PCDDs/PCDFs IN 22 CATEGORIES OF FOOD COLLECTED FROM SIX CANADIAN CITIES BETWEEN 1985 AND 1988 . John J. Ryan*, Luz G. Panopio, David A. Levis, Dorcas F. Veber and Henry B.S. Conacher. Food Research Division, Health and Welfare Canada, Ottava KIA 012, CANADA.

ABSTRACT

More than 160 fatty food composites of mostly animal foods originating from six cities across Canada were analysed for PCDDs/PCDFs. A high frequency of low levels (0.1 to 10 ng/kg on whole weight basis) of hexa-, hepta- and octa- PCDDs/PCDFs were found in meat samples (beef, pork, and, less so, poultry) and milk products. 2,3,7,8-TCDF and 2,3,7,8-TCDD at levels less than 1 ng/kg were also detected in some fish and shellfish samples and in milk products packaged in bleached carton containers.

INTRODUCTION

2,3,7,8-substituted PCDDs/PCDFs are known to be present in the adipose tissue of most people from industrialized countries (1-3). In defining the source of these contaminants in people, most estimates have indicated that food contributes more than 90% to this human burden. This conclusion has been reached by comparison of known concentrations of PCDDs/PCDFs in ambient air, drinking water, and food available for consumption. However the data on food (4-6) with respect to food types and detectable values are limited and not extensive. For this reason we analysed more than 160 selected fatty food composites from the Canadian Total Diet Program (7).

EXPERIMENTAL

Sampling

A detailed description of the Total Diet Program has been published elsewhere (?). Briefly, representative food samples were collected from each of six major Canadian cities (Ottawa (x2), Halifax, Winnipeg, Vancouver, Hontreal and Toronto) between 1985 and 1988. Each sample for analysis was a composite of four brands from different retail outlets and was used 's such (e.g. milk) or prepared in a manner suitable for consumption (e.g. raw meats were zooked) to yield approximately 112 composite from each city. Of these set of composites, 72 of nigh fat content, milk products (7 types), meat products (9 types), fish (4 types), and miscellaneous (2 types) were taken for analysis. In addition a number of other high consumption food composites were also analysed. The amount of sample used for analyses was thosen to contain either a high lipid content (up to 10 g) or a high wet weight (up to 250 g) in order that the anticipated low levels (sub ng/kg in most samples) would yield discrete analytical numbers in many cases.

<u>Analysis</u>

The samples were analysed by adding a nixture of isotopically labelled PCDDs/PCDFs. Extracting with acetone-hexane (2:1 v/v), determining the hexane soluble portion on an aliquor, and defacting the remaining portion by partitioning with sulfuric acid. Sample purification was carried out in sequence on columns of Florisil, carbon and acid-base silica. Measurement was by gas chromatography-mass spectrometry (GC-MC) using the isotope dilution technique. Each set of 9 to 12 samples consisted of a reagent blank, 7 to 10 unknowns, and 1 or 2 quality control samples such as duplicates, spikes or reference materials. Detection limits in the food samples on a whole weight basis varied depending on congener and food type. The limits were usually lower than 1 mg/kg and as low as 10 pg/kg for milk samples.

RESULTS AND DISCUSSION

Virtually all the PCDDs/PCDFs present in ordinary foods were those with 2.3.7.8substitution. Of the 17 members of this class with 4 to 8 chlorines, the major compounds found with respect to both frequency and concentration were the 2.3.7.8-HxCDDs (3 isomers). 1.2.3.4.6.7.8-HpCDF, 1.2.3.4.6.7.8-HpCDD and OCDD. These congeners were present in a variety of foods of animal origin, including dairy products (milk, cheese, cream), beef (steak, hamburger and organ Deats), pork (fresh and cured) and, less so, in poultry products (chicken, turkey, and eggs). Concentrations of the above higher chlorinated congeners in the six composite samples of hamburger are shown in Table I where levels vary from 0.2 ng/kg up to values for 2.3.7,8-TCDF and 2.3.7,8-TCDD in 2% defatted milk (Table II) were 1.1 and 0.038 ng/kg, respectively. As a result of recent reductions in the levels of 2.3.7,8-TCDF and 2.3.7,8-TCDD in bleached cartons used as milk containers, it is to be expected that milk samples taken from 1989 will have lower concentrations of these contaminants. The highest level found of any congener was in organ meats (liver and kidney) where OCDD levels were over 50 ng/kg in 4 of 6 composites. In most cases no congeners could be found in foods of vegetable origin such as shortening, peanut butter, fruits or cereal products such as flour. No obvious difference was evident in the levels of these compounds as a function of the city from across Camada where it was purchased.

The results show a background level primarily of higher chlorinated PCDDs/PCDFs in certain foods of animal origin and, secondarily, of the tetra-congeners in milk products from bleached containers and fish from fresh and salt water On a 2.3.7.8-TCDD toxic equivalents basis, the average level found calculated on the whole weight was between 0.1 and 0.2 ng/kg. The relationship of these concentrations with regard to intake and body burden is being assessed.

REFERENCES

- J.J. Ryan, R. Lizotte and B.P.-Y. Lau, <u>Chemosphere</u> 14 (1985) 697.
- M. Nygren, C. Rappe, C. Lindström, M. Hansson, P. A. Bergquist, S. Marklund, L. Domellof,
 L. Hardell and M. Olsson, In: <u>Chlorinated Dioxins and Dibenzofurans in Perspective</u>, eds
 C. Rappe, G. Choudhary, and L.H. Keith, Lewis Publishers, Michigan, U.S.A., Chp. 2, pp
 15-34 (1986).
- J.S. Stanley, K.E. Boggess, J. Onstat, T.M. Sack, J.C. Remmers, J. Breen, F.W. Kutz, J Carra, P. Robinson and G.A. Mach, <u>Chemosphere</u> 15 (1986) 1605.
- H. Ono, K. Kashima, T. Wakimoto and R. Tatsukawa, <u>Chemosphere</u> 16 (1987) 1823.
- 5. H. Beck, K. Echart, W. Mathar and K. Wittkowski, Chemosphere 18 (1989) 417.
- B. Birmingham, B. Thorpe, R. Frank, R. Clement, H. Tosíne, G. Fleming, J. Ashman, J Wheeler, B.D. Ripley and J.J. Ryan, <u>Chemosphere</u> 19 (1989) 507.
- H.B.S. Conacher, R.A. Graham, W.H. Newsome, G.F. Graham and P. Verdier, <u>Can. Inst. Foc.</u> <u>Sci. Technol. J.</u>, 27 (1989) 322.

Sample No	City	۹ Lipid	2378- HxCDFs®	2378- HxCDDs ^b	1234678- HpCDF	1234678- HpCDD	OCDD	TEQC
1	Ottawa	17	.87	1.6	2.7	6.4	9.2	. 34
2	Halifax	19	ND(.2) ^d	. 53	1.1	2.9	8.1	. 10
3	Winnipeg	18	ND(.2)	. 81	ND(.2)	2.3	2.1	.11
4	Vancouver	21	.46	1.5	1.1	4.0	6.3	. 32
5	Montreal	14	.18	. 65	. 47	1.7	3.2	.11
6	Toronco	21	. 39	. 89	1.5	3.2	4.7	. 18
Mean ^e ±SD		16 <u>+</u> 6.9	.48 <u>+</u> .29	1.0 ±.45	1.4 ±.83	3.4 ±1.2	5.7 ±2.6	.19 <u>+</u> .11

Table 1: Concentrations (ng/kg whole weight) of higher chlorinated PCDDs/PCDFs in beef hamburger composite samples from six Canadian cities.

a 123478/123678/234678-inomers; b 123478/123678/123789- isomers; C 2378-TCDD toxic equivalents; d non-detected followed by limit of detection in brackets; C positive samples only

Table 11: Concentrations (ng/kg whole weight) of tetra- and penta- PCDDs/PCDFs in partially defatted cows' milk composite samples from six Canadian cities.

Sample No	City	% Lipid	1278. TCDF	2378- TCDF	2378- TCDD	23478- PnCDF	12378 PnCDD	TEQª
1	Ottawa	1.45	. 08	.08	ND(.01) ^b	ND(.02)	ND(.02)	.008
2	Halifax	1.52	.81	1.0	.039	ND(.02)	ND(.02)	. 15
3	Winnipeg	1.85	. 79	1.0	ND(.02)	ND(,02)	ND(02)	. 10
4	Vancouver	1.10	. 27	.45	. 073	. 033	. 025	. 11
5	Montreal	1.45	2.8	2.1	.038	.017	ND(.01)	. 26
6	Toronto	1.62	2.7	2.0	. 052	.023	ND(.01)	. 27
Mean ^c ±SD		1.5 <u>+</u> .25	1.2 <u>+</u> 1.2	1.1 ±.81	.038 <u>+</u> .012	.024 <u>+</u> .007		.15 ±.10

 2378-TCDD toxic equivalents including that from higher chlorinated congeners not listed; ^b non-detected followed by detection limit (ng/kg) in brackets; ^c positive samples only

Organohalogen Compounds 1

1

500