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Levels and congener profiles of PCBs and PCDD/Fs in blue shark (*Prionace glauca*) liver from the South-Eastern Mediterranean Sea (Italy)

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ABSTRACT

Liver of blue shark (*Prionace glauca*) specimens from the South-Eastern Mediterranean Sea were analyzed for the presence of polychlorinated biphenyls (PCBs), including coplanar congeners, polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). PCBs were the dominant chemicals, followed by PCDFs and PCDDs. The pattern of PCB congener concentrations in the hepatic tissue was dominated by higher chlorinated compounds. The specific profile of toxic PCDD/F congeners was characterized mainly by 2,3,7,8-TCDF and 2,3,7,8-TCDD, followed by 1,2,3,6,7,8-HxCDD and 2,3,4,6,7,8-HxCDF. The total 2,3,7,8-TCDD toxic equivalent (TEQs) was 149 pg g^{-1} lipid wt. The profile of TEQ shows that PCDDs present the greatest risk to this species contributing to total toxicity with a percentage approximately of 60%, while the contribution of PCDFs and DL-PCBs is almost the same being 22.4% and 21.6%, respectively. Further investigations are urgently needed to characterize the PCDD/Fs contamination levels not only in elasmobranch fish but in all Mediterranean marine biota.

1. Introduction

Persistent organic pollutants (POPs) are organochlorinated compounds of concern to the international community because are highly toxic to human and wildlife, persistent in the environment, resisting biodegradation, taken up and bioaccumulated in terrestrial and aquatic ecosystems, and capable of long-range trans-boundary atmospheric transport and deposition (Gramatica and Papa, 2007). Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are among the most known and investigated POPs. PCDD/Fs are unwanted and often unavoidable by-products in a number of industrial and thermal processes, while PCBs have been produced for specific industrial uses. In aquatic systems these chemicals are strongly bound to particulate material and accumulate in sediments, but they are taken up by benthic biota and so enter marine food webs, becoming concentrated at high trophic levels. It is, often, suggested that sharks may function as keystone predators (Stevens et al., 2000) being essential to the maintenance and stability of food webs. The mean trophic levels of these organisms (Cortès, 1999) are similar to those described for marine mammals (Pauly et al., 1998) and are somewhat higher than those of seabirds (Hobson et al., 1994). As marine mammals and seabirds, sharks are particularly susceptible of accumulating significant levels of these contaminants in their body resulting sentinel species of great potency for monitoring of such contaminants in marine environment (Serrano et al., 1997, 2000; Strid et al., 2007). Furthermore, the potential effects of POP exposure may have drastic implications for the health and survival of shark populations because these organisms generally tend to exhibit life history characteristics consistent with limited reproductive potential and low rates of population growth (Gelsleichter et al., 2005). It is not a coincidence that Species Survival Commission of International Union for Conservation of Nature (IUCN) has formed a Shark Specialist Group (SSG) which has developed an international plan of action for conservation and management of sharks. Given these points, there is a need to characterize levels of these contaminants in elasmobranch fish. Nevertheless, so far very limited data are available on the contamination of sharks by organohalogen pollutants (Serrano et al., 1997, 2000; Gelsleichter et al., 2005; Strid et al., 2007), with a particular paucity for data relating to Mediterranean Sea (Corsolini et al., 1995; Storelli and Marcotrigiano, 2001; Storelli et al., 2005); marine area that for the reduced hydrodynamics, high riverine inputs and intensive agricultural and industrial activities is subjected to a high anthropogenic impact (Frignani et al., 2004; Solis-Weiss et al., 2004). In this study, we report the occurrence of PCBs and PCDD/Fs in blue shark (*Prionace glauca*) liver from the Mediterranean Sea and assess the potential wildlife health risk to this species

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associated with the exposure to these contaminants. The toxicological significance of these levels and a comparison of concentrations to those reported for other marine organisms are also discussed.

2. Materials and methods

2.1. Sample collection

Twenty-two specimens of *P. glauca* (blue shark) were caught in the South-Eastern Mediterranean Sea (Fig. 1) during the period from June to August 2008. From each specimen (weight: 5.0–21.0 kg, total length: 105–124 cm) liver was taken and kept in a deep freeze at −20 °C until chemical analysis.

2.2. Sample preparation and clean up

Concentrations of 17 individual PCB congeners (PCBs: 8, 20, 28, 35, 52, 60, 77, 101, 105, 118, 126, 138, 153, 156, 169, 180 and 209), including only six of the twelve "dioxin–like" PCBs (non-*ortho* DL-PCBs: 77, 126, 169, mono-*ortho* DL-PCBs: 105, 118, 156), together with the seventeen 2,3,7,8- substituted PCDD/F congeners were determined. A complete description of the experimental procedure relative to PCBs has been recently described and validated (Storelli et al., 2007, 2009). Briefly, fish liver were ground in a porcelain mortar and pestle with Na_2SO_4 and spiked with PCB 143 used as internal standard. The mixture was extracted with hexane 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 (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 (1/1, 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 (Nos. 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. The determination of PCDD/Fs was based on the US EPA method 1613. Briefly, the samples extracted as above reported have been subjected to a multi-step clean-up to remove the matrix and the potential interfering components. The first stage was a fat destruction step consisting of a treatment of the sample solution with sulfuric acid and base back-extraction. The obtained extracts were then subjected to a pre-conditioned florisil clean-up column, that was eluted with different solutions in order to remove interfering components. The first eluted solvent was discarded, while the second eluate which contained PCDD/Fs was collected. The extracts were evaporated to dryness and redissolved in iso-octane. Appropriate ^{13}C-labeled extraction standards (1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD) were added to the samples in accordance with EPA method 1613, in order to control the whole sample preparation process. Recoveries of the ^{13}C-labeled standards ranged from 89% to 101%.

2.3. High resolution gas chromatography–mass spectrometry (GC–MS)

The final obtained PCBs and PCDD/Fs extracts were injected and analyzed separately on a high-resolution gas-chromatograph interfaced with a high-resolution mass spectrometer (HRGC-HRMS). Instrumentation included a Thermo Trace GC Ultra (Austin, TX), connected to a PolarisQ high-resolution mass spectrometer. The PCB chromatographic separation was achieved by splitless injection of 2 μL on a capillary column with length of 30 m, i.d. 0.25 mm and 0.25 μm thickness stationary phase film (RTX-5, Restek US, Bellefonte, PA, USA). The gas chromatography oven was programmed as follows: initial temperature 90 °C, held for 1.50 min, then increased to 180 °C at a rate of 15 °C min^{-1}, further increased to 280 °C at a rate of 5 °C min^{-1}, further increased to 300 °C at a rate of 40 °C min^{-1}, held for 7 min. Helium was used as carrier gas at constant flow (1.0 mL min^{-1}). For the PCDD/Fs chromatographic separation was achieved by splitless injection of 1 μL on a capillary column with length of 30 m, i. d. 0.25 mm and 0.25 μm thickness stationary phase film (RTX-200, Restek U.S., Bellefonte, PA, USA). The gas chromatography oven was programmed as follows: initial temperature 150 °C, held for 1 min, then increased to 200 °C at a rate of 10 °C min^{-1}, further increased to 310 °C at a rate of 5 °C min^{-1}, held for 5 min. Helium was used as carrier gas at constant flow (1.0 mL min^{-1}). The mass spectrometer was operated in EI mode at 70 eV. The MS was used in the SIM mode with the two most intensive ions of the molecular ion cluster monitored in specific windows.

2.4. Quality assurance and quality control

QA/QC was performed through the analysis of procedural blanks, a duplicate sample and a standard reference material [CRM 349 (cod liver oils) (BCR, Brussels)] for each set of samples. For the replicate and standard reference materials, the relative

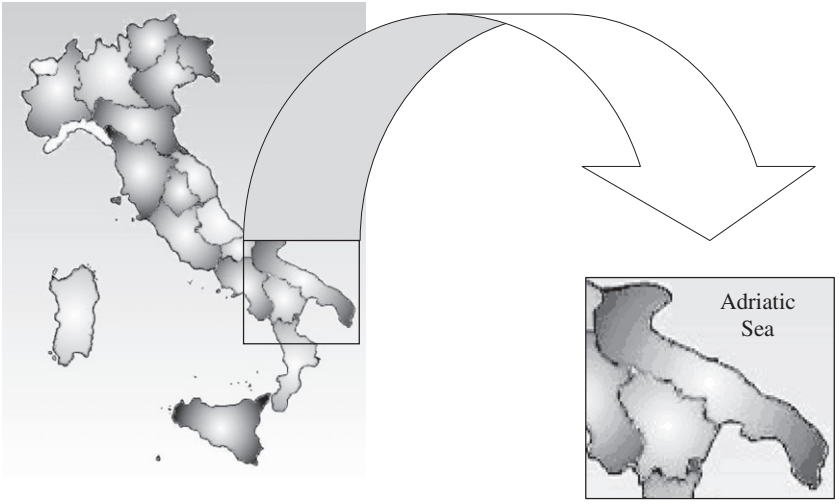

Fig. 1. Sampling site.