

PCDD/Fs, PCBs, AND PBDEs IN FINNISH GAME AND SEMI-DOMESTICATED ANIMALS IN 2006-7

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Introduction

Elevated polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) and biphenyl (PCB) levels were found in Finnish reindeer calves in regular market surveillances in 2003-2005¹ which launched a project in 2006 to learn more of the levels of PCDD/Fs and PCBs in reindeer and the causes of these elevated levels. First results of this project were published in DIOXIN2007 conference in Tokyo 2007². Additional reindeer samples and also other game meat samples have been studied in 2007. We present here data of PCDD/Fs, PCBs, and polybrominated diphenylethers (PBDEs) in Finnish game and semi-domesticated animals.

In Finland hunting is a popular hobby among population and over 300,000 people had an official hunting card in 2005 allowing them to hunt according to legislation (www.mmm.fi). Hunting big game, like elks (60,000 elks annually, about 10 million kg; www.rktl.fi), results that a group of people might consume more e.g. elk meat than ruminant, pork, or poultry meat. On the other hand reindeer husbandry (incl. meat production, tourism, by-products) is an important livelihood in the northern Finland. The indigenous Sami people carry out traditional reindeer herding. It has a highly important social and cultural role to people in the north. In the autumn the number of reindeer is about 270,000 – 300,000, of which about a third are slaughtered (70% of these calves). The annual reindeer meat production totals about 2.5 million kg, and the value of this in retail trade is estimated at about 50 million euros. Knowledge of organic pollutants in Finnish game and semi-domesticated animals is highly needed in order to give advice, if needed, to minimize the exposure of the hunting/indigenous population. The Commission Regulation (EC) No 1881/2006³, setting maximum levels for PCDD/Fs and PCBs in foodstuffs excludes meat of wild and farmed game.

Materials and Methods

In 2007 in a regular market surveillance, meat samples of semi-domesticated reindeer [*Rangifer tarandus tarandus*] (n=9), and red deer [*Cervus elaphus*] (n=1); and wild elk [*Alces alces*] (n=3), a mixture of elk and red deer (n=1), hare [*Lepus europaeus*] (n=1), mallard [*Anas platyrhynchos*] (n=1), and the Baltic Sea seal [*Halichoerus grypus*] (n=6) were taken. Sampling and pooling complied the Commission regulation 1883/2006/EC⁴ and was targeted to the game or semi-domesticated reindeer sold in food stores representing different types and quality of meat. Samples included fillet, tenderloin, flank, rump, and sliced meat for sautéed reindeer or red deer (steak or back) or other pooled meat samples. All samples were Finnish origin except red deer meat which was imported from New Zealand.

In addition to market surveillance samples, in 2006 a three-year study was launched on the sources of dioxin exposure in reindeer and elks. Pooled meat samples of adult and calves of reindeer (n=11 adults and n=32 calves) and elks (n=6, both adults and calves) have been collected in the reindeer management area in Finnish Lapland. The meat samples have been taken so that they represent all of the meat derived from animal in proportion to the weight shares of different types of meat and the whole individual animal as foodstuff. Besides meat samples liver samples of four reindeer adults and 11 calves have been analyzed for PCDD/Fs and PCBs.

Analytes measured comprised of PCDD/Fs, PCBs, and PBDEs, see table 1. After homogenisation sample was freeze dried and fat was extracted with ethanol-toluene using an Accelerated Solvent Extractor (ASE 300). After extraction solvent was exchanged to hexane and the fat content was determined gravimetrically. The sample was then defatted on an acidic silica column and further purified and fractionated on alumina and carbon columns, respectively. Analyses of PCDD/Fs, PCBs and PBDEs were performed with HRGC/HRMS using SIR and resolution of 10 000. Toxic equivalents (TEQ) for PCDD/Fs (WHO_{PCDD/F}-TEQ) and PCBs (WHO_{PCB}-TEQ) were calculated with two sets of toxic equivalency factors (TEF) defined by WHO in 1997⁵ and 2005⁶. Concentrations are reported with upper bound method. In the upper bound method, the results of congeners with concentrations below LOQ were designated as LOQ. The laboratory is an accredited testing laboratory (No T077) in Finland

(current standard: EN ISO/IEC 17025). The scope of accreditation includes PCDD/Fs, non-*ortho*-PCBs, PCBs, and PBDEs from food samples.

Results and discussion

In Tables 1 and 2 there are median concentrations and ranges of sums of PCDD/Fs, PCBs, indicator- and marker-PCBs, and PBDEs along with TEQs of dioxins and PCBs in different games and semi-domesticated animals analysed in Finland during 2006-7. Lowest median concentrations of WHO_{PCDD/F-PCB}-TEQ/g fat were measured among meats of elk, red deer, mallard and hare, 1.7 pg/g fat, followed by reindeer meat concentrations (2.8 WHO_{PCDD/F-PCB}-TEQ/g fat). Reindeer liver contained about 17 times more dioxins and PCB as TEQ when compared to meat concentrations (46 pg WHO_{PCDD/F-PCB}-TEQ/g fat) and above that were the concentrations of the marine mammal Baltic Sea seal, 220 pg WHO_{PCDD/F-PCB}-TEQ/g fat. Several interesting details of the result can be detected:

- Flank meat of reindeer did contain more PCDD/Fs and PCBs when compared to other meats in reindeer, the reason for this remained unclear.
- In reindeer calves the concentrations were higher when compared to adults, and this applied also to liver samples of reindeer.
- In elks the adult animals had equal or higher concentrations of contaminants when compared to calves.
- The contribution of PCB to WHO_{PCDD/F-PCB}-TEQ was higher in meats of reindeer and especially in Baltic Sea seal while the opposite was true for meat of elk, red deer, mallard, and hare as well as for liver of reindeer.
- The concentrations of 15 PBDE congeners were all below 10 ng/g fat in terrestrial animals which can be considered as low concentrations even though concentrations reported in here are upper bound result and BDE 209 has quite a high LOQ. When only five congeners of PBDEs (BDE 47, 99, 100, 153, and 154) were considered the sums of PBDEs were all below 1 ng/g fat.
- In the meats of Baltic Sea seals the PBDE concentrations reached 210 ng/g fat implicating different position of the seals in the food chain when comparing with terrestrial game.

Two interesting points regarding needs for possible changes in EU legislation of maximum levels of contaminants in foodstuffs: a) applying new TEFs⁶ resulted an average a decrease of 12% and 9% in WHO_{PCDD/F}-TEQs and WHO_{PCB}-TEQs, respectively, the effect was most dramatic with the Baltic Sea seals in which WHO_{PCB}-TEQ decreased by 60% resulting from high contribution of mono-*ortho*-PCBs to TEQ; b) using marker PCB concentrations as a proxy for TEQs might have application in routine food monitoring as a screening method, since in this study a correlation between marker-PCBs and WHO_{PCDD/F-PCB}-TEQ was about 0.8 for reindeer, elk, and the Baltic Sea seal samples.

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Table 1. Median upper bound concentrations and ranges of PCDD/Fs, PCBs, indicator and marker PCBs, and PBDEs along with TEQs of dioxins and PCBs in different market surveillance foodstuffs in Finland in 2007.

Market surveillance Samples 2007	n	Fat %	PCDD/F ₁₇ ^a	PCB ₃₇ ^b	Indicator PCB ₇ ^c	Marker PCB ₆ ^d	WHO _{PCDD/F-TEQ} 1998	WHO _{PCB-TEQ} 1998	PBDE ₁₅ ^e	PBDE ₅ ^f
			pg/g fat	ng/g fat	ng/g fat	ng/g fat	pg/g fat	pg/g fat	ng/g fat	ng/g fat
Reindeer										
Fillet	1	3.8	4.8	6.7	4.0	3.0	1.0 0.87	1.7 1.6	0.46	0.11
Rump	3	2.7 (2.0-3.8)	5.7 (4.8-11)	8.7 (7.2-25)	5.5 (4.2-15)	4.4 (3.2-13)	1.2 (1.2-2.4) 1.0 (0.98-2.1)	1.9 (1.7-4.7) 1.7 (1.5-4.2)	0.68 (0.55-7.7)	0.22 (0.15-0.64)
Tenderloin	1	2.8	5.7	8.0	5.0	3.9	1.1 0.92	1.8 1.6	0.67	0.15
Flank	1	4.0	8.3	77	52	49	2.2 1.9	6.9 5.6	0.87	0.39
Sautéed meat	3	5.7 (5.0-5.8)	6.4 (5.6-8.0)	8.1 (7.1-13)	5.1 (4.2-8.1)	4.1 (3.3-6.2)	0.94 (0.90-1.3) 0.81 (0.79-1.1)	1.8 (1.4-2.8) 1.7 (1.3-2.6)	0.59 (0.52-7.6)	0.13 (0.12-0.19)
Red deer										
Sautéed meat	1	2.2	6.2	1.7	0.82	0.71	0.77 0.74	0.22 0.21	1.5	0.11
Elk + red deer										
Sautéed meat	1	7.5	6.5	1.8	1.0	0.96	0.80 0.78	0.13 0.13	0.49	0.067
Elk										
Rump	3	1.7 (1.0-3.3)	7.8 (4.2-11)	2.7 (2.2-7.2)	1.5 (1.2-4.3)	1.3 (1.0-3.5)	0.92 (0.48-1.9) 0.88 (0.46-1.5)	0.25 (0.24-1.3) 0.22 (0.22-1.2)	0.84 (0.38-2.6)	0.11 (0.07-0.43)
Mallard										
	1	19	7.7	1.4	0.86	0.78	0.88 0.85	0.047 0.032	1.1	0.86
Hare										
	1	3.3	20	4.9	2.7	2.3	1.2 1.0	0.89 0.84	1.7	0.51
Baltic Sea seal										
	6	3.0 (0.8-9.5)	94 (60-190)	19 (7.6-53) ^g	14 (5.8-39) ^g	14 (5.7-39) ^g	22 (8.8-34) 19 (8.2-29)	191 (71-320) 66 (26-99)	113 (46-210)	97 (45-210)

^a 17 toxic 2,3,7,8- Cl substituted PCDD/F congeners; ^b PCB congeners: 18, 28/31, 33, 47, 49, 51, 52, 60, 66, 74, 77, 81, 99, 101, 110, 105, 114, 118, 122, 123, 126, 128, 138, 141, 153, 156, 157, 167, 169, 170, 180, 183, 187, 189, 194, 206, and 209; ^c PCB congeners: 28/31, 52, 101, 118, 138, 153, and 180; ^d PCB congeners: 28/31, 52, 101, 138, 153, and 180; ^e PBDE congeners: 28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 183, and 209; ^f PBDE congeners: 47, 99, 100, 153, and 154; ^g µg/g fat

Table 2. Median upper bound concentrations and ranges of PCDD/Fs, PCBs, indicator, and marker PCBs along with TEQs of dioxins and PCBs in reindeer meat and liver and in elk meat in Finland in 2006.

Samples	n	Fat	PCDD/F ₁₇ ^a	PCB ₃₇ ^b	Indicator PCB ₇ ^c	Marker PCB ₆ ^d	WHO _{PCDD/F-TEQ} ₁₉₉₈	WHO _{PCB-TEQ} ₁₉₉₈
Reindeer-elk study 2006		%	pg/g fat	ng/g fat	ng/g fat	ng/g fat	WHO _{PCDD/F-TEQ} ₂₀₀₅	WHO _{PCB-TEQ} ₂₀₀₅
							pg/g fat	pg/g fat
Reindeer meat								
Calf	32	4.3 (2.1-7.2)	7.4 (5.1-29)	7.9 (3.7-19)	4.7 (2.0-13)	3.8 (1.5-11)	1.2 (0.90-2.0) 1.1 (0.78-1.7)	1.7 (1.6-3.6) 1.5 (0.93-3.2)
Adult	11	4.3 (1.7-9.0)	6.6 (4.0-10)	5.0 (3.6-7.0)	2.8 (1.8-3.9)	2.1 (1.5-3.0)	0.96 (0.69-1.6) 0.83 (0.62-1.5)	1.1 (0.62-2.1) 1.0 (0.57-1.9)
Reindeer liver								
Calf	10	5.6 (4.6-9.1)	220 (120-530)	13 (8.5-32)	8.6 (4.8-22)	7.0 (3.9-19)	36 (25-110) 28 (19-82)	20 (11-53) 20 (11-53)
Adult	4	5.9 (5.1-7.2)	130 (75-270)	7.7 (5.6-9.9)	4.4 (3.4-5.8)	3.6 (2.8-4.6)	21 (19-61) 16 (14-46)	11 (8.3-18) 11 (8.3-18)
Elk meat								
Calf	6	1.7 (1.3-3.5)	8.2 (6.2-42)	4.4 (3.7-6.8)	2.8 (1.9-4.3)	2.2 (1.5-3.1)	1.2 (0.66-2.0) 1.1 (0.56-1.9)	0.64 (0.35-1.1) 0.56 (0.31-0.92)
Adult	6	3.0 (0.8-6.6)	10 (5.2-13)	5.3 (2.2-11)	3.3 (1.3-7.3)	2.6 (1.0-5.9)	1.2 (0.74-2.0) 1.1 (0.71-1.6)	0.84 (0.32-1.7) 0.73 (0.28-1.5)

^a 17 toxic 2,3,7,8- Cl substituted PCDD/F congeners; ^b PCB congeners: 18, 28/31, 33, 47, 49, 51, 52, 60, 66, 74, 77, 81, 99, 101, 110, 105, 114, 118, 122, 123, 126, 128, 138, 141, 153, 156, 157, 167, 169, 170, 180, 183, 187, 189, 194, 206, and 209; ^c PCB congeners: 28/31, 52, 101, 118, 138, 153, and 180; ^d PCB congeners: 28/31, 52, 101, 138, 153, and 180