	1.6	<LOD
CB 180	<LOD	2.8	<LOD	12.6	<LOD	7.9	2.5	26.0	1.9	3.2
Σ_{28}PCBs	43.8	51.6	162.9	157.9	381.7	168.6	192.2	621.2	166.9	95.6
Σ_{7}PCBs	21.6	32.3	92.3	111.6	226.7	110.2	105.0	440.6	92.6	54.3
Σ_{6}DL-PCBs	8.0	5.2	20.9	14.2	37.5	16.2	28.5	75.1	16.3	10.9

Σ_{28}PCBs = sum of the 28 PCB congeners; Σ_{7}PCBs = sum of the 7 priority PCBs; Σ_{6}DL-PCBs = sum of the 6 mono-ortho dioxin-like PCBs.

The distribution of PCBs in YFT tissues from the western Indian Ocean is presented in Figure 1. Similar patterns were reported in the muscle and liver of the different YFT specimens, although for some congeners, high standard deviations were observed. The main PCB congeners and their relative abundance were as follow: CB153 (8-26%) ≈ CB52 (5-26%) > CB138 (6-21%) > CB110 (9-12%) ≈ CB118 (6-12%) ≈ CB101 (6-10%). These fingerprints were unexpected. Indeed, they were predominated on the one hand by the more hydrophobic compounds (CB153, CB138 and CB118) present in all aquatic biota and known to be bioaccumulated and biomagnified in the food chain and to resist to biotransformation. On the other hand, they revealed the prevalence of the least chlorinated congeners and consequently the more soluble and the less persistent ones (CB52, CB101 and CB110). Previous works on PCB contamination in tunas emphasized the prevalence of the more persistent PCBs (CB153>CB138>CB180>CB118) in muscle[2,13-16] and liver[9,12,14,16] of tuna species (bluefin and skipjack tunas) from different geographical regions. Nonetheless, Ueno et al.[9] highlighted the predominance of less chlorinated PCB congeners in skipjack tuna samples from cold waters in the northern regions compared to those from tropical areas, hypothesizing that it was the consequence of a higher atmospheric transport of these compounds. However, our first results on PCB contamination of YFT from the Indian Ocean did not match with these observations.

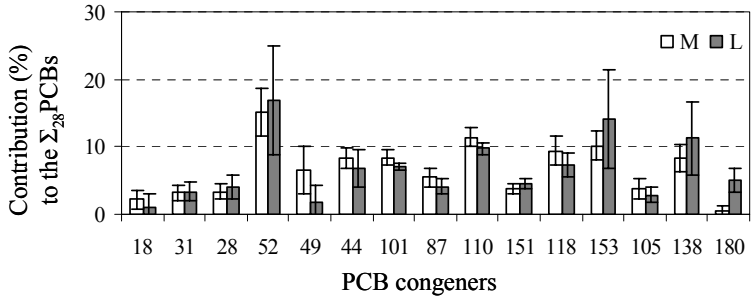

Figure 1. PCB patterns in the muscle (M) and liver (L) of yellowfin tunas (n=5) from the western Indian Ocean. Mean values (± standard deviation) of the contribution of each congener to the Σ_{28}PCBs.

Among the 17 analysed organochlorine pesticides, only HCB, lindane, DDTs and chlordane compounds were detected in the YFT muscles and livers (Table 3). All YFT exhibited high concentrations of HCB, mainly stored in muscle (121 to 601 ng.g^{-1} lw) compared to liver (18 to 82 ng.g^{-1} lw). Ueno et al.[9] reported lower HCB levels of 1-3, 3-11 and 1-3 ng.g^{-1} lw in the liver of skipjack tunas collected from the Indian Ocean, the northern Pacific Ocean and the southern Atlantic Ocean, respectively. Another tuna species, the bluefin tuna collected from the Mediterranean Sea, exhibited HCB residues of 0.003-19 ng.g^{-1} lw in muscle[17]. The study of YFT contamination by lindane revealed very inter-individual variable results, with levels ranging from <LOD to 250 ng.g^{-1} lw and from 4 to 22 ng.g^{-1} lw in muscle and liver, respectively. Immature yellowfin tuna (YFT1 and YFT2) presented the higher lindane concentrations in liver compared to muscle, whereas this opposite trend was observed for male specimen (YFT3, YFT4 and YFT5). These results were in the same range than those observed in bluefin tuna liver collected from Japanese coastal waters, but were higher than those measured in tuna species from the Mediterranean Sea and open oceans[9,16,18].

Table 3. Organochlorine pesticides (ng.g^{-1} lw) in the muscle (M) and liver (L) of yellowfin tuna (YFT, n=5) from the western Indian Ocean.

	YFT1		YFT2		YFT3		YFT4		YFT5	
	M	L	M	L	M	L	M	L	M	L
pp'-DDE	2.3	5.1	16.2	17.5	24.1	15.0	16.1	34.8	13.6	10.8
pp'-DDD	1.2	1.5	3.7	7.8	6.4	8.3	4.4	22.5	<LOD	5.8
pp'-DDT	<LOD	<LOD	5.9	<LOD	10.5	<LOD	7.5	0.8	7.1	0.9
op'-DDD	0.9	<LOD	2.1	<LOD	2.3	<LOD	<LOD	4.6	<LOD	2.8
ΣDDTs	4.4	6.6	27.8	25.3	43.2	23.3	28.0	62.7	20.7	20.3
HCB	378.8	17.6	121.2	53.4	185.9	82.3	196.5	58.8	601.5	78.7
lindane	<LOD	4.3	17.9	22.0	39.8	17.5	250.2	3.8	40.9	17.3
trans-chlordane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.0	<LOD	1.0
cis-chlordane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.6	<LOD	0.8
trans-nonachlor	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.3	<LOD	0.6
cis-nonachlor	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.1	<LOD	<LOD

Chlordane compounds were detected only in the liver of YFT4 and YFT5 at very low levels (6 and 2 ng.g^{-1} lw, respectively).

DDT and its metabolites were present in all yellowfin tunas collected from the western Indian Ocean. Concentrations of DDTs ranged from 4 to 43 ng.g^{-1} lw and from 7 to 63 ng.g^{-1} lw in muscle and liver, respectively. The lowest contamination levels were measured in the immature specimen (YFT1). Compared to previous works, our results revealed a weak DDT contamination of YFT from the western Indian Ocean. Indeed, DDT concentrations of 20-430 ng.g^{-1} lw, 21-190 ng.g^{-1} lw and 45-150 ng.g^{-1} lw were measured in the liver of skipjack tunas collected from the Indian Ocean, the northern Pacific Ocean and the southern Atlantic Ocean, respectively[9]. The liver of bluefin tuna from the Mediterranean Sea[12,16] and Japanese coastal waters[18] exhibited

DDT levels of 12-435 and 140-2900 ng.g^{-1} lw, respectively. The more persistent metabolite *p,p'*-DDE was the predominant compound among DDTs in YFT tissues, accounting for 55 to 75% of the sum of DDTs (Figure 2). Similar patterns were observed in the muscle and liver of bluefin tuna (*Thunnus thynnus*) from the Mediterranean Sea[14,16] and Japanese coastal waters[18].

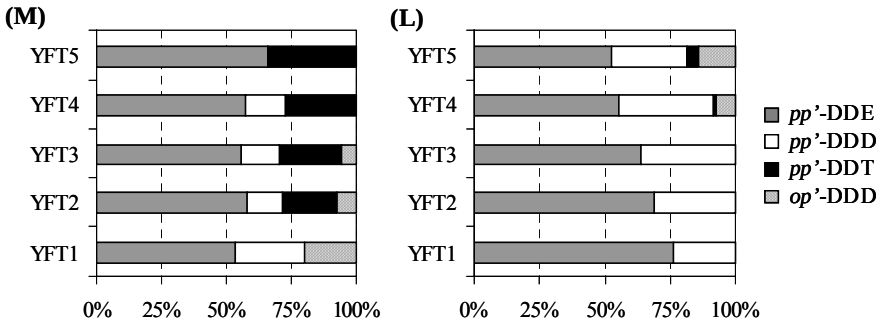

Figure 2. Composition of DDTs in the muscle (A) and liver (B) of yellowfin tunas (YFT, n=5) from the western Indian Ocean.

Conclusion

The results presented here provide reference data on POP contamination in an exploited top marine predator, the yellowfin tuna (*Thunnus albacares*), from the western Indian Ocean. In a worldwide context, the muscle and liver of this species appeared moderately contaminated by PCBs and DDTs, whereas high concentrations of HCB and lindane were reported. Moreover, it must be noted that residues of PCBs, DDTs, lindane and HCB were higher than those measured in 1999 in previous surveys on POP contamination in skipjack tuna from the Indian Ocean[9,10], suggesting active ongoing sources at the vicinity countries of this region. Indeed, such an hypothesis may be related to the agricultural and industrial growth in these countries in recent years, as well as the possible impacts from northern developed nations which used developing countries in the southern hemisphere as dumpsite for used transformers and capacitors for example. As regards PBDEs, this study adds information on the scarce literature data that exist on brominated compounds in tunas, revealing the absence of PBDE pollution sources in the western Indian Ocean.

In the future, further investigations based on POP contamination in exploited tunas and associated species (i.e., swordfish, sharks) from the Indian Ocean should be conducted in order to improve our understanding on the distribution and transport of these contaminants (influence of biological factors such as sex, age, reproduction status, migration, etc), to identify the possible direct and/or indirect pollution sources in this region, and to participate to the assessment of the potential health risk to local populations.

Acknowledgements

JPM Torres is indebted to the CAPES Foundation of the Ministry of Education (Brazil) for the Post-Doctoral Fellowship. Dr. Torres is Associate Professor I and Researcher of the Brazilian Research Council (CNPq – Level 2), Fellow of FAPERJ (Cientista Jovem do Nosso Estado) and Advance Sellikoff Fellow of the Mount Sinai School of Medicine and supported in part by NIH-Fogarty Grant No: 1D43 TW 00640.

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