ELSEVIER

Chemosphere 62 (2006) 375–380

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Occurrence and accumulation of organochlorine contaminants in swordfish from Mediterranean Sea: A case study

M.M. Storelli, G.O. Marcotrigiano *

Pharmacological-Biological Department, Chemistry and Biochemistry Section, Veterinary Medicine Faculty, University of Bari, Strada prov. le per Casamassima, km 3, 70010 Valenzano, (BA), Italy

Received 31 January 2005; received in revised form 1 April 2005; accepted 18 April 2005
Available online 27 June 2005

Abstract

Polychlorinated biphenyls including coplanar congeners and DDT compounds were measured in the liver of a teleost species: namely, *Xiphias gladius*. PCB concentrations (median: 1121 ng/g lipid wt) were comparable with DDT levels (median: 1236 ng/g lipid wt). PCBs revealed a profile dominated by hexa-, penta- and heptachlorinated congeners. Among DDTs, the compound in the greatest concentration was *p*,*p*′-DDE, representing 70% of the total DDT burden, followed by *o*,*p*′-DDT > *p*,*p*′-DDT > *p*,*p*′-DDD = *o*,*p*′-DDD. Mean total 2,3,7,8-TCDD equivalent of five coplanar PCBs was 8.83 pg/g lipid weight. The isomers with higher TEQs values were non-*ortho* congeners than mono-*ortho* ones.

Keywords: DDTs; PCBs; Swordfish liver; TEQs

1. Introduction

Pollution by persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (DDTs), has spread all over the world as evidenced by their detection both in human and wildlife. Within marine environment, the coastal areas have deserved special consideration as primary receivers of urban, industrial and riverine inputs. Little attention has, instead, been paid to open-sea waters, although POPs extend the boundaries of their distribution all over the marine ecosystem. In this regard it has been emphasized that open seas play the role of final sink for persistent contaminants (Tanabe, 2000). For example, it has been reported, that the open-sea waters contain the major portion of residual PCBs, accounting for 61% of the total load in the environment (Tatsukawa and Tanabe, 1990). In this perspective large fish, such as shark, tuna and swordfish, as upper links in the pelagic food chain, may exhibit a high potential for the accumulation of these pollutants (Stefanelli et al., 2002; Ueno et al., 2002; Storelli et al., 2003a; Stefanelli et al., 2004).

Recent studies have indicated Mediterranean swordfish and tuna as species potentially "at risk" for the reproductive function because a dramatic induction of typically female proteins, such as vitellogenin and zona radiata proteins, have been detected in adult males of

* Corresponding author. Tel.: +39 80 5443866.
E-mail address: g.o.marcotrigiano@veterinaria.uniba.it (G.O. Marcotrigiano).

0045-6535/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2005.04.099

these species (Fossi et al., 2001; Fossi et al., 2002; De Metrio et al., 2003). The same investigations support the hypothesis that organochlorine with endocrine disrupting capacity, among which polychlorinated biphenyls and organochlorine pesticides, may have played a significant role in this process. The need for a continuous monitoring of organochlorine load in these species is, hence, obvious. Therefore, this study intended to investigate the status of PCBs and DDTs contamination and the accumulation profile of individual PCB congeners in the liver of swordfish from Mediterranean Sea. Furthermore, 2,3,7,8-TCDD of mono- and non-*ortho* congeners were estimated (TEQs), using toxic equivalents factors (TEFs) based on fish toxicity data according to Van den Berg et al. (1998), in order to assess the relative toxicological impact of these highly toxic PCBs in the organisms in question.

2. Materials and methods

Specimens of *Xiphias gladius* (swordfish), weighing between 5.3 and 83.0 kg, were caught in the Ionian Sea during June–September 2003 (Table 1). The livers of the specimens of similar size were grouped, homogenised and analysed. To determine polychlorinated biphenyl (PCBs = 8, 20, 28, 35, 52, 60, 77, 101, 105, 118, 126, 138, 153, 156, 169, 180 and 209) and DDT compound (DDTs = *p*,*p*′-DDT, *o*,*p*′-DDT, *p*,*p*′-DDE, *p*,*p*′-DDD, *o*,*p*′-DDD) concentrations the following method was used. Aliquots (2–3 g) of the homogenised samples were ground with anhydrous sodium sulphate in a mortar. The mixture was extracted with petroleum ether according to Erney's procedure (Erney, 1983). The extracts were then concentrated and subsamples were taken in order to determine the tissue fat content by gravimetry. An aliquot of the remaining extract was dissolved in hexane (5 ml) and mixed with H_2SO_4 conc. for the clean up, following the procedure described by Murphy (1972). After centrifugation, the hexane solution was concentrated (about 1 ml) and transferred on a glass column (i.d. 5 mm) filled with 1 g of florisil (activated at 120 °C for 16 h) for the separation of PCBs from other organochlorine compounds. The first fraction eluted with hexane (12 ml), contained PCBs and some DDTs, whereas the second fraction, eluted with 10 ml of 15% ethylether in hexane, contained the remaining DDTs and other organochlorine compounds. An aliquot of initial fraction was run on a column (i.d. 5 mm) packed with 125 mg of activated carbon (434455 C. Erba, Milano, Italy) for the separation of non-*ortho* PCB congeners, 3,3′,4,4′-T_4CB, (IUPAC 77), 3,3′,4,4′,5-P_5CB (IUPAC 126), and 3,3′,4,4′,5,5′-H_6CB (IUPAC 169) from other PCBs following the method reported by Tanabe et al. (1987). Analyses were made on a Carlo Erba HR gas chromatograph 8000 Top with automatic injection system and with an electron capture detector ECD-400, Ni^{63} (temperature: 330 °C). The GC was connected to a PC-Pentium III IBM equipped with Chrom-Card version 1.2 software program for integration purposes (C. Erba). For all the analyses a fused-silica capillary column DB-5 Supelco (length = 30 m, inside diameter 0.25 mm and film thickness 0.25 μm), was used. Hydrogen at a flow rate of 1 ml/min was used as gas carrier, nitrogen as make-up gas 60 ml/min. Temperature was programmed according to the following sequence: injection at 90 °C. Oven steady for the first min and then an increased from 90 to 180 °C at a rate of 15 °C/min. Oven maintained at steady temperature for 1 min and then increased from 180 to 220 °C at a rate of 4 °C/min; oven maintained at steady temperature for 20 min and then increased from 220 to 275 °C at a rate of 5 °C/min; from this point until the end of the analytical run, the column remained isothermal at a temperature of 275 °C. The individual PCB congeners were determined against the corresponding individual standards obtained from ULTRA Scientific, Inc. (chemical purity 99%). The reference material employed was BCR 349 (cod liver oil). The identity of the DDT group compounds was confirmed by an alkali conversion to their respective olefins and re-analysis by GLC. Analytical data, as for DDT group compounds were obtained by a comparison between sample peak area and external standards peaks area (POCs mixture, bought from Supelco). Recoveries were determined by adding known amounts of PCBs and DDTs standards (at three levels of concentrations) to empty samples before extraction (method of additions). The recoveries were within 80–110%. The limits of quantification were from 0.1 to 0.4 ng/g on a wet wt basis for the PCB congeners and DDTs. Quantification

Table 1
Details of swordfish

Code	No. of specimens	Length (cm)	Weight (kg)
1	4	88.5 ± 0.4	5.3 ± 0.3
2	4	92.0 ± 0.7	7.0 ± 0.4
3	9	102.2 ± 0.3	10.8 ± 0.7
4	4	107.0 ± 0.6	12.8 ± 0.6
5	4	107.5 ± 0.7	14.1 ± 0.3
6	5	112.2 ± 0.4	16.6 ± 0.7
7	6	118.2 ± 0.7	18.8 ± 0.7
8	3	116.8 ± 0.5	22.0 ± 0.3
9	2	132.0 ± 0.4	25.5 ± 0.7
10	2	132.5 ± 0.7	28.0 ± 0.3
11	4	135.7 ± 0.9	30.1 ± 0.3
12	3	134.3 ± 0.5	32.8 ± 0.8
13	2	144.5 ± 0.4	37.3 ± 0.1
14	2	148.0 ± 0.2	40.5 ± 0.7
15	1	157.0	44.0
16	1	166.0	60.5
17	1	167.0	66.0
18	1	172.0	83.0