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Tissue-specific bioaccumulation of a wide range of legacy and emerging persistent organic contaminants in swordfish (*Xiphias gladius*) from Seychelles, Western Indian Ocean

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Abstract :

Swordfish (Xiphias gladius) is a major marine resource of high economic value to industrial and artisanal fisheries. As a top predator with a long lifespan, it is prone to accumulate high levels of contaminants. The bioaccumulation of a wide range of both legacy and emerging persistent organic contaminants was investigated in the muscle, liver and gonads of swordfish collected from the Seychelles, western Indian Ocean. The detection of all target contaminants, some at frequencies above 80%, highlights their widespread occurrence, albeit at low levels. Mean concentrations in muscle were 5637, 491 and 331 pg g−1 ww for organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and perfluoroalkyl substances (PFASs), respectively. ∑BFR mean concentrations were far below, i.e. 47 pg g−1 ww. The data are among the first obtained for such a high diversity of contaminants in an oceanic top predator worldwide and constitute a benchmark of the contamination of Indian Ocean ecosystems.

Highlights

► Wide range of organic contaminants investigated in swordfish from the Seychelles ► Major contaminants were chlorinated (OCPs, PCBs) and fluorinated (PFASs) compounds. ► All contaminants at low levels in Indian Ocean compared to other oceans worldwide ► Tissue-specific distribution driven by contaminant affinities to lipids or proteins ► No difference in contaminant concentrations in male and female swordfish

Keywords : Persistent organic pollutants (POPs), Brominated flame retardants, Perfluoroalkyl substances, Synthetic musks, Organotropism, Large pelagic fish

1. Introduction

Apical marine fish predators represent a major marine resource and play an essential role in marine ecosystems. In addition, they are of high economic value to industrial and artisanal fisheries and provide important nutrients to local populations (Sioen et al., 2009). However, due to their position at the top of trophic webs, coupled with a long lifespan, they are prone to accumulate high levels of various contaminants, including toxic compounds such as Persistent Organic Pollutants (POPs) and various other persistent hydrophobic contaminants. POPs are defined by their persistent, bioaccumulative, toxic properties and propensity to travel far from their emission sources, hence leading to global distribution (Wania and Mackay, 1996; Lohmann et al., 2007). Various classes of organic contaminants, although not listed under the United Nations Stockholm Convention for POPs, share similar properties and are therefore raising concerns with regards to ocean health. The contaminants reported in this study were organochlorines (OCs), including polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and organochlorinated pesticides (OCPs) (namely, dichlorodiphenyl-trichloroethane –DDT and its isomers, hexachlorobenzene –HCB, hexachlorocyclohexanes –HCHs), brominated flame retardants (BFRs) including polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDDs) and various other non-PBDE BFRs, perfluoroalkyl substances (PFASs) including perfluorosulfonates (PFSAs) and perfluorocarboxylic acids (PFCAs), and synthetic musks (SMs). These diverse contaminant families feature various physico-chemical properties and anthropogenic pressures, i.e. industrial, domestic and agricultural usages. Most of them have been phased-out, especially in the Northern Hemisphere, but their global distribution, in addition to potential contemporary use and

secondary emissions, emphasize the need to characterize their occurrence in the marine environment.

Swordfish (*Xiphias gladius)* is a highly-migratory large pelagic species inhabiting tropical and temperate waters in world oceans (Varghese et al., 2013). This top predator species is kwown to undertake large diel vertical migrations from the surface to more than 1000 m depth, foraging in deep waters during the day and staying in the mixed layer at night (Abascal et al., 2010). Although swordfish are opportunistic predators, their diet in the western Indian Ocean is dominated by mesopelagic fishes and cephalopods (Potier et al., 2007).

The main objectives of this study were i) to assess the state of contamination of the Seychelles marine ecosystem using swordfish as a high bioaccumulating species at the top end of the pelagic food chain, ii) to characterize the bioaccumulation of a wide range of persistent hydrophobic organic contaminants, both legacy and of emerging concern, iii) to determine contaminant sources through levels and profiles iv) to explore the distribution of the studied contaminants in various fish tissues. To the best of our knowledge, the data presented here are among the first obtained for such a high diversity of organic contaminants in swordfish from this part of the world. In particular, some contaminants, such as non-PBDE BFRs and synthetic musks are reported for the first time. As such, the results could serve as a benchmark for future evaluation of the contamination of Indian Ocean ecosystems.

2. Material and Methods

2.1. Sample collection

Ethical approval was not required for this study, as all fish were collected as part of routine professional fishing procedures. A total of 17 fish (9 males and 8 females) were collected

between November 2013 and November 2014 offshore of the Seychelles islands (Figure 1), on board a pelagic semi-industrial longline vessel fishing.

All fish were measured (lower jaw fork length – LJFL- in cm), sexed and further processed at sea: whole liver, whole gonads and 5 cm^3 squares of front dorsal (FD) muscle were collected from each specimen, stored in aluminium foil taking all necessary precautions to avoid external contamination and kept frozen on board until landing (for a maximum of 10 days). On selected individuals (n = 5 males and 3 females), additional muscle samples were collected from back dorsal (BD), middle dorsal (MD) and middle ventral (MV) parts of the fish and analysed for contaminants (Table 3). Upon unloading at Victoria Fishing Port (Mahe, Seychelles), vessel logbook information (sampling dates and coordinates) were retrieved and the samples were rapidly transferred to the Seychelles Fishing Authority Research Laboratory for further processing: a sub-sample was collected from the central part of each liver (L), gonad (G) and muscle (FD, BD, MD, MV) sample and stored frozen in amber glassware prior to freeze-drying. The freeze-dried samples were transported to the IFREMER Laboratory of Biogeochemistry of Organic Contaminants (Nantes, France), homogenized using a blender and finely ground with a ball mill MM400 (Retsch) prior to organic contaminant and total lipid content analysis.

2.2. Total lipid content (TLC) analysis

An aliquot of each freeze-dried sample (0.5 g dw) used for organic contaminant analysis was extracted with a mixture of hexane / acetone (80:20) at 100 °C under 100 bars using pressurized liquid extraction (PLE) with a Dionex accelerated solvent extractor (ASE 200, Dionex Corp., USA). The extracts were evaporated to dryness at 105°C for 12 hr to determine total lipid content (TLC) expressed in % of wet weight (ww).

2.3. Contaminant analysis

Detailed analytical procedures for PCDD/Fs, PCBs-OCPs, BFRs and PFASs can be found in Munschy et al. (2008), Munschy et al. (2016), Munschy et al. (2011; 2015) and Munschy et al. (2019), respectively. The analyses were processed using gas chromatography coupled to high resolution mass spectrometry (GC-HRMS), ultra performance liquid chromatograph (UPLC)-MSMS.

Synthetic musk analysis was described in Tixier et al. (2017) for musk xylene (2,4,6-trinitro-1,3-dimethyl-5-*tert*-butylbenzene - MX) and musk ketone (4'-*tert*-butyl-2',6'-dimethyl-3',5'-dinitroacetopheneone – MK). HHCB (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran - Galaxolide) and AHTN (7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene - Tonalide) were analysed using an Agilent 7890 gas chromatograph coupled to a Waters Xevo® TQ-S micro (Waters Corp.) mass spectrometer (GC-MS/MS) using multiple reaction monitoring (MRM). Quantification and confirmation were performed in the multiple reaction monitoring using atmospheric pressure chemical ionization (APCI) mode (HHCB, MRM = 258.1 > 243.1, 258.1 > 213.1; AHTN, MRM = 273.4 > 255.2, 258.1 > 243.1).

Table 1 summarizes the general analytical procedures used for the various contaminant classes. PCDD/Fs, PCBs, OCPs and BFRs were analysed in all samples (n = 74, see Table 3), while HBCDDs and SMs were analysed in a limited number of samples (n = 6 male and 4 female muscle, n = 5 male and 3 female gonads and n = 5 male and 3 female liver for HBCDDs and n = 5 male and 5 female muscles for SMs). Contaminant concentrations were calculated in pg g^{-1} wet weight (ww), with a mean humidity percentage of 75% (mean value calculated on all samples). Concentrations were converted into ng g^{-1} lipid weight (lw) using the total lipid content determined in each sample.

2.4. QA/QC

In order to minimize external and cross-contaminations, all samples were processed in the laboratory in a clean, low-dust atmosphere and under positive pressure, and windows were UV-protected. All chemicals were carefully selected to satisfy trace analysis requirements. Glassware was oven-baked at 450°C for 8 hr.

QA / QC procedures were followed during each sequence analysis; they included the analysis of in-house quality control samples, procedural blanks, quantifications using external calibration (5 to 6 calibration levels), addition of labelled compounds before extraction, used to calculate recoveries, and participation in interlaboratory comparison tests for the marine environment. Detailed information on QA/QC performances can be found in the supplementary material.

2.5. Statistical analysis

Statistical analyses were performed using StatSoft Statistica software v 7.1. Correlations (e.g. between total lipid content, fish size / age and POP concentrations) were tested using simple linear regression coefficients. In view of the small sample size per group, data comparisons (biological parameters, POP concentrations and ratios) across fish groups were performed using non-parametric tests (Mann–Whitney test for comparison of two independent samples, or one-way ANOVA Kruskal-Wallis's test), with a significance level (α) of 0.05. Results were considered to be significant only when both tests gave significant results.

3. Results and discussion

3.1. *Biometric parameters*

The analysed samples were chosen to cover a broad range of swordfish sizes: female and male fish analysed for organic contaminants were 124-203 and 110-204 cm LJFL, respectively (Table 2). Swordfish age was estimated using growth curves from Farley et al. (2016). Calculations gave estimated ages ranging from 2 to 20 years in males and between 2 and 9 years in females.

Fish sizes and ages showed no significant differences between males and females, although female swordfish are reported to grow faster and to longer lengths than males (Varghese et al., 2013). The biometric characteristics were in the range of those collected in 1998-2001 in the western Indian Ocean (around Reunion Island) (Poisson and Fauvel, 2009). Most swordfish were collected during the reproduction season identified in the western Indian Ocean, i.e. from October to April (Poisson and Fauvel, 2009); only two females were collected during the resting season.

3.2. Total lipid content

TLC values in all tissues of fish of both sexes showed high variability, with mean values ranging from 4.0 ± 2.6 (gonads) and 7.9 ± 5.4 (muscles) % ww in females and from 3.7 ± 2.1 (gonads) to 7.7 ± 5.4 (muscles) % ww in males (Table 3), i.e. similar to the values reported in swordfish specimens worldwide (Kannan et al., 2002a; Stefanelli et al., 2004; Corsolini et al., 2008). No significant differences in TLC were found in males and females in any tissue. TLC was not significantly different in the various muscle parts; gonads showed significantly lower TLC than liver and muscle.

3.3. Major contaminant levels and biological parameters

Concentrations of the major studied classes of contaminants are presented in Table 3. Globally, in all swordfish, contaminants ranked in the order OCPs > PCBs > PFASs > PBDEs in muscle (Figure 2), which reflects a higher exposure of swordfish to OCPs in this oceanic region. Organochlorinated and organobrominated contaminants covariated strongly with each other, but not with PFASs, highlighting the different sources and bioaccumulation behaviours of these contaminant families. Different contaminant distributions were observed in gonads and liver, where PFASs and OCPs showed the highest levels (Figure 2). Lipophilic contaminants such as PCBs and OCPs showed similar distribution to TLC, to which they were significantly correlated ($p < 0.001$ for PCBs and OCPs). As a result, when normalized to TLC, the differences in PCB and OCP concentrations across tissues were not significant. PBDE concentrations expressed in ww did not show any significant differences across tissues, although TLC and PBDE concentrations were positively correlated ($p < 0.01$). Conversely, PFOS and PFCAs were significantly higher in liver and gonads than muscle. PFASs have been previously shown to partition preferentially to phospholipids and protein-rich tissues such as gonads and liver in various fish species (Martin et al., 2003; Zafeiraki et al., 2019). Liver to muscle and gonads to muscle concentration ratios (on a ww basis) were 21 ± 8 and 12 ± 6, respectively, for PFASs, 1.4 ± 0.6 and 0.6 ± 0.1 for PCBs and 2.1 ± 2.0 and 0.5 ± 0.1 for OCPs. These ratios calculated with lipid-normalized concentrations were 1.0 ± 0.3 and 0.9 ± 0.3, respectively, for PCBs and 1.0 ± 0.3 and 0.8 ± 0.3 for OCPs.

The various muscle parts (FD, BD, MD, MV) did not show major differences in contaminant concentrations (in ww or in lw), hence highlighting the homogeneity in contaminant distribution in the studied muscle parts and suggesting that contaminant transfer in swordfish muscle is homogeneous. This could have a practical outcome for the design of future tissue

sampling strategies, enabling sampling of any muscle part without affecting organic contaminant bioaccumulation results.

Although globally (all contaminant families considered together), a tendency towards higher contamination levels in male tissues was observed, due to high inter-individual variability in concentrations, the difference was significant for DDTs in the liver of males only (in ww and lw). As male and female individuals have similar feeding habits, supported by similar carbon and nitrogen stable isotope signatures in both sexes ($\delta^{13}C$: -16.3 ± 0.4 ‰ in males versus -16.5 ± 0.3 ‰ in females; $\delta^{15}N$: 14.2 ± 0.6 ‰ in males versus 14.0 ± 0.4 ‰ in females, as determined in the muscle of the same individuals; Munschy et al., 2020), the lack of differences in contaminant burden between sexes suggests that female swordfish spawning did not lead to significant decontamination over time in the studied individuals. Similarly, some authors have suggested that spawning does not lead to a significant drop in contaminant concentrations in female fish in response to growth rate and other life history characteristics (Madenjian et al., 2010; Ng and Gray, 2009). In fact, the importance of contaminant loss through spawning depends upon lipid utilisation and spawning strategies (Larsson et al., 1993; Rypel et al., 2007). In tropical areas such as the south Indian Ocean, swordfish has multiple spawnings with extended spawning periods (Poisson and Fauvel, 2009). However, their high and continuous feeding rate may counteract contaminant loss through spawning.

3.4. Organochlorinated pollutants levels and profiles

3.4.1. PCDD/Fs

PCDD/Fs were seldom detected in swordfish samples. 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF were the two most-detected congeners (24% of the samples) above the limits of quantification, at levels ranging from 0.02 to 0.14 pg g^{-1} ww and from 0.03 to 0.19 pg g^{-1} ww, respectively. 1,2,3,7,8-PeCDF was the second most-detected congener (7% of the samples) at 0.02-0.09 pg g^{-1} ww. The concentrations of ∑PCDD/Fs expressed in TEQ were, on average, 0.0038 ± 0.020 pg TEQ g^{-1} ww in muscle (lower bound values, < LOQ = 0), i.e. 93 times below EU regulations for food consumption (EU, 2011). These levels are among the lowest found in marine biota worldwide, including in long-lived predatory fish. Indeed, in swordfish collected from Spanish markets, PCDD/F concentrations were 0.050 pg WHO-TEQ g^{-1} ww (lower bound) in 2005 (Bocio et al., 2007) and 0.079 pg WHO-TEQ g^{-1} ww (middle bound, < limit of detection -LOD = LOD / 2) in 2012 (Perello et al., 2015).

3.4.2. PCBs

Among the 6 i-PCBs, CB-180, CB-153 and CB-138 were detected in the majority of samples (in 91%, 88% and 87% of samples respectively). The frequency of detection of CB-101, CB-52 and CB-28 was 81%, 69% and 51% respectively. Regarding dl-PCBs, CB-114 was below the limit of detection in all samples, CB-77 and CB-81 were detected in 47% and 43% of samples respectively, while the other dl-PCBs were detected in 71% (CB-123) to 93% (CB-167) of samples. ∑i-PCB concentrations in male swordfish were between 59 and 1514 pg g^{-1} ww in muscle (FD, MD, BD and MV muscle samples mixed), between 149 and 592 pg g^{-1} ww in liver and between 196 and 726 pg g^{-1} ww in gonads. In females, i-PCB concentrations ranged from 169 to 1007 pg g^{-1} ww, from 133 to 453 pg g^{-1} ww and from 38 to 382 pg g^{-1} ww in muscle, liver and gonads respectively. ∑dl-PCB concentrations were found to be about 5 times lower and strongly correlated to ∑i-PCB concentrations (r = 0.99, all tissues). Mean

concentrations of quantified PCBs in muscle, liver and gonads of swordfish analysed in this study are summarized in Table 3. The levels are far lower than those reported in swordfish from the Mediterranean Sea (13-399 ng g^{-1} ww) (Kannan et al., 2002a; Stefanelli et al., 2004; Corsolini et al., 2005; Bocio et al., 2007; Perello et al., 2015) and from the Brazilian coast (6.5 ng g^{-1} ww) (de Azevedo e Silva et al., 2007). ∑dl-PCB levels reported in swordfish from the North Atlantic Ocean were 0.28 ng g^{-1} ww (Mezzetta et al., 2011), i.e. in the range of those found in our study.

On average, i-PCB profiles were dominated by CB-153 > CB-180 > CB-138 in all tissues and in both sexes. These three highly bioaccumulative and non-metabolizable congeners accounted for 85% of ∑i-PCBs. Among dl-PCBs, CB-118 was predominant (49 ± 3% of ∑dl-PCBs), followed by CB-105, CB-156 and CB-167 (each between 12% and 16%). Non-ortho PCBs (CB-77, -81, -126 and -169) represented 6% of ∑dl-PCBs, with CB-126 and CB-169 being the most prevalent. Similar profiles have already been reported worldwide in marine fish including top predators (Ueno et al., 2005; Bhavsar et al., 2007; Corsolini et al., 2007; Munschy et al., 2016). Globally, hexachlorinated congeners were predominant in all tissues, followed by heptachlorinated and pentachlorinated congeners (Figure 3).

3.4.3. OCPs

All DDT isomers were identified at concentrations above the limits of quantification in 100% of the samples. HCB was detected in 91% of the samples, while β-HCH and α-HCH were detected in 49% and 24% of the samples, respectively. γ-HCH was below the limit of quantification in all samples. Concentrations of the main detected OCPs are shown in Table 3. In males, ∑DDT concentration ranges (min-max) were between 196 and 16567 pg g^{-1} ww

in muscle (FD, MD, BD and MV muscle samples mixed), between 1804 and 9146 pg g^{-1} ww in liver and between 210 and 8852 pg g^{-1} ww in gonads. In females, ∑DDT concentrations ranged from 313 to 13790 pg g^{-1} ww in muscle, from 1184 to 4294 pg g^{-1} ww in liver and from 186 to 4020 pg g^{-1} ww in gonads. These concentrations are lower than those reported in swordfish from the Mediterranean Sea (38-57 ng g^{-1} ww range) (Kannan et al., 2002a; Stefanelli et al., 2004; Corsolini et al., 2008) and in a similar range to those from specimens collected from the Brazilian coast (2.47 ng g^{-1} ww) (de Azevedo e Silva et al., 2007). HCB concentrations in males were in the 33-638 pg g^{-1} ww range, and in the 34-472 pg g^{-1} ww range in females, i.e. much lower than those reported in specimens collected in 2005 in the Southern Tyrrhenian Sea (Corsolini et al., 2008). β-HCH concentrations were in the 2-90 pg g^{-1} ww range in males and in the 1-83 pg g^{-1} ww range in females. All OCP concentrations were cross-correlated, indicating similar sources and behaviour in the analysed fish. Overall, the organochlorine concentrations determined in our study were low in comparison to those reported in other oceans, in particular in the Northern Hemisphere. These results are coherent with previous studies on various top predator fish worldwide (Ueno et al., 2003; Nicklish et al., 2017) and reflect higher contaminant inputs in the Northern Hemisphere from industrialized and urban areas (Gioia et al., 2012; Tanabe and Ramu, 2012).

DDT profiles in swordfish muscle were dominated by *p,p'*-DDE (71% ± 6% of DDTs), followed by *p,p'*-DDT (19% ± 5%), *p,p'*-DDD (5% ± 1%), *o,p'*-DDT (4% ± 0.5%) and *o,p'*-DDD (0.9% ± 0.2%). Due to the higher stability of the *p,p'* metabolites DDE and DDD versus the parent compound *p,p'*-DDT, DDT isomeric profiles in fish are mainly dominated by *p,p'*-DDE followed by *p,p'*-DDD (Binelli and Provini, 2003a; Jürgens et al., 2015). Contamination profiles similar to the one found in our study (i.e. *p,p'*-DDE > *p,p'*-DDT > *p,p'*-DDD) have been reported in fish from Southern China coasts where DDT originates from antifouling paints

and dicofol impurities (Guo et al., 2008). Based on the knowledge of technical DDT isomeric composition (i.e. 75% of *p,p'*-DDT, 15% of *o,p'*-DDT, 5% of *p,p'*-DDE and 5% of other isomers, Zhou et al., 2014), several ratios using DDT isomers are commonly-used to investigate DDT origin and ageing. The *o,p'*-DDT / *p,p'*-DDT ratio, used to determine the origins of DDT, was similar in all samples (0.25 ± 0.14 on average, regardless tissue or sex), indicating similar exposure sources for all fish and indicative of technical DDT (Suarez et al., 2013). The ratio of (*p,p'*-DDE + *p,p'*-DDD) / ∑ DDTs, commonly-used to distinguish new and old DDT sources, showed an average value of 0.77 ± 0.06 in muscle, characteristic of relatively old DDT inputs (recent DDT inputs would be characterized by a ratio < 0.5, Suarez et al., 2013). The fact that *p,p'*-DDT, which half-life in fish is 8 months (Binelli and Provini, 2003a), ranked second, suggests continuous inputs of DDT , which is consistent with various publications reporting DDT use in Southern Asia, South-Eastern Africa and India (Bogdal et al., 2013; Ali et al., 2014; Bouwman et al., 2015; van den Berg et al., 2017). The past and potential contemporary use of DDT in various Southern countries is also reflected by the ∑DDT / ∑PCB concentration ratio of 13.7 ± 3.8 (average value in muscle), which reveals a higher DDT exposure of swordfish from the Seychelles islands versus PCBs. Interestingly, this ratio was far higher than that determined in albacore tuna from another location in the southwestern Indian Ocean (i.e. 3.33 ± 1.39 at Reunion Island, Munschy et al., 2016), which suggests higher inputs of DDTs in the northern and central western Indian Ocean versus southwestern areas. In addition, higher emissions due to increased volatilization of DDT are more likely to occur in tropical regions than temperate regions. Together, higher usage and higher emissions would explain the higher ∑DDT / ∑PCB concentration ratio found in swordfish inhabiting tropical and subtropical regions of the western Indian Ocean versus albacore tuna inhabiting more temperate waters.

No significant differences in *p,p'*-DDE contributions were observed across tissues in either sex. Conversely, higher *p,p'*-DDD and *o,p'*-DDD contributions and lower *p,p'*-DDT and *o,p'*-DDT contributions were found in liver versus gonads and muscle (Figure 3). The ratio of *o,p'*-DDD + *p,p'*-DDD / ∑ DDTs was significantly higher in liver followed by gonads and muscle (both genders). It has previously been reported that fish are able to metabolize DDT and that the bioaccumulation of DDT metabolites and biotransformation are tissue-specific (Kwong et al., 2008). The higher contribution of the DDT metabolites *p,p'*-DDD and *o,p'*-DDD in liver suggests that DDT degradation occurred preferentially in liver.

3.5. BFR concentrations and profiles

BDE-28, -47, -49, -66, -100, -154 and -155 were quantified in over 50% of the samples. The detection frequency of the remaining congeners decreased in the order BDE-208 (31%) > BDE-153 (29%) > BDE-99 (22%). ∑ 8 PBDE (BDE-28, -47, -49, -99, -100, 153, -154, -183) concentrations in male swordfish ranged from 12 to 242 pg g^{-1} ww in muscle (FD, MD, BD and MV muscle samples mixed), 24 to 55 pg g^{-1} ww in liver and 13 to 36 pg g^{-1} ww in gonads. In females, ∑PBDE concentrations ranged from 14 to 86 pg g^{-1} ww in muscle, 13 to 124 pg g^{-1} ww in liver and 14 to 72 pg g^{-1} ww in gonads. Mean PBDE concentrations are presented in Table 3 and are similar to those reported in swordfish from markets in Valencia, Spain in 2007-2012 (Pardo et al., 2014), but lower than those reported in the muscle and liver of male and female individuals collected in 2005 in the Southern Tyrrhenian Sea (Italy) (Corsolini et al., 2008), or in swordfish from fish markets in Catalonia, Spain in 2005 (Domingo et al., 2006). Concerns have been raised over a possible future increase in BFR inputs in Southern Hemisphere countries such as South Africa due to the absence of

restrictions or regulations on imports of BFRs and BFR-containing products (Quinn et al., 2020).

PBDE profiles in muscle were dominated by BDE-47 (49% ± 14% of the ∑PBDE), followed by BDE-154 (22% ± 7%) and BDE-49 (16% ± 3%). PBDE profiles were significantly different between male and female fish muscles, with higher contributions of BDE-28 and BDE-47 and a lower contribution of BDE-100 in females versus males. BDE-47 contributed to 43% ± 15% and 45% ± 12% of the ∑PBDE in gonads and liver, respectively, i.e. similar to contribution in muscle.

PBDEs undergo metabolism in marine biota, including fish, which metabolise PBDEs via debromination processes in a species-specific way (Roberts et al., 2011). Although BDE-47 was -as often in marine biota- found to be the predominant PBDE congener in all tissues, BDE-154 was also shown to be a fairly large contributor in swordfish. This congener may originate from the degradation of higher brominated congeners such as BDE-183, as shown in other fish species (Roberts et al., 2011). BDE-183 was indeed seldom detected (i.e. in only 7 samples in total) and its contribution was low (2% ± 2%), hence supporting the degradation hypothesis. Similarly, BDE-49, which can result from BDE-99 debromination, was found in relatively high proportions in swordfish (17 ± 4%). The BDE-99 / BDE-100 ratio, used as an indicator of fish capacity to metabolize PBDEs (Voorspoels et al., 2003), was 0.4 ± 0.1 on average in muscle. This ratio has been shown to decrease with increasing trophic levels (Wan et al., 2008) and would suggest swordfish are capable of metabolizing PBDEs. However, determining the PBDE profiles of main swordfish preys would be essential to determine if these profiles originated from metabolism in swordfish or from its prey.

Non-PBDE BFRs were detected in less than 50% of the analysed samples and ranked in the order BB-153 (46%) > HBB (26%) > BTBPE (22%) > DBDPE (18%). Their concentrations

ranged from 0.1 to 1.7 pg g^{-1} ww, 0.2 to 0.8 pg g^{-1} ww, to 11 pg g^{-1} ww and 4 to 26 pg g^{-1} ww, respectively. Average concentrations ranked in the order DBDPE > BTBPE ~ HBB ~ BB-153. This low occurrence is consistent with low biomagnification capacities, although reported results remain inconclusive for DBDPE and BTBPE (Tao et al., 2019). To our knowledge, these results are the first to be reported for top predator fish from the Indian Ocean.

HBCDDs were analysed in a selection of samples (n = 10 and 16 female and male tissues, respectively). Among the three HBCDD analysed isomers, α-HBCDD was the only one detected, at a frequency of 38%. In female individuals, α-HBCDD was detected at concentrations ranging from 4 to 29 pg g^{-1} ww in muscle, of 9 pg g^{-1} ww in liver and below the limits of quantification in gonads. In males, α-HBCDD was detected at 7-17 pg g^{-1} ww in muscle, 6-13 pg g^{-1} ww in liver and below the limits of quantification in gonads. In swordfish collected from Italian markets but originating from western Indian Ocean (i.e. FAO zone 51), HBCDDs were detected in one sample out of two at 16 pg g^{-1} ww (Tavoloni et al., 2020), i.e. similar to the levels found in this study.

3.6. PFAS concentrations and profiles

Among the analysed PFASs, PFOS, PFDA and PFUnDA were detected in 100% of samples. PFDoDA and PFTrDA were detected in 91% of samples and PFNA and PFTeDA in 77% and 59% of samples, respectively. The presence of both PFOS and PFCAs in swordfish indicates biomagnification of these compounds at the top of food webs and is consistent with their global distribution in tropical and subtropical oceans (Gonzalez-Gaya et al., 2014). Table 3 shows the mean concentrations of PFOS and ∑PFCAs in the various tissues of male and female swordfish. PFOS concentrations in all tissues were in the 23-1713 pg g^{-1} ww range, while remaining PFASs, i.e. long chain PFCAs, were in the 9-4777 pg g^{-1} ww range. PFOS

was identified at < 1 to 8 ng g^{-1} ww in the liver of swordfish from the Southern Tyrrhenian Sea in 1999 (Kannan et al., 2002b) and was below 1.5 ng g^{-1} ww in both muscle and liver of male and female individuals collected from the same area in 2005 (Corsolini et al., 2008). In swordfish consumed in France (no reported geographical origin), ∑ PFASs were in the 0.28-1.11 ng g^{-1} ww range (Yamada et al., 2014).

PFCA concentrations were higher than PFOS concentrations in all samples. PFCA / PFOS ratio was significantly higher in gonads (9.0 ± 3.2) than in liver (6.3 ± 2.3) or muscle (6.1 ± 2.5), which highlights a tissue-specific distribution of PFASs. Only long-chain PFASs (C ≥ 8) were detected in swordfish tissue samples, corresponding to the higher bioaccumulative abilities and biomagnification propensities of PFASs of higher carbon-chain length in trophic webs versus their short-chain counterparts (Martin et al., 2003; Conder et al., 2008;). More specifically, PFCA profiles showed a predominance of odd-chain length compounds (PFUnDA and PFTrDA) versus even-chain ones (PFDA and PFDoDA). This has previously been observed in fish and partially explained by the degradation of neutral precursors such as 10:2 perfluorodecanol (fluorotelomer alcohol – FTOH) (Ellis et al., 2004; Hart et al., 2008). The origin of PFUnDA has also been attributed to the industrial production of fluoropolymers or impurities from the oxidation of fluorotelomer olefins (Prevedouros et al., 2006; Harada et al., 2011).

No differences in PFAS profiles were observed between sexes. PFOS and some PFCAs showed different relative contributions according to tissue: PFOS was more abundant in liver than in gonads, while the opposite was observed for PFTrDA; PFDA and PFUnDA were more abundant in muscle than in gonads (Figure 3). These results demonstrate tissue-specific and compound-specific PFAS distribution, probably reflecting complex interrelated

effects according to tissue biochemical composition and PFAS binding affinities (Verreault et al., 2005).

3.7. Synthetic musk concentrations and profiles

The contamination of swordfish by synthetic musks (SMs) was investigated in a limited number of muscle samples (n = 5 males and 5 females). Among the four investigated SMs, the two polycyclic musks, HHCB and AHTN were found in the highest concentrations, at 428 ± 221 and 274 ± 238 pg g^{-1} ww respectively. HHCB was detected in all samples, while AHTN was only detected in four samples. MX and MK were detected in four samples only, at 10 ± 3 and 69 ± 54 pg g^{-1} ww respectively. The differences observed in nitromusk and aromatic musk contamination levels is consistent with current usages and regulations (Rimkus et al., 1999). High variations were observed across individuals and globally, no differences in HHCB or AHTN were observed according to sex. Levels in swordfish from the western Indian Ocean were in the lower ranges of those measured in other marine fish species worldwide (Rainieri et al., 2017). For instance, in hammerhead shark livers collected in 2004 in the Ariake Sea in Japan, only HHCB was detected at 16-48 ng g^{-1} ww, i.e. 1 or 3 orders of magnitude below those in fish from Canada, the US and Europe (Nakata, 2005).

3.8. *Contaminant levels versus human health regulations*

Due to POP toxicity and accumulation in seafood, which is one of the major routes of human exposure to these pollutants (Törnkvist et al., 2011; Shin et al., 2015), maximum POP residues in foodstuffs have been established in various countries worldwide. Globally, contamination levels were several orders of magnitude below regulations. i-PCBs were 26 to 1200 times lower in muscle, and 200 to 1400 times lower in liver, than the maximum levels

set by the European Commission for non dl-PCBs in foodstuffs (EU, 2011), i.e. 75 ng g^{-1} ww and 200 ng g^{-1} ww in muscle and liver respectively, and below the maximum values set by the governments of Japan (500 ng g^{-1} ww), Australia (500 ng g^{-1} ww) and the US (2000 ng g^{-1} ww) for total PCBs (Vizzini et al., 2010). dl-PCB concentrations calculated in toxic equivalents (TEQs) using the toxic equivalent factors (TEFs) set by the World Health Organization in 2005 (Van den Berg et al., 2006) showed average levels of 0.35 ± 0.24 pg TEQ g^{-1} ww, i.e. below the maximum level set by the European Commission for dl-PCBs in foodstuffs of 3 pg TEQ g^{-1} ww in muscle (EU, 2011). Non-ortho PCBs and, in particular, CB-126 (74% of dl-PCB TEQs) and CB-169 (24%), contributed the most to TEQ values. They were also below the guideline value of 0.79 pg TEQ g^{-1} ww set by Canada to protect wildlife consumers of aquatic biota (CCME, 2001). *p,p'*-DDE maximum levels were below those set by Japan (3000 ng g^{-1} ww) and Australia (1000 ng g^{-1} ww) (Vizzini et al., 2010). DDT concentrations were below the maximum admissible concentrations set by the EU (Binelli and Provini, 2003b) but slightly exceeded the limit of 14 ng g^{-1} ww set by Canada (CCME, 1999) in two male muscle samples (at 17.7 and 16.6 ng g^{-1} ww). Other OCPs were below EU and China maximum limits for lindane and HCH and below the environmental quality standards (EQS) of 10 µg kg^{-1} set by the European Union (EU, 2013) for HCB to protect human health. PBDEs (sum of 6 congeners = BDE-28, 47, 99, 100, 153 and 154) were above the EQS of 0.0085 µg kg^{-1} in muscle set to protect human health (7 times higher in muscle on average) in 78% of muscle samples. However, the EQS set by the EU for PBDEs is recognized as being extremely low, leading to environmental concentrations exceeding EQS in most cases (Fliedner et al., 2016). The HBCDD EQS of 167 µg kg^{-1} ww, although established on whole fish to protect wildlife (secondary poisoning of fish-eating predators),

was never exceeded, nor was the PFOS NQS of 9.1 µg kg^{-1} ww in muscle (human health purpose).

4. Conclusions

This study provides the first data on the contamination of the top predator swordfish by a wide range of persistent organic contaminants in the Seychelles archipelago, western Indian Ocean. The results highlight the widespread contamination of southern oceans by persistent organic contaminants, albeit at low levels. Swordfish from the study area were more impacted by DDTs than PCBs, which is consistent with current knowledge on global environmental inputs of these POPs in the Southern Hemisphere. PFASs and, in particular, long-chain PFCAs, were found in relative abundance, especially in gonads and liver.

Further studies on the contamination of top predators and their prey in the Indian Ocean would be required on a larger geographical scale to gain more insight into global ocean contamination in this part of the world and better characterize contaminant biomagnification in tropical food webs.

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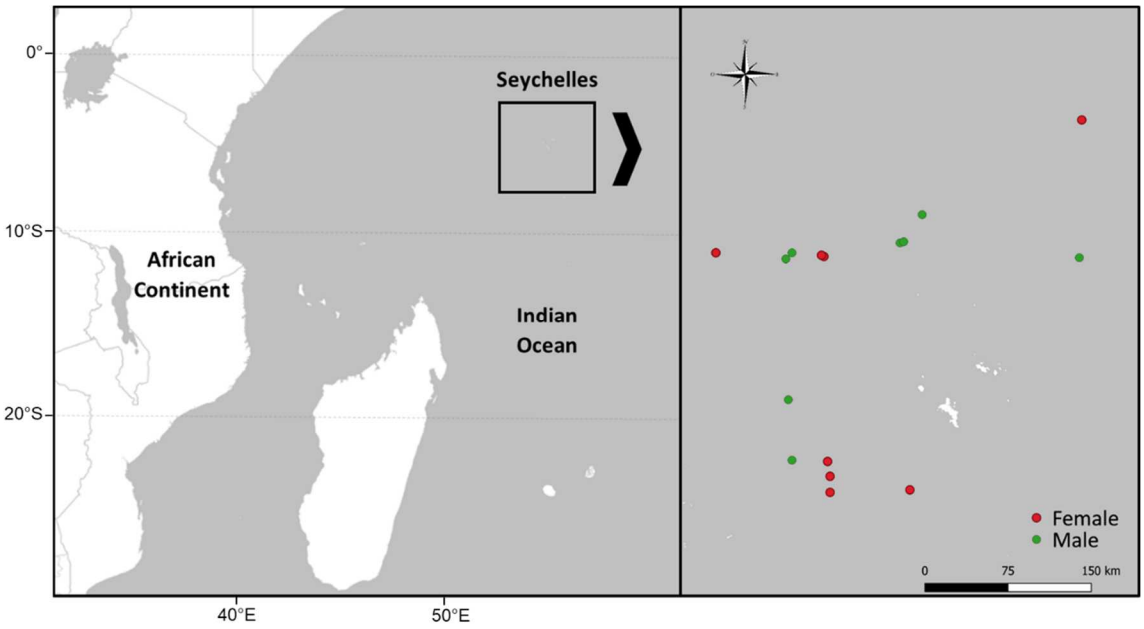
Figure 1: Map of swordfish fishing positions in the Seychelles, western Indian Ocean in 2013-2014.



2 columns

Figure 2. PCB (∑18 congeners), OCP (∑5 DDT isomers + HCB + HCH), PFAS (∑PFSAs + PFCAs) and PBDE (∑8 congeners -inside box), concentrations (pg g^{-1} ww) in the muscle, gonads and liver of swordfish collected in the western Indian Ocean in 2013-2014. The lower and upper ends of boxplots depict the 25th and 75th percentiles of the data, the lower and upper whiskers correspond to the minimum and maximum values, respectively, the black squares represent the median.

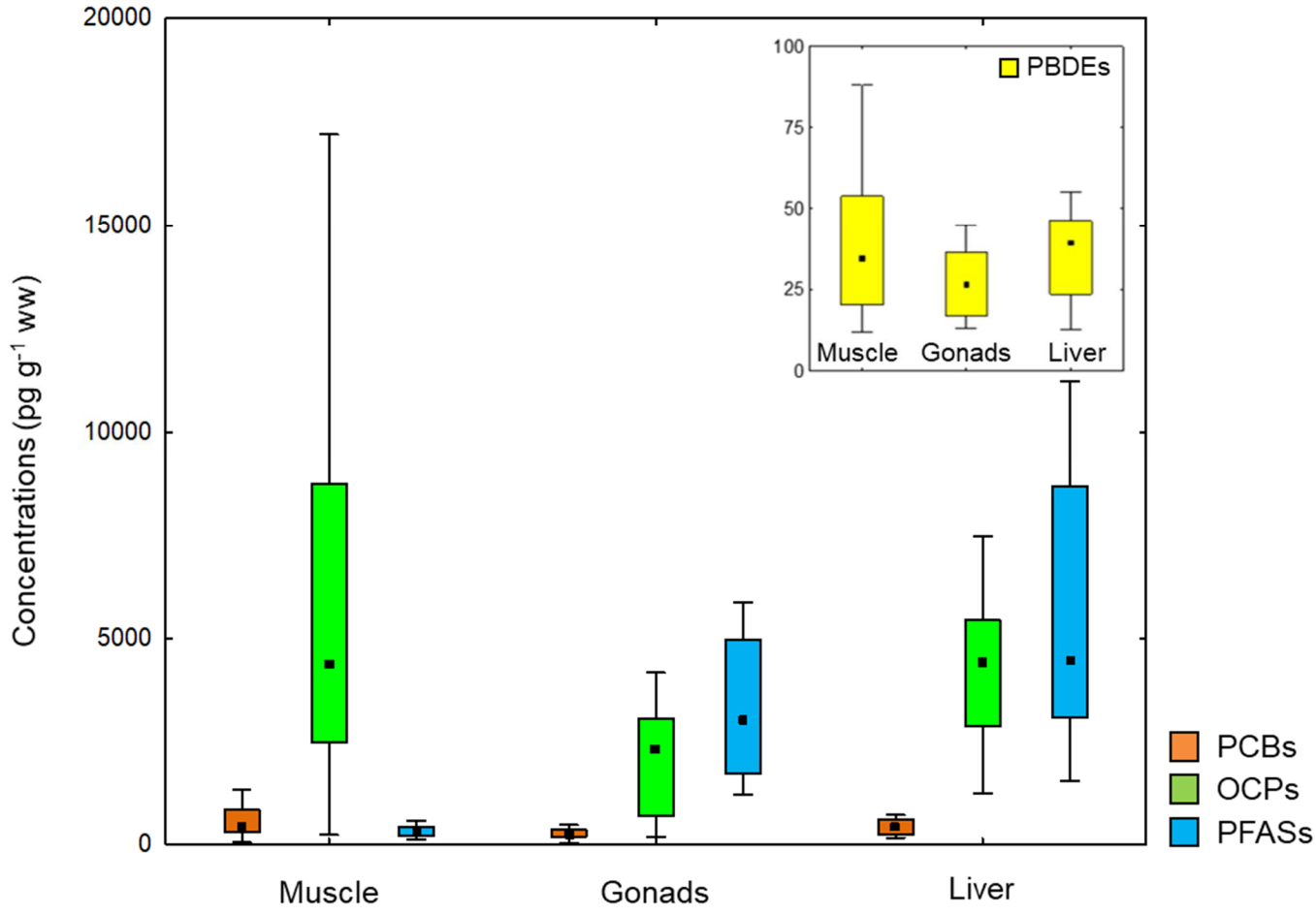


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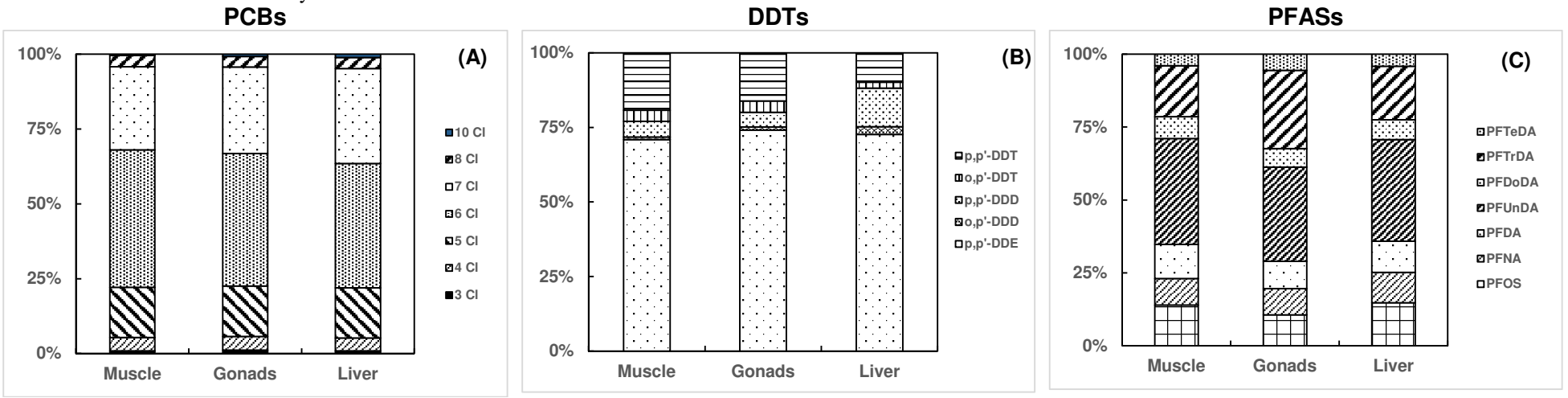
Figure 3. Contributions (%) of (A) PCBs (grouped per number of chlorine atom), (B) DDTs (5 isomers) and (C) PFASs (PFOS and long-chain PFCAs) in the muscle, gonads and liver of swordfish collected in Seychelles in 2013-2014.



2 columns

Table 1. General description of the analytical procedures used for PCDD/F, PCB, OCP, BFR, PFAS and SM analyses in the various tissues of swordfish collected in Seychelles in 2013-2014. PLE = pressurized liquid extraction, LSE = liquid solid extraction, DCM = dichloromethane, GPC = gel permeation chromatography, si-al = silica-alumina column, nitro-PYE = nitrophenylpropylsilica column - 2-(1-pyrenyl)ethyldimethylsilylated silica column. Other abbreviations are given in 2.3 section.

Contaminants		**Organochlorinated Contaminants**			**Brominated Flame Retardants**		**Synthetic Musks**	**Perfluoroalkyl Substances**
Congeners		7 PCDDs 10 PCDFs	36 PCBs	OCPs 5 DDT isomers, HCB, γ-HCH	34 PBDEs, BTBPE, DBDPE, HBB, BB-153	3 HBCDD enantiomers	2 polycyclic musks 2 nitro-musks	5 PFSAs 9 PFCAs
Freeze-dried sample mass (g dw)	Muscle	1-3	1-3	1-3	1-3	2	3	1
	Liver	1-3	1-3	1-3	1-3	1	--	0.25
	Gonads	1-3	1-3	1-3	1-3	1	--	0.5
Extraction Solvent		PLE DCM (100%)	PLE DCM (100%)	PLE DCM (100%)	PLE DCM (100%)	PLE DCM/hexane (50:50, v:v)	PLE DCM/Hexane (50:50, v:v)	LSE MeOH / KOH
Clean-up		GPC- sial-nitro-PYE	GPC- sial-nitro-PYE	GPC- sial-nitro-PYE	GPC- sial-nitro-PYE	GPC-acid treatment-NaOH	GPC-Florisil-sial	SPE: WAX-Envicarb
Internal standards (added before extraction)		^{13}C-PCDDs (6) and PCDFs (9)	^{13}C-dl-PCBs (12) and i-PCBs (6)	^{13}C-DDTs (5), ^{13}C-HCB, ^{13}C-γ-HCH	^{13}C- BDE-15, -28, -47, -77, -99, -100, -126, -153, -154, -169, -183, -197, -205, -207, -209, HBB, BTBPE, BB-153, DBDPE	β-HBCDD-d18	MX-d15	^{13}C- PFOS, PFHxA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTeDA and $^{18}O_2$PFHxS
External standards (added before injection)		^{13}C-1,2,3,4-TCDD and 1,2,3,7,8,9-HCDD	^{13}C- CB-70, -111, -170	d8- p,p'-DDD and o,p'-DDT	^{13}C- BDE-79, -139, -180, -206	^{13}C- HBCDDs	Phe-d10	$^{13}C_8$ PFOS
Instrument		GC/HRMS	GC/HRMS	GC/HRMS	GC/HRMS	UPLC-MS/MS	GC/MS GC-MS/MS	UPLC-MS/MS
Column		RTX-Dioxin2 (40 m x 0.18 mm x 0.18 µm)	HT-8 (50 m × 0.22 mm × 0.2 µm)	HT-8 (50 m × 0.22 mm × 0.2 µm)	RTX-1614 (30 m x 0.25 mm x 0.10 µm)	BEH C_{18} (150 mm × 2.1 mm, 1.7 µm)	DB-5 MS (40 m × 0.18 mm × 0.18 µm)	BEH C_{18} (50 mm × 2.1 mm, 1.7 µm)
LOQs (pg g^{-1} ww)	Muscle	0.04-0.16	0.1-13	0.3-24	PBDE: 0.1-6 except BDE-209: 87 non-PBDEs: 0.1-9	1-6	6-82	1-174
	Liver	0.02-0.07	0.1-10	0.6-14	PBDE: 0.1-8 except BDE-209: 86 non-PBDEs: 0.2-4	4-19	--	6-660
	Gonads	0.01-0.06	0.1-10	1-16	PBDE: 0.1-7 except BDE-209: 91 non-PBDEs: 0.2-6	2-20	--	3-275
Reference		Munschy et al., 2008	Munschy et al., 2016	Munschy et al., 2016	Munschy et al., 2011	Munschy et al., 2015	Tixier et al., 2017	Munschy et al., 2019

Table 2. Biometric parameters (lower jaw fork length –LJFL in cm, age in year) of swordfish (*Xiphias gladius*) collected in Seychelles in 2013-2014 and analysed for organic contaminants. M = male, F = female.

Sex	n	Size (cm)	Age (year)
All	17	165 ± 29 (110-204)	6.4 ± 4.7 (2.0-20.0)
M	9	160 ± 32 (110-204)	7.3 ± 6.2 (2.0-20.0)
F	8	172 ± 26 (124-203)	5.4 ± 2.1 (2.3-8.6)

Table 3. TLC (% ww), PCB (∑i-PCBs and ∑dl-PCBs), OCP (∑DDTs, HCB, β-HCH), ∑PBDE, PFOS and ∑PFCA concentrations (pg g^{-1} ww) in different muscle parts (FD = front dorsal, BD = back dorsal, MD = middle dorsal and MV = middle ventral parts); in the liver and gonads of male (M) and female (F) swordfish collected in the Seychelles in 2013-2014. The values are given as mean ± sd except for MV, MD and BD in females for which min-max are given due to the small number of samples.

Tissue		Sex	n	TLC	∑i-PCBs	∑dl-PCBs	∑DDTs	HCB	β-HCH	∑PBDEs	PFOS	∑PFCAs
Muscle	All	F	17	7.9 ± 5.4	420 ± 265	85 ± 66	4086 ± 3655	265 ± 141	41 ± 42	38 ± 26	46 ± 17	296 ± 109
	FD	F	8	7.5 ± 4.5	500 ± 320	101 ± 82	5392 ± 4509	301 ± 148	52 ± 44	46 ± 30	46 ± 14	300 ± 118
	MV	F	3	1.1-14.0	253-628	44-135	641-8029	274-330	< LOQ	24-48	23-75	183-450
	MD	F	3	1.0-11.9	229-373	49-62	537-4371	99-378	< LOQ	18-53	30-45	186-313
	BD	F	3	1.0-7.2	169-312	31-72	556-3620	34-219	8[(a)]	14-15	36-80	243-486
Liver	-	F	8	6.9 ± 3.1	301 ± 113	57 ± 24	3171 ± 1142	235 ± 101	32 ± 16	39 ± 39	829 ± 467	4508 ± 3019
Gonads	-	F	8	4.0 ± 2.6	177 ± 117	51 ± 28	1703 ± 1264	133 ± 84	17 ± 12	36 ± 23	422 ± 261	3014 ± 1531
Muscle	All	M	24	7.7 ± 5.4	535 ± 387	124 ± 72	6336 ± 4923	240 ± 161	51 ± 26	56 ± 56	45 ± 15	276 ± 196
	FD	M	9	7.5 ± 4.5	588 ± 327	119 ± 64	6427 ± 4192	254 ± 131	51 ± 26	57 ± 42	48 ± 15	368 ± 222
	MV	M	5	11.7 ± 7.3	811 ± 500	166 ± 100	9215 ± 6441	347 ± 232	< LOQ	43 ± 13	37 ± 3	131 ± 51
	MD	M	5	6.8 ± 5.3	384 ± 353	121 ± 53	5617 ± 4862	212 ± 144	< LOQ	79 ± 109	37 ± 8	145 ± 17
	BD	M	5	5.0 ± 3.7	343 ± 371	85 ± 73	4011 ± 4613	133 ± 102	< LOQ	39 ± 43	55 ± 25	278 ± 171
Liver	-	M	9	7.2 ± 3.5	454 ± 164	90 ± 32	5838 ± 2477	257 ± 132	40 ± 20	44 ± 11	737 ± 333	5204 ± 3047
Gonads	-	M	8	3.7 ± 2.1	359 ± 248	69 ± 46	3515 ± 3226	164 ± 42	20 ± 13	24 ± 11	343 ± 243	3352 ± 705

(a) n = 1