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CHLORINATED HYDROCARBON CONCENTRATIONS IN THE GULF OF CALIFORNIA

HARBOR PORPOISE (PHOCOENA SINUS)

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INTRODUCTION

High concentrations of chlorinated hydrocarbon contaminants have been noted in coastal odontocetes from a number of areas (Gaskin et al. 1971, 1974, 1982, 1983, Calambokidis 1986, Calambokidis et al. 1984, O'Shea et al 1980, Taruski et al. 1975). Many of these contaminants are stable, tend to concentrate up food chains, and are lipophilic accumulating in fatty tissues such as blubber. Coastal odontocetes occurring in nearshore waters near industrial or agricultural areas are particularly susceptible to accumulation of these contaminants. Impacts of chlorinated hydrocarbons on wild marine mammal populations have been hard to demonstrate conclusively because of the complexity of proving such a relationship in an uncontrolled environment. A number of studies have documented apparent relationships between chlorinated hydrocarbons (PCBs or DDE) and reproductive difficulties in pinnipeds (Helle et al. 1976a, 1976b, Gilmartin et al. 1976, Reijnders 1982a, 1982b). A recent study with captive seals has demonstrated a cause and effect relationship between reproductive failure in harbor seals and consumption of fish from a contaminated area (Reijnders 1986).

The Gulf of California harbor porpoise (Phocoena sinus) also known as cochito and vaquita is restricted to the northern waters of the Gulf of California (Brownell 1983, 1986, Brownell et al. 1987). The limited range of this species and low population size underscores the importance of research on this species. A series of tissues recently became available from 13 fresh animals examined in 1985 and described in Brownell et al. (1987).

This report summarizes results of analysis for chlorinated hydrocarbon concentrations in the blubber of eight vaquita. These results will be incorporated into a publication authored by the individuals involved in the collection and analyses of these samples.

METHODS

Samples were collected as described in Brownell et al. (1987). Tissues samples were collected in aluminum foil and stored frozen. During shipment some of the samples thawed but remained chilled. Because the samples were transported between a number of locations this may have occurred on several occasions.

Blubber samples from eight vaquita were analyzed for pesticides and PCBs by Analytical Resources Inc. (ARI), an EPA contract laboratory in Seattle, Washington. All tissue samples were received frozen by ARI and maintained at -20°C until thawed for extraction.

Sample Extraction: After thawing, 10 ml of methylene chloride (CH_2Cl_2) was added to each sample. The samples were then ground into a paste using a Tekmar Tissumizer, and 25 grams of sodium sulphate (Na_2SO_4) was blended into each sample. Another 50 ml of CH_2Cl_2 was added, along with 200 μl of the surrogate standard solution containing 12 μg of d8-naphthalene, 15 μg of d10-acenaphthene, and 11 μg of d12-perylene. The entire sample mixture was then homogenized using the Tissumizer on high speed for one minute. The solvent portion was decanted off, passed through more Na_2SO_4 , and collected in a prepared Kuderna Danish (KD) concentration apparatus. Each sample was similarly extracted three additional times (making a total of four) and the extracts composited in the KD. Each sample was then concentrated to approximately 10 ml.

GPC Cleanup: Sample extracts were injected on a Biobeads SX-3 column (2.5 cm id x 55 cm) and eluted with CH_2Cl_2 at 5 ml per minute. The column was calibrated with a mixture of corn oil, ethylhexyl phthalate, and pentachlorophenol. A single fraction containing all of the targetted compounds was collected, and the fraction containing the higher molecular weight compounds was discarded. The fraction collected was then concentrated to 1 ml using the water bath and evaporator as before.

Alumina Cleanup: The extract was passed through an alumina column containing approximately 3 grams of alumina. The extracts were eluted with a solution of 10% CH_2Cl_2 in hexane and a 10 ml volume was collected.

Pesticide/PCB Analysis: Following alumina cleanup, approximately 1 ml of each 1:10 extract was analyzed for pesticides/PCBs by GC/ECD using a 30 meter, DB-5 silica column. The results from the DB-5 column were then confirmed using a DB-1701 (14% cyanopropylphenyl) column.

RESULTS AND DISCUSSION

Results of analyses are summarized in Table 1 with detailed results included in the Appendix. Concentrations of only four pesticide related compounds and PCBs exceeded detection limits (see Appendix). DDE (4,4'-DDE), the primary breakdown product of the pesticide DDT, was the only pesticide recovered from all samples with concentrations ranging from 530 to 7,500 ppb (ug/kg by wet weight). Concentrations based on lipid weight are only slightly higher because samples consisted of 67 to 100% lipids. Two other DDT-related compounds were also recovered, DDD (4,4'-DDD) and DDT (4,4'-DDT), though in much lower concentrations than the DDE. Five samples contained detectable concentrations of DDD, ranging from 34 to 600 ppb and four samples contained detectable concentrations of DDT, ranging from 50 to 1,000 ppb. Both DDD and DDT concentrations were significantly correlated with DDE concentrations ($r=.82$, $p<0.01$ for both cases). Alpha-BHC was only detected in three samples at concentrations of 5 to 49 ppb. PCBs were detected in a single animal at 200 ppb.

Concentrations of total DDT (4,4'-DDE + 4,4'-DDD + 4,4'-DDT) in relation to sex and lengths of porpoise are shown in Figure 1. Though sample size is small, the results suggest several patterns consistent with findings in other marine mammals. Concentrations appear to increase with length in males with the highest concentration in any animal occurring in the only mature adult male. Concentrations in subadult females are similar to the males but the three adult females showed concentrations that were lower than the subadult females and dramatically lower than the single adult male.

This pattern is consistent with studies of concentrations in other marine mammals. Increasing concentrations of DDT compounds and PCBs in males with age or length has been reported for pinnipeds (Calambokidis et al. 1984, Addison and Smith 1974, Addison et al. 1973, Donkin et al. 1981) and odontocetes (Gaskin et al. 1982, 1983). Concentration increases in females have generally been found to remain constant or decline once reproductive age is reached (Gaskin et al. 1982, 1983, Calambokidis et al. 1984, Addison and Smith 1974). These results reflect the low rates of metabolism and excretion of these compounds with adult females being able to partially purge these compounds through transplacental transfer and lactation.

Concentrations of both DDT compounds and PCBs were generally lower than has been reported for odontocetes in many areas (see Risebrough 1978, Calambokidis et al. 1984, and Wagemann and Muir 1984 for reviews). Table 2 and Table 3 show concentrations of total DDT and PCBs, respectively,

Table 1. Concentrations of chlorinated hydrocarbons in *Phocoena sinus* recovered from the Sea of Cortez, Mexico in 1985. Life history data from Brownell et al. (1987).

No.	Date	Sex	Mat.	Wt. Kg	Leng. cm	Girth cm	Perc. lipid	Concentration (ug/kg, wet weight)					
	Mo/Dy/Yr							ppDDE	ppDDD	ppDDT	TDDT	A-BHC	PCB
3	3/14/85	F	N	22.2	106.9	64.3	75%	2400	-	-	2400	33	-
4	5/12/85	F	N	23.7	110.0	64.0	85%	3500	400	100	4000	-	-
5	5/14/85	M	N	16.7	93.5	60.5	82%	1200	80	50	1330	-	-
9	5/17/85	M	N	23.2	110.0	51.5	83%	4300	37	-	4337	49	-
6	5/14/85	F	Y	45.7	143.5	75.5	67%	590	34	50	674	5	-
26	3/13/85	F	Y	42.7	135.0	75.0	100%	620	-	-	620	-	-
27	3/13/85	F	Y	43.7	135.0	75.5	84%	530	-	-	530	-	-
24	3/13/85	M	Y	46.7	134.5	75.5	70%	7500	600	1000	9100	-	200

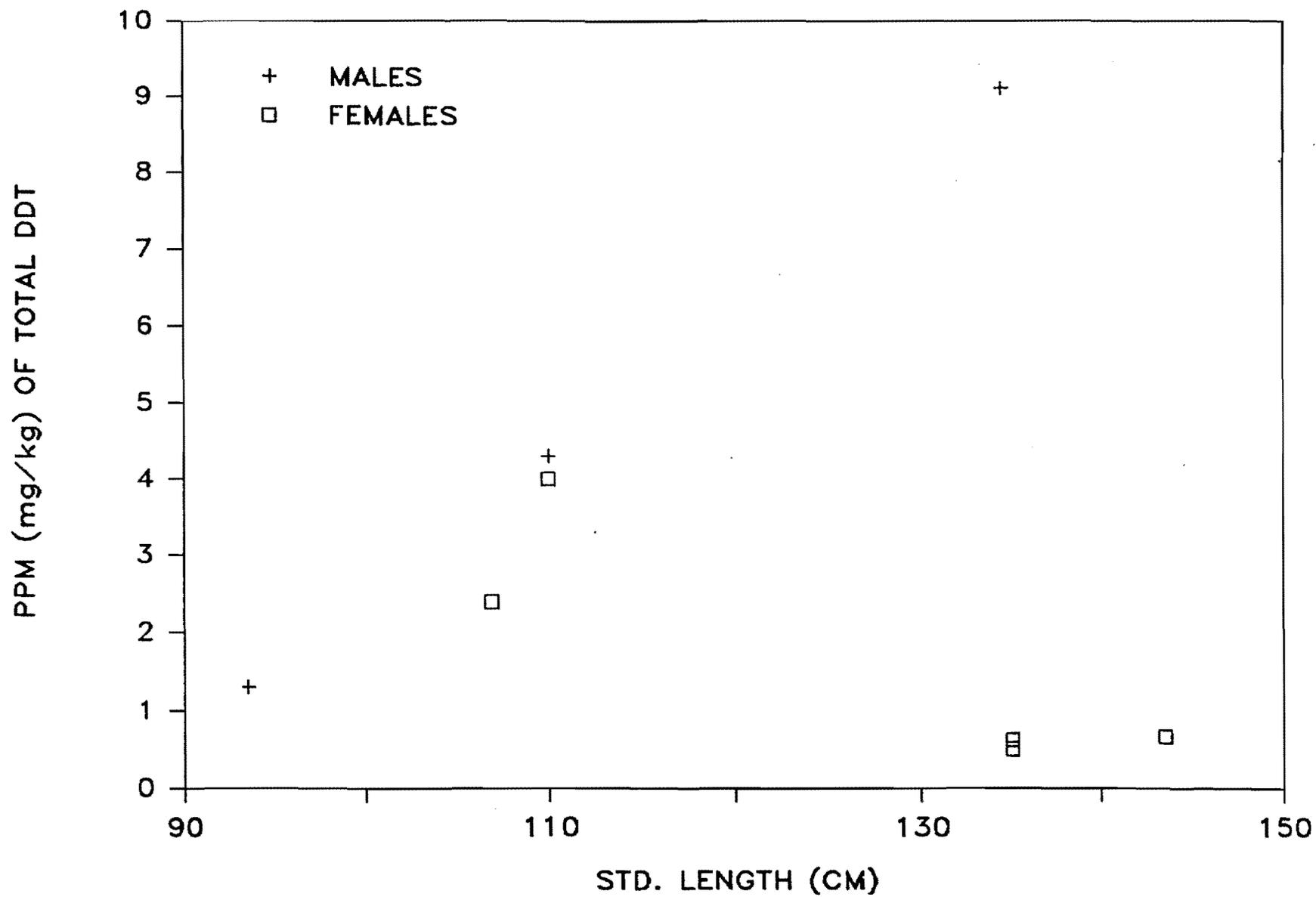


Figure 1. Concentration of total DDT in the blubber of male and female vaquita in relation to body length.

Table 2. Total DDT concentrations in harbor porpoise blubber. See footnotes at end of table for explanation of symbols and abbreviations.

Location	Year	Age	Sex	Wt	N	Concentration, ppm			Reference
						Mean	Low	High	
Netherlands	78	F	U	L	1	6.7	-	-	Duinker and Hillebrand 1979
Rhode Is	73	A	F	W	1	57.5	-	-	Taruski et al 1975
Canada Atlantic	70	A	M	W	12	306.7	150.8	520.0	Gaskin et al 1971
Canada Atlantic	70	N	M	W	2	130.9	75.1	186.7	Gaskin et al 1971
Canada Atlantic	70	N	F	W	1	154.8	-	-	Gaskin et al 1971
Canada Atlantic	70	A	F	W	15	214.2	111.6	447.9	Gaskin et al 1971
Canada Atlantic	70	L	F	W	6	69.0	40.0	122.0	Gaskin et al 1971
Orkney, N Scotland	67	A	U	W	1	3.9	-	-	Holden and Marsden 1967
East Scotland, N Sea	66	A	U	W	3	43.0	27.9	55.3	Holden and Marsden 1967
North Sea	70	U	U	W	7	41.2	11.1	102.0	Koeman et al 1972
Baltic, German coast	76	U	B	W	2	37.6	29.3	45.9	Harms et al 1978
North Sea, Ger coast	76	U	F	W	1	2.4	-	-	Harms et al 1978
So. Calif. coast	75	S	F	W	1	335.0	-	-	O'Shea et al 1980
So. Calif. coast	75	S	F	W	1	2.3	-	-	O'Shea et al 1980
Coast of France	77	F	U	D	1	0.4	-	-	Alzieu and Duguy 1979
Coast of France	77	P	F	D	1	1.7	-	-	Alzieu and Duguy 1979

Table 2. Continued

Location	Year	Age	Sex	Wt	N	Concentration, ppm			Reference
						Mean	Low	High	
Baltic Sea	72	U	B	L	8	171.0	30.0	289.0	Otterlind 1976
West coast, Sweden	74	U	U	L	6	160.0	24.8	560.0	Otterlind 1976
East coast, Denmark	75	U	U	L	4	8.1	2.2	12.0	Otterlind 1976
Baltic Sea	76			W	2	37.6	29.3	45.9	Huschenbeth 1977
Bay of Fundy	75	T	M	W	-	103.4	22.8	227.0	Gaskin et al. 1983
Bay of Fundy	75	T	F	W	-	39.3	21.4	55.7	Gaskin et al. 1983
Puget Sound	77	T	U	W	2	8.0	1.4	14.0	Calambokidis et al. 1984
California	85	T	B	W	16	46.0	6.2	132.	Calambokidis 1986
Oregon	85	T	B	W	13	19.0	2.1	52.1	Calambokidis 1986
Washington	85	T	B	W	7	13.0	0.2	26.4	Calambokidis 1986

Year: Collection year, midpoint if samples were collected over several years.

Age: A = adults
 S = subadults
 N = pup
 T = all age classes mixed
 P = pregnant female
 F = fetus
 U = unknown

Sex: F = female
 M = male
 B = mixed sexes
 U = unknown

Wt: weight basis for concentration, L = lipid weight, W = wet weight, D = dry weight

Table 3. PCB concentrations in harbor porpoise blubber. See footnotes at end of Table 2 for explanation of symbols and abbreviations.

Location	Year	Age	Sex	Wt	N	Concentration, ppm			Reference
						Mean	Low	High	
Netherlands	78	F	U	L	1	59.0	-	-	Duinker and Hillebrand 1979
Rhode Is	73	A	F	W	1	74.0	-	-	Taruski et al 1975
W coast Greenland	72	U	U	W	2	6.6	1.9	11.4	Clausen et al 1974
North Sea	70	U	U	W	7	88.0	35.0	148.0	Koeman et al 1972
Baltic, German coast	76	U	B	W	2	114.0	88.6	140.0	Harms et al 1978
So. Calif. coast	75	S	F	W	1	84.0	-	-	O'Shea et al 1980
So. Calif. coast	75	S	F	W	1	0.6	-	-	O'Shea et al 1980
Coast of France	77	T	U	D	2	3.8	1.4	6.1	Alzieu and Duguy 1979
Baltic Sea	72	U	B	L	8	93.4	28.0	190.0	Otterlind 1976
West coast, Sweden	74	U	U	L	6	159.0	56.4	260.0	Otterlind 1976
East coast, Denmark	75	U	U	L	4	142.0	68.0	210.0	Otterlind 1976
Baltic Sea	76			W	2	114.3	88.6	140.0	Huschenbeth 1977
Bay of Fundy	71	T	M	W	62	78.7	0.0	0.0	Gaskin et al. 1983
Bay of Fundy	71	T	F	W	40	46.6	0.0	0.0	Gaskin et al. 1983
Puget Sound	77	T	U	W	2	28.0	1.7	55.0	Calambokidis et al. 1984
California	85	T	B	W	16	14.0	2.5	42.0	Calambokidis 1986
Oregon	85	T	B	W	13	11.0	1.4	49.6	Calambokidis 1986
Washington	85	T	B	W	7	17.0	0.2	29.8	Calambokidis 1986

reported in the blubber of harbor porpoise from different parts of the world. Concentrations found in the vaquita are generally much lower than reported for harbor porpoise for most regions examined to date. In dramatic contrast to the vaquita are the concentrations of up to 2,000 ppm found in the blubber of coastal bottlenose dolphins from southern California (Schafer et al. 1984).

Aguilar (1984) concludes that the DDE / total DDT ratio in marine mammal tissues is indicative of the length of time DDT has been in the biota with .6 as the likely equilibrium ratio after a long period of degradation. The ratios found in this study are generally greater than .6 and indicate that the DDT input into this area is not recent. Borrell and Aguilar (1987) report a high percent DDE may also be the result of high overall contamination with DDT, but is clearly not the case for the vaquita.

Both DDE and PCBs have been linked to reproductive problems in marine mammals (Gilmartin et al. 1976, Reijnders 1982a, 1982b, 1986, Helle et al. 1976a, 1976b, Helle 1980). These problems have all been noted in species with accumulations of PCB and DDT products several orders of magnitude higher than found in the vaquita. Chlorinated hydrocarbon pesticides and PCBs do not appear to pose a threat to the small number of remaining vaquitas.

CONCLUSIONS

- Relatively low concentrations of DDT compounds, alpha-BHC, and PCBs were recovered from the tissues of 8 vaquita. DDT compounds occurred in the highest concentrations and the DDT metabolite DDE was the only compound recovered from all animals.
- Concentrations of DDT compounds suggested an accumulation with age in males and a declining concentration in females after reproductive maturity. This is consistent with findings in other studies of marine mammals.
- The proportion of DDE to total DDT suggest that the source of the DDT compounds is not from recent applications of DDT.
- Chlorinated hydrocarbon pesticides or PCBs do not appear to pose a hazard to the remaining vaquita.

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