

POLYCHLORINATED -NAPHTHALENES, -BIPHENYLS, -DIBENZO-*p*-DIOXINS AND -DIBENZOFURANS IN TUNA, SWORDFISH, CORMORANTS AND SWALLOWS FROM ITALY

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Introduction

Although several studies have reported concentrations of PCBs and DDTs in cetaceans from the Mediterranean Sea, occurrence of these compounds in tuna, swordfish and cormorants is less known. Similarly no studies have reported concentrations of polychlorinated-dibenzo-*p*-dioxins (PCDDs), -dibenzofurans (PCDFs) or -naphthalenes (PCNs) in fishes and birds from the Italian coast. In this study, tissues of bluefin tuna (*Thunnus thynnus thynnus*), swordfish (*Xiphias gladius*) and common cormorants (*Phalacrocorax carbo*) collected from the Italian coasts were analyzed for the presence of *p,p'*-DDE, PCBs, PCDDs, PCDFs and PCNs. Barn swallows (*Hirundo rustica*) collected from agricultural areas near Milan, northern Italy, were analyzed for the presence of the target organochlorines. 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) were calculated by multiplying the concentrations of toxic congeners with their corresponding toxic equivalency factors (TEFs) derived from H4IIE in vitro bioassays^{1,2}.

Materials and Methods

Samples of liver, muscle and fat from sexually mature (fork length >110 cm) bluefin tuna were collected in Palizzi, southern coast of Italy, during October- November 1999. Liver and muscle were taken from mature swordfish, which were harpooned in Stretto di Messina in the Ionian - Tyrrhenian Seas during July 1999. Tissues from several individuals were pooled to obtain representative samples. Livers of cormorant were collected from the birds that were originally sacrificed in 1997 by the Department of Sanitary, Division of Rearing and Zootechnical Resources. Cormorants were from Cabras lagoon in the Sardinian Sea. Barn swallows were collected in 1995 at farms located in Milan, northern Italy. Chloronaphthalene (CN), chlorobiphenyl (CB) and 2,3,7,8-substituted congeners of PCDDs and PCDFs were analyzed following the method described elsewhere with some modifications³. PCB congeners were identified and quantified using a gas chromatograph (Perkin Elmer series 600) equipped with ⁶³Ni electron capture detector (GC-ECD). Identification and quantification of individual PCN and PCDD/DF congeners were accomplished with a Hewlett Packard 6890 series high resolution gas chromatograph (HRGC) coupled to a JEOL JMS-700 high resolution mass spectrometer (HRMS). CN and dioxin congeners were determined by selected ion monitoring (SIM) at the two most intensive ions of the molecular ion cluster.

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Results and Discussion

Bluefin Tuna. Concentrations of total PCBs in livers of bluefin tuna ranged from 224 to 1660 ng/g (mean: 934; n=3) wet wt (Table 1). Mean concentrations of total PCBs in tuna muscle and fat were 280 (n=2) and 817 ng/g, wet wt, respectively. Muscle of bluefin tuna collected in 1993 contained total PCB concentrations in the range of 170 to 2200 ng/g, wet wt ⁴. Mean concentrations of *p,p'*-DDE in liver, muscle and fat of tuna were 82, 49 and 135 ng/g, wet wt, respectively (Table 1). The observed concentrations of *p,p'*-DDE in the muscle of tuna were less than those reported for relatively larger size tuna collected in 1993 (56-270 ng/g, wet wt) ⁴. PCNs were found in all the analyzed tissues of bluefin tuna at concentrations ranging from 7 (muscle) to 550 pg/g, wet wt (fat) (Table 1). However, the observed concentrations of PCNs in livers of tuna from Italy were less than those found in the livers of cod from the Baltic Sea ⁵. Concentrations of 2,3,7,8-substituted congeners of PCDDs/DFs were generally less than the limits of detection, which varied from 1 to 75 pg/g, wet wt, depending on the congeners and tissue (Table 2a,b). Previous studies have not reported concentrations of PCDDs/DFs in tuna from Italian coast of the Mediterranean.

Swordfish. Concentrations of total PCBs in pooled samples of liver and muscle of swordfish were 745 and 329 ng/g, wet wt (mean: n=2), respectively (Table 1). Similarly, concentrations of *p,p'*-DDE in swordfish liver and muscle were 135 and 57 ng/g, wet wt, respectively. PCDD/DF congeners were not found in swordfish above the limits of detection (Table 2a,b). This study provides baseline measurements of organochlorines in swordfish for the first time.

Cormorants. Concentrations of total PCBs in livers of cormorants ranged between 722 and 2300 ng/g, wet wt (Table 1). Concentrations of *p,p'*-DDE in cormorant livers ranged from 144 to 190 ng/g, wet wt (mean: 166). Concentrations of PCNs in cormorant livers ranged from 130 to 795 pg/g, wet wt (mean: 424). Mean PCN concentration in cormorant livers were 7-times greater than those found in the livers of tuna and swordfish. Estimated concentration of total PCNs in livers of cormorants collected from the Baltic Sea was 14,000 pg/g, wet wt ⁶.

Barn Swallows. Barn swallows collected from agricultural areas near Milan contained remarkable concentrations of PCBs. Mean concentrations of PCBs in liver and muscle of barn swallows were 1230 and 716 ng/g, wet wt, respectively (n=2). Concentrations of *p,p'*-DDE in liver and muscle of swallows were 95 and 75 ng/g, wet wt, respectively (Table 1). PCNs were also found in swallows at concentrations ranging from 116 to 215 pg/g, wet wt.

Toxic Equivalents. To our knowledge, no previous studies have reported the occurrence of PCNs in biota from the Mediterranean Sea. The results of this study permitted the analysis of relative contribution of PCNs to total TEQs (sum of TEQs of coplanar PCBs, PCDDs/DFs and PCNs). Calculated concentrations of total TEQs (sum of TEQs of PCBs, PCNs and PCDDs/DFs) in the tissues of tuna ranged from 0.99 to 28 pg/g, wet wt. Total TEQs in swordfish tissues were in the range of 1.47 to 3.55 pg/g, wet wt. Non- and mono-*ortho* PCBs were the major contributors to total TEQ concentrations in fishes. In particular, non-*ortho* coplanar PCB congener 126 accounted for 80 to 90% of the total TEQs in fishes. Contribution of this congener to total TEQs was relatively less in birds accounting for 52 to 76% of the total TEQs. In livers of cormorants and muscle tissues of swallows, PCDDs/DFs contributed up to 80 and 45%, respectively, of the total TEQs. Contribution of PCNs to total TEQs in fishes and birds from the Mediterranean Sea was

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less than 2%. This is less than those that have been reported to occur in earlier studies in which PCNs contributed up to 50% of the total TEQs in fishes from the Detroit River^{3,7}.

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Table 1. Concentrations (wet weight) of *p,p'*-DDE (ng/g), total PCBs (ng/g) and total PCNs (pg/g) in fishes and birds from Italy

Species	Tissue	Fat (%)	Date of colln	Location	n	<i>p,p'</i> -DDE	PCBs	PCNs
Tunafish	Liver	11.5	Oct-Nov 1999	Palizzi	1	75	1660	NA
Tunafish	Liver	3.95	Oct-Nov 1999	Palizzi	1	61	224	53.8
Tunafish	Liver	10	Oct-Nov 1999	Palizzi	5	110	920	NA
Tunafish	Muscle	5.3	Oct-Nov 1999	Palizzi	3	67	363	22.6
Tunafish	Muscle	2.92	Oct-Nov 1999	Palizzi	2	30	197	6.97
Tunafish	Fat	85	Oct-Nov 1999	Palizzi	3	135	817	552
Swordfish	Liver	16.2	July 1999	Stretto Messina	4	135	745	62.9
Swordfish	Muscle	8.78	July 1999	Stretto Messina	4	45	258	14.8
Swordfish	Muscle	9.5	July 1999	Stretto Messina	6	69	399	14.6
Cormorant	Liver	7.6	1997	Cabras lagoon	3	164	722	130
Cormorant	Liver	7.76	1997	Cabras lagoon	1	190	2300	795
Cormorant	Liver	4.55	1997	Cabras lagoon	1	144	1230	347
Swallow	Liver	45	1995	Milan	5	84	954	215
Swallow	Liver	6.2	1995	Milan	4	105	1510	126
Swallow	Muscle	4.7	1995	Milan	4	67	733	116
Swallow	Muscle	5.1	1995	Milan	5	82	700	142

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N= number of samples pooled.
NA= not analyzed.

Table 2a. Concentrations of 2,3,7,8-substituted PCDDs (pg/g, wet wt) in fishes and birds from Italy

Species	Tissue	PCDD congeners						OCDD
		2378	12378	123478	123678	123789	1234678	
Tuna	Liver	<2	<2	<10	<10	<10	<5	<50
Tuna	Muscle	<1	<1	<2	<3	<2	<3	<2
Tuna	Muscle	<3	<1	<3	<4	<3	<3	<2
Tuna	Fat	<40	<20	<15	<25	<25	<10	<7
Swordfish	Muscle	<1	<4	<6	<6	<2	<10	<4
Swordfish	Muscle	<3	<2	<10	<10	<10	<10	<4
Swordfish	Liver	<10	<10	<20	<20	<20	<30	<30
Cormorant	Liver	<15	<75	<10	<10	<10	<5	<2
Cormorant	Liver	<3	<5	<8	<8	<8	<30	<10
Cormorant	Liver	<10	5.56	<3	5.07	<3	<10	<6
Swallow	Liver	<10	5.77	<0.01	12.6	<13	<50	<25
Swallow	Liver	<10	<10	<15	9.37	<15	<6	<3
Swallow	Muscle	1.41	2.62	<3	<3	<3	<8	<6
Swallow	Muscle	1.81	2.36	<3	5.7	<3	<10	<5

Table 2b. Concentrations of 2,3,7,8-substituted PCDFs (pg/g, wet wt) in fishes and-birds from Italy

	2378	12378	23478	123478	123678	123789	²³⁴⁶⁷ ₈	1234678	1234789	OC DF
Tuna L	<6	NA	NA	NA	NA	NA	NA	<6	<6	<10
Tuna M	<2	<2	<2	3.21	<1.5	<2	<3	<4	<3	<2
Tuna M	<3	<5	<6	<2	<2	<10	<2	<4	<4	<3
Tuna F	<18	<10	19	19.8	<5	<5	<10	<12	<25	<5
Swordfish M	<5	<4	<4	<5	<4	<4	<4	<12	<14	<3
Swordfish M	<6	<6	<6	<5	<5	<5	<5	<10	<8	<6
Swordfish L	<20	<20	<20	<10	<60	<10	<10	<25	<25	<20
Cormorant L	<4	<2	<10	<4	6.36	<4	<4	<6	<8	<4
Cormorant L	<8	<3	<3	<10	<10	<10	<10	<30	<30	<16
Cormorant L	<3	<2	7.7	<5	<5	<5	<6	<14	<12	<8
Swallow L	<12	9.11	<12	<15	<15	<15	<15	<40	<40	<25
Swallow L	<2	<1	<2	<6	<6	<6	<6	<20	<15	<3
Swallow M	13.1	4.48	10.4	<4	<3	<4	<4	<4	<4	<6
Swallow M	<3	<5	15	<4	<4	<3	<3	<10	<20	<6

NA = Not analyzed; M= Muscle; L= Liver; F= Fat

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