

## ACCUMULATION AND ELIMINATION OF PCDD/DFS, DIOXIN-LIKE PCBs AND ORGANOCHLORINE PESTICIDES IN BALD EAGLES FROM MICHIGAN, USA

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### Introduction

Bald eagles are predatory birds, which feed at the top of the aquatic food web. Since bald eagles are relatively long-lived birds (up to 30 years in wild), they remain sensitive to environmental toxicants that bioaccumulate and affect critical biological processes such as reproduction. Regulation of the use of DDT in the early 1970s has resulted in the recovery of bald eagle populations in the USA, although, in some locations, PCBs and other chlorinated hydrocarbons continue to affect bald eagle production. Bald eagle was listed as an endangered/threatened species in the USA until 1999. Reports of PCB or DDT concentrations in bald eagle tissues such as liver, muscle, fat, kidney or gall bladder are sparse due to the difficulties in obtaining such tissues. Tissues of freshly dead bald eagles collected from the Upper Peninsula of Michigan, USA, provided an opportunity to analyze chlorinated hydrocarbons in several body tissues. Considering the lack of information on tissue-specific accumulation of PCDDs, PCDFs, dioxin-like and total PCBs, *p,p'*-DDE and HCB, concentrations of these compounds were measured in liver, kidney, muscle, fat, blood plasma and gall bladder of bald eagle collected from the Upper Peninsula of Michigan, USA. Elimination rates of target analytes were also calculated based on the concentrations in bile/gall bladder.

### Materials and Methods

Carcasses of bald eagles were collected in the Upper Peninsula of Michigan in 2000 were collected by or submitted to Rose Lake Wildlife Research Center, Lansing, Michigan. The carcasses were transported to the wildlife research center and upon receipt, they were necropsied and cause of death determined. Liver, muscle, fat, kidney and gall bladder were wrapped in solvent clean aluminum foil and stored at  $-20^{\circ}\text{C}$  until analysis. The gall bladder analyzed in this study was filled with bile. In addition, blood plasma of nestling bald eagles (approximately <60 d old), collected during 1993 were also analyzed. To separate blood plasma, approximately 10 mL of whole blood was centrifuged and stored at  $-20^{\circ}\text{C}$  until analyzed. Details of the samples and sampling locations are discussed elsewhere<sup>1</sup>.

Details of the analytical procedures have been reported earlier<sup>1-4</sup>. Identification and quantification of 2378-substituted congeners of PCDD/DFs, dioxin-like PCBs (non- and mono- *ortho*- substituted congeners) and organochlorines pesticides was performed by, Hewlett Packard 6890 Series high-resolution gas chromatography interfaced with a Micromass Autospec - Ultima high-resolution mass spectrometer and Hewlett Packard 6890 Series gas chromatograph with electron capture detector (GC-ECD).

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## Results and Discussion

### PCDD/DFs

Average concentrations of PCDD/DFs were greater in livers than in kidney, muscle, gall bladder, fat or blood plasma (Table 1). The wide variation in concentrations of PCDD/DFs in livers suggests exposure to localized sources of contamination. A few studies have measured concentrations of PCDDs/DFs in livers of bald eagles from British Columbia, Canada<sup>5</sup>. Concentrations of PCDD/DFs measured in livers and blood plasma of bald eagles from the Upper Peninsula of Michigan were similar to those reported for eagles collected near a kraft pulp mill in British Columbia<sup>5,6</sup>. The limited data suggest that concentrations of PCDD/DFs in livers of juvenile bald eagles (mean: 180 pg/g, wet wt) were less than that in adults (mean: 1600 pg/g, wet wt). Livers of adult male bald eagles (mean: 2300 pg/g, wet wt) contained greater concentrations of PCDD/DFs than did adult female bald eagle (110 pg/g, wet wt). Bald eagles from Cecil Bay and Mackinac contained greater concentrations of PCDD/DFs than those from the Paint River, Fence River, Kallio and Menominee.

**Table 1.** Mean concentrations of 2378-chlorine substituted PCDD/DFs (pg/g wet wt.), dioxin-like PCBs, total PCBs, *p,p'*-DDE and HCB (ng/g wet wt) in bald eagle tissues.

Tissues*	L (n=6)	M (n=6)	K (n=2)	F (n=2)	GB (n=1)	P (n=4)
Fat (%)	6.3	1.6	4.6	79	1.6	0.61
2378-D	70	70	220	9.1	100	0.23
12378-D	140	110	260	27	200	0.46
123478-D	30	13	32	10	54	0.21
123678-D	100	49	160	26	220	0.35
123789-D	0.60	0.32	2.1	1.8	1.8	0.023
1234678-D	7.8	1.5	19	24	19	0.70
OCDD	170	26	50	13	73	5.4
2378-F	13	6.1	8.9	22	25	0.55
12378-F	3.8	0.14	<0.01	2.1	<0.01	0.076
23478-F	170	110	240	6.0	290	0.37
123478-F	71	55	250	11	130	6.0
123678-F	16	13	24	2.2	53	0.25
234678-F	21	19	30	1.8	81	0.18
123789-F	<0.01	<0.01	0.46	0.51	<0.01	0.024
1234678-F	28	35	29	2.9	98	0.33
1234789-F	12	12	20	1.4	32	0.15
OCDF	21	24	27	1.8	56	0.15
Dioxin-like PCBs						
TeCB (81)**	0.94	0.95	1.5	0.37	1.6	0.00095
TeCB (77)	9.2	7.2	32	12	22	0.056
PeCB (126)	8.0	5.7	21	5.8	28	0.023
HxCB (169)	4.1	2.7	4.3	1.1	7.2	0.0050
PeCB (105)	750	550	2300	500	3900	1.2
PeCB (114)	260	250	320	64	640	0.084
PeCB (118)	940	830	3900	1100	6200	3.4
PeCB (123)	210	180	270	69	480	0.11
HxCB (156)	350	360	920	250	1400	0.52
HxCB (157)	140	140	220	61	290	0.16
HxCB (167)	260	270	590	170	850	0.36
HpCB (189)	91	91	120	28	180	0.058
HpCB (170)	7500	3800	2200	410	2700	1.4
HpCB (180)	17000	4800	4900	1600	5400	4.7
Total PCBs	51000	15000	32000	13000	48000	56
<i>p,p'</i> -DDE	3600	440	1600	2000	2800	10
HCB	31	9.4	37	30	18	0.20

\* L, M, K, F, GB and P respectively indicates, liver, muscle, kidney, fat, gall bladder and plasma;\*\* The numbers in parentheses indicates IUPAC numbers; The values rounded.

## *PCBs and DDT*

Concentrations of total PCBs in livers of bald eagles ranged from 450 to 280,000 ng/g, wet wt. (Table 1). *p,p'*-DDE concentration in the liver of a diseased bald eagle was 17,000 ng/g, wet wt. (Table 1). The concentration of 280,000 ng PCBs/g, wet wt, is the greatest value reported for a bald eagle liver so far. Concentrations of total PCBs in blood plasma ranged from 46 to 67 ng/g, wet wt. The mean concentrations of fourteen dioxin-like PCB congeners in bald eagle tissues (all the tissues) collectively accounted for 50 % of the total PCB concentrations. Concentrations of fourteen dioxin-like PCBs in blood plasma of eagles ranged from 10-14 ng/g, wet wt (Table 1). This was 15 to 30 % of the total PCB concentrations.

## *Toxic Equivalents*

Concentrations of TEQs in livers of bald eagles ranged from 95 to 8400 pg/g, wet wt, followed by kidney (930-9100 pg/g, wet wt), muscle (150-6000 pg/g, wet wt), gall bladder (5500 pg/g, wet wt), fat (850-2000 pg/g, wet wt) and blood plasma (2-12 pg/g, wet wt). These values are greater than those reported for dead bald eagle livers collected near a kraft pulp mill in British Columbia<sup>6</sup>. Concentrations of TEQs in bald eagle tissues fall within the range of toxic threshold values reported for chicken, pheasant or Caspian tern eggs<sup>1</sup>. A lowest-observed-effect level (LOEL) of 25 ngTEQ/g in liver on a lipid weight basis has been suggested for CYP1A induction and 50 % reduction of plasma thyroxine levels in common tern chicks. On a lipid weight basis, concentrations of TEQs in livers of all the birds analyzed in this study were greater than 1000 pg/g. A threshold reference value of 2300 pgTEQ/g, wet wt, in eggs has been proposed for American kestrels. The concentrations of TEQs in livers of all the bald eagles analyzed, except one, were greater than the toxic reference values reported for American kestrels. The concentrations of TEQs in tissues were greater than the no-observed adverse effect level (NOEL) of 100 pg/g, wet wt, proposed for bald eagle eggs. The contribution of non-*ortho* PCBs to total TEQs in eagle tissues ranged from 48 to 94 % in liver, 65 to 87 % in muscle, 75 to 84 % in kidney, 79 to 92 % in fat, 75 % in gall bladder and 52 to 84 % in plasma (Figure 1).

## *Biliary Excretion of Organochlorines*

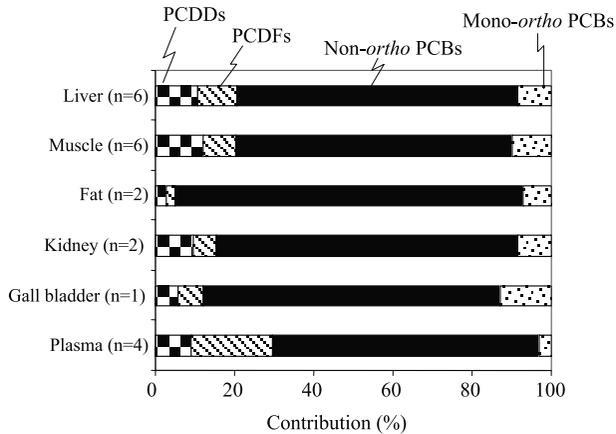
Gall bladder analyzed in this was filled with bile. Assuming that the organochlorine concentrations measured in gall bladder would reflect that of bile, biliary excretion of organochlorines analyzed in this study could be estimated. Biliary excretion rate can be calculated as:

$$\begin{aligned} \text{Biliary excretion rate (\% per day)} &= [\text{Amount in bile/gall bladder (mg)} / \text{Amount in body fat (mg)}] \times 100 \dots\dots\dots (1) \\ \text{Organochlorine burden in body fat (mg)} &= \text{Mean concentration in muscle and liver (mg/g on a lipid weight basis)} \times 660 \text{ g (mass of fat)} \dots\dots\dots (2) \\ \text{Organochlorine burden in bile (mg)} &= \text{Concentrations in bile/gall bladder (mg/g, lipid wt)} \times 0.16 \text{ g (mass of fat)} \dots\dots\dots (3) \end{aligned}$$

Excretion rates of PCDDs, PCDFs, PCBs, *p,p'*-DDE and HCB ranged from 0.015 to 0.025 % per day (Table 2).

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**Figure 1.** Relative contribution (%) of PCDDs, PCDFs, non-ortho PCBs and mono-ortho PCBs to total TEQs in tissues of bald eagles

**Table 2** . Estimated Burdens of Organochlorines in Body Fat and Biliary Excretion Rates in Bald Eagles.

Compound	Mean concentration in body fat (mg/g)*	Amount (burden) in body fat (mg)*	Concentration in bile/gall bladder (mg/g)*	Amount (burden) in bile (mg)*	Biliary excretion rate (% per day)
PCDDs	0.066	43.6	0.042	0.0067	0.015
PCDFs	0.059	38.7	0.048	0.0077	0.02
PCBs	4430	2920000	3000	480	0.016
<i>p,p'</i> -DDE	170	113000	175	28	0.025
HCB	1.7	1100	1.13	0.18	0.016

\*Mean of muscle and liver concentrations (lipid weight basis)

## References

1. Senthil Kumar K., Kannan K., Giesy J.P and Masunaga S. (2002) Environ Sci Technol. (in press)
2. Senthil Kumar K., Kannan K., Paramasivan O.N., Shanmugasundaram V.P., Nakanishi J and Masunaga S. (2001) Environ Sci Technol. 35, 3448
3. Senthilkumar K., Iseki N., Masunaga S., Hayama S.I. and Nakanishi J. (2002b) Arch Environ Contam Toxicol. 42, 244
4. Senthil Kumar K., Kannan K., Corlsolini S., Evans T., Giesy J.P., Nakanishi J and Masunaga S. (2002c) Environ Pollut. (in press)
5. Elliott J.E., Wilson L.K., Langelier K.W and Norstrom R.J. (1996) Environ Pollut. 94, 9
6. Elliott J.E and Norstrom R.J. (1998) Environ Toxicol Chem. 17, 1142