Assessing the Risks from 2,3,7,8 TCDF in Milk Packaged in Paper

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ABSTRACT

PCDD and PCDF measurements were made on selected retail milk products including paper packaged milk samples covering all known paper carton suppliers in the state of California. Significant levels of 2,3,7,8 TCDF were found in the paper packaged milk in all brands investigated except one. All other 2,3,7,8 substituted PCDFs and PCDDs were either not detected or detected at very low levels. Two *non 2,3,7,8 substituted TCDFs were consistently detected in the contaminated milk samples. Using the mean concentration of 2,3,7,8* TCDF detected and assuming a 240 ml daily consumption of milk for an adult, we estimated that the milk represented a doubling of the daily TCDD equivalent exposure based on the CA TEF, but only a 10% increase using the International TEF. The lifetime cancer risk was calculated to be $218/10^6$ (CA TEF) and $22/10^6$ (ITEF).

INTRODUCTION

Dioxin and furan isomers are often detected in bleached pulps, but those most frequently detected and consistently at the highest levels are the 2,3,7,8 TCDD, 2,3,7,8 TCDF and 1,2,7,8 TCDF[1,2]. *Usually 2,3,7,8 TCDF is at about 5-10 times higher concentration than 2,3,7,8* TCDD[1,3]. Products made using bleached paper may present a source of exposure to people using them. In the past two years we have been investigating dioxin and furan contamination of farm animals in Oroville California[3,4]. During the course of our investigation milk from a cow raised in Oroville was sampled along with commercially produced milk sold in two areas in California. The analysis of the commercial milk revealed surprisingly elevated levels of 2,3,7,8 TCDF in both commercial milk samples (2,3,7,8 TCDD was not analyzed due to the lack of adequate sensitivity of the method).

We conducted a preliminary investigation of dioxin and furan levels in California commercial milk The questions we wished to address were the following:

- What is the source of the milk contamination?
- How many commercial brands of milk are affected?
- How widespread and variable is the contamination?
- Do the size of the carton and the fat content of the milk affect the levels?
- How much milk in contaminated packaging is consumed in California?

METHODS

Cow's milk packaged in paper and plastic was collected from retail stores in one area of California. A latin squares sampling design was used to economically cover all the variables of interest (container source, size and milk fat content). All samples were collected on the same day with the same or nearly the same shelf pull date. This was necessary to reduce potential variability resulting from the length of time the milk is in contact with the container. Inquiries of milk packaging plant operations suggested that shelf pull dates would correlate well with the filling date of the carton. The sampled milk was immediately brought to the laboratory and the milk transferred to clean glass jars and frozen at -20 degrees Celsius until dioxin and furan analysis could be performed.

We decided to analyze only the milk from the packaged products and did not look at dioxins and furans in the paper for two reasons. First, calculating a hypothetical exposure to people from dioxins in the milk they consume is relatively simple and is likely to be more important than their contact with the container itself. Also, the analytical method for milk is rapid and allows the use of large sample sizes and therefore facilitates high sensitivity and selectivity for PCDDs and PCDFs.

The cow's milk was analyzed by adding carbon 13 labelled 2,3,7,8 substituted PCDDs and PCDFs to usually 150g portions of milk. Following the addition of 150 ml ethanol, the lipophilic components were removed by extraction with 50:50 hexane/ethyl ether. The PCDDs and PCDFs were rapidly purified by a modified procedure based on the method described by Smith and Stalling[5]. The PCDDs and PCDFs were separated and detected using a 60 meter DB-5 capillary column interfaced to a Finnigan 4500 quadrupole mass

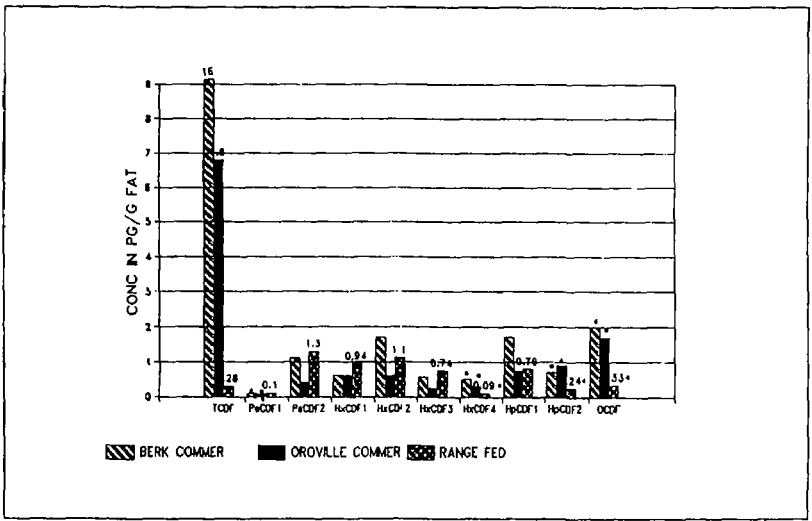

Figure 1 Berkeley commerical and Oroville commerical cow's milk from paper cartons; Oroville range feed cow's milk: note that the detection limits for range fed cow's milk are much lower(41g milk fat analyzed verses 5g for commerical milk).

spectrometer operating in methane negative ion mode.

Risk calculations were performed on the 2,3,7,8 TCDF values by using the unit cancer risk (UCR) derived from an application of the linearized multistaged model to animal bioassay data for 2,3,7,8 TCDD. The UCR employed was 1.56×10^5 $(mg/kg/day)^{-1}$ that is used by the U.S. EPA[6]. We assumed 2,3,7,8 TCDF to be a complete carcinogen with no threshold. There are many uncertainties in applying this procedure but use of the UCR accepted by the U.S. EPA allows comparison with other risk assessments.

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RESULTS

Figure 1 illustrates two typical patterns of 2,3,7,8 substituted chlorofuran isomers seen in contaminated commercial milk contrasted with the quite different pattern seen in the milk from range fed Oroville cows. The commercial milk contains an elevated and easily detected 2,3,7,8 TCDF concentration with a mean level of 0.45 pg/g whole milk (* indicates analytes not detected; values are the detection limits). All other furan isomers are either not detected or detected at much lower amounts. In addition to the elevated levels of 2,3,7,8 TCDF two other TCDF isomers were consistently detected in contaminated commercial milk. They have been identified as the 1,2,7,8 TCDF and the 2,4,6,8 TCDF (Figure 2).

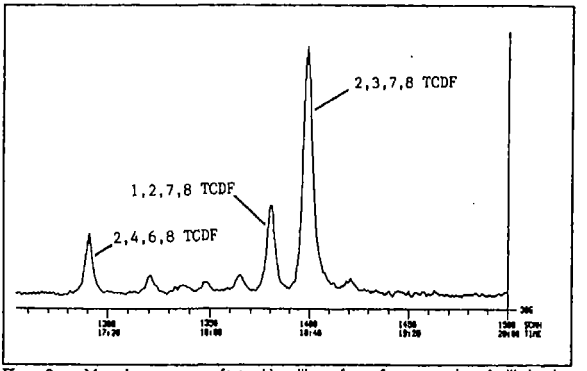

Figure 2 Mass chromatogram of tetrachlorodibenzofurans from contaminated milk showing 2,4,6,8; 1,2,7,8 and 2,3,7,8 TCDF.

The strongest predictor of 2,3,7,8 TCDF concentration was the source of the paper. The 2,3,7,8 TCDF concentrations demonstrated the widest range in the most contaminated samples (table). All paper container sources demonstrated detectable levels of 2,3,7,8 TCDF in the milk with the exception of Paper Company C. For companies A and B size of the paper container had little affect on the observed concentrations and milk packaged in plastic was always uncontaminated.

The risk calculations for exposure to 2,3,7,8 TCDF in milk packaged in contaminated paper require the acceptance of several simplifying assumptions. The ones used here are as follows:

1) Assume a 70 kg individual will consume 240g milk per day for 70 years.
2) Assume 90% of the TCDF is absorbed[7].
3) Assume that all milk consumed is packaged in contaminated paper with a mean concentration for 2,3,7,8 TCDF = 0.45 pg/g whole milk.
4) Assume humans are as sensitive to the carcinogenic risk as animals.

Using the California TEF, which weights 2,3,7,8 TCDF the same as 2,3,7,8 TCDD, the lifetime cancer risk is 218 excess cases in one million exposed people. Using the International TEF for 2,3,7,8 TCDF the risk becomes 22 in one million exposed persons. These estimates reflect the upper limit of the risk. The actual risk could be much less.

DISCUSSION

The elevated levels of 2,3,7,8 TCDF found in most samples compared with all other isomers investigated strongly suggest a bleach paper source for the contamination. This conclusion is further supported by the detection of 1,2,7,8 TCDF in all contaminated samples and lack of contamination in milk packaged in plastic containers. In our risk calculations we assume that a person would only drink contaminated milk, which could be interpreted as an overestimation of the risk. We feel that it is justified, since people consuming may habitually buy milk from a particular store, however this represents a theoretical upper bound risk and there are many uncertainties in the risk assessment model. Accounting for higher milk consumption per body weight in childhood would have increased the risk. In addition inclusion of unmeasured quantities of 2,3,7,8 TCDD in the risk calculation would have resulted in a slightly higher risk estimate. Since two of the three paper suppliers to California produce contaminated products, the chances of large numbers of people

drinking only from contaminated containers is more likely. The assumption we use for daily milk intake, however, is conservative. Using the US FDA estimate of 480 ml/day as an average intake would double the estimated risk[8].

Based on our estimates the potential daily exposure of a person to 2,3,7,8 TCDF from milk is between 10 and 100% of the daily exposure that has been estimated by other investigators from all PCDD and PCDF isomers and all sources[9,10]. Elimination of this source of exposure is practical because it is easily identified and paper suppliers can produce economically competitive bleached paper that will result in very low or nondetectable 2,3,7,8 TCDF levels in the packaged milk product.

TABLE 1

LEVELS OF 2,3,7,8 TCDF IN COW'S MILK, PG/G FAT BY PAPER MANUFACTURER AND CONTAINER SIZE

CONTAINER SOURCE	COMPANY A	COMPANY B	COMPANY C	UNKNOWN PLASTIC
SIZE				
1/2 PT. PAPER	-	-	<0.4	-
1/3 PT. PAPER	38,40+ 16*	3.7	-	-
PINT PAPER	10.3	-	-	-
1/2 GAL. PAPER	6.5	3.2	-	-
GALLON PLASTIC	-	-	-	<0.6

\+ TWO DETERMINATIONS FROM THE SAME MILK CARTON
* DETERMINATION OF MILK FROM A CARTON COLLECTED TWO WEEKS EARLIER

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