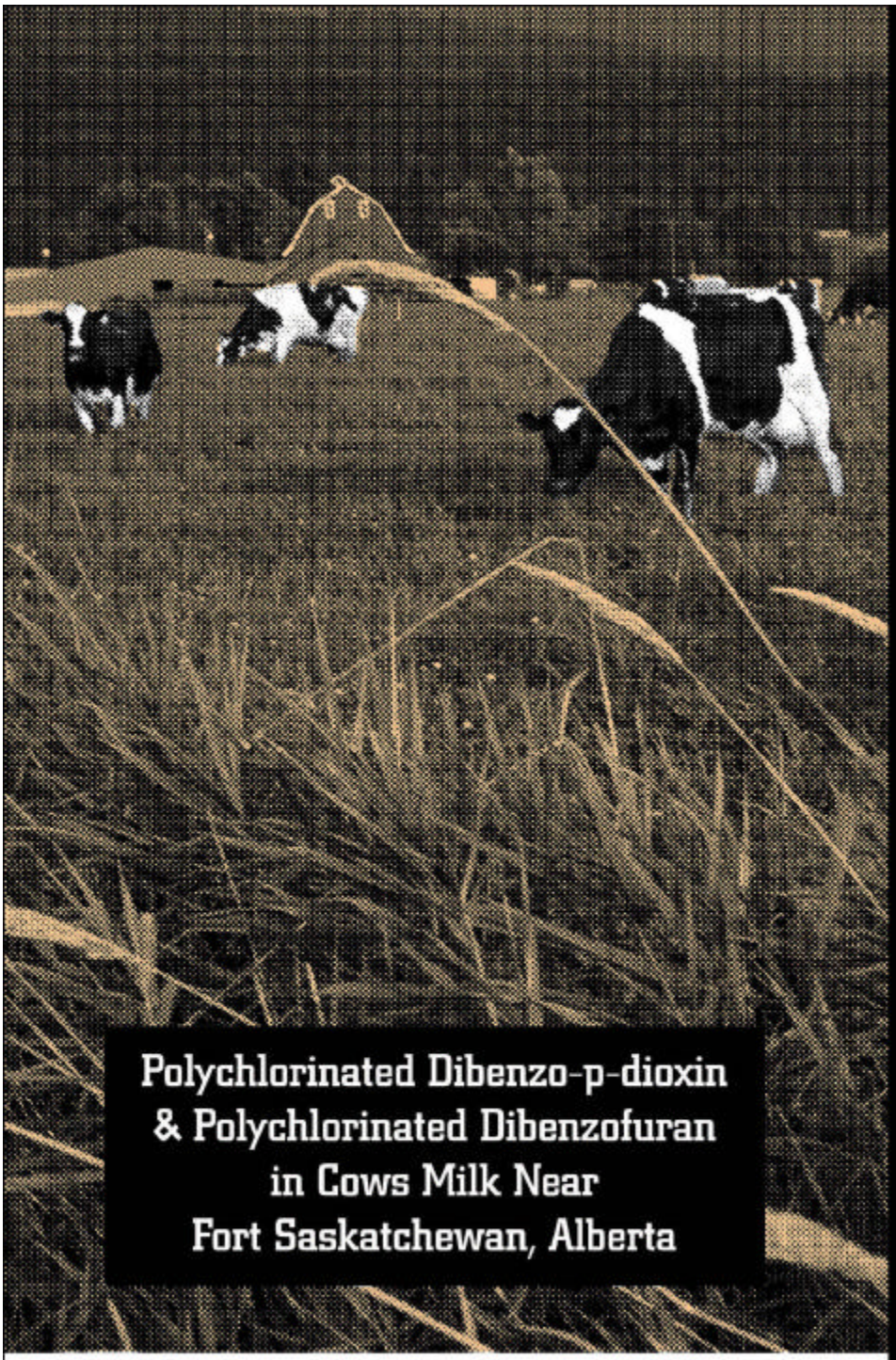

Polychlorinated Dibenzo-p-dioxin & Polychlorinated Dibenzofuran in Cows Milk Near Fort Saskatchewan, Alberta

REPORT

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Introduction

The potential exposure of residents of Ft. Saskatchewan and Dow Chemical employees to polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD/F) has been investigated in previous reports (Hicks, McColl, and Paoli 1997; Hicks and McColl 1995). These investigations employed exposure modeling to estimate the distribution and subsequent potential exposure routes for PCDD/F from the Dow Ft. Saskatchewan EDC/VCM thermal oxidizer units. In the second report (Hicks, McColl, and Paoli 1997), it was conservatively estimated that deposition of PCDD/F on agricultural land could, in a "worst case" scenario, lead to an incremental increase of 38% in human exposure, of which uptake through milk consumption is a significant component. This project was conducted in response to the potential concern of whether human health might be affected by PCDD/F emissions from Ft. Saskatchewan area sources.

In this study, cow's milk from farms which are potentially affected by PCDD/F emissions from various industries in Ft. Saskatchewan, including the Dow Chemical EDC/VCM facility, were sampled and analyzed for PCDD/F. The results were compared with samples from reference farms as well as supermarket milk.

Materials and Methods

Sampling

The initial sampling plan is attached as Appendix I. Some changes have been made during the field collection in terms of availability. The blank samples were supermarket milk from Edmonton. Two samples were obtained from each site. Two laboratory method duplicates were processed (Farms A and C). Two system (sampling + analysis) triplicates were processed (Farms D and E). System duplicates were processed for each farm for the first sampling set.

Four farms within 15 km of the Ft. Saskatchewan industrial area, one of which is a Hutterite farm, were selected for milk sampling. The reference farms are located near Calmar, 20 km south and 30 km east of Edmonton, and near Brooks, approximately 100 km east of Calgary. These reference sites are considered to be sufficiently removed from potential local industrial PCDD/F sources. Alphabetical designations for the farms were used in the sampling procedure, however, in order to avoid confusion with the farms noted in Hicks, McColl and Paoli (1997), the farms were given alphanumeric coding as listed in Table 1. The farms used in this study were not selected with respect to their inclusion in or exclusion from the Hicks et al.'s study.

Table 1 Designation of Farm Identification

Fort Saskatchewan		Reference	
Farm Identification	Sample Identification	Farm Identification	Sample Identification
FS_1	A	R_1	D
FS_2	B	R_2	F
FS_3	C		
FS_4	E		

Laboratory Analysis

All samples were forwarded to the MAXXAM laboratory, in Missisauga, Ontario. The laboratory is accredited by the Standards Council of Canada to ISO Guide 25. All individual samples were analyzed for total tetra- to octo- dioxin and furan homologs, and all 2,3,7,8-substituted tetra- to octo- dioxin and furan isomers. The analytical procedures are presented in Appendix II.

Reported MDLs were corrected for surrogate recovery. MDLs were 0.015 - 0.3 pg/g, whole weight, for PCDD/F congeners. Quality assurance and quality control were maintained by analysis of method blank (lab reagents), spiked blank and sample duplicate every batch of samples. Instrument performance and stability were monitored on a regular basis.

Statistical Analysis

All statistical analyses were done using SPSS for Windows v. 6.1. Method replicates and Farm FS_2 were not included in statistical tests. Sample C210897D was rejected as an outlier and was not included in statistical tests. Significance was set at 0.05 (95% confidence level) for all statistical tests. Non-parametric tests (Wilcoxon Rank Sum Test) were performed. Examination of the lipid determinations for the duplicate samples (marked with suffix D) indicates a high degree of variability. Deviations from the average of the duplicates range from 4.3% to 51%. Thus, the reported statistical analysis has been limited to Toxic Equivalencies (TEQs) values on a whole weight basis (TEQ_{ww}). International Toxic Equivalency factors (NATO-CCMS for dioxin/furan) were used for calculating TEQ values.

Farm FS_2 could not be sampled in a similar manner as all other farms, thus reducing confidence in comparing data from this farm with others in the study. Therefore, sampling at Farm FS_2 was halted after the first sampling week. Additionally, examination of the data from Farm FS_2 suggests that an additional source of PCDD/F is present, which closely resembles PCDD/F contamination from pentachlorophenol (PCP) treated lumber. This may be related to building materials used in the barn or

feed storage facilities. Statistical tests for difference between farms have not included data from Farm FS_2.

The variability in the data do not allow for evaluation of temporal variation in PCDD/F concentration (e.g. due to differences in feed supply) within the time-scale tested in the study. Supermarket milk from Clareview and Manning Crossing was reported as having non-detectable levels of PCDD/F.

Results

Appendix III presents the summary concentrations of TEQ_{ww} values for PCDD/F for the individual samples. The means and ranges of TEQ values are tabulated in Table 2. Non-parametric tests allow the following observations for comparisons between individual farms and groups of farms:

- The TEQ_{ww} are significantly different between the two Hutterite farms (FS_4 and R_2) with FS_4 having the higher concentration of PCDD/F.
- TEQ_{ww} are greater in milk from FS_1 and FS_3 than in milk from R_1 (Calmar) – i.e. non-Hutterite farms.
- The TEQ_{ww} are greater in all Ft. Saskatchewan area farms than non-Ft. Saskatchewan farms.

The observations indicate that cow's milk concentrations of 2378-substituted PCDD/F congeners are greater in the urban/industrial Ft. Saskatchewan area than at the 2 rural reference farms, Calmar and Brooks. However, one should note that the greater concentration of PCDD/F in the Ft. Saskatchewan area vs. the reference farms is normally observed when comparing urban and rural sites.

Table 2 Ranges and Means of TEQ for Each Farm

Farm ID	TEQ_{ww}		TEQ_{ww} - 1/2MDL		TEQ_{ww} - MDL	
	Mean	Range	Mean	Range	Mean	Range
FS_1	0.023	0.016 - 0.03	0.038	0.032 - 0.044	0.053	0.048 - 0.057
FS_3	0.033	0.026 - 0.037	0.048	0.041 - 0.054	0.060	0.057 - 0.064
FS_4	0.019	0.01 - 0.028	0.034	0.029 - 0.040	0.052	0.048 - 0.058
R_1	0.0097	0.0045 - 0.017	0.030	0.026 - 0.036	0.050	0.047 - 0.055
R_2	0.0075	0.0016 - 0.01	0.027	0.023 - 0.029	0.047	0.045 - 0.048

Unit = pg TEQ/g; ww= whole weight; MDL = method detection limit

An estimated daily intake of 0.2 pg TEQ/kg/day was calculated based on the highest TEQ_{ww} - MDL concentration of 0.064 pg/g whole weight, whole milk consumption rate of 214 g/day per person (Conacher *et al.* 1989) and the average body weight of 73 kg.

The estimated daily intake does not exceed the tolerable daily intake of 10 pg/kg/day for TCDD proposed by Health Canada.

Discussion

The TEQ_{ww} represents the total TEQ from only those PCDD/F congeners that were observed above the method detection limits (MDL). However, it is probable that some additional amount of PCDD/F is present but below the congener detection limits. A conservative assumption is made that the potential range of the TEQ_{ww} is from the measured TEQ_{ww} to that calculated by replacing non-detects with the value for the MDL. Mean TEQ_{ww} in Table 2 can be understood as the minimum TEQ_{ww} and TEQ_{ww}-MDL as the maximum or potential TEQ_{ww} which represents a "worst case" scenario. A maximum potential TEQ_{ww} of 0.064 pg/g or 64 pg/kg was determined for FS_3.

Cow's milk PCDD/F concentrations have been tabulated from recent literature (Table 3). The ranges of mean TEQ_{ww} including a maximum potential TEQ_{ww} in this study fall within or below those ranges reported in the literature for cow's milk samples from Europe, USA and Canada. In general, literature values reflect the TEQ-½MDL – i.e. when a congener is listed as not detected, one-half the method detection limit is used in the calculation of the total TEQ for that sample.

Table 3 Concentration Ranges of PCDD/F in Whole Milk from Various Countries

TEQ_{ww}		TEQ_{lipid}			
mean	range	mean	range	Region	Reference
	0.012 - 0.026	0.68	0.42-0.81	Mississippi	Cooper et al. 1995
		1.1		Switzerlan	Schuler et al. 1995
		1.0	0.61 - 1.8	Germany 1994	Fuerst and Wilmers 1995
		0.87	0.69 - 1.1	Bavaria , Germany	Mayer 1995
0.04	0.04 - 0.04			USA	Schecter et al. 1995
0.04	0.018 - 0.061			Canada	Ryan et al. 1991
0.07	0.055 - 0.086	1.8	1.4 - 2.2	Netherlands	Hendriks et al. 1996
			4.1 - 5.0	UK	Harrison et al 1996
			0.7 - 2.5 (bkgd)	Netherlands	Liem et al. 1991
			1.2 - 13.5 (MSW)*		

Unit = pg TEQ/g; * Concentrations near municipal waste incinerators (MSW) in the Netherlands

The "worst case" maximum potential PCDD/F concentrations in milk in the Ft. Saskatchewan area farms were contributed by all sources. In contrast, a "worst case" increment of 0.062 pg TEQ/g estimated by Hicks, McColl, and Paoli (1997) is attributed only to emissions from the Dow EDC/VCM facility. The calculations of incremental

increase in exposure to PCDD/F TEQs were based on the conservative assumptions that the highest potential concentration is attained in the meat and dairy products and that 100% of meat and dairy consumption is from that farm. However, since the conservative total TEQ_{ww} for the Ft. Saskatchewan farms is approximately equal to the estimated incremental TEQ_{ww} as calculated in the modeling study, the conclusion may be drawn that, for the cow's milk, the model data is not supported by measured concentrations.

The daily intake of PCDD/F comes mainly from the diet through commercial food sources, and to a lesser extent, from breathing air and drinking water. The daily intake from background exposure for adult Canadians is estimated to be 2 - 4 pg TEQ/kg/d (Gilman *et al*. 1991). The estimated daily intake in this study indicates that the consumption of whole milk from the Ft. Saskatchewan area, based on lifetime daily consumption, would not exceed the tolerable daily intake for PCDD/F proposed by Health Canada.

Conclusions

A number of conclusions are drawn from the analysis of the PCDD/F data presented above:

1. The range of TEQ_{ww} determined for all farms falls within or below the ranges of cow milk TEQww reported in the literature.
2. PCDD/F TEQ_{ww} concentrations in cow's milk are greater in the farms close to urban sources than in milk from two reference farms in rural areas (Calmar and Brooks). Such a difference is commonly observed when comparing an urban/industrial region with a rural area.
3. The measured concentrations in whole milk do not support the "worst case" incremental estimates from the model study.
4. The estimated daily intake does not exceed the Health Canada Tolerable Daily Intake for PCDD/F.

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Appendix I Sampling Plan and Protocol

A. Milk sampling, Fort Saskatchewan, August 1997

- 4 dairy herds (3 near Fort Saskatchewan, 2 reference herds)

  Sample herds: Hutterite colony
  Farm A
  Farm B
  Farm C
  Reference herds: Hutterite colony (Brooks)
  Farm D (Devon/Leduc area)
  Blank: Supermarket milk (Red Deer): buy in plastic jugs, not paper milk cartons.

- 3 samples, 1 week apart; on Week 1, take duplicate samples at each farm

  - ◆ Samples would be taken from mixed/cooled bulk tank (integrating across all producing cows) at the end of one day (2 milkings: this integrates across the effect of the daily milk production cycle).
  - ◆ Obtain milk from the outflow valve at the bottom of the tank using a cleaned and solvent rinsed 1L glass jar (provided by MAXXAM) to obtain the sample.
  - ◆ Store the sample at 4 ^{o}C until extraction and analysis can take place, but not longer than 4 days.
  - ◆ Freeze sample if necessary.
  - ◆ Samples from one of the potentially affected herds and the reference herd would be analyzed in triplicate in Week 1 samples to establish analytical variability and method quantitation limits.

- Week 1: take 2 x 1.0L samples (sample + duplicate) from each herd including reference herds and Red Deer supermarket blank. Samples should be taken from the well mixed bulk tank after the final milking for one day - i.e. the milk from only two milkings (am + pm) in the bulk tank. If the tank has not been mixing when technician arrives to take samples, turn on mixer for at least 15 minutes prior to sampling.

  Total samples for Week 1 = 14.

- Week 2: take 1 x 1.0L samples from each herd including reference herds and Red Deer blank.

  Total samples for Week 2 = 7.

- Week 3: take 1 x 1.0L samples from each herd including reference herds and Red Deer blank.
  Total samples for Week 3 = 7.

- At least one sample from the sample herds and one from the reference herds should be subsampled/analyzed in triplicate in the laboratory.

- Questionnaire for sampling farms and reference farms: include the following questions:
  - ◆ source of feed - local (same farm), local commercial, external sources (provide supplier name)
  - ◆ # of cows currently milked.
  - ◆ # of cows in their first milk cycle.
  - ◆ where milk shipped.
  - ◆ how much milk used by farmer/family.

B. Sampling Protocol

1. Supplies needed:
   - ultra clean collection containers (1 L glass bottles, wide mouth, supplied by MAXXAM);
   - latex gloves;
   - label marker;
   - hardbound notebook;
   - clean pail (e.g. 4L ice cream pail should suffice)
   - cooler and cold-packs
   - labels for samples
   - aluminum foil (optional)

2. Timing of milk collection.
   - Ensure that milk can be collected at such a time that the bulk tank contains a morning and evening milking.

3. Arrival at farm.
   - Ensure that 2 complete milkings are in the bulk tank.
   - Turn on the tank homogenizer, if it is not already on.
   - Let the tank mix for at least 15 minutes.

4. Fill out questionnaire.
   - While tank is mixing, work with dairy operator to fill out the questionnaire.

5. Obtaining the sample:
   - After tank has mixed for at least 15 minutes, locate outflow valve on bulk tank

(should be at one end at the bottom of the tank).
- Put on a fresh pair of latex gloves.
- Fill the clean pail once with milk to purge the valve. Set the pail aside for now.
- Uncap the bottles just before filling, recap immediately afterwards. If possible, don't set the cap down at all. If that's impractical, set it open side up on a clean surface such as the notebook or a clean piece of aluminum foil.
- Fill the required number of 1 L sample bottles,. (i.e. 2 at each farm for Week 1, labeling the 2nd bottle as the duplicate sample. The exception to this in Week 1 will be Farm H at which 4 bottles will be filled (to obtain enough volume for first triplicate sample) - in this case, label the first 3 bottles the same, and the 4th as the duplicate.)
- only after the required number of sample bottles have been filled, capped and labeled, pour the pail of milk back into the tank (there should be a lid on the top). It may be prudent to ask the diary operator if he/she wants the milk back in the tank - they may have reasons for not wanting it to go back in.

6. Labeling and transporting the samples.
   - Samples should be labeled clearly with water-proof ink. Large sticky labels (e.g. Avery) work well. Include Farm i.d., date, and sample code, sampler's initials. The sample code could be, for example, Farm i.d. - date - duplicate (e.g. H-130897 and H-130897-d).
   - Duplicate the label in the hardbound notebook and add any comments to the notebook, particularly if anything unusual occurred during sampling.
   - pack the samples into the cooler in such a way so that they will not break or leak.
   - Deliver to MAXXAM in Edmonton ASAP.
   - At MAXXAM, you should obtain a receipt for the samples you drop off. This should be part of their Chain-of-Custody procedure. Staple receipts into the hardbound notebook.
   - If sending samples from Brooks, staple the courier way-bill into the notebook. MAXXAM will send the receipt copy to Alberta Health. (Confirm with Susan Shaw). Send via same-day service from Brooks.

7. Trouble Shooting
   - Things don't always go according to plan, but don't panic if things aren't happening perfectly. Do the best you can according to the circumstances, and WRITE IT DOWN. If we have complete documentation, we have options available to us regarding data interpretation.
   - Take extra sample bottles and gloves along on each sample collection trip. Glass bottles break or can get contaminated. Don't use a bottle if anything other than milk goes into the opening. MAXXAM should provide a few extra bottles.

Appendix II Laboratory Analytical Procedures

All individual samples were analyzed for total di- to deca-PCB homologs, 44 PCB isomers, total tetra- to octo- dioxin and furan homologs, and all 2,3,7,8-substituted tetra- to octo- dioxin and furan isomers. The results for PCBs are not presented in this report.

Each sample was homogenized and a known weight was subsampled for analysis. Prior to the initial extraction, samples were fortified with fifteen $^{13}C_{12}$-labeled PCDD/F with exception of OCDF and eight $^{13}C_{12}$-labeled PCBs (IUPAC nos. 31, 52, 118, 153, 180, 194, 206 and 209). These internal standards represent each of the PCDD, PCDF and PCB homologs. Samples were digested overnight in 200 ml of concentrated hydrochloric acid and then extracted with 30 ml of 50:50 Dichloromethane/Hexane by tumbling in a roto-rack for one hour. Acetone was added to break up the emulsions. This extraction was repeated twice more. Extracts were dried over sodium sulphate and then concentrated to 1 ml and transferred with solvent rinsing to a clean glass bottle. Lipid content was determined gravimetrically from the remaining extract. The extracts were subjected to an acid/base silica cleanup, reconcentrated and split into two equal portions by weight. One portion, for PCDD/F analysis, was cleaned up on alumina following the standard operating procedure for dioxins/furans. The PCB portion was cleaned up on a modified alumina column. The cleaned fractions were concentrated to approximately 200 µl for PCBs and 20 µl for PCDD/Fs. Performance standards were added to the cleaned-up extracts immediately prior to sample injection. Extracts were analyzed separately for PCBs and PCDD/Fs on an Autospec Ultima High Resolution Mass Spectrometer, interfaced with a Hewlett Packard Gas Chromatograph. Fused silica capillary columns (60 meter, 0.25 mm ID, 0.25 µm film thickness) were used for determining PCDD/Fs and PCB congeners. Injector temperature was 265 ^{o}C. The GC temperature program was as follows: initial temp 80 ^{o}C, hold 1 min; ramp to 205 ^{o}C @ 40 ^{o}C/min; ramp to 220 ^{o}C @ 3 ^{o}C/min, hold 16 min; ramp to final temp of 310 ^{o}C @ 15 ^{o}C/min, hold 15 min. The total time of the GC run was 50 min. Congeners were detected in the selected ion monitoring (SIM) mode. Concentrations were quantified from the peak area of all the homologos and individual congeners to that of the corresponding internal standards. Method detection limits (MDLs) were defined as three times the background noise in the surrogate peak area.

Appendix III Summary Concentrations for the Individual Samples

Lab Identification	Lipid Content (%)	TEQ_{ww}- MDL (pg/g)	TEQ_{ww}- 1/2MDL (pg/g)
8009-300A-210897	2.4	0.0574	0.05465
8009-301A-210897D	2.2	0.0526	0.03755
8009-302B-210897	2.9	0.0582	0.04370
8009-303B-210897D	1.9	0.0989	0.09066
8009-304C-210897	4.6	0.0601	0.04860
8009-305C-210897D	1.5	0.0690	0.05375
8009-306E-210897	3.4	0.0478	0.03180
8009-307E-210897D	2.5	0.0575	0.04257
8009-308E-210897	2.8	0.0479	0.02915
8009-309E-210897D	1.2	0.0481	0.02910
8009-310D-220897	1.5	0.0515	0.03250
8009-311E-220897D	1.3	0.0549	0.03590
8009-312A-270897	2.1	0.0484	0.03240
8009-313C-270897	2.5	0.0565	0.04125
8009-314E-270897	1.3	0.0535	0.03900
8009-315D270897	2.2	0.0488	0.02905
8009-316D-280897	2.5	0.0507	0.03020
8009-317D-280897	2.3	0.0496	0.02910
8009-318C-040997	2.9	0.0638	0.04930
8009-319CE040997	2.5	0.0544	0.03990
8009-320D110997	2.7	0.0472	0.02595
8009-321D-050997	0.73	0.0474	0.02615
8009-322F290897	2.4	0.0484	0.02940
8009-323F-290897D	3.5	0.0480	0.02900
8009-324F-040997	3.0	0.0446	0.02310
8009-325F100997	3.1	0.0450	0.02650
8009-326Y-190997	3.0	0.0433	0.02165
8009-327Z-190997	1.8	0.0433	0.02165