PCDD/F, PCB, AND PBDE LEVELS IN FINNISH FOODSTUFFS IN 2003-2005

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Introduction
In order to generate reliable background occurrence data on polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs, dioxin) and polychlorinated biphenyls (PCBs) the Commission of the European Communities has a recommendation for member countries to monitor these substances in foodstuffs[1]. A minimum number of analysed samples per country per year in different food categories is recommended, and for Finland the amount of annual samples is 45. In Finland, along with PCDD/Fs and PCBs the occurrence of polybrominated diphenyl ethers (PBDEs) has been measured since 2003 from analysed food samples. We present here monitoring data of PCDD/Fs, PCBs, and PBDEs in meat, milk, cheese, egg, oil and fat samples during 2003-2005. Fish samples have been excluded from this presentation since the results of those samples have been published in two recent papers[2,3].

Materials and Methods
Representative meat samples (n=34) were collected from major slaughter houses, milk samples (n=13) either from the dairies or from individual farms, and samples of cheese, egg, oil and fats (n=5, 16, and 7, respectively) were obtained from retails. Sampling and pooling complied the Commission directive 2002/69/EC[4].
Analytes measured comprised of 17 2,3,7,8-chlorine substituted "toxic" PCDD/F congeners, 37 PCB congeners (including 12 DL-PCBs, 6 indicator-PCBs, and congeners PCB 18, 33, 47, 49, 51, 60, 66, 74, 99, 110, 122, 128, 141, 170, 183, 187, 194, 206, 209), and 15 PBDE congeners (BDE 28, 47, 66, 71, 75, 77, 85, 99, 100, 119, 138, 153, 154, 183, and 209).

After homogenisation solid sample was freeze dried and fat was extracted with toluene using a Soxhlet apparatus or with acetone-hexane (35/65, v/v) using Accelerated Solvent Extractor (ASE). Liquid sample was extracted with liquid-liquid extraction (hexane or diethyl ether-hexane). Oil sample was dissolved in hexane. After extraction solvent was exchanged to hexane and the fat content was determined gravimetrically. The sample was then defatted on an acidic silica column. PCDD/Fs, PCBs, and PBDEs were fractionated on a carbon column and further purified on alumina column. Analyses of PCDD/Fs, PCBs and PBDEs were performed with HRGC/HRMS using SIR and resolution of 10 000[5]. Toxic equivalents (TEq) for PCDD/Fs ($WHO_{PCDD/F}$-TEq) and PCBs (WHO_{PCB}-TEq) were calculated with toxic equivalency factors (TEF) defined by WHO in 1998[6]. Concentrations were calculated with upper bound method. In the upper bound method, the results of congeners with concentrations below LOQ were designated as LOQ.

As an analytical quality assurance the laboratory of chemistry at the National Public Health Institute has participated in several international quality control studies for the analysis of PCDD/Fs, PCBs, and PBDEs. The matrixes in these studies have included milk, egg, meat, oil and fat and fish samples[7,8,9]. 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 and feed samples.

Results and discussion
In Table 1 there are median concentrations and ranges of sums of PCDD/Fs, PCBs, indicator PCBs, and PBDEs along with TEqs of dioxins and PCBs in different foodstuff samples analysed in Finland during 2003-2005. Overall measured concentrations were quite low in all domestic animals' samples and products there off. In meat, milk, cheese, and egg samples the median concentrations of PCDD/Fs were below 10 pg/g fat, below 10 ng/g fat in PCBs, and below 3 ng/g fat in PBDEs. Samples of liver of bovine and pork suggest that PCDD/Fs accumulate to greater extent in liver than PCBs and PBDEs do. There was some 5-8 times higher concentrations of PCDD/Fs in liver than in meat of bovine or pork. The corresponding ratio for PCBs and PBDEs varied

between 0.5 and 2. Concentrations of meats of elk and adult reindeers corresponded quite well with domestic animals' meat concentrations but in reindeer calves' meat samples the concentrations of PCDD/Fs and PCBs were ten times as high as in other meat samples. With PBDEs there was no difference between reindeer calves and other animals. The TEq concentrations were very low almost in all samples. Especially with $WHO_{PCDD/F}$-TEq the lowest concentrations originate almost entirely from results based solely on LOQs, since most of the congeners in a sample were unquantifiable. Compared to domestic animals the TEq concentrations in farmed game (reindeer) and in wild game (elk) were somewhat higher. Especially in reindeer calves the TEqs were higher than in other samples. The ratio between two TEqs also changed clearly when moving from domestic animals to elks and reindeers. In the former group $WHO_{PCDD/F}$-TEq dominate over the WHO_{PCB}-TEq, while the opposite was true for elks and reindeers.

Table 1. Median upper bound concentrations and ranges of sums of PCDD/Fs, PCBs, indicator PCBs, and PBDEs along with TEqs of dioxins and PCBs in different foodstuffs in Finland in 2003-2005.

		Sum of PCDD/Fs	Sum of PCBs	Sum of Indicator PCBs	Sum of PBDEs[a]	$WHO_{PCDD/F}$-TEq	WHO_{PCB}-TEq
Samples	n	pg/g fat	ng/g fat	ng/g fat	ng/g fat	pg/g fat	pg/g fat
Meat							
Bovine	3	**2.46** (1.83-6.73)	**1.74** (1.39-3.22)	**0.91** (0.68-1.83)	**0.60**, *0.21* (0.59-0.68)	**0.24** (0.23-0.27)	**0.13** (0.083-0.20)
Pork	3	**6.21** (3.53-11.5)	**2.67** (0.44-3.70)	**1.61** (0.20-2.25)	**0.77**, *0.25* (0.61-1.43)	**0.20** (0.18-0.20)	**0.059** (0.010-0.067)
Poultry	9	**9.23** (2.76-27.8)	**5.58** (1.39-14.0)	**2.99** (0.18-7.24)	**2.58**, *0.50* (0.93-4.04)	**0.40** (0.18-0.70)	**0.14** (0.035-0.89)
Sheep	3	**2.60** (1.15-19.0)	**1.60** (1.22-3.59)	**1.01** (0.73-2.03)	*0.092* (*0.065-0.13*)	**0.25** (0.10-0.36)	**0.14** (0.11-0.32)
Elk	3	**5.12** (2.90-10.4)	**5.47** (2.63-6.27)	**2.36** (0.89-2.64)	*0.53* (*0.40-2.79*)	**0.35** (0.29-0.38)	**0.92** (0.59-1.08)
Reindeer	4	**11.6** (3.14-46.3)	**5.71** (5.52-14.2)	**2.56** (2.42-7.74)	**1.72**, *0.26* (1.26-2.19)	**0.71** (0.50-1.02)	**1.28** (1.15-1.44)
Reindeer calf	4	**68.2** (11.7-207)	**44.4** (25.5-79.3)	**24.3** (13.5-46.3)	**1.52**, *0.68* (1.35-1.57)	**2.55** (1.79-2.79)	**4.20** (3.49-6.65)
Liver							
Bovine	3	**12.9** (5.69-420)	**3.68** (3.43-9.06)	**2.55** (2.39-.03)	*0.14* (*0.11-0.37*)	**0.19** (0.090-1.34)	**0.33** (0.29-0.49)
Pork	2	**46.8** (30.5-63.2)	**3.57** (2.62-4.53)	**2.16** (1.62-2.70)	*0.47* (*0.20-0.73*)	**0.83** (0.73-0.93)	**0.15** (0.15-0.15)
Milk	13	**1.49** (0.95-3.03)	**2.21** (1.87-7.79)	**1.20** (1.09-3.52)	**1.51**, *0.22* (0.40-1.66)	**0.20** (0.11-0.45)	**0.16** (0.10-0.37)
Cheese	5	**2.87** (2.26-3.38)	**5.31** (2.24-11.5)	**2.94** (1.22-6.72)	**0.39**, *0.16* (0.27-0.85)	**0.16** (0.15-0.43)	**0.19** (0.065-0.91)
Eggs	16	**6.88** (3.70-24.7)	**8.08** (1.81-16.2)	**4.16** (0.73-8.76)	**1.42**, *0.64* (0.82-8.18)	**0.75** (0.34-1.60)	**0.56** (0.14-1.50)
Oils and fats	7	**4.07** (1.74-44.3)	**0.85** (0.10-0.92)	**0.51** (0.019-0.56)	**0.42**, *0.14* (0.37-0.46)	**0.17** (0.14-0.21)	**0.031** (0.010-0.034)

[a]Number in *Italics*-font represents median concentration of the samples when BDE 209 is excluded.

In Figure 1, $WHO_{PCDD/F}$-TEq and WHO_{PCB}-TEq in different foodstuffs are depicted. In all domestic animal meat and also in liver samples the combined TEq of PCDD/Fs and PCBs was below the maximum level of these compounds set by the Commission of the European Communities in Council regulations 2375/2001 and 199/2006[10,11]. The latter of these regulations shall be applied from 4th November 2006. The combined TEq and also $WHO_{PCDD/F}$-TEq in elk and reindeer meat samples were higher than in domestic animals but remained still under the maximum limits. When WHO_{PCB}-TEq was combined with the dioxin TEq in reindeer calf samples the maximum limit of 4,5 pg $WHO_{PCDD/F+PCB}$-TEq/g fat was exceeded by 50%, which is more than the uncertainty of the analysis in the laboratory.
With milk, cheese, egg, and oil and fat samples the maximum limit values lie far above the measured values.

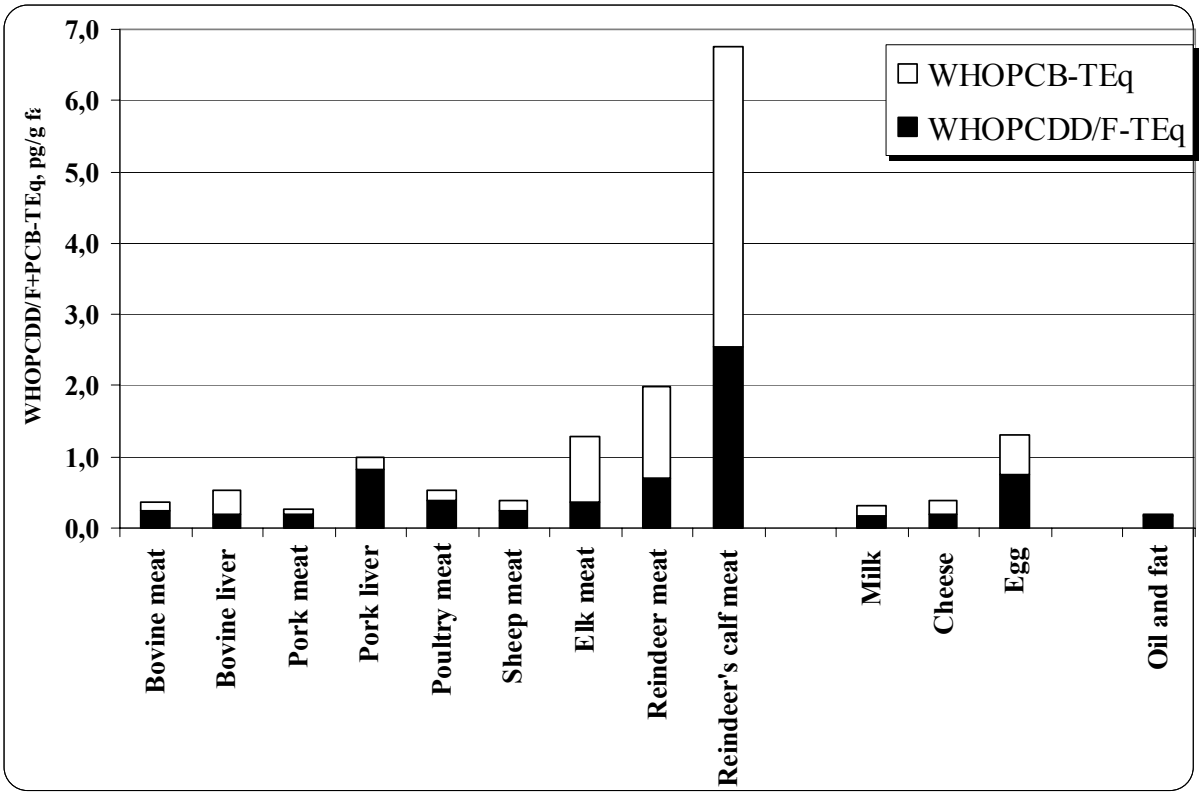

Figure 1. $WHO_{PCDD/F}$-TEq and WHO_{PCB}-TEq in different foodstuff in Finland in 2003-2005.

These 75 samples analysed in Finland during 2003-2005 as official dioxin monitoring samples indicate that the meats from domestic animals and other food stuffs there off are relatively contaminant free products. On the other hand the meat from farmed game and wild game showed somewhat higher concentrations. This might be due to longer life cycle of these animals compared to domestic animals allowing contaminants accumulate into the animal a longer period of time. With reindeer calves the most obvious reasons for relatively high concentrations are that the size of the animals is smaller than the size of on adult reindeers, especially the proportion of fat might be smaller in young animals when compared to older ones. Another reason for the elevated concentrations in reindeer calves might be that the period of using mother's milk by a calf is quite close to the time the calf was slaughtered and due to extensive exposure through mother's milk can still reflect in to the levels of PCDD/Fs and PCBs in calf meat.

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