



ORGANOCHLORINE LEVELS IN CUVIER'S GOOSEBEAKED WHALES FROM IONIAN SEA, HELLAS

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Summary

Polychlorinated biphenyls (PCBs) and organochlorine pesticides were determined in subcutaneous blubber of 10 Cuvier's beaked whales (*Ziphius cavirostris*), stranded in a beach of Kyparissiakos Gulf (SE Ionian Sea, Hellas) on May 1996. DDTs were always the most abundant compounds with concentrations ranged between 11.2 and 35.1 $\mu\text{g/g}$ wet wt (mean value 20.9 $\mu\text{g/g}$), followed by the PCBs. Total PCBs concentrations (the sum of thirteen congeners) varied between 3.0 and 12.4 $\mu\text{g/g}$ wet wt (mean value 7.5 $\mu\text{g/g}$). Trans-nonachlor, hexachlorobenzene and dieldrin were also detected in lower concentrations.

Key words: whales, organochlorines, PCBs, Ionian sea

INTRODUCTION

Organochlorinated hydrocarbons, including the chlorinated pesticides (especially the DDT group) and the polychlorinated biphenyls (PCBs), are known to be ubiquitous environmental contaminants that have penetrated all marine ecosystems. Because of their considerable chemical stability and high fat solubility, they present high capability for bioaccumulation in marine organisms through the food chain¹. Fish eating cetaceans with long life-spans and low metabolic capacities, occupying a high trophic level form ideal depositories for this class of pollutants². There is evidence that exposure to high levels of organochlorines reduces the ability of the contaminated mammals to resist various diseases or illnesses and also exhibits negative influences on their reproductive activities^{3,4}. The present work reports the concentration of organochlorine compounds in the blubber of a common Mediterranean cetacean species the Cuvier's Beaked whale (*Ziphius cavirostris*). This whale is a toothed species feeding mainly on squid and deep water fish and is thus situated at a high stage in the trophic web resulting in high bioaccumulative capability. It is generally considered to be extremely difficult to observe at sea because of its unobtrusive and shy behaviour. However, an important number of direct observations were recently made in both the Ionian and Aegean

sea^{5,6} while during the last five years 10 strandings were reported in the Ionian and 13 in the Aegean sea. These data indicate that *Z. cavirostris* could be a frequent species in the hellenic seas⁷. Although there are some recent data on the concentrations of organochlorine residues in other marine mammals from hellenic waters, such as seals and dolphins⁸, no data exist on these compounds in whales.

MATERIALS AND METHODS

Blubber samples were collected from 10 specimens (8 males and 2 females) stranded in a sandy beach of Kyparissiakos gulf (South Ionian Sea, Hellas) on May 1996 (Fig. 1). The total lengths of the 8 males were between 4.4 and 5.2 m and none of them had apparent teeth. However, most of them had typical tooth scars on their skin. The two females were 4.7 m long and didn't present any tooth scar. The samples were taken approximately 50 cm behind the blowhole and slight laterally, wrapped in aluminum foil and kept in deep freeze until analysis.

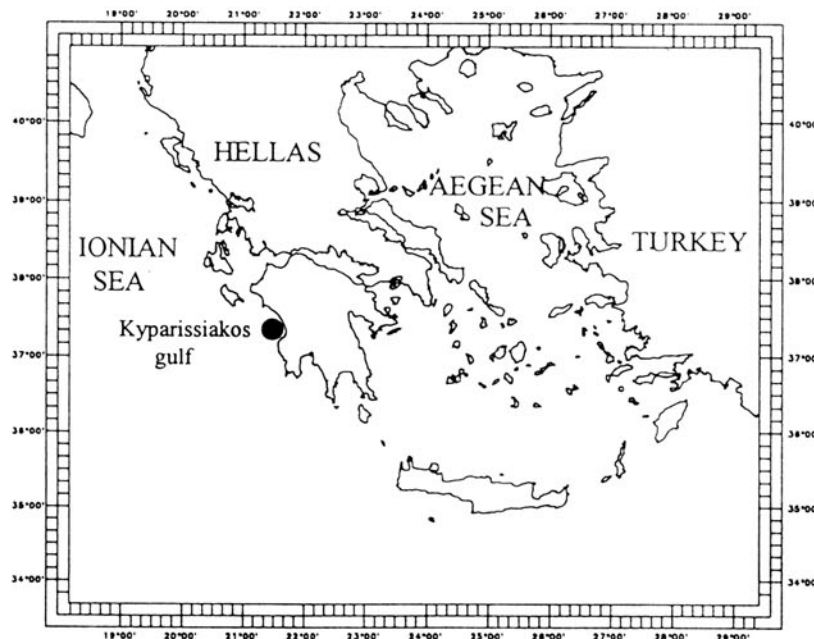


Fig. 1. Location where the Cuvier's Beaked whales stranded

At the laboratory, sub-samples of frozen tissue after lyophilization and grinding were soxhlet extracted with a 1:1 mixture of pentane-dichloromethane for nine hours. The lipids

content determination (as the extractable organic material) was performed in an aliquot of this extract and the rest of it was cleaned up by passage through a column containing 5% deactivated alumina⁹. The eluant was n-hexane. The cleaned extract was concentrated under a stream of pure nitrogen to a final volume of 0.5 ml and the organochlorines were determined by gas chromatography - mass spectrometry. A Hewlett - Packard 6890 GC-MS operating in selected-ion monitoring mode (SIM) with programmable time windows was used. The analytical column was a HP-5 MS capillary column (30 m X 0.25 mm) and the oven temperature was programmed from 60 °C (1.5 min) to 190 °C at 15 °C/min and then to 240 °C at 3.6 °C/min (10 min). The masses selected (m/z) were 79 for dieldrin, 235 for DDT and DDE, 246 for DDE, 284 for HCB, 409 for trans-nonachlor and 292, 326, 360, 394, 430 for the tetra-, penta-, hexa-, hepta- and octa- chlorobiphenyls respectively.

RESULTS AND DISCUSSION

The organochlorine concentrations in the blubber of the examined specimens are presented in Table 1. Total DDTs were calculated as the sum of the p,p' forms of DDT and its metabolites DDE and DDD, while total PCBs correspond to the sum of thirteen congeners with IUPAC Nos 52, 87, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183 and 194. PCBs mixtures are theoretically composed of 209 congeners about 50 of which are found in the environment, but it has been shown that the toxic nature of these mixtures can principally be attributed to the presence of a small group of chlorobiphenyls¹⁰. The above mentioned 13 congeners determined in this study were selected in accordance with the recommendation of ICES and taking into consideration the following criteria: a) they occur in relatively high concentrations in the technical PCB mixtures, b) they cover the chlorination range from 4 to 8 Cl atoms c) some of them with mono-ortho and di-ortho substitution are highly toxic. The rest of organochlorines analyzed were: hexachlorobenzene (HCB), dieldrin and trans-nonachlor.

In all cases the residue levels of DDTs predominated with concentrations ranging from 11.2 to 35.1 µg/g wet wt (mean 20.9 µg/g wet wt). The PCBs concentrations were lower and varied between 3.0 and 12.1 µg/g wet wt (mean 7.5 µg/g wet wt). Considering the other organochlorines, trans-nonachlor presented the higher concentrations (92-260 ng/g wet wt,

Table 1. Organochlorine residue levels (ng/g wet wt) in the blubber of the Cuvier's Beaked whale

Whale No sex	1 male	2 male	3 male	4 female	5 female	6 male	7 male	8 male	9 male	10 male	Mean value
Length (m)	4.4	5.1	4.6	4.7	4.7	4.9	4.5	5.2	4.7	4.9	
Lipids %	92	80	88	92	86	77	81	78	59	60	79
p,p'-DDE	9227	20316	8843	11024	24912	29740	10245	21329	13771	22649	17206
p,p'-DDD	739	2119	944	963	2560	2308	1209	316	1600	2106	1486
p,p'-DDT	1454	3762	1404	1415	3082	3089	1944	670	1583	3401	2180
ΣDDTs	11421	26196	11191	13402	30554	35138	13397	22315	16955	28156	20873
HCB	33.6	62.1	46.7	49.8	46.0	47.6	65.3	47.5	23.0	28.3	44.9
Trans- nonachlor	92	266	126	138	260	244	152	211	127	161	178
Dieldrin	21.4	8.4	25.3	12.6	2.6	15.2	9.6	19.0	12.1	1.6	12.8
Polychlorinated biphenyls											
52 (4Cl)	29	87	57	45	97	70	74	59	187	46	80
101 (5Cl)	129	455	270	326	412	401	323	391	188	208	300
87 (5Cl)	37	107	67	73	95	88	80	96	47	51	83
118 (5Cl)	244	922	448	437	909	729	571	618	451	438	589
153 (6Cl)	792	3192	1482	1472	3083	2627	1800	1896	1551	1459	1951
105 (5Cl)	nd	56	41	32	nd	50	44	41	nd	22	29
138 (6Cl)	879	3527	1525	1421	3608	2919	1773	2294	1776	1510	2137
183 (7Cl)	nd	410	196	189	351	308	216	250	177	174	227
128 (6Cl)	99	259	157	180	233	205	180	210	108	127	189
156 (6Cl)	71	212	107	96	211	169	110	138	100	104	147
180 (7Cl)	549	2330	1091	1047	2171	1774	997	1353	966	922	1338
170 (7Cl)	241	804	445	423	827	615	393	492	406	392	521
194 (8Cl)	nd	187	135	109	179	123	86	98	96	84	110
ΣPCBs	3041	12462	5966	5805	12078	10009	6573	7877	5868	5491	7517

mean 178 ng/g), while HCB and dieldrin levels were significantly lower (33.6-49.8 ng/g wet wt, mean 44.9 ng/g and 8.4-21.4 ng/g wet wt, mean 12.8 ng/g, respectively). These values are quite similar to those found in a previous study on the same species¹¹ and in general they are within the range reported for other odontocetes in the Ionian and Aegean sea^{1,4,8}. They are not considered high enough to cause the death of these cetaceans but they may increase their vulnerability to various pathogens.

The toxicity of individual PCB congeners depends on the degree and position of chlorine substitution on the biphenyl ring. The relative percentages of the congeners determined in this study are given in Fig. 2. The hexachlorobiphenyls 138 and 153 were the

dominant congeners (average 27.4% and 25.5 % of the total PCBs) followed by the heptachloro- 180 (17.3%) , the pentachloro- 118 (7.6%), the heptachloro- 170 (6.8%) and the pentachloro congener 101 (4.3%). All these compounds are considered as persistent due to 2,4,5 or 2,3,5 chlorine substitution¹. Hexa- and heptachlorobiphenyls together constituted on average 86 % of the total PCBs, in agreement with observations made in striped dolphins from the Mediterranean sea and in contrast with measurements in marine cetaceans from others parts of the world, where the penta- and hexachlorobiphenyls predominate¹².

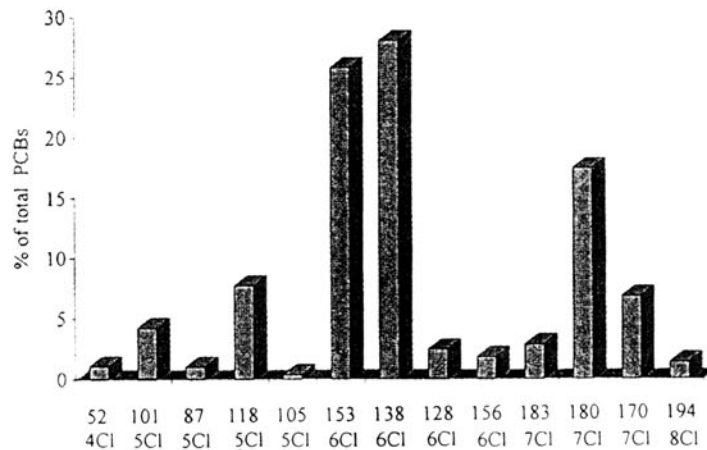


Fig. 2 . Percentage composition of PCB congeners in the blubber of the Cuvier's Beaked

DDE was always the main component of the DDT group and accounted for the 80-96 % of the total DDTs, with only 1.5-9% being found as DDD. It is known that DDE is the main metabolite of DDT and it is not usually introduced in the ecosystem directly but it originates from a degradative dehydrochlorination of DDT taking place both in living organisms and in non-living environmental systems¹³. The high DDE percentage found in this study could probably be attributed to a decreasing exposure of the marine mammals to new sources of DDT¹⁴.

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