HARBOR SEALS AS INDICATORS OF HALOGENATED CONTAMINANTS IN SAN FRANCISCO BAY

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Introduction

Significant accumulations of persistent organochlorines, from both historical and on-going waste discharges, have been documented in the estuarine environment of San Francisco Bay. Harbor seals (*Phoca vitulina richardsii*), as year-round residents of the Bay[1] and upper trophic level piscivores, are exposed to those contaminants which bioaccumulate in the food web. Elsewhere, regional studies[2,3] have documented high residue levels of organochlorine contaminants in pinnipeds. Studies of harbor seals eating contaminated fish from the Baltic Sea found both reduced reproduction[4] and immune suppression associated with elevated organochlorine residues. To assess contaminant levels in upper trophic level biota of San Francisco Bay, harbor seal blubber samples were analyzed for PCDD/PCDFs, OCPs, PCBs and PBDEs.

Materials and Methods

Blubber samples were collected between 1989–1998, from beach-cast harbor seals found along the San Francisco Bay shoreline. Tissue collections were part of a larger study of harbor seal population dynamics, health, contaminant residues and prey selection[1]. Gross blubber samples collected in the field were sub-sampled, and archived at the UC Berkeley Museum of Vertebrate Zoology until they were brought to the laboratory where they remained at –20°C until analysis. The samples chosen for this analysis were gender balanced, sexually mature adults, as defined by length and weight, and one mother fetus pair that died during birth. Some individuals chosen had been tagged and sampled, 2-4 years prior to dearth, for health and contaminant residues.

Samples were thawed, weighed, mixed with Na_2SO_4, homogenized with 1:1 dichloromethane : hexane, and spiked with ^{13}C-labelled internal standards (all seventeen 2,3,7,8-substituted PCDD/PCDFs; PCBs 77, 126, 169, 28, 52, 47, 101, 105, 118, 153, 180, 194, 209; HCB, □-HCH, DDE, DDT, Dieldrin, Mirex and PBDE 77). □pproximately 1/10 of the extract was analyzed for OCPs, PCBs and PBDEs, and 9/10 analyzed for PCDD/Fs and non-ortho PCBs. Lipid content was determined gravimetrically. Samples were serially processed through columns containing Na_2SO_4 and AX21 carbon. The first fraction off the carbon column was further cleaned up by GPC and Florisil, recovery standards were added and the sample concentrated to 10 □L for PCB, OCP and PBDE analysis. PCDD/Fs and non-ortho PCBs were eluted from the carbon column with toluene and the eluate cleaned up with alumina and acid silica columns; recovery standards were added and the sample concentrated to 10 □L. PCDD/Fs and PCBs were analyzed by HRGC/HRMS (Finnigan MAT 90) with a 60 m, 0.25 mm ID, 0.25 □m film thickness, DB-5ms column. PFK was used for the lock masses and the MS was operated in an EI mode with multiple ion monitoring. OCPs and PBDEs were analyzed by LRMS in NCEI mode (Finnigan 4510) with a 60 m, 0.25 mm ID, 0.25 □m film thickness, DB-5ms column, with methane as the reagent gas. The ion source pressure was 0.6 Torr and ion source temperature was 100 °C. The electron energy was typically 70 eV and the electron current was kept at 0.3 mA.

Results and Discussion

The major PCDD/PCDFs and non-ortho PCBs in harbor seal blubber are shown in Table 1. Only 1,2,3,6,7,8 HxCDD, 2,3,7,8 TCDF and OCDD were consistently measured above the detection limit. Overall, concentrations of PCDD/PCDFs were low in all analyzed samples. This finding is consistent with other reports on low PCDD/PCDF levels in harbor seal blubber from the New York area[5], and from the north coast of Europe[6]. Higher levels of a broader range of PCDD/PCDF congeners have been reported in other pinniped species, including the Baikal seal[3], and the ringed seal[2].

The major congeners found in harbor seals were compared to those found in San Francisco Bay white croaker, one of six primary seal prey species (Table 1). In white croaker[7], the concentration of total PCDFs was higher than that of total PCDDs, and the concentration of PCDD/PCDFs on a lipid basis was similar to that in the seals. Fewer detectable congeners and low concentrations of PCDD/PCDFs in harbor seals suggest a rapid metabolism of PCDD/PCDFs and no bioconcentration.

The mean non-ortho coplanar TEQ[8] for San Francisco Bay seals is 68 ng/g lipid (Table 1), exceeding levels reported for pinnipeds throughout the Northern Hemisphere[5,6]. The congener order is: PCB126 >PCB77 > PCB169, the same relative order reported in other studies. However, the relative order of non-ortho coplanar residues in white croaker is: PCB77> PCB126 > PCB169, which is similar to the pattern found in environmental samples, reflecting the relative positions on the food web, again indicating differential metabolism and excretion of selected congeners.

The major PCB congeners found in San Francisco Bay seals are listed in Table 2. The mean ΣPCB blubber residue was 71 ppm lipid. This value is substantially higher than reported for immuno-compromised harbor seals fed Baltic fish, and from wild seals from other regions[5]. Higher chlorinated biphenyls constituted major proportions of total PCBs. All 13 top PCB congeners in the seal samples contain six or more chlorines, which may suggest metabolism of lower chlorinated PCBs and biomagnification of highly chlorinated congeners.

DDE, the prime DDT metabolite, was the major OCP in the seals (Table 2). The large DDE/DDT ratio (56) for this sample population indicates limited recent exposure to the parent compound and contrasts sharply with the DDE/DDT ratio (6.5) found in the white croaker. This finding is supported by low p,p'-DDT (106 ng/g lipid) levels in our sample when compared to mean levels reported for harbor seals eating contaminated Baltic fish[6]. Higher oxychlordane:trans-nonachlor ratios were found in seals (0.65) compared to white croaker (0.12). Additionally, □-HCH was the most abundant of the HCH-isomers in most samples in accordance with other reports of HCHs in pinnipeds[6,9], but in contrast to the findings of Tanabe et al[10] (1982) where the □-HCH isomer was dominant in striped dolphins. In contrast, □-HCH is the most abundant isomer in fish and humans.

PBDE levels in San Francisco Bay harbor seals (Table 2) were comparable to levels reported in pinnipeds from the Baltic and Swedish coasts[9]. Mean levels of PBDE 47 were found to be an order of magnitude greater than either PBDE 99 or PBDE 153. In contrast to PCBs, only lower halogenated PBDE congeners seem to bioconcentrate in the seals.

Conclusions

The levels of PCDDs/PCDFs, PCBs, OCPs and PBDEs found in seals indicated that biota of San Francisco Bay are contaminated. Comparison of levels and patterns of contaminants in seals and fish suggest that bioaccumulation mechanisms at low trophic levels (fish) depend primarily on the physicochemical properties of the pollutants. At high trophic levels (seal), bioaccmulation mechanisms are primarily affected by the metabolic capacity of the animal species.

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Table 1. Major PCDD/Fs and non-ortho PCBs in harbor seals and fish from SF Bay*.

	Seals (pg/g fat)			White Croaker (pg/g wet)
	Adult Seals n=10	Fetus n=1	Mother # n=1	Fillet n=8 composites
2378TCDD	ND	ND	ND	0.3 (0.04)
12378PCDD	ND	ND	ND	0.52 (0.04)
123678HxCDD	11.5 (2.3)	9.3	19	0.28 (0.03)
OCDD	13.2 (1.9)	19	22	0.3 (0.02)
2378TCDF	4.55 (0.5)	4.3	5.9	2.26 (0.26)
12378PCDF	ND	ND	ND	0.25 (0.04)
23478PCDF	ND	ND	3.8	0.99 (0.1)
PCB 77	68.3 (6.2)	52	98	158 (29)
PCB 126	587 (100)	418	585	50 (9.9)
PCB 169	37.2 (8.6)	13.7	ND	3.4 (0.5)
TEQ-non-ortho PCBs	67.9 (10.5)	42	59	5.1 (0.1)
TEQ-PCDD/Fs	6.22 (0.8)	4.4	6.7	1.3 (0.1)

*Mean, with Standard Error in parentheses
# Mother of fetus, also included in the 10 adults.
ND= Not Detected

Table 2. Major PCBs, OCPs and PBDEs in seal blubber (ng/g, fat)

Analyte	Min	Max	Median	Mean	SD
153/132	3043	71685	13441	17486	19247
138	1623	39427	6077	10388	10845
180	887	26882	5040	7349	7198
182/187	558	35842	4218	8359	9990
99/113	795	11828	1644	2844	3188
170	275	9473	2138	2788	2599
183	162	10753	1905	2764	3063
196/203	152	7885	1212	1999	2275
194	152	7168	1212	1884	2082

199	152	7527	1279	1839	2153
146/161	66	9319	975	1723	2658
177	67	6093	707	1490	1758
178	85	3943	599	1069	1150
□PCBs	9960	277500	41280	71290	74840
p,p'-DDE	2331	21147	3886	5950	5665
trans-nonachlor	161	1720	275	518	477
Oxychlordane	103	1254	183	337	337
Mirex	39	538	95	139	148
p,p'-DDT	32	264	86	106	72
□-HCH	0.1	84	19	29	26
Dieldrin	10	42	25	24	10
□-HCH	0.2	78	10	19	25
HCB	3	47	15	18	15
□-HCH	2	30	6	10	9
PBDE 47	46	6996	331	1251	2041
PBDE 99	16	301	95	110	82
PDBE 153	4	968	39	135	281

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