# Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans in Canadian Bleached Paperboard Milk Containers (1988–1989) and Their Transfer to Fluid Milk

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Bleached paperboards used for milk cartons were examined for their PCDD/PCDF content. Those manufactured in Canada prior to mid-1989 tested positive for 2,3,7,8-tetrachlorodibenzofuran (TCDF) and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) with levels on a TCDD toxic equivalency (TEQ) basis varying between 1.4 and 55 ng/kg of board. Bleached paperboard produced subsequent to mid-1989 tested negative for these compounds at a limit of detection of 1 ng of TEQ/kg of board. Storage of three types of fluid milk in pre-mid-1989 low- and high-level board cartons resulted in the transfer of the TCDF/TCDD into the milk, most of which occurred in the first 7 days. The transfer varied between 3 and 25%, with whole and 2% fat milk accumulating about double the concentrations of skim milk. On the basis of these results, fluid milk stored for up to 14 days at 5 °C in currently produced bleached paperboard containers with less than 1 ng of TEQ/kg of board would not contain any detectable PCDDs/PCDFs, i.e., less than 0.005 ng of TEQ/kg of fluid milk.

## INTRODUCTION

In 1987 the U.S. Environmental Protection Agency (EPA) (Amendola et al., 1989) documented that the chlorine bleaching of pulp in the kraft process generated certain polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). These PCDDs and PCDFs are now known to consist of approximately equal amounts of 1,2,7,8-tetrachlorodibenzofuran (TCDF) and 2,3,7,8-TCDF and lesser amounts of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). Collectively, the presence and relative distribution of these compounds is diagnostic of PCDDs/PCDFs from chlorine bleaching of pulp and is different from the pattern associated with other sources of PCDDs/PCDFs such as incineration and chlorinated aromatics. Subsequent to this finding by the EPA, Health and Welfare Canada reported in 1988 (Ryan et al., 1988, 1991a) that cows' milk packaged in polyethylene-coated bleached paperboard containers contained higher levels of 1,2,7,8-TCDF, 2,3,7,8-TCDF, and, in some cases, 2,3,7,8-TCDD than those milks packaged in other types of containers such as plastic or glass. This additional concentration of those PCDDs/PCDFs associated with chlorine bleaching was suggested to originate by transfer from the paperboard to the plastic film and then by leaching into the milk itself. However, this supposed route could not be specifically substantiated, nor could the amount and rate of transfer be ascertained. The difference in the PCDD/PCDF content of fluid milk as a function of its packaging has subsequently been noted in a number of countries such as the United States (Glidden et al., 1990; LaFleur et al., 1990), Sweden (Rappe et al., 1990), New Zealand (Buckland et al., 1990), Great Britain (Startin et al., 1990), and Germany (Beck et al., 1990b; Päpke et al., 1990). Some of these groups have addressed briefly the PCDD/PCDF content of the milk as a function of length of storage, fat content of milk, and content of the board. However, most of these studies have not been extensive, are incompletely documented, and have sometimes led to contradictory findings.

For this reason, we decided, in cooperation with the National Dairy Council of Canada and Carleton University, to study the migration of PCDDs/PCDFs from bleached paperboard containers of different PCDD/PCDF content into fluid milk in a controlled experiment using the parameters of time and fat content of milk. At the same time, we evaluated and modified methods to measure PCDDs/PCDFs in board samples. These methods were then used to evaluate the effect of the change in bleaching of the boards during mid-1989 designed to reduce significantly their PCDD/PCDF content. This paper gives the results of the PCDD/PCDF content of boards fabricated by the older and newer technologies and documents the rate and amount of transfer from two boards (high and low PCDD/PCDF content) to three types of fluid milk.

## EXPERIMENTAL PROCEDURES

**Sampling.** (*i*) *Boards.* In Canada all milk carton boards that are formed into milk containers are furnished by two suppliers who obtain their boards from four primary producers (designated A–D). Uncoated boards vary in surface density from about 280 to 330 g/m$^2$ depending on the size of the milk carton to be formulated (200 mL–2 L). Boards were obtained from the two suppliers either uncoated, coated with a thin film of polyethylene, or formulated into flat templates ready for pressing into containers. Boards were obtained prior to mid-1989 from three of four primary producers (A, B, D) using the older bleaching processes (board from supplier C was not available during this period) and from all four producers subsequent to mid-1989 when newer methods of bleaching had been introduced. The quality control (QC) board sample used to test the precision and reliability of the analytical methodology was available from a related study.

Two sets of coated boards, approximately 20 × 30 cm for 500-mL containers, are designated high- and low-level board per their PCDD/PCDF content (cf. below) for the leaching study. When these boards are pressed into 500-mL containers, there is an overlap of the board in making the seals on the side, bottom, and pouring spout, so only about 75% of the original board is in actual contact as a container with the fluid milk. This factor has been used in calculation of percent migration.

(*ii*) *Milks.* Two sets of 500-mL containers made from board of high and low PCDD/PCDF content were filled at a local dairy

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with three types of bulk fluid milk, whole (3.5% fat), partly skimmed or low fat (2% fat), and completely defatted or skim milk (less than 0.1% fat). At the same time 500-mL aliquots of the three bulk milks were filled into clean polycarbonate plastic jars previously analyzed for PCDDs/PCDFs and found to test negative. All milk samples were then transferred from the dairy to the laboratory on the same day. Aliquots of the bulk milk samples were immediately stored frozen at -18 °C, and these are designated as time 0. The milk samples in the 500-mL bleached carton containers were stored at 4–5 °C for 2, 7, 14, and 21 days. At the specified times, the stored milks were poured from the cartons into a 500-mL polycarbonate plastic container and stored frozen at -18 °C until analyzed. The recommended shelf life of fluid milk stored at 4–5 °C is up to 14 days, so that 21 days represents an out-of-date product. QC samples of fluid whole and skim milk used to verify the method performance were purchased randomly at local stores. These samples in 1-L bleached carton containers were stored at 4–5 °C until their expiry date, composited into one large pool of 4 L, aliquoted into 500-mL portions in polycarbonate jars, and stored frozen at -18 °C until analyzed.

**Analyses.** The determination of PCDDs/PCDFs in both milk and board samples has been reported in detail previously (Ryan et al., 1990, 1991a). The only major change from the early procedures was in the extraction of the carton samples, which were processed as follows. The cartons, which were analyzed in several forms such as flat or folded, bleached or not, plastic-coated or not, were cut up with scissors to about 1 cm square pieces. The pieces were placed in a plastic bag and shaken to randomize them. About 5-g aliquots were used for analysis, two 2.5-g portions of which were placed separately in a Waring blender and pulverized or "fluffed" for about 30–45 s to give a product looking like candy floss. The combined fluffed portions were added to a 1-L Erlenmeyer flask with a pouring spout and spiked with the isotopically labeled quantification standards. To the sample was then added 400 mL of aqueous ethanol (1:1 v/v), and the mixture was allowed to soak for 24 h at room temperature with occasional shaking. Then 200 mL of hexane was added and the mixture homogenized for 30–45 s with the mechanical probe. After phase separation, the hexane was decanted from the Erlenmeyer flask with its pouring spout through a toluene-washed filter paper containing a little anhydrous sodium sulfate into a 1-L round-bottom flask. Residual hexane from the extraction vessel was transferred with the aid of a glass pipet. The extraction, homogenization, and transfer were repeated with two more aliquots of 200 mL of hexane. The combined hexane extracts were reduced to about 150 mL on a rotary evaporator under vacuum, transferred to a 250-mL separatory funnel, and washed with a little water prior to extract purification. For comparison, this method was tested simultaneously using the same amount and type of board with two other methods. One was a 2-h reflux and stirring with 2:1 (v/v) acetone/hexane and the other a 20-h Soxhlet extraction with toluene.

Cleanup procedures (lipid degradation), column chromatography (acid–base silica; Florisil and carbon columns), and measurement and quantification with high-resolution (HR) gas chromatography–mass spectrometry (HRGC–MS) have been described (Ryan et al., 1990, 1991a). Recoveries of three of the isotopically labeled internal standards, [$^{37}Cl_4$]-1,2,7,8-TCDF, [$^{37}Cl_4$]-2,3,7,8-TCDF, and [$^{13}C_{12}$]-2,3,7,8-TCDD, from milk samples averaged (±SD; $n$ = 7) 68 ± 10, 78 ± 9.5, and 65 ± 7.7%, respectively. Many of the milk samples in the storage experiments were analyzed in duplicate, and average values are reported.

A combination of high-resolution GC with a methyl silicone column (DB-5) and a polar cyanopropyl phase column (e.g., CP-Sil 88) along with high mass resolution mass spectrometry is usually adequate to specify the isomeric content of a sample extract, particularly for the biologically important 2,3,7,8-substituted congeners (Ryan et al., 1991b). However, as has been documented by Buser et al. (1989), wood and lignin contain high amounts of creosols (alkylalkyoxyphenols) which are converted in significant amounts in the bleaching process to alkylated PCDFs. Dimethyl (or ethyl) TCDF and $^{13}C$-labeled TCDD have the same nominal mass of 332, which can only be mass separated with a resolution of 80 000. On a nonpolar GC column such as a DB-5 (methyl silicone), the alkylated analogues elute later than the TCDDs/TCDFs. However, with a polar column (e.g., cyanopropyl silicone), which is better for PCDD/PCDF isomeric specificity, there is significant overlap in elution times between the two classes of compounds when [$^{13}C$]TCDD ($m/z$ 332, 334) is measured and less when native ($^{12}C$) TCDD ($m/z$ 320, 322) is measured (Charles and Tondeur, 1990). Thus, for sample extracts originating from bleached cartons and milk stored therein, reliance is largely made on the nonpolar GC capillary phases.

**Table I. Repetitive Determinations of PCDDs/PCDFs in Bleached Milk Carton Board/Containers and QC Fluid Milk Samples Stored in Bleached Carton Containers[a]**

| | analyte | | | |
|---|---|---|---|---|
| | 1,2,7,8-TCDF | 2,3,7,8-TCDF | 2,3,7,8-TCDD | TEQ[b] |
| | | Board Samples | | |
| Finnish[c] ($n$ = 4) | 49 ± 9.9 | 41 ± 7.3 | 2.7 ± 0.15 | 6.8 ± 0.81 |
| high level[d] ($n$ = 4) | 130 ± 21 | 140 ± 24 | 8.4 ± 2.1 | 22 ± 1.6 |
| low level[d] ($n$ = 3) | 20 ± 3.2 | 21 ± 0.58 | 5.5 ± 0.75 | 7.7 ± 0.72 |
| | | Milk Samples | | |
| whole[e] ($n$ = 3) | 0.017 ± 0.003 | 0.020 ± 0.006 | ND[f] (0.005) | 0.002 |
| skim[e] ($n$ = 5) | 0.14 ± 0.012 | 0.16 ± 0.023 | 0.033 ± 0.004 | 0.049 |

[a] Average values ± SD in nanograms per kilogram (ppt) of board or whole weight milk. [b] 2,3,7,8-TCDD toxic equivalents based on international toxic equivalency factors (I-TEF) (Kutz et al., 1990). [c] Aliquots of a composite of homogenized 1-L boards (20 × 30 cm) used as QC samples. [d] Individual coated board samples. [e] Aliquots of a composite bulk milk sample. [f] Nondetected (detection limits in parentheses).

## RESULTS

Extracting the pulverized cardboard with toluene in a Soxhlet or refluxing with acetone–hexane (2:1 v/v) produced similar concentrations of PCDDs/PCDFs. Results for two different boards using (a) ethanol soaking/hexane extraction, (b) acetone/hexane stirring, and (c) toluene Soxhlet extraction were 7.1, 6.6, and 6.3 ng of TEQ/kg, respectively, for the first board and for the second board, in which only 2,3,7,8-TCDF was detected, 2.1, 1.5, and 1.6 ng of TEQ/kg, respectively. As the room temperature soaking with aqueous ethanol followed by hexane extraction was simple and analogous swelling and extraction techniques had been used successfully by other groups (LaFleur et al., 1989; Beck et al., 1989, 1990a) for paper analyses, this method was used for all board samples. The precision in the analysis of three types of board samples, a QC carton of Finnish origin and the two cartons used for the migration studies (designated high and low, respectively), is shown in Table I. The typical pattern associated with the bleaching phenomena, i.e., about equal amounts of the two TCDFs and about 5–15 times less of 2,3,7,8-TCDD, is evident from the results. The relative standard deviation (RSD) of the repetitive carton analysis averages 15%.

The results of the board analyses are shown in the first part of Table II (old process) for three of the four producers (A, B, D) (samples of old boards from producer C were not available) and in the second part of Table II for all four producers (new process). Prior to mid-1989, the boards from three of the four producers showed readily measurable levels of the two TCDFs and 2,3,7,8-TCDD associated with the bleaching process. The TEQ method of calculation adds concentrations of only the 2,3,7,8-substituted congeners and assigns relative toxicity factors of 1.0, 0.1, and 0.0, respectively, to 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 1,2,7,8-TCDF (Kutz et al., 1990). On this basis the total concentrations in the board varied greatly between 1.4

**Table II. PCDDs/PCDFs Associated with Chlorine Bleaching in Milk Carton Boards from Canadian Producers up to Mid-1989 (Older Process) and Subsequent to Mid-1989 (New Process)[a]**

| | analyte | | | |
|---|---|---|---|---|
| producer | 1,2,7,8-TCDF | 2,3,7,8-TCDF | 2,3,7,8-TCDD | TEQ |
| | | Old Process | | |
| A | 73 | 59 | 8.4 | 14 |
| A | 33 | 28 | 4.1 | 6.9 |
| A | 8.4 | 7.4 | 0.7 | 1.4 |
| A | 14 | 15 | 1.8 | 3.3 |
| B | 19 | 15 | 14 | 16 |
| D | 130 | 140 | 8.4 | 22 |
| D | 400 | 420 | 13 | 55 |
| | | New Process | | |
| A | 4.1 | 3.1 | ND[b] | ND |
| A | 4.2 | 3.9 | ND | ND |
| A | ND | ND | ND | ND |
| A | ND | ND | ND | ND |
| A | ND | 2.1 | ND | ND |
| A | ND | ND | ND | ND |
| B | 1.5 | 1.2 | ND | ND |
| B | 1.9 | 3.1 | ND | ND |
| C | 13 | 9.4 | 4.8 | 5.7 |
| C | 20 | 21 | 5.5 | 7.7 |
| C | 21 | 19 | 6.5 | 8.4 |
| C | 9.5 | 8.0 | 2.6 | 3.4 |
| D | 2.1 | 2.0 | ND | ND |
| D | ND | ND | ND | ND |
| D | ND | ND | ND | ND |

[a] Values in nanograms per kilogram of board. [b] Not detected at limit of detection of 1 ng/kg.

and 55 ng of TEQ/kg with a geometric mean of 9.8 ng/kg. Subsequent to mid-1989, using newer bleaching processes, three of the four producers showed markedly reduced levels of these contaminants. Except for producer C, all were below the detection limit of 1 ng of TEQ/kg of board (1 ppt)—the practical limit at which board samples are deemed to contain nondetectable concentrations of these contaminants. In a few instances some of these board samples showed the presence of additional PCDD/PCDF congeners. These analytes, such as 1,3,6,8-TCDD, 1,2,3,6,7,9- and 1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin (HxCDD), 1,2,4,6,8,9-hexachlorodibenzofuran (HxCDF), 1,2,3,4,6,7,8- and 1,2,3,4,6,7,9-heptachlorodibenzo-*p*-dioxin (HpCDD), 1,2,3,4,6,7,8- and 1,2,3,4,6,8,9-heptachlorodibenzofuran (HpCDF), and octachlorodibenzo-*p*-dioxin (OCDD), are not related to the bleaching process. Instead, they arise from the use of wood chips treated with chlorophenols, the latter containing specific PCDDs/PCDFs as listed above.

The results of the analyses of the QC whole and skim milk samples used to support method performance are shown in the lower part of Table I. Both milk types showed the presence of the two TCDFs, and only the skim milk QC sample tested positive for a lower concentration of 2,3,7,8-TCDD. In these samples of milk taken randomly from the market in early 1989, skim milk showed higher levels of the PCDDs/PCDFs than did the whole milk. The relative standard deviation of these analyses varied between 5 and 30% depending on analyte, with the greatest variation found for 2,3,7,8-TCDF. This may reflect the occurrence of small amounts of this analyte in some laboratory blanks.

The PCDD/PCDF results of the storage of whole milk, 2% fat milk, and skim milk for 2, 7, 14, and 21 days in both the low- and high-level board containers are given in Table III. As anticipated from previous surveys of milk and board, concentrations of the two TCDFs in the stored milk were higher than 2,3,7,8-TCDD, and the milks stored in the high board showed higher amounts of transfer than those stored in the low board. A very low concentration (ca. 0.01 ng/kg of whole weight) of 2,3,7,8-TCDF was detected at time 0 in whole and 2% fat milk and none in skim milk. In most cases, the most rapid transfer occurs in the first 7 days, with less taking place thereafter. This can be seen graphically on a TEQ basis for 2% fat milk in Figure 1. Even on storage for 21 days, i.e., 7 days beyond the recommended shelf time, the concentrations in the milk samples changed appreciably only in the high-level board. On a TEQ basis after 14 days, milk values varied between 0.007 and 0.036 ng/kg for the low board and between 0.069 and 0.13 ng/kg for the high board. Concentrations of the PCDDs/PCDFs in the whole and 2% fat milks were similar in most cases and about double that for completely defatted (skim) milk.

The percent migration or transfer of 2,3,7,8-TCDF, 2,3,7,8-TCDD, and TEQ from both the high and low 500-mL milk cartons (average weight 18.4 g) could be calculated from the residue levels in the cartons and the milk. Moreover, it is assumed from the geometry of the milk cartons that only 75% of the milk in the container is in actual contact with the original board. These calculated data are given in Table IV for 14 days of storage, i.e., the maximum recommended shelf time. Generally, 2,3,7,8-TCDF is transferred more (11–25%) than 2,3,7,8-TCDD (7.2–19%), and whole and 2% fat milk leach more of these compounds than does skim milk. Small concentrations (1–20 ng/kg) of the higher chlorinated congeners (hexa, hepta, and octa) were detected in both the high- and low-level boards. Fluid milk stored in these two boards did not result in a measurable increase in the milk levels of the higher chlorinated PCDDs/PCDFs.

## DISCUSSION

The PCDD/PCDF content in the milk carton boards supports the original findings in 1987 of the U.S. EPA that chlorine bleaching of pulp generates TCDFs, mainly the 1,2,7,8 and 2,3,7,8 isomers, and lesser amounts of 2,3,7,8-TCDD. Milk cartons produced for Canadian use prior to mid-1989 contained readily measurable amounts of these contaminants, although the variation among the individual samples both within and between producers was large. Subsequent to mid-1989, bleached board from three of the four producers showed nondetectable TEQ (limit of detection 1 ng/kg of board; i.e., 1 ppt). In fact, more recent data from the producer of board C have demonstrated that their boards are now below the limit of detection (LOD) for the above-mentioned analytes characteristic of chlorine bleaching.

Storage of fluid milk in positive-testing board containers results in the migration of bleaching analytes from the board into the milk as originally hypothesized (Ryan et al., 1988, 1991a) and supported independently by other groups in the United States (LaFleur et al., 1990), Sweden (Rappe et al., 1990), New Zealand (Buckland et al., 1990), Great Britain (Startin et al., 1990), and Germany (Beck et al., 1990b). With regard to the rate of migration, most of the above studies, including the present one, have reported that the most rapid transfer occurs soon after contact (within the first 7 days) as shown in Figure 1. Presumably a portion of the analytes in some board containers migrates at a slower rate into the milk even when samples are stored longer than the recommended time of 14 days. Such a change in rate would be predicted from simple laws of diffusion. These results also indicate that TCDF migrates more quickly and in greater amounts than TCDD and both probably more than the higher

**Table III. Effect of Storage on PCDD/PCDF Content of Fluid Milk in Low (7.7 ng of TEQ/kg) and High (22 ng of TEQ/kg) Bleached Board Containers[a]**

| time, days | board: | low | | | | high | | | |
|---|---|---|---|---|---|---|---|---|---|
| | analyte: | 1,2,7,8-TCDF | 2,3,7,8-TCDF | 2,3,7,8-TCDD | TEQ | 1,2,7,8-TCDF | 2,3,7,8-TCDF | 2,3,7,8-TCDD | TEQ |
| | | | | Whole Milk | | | | | |
| 0 | | ND[b] (0.005) | 0.011 | ND (0.003) | ND | ND (0.005) | 0.011 | ND (0.003) | ND |
| 2 | | 0.055 | 0.059 | 0.005 | 0.011 | 0.38 | 0.35 | 0.016 | 0.051 |
| 7 | | 0.11 | 0.12 | 0.016 | 0.028 | 0.62 | 0.56 | 0.040 | 0.096 |
| 14 | | 0.14 | 0.14 | 0.022 | 0.036 | 0.76 | 0.68 | 0.044 | 0.11 |
| 21 | | 0.13 | 0.13 | 0.024 | 0.037 | 1.00 | 1.23 | 0.038 | 0.16 |
| | | | | 2% Fat Milk | | | | | |
| 0 | | ND (0.005) | 0.008 | ND (0.003) | ND | ND (0.005) | 0.008 | ND (0.003) | ND |
| 2 | | 0.059 | 0.093 | 0.013 | 0.022 | 0.39 | 0.37 | 0.040 | 0.077 |
| 7 | | 0.11 | 0.11 | 0.014 | 0.025 | 1.06 | 1.12 | 0.044 | 0.15 |
| 14 | | 0.12 | 0.12 | 0.017 | 0.029 | 0.94 | 1.04 | 0.034 | 0.13 |
| 21 | | 0.12 | 0.13 | 0.024 | 0.037 | 0.95 | 1.13 | 0.068 | 0.18 |
| | | | | Skim Milk | | | | | |
| 0 | | ND (0.005) | ND (0.005) | ND (0.003) | ND | ND (0.005) | ND (0.005) | ND (0.003) | ND |
| 2 | | 0.046 | 0.035 | ND (0.005) | ND | 0.36 | 0.24 | 0.012 | 0.036 |
| 7 | | 0.080 | 0.067 | ND (0.005) | 0.007 | 0.68 | 0.46 | 0.016 | 0.062 |
| 14 | | 0.091 | 0.067 | ND (0.005) | 0.007 | 0.74 | 0.52 | 0.017 | 0.069 |
| 21 | | 0.094 | 0.074 | 0.010 | 0.017 | 0.80 | 0.70 | 0.019 | 0.089 |

[a] 2,3,7,8-TCDD toxic equivalents. Values in nanograms per kilogram of whole weight. [b] Not detected (detection limits in parentheses).

**Table IV. Percent Migration of 2,3,7,8-TCDF, 2,3,7,8-TCDD, and TEQ from Low- and High-Level Bleached Carton Containers into Fluid Cows' Milk After 14 Days of Storage[a]**

| | analyte: | 2,3,7,8-TCDF | | 2,3,7,8-TCDD | | TEQ | |
|---|---|---|---|---|---|---|---|
| | board: | low | high | low | high | low | high |
| | | | Whole Milk | | | | |
| % migration | | 24 | 17 | 15 | 19 | 17 | 19 |
| | | | 2% Fat Milk | | | | |
| % migration | | 20 | 25 | 11 | 15 | 13 | 21 |
| | | | Skim Milk | | | | |
| % migration | | 11 | 13 | ND | 7.2 | 3.1 | 11 |

[a] Based on board weight of 18.4 g, 75% contact of board area to milk, 500-mL milk samples, and residue levels in Tables I (boards) and Table III (milks).

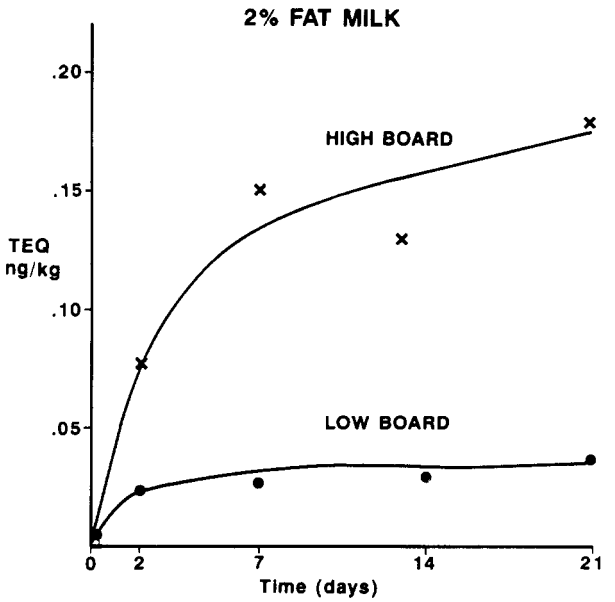


**Figure 1.** Time course of the transfer on storage at 5 °C of 2,3,7,8-TCDD and 2,3,7,8-TCDF expressed as TEQ from a high (22 ng of TEQ/kg) and low (7.7 ng of TEQ/kg) board into 2% fat milk.

chlorinated homologues. In those cases where some of the higher chlorinated 2,3,7,8-substituted PCDDs/PCDFs are present in milk cartons from chlorophenol-treated wood, their transfer into fluid milk does not appear as likely. As such, these results on the differential transfer of congeners agree with three previous studies (Buckland et al., 1990; LaFleur et al., 1990; Päpke et al., 1990). The present study also shows about a 2-fold difference in the percent transfer between whole/2% fat milk, on one hand, and skim milk. Such a finding is corroborated by our previous survey (Ryan et al., 1991b). However, the only other study that addressed in any detail the fat content of milk as a function of migration (Buckland et al., 1990) found transfer, in decreasing order, of cream, partially defatted (1.5%) milk, and whole milk, i.e., somewhat different from that reported here. LaFleur et al. (1990) have examined the migration of PCDDs/PCDFs from bleached paper wrappings in contact with food and concluded that the transfer was greatest for fatty foods. Moreover, in studies of the migration of plasticizers from food wrappings into food, it is believed that the amount of transfer depends on the fat content of the food (D. Page, Health Protection Branch, Ottawa, personal communication), although this has not been specifically demonstrated. For example, transfer of phthalate esters in food grade plastic wrappings is greater in hamburger than in steak.

The percent migrations of the TEQ as listed in Table IV (3–21%) are somewhat higher than those reported in other milk studies. Some of this difference is due to the method of calculation adopted here, where it is assumed that only 75% of the area of the board is in actual contact with the milk when made into the carton. However, even with this calculation difference, the relative transfers reported here are still somewhat higher than those from Germany (Beck et al., 1990b) and the United Kingdom (Startin et al., 1990). Such a difference may reflect the higher concentration of contamination of the board chosen for part of the present study.

In summary, except for one producer (which has subsequently been rectified), bleached board used as milk containers and manufactured in Canada after mid-1989 contained no detectable amounts of TEQ at a LOD of 1 ng of TEQ/kg of board (1 ppt). Fluid milk stored in board containers of two different concentration levels manufactured prior to mid-1989 resulted in the transfer of both 2,3,7,8-TCDF and 2,3,7,8-TCDD into the milk with the precent migration varying between 7 and 25%. At 5 °C

most of the transfer occurred in the first 7 days, with both whole and 2% fat milk accumulating more than completely defatted milk. Assuming a 20% transfer, it can be calculated that fluid milk stored at 5 °C for up to 14 days in the present bleached paperboard containers testing less than 1 ng of TEQ/kg of board should contain no detectable PCDDs/PCDFs, i.e., less than 0.005 ng of TEQ/kg of milk or 5 parts per quadrillion (ppq).

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LITERATURE CITED

Amendola, G.; Barna, D.; Blasser, R.; LaFleur, L.; McBride, A.; Thomas, F.; Tiernan, T.; Whittemore, R. The occurrence and fate of PCDDs and PCDFs in five bleached kraft pulp and paper mills. *Chemosphere* **1989**, *18*, 1181–1188.

Beck, H.; Dross, A.; Eckart, K.; Mathar, W.; Wittkowski, R. PCDDs, PCDFs and related compounds in paper products. *Chemosphere* **1989**, *19*, 655–660.

Beck, H.; Dross, A.; Mathar, W. Interlaboratory study on PCDDs and PCDFs in coffee filter paper. *Chemosphere* **1990a**, *20*, 1307–1312.

Beck, H.; Dross, A.; Mathar, W.; Wittkowski, R. Influence of different regional emissions and cardboard containers in levels of PCDD, PCDF and related compounds in cow milk. *Chemosphere* **1990b**, *21*, 789–798.

Buckland, S. J.; Hannah, D. J.; Taucher, J. A.; Weslon, R. J. The migration of polychlorinated dibenzo-p-dioxins and dibenzofurans into milks and cream from bleached paperboard packaging. Presented at the 10th International Symposium on Chlorinated Dioxins and Related Compounds, Sept 1990; Eco-Informa Press: Bayreuth, Germany; Short Papers, Vol. 3, pp 223–226.

Buser, H. R.; Kjeller, L.-O.; Swanson, S. E.; Rappe, C. Methyl-, polymethyl-, and alkylchlorodibenzofurans identified in pulp mill sludge and sediments. *Environ. Sci. Technol.* **1989**, *23*, 1130–1137.

Charles, M. J.; Tondeur, Y. Choosing between high-resolution mass spectrometry and mass spectrometry/mass spectrometry: Environmental applications. *Environ. Sci. Technol.* **1990**, *24*, 1856–1860.

Glidden, R. M.; Brown, P. J.; Sittig, R. A.; Syverlson, C. N.; Smith, P. V. Determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzofuran in cow's milk. *Chemosphere* **1990**, *20*, 1619–1624.

Kutz, F. W.; Barnes, D. G.; Bottimore, D. P.; Greim, H.; Bretthauer, E. W. The international toxicity equivalency factor (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds. *Chemosphere* **1990**, *20*, 751–757.

LaFleur, L. E.; Ramage, K.; Gillespie, W. J.; Miille, M. J.; Lukemburg, W. J.; Valmores, S. Optimization of extraction procedures for the analysis of TCDD/TCDF in pulp, paper base stocks, and pulp industry solid wastes. *Chemosphere* **1989**, *19*, 643–648.

LaFleur, L.; Bousquet, T.; Ramage, K.; Burnck, B.; Davis, T.; Luksemburg, W.; Peterson, B. Analysis of TCDD and TCDF in the ppq-level in milk and food sources. *Chemosphere* **1990**, *20*, 1657–1662.

Päpke, O.; Ball, M.; Lis, A. Z. Concentration and time dependence of migration of PCDD/PCDF from paperboard cartons into milk. Presented at the 10th International Symposium on Chlorinated Dioxins and Related Compounds, Sept 1990; Eco-Informa Press: Bayreuth, Germany; Short Papers, Vol. 4, pp 365–370.

Rappe, C.; Lindström, G.; Glas, B.; Lundström, K.; Borgström, S. Levels of PCDDs and PCDFs in milk cartons and in commercial milk. *Chemosphere* **1990**, *20*, 1649–1656.

Ryan, J. J.; Panopio, L. G.; Lewis, D. A. Bleaching of pulp and paper as a source of PCDDs and PCDFs in foods. *Abstracts of Papers*, 8th International Symposium on Chlorinated Dioxins and Related Compounds, Aug 1988; University of Umeå: Umeå, Sweden, 1988; Abstract SOU 07.

Ryan, J. J.; Panopio, L. G.; Sun, W.-F.; Shewchuk, C. Measurement of dioxins and furans in milk products and their carton containers. Presented at the 23rd International Dairy Congress, Oct 8–12, 1990, Montreal, Canada; Mutual Press: Ottawa, 1990; Vol. 2, pp 1387–1392.

Ryan, J. J.; Panopio, L. G.; Lewis, D. A.; Weber, D. F. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in cows' milk packaged in plastic-coated bleached paperboard containers. *J. Agric. Food Chem.* **1991a**, *39*, 218–223.

Ryan, J. J.; Conacher, H. B. S.; Panopio, L. G.; Lau, B. P.-Y.; Hardy, J. A.; Masuda, Y. Gas chromatographic separations of all 136 tetra- to octapolychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans on nine different stationary phases. *J. Chromatogr.* **1991b**, *541*, 131–183.

Startin, J. R.; Rose, M.; Wright, C.; Parker, I.; Gilbert, J. Surveillance of British foods for PCDDs and PCDFs. *Chemosphere* **1990**, *20*, 793–798.

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