Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans in Cows' Milk Packaged in Plastic-Coated Bleached Paperboard Containers

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Milk products purchased between 1985 and 1988 and packaged in plastic-coated bleached paperboard cartons were analyzed for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Whole and 2% milk samples showed concentrations of 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) on a whole weight basis of about 1.0 pg/g and, in some cases, of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) about 20-fold less. On a TCDD equivalent (TEQ) basis, cream samples (0.3 pg of TEQ/g) contained about twice as much as whole and 2% fat milk samples, which in turn were about double that of skim milk. A number of bleached paper containers from contaminated food samples analyzed positive for TCDF and TCDD at higher concentrations and in similar proportions. This paper is the first to show a difference in the levels of 2,3,7,8-TCDF and 2,3,7,8-TCDD between milk samples from bleached paperboard containers and those from paper or glass containers. Pharmacokinetic considerations of half-lives and known human adipose tissue levels indicate that the consumption of cows' milk products containing TCDF and TCDD at the above levels could significantly contribute to our body burden of these toxic compounds.

INTRODUCTION

In the autumn of 1985 the first indication that the chlorine bleaching used in the pulp and paper industry could be a source of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) arose from analyses of fish samples in the vicinty of paper-manufacturing plants. This work (U.S. Environmental Protection Agency, 1986; Kuehl et al., 1987), referred to as the National Dioxin Study, led to findings of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) in bleached kraft pulp and mill wastewaters. Subsequent work by the EPA begun in 1986 and reported in September 1987 (Amendola et al., 1989), the so-called five mill study, confirmed these first reports and showed the extent of the contamination from the bleaching process. The occurrence of PCDDs and PCDFs from chlorine bleaching in pulp and paper manufacturing has been reported simultaneously from several countries (Clement et al., 1989; Swanson et al., 1988). Typical analyses from many locations showed median levels of 2,3,7,8-TCDF and 2,3,7,8-TCDD in paper samples to be 50 and 5 pg/g [parts per trillion (ppt)], respectively. Sludges contained levels 5–10 times higher and aqueous effluents about 100 times less. The other 2,3,7,8-substituted PCDDs/PCDFs were not reported at these concentrations, although other TCDFs, later identified as mainly the 1,2,7,8-TCDF isomer, were found.

Bleached (whitened) paper products are used to package a great variety of foods, but it was not suspected that small amounts of PCDDs and PCDFs in paper packaging material could readily contaminate a food sample. About this time the Canadian Health Protection Branch was conducting an extensive analytical program of total diet food samples for PCDDs/PCDFs. These samples originated from food samples as purchased in retail stores across the country. In the course of this work we noticed an unusual combination of TCDF responses in cows' milk products packaged in plastic-coated bleached paperboard containers. This paper contains the results of analyses of milk products and their containers for PCDDs/PCDFs which indicate the migration of trace amounts of these toxic compounds from the bleached container into the food.

EXPERIMENTAL PROCEDURES

Sampling. All milk products were purchased from retail stores in five major cities across Canada from 1985 to 1988. Those samples packaged in bleached paperboard containers that had been coated with a thin film of plastic were stored at 5 °C no longer than their expiry date (up to 14 days), transferred to plastic containers, and stored frozen at −20 °C until analyzed. Milk samples used as controls were also purchased in commercial outlets and were packaged in either pliable plastic bags or glass containers and were kept frozen (−20 °C) until analyzed. Most of the samples for analysis contained the milk from four separate brands as a composite sample of equal portions and purchased from separate stores. Milk containers were either 500-mL, 1-L, or 2-L sizes.

Extraction. (*i*) *Milk.* The milk sample (up to 250 mL for whole, 2%, and skim milk; 30–40 mL for cream) was weighed into a tared suitably sized separatory funnel. The internal or quantification standard as a composite mixture was then added to the milk sample to correct for losses of analytes during the extensive extraction and cleanup procedures. This single solution of 25 μL of toluene contained (1) seven carbon-13 labeled PCDDs with 2,3,7,8-substitution, chlorinated from tetra to octa, and (2) seven chlorine-37 and one carbon-13 labeled PCDF, all of which were 2,3,7,8-substituted except 1,2,7,8-TCDF and of homologue from tetra to hepta. The amount added per sample varied for the particular PCDD from 20 to about 300 pg. For the PCDFs, most were added in an amount of about 50 pg.

To the milk sample was then added 5 volumes of glass-distilled acetone–hexane (2:1 v/v) per volume of sample, and the mixture was shaken vigorously manually for 2 min. After phase separation, which readily took place when this large volume of extraction solvent was used, the bottom aqueous layer was drained into a 2-L flask and the upper hexane layer filtered through a toluene-washed paper filter into a 2-L round-bottomed flask. The aqueous layer and suspended solids portion were then returned to the 2-L separatory funnel, 600 mL of hexane was added, and the mixture was shaken vigorously for 2 min. After phase separation, the aqueous layer was removed and the hexane combined with that

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of the first extract. The hexane extracts were concentrated in a rotary evaporatory under reduced pressure to about 75 mL, transferred to a 250-mL separatory funnel, and washed with 30 mL of water to remove residual acetone. The extract was then filtered through a small amount of anhydrous sodium sulfate into a 100-mL volumetric flask and the extract made up to the mark. An aliquot of 5–10 mL of the hexane extract was used to determine the lipid content gravimetrically and the rest made up to about 150 mL with hexane in a 250-mL separatory funnel prior to treatment with concentrated sulfuric acid.

(*ii*) *Cartons, Bleached with or without Plastic Coating.* The board (~5 g) was cut into 1-cm squares and refluxed with 120 mL of acetone–hexane (2:1 v/v) for 1 h by using a water-cooled condenser while stirring with a magnetic bar. After cooling, the mixture was filtered into a 250-mL separatory funnel and the liquid extract washed with 30 mL of water, which was discarded. The hexane extract remaining was made up to 50 mL in a volumetric flask, and an aliquot of 10 mL, corresponding to about 1 g of board, was taken.

Cleanup Procedures. All sample extracts were then purified by an extensive procedure, most of which has been described previously (Ryan et al., 1986a,b). This consisted of (a) lipid degradation by partitioning the hexane extract with concentrated sulfuric acid, (b) chromatography on disposal Florisil columns to remove PCBs, other organochlorine compounds, and residual fat, and (c) separation of the planar PCDDs/PCDFs from nonplanar less adsorbed compounds on disposable columns of carbon dispersed on silica. Some extracts of milk products were also filtered through a minicolumn of cesium silicate and sulfuric acid adsorbed on silica gel (Patterson et al., 1986) that removed some unknown components which, after several injections, interfered on the gas chromatographic (GC) column and coated the ion source of the mass spectrometer (MS). Furthermore, the presence of unknown peaks in the GC–MS originating from the paperboard samples, particularly with polar columns, necessitated additional cleanup of these samples for which an alumina column in tandem with the cesium silicate was used (Patterson et al., 1986).

Measurement and Quantification. For most samples a VG Analytical MS instrument was used, either a ZAB-2F or a 7070 EQ, with electron impact ionization. Varian GCs, either 3700 or Vista 6000, with capillary columns and on-column injectors were coupled directly via heated interfaces to the MSs. Multigroup-selected ion monitoring of appropriate masses at mass resolution of 2K was controlled by a VG 11/250 data system based on a DEC PDP 11/24 computer. For the PCDDs, these ions consisted of the two most abundant molecular ions on the basis of chlorine for the native carbon-12 and the stable isotope carbon-13 isotopomers. For the PCDFs, the ions were the two most abundant molecular ions for the native carbon-12 and the most abundant molecular ion for the chlorine-37 labeled isotopomer. For most analyses, a DB-5 bonded phase capillary column of length 20–30 m, 0.25 mm i.d., 250-μm thickness, was used. About 25% of all samples selected in proportion as to their contribution to the total number were confirmed by using a polar nonbonded cyanopropyl CP-Sil 88 capillary column of length 50 m, 0.25 mm i.d., 200-μm, thickness at high mass resolution (8–10K) with perflurokerosene as reference.

Quantification of the response from the normal and stable isotopic channels of the MS in a sample was carried out by the isotope dilution method using relative response factors (RRF). These were obtained from the MS by using a standard curve constructed from a series of eight calibration standards containing the isotopically labeled PCDDs/PCDFs identical with those in the sample spiking mixture (typically 5 pg/μL) and various concentrations of the normal (nonenriched or natural) PCDDs/PCDFs in the range 0.1–25 pg/μL or higher. These calibration standards contained all 2,3,7,8-substituted PCDDs/PCDFs, the first and last eluting isomers from each homologue group of the PCDD and PCDF, and other congeners readily separated from each other by GC. The relative response ratio for a standard on a daily basis and for unknown samples had to be within 15% of those from the calibration curve. The concentration of any native analyte in an unknown sample was given by

$$\text{concn} = (R_x/R_{is})(Q_{is}/\text{RRf})(1/W)$$

where R_x is the response of any native analyte at any mass, Q_{is} is the amount of quantification standard added at the beginning, R_{is} is its response, RRF is the relative response factor of native analyte x to the isotope used for its quantification, and W is the weight of the sample.

Method Characteristics and Quality Assurance. A combination of the high-resolution GC with both the methyl silicone column (DB-5) and the polar cyanopropyl column along with high mass resolution gave specificity for virtually all the PCDDs/PCDFs and, in particular, the biologically important ones with 2,3,7,8 substitution. Of the 7 possible 2,3,7,8-PCDDs and 10 possible 2,3,7,8-PCDFs with four or more chlorines, 7 and 6, respectively, are often found in biological samples, and these 13 analytes can be separated by using these two GC columns (Ryan et al., 1990). Recoveries of the isotopic standards using 1,3,6,9-TCDD as recovery standard were usually 60–80% except for OCDD, which was 30–40% (incompletely recovered from the carbon column). Samples were usually processed in batches of nine containing a laboratory reagent blank to check for contamination in the sample purification, quality control samples of similar matrix to the unknowns (milk pools and board samples) to verify repeatability, and the unknown samples to be analyzed. Results of analyses (n = 4) of aliquots of a pooled skim milk QC sample showed average values ± SD for 1,2,7,8-, 2,3,7,8-TCDF, and 2,3,7,8-TCDD, respectively of 0.14 ± 0.04, 0.15 ± 0.03 and 0.030 ± 0.004 pg/g. Method blanks, containing all components of the analysis except the unknown sample, showed less than 2 pg total of any TCDD/TCDF congener corresponding to a detection limit for a 250-g milk sample of 0.01 parts per trillion. Detection limits of standards varied from about 0.1 to 1.0 pg depending on the congener. For the carton samples using 1.0-g samples, the detection limit was 2–3 pg/g.

RESULTS

The prominent PCDDs/PCDFs in cows' milk products, particularly those associated with the bleaching process, are 1,2,7,8-TCDF, 2,3,7,8-TCDF, and 2,3,7,8-TCDD. The contents of these three analytes in whole milk, 2% milk, skim milk (defatted or low fat), and 10–12% table cream, are shown in Tables I, II, III, and IV, respectively, along with other samples not packaged in bleached paperboard containers. Also listed are the TCDD equivalents (TEQ) of each sample based on the toxic equivalency factors (TEF) as suggested by an international group (NATO Committee on the Challenge of Modern Society, 1988) in which 2,3,7,8-TCDF is alotted a value of 0.1 times the toxicity of 2,3,7,8-TCDD. 1,2,7,8-TCDF and the other non-2,3,7,8-substituted PCDDs/PCDFs are assigned a value of zero. Samples of both whole and 2% fat milk all contain the 1,2,7,8- and 2,3,7,8-TCDF isomers with levels averaging about 1 pg/g. 2,3,7,8-TCDD is much lower in concentration and could only be detected in about half the samples. Mean TEQ values for both types of milk samples are about 0.15 pg/g. Skim milk samples contain lower levels of all three analytes which, on a TEQ basis, give about half the value of samples with a higher fat content. The six samples of cream all contained the highest levels of contaminants associated with bleaching and averaged about twice the whole and 2% milk values. In all cases average values of 1,2,7,8-TCDF, 2,3,7,8-TCDF, 2,3,7,8-TCDD, and TEQ were substantially higher in milks packaged in paperboard containers than in those from plastic or glass containers.

All samples were also analyzed for the penta- to octa-PCDDs/PCDFs. Small amounts of hexadioxin (up to 0.15 pg/g), heptadioxin (to 0.5 pg/g), and octadioxin (up to 1.0 pg/g) were found in some of these samples including those in containers other than bleached paperboard. In almost all cases these compounds were the 2,3,7,8-substituted congeners and are not believed to be associated with the

Table I. Levels[a] of Selected PCDDs/PCDFs in Whole Milk Samples

no.	origin or type	vol analyzed, mL	1,2,7,8-TCDF	2,3,7,8-TCDF	2,3,7,8-TCDD	TEQ[b]
			Bleached Paperboard Containers			
1	Ottawa	68	ND[c] (0.2)	0.40	ND (0.1)	0.040
2	Ottawa	125	0.36	0.59	ND (0.02)	0.059
3	Ottawa	180	0.020	0.064	ND (0.01)	ND (0.01)
4	Halifax	220	1.2	1.4	0.052	0.20
5	Ottawa	80	0.59	0.83	0.014	0.10
6	Ottawa	80	0.79	1.2	0.042	0.16
7	Ottawa	80	0.30	0.95	0.056	0.15
8	Winnipeg	188	2.1	2.5	0.028	0.28
9	Quebec	250	0.66	1.5	0.061	0.21
10	Vancouver	200	0.54	0.59	ND (0.03)	0.06
11	Ottawa	250	0.032	0.039	ND (0.01)	ND (0.01)
12	Montreal	250	2.9	2.0	0.036	0.24
13	Toronto	250	1.4	1.0	0.045	0.15
	mean of positives ± SD (number)		0.91 ± 0.87 (12)	1.0 ± 0.71 (13)	0.042 ± 0.015 (8)	0.15 ± 0.08 (11)
			Noncarton Containers			
14	plastic	255	0.04	0.18	ND (0.01)	0.018
15	plastic	250	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)
16	glass	250	ND (0.01)	0.61	ND (0.01)	0.061
17	glass	250	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)
18	glass	250	ND (0.02)	0.073	ND (0.02)	ND (0.02)

[a] Picograms per gram whole weight. [b] 2378-TCDD toxic equivalents. [c] Not detected followed by detection limits in parentheses.

Table II. Levels[a] of Selected PCDDs/PCDFs in 2% Milk Samples

no.	origin or type	vol analyzed, mL	1,2,7,8-TCDF	2,3,7,8-TCDF	2,3,7,8-TCDD	TEQ[b]
			Bleached Paperboard Containers			
1	Ottawa	125	0.64	0.84	0.050	0.13
2	Ottawa	196	0.08	0.08	ND[c] (0.01)	ND (0.01)
3	Halifax	207	0.81	1.0	0.039	0.14
4	Winnipeg	168	0.79	1.0	ND (0.01)	0.10
5	Vancouver	196	0.27	0.45	0.023	0.07
6	Ottawa	250	0.030	0.033	ND (0.01)	ND (0.01)
7	Montreal	250	2.8	2.1	0.038	0.25
8	Toronto	250	2.7	2.0	0.052	0.25
	mean of positives ± SD (number)		1.0 ± 1.1 (8)	0.94 ± 0.78 (8)	0.040 ± 0.012 (5)	0.16 ± 0.08 (6)
			Noncarton Containers			
9	glass	68	ND (0.1)	ND (0.1)	ND (0.1)	ND (0.1)
10	plastic	150	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)
11	plastic	240	ND (0.01)	ND (0.02)	ND (0.01)	ND (0.02)

[a] See Table I footnotes.

Table III. Levels[a] of Selected PCDDs/PCDFs in Skim (Defatted) Milk Samples

no.	origin or type	vol analzyed, mL	1,2,7,8-TCDF	2,3,7,8-TCDF	2,3,7,8-TCDD	TEQ[b]
			Bleached Paperboard Containers			
1	Ottawa	145	0.11	0.15	ND[c] (0.02)	0.015
2	Halifax	218	0.76	0.50	ND (0.01)	0.050
3	Winnipeg	230	0.70	0.68	ND (0.01)	0.068
4	Vancouver	200	0.21	0.16	ND (0.02)	0.016
5	Ottawa	250	0.13	0.13	0.032	0.045
6	Montreal	250	2.2	1.4	0.024	0.16
7	Toronto	250	2.0	1.0	0.030	0.13
	mean of positives ± SD (number)		0.87 ± 0.88 (7)	0.57 ± 0.49 (7)	0.029 ± 0.004 (3)	0.069 ± 0.056 (7)
			Noncarton Containers			
8	plastic	250	ND (0.01)	ND (0.01)	ND (0.01)	ND (0.01)
9	plastic	250	ND (0.01)	ND (0.01)	ND (0.01)	ND (0.01)

[a] See Table I footnotes.

bleaching process. Other PCDDs and PCDFs of homologue penta- to octa- and non-2,3,7,8-substituted (e.g., 1,2,4,7,8-PnCDD and 1,2,3,6,7,9-HxCDD), have been found in marine species from the vicinity of pulp and paper mills. These additional compounds were not present in the milk samples packaged in bleached paperboard carton containers.

The results of Tables I–IV show a wide variability in the levels of PCDDs/PCDFs associated with milk in the bleached containers. Some milk in paperboard containers contained little or none of these contaminants. This probably reflects the known wide variability of the 2,3,7,8-TCDF/TCDD content of bleached pulp (Amendola et al., 1989) and milk cartons prepared from it (J. Ryan, unpublished observations). On the other hand, milk samples in nonpaperboard containers did not show elevated levels of the two indicative TCDFs. Levels of 2,3,7,8-TCDD were often at or near the detection limit such that the reliability of the TCDD results is lower than those for the TCDFs, where the MS signals were often much

Table IV. Levels[a] of Selected PCDDs/PCDFs in Table Cream Samples Packaged in Bleached Paperboard Containers

no.	origin	vol analyzed, mL	1,2,7,8-TCDF	2,3,7,8-TCDF	2,3,7,8-TCDD	TEQ[b]
1	Ottawa	40	0.40	0.68	ND[c] (0.05)	0.068
2	Halifax	40	2.6	3.3	0.10	0.43
3	Winnipeg	40	1.6	2.6	ND (0.05)	0.26
4	Vancouver	50	1.7	1.9	0.050	0.24
5	Montreal	70	3.9	3.2	0.11	0.43
6	Toronto	70	2.4	2.0	0.10	0.30
	mean of positives ± SD (number)		2.1 ± 1.2(6)	2.3 ± 0.98(6)	0.09 ± 0.03 (4)	0.29 ± 0.14(6)

[a] See Table I footnotes.

Table V. Levels[a] of Selected PCDDs/PCDFs in Nondairy Food Products Packaged in Bleached Paperboard Containers

no.	sample type	vol analzyed, mL	1,2,7,8-TCDF	2,3,7,8-TCDF	2,3,7,8-TCDD	TEQ[b]
1	orange juice	240	0.029	0.042	ND[c] (0.01)	ND (0.01)
2	orange juice	250	0.44	0.79	ND (0.02)	0.079
3	lemonade	250	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)
4	apple juice[d]	250	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)
5	lemonade	250	ND (0.07)	ND (0.02)	ND (0.02)	ND (0.02)
6	synthetic creamer	50	ND (0.05)	ND (0.05)	ND (0.05)	ND (0.05)
7	liquid diet	100	ND (0.02)	ND (0.02)	ND (0.02)	ND (0.02)
8	liquid diet	100	ND (0.03)	ND (0.03)	ND (0.03)	ND (0.05)

[a] See Table I footnotes. [d] Aluminum lined.

Table VI. Comparison of PCDD/PCDF Levels[a] in Contaminated Foods and Their Packaging Material

analyte	1,2,7,8-TCDF	2,3,7,8-TCDF	2,3,7,8-TCDD
2% milk	0.81	1.0	0.039
milk carton	10	51	5.8
cream	2.6	3.3	0.10
cream carton	25	107	ND[b] (2)
orange juice	0.44	0.79	ND (0.02)
orange juice carton	23	18	ND (2)

[a] Picograms per gram. [b] Not detected followed by detection limits in parentheses.

stronger. The levels in the milk samples do not appear to depend markedly on the region of the country where the samples were purchased since no trend or indication is evident.

Limited data are available on the PCDD/PCDF content of other nondairy food products also packaged in bleached paperboard containers, and this information is listed in Table V. These samples include fruit juices and drinks, a synthetic nondairy creamer, and two liquid diets used in clinical and nursing institutions. No 2,3,7,8-TCDD was detected (limit of detection 0.01–0.03 ppt) in any of these samples, and in only one sample, orange juice, were low but measurable amounts of 1,2,7,8- and 2,3,7,8-TCDF found. This limited information suggests less contamination of these products associated with bleached paperboard containers.

In some cases, the carton used to package the food sample that showed positive for TCDF/TCDDs was available for analyses. Because of the smaller sample size used when paperboard samples for these compounds were analyzed, their detection limits are higher. Nevertheless, three paperboard cartons from contaminated foods were available for study, and the results of their PCDD/PCDF content along with the associated food sample are shown in Table VI. These results show, as anticipated, a higher level in the cartons than in the food sample. In addition, particularly for the TCDFs, the same isomers present in the food are also present in the board. The analytical values indicate that the level of TCDFs in the board are about 10–50 times higher than in the food.

DISCUSSION

This work, reported previously at Dioxin 88 (Ryan et al., 1988), is the first to show that milk products packaged in plastic-coated bleached paperboard cartons contain TCDFs at about 1 pg/g and, in some cases, lower levels of 2,3,7,8-TCDD, and these levels are substantially higher than those in milk samples from plastic or glass containers. Previous analysis of milk samples (Fuerst et al., 1988; Bückert, 1988) by other groups had shown small amounts (less than 1 pg/g) of 2,3,7,8-TCDF in some samples, but its origin was unknown. Other analyses of cows' milk samples (Beck et al., 1988; Rappe et al., 1987) using methodology with low detection limits have failed to report this presence, possibly because the milk samples were collected directly from the manufacturer without being packaged in bleached paperboard cartons. Very high levels of TCDFs (over 100 pg/g) have been reported from a milk composite sample from Ontario (Davies, 1988), but analytical criteria to support this level were lacking and the result could not be repeated by other groups.

It is well established that the chlorine bleaching of pulp to produce an aesthetically pleasing paper material yields similar amounts of 2,3,7,8- and 1,2,7,8-TCDF and smaller levels of 2,3,7,8-TCDD. These analytes collectively produce an analytical pattern for the PCDD/PCDF content that is diagnostic for the bleaching process and is completely different from the PCDD/PCDF pattern associated with incineration (most congeners present in similar concentrations), PCBs (PCDFs only present; many 2,3,7,8-substituted), and other chloroaromatics (specific congeners). In our study the presence of 1,2,7,8-TCDF indicates an adventitious contamination of the milk and not the cow or its feed. If the cow were exposed to these analytes through the food chain, only the 2,3,7,8-substituted congeners would be expected to be detected in the milk after metabolism. In addition, the fact that in all cases where milk samples tested positive for PCDDs/PCDFs measurable levels were readily detected in their cartons strongly suggests the carton as the original source. However, it is not clear how the TCDFs and TCDD could migrate through the plastic moisture barrier into the milk. The lipid content of the sample may be a contributing factor since whole and 2% milk (2–3.5% lipid) have about double the levels of TCDFs and TCDD than skim milk (less than 0.1% lipid) but only about half the level of table cream (about 10% lipid). A GC–MS tracing of the TCDF region from several samples is shown in Figure 1. A skim milk sample from a paperboard carton shows the presence

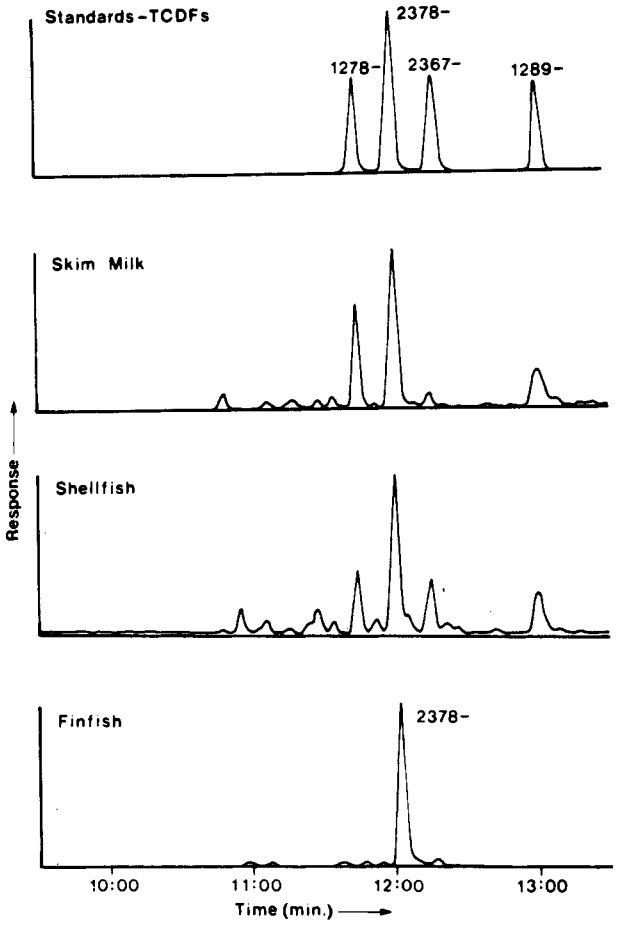

Figure 1. GC–MS tracing of the TCDF region of a skim milk sample packaged in a bleached paperboard container and two marine species taken from the vicinity of a pulp and paper manufacturer.

of both 2,3,7,8- and 1,2,7,8-TCDF along with smaller amounts of other TCDFs. Two marine samples taken from the vicinity of a pulp and paper manufacturer are available for comparison. The shellfish does not appear to metabolize any of the TCDFs and shows a distinctive "bleaching pattern" comparable to that of the milk sample, while the fish sample shows the presence only of 2,3,7,8-TCDF with the other TCDFs presumably excreted or not absorbed.

It has been known for some years that the general human population from industrialized countries contains a variety of PCDDs/PCDFs, all 2,3,7,8-substituted, with the highest concentration in the adipose tissue (Ryan et al., 1985; Stanley et al., 1986). The half-life for elimination of 2,3,7,8-TCDD in human has been reliably measured at about 7 years (Poiger and Schlatter, 1986; Pirkle et al., 1989), while that for 2,3,7,8-TCDF is unknown but, from information on other PCDFs in humans from incidents of rice oil poisonings (Kunita et al., 1984), is less than 7 years and possibly around 2 years. Calculation of the total human body burden of these analytes can be made from the known concentrations in adipose tissue of about 5 and 3 pg/g for TCDD and TCDF, respectively (Ryan et al., 1985). By use of pharmacokinetic considerations of equilibrium and first-order kinetics, for a 70-kg person of 18% lipid, the daily dosing rates to maintain current body levels of TCDD and TCDF would be about 20 and 40 pg of TCDD and TCDF, respectively. Daily consumption of 500 mL of milk containing levels of TCDD and TCDF as described in this paper along with complete absorption would readily equal or, in the case of 2,3,7,8-TCDF, surpass this body burden. In other words, continuous consumption of milk from bleached cartons could easily contribute significantly to the known human body burden of 2,3,7,8-TCDD and 2,3,7,8-TCDF in humans. Over the past year efforts in Canada have been successful in producing paperboard containers and, subsequently, milk packaged therein with nondetectable levels of these compounds.

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LITERATURE CITED

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