

**Polychlorodibenzo-p-dioxin and polychlorodibenzofuran (PCDD/F)
levels in Baltic herring and rainbow trout samples in Finland**

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Chlorinated dioxins and furans have been found all around the world and also in human tissue and milk samples. Food have been assumed to be the most probable way of exposure to PCDD/Fs. However, before some recommendations or guidelines for food can be provided the level of PCDD/Fs in food must be known. Finland is facing this problem with many other countries. Possible sources of PCDD/Fs in Finland might be the waste water and flue gas emissions of many pulp mills which have used chlorine bleaching process in their cellulose production. Contrary to the other European countries, practically all the municipal wastes in Finland are disposed at the landfills and not burned or incinerated. In addition, a lot of efforts have nowadays been made to change chlorine bleaching to other enzyme processes or chlorine dioxide bleaching which minimize the formation of dioxins.

Although the emissions of the dioxins will be decreased with new efforts and processes the situation continuously need the control. The local contamination or that of the special food items may be remarkable and even cause the tolerable intake limits to be exceeded.

A Canadian study¹ has suggested that 90% of dioxin exposure come from food and the rest from air, water, soil, and consumer products. The German Federal Health Office² has found that dioxins were highest in fish, chicken, eggs, sheep, beef, and cow milk, in that order. Many other governments have also programs for the control of dioxins in food and food packaging material. At least two countries have established tolerances for fish (Canada³) or level of concern (USA⁴) which would result in warnings to the fish consuming public.

A number of governments and Nordic Countries together have established the acceptable daily intake (ADI) value, tolerable daily intake value (TWI), or virtually safe dose value for dioxins. Joint Expert Committee on Food Additives (JECFA) has established TWI of 70 pg TCDD equivalents that is twice as high as that of the Nordic value, 35 pg. There is no agreement about how a limit might be established. There are also difficulties in methods of analysis. The costs of analyses at levels of picograms or even femtograms per gram are high, too.

Although it was unlikely that average levels of dioxins in Finland vary from those found in the other countries it was decided to follow the situation in the other Nordic Countries. In Finland the dioxin program has been made by National Food Administration and analyzed by the National Public Health Institute. For the purposes of reference values and daily intakes of dioxins the basic food, milk, meat, eggs, and fish were chosen to control.

Materials and Methods

From each food item, milk, meat, egg, and fish, 20 samples were analyzed. Each sample was a pool of five samples except of the ten Baltic herring samples which were pooled from 20 fish filets. Eight of the ten rainbow trout samples had been fed with normal nourishment, one pooled sample with Baltic herrings and one pooled sample both with normal nourishment and with Baltic herrings (1:1) for three months.

The solid samples were pooled by the weight basis but the milk samples were already pooled in the dairy. Milk samples were analyzed according to Lindström and co-workers⁵. Meat samples were homogenized and fat from meat was extracted in Soxhlet with toluene for 24h. Fat from egg samples was extracted according to Jasinski⁶. Fish samples were dried with fourfold amount of activated sodium sulphate at 120 °C and fat from the fish samples was extracted in Soxhlet with toluene for 24 h. The different fat samples were purified with Silica Gel column according to Lindström and Rappe⁷, and fractionated in activated carbon and aluminum columns according to Jimenez¹ and co-workers⁸. PCDD/F analyses of the separated, purified fractions were performed with a high resolution mass spectrometry equipped with a quartz capillary column (HP5). The quantitation was made by a selective ion recording method using the VG 70 SE mass spectrometry (resolution 10,000). Total of 16 ¹³C-PCDD/Fs congeners (ED-998 tetra-octa chlorodioxin standard solution and EF-999 tetra-octa chlorofuran standard solution, Cambridge Isotope Laboratories) were used as internal standards which were added to the samples before extractions.

Results and Discussion

The results of fish samples are shown in Table. Rainbow trout fish samples (on average 0.53 pg/g wet weight or 4.17 pg/g fat) contained PCDD/Fs about half of that of Baltic herring samples (on average 0.94 pg/g wet weight or 30.2 pg/g fat) calculated as Nordic toxic equivalents. The rainbow trout sample (2.10 pg/g wet weight or 33.4 pg/g fat) fed with Baltic herrings for three months contained two times as much PCDD/Fs as Baltic herrings on an average and as much as the highest sample of Baltic herrings. The rainbow trout sample fed both with herrings and normal food was between those values.

The preliminary results of Finnish milk samples showed very low levels of PCDD/Fs. Dioxin concentrations of egg samples were a little bit higher than those of the milk samples. Pork samples were quite clean from PCDD/Fs but bovine meat samples contained low levels of dioxins.

Fish food has been shown to be healthy especially for population with high incidence of cardiovascular diseases and high mortality in them^{9,10,11} as the situation is in Finland. Fish

consumption should be increased among the whole population. However, we do not know the real effects of dioxins for human people and for that reason some care must be taken. Depending on the nourishment and age of rainbow trouts, this fish species could be almost clean from dioxins as seen in Table. However, feeding of rainbow trout with Baltic herrings as the only feed might increase the level of dioxins even to a higher level than they were in the Baltic herrings. Further studies are therefore needed to find out the maximum amounts of Baltic herrings suitable for the nourishment of rainbow trouts without considerable increase of PCDD/Fs in them.

Table. PCDD/F concentrations of 10 pooled Baltic herring samples (20 fish in a pool) and 7 pooled rainbow trout samples (5 fish in a pool) as pg/g wet weight and the sum Nordic toxic equivalents (TEQs).

| congener | Baltic herring | | | rainbow trout | | | * |
|----------------------------------|----------------|-------|-----------|---------------|-------|-----------|-------|
| | average | std | range | average | std | range | |
| 2,3,7,8-Cl ₄ DF | 0.80 | 0.22 | 0.49-1.21 | 0.33 | 0.27 | 0.02-0.87 | 1.32 |
| 2,3,7,8-Cl ₄ DD | 0.09 | 0.06 | <0.20 | <0.05 | <0.05 | <0.07 | 0.07 |
| 1,2,3,7,8-Cl ₅ DF | 0.13 | 0.08 | 0.05-0.32 | 0.11 | 0.06 | 0.02-0.21 | 0.07 |
| 2,3,4,7,8-Cl ₅ DF | 1.08 | 0.47 | 0.65-2.31 | 0.72 | 0.67 | 0.12-2.36 | 3.32 |
| 1,2,3,7,8-Cl ₅ DD | 0.26 | 0.08 | 0.16-0.46 | 0.13 | 0.05 | 0.06-0.23 | 0.38 |
| 1,2,3,4,7,8-Cl ₆ DF | 0.11 | 0.08 | <0.20 | <0.05 | <0.05 | <0.18 | 0.06 |
| 1,2,3,6,7,8-Cl ₆ DF | 0.11 | 0.08 | <0.20 | <0.05 | <0.05 | <0.18 | 0.06 |
| 1,2,3,7,8,9-Cl ₆ DF | <0.05 | <0.05 | <0.17 | <0.05 | <0.05 | <0.18 | 0.15 |
| 2,3,4,7,8,9-Cl ₆ DF | 0.12 | 0.05 | <0.17 | 0.08 | 0.09 | <0.27 | <0.05 |
| 1,2,3,4,7,8-Cl ₆ DD | 0.22 | 0.20 | <0.76 | <0.05 | <0.05 | <0.08 | <0.05 |
| 1,2,3,6,7,8-Cl ₆ DD | 0.23 | 0.12 | 0.02-0.45 | <0.05 | <0.05 | <0.50 | <0.05 |
| 1,2,3,7,8,9-Cl ₆ DD | 0.06 | 0.07 | <0.18 | 0.10 | 0.17 | 0.53 | 0.09 |
| 1,2,3,4,6,7,8-Cl ₇ DF | 0.12 | 0.07 | 0.01-0.26 | 0.06 | 0.05 | <0.10 | 0.07 |
| 1,2,3,4,7,8,9-Cl ₇ DF | <0.05 | <0.05 | <0.10 | <0.05 | <0.05 | <0.05 | <0.05 |
| 1,2,3,4,6,7,8-Cl ₇ DD | 0.34 | 0.17 | 0.16-0.74 | 0.10 | 0.10 | <0.31 | 0.07 |
| OCDF | 0.08 | 0.08 | <0.28 | <0.05 | <0.05 | <0.08 | <0.05 |
| OCDD | 1.84 | 0.68 | 0.54-2.99 | 0.23 | 0.23 | <0.81 | 0.59 |
| TEQs | 0.94 | 0.34 | 0.64-1.89 | 0.53 | 0.38 | 0.23-1.47 | 2.10 |

* a pool of rainbow trouts fed with Baltic herrings

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