



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

OFFICE OF  
PESTICIDES AND TOXIC  
SUBSTANCES

May 19, 1998

**MEMORANDUM**

SUBJECT: Chlorpyrifos. Case 0100. PC Code 059101. Results of the National Food Survey Conducted in 1993-1994. MRID 43721601. DP Barcode: D217707, D242445.

FROM: Leung Cheng, Chemist *Lee Cheng*  
Chemistry & Exposure Branch 1  
Health Effects Division (7509C)

THROUGH: Francis Suhre, Branch Senior Scientist *Francis B. Suhre*  
Chemistry & Exposure Branch 1  
Health Effects Division (7509C)

TO: Mary Rust  
Risk Characterization & Analysis Branch  
Health Effects Division (7509C)

DowElanco (now Dow AgroSciences) initiated a market basket survey in 1993 to better determine the acute dietary exposure of chlorpyrifos to consumers. The survey was conducted at the registrant's own initiative. A study protocol had previously been submitted and was reviewed by CBRS with few comments (M. Clifford & S. Knizner, 4/8/94).

*Sampling Design*

Samples of fresh apple, applesauce, apple juice, orange juice, peanut butter, whole milk, ground beef and pork sausage were collected from grocery stores located in the 48 contiguous states in a year-long period; for fresh tomatoes, sampling was conducted in Florida only over a period of 9 months, because the use of chlorpyrifos was restricted to Florida at the time of sampling. The 9 food items were selected because of their significant contributions in the dietary exposure in general and in infants and children, and the potential of high residues based on modes of application (therefore excluding seed treatment of beans, dormant use, use in food handling establishments), and the percentage of the crops that are treated with this insecticide.

The collection of food items was conducted at the retail level and the retail outlets were selected using a national database (1991) containing more than 95,000 supermarkets, superettes and convenience stores. Convenience stores were not included since they are not consistent in the food items they provide and their contribution to the total volume of sales was only 7%. The variables used in the stratification of the store population are: Census Region (North East, North Central, West, South, same regions that EPA and USDA have compiled consumption pattern data), sales volume (ACV category or all commodity volume of sales - a measure of the annual sales of a retail store), geographical areas (specific states or group of states in the 4 regions), and degree of urbanization (largest metropolitan areas, counties with various specified population levels). The survey was designed to be self-weighting with respect to ACV since each store's chance of being selected is proportional to its volume of sales (that is, the allocation of the total sample size would be proportional to the distribution of the total ACV over all strata). In the case of tomato, sampling was restricted to Florida, and therefore only ACV and urban-rural nature of the community were considered.

The size of the samples collected for each food item was derived from a predetermined error of 0.01 ppm and the standard deviations from the controlled field trials of apple, orange, and tomato, and the California state monitoring data, using the formula  $A_o = sd/\sqrt{n}$  (where  $A_o$  is the error,  $sd$  is the standard deviation, and  $n$  is the number of samples). The number of fresh tomato samples collected (54) was reduced by roughly 75% because use of chlorpyrifos on tomato was restricted to Florida in 1993 and because of the harvesting period (typically October through June).

The sample of 200 stores was assigned to the individual collection periods (one of the 25 sampling dates) and divided equal-sized among the variables. For tomato, the sample of 54 stores was divided into 3 subsamples of 18 sampling dates.

### *Survey Information*

Collection of food samples started on 11/29/93 and continued approximately every two weeks through 11/7/94, except during Thanksgiving week and during Christmas holiday season. Mondays were scheduled as the primary day for sampling since survey results of grocery stores indicated restocking on Sunday night and Monday morning. When a holiday occurred on a Monday, shopping was scheduled for Tuesday. For all food items (except apple and tomato), duplicate samples were collected. One sample was used to analyze chlorpyrifos residues, and the backup sample was available for repeat analysis.

According to the original protocol and the Field Phase Report of 7/12/95, six instead of four fresh apples of the same type from the same produce bin were selected. The apples were picked at random from different areas in the bin and were without bruises, blemishes, or breaks in the skin. Apples labeled "organic" or "organically grown" were not selected. For applesauce, two jars (24 to 26 oz size) of the same brand and from the same lot were purchased; these were not from "organically grown" or "organic" in nature. For apple juice,

two 64-oz bottles not labeled "organically grown" or "organic" were purchased. Four firm tomatoes from the same bin, without blemishes, breaks in the skin, or bruises were collected. Two packages of ground beef at about a pound each were purchased; the fat content in the meat was in the range of 15 to 30%. Whole milk containing 1%, 2% or 2½% fat was purchased. Two 16 to 64 oz cartons instead of half-gallon containers of ready-to-drink 100% orange juice (not "orange drink") from the same lot were purchased. Two jars of smooth peanut butter from the same lot were purchased. Two one-pound packages of ground mild sausage (not link or brown-and-serve type) were purchased. The 7/12/95 Field Phase Report also stated some other minor deviations and difficulties but none were serious enough to affect the outcome of the survey.

All samples were received at the DowElanco laboratories on the day following purchase from the grocery store. Samples of fresh apple, orange juice, ground beef, whole milk, pork sausage and fresh tomato were received chilled; samples of applesauce, apple juice and peanut butter were received at ambient temperature. Preparation of the bulk samples and transfer to long term frozen storage were completed within 3 days of receipt. The majority of the bulk samples required no preparation beyond transfer to glass jars with or without plastic coating with Teflon®-lined screw cap lids (apple juice, orange juice, whole milk) or foil-lined lids (apple, tomato, ground beef, pork sausage). All samples were stored refrigerated (3 C) or frozen (-20 C) prior to residue analysis at the DowElanco North American Environmental Chemistry Laboratory, Indianapolis, Indiana. All analyses for chlorpyrifos were completed within 140 days after sample collection (12/10/93-1/11/95).

Samples of apple, applesauce, orange juice and tomato were analyzed according to DowElanco ACR 84.4.S3 with slight modification. Aliquots of food samples were extracted/sonicated with acetone, concentrated, and diluted with water. The residue was cleaned up on a C18 solid phase extraction (SPE) column before being dissolved in hexane. Analysis was by capillary GC equipped with flame photometric detection.

Samples of apple juice were analyzed according to DowElanco ACR 79.8.S1 with slight modification. An aliquot was extracted with hexane in the presence of 1% phosphoric acid. After centrifugation, a hexane aliquot was analyzed by capillary GC/FPD.

Samples of ground beef and pork sausage were analyzed according to DowElanco GRM 95.08. Aliquots of finely divided tissues were extracted with 9:1 hexane:*t*-butyl methyl ether. After centrifugation, the sample was chilled to solidify the fat. An aliquot of the liquid was partitioned 3x with acetonitrile and the combined acetonitrile extracts were evaporated to dryness. The residue was dissolved in aqueous acetone, cleaned up on a C18 SPE column eluting with hexane. An aliquot was analyzed by capillary GC/FPD.

Samples of peanut butter were analyzed according to GRM 95.08 except with 1:1 hexane:*t*-butyl methyl ether.

Samples of whole milk were analyzed using DowElanco GRM 95.09. Aliquots were heated briefly at  $\approx 45$  C to liquify any solid fats and then extracted with acetone in the presence of sodium chloride. Following centrifugation, an aliquot was acidified with 1% phosphoric acid and then extracted 2x with hexane. The residues in hexanes were extracted into acetonitrile before analysis on capillary GC/FPD.

### Analytical Results

For each matrix, a target limit of quantitation (LOQ) of 0.01 ppm or 0.005 ppm was defined. With each analytical set, recovery data (see Table 1) were collected at the target LOQ, at  $\frac{1}{2}$  the LOQ, and at levels above the LOQ.

Table 1. Recovery Data for Chlorpyrifos in Selected Food Items\*

	0.00125 ppm	0.0025 ppm	0.005 ppm	0.010 ppm	0.050 ppm	0.10 ppm
Apple		69-122%† (n=6)‡	72-127% (n=18)	71-116% (n=28)		71-120% (n=21)
Applesauce		83-128 † (n=6)	71-114 (n=19)	61-113 (n=26)		60-78 (n=19)
Apple Juice	91-114%† (n=6)	86-129 (n=19)	83-125 (n=29)		81-116% (n=16)	
Orange Juice		66-114† (n=6)	62-119 (n=19)	66-106 (n=27)		63-89 (n=16)
Tomato		76-90† (n=3)	75-107 (n=12)	74-113 (n=21)		73-115 (n=17)
Peanut Butter		61-87† (n=6)	68-106 (n=19)	63-94 (n=26)		64-104 (n=20)
Whole Milk		77-105† (n=6)*	79-133 (n=19)	62-121 (n=26)		81-115 (n=14)
Ground Beef		77-127† (n=6)	80-114 (n=19)	75-115 (n=26)		70-116 (n=13)
Pork Sausage		65-86† (n=6)	71-118 (n=19)	68-120 (n=26)		73-114 (n=14)

\* All controls contained "0.00 ppm" chlorpyrifos. † Recovery sample analyzed to demonstrate ability to detect chlorpyrifos between the LOD and LOQ. ‡ Number of spike samples.

4

The limit of detection (LOD) and LOQ were derived following the established guidelines described in "Principles of Environmental Analysis", *Analytical Chemistry*, 55, 14, 2210-2218 (1983). For each matrix, the LOQ was calculated as the blank plus 10 times the standard deviation, and the LOD the blank plus 3 times the standard deviation. Based on the method recovery data at 0.005 ppm for individual food items (except apple juice which was at 0.0025 ppm), the calculated LOQ's ranged from 0.003 ppm (apple juice) to 0.008 ppm (applesauce); the calculated LOD's ranged from 0.0008 ppm (apple juice) to 0.002 ppm (tomato).

Aside from double entry and replicate or triple sample analysis, the number of samples collected for each food item surveyed were at least the stated 200 or 54: 204 for fresh apple, 207 for applesauce and apple juice, 203 for whole milk and pork sausage, 200 for orange juice, peanut butter and ground pork, and 55 for tomato. Overall, the recovery data at the various spike levels approach the 70-120% range. Representative chromatograms depicting calibration standards, untreated controls, fortified controls, and surveyed food samples are deemed acceptable.

When levels of chlorpyrifos in samples were greater than 0.03 ppm (3 x target LOQ) or greater than 0.015 ppm in apple juice, the concentration in these samples were usually confirmed by mass spectroscopy. The mass spec analysis was conducted along with a standard of similar concentration with the detector set to monitor  $m/z$  314 and 316, two of the major ions. For confirmation, the ion ratio of  $m/z$  314 to 316 of the samples were within 10% of the standard.

All food samples with chlorpyrifos less than the LOQ but greater than or equal to the LOD, were reported as <LOQ. All samples with <LOD chlorpyrifos were reported as non-detects (ND). Results are summarized in Table 2.

5

Table 2. Survey Results of Chlorpyrifos in Selected Food Items

Matrix <sup>a</sup>	% RAC Treated (1992) <sup>b</sup>	LOQ <sup>c</sup> (ppm)	% Samples > LOQ	LOD <sup>c</sup> (ppm)	% Samples < LOQ but > LOD	% Samples < LOD	Maximum Chlorpyrifos (ppm)	Tolerance (ppm)
Fresh Apple	58	0.007	19.5	0.002	14.5	66	0.052	1.5
Applesauce		0.008	0	0.002	2	98	< LOQ	
Apple Juice		0.003	0	0.0008	1	99	< LOQ	
Orange Juice	24	0.007	0.5	0.002	0	99.5	0.015	1.0 (citrus)
Tomato <sup>d</sup>	2	0.005	18.5	0.002	11.1	70.4	0.058	0.5
Peanut Butter <sup>e</sup>	31	0.005	46	0.002	38.5	15.5	0.021	0.2 (peanut)
Whole Milk		0.006	0	0.002	0	100	< LOD	0.01
Ground Beef		0.005	0	0.002	0.5	99.5	< LOQ	0.05 (meat)
Pork Sausage		0.007	0	0.002	0.5	99.5	< LOQ	0.05 (mbpt)

<sup>a</sup> Number of samples analyzed: 200 for apple, applesauce, apple juice, peanut butter, whole milk, ground beef and pork sausage; 195 for orange juice (for lack of ready-to-drink 100% o.j. at the predetermined stores); and 54 for tomato. <sup>b</sup> Percent of raw agricultural commodity treated nationally. <sup>c</sup> Calculated. <sup>d</sup> Collected in Florida only due to regional registration. <sup>e</sup> It is not apparent why the percent of detects (> LOD) is substantially higher than the percent of peanut treated with chlorpyrifos.

6

## CONCLUSIONS AND RECOMMENDATION

For Monte Carlo analysis of chlorpyrifos in acute dietary exposure assessment, the chlorpyrifos levels for the food items surveyed are tabulated in Table 3. We recommend that for samples containing chlorpyrifos at < LOD, half the calculated LOD be assumed, for samples containing < LOQ but > LOD chlorpyrifos, half the calculated LOQ be assumed, and for samples containing > LOQ chlorpyrifos, the reported levels be used. Also, for foods that can be eaten unmixed such as apple and tomato, it is assumed that the amount of chlorpyrifos found in the composite samples all came from a single apple or tomato. Since there were six apples and four tomatoes in the composite samples, the chlorpyrifos level found should be multiplied by a factor of 6 or 4. The latter should be applied to all values > LOD. In the case of samples > LOD but < LOQ, half the LOQ should be multiplied by the factor.

Table 3. Levels of Chlorpyrifos (ppm) in Selected Food Items

Commodity	Samples < LOD	Samples > LOD but < LOQ*	Single Serving Size Factor*	Level used in 1996 DRES
Fresh Apple	0.001	0.0035	6	1.5
Applesauce	0.001	0.004	N/A**	0.047
Apple Juice	0.0004	0.0015	N/A	0.062
Orange Juice	0.001	0.0035	N/A	0.015
Tomato	0.001	0.0025	4	1.0
Peanut Butter	0.001	0.0025	N/A	
Whole Milk	0.001	0.003	N/A	0.01
Ground Beef	0.001	0.0025	N/A	0.05
Pork Sausage	0.001	0.0035	N/A	0.05

\* The reported values should be used for samples bearing chlorpyrifos at > LOQ. \* Applied to samples bearing chlorpyrifos at > LOD. \*\* Not applicable.

cc:RF, Reg Std File, Cheng

RDI:ResChemTeam:5/7/98:ChemSAC:5/13/98:FBSuhre:5/19/98

7509C:CEB-1:LCheng:CM#2:RM805:5/5/98:08:CHLORPYRIFOS/MARKET

7