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A National Survey of Dioxin-Like Compounds in the United States Milk Supply

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Introduction

The exposure portion of the United States Environmental Protection Agency's (EPA) Dioxin Reassessment has concluded that over 90% of human exposure to dioxin (and related compounds) occurs via food ingestion, primarily meats, dairy products, and fish[1]. Therefore, EPA has undertaken a program to monitor the national food supply for dioxin-like compounds. Surveys have now been completed for beef[2,3], pork[4], and poultry[5]. This paper reports on a national survey for dioxins in milk.

The purpose of this survey was to assess the national prevalence and concentrations of polychlorinated dibenzo-p-dioxins (CDDs), polychlorinated dibenzofurans (CDFs), and dioxin-like polychlorinated biphenyls (dioxin-like PCBs) in the general pasteurized milk supply of the United States. This survey was not designed to be statistically rigorous. That is, it was not the intention to randomly sample a defined population of milk such that the results could be extrapolated back to the nation's total milk supply with a known degree of precision. This milk survey had three primary objectives: 1) to provide a non-statistical estimate of the average concentrations of the dioxin-like compounds in pasteurized milk in the United States milk supply; 2) to assess geographic variability of dioxins in this milk supply; and 3) to assess temporal variability of dioxins in this milk supply.

Study Design

This study utilized the EPA Environmental Radiation Ambient Monitoring System (ERAMS)[6] for collecting milk samples. The overall objectives of ERAMS are to estimate ambient levels of radioactivity in the environment, follow trends in environmental radioactivity levels, and assess the impact of fallout and other intrusions of radioactive materials. In addition to milk, ERAMS has stations which monitor radioactivity in airborne particulates, precipitation, drinking water, and surface water. ERAMS has 51 milk sampling stations in 41 (of 50) US states, and Panama and Puerto Rico. ERAMS stations are located within the major population centers of the 41 states. Individual stations send milk to a central EPA ERAMS facility located in Montgomery, AL. The milk sample from each ERAMS station is a proportional composite from large dairy plants supplying the population centers; that is, the amount of milk obtained from each of the dairy plants contributing to the sample is roughly proportional to the amount of milk the dairy plant supplies to the region. It is estimated that the ERAMS milk samples represent roughly 20% of the US milk supply.

To address the first objective of the study, establishing a representative profile of concentrations of dioxin-like compounds for the U.S. milk supply, milk collected from each ERAMS station was combined to form a grand composite. This composite was always made up of less than 51 samples since some ERAMS stations are unable to collect a sample every month of the year. Make up of the grand composite was proportionally weighted by the volume of milk sold in each reporting area. Composite samples were collected over 4 time periods: April, July, and October of 1996 and January of 1997. Duplicate analyses were performed on each grand composite and the results averaged to generate national estimates of concentrations of the dioxin-like compounds in milk.

In addition to the composite sample each quarter, there were 10 samples from individual ERAMS stations. The 10 quarterly station samples were split into two groups of 5. One of the groups of 5 consisted of unique stations each quarter, leading to a total of 20 unique stations over the course of the survey (5 stations in 4 quarters). These stations were selected to evaluate geographic variability. The other 5 stations were resampled each quarter, so that some temporal variability information from set locations could possibly be gained. In summary, then, there were 25 stations sampled at least once; 20 sampled once and 5 sampled 4 times. The final sample count was 48: 8 grand composite and 40 station samples.

Each sample of milk was preserved with formaldyhyde and sent to the EPA's Environmental Chemistry Laboratory at the Stennis Space Center in Mississippi (the EPA laboratory). The formaldehyde and shipping containers were tested prior to sampling to confirm that they did not significantly contribute to levels of the dioxin-like compounds in milk. Sample analyses were based on a modified AOAC method. Five hundred milliliter sub samples were extracted with hexane after being acidified and denatured by the addition of potassium hydroxide and ethyl alcohol. The hexane extracts were combined, dried over sodium sulfate and the lipid removed by stirring the crude extract with acidified silica gel. The samples were further cleaned up utilizing combined acid/base silica columns, neutral alumina and the PCBs separated from the dioxins/furans using PX21 graphitized carbon columns. The lipid content of each sample was determined using a modified AOAC Mojonnier ether extraction method. Samples were analyzed for fifteen different CDD and CDF congeners, and octa CDD and CDFs (the seventeen compounds which have toxicity equivalency to 2,3,7,8-TCDD) and a set of dioxin-like coplanar PCBs, including PCBs 77, 105, 118, 126, 156, 157, and 169. Samples were stored at 4 °C and

protected from light. Once removed from storage for analysis, the samples were extracted within 24 hours. Following extraction, sample extracts were stored at 4 °C until dioxin analysis. Preliminary method development work determined the target Limits of Quantitation (LOQs); Limits of Detection (LODs) were estimated to be one half of the target LOQs. The final LODs for the CDD/CDFs were, on a lipid basis: 0.04 pg/g lipid for the tetra congeners, 0.12 pg/g lipid for the penta through hepta congeners, and 0.40 pg/g lipid for the octa congeners (based on a 500 ml sample with 2.5% lipids). Final LODs (in pg/g lipid) for the coplanar PCBs were: 1.0 for PCB 77, 16.0 for PCB 118, 8.0 for PCB 105, 0.2 for PCB 126, 5.0 for PCB 156, 1.5 for PCB 157, and 0.1 for PCB 169. Further details on the EPA laboratory procedures for measuring dioxin-like compounds in animal fat matrices, developed during the first of the food surveys, the beef survey, and subsequently applied to the pork and poultry surveys, can be found in Ferrario, et al[7, 8].

Results

For all results, the lipid-adjusted concentrations were converted to the 2,3,7,8-TCDD toxic equivalence (TEQ) using the International-Toxic Equivalence Factor (I-TEFs) scheme[9] for CDD/CDFs and the WHO recommendations for coplanar PCBs[10].

Although there was an expectation that whole milk samples were to be collected, 14 of 40 non-composite samples had lipid contents under 1.5%. At low lipid content, the capability of the methods to measure for the dioxin-like compounds was compromised - the frequency of detection was found to decrease and the lipid-based detection limits increased for these low lipid samples. For these reasons, these 14 samples of low lipid content were not considered further. All 8 composite samples had sufficiently high lipid contents at 2.6% and higher.

Results from this survey are shown in Tables 1 through 4. Table 1 displays the TEQ concentration of each of the composites, as well as a summary of TEQ results comparing the composites and the 26 study samples. Table 2 shows the mean concentrations of the congeners in the 8 composite samples. Table 3 shows the CDD/CDF and PCB TEQ concentrations of the four stations which were sampled four times each. Table 4 shows the CDD/CDF and PCB concentrations for groupings of the 26 station samples as a function of geographic setting in the US and month. Results in Tables 1, 3, and 4 were calculated at ND = ½ DL; TEQ concentrations were lower by no more than 0.02 pg TEQ/g lipid when calculated at ND = 0. Conclusions from these results are:

1) Based on the composite samples, the national average CDD/CDF and PCB TEQ concentrations in milk are 0.82 pg/g lipid and 0.50 pg/g lipid, respectively. Table 1 shows that, as a group, the 26 station samples had similar average TEQ concentrations compared to the composites, but the variation in concentrations measured by the standard deviation and standard error is larger, as might be expected.

2) Tables 3 and 4 show little evidence of a temporal trend for TEQ concentrations. The summer months represented by the July samples may be the time of lowest milk concentrations for both CDD/CDFs and PCBs, but this does not appear to be a strong trend. Table 4 suggests a geographic trend in that CDD/CDF concentrations of milk may be lowest in the Southwest and highest in the Southeast. A weaker geographic trend for PCBs suggests that the highest concentrations may be in the Northwest and the lowest in the Southeast.

3) Results suggest more variability and CDD/CDF TEQ concentrations than in PCB TEQ concentrations. This trend pertains to the station samples rather than the composite samples. As seen in Table 1, the standard deviation is over half the mean for the CDD/CDF TEQ

concentration whereas it is about one-third the mean for the PCB TEQ. Similarly, there is a factor of 8 span in the minimum and maximum CDD/CDF TEQ concentration, while the PCB TEQ concentration spans a range of 4.

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Table 1. Overall comparison of the composite samples with the individual station samples.

Description	Composite	Station Samples
number of samples	8	26
CDD/CDF TEQ, pg/g lipid, average	0.82	0.84
standard deviation, standard error of mean	0.07, 0.02	0.44, 0.09
minimum, maximum pg TEQ/g lipid	0.75, 0.94	0.25, 2.01
PCB TEQ, pg/g lipid, average	0.50	0.43
standard deviation, standard error of mean	0.05, 0.02	0.15, 0.03
minimum, maximum pg TEQ/g lipid	0.42, 0.60	0.18, 0.75

Table 2. Average congener concentrations of 8 composite samples (pg/g lipid; ND=0 in parenthesis).

CDDs	Concentration	CDFs	Concentration	PCBs	Concentration
2378-TCDD	0.07 (0.07)	2378-TCDF	0.08 (0.08)	PCB 77	10.6 (10.6)
12378-PCDD	0.32 (0.32)	12378-PCDF	0.05 (0)	PCB 118	685.3 (685.3)
123478-HxCDD	0.39 (0.39)	23478-PCDF	0.28 (0.28)	PCB 105	170.3 (170.3)
123678-HxCDD	1.87 (1.87)	123478-HxCDF	0.39 (0.39)	PCB 126	3.6 (3.6)
123789-HxCDD	0.55 (0.55)	123678-HxCDF	0.25 (0.25)	PCB 156	60.1 (60.1)
1234678-HpCDD	5.03 (5.03)	123789-HxCDF	0.05 (0)	PCB 157	13.8 (13.8)
OCDD	4.89 (4.89)	234678-HxCDF	0.28 (0.28)	PCB 169	0.5 (0.5)
		1234678-HpCDF	0.83 (0.83)		
		1234789-HpCDF	0.05 (0)		
		OCDF	0.05 (0)		

Table 3. Temporal variation of CDD/CDF and PCB TEQ concentrations from stations sampled more than once (pg TEQ/g lipid; NA = low lipid sample not available; CDD/CDF TEQ listed first).

Station	April, 96	July, 96	October, 96	January, 97
Boston, MA	1.26, 0.43	0.68, 0.42	0.91, 0.64	0.79, 0.48
Wichita, KS	0.36, 0.42	NA	0.64, 0.42	0.35, 0.58
St. Paul, MN	NA	0.74, 0.36	0.92, 0.35	0.59, 0.29
Charleston, SC	1.13, 0.18	NA	NA	0.82, 0.30

Table 4. Temporal and geographical variation of CDD/CDF and PCB TEQ concentrations compiled from clusters of stations (pg TEQ/g lipid; first number in pair is CDD/CDF TEQ; number of stations in parenthesis; NA = low lipid sample not available).

US Quadrant	April, 96	July, 96	October, 96	January, 97	AVERAGE
Northeast	0.94, 0.43 (2)	0.67, 0.44 (2)	0.91, 0.64 (1)	0.79, 0.48 (1)	0.82, 0.48 (6)
Southeast	1.32, 0.29 (2)	0.88, 0.31 (1)	1.64, 0.33 (1)	0.81, 0.31 (2)	1.13, 0.31 (6)
Midwest	NA	0.74, 0.36 (1)	0.92, 0.35 (2)	0.91, 0.47 (2)	0.87, 0.41 (4)
Southwest	0.36, 0.42 (1)	0.25, 0.32 (1)	0.64, 0.42 (1)	0.79, 0.50 (2)	0.51, 0.37 (5)
Northwest	0.32, 0.49 (2)	NA	0.87, 0.72 (1)	1.23, 0.50 (2)	0.80, 0.54 (5)
AVERAGE	0.74, 0.41 (7)	0.64, 0.37 (5)	1.00, 0.49 (5)	0.92, 0.45 (9)	0.78, 0.43 (26)