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Persistent Organic Pollutants (PCBs and DDTs) in European Conger Eel, *Conger conger* L., from the Ionian Sea (Mediterranean Sea)

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Abstract The present study provides novel data regarding levels of polychlorinated biphenyls (PCBs) and organochlorine pesticides (DDTs) in muscle tissue of European conger eel (*Conger conger*) from Ionian Sea (Mediterranean Sea). The mean concentration of PCBs (891 ng g^{-1} lipid weight) was higher than those of DDTs (543 ng g^{-1} lipid weight). PCB pattern was dominated by higher chlorinated congeners (hexa-CBs: 69.3 %, penta-CBs: 17.2 %, hepta-CBs: 13.3 %). Regarding DDT pattern, *p,p′*-DDE was prevalent in all samples (85.5 %), suggesting no recent DDT input. The total 2,3,7,8-TCDD toxic equivalent (TEQs) of coplanar PCBs, including mono-and non-*ortho* congeners was 0.41 pg g^{-1} wet weight (29.92 pg g^{-1} lipid weight). The PCB and DDT levels, as well as TEQ concentrations were lower than most of the corresponding published data for fish from Mediterranean and non-Mediterranean regions, probably reflecting a moderately contaminated area.

Keywords Mediterranean Sea · European conger eel · DDTs · PCBs · TEQs

Organochlorine compounds such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (DDTs) are a group of structurally similar compounds globally distributed. Because of their toxicity, stability, long biological half-life and high liposolubility, they may bioaccumulate and biomagnify along food chains, with a potential risk especially for high trophic level predators. These compounds exhibit, in fact, a broad spectrum of toxicological responses affecting development, reproduction, and behaviour of wildlife. In particular, in the aquatic ecosystems these compounds become distributed between water phase and particulate matter which act as a sorbent for them and transports them into sediment, which serves both a sink and a source of contamination to the biota. As a result the fauna inhabiting deep-sea waters, because of interactions with bottom environment might be more subject to bioaccumulation of these organochlorine compounds. This aspect acquired a particularly alarming dimension for organisms from marine areas with strong anthropogenic impact. In this picture one location of special concern is the Mediterranean Sea, which for its peculiar oceanographic characteristics, such as relatively shallow, semi-enclosed and with limited natural water exchanges, favours the accumulation rather than the dispersion of contaminant inputs, turning so a particularly vulnerable and potentially threatened ecosystem. European conger eel (*Conger conger*) is an important commercial species of the Mediterranean Sea. It is a strictly benthic fish that lives on the continental shelf on rocky and sandy bottoms, from the shorelines to depth of 1,000 m. European conger eel is carnivorous fish and its diet consist mainly of bottom-living fish, crustaceans and cephalopods. Because of high trophic level (Stergiou and Karpouzi 2002) and nature of its habitat, this species might have a propensity to accumulate these pollutants. Nevertheless, there are only few reports regarding status of contamination of these organisms either for Mediterranean Sea (Storelli et al. 2003, 2011; Storelli 2008) or other marine areas (Miao et al. 2000; Takahashi et al. 2001; Tanabe et al. 2005). To fill this knowledge gap the present study reports the occurrence of PCBs and DDTs in European conger eel from the Ionian Sea

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(Mediterranean Sea). The toxicological significance of these levels and a comparison of concentrations to those reported for other marine organisms are also discussed.

Materials and Methods

Specimens of *C. conger* (European conger eel) (specimen number: 137; weight range: 469.0–1,057.0 g; length range: 64.5–85.0 cm) were caught in the Ionian Sea (Mediterranean Sea) (Fig. 1) from June to September 2010. From the total number of specimens were formed pools (no 10) within which individual fish were gathered as a function of their similar size. From fish of each pool, muscle tissue was taken, homogenised and kept in a deep freeze at –20°C until chemical analysis. The following PCB congeners (no. 8, 20, 28, 35, 52, 60, 77, 101, 105, 118, 126, 138, 153, 156, 169, 180 and 209), together with the DDT compounds (*p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD, *o,p′*-DDT, *o,p′*-DDD) were determined using analytical procedures previously described and validated (Storelli et al. 2009). Briefly, approximately 12 g of pooled fish muscle was grinded with Na_2SO_4 and spiked with 20 ng of 2,2′,3,4,5,6′-H_6CB (PCB 143) used as internal standard. The mixture was extracted with petroleum ether and concentrated. Subsamples were taken in order to determine the tissue fat content by gravimetry. An aliquot (about 100 mg) of the remaining extract was dissolved in hexane and cleaned by passing through 8 g of acid silica (H_2SO_4, 44 %w/w.), using 50 mL of a mixture of hexane/dichloromethane (L/L, v/v) for elution of the analytes. The eluate was evaporated to dryness and redissolved in 100 µL of iso-octane. For the separation of non-*ortho* PCB congeners (no. 77, 126 and 169) from other PCBs, the method reported by Tanabe et al. (1987), involving fractionation on 125 mg of activated carbon (434455 C. Erba, Milano, Italy), was used. For the analysis of organochlorine compounds, a Thermo Trace GC connected with a Thermo PolarisQ MS operated in electron impact ionization (EI) mode was equipped with a 30 m × 0.25 mm × 0.25 µm Rtx 200 capillary column (Thermo, Austin, Texas, USA). The MS was used in the SIM mode with two ions monitored for each PCB homologue group or pesticide in specific windows. 1 µL of the cleaned extract was injected in splitless mode (injector temperature 90°C then to 300°C with 70°C/min), splitless time 1.50 min, pulse pressure time 1.50 min, pressure pulse 25 psi. Helium was used as carrier gas at constant flow (1.0 mL/min). The temperature of the Rtx 200 column was held at 90°C for 1.50 min, then increased to 180°C at a rate of 15°C/min, further increased to 280°C at a rate of 5°C/min, further increased to 300°C at a rate of 40°C/min, held for 7 min. QA/QC was performed through the analysis of procedural blanks, a duplicate sample and a standard reference material [CRM349 for PCBs and CRM598 for DDTs (cod liver oils) (BCR, Brussels)] within each batch of samples. For the replicate and standard reference materials, the relative standard deviations (RSD) were <10 % for all the detected compounds. Additionally, the method performance was assessed through participation in interlaboratory studies organized by QUASIMEME (Laboratory Performance Studies, Year 9, June 2004 to May 2005). The limit of detection for PCBs ranged from 0.02 to 0.50 ng g^{-1} on a lipid weight basis, while for DDTs it was 2.0 ng g^{-1} on a lipid weight basis. Concentrations of PCBs and DDTs, means of two replicate measurements, are presented as ng g^{-1} on a lipid weight basis, while for comparative purposes TEQ concentrations are expressed either in pg-TEQ g^{-1} wet weight or in pg- TEQ g^{-1} lipid weight.

Fig. 1 Sampling site

Results and Discussion

Concentrations of PCBs and DDTs (ng g^{-1} lipid weight) in the muscle tissue of European conger eel are summarized in Table 1. As revealed by the statistical analysis (Mann–Whitney's *U* test) PCB concentrations, ranging from 518 to 1,724 ng g^{-1} lipid weight (average: 891 ng g^{-1} lipid weight), were significantly higher than those of DDTs, which varied from 271 to 865 ng g^{-1} lipid weight (average: 543 ng g^{-1} lipid weight) ($p < 0.05$). The legal restrictions

Table 1 Minimum, maximum and mean concentrations (ng g^{-1} lipid weight) of individual PCB congeners and DDTs in European conger eel muscle from Ionian Sea

	Min	Max	Mean	SD
Lipid %	0.3	4.0	1.4	1.2
PCB 77	0.5	4.0	2.0	1.0
PCB 101	ND	31.0	11.0	14.0
PCB 105	12.0	70.0	37.0	19.0
PCB 118	53.0	201.0	99.0	48.0
PCB 126	ND	33.0	5.8	10.0
PCB 138	89.0	435.0	226.0	104.0
PCB 153	241.0	707.0	373.0	161.0
PCB 156	ND	47.0	18.0	20.0
PCB 180	30.0	268.0	119.0	69.0
∑PCB	518.0	1,724.0	891.0	398.0
p,p′-DDE	248.0	769.0	464.0	175.0
p,p′-DDT	7.0	84.0	46.0	28.0
p,p′-DDD	ND	38.0	14.0	13.0
o,p′-DDD	5.0	34.0	19.0	10.0
∑DDT	271.0	865.0	543.0	201.0

introduced in most parts of developed world since the 1970s for production and use of persistent pesticides, have undoubtedly determined a decline in the environmental concentrations of these compounds. Consequently this chemical class often occurs into the biota in low concentrations and with a profile dominated by *p,p′*-DDE, the main product of metabolic oxidation of *p,p′*-DDT. In line with this observation, in our samples *p,p′*-DDE was predominant, accounting for 85.5 % of the total DDTs, followed by *p,p′*-DDT (8.5 %), *o,p′*-DDD (3.5 %) and *p,p′*-DDD (2.6 %), while *o,p′*-DDT resulted below the limit of detection in all the organisms analyzed. Also the high value of *p,p′*-DDE/DDTs ratio (0.9) encountered in the current study indicated a remote use of *p,p′*-DDT in agricultural activities. Concerning PCBs, of the 17 congener peaks for which analyses were conduct in this study PCBs 77, 105, 118, 138, 153, and PCB 180 were detected in all samples, PCBs 101, 126 and 156 were encountered in 40.0 %, 41.5 % and 50.0 % of samples respectively, while the remaining congeners PCBs 8, 20, 28, 35, 52, 60, 169, 209 were below the limit of detection in all organisms examined. The PCB profile was characterized by the predominance of the hexachlorobiphenyls (69.3 %), followed by penta- (17.2 %), hepta- (13.3 %) and tetra- (0.2 %). Among hexa- congeners, PCB 153 and PCB 138 were predominant analytes, accounting for 41.9 % and 25.4 % of the total PCBs respectively, followed by hepta-PCB 180 (13.3 %), pentacholobiphenyls PCB 118 (11.2 %) and PCB 105 (4.2 %), while the other chlorobiphenyls accounted for less 5 % of the total PCB residue. To our knowledge, few information is available on the occurrence of organochlorine residues in these organisms from Mediterranean Sea. Some studies carried out by Storelli et al. (2003, 2008, 2011), (Table 2) regarding PCBs contamination in European conger eel specimens from Adriatic Sea, reported concentrations higher than those encountered in the sample here investigated. These differences may be attributed to various factors, first of all the level of pollution of the site

Table 2 Comparison of PCB and DDT concentrations (ng g^{-1} lipid weight) in fish muscle measured in this study with those from Mediterranean and non-Mediterranean regions

Species	Location	PCBs	DDTs	References
C. conger	Mediterranean Sea (Ionian Sea)	891	543	This study
C. conger	Mediterranean Sea (Adriatic Sea)	3,481	–	Storelli et al. (2003)
C. conger	Mediterranean Sea (Adriatic Sea)	3,406	–	Storelli, (2008)
C. conger	Mediterranean Sea (Adriatic Sea)	1,980	–	Storelli et al. (2011)
Mullus barbatus	Mediterranean Sea (Tyrrhenian Sea	1,421	221	Naso et al. (2005)
Mugil cephalus	Mediterranean Sea (Tyrrhenian Sea)	16,515	703	Naso et al. (2005)
Conger cinereus	Pacific Ocean	1,678[a]	–	Miao et al. (2000)
Conger myriaster	Pacific Ocean (China Sea)	80	7,900	Tanabe et al. (2005)
Conger myriaster	Pacific Ocean (China Sea)	130	1,700	Tanabe et al. (2005)
Congriscus megastomus	Pacific Ocean (Tosa Bay)	1,600	1,200	Takahashi et al. (2001)
Hoplobrotula armata	Pacific Ocean (Suruga Bay)	1,900	51	Lee et al. (1997)
Helicolenus hilgendorfi	Pacific Ocean (Suruga Bay)	1,200	770	Lee et al. (1997)
Sebastolobus altivelis	Pacific Ocean (Monterey Bay)	1,400	–	Froescheis et al. (2000)
Microstomus pacificus	Pacific Ocean (Monterey Bay)	–	2,380	Looser et al. (2000)
Sebastolobus altivelis	Pacific Ocean (Monterey Bay)	–	2,420	Looser et al. (2000)
Coryphaenoides armatus	Atlantic Ocean	–	1,090	Looser et al. (2000)

[a] Dry weight

where the organisms are caught. In this regard has been often reported that marine organisms from the Adriatic Sea are more contaminated in comparison to those from Ionian Sea (Storelli et al. 2005), probably because of more intensive industrial activities, typical of the north Italian regions (Frignani et al. 2004; Solis-Weiss et al. 2004). In the same way, higher concentrations were detected in benthic fish from other Mediterranean marine waters strongly contaminated by anthropogenic input, such as Gulf of Naples (Naso et al. 2005) (Table 2). An other important factor having a considerably effect on the magnitude of accumulated organochlorines is the fish size. In accordance to this assumption the concentrations of PCBs in the organisms investigated varied with size resulting in higher amount in larger fish as evidenced by positive relationship ($R = 0.75$, $p < 0.02$). However independently from the complexity of factors leading to a different bioaccumulation of these contaminants in marine organisms, our results generally indicated that organochlorine contamination was lower compared not only to the levels encountered in organisms from various areas of Mediterranean Sea, but also to those in fish from other locations comprising industrialised areas such as Japanese (Lee et al. 1997; Takahashi et al. 2001), Atlantic (Looser et al. 2000; Tanabe et al. 2005) and Pacific waters (Froescheis et al. 2000) (Table 2). On the contrary when comparing the homolog pattern of current study to those reported for marine organisms from Mediterranean Sea and other marine areas a similarity emerged, being hexa-, hepta- and pentachlorinated biphenyls among the top contributors to the sum of total PCBs, with a dominance of PCB 153, 138, 118 and 180. On the other hand, these PCBs are the most abundant in commercial PCB mixtures commonly used in European countries, such as Aroclor 1254 and 1260. In addition they exhibit higher persistence in most biota due to their high octanol-water coefficients (log K_{ow}) and high persistence and because they have structures difficult to metabolise. Of interest for the toxicological implications on organisms is the accumulation of those congeners isostereomers of 2,3,7,8-TCDD, including non-*ortho* coplanar PCB congeners 77, 126 and 169 and mono-*ortho* PCB 105, 118 and 156. In our samples concentrations of these dioxin-like PCBs varying from 86.5 to 314.5 ng g^{-1} lipid weight with a mean value of 162.3 ng g^{-1} lipid weight, accounted for a moderate part of the total PCBs (18.2 %). Mono-*ortho* PCBs were predominant respect to non-*ortho* PCBs, contributing for 95.2 % of the total dioxin-like-PCBs. Among the mono-*ortho* congeners, PCB 118 was prevalent constituting 64.3 %, followed by PCBs 105 (24.0 %) and PCB 156 (11.7 %). In the case of non-*ortho* DL-PCBs, the contribution by congener PCB 77 was lower than that PCB 126 which constituted 74.6 %, while PCB 169 was not encountered in any of samples investigated. The TEQ concentrations (0.41 pg g^{-1} wet weight; 29.92 pg g^{-1} lipid weight), calculated using the TEFs for fish developed by Van den Berg et al. (1998), showed that non-*ortho* congeners contributed principally to the total toxicity with the pentachlorinated non-*ortho* congener PCB 126 having percentage above 97.0 %. Looking at the our TEQs concentration the comparison with the data from other studies is rather complicated because of differences among various reports, including sampled tissue examined, the way of expressing concentrations (wet weight, lipid weight), the use of different TEF values and other factors influencing the final result. However overall, the data observed in European conger eel was lower to those encountered in muscle tissue of fish and marine organisms located in highest position of trophic webs such as swordfish, tuna fish and marine turtles from Adriatic and Tyrrhenian Sea, confirming a situation of moderate contamination of the Ionian Sea in comparison with those of other Mediterranean regions. Anyhow, this finding needs to be verified by further research involving different marine organisms from Ionian Sea because the accumulation processes of these pollutants in fish are complex and are species-specific. Therefore continuous monitoring should be instituted so as to acquire further information on the environment quality of this marine area even if there seems, at present, to be no marked threat for biota from the examined water body.

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