# **LEVELS IN FOOD**

### Dioxin-like compounds in total diet food, Canada 1992-93

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#### Abstract

About 100 total diet food samples from Toronto in 1992 and Montreal in 1993 were analysed for PCDDs, PCDFs and *no* PCBs. On a TEQ basis, beef had higher concentrations than either pork or poultry with values for ground beef between 0.3 and 0.4 ng/kg whole weight. The TEQ for dairy products depended on the lipid content with butter containing more than ten times higher amounts than fluid milk. The only detectable change in TEQ since the mid 1980's for the most important foods was the lower level in fluid milk attributed to changing of the technique for bleaching of milk cartons.

#### Introduction

It has been recognized for some time<sup>1.2</sup> that more than 95% of human exposure to dioxins (PCDDs), furans (PCDFs) and probably PCBs occurs through ingestion of common foods. The dioxin-like compounds, here defined as PCDDs/PCDFs and *non-ortho* PCBs, occur ubiquitously in the environment particularly in industrial countries and have recently been implicated in human health end points such as reproduction and development at doses lower than those for the more conventional carcinogenic effects. In the on-going review by the US Environmental Protection Agency (EPA) of exposure and health effects of dioxin-like compounds, foods particularly beef products were acknowledged as major contributors to exposure from these compounds although data to support this conclusion were not extensive.

A total diet food program<sup>3</sup> is a means of estimating human intake of chemical substances based on the analysis of foods commonly consumed by the normal or general population. In Canada this food safety program has been carried out a least three times on foods purchased at commercial outlets and then prepared domestically for consumption. We report here on the PCDD/PCDF/*no* PCB content of selected total diet foods mostly of animal origin from two Canadian cities in 1992-3. These results are compared to similar sampling from 1988 and, where possible, to recent US data on the same food commodities.

#### Experimental

<u>Sampling</u> Total diet food samples were purchased from four commercial outlets in the summers of 1992 in Toronto and of 1993 in Montreal, prepared for consumption where applicable, and 135 food composites were constituted from each of the two cities. Forty-four (44) of these

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composites, mostly fatty foods of animal origin, were selected from each centre (total 88 analyses) for the determination of PCDDs/PCDFs and *non ortho* PCBs.

Analysis Concentrations of the above analytes in common foods are low (usually less than 1 ng/kg (ppt)). In order to ensure that as many as possible samples gave discrete positive results (as few as possible non- detectable (ND) numbers), a large sample size was used compatible with the method capacity. This ensured that the problem of dealing with large numbers of NDs will be minimal when conducting intake estimates. The actual sample size used was up to 8 g of extractable fat to a maximum whole weight size of about 100 g. Samples were analysed by solvent extraction with acetone-hexane (a small aliquot was used for the lipid determination gravimetrically), defatting with strong sulfuric acid, purification on adsorbents of acid/base silica and Florisil, and separation of chemical classes on activated carbon. Identification was by gas chromatography-mass spectrometry and quantification by the isotope dilution internal standard method<sup>4.5</sup>. Detection limits varied depending on congener and sample size, were always below 1 ppt, and were as low as 5 pg/kg (parts per quadrillion) for the tetra and penta congeners in large samples such as fluid milk.

#### **Results and Discussion**

Table 1 shows the TCDD toxic equivalents (TEQ) for both the FCDDs/PCDFs and *no* PCBs for some of the main categories of foods which are known to contain these contaminants. On a TEQ basis and using whole weights, all concentrations are below 1 ppt. Beef products contain more TEQ than either pork or poultry and all three of these important food categories have more TEQ from the PCDD/PCDF portion than from the planar PCBs. The concentrations of TEQ in dairy products depend particularly on the lipid content and the planar PCBs contributes a greater proportion of TEQ than in the case with meat samples. As expected freshwater fish has higher TEQ than marine fish and most of this originates from PCBs.

The values which we report here for beef can be compared to the recent results of the US EPA in their study of beef fat from samples taken country wide in 1994<sup>6</sup> and by Schecter et al.<sup>7</sup> from New York state in 1993. In the former study the mean TEQ (PCDD/PCDF) using one-half the detection limit was 0.89 ng/kg on a lipid basis or an estimated 0.17 ng/kg on whole weight (19% fat). The latter value is somewhat lower than but similar to our value for ground beef (about 20% fat). The TEQ numbers we find are within the rather wide range of those from the New York study.

Table 2 lists the TEQ for certain food composites in both cities over a period of 4-5 years using data from our previous total diet study<sup>8</sup> which incorporated the same sampling protocol and analytical methods as described here. Most food composites do not appear to have changed their contaminant level significantly over this time period with the notable exception of fluid milk. The major decrease in TEQ for this food is attributed to bleaching techniques which have minimized the formation of dioxins and furans<sup>4</sup>.

This data on the TEQ of total diet foods will be supplemented with that from 3 other major cities. Along with the major PCB content of the same foods<sup>9</sup> and food intake information, a more detailed estimate of the daily intake will be made and comparison made to national guidelines both

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within and without Canada.

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#### References

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- (1) Birmingham, B.; Thorpe, B.; Frank, R.; Clement, R.; Tosine, H.; Fleming, G.; Ashman, J.; Wheeler, J.; Ripley, B.D.; Ryan, J.J. Chemosphere 1989, 19,507-512.
- (2) Fürst, P.; Beck, H.; Theelen, R. Toxic Substances J. 1992, 12, 133-150.
- (3) Conacher, H.B.S.; Graham, R.A.; Newsome, W.H., Graham, G.F.; Verdier, P. Can. Inst. Food Sci. Tech. J. 1989,322-326.
- (4) Ryan, J.J.; Shewchuk, C.; Lau, B.P.-Y.; Sun, W.F. J.Agr.Food Chem. 1992,40,919-923.
- (5) Ryan, J.J.; Lau, B.P.-Y.; Boyle, M.J. *Biological Mass Spectrometry*, eds. Matsuo, T.; Caprioli, R.M.; Gross, M.L.; Seyama, Y. 1994, chp3.16,583-602.
- (6) Winters, D.; Cleverly, D.; Meier, K.; Dupuy, A.; Bryne, C.; Deyrup, C.; Ellis, R.; Ferrario, J.; Harless, R.; Leese, W.; Lorber, M. McDaniel, D.; Schaum, J.; Walcott, J. Chemosphere 1996,469-478.
- (7) Schecter, A.; Startin, J.; Wright, C.; Kelly, M.; Päpke, O.; Lis, A.; Ball, M.; Olson, J.R. Environ. Health Persp. 1994, 102,962-966.
- (8) Ryan, J.J.; Panopio, L.G.; Lewis, D.; Weber, D.F.; Conacher, H.B.S. Organohalogen Compounds 1990,497-500.
- (9) Newsome, W.H.; Davies, D.J.; Sun, W.F. Food Add. Contamin. 1997, in press.

		Toronto			Montreal		
Composite	1988	<u>19</u> 92	% change	1988	1993	% change	
ground beef	0.31	0.32	+ 3	0.21	0.32	+52	
whole milk	0.16	0.038	-76	0.24	0.031	-87	
butter	0.40	0.50	+25	0.46	0.33	-28	
wieners	0.31	0.27	-15	0.19	0.24	+26	
shellfish	0.033	0.068	+106	0.30	0.28	-6	

#### Table 2: Comparison of changes in TEQ (ng/kg whole weight) in selected total diet foods for Toronto between 1998 and 1992 and for Montreal between 1988 and 1993

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Table 1: TCDD toxic equivalents (TEQ) and their lipid content in fatty animal total
diet composites from Toronto (TO) 1992 and Montreal (MT) 1993;
values ng/kg (ppt) on whole weight basis

		% lipid		PCDD/ PCDF		rio PCB		Σ TEQ	
Food Category	Composite Sample	то	MT	то	MT	ТО	MT	то	MT
Meat	beef ground	20.0	19.5	0.32	0.32	0.067	0.045	0.39	0.37
	beef steak	7.0	6.9	0.18	0.17	0.017	0.016	0.19	0.18
	beef roast	6.8	6.1	0.087	0.14	0.014	0.018	0.10	0.16
	pork cured	18.5	17.9	0.045	0.044	0.007	0.004	0.053	0.049
	organ meat	5.3	5.2	0.29	0.37	0.034	0.052	0.32	0.42
	poultry	3.6	5.5	0.066	0.043	0.010	0.019	0.076	0.062
Dairy	whole milk	2.72	1.41	0.038	0.031	0.033	0.096	0.072	0.041
	1 % milk	0.62	0.33	0.024	0.021	0.012	0.004	0.036	0.025
	cream	8.86	10.4	0.079	0.076	0.066	0.062	0.145	0.138
	cheese cheddar	30.9	31.6	0.24	0.20	0.15	0.16	0.39	0.36
	butter	76.7	67.2	0.50	0.33	0.42	0.29	0.93	0.62
Fish	fresh water	3.3	5.9	0.26	0.16	0.36	0.32	0.62	0.48
	marine	1.7	0.75	0.033	0.013	0.24	0,105	0.28	0.12
Oils	cooking fats and salad oil	94,2	84.4	0.42	0.28	0.019	0.029	0.44	0.31

For non detected congeners used one-half the limit of detection