U.S. Market Basket Study To Determine Residues of the Insecticide Chlorpyrifos

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A market basket study was conducted to measure residues of the insecticide chlorpyrifos in samples of apples, applesauce, apple juice, fresh orange juice, tomatoes, peanut butter, whole milk, ground beef, and pork sausage collected during a 12-month period from 200 grocery stores across the United States. Approximately 90% of the samples contained no detectable levels of chlorpyrifos, and all residues detected were below tolerances, the legal limits for the United States. No values greater than the limit of quantitation (LOQ) were found in applesauce (LOQ = 0.008 ppm), apple juice (LOQ = 0.003 ppm), whole milk (LOQ = 0.006 ppm), ground beef (LOQ = 0.005 ppm), or pork sausage (LOQ = 0.007 ppm) samples. Only one fresh orange juice sample contained residues greater than the LOQ at 0.015 ppm. Only about 20% of the apples (maximum = 0.052 ppm), 20% of the tomato samples (maximum = 0.058 ppm), and 50% of the peanut butter samples (maximum = 0.021 ppm) contained quantifiable residues.

Keywords: *Chlorpyrifos; food residues; grocery store commodities; tolerances; exposure assessment*

INTRODUCTION

Dietary risk assessment is an important component for considering potential human health risks from pesticide exposure. Assessments of risk from dietary exposure to pesticides depend upon toxicity of the pesticide, magnitude of pesticide residues in food, and food consumption patterns (Parmar et al., 1997). Consequently, improvements in the accuracy of dietary risk assessments depend upon improved understanding of toxicity, food residues, and consumption. This paper presents a method for measuring pesticide residues in or on food that affords a more refined and reliable assessment of dietary exposure and risk.

Assessment of dietary risk typically follows a tiered sequence that progresses from the use of conservative pesticide residue values to more realistic values. Regulatory authorities such as the U.S. Environmental Protection Agency (EPA) use a tiered approach to conserve resources. If a risk determined in the assessment conducted at a lower tier is acceptable, further analysis is not needed. Preliminary risk assessments typically utilize tolerance values. Tolerances are intended to be enforcement tools and are based on the highest residue values found in pesticide registration field residue studies using the maximum application rates and shortest intervals from application to harvest (U.S. EPA, 1997). These studies are conducted by the registrant during the development of a pesticide to register the product with the EPA. Thus, risk assessments using tolerances constitute a high-end estimate of pesticide residues in food. At the next stage of refinement of dietary risk assessment, tolerance values are replaced by average residue values, sometimes referred to as anticipated residues, calculated from a series of samples from registration field residues studies.

At early stages of risk assessment, pesticide residues in processed commodities such as juice or oil are calculated from anticipated residues by applying a residue concentration factor that is determined from processing studies (U.S. EPA, 1997). Pesticide residues potentially found in meat, milk, poultry, and eggs resulting from the consumption of treated feed by these animals are determined from feeding studies (U.S. EPA, 1997).

A source of refined pesticide residue data for higher tiers of assessment may be available from monitoring data. Monitoring data are collected for tolerance enforcement and dietary risk assessment (U.S. EPA, 1997). In a monitoring program, samples of agricultural commodities are obtained and analyzed for pesticide residues. Monitoring data are available from the Food and Drug Administration (FDA), the U.S. Department of Agriculture (USDA), and the California Environmental Protection Agency (Cal EPA; California food only). Not all of these monitoring programs are suitable for use in assessing dietary exposure. The FDA focuses on collecting compliance data that target commodities suspected of containing residues above the legal limit at the point of entry into interstate commerce. The FDA also conducts a Total Dietary Study, but it is of limited value for risk assessment because sampling is limited to only 12 retail outlets. The USDA established the Pesticide Data Program (PDP) to provide residue moni-

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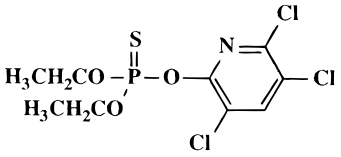

Figure 1. Structure of chlorpyrifos [CAS Registry No. 2921-88-2 (supplied by the author)].

toring and application data useful for dietary risk assessment of chronic or long-term dietary risk (USDA, 1995).

As a further refinement of dietary risk assessment and validation of federal monitoring data, market basket studies may be conducted by the pesticide registrant to obtain data on samples collected at the point of consumer purchase (U.S. EPA, 1998a). In a market basket study, samples of food are collected from grocery stores and analyzed for residues of a pesticide. Market basket studies provide more realistic data on residues of a pesticide reaching the consumer. These studies have rarely been conducted because of the complexity and cost. When conducted, registrants collect the food forms that provide the highest theoretical exposure to the pesticide of interest. This exposure calculation relies on less realistic data such as field residue data that do not account for the reduction of residues between the field and consumer purchase. Because sampling at the point of consumer purchase provides a more realistic measure of the residues on commodities as obtained by consumers, an objective of this study was to determine nationally representative residue levels of chlorpyrifos [*O*,*O*-diethyl-*O*-(3,5,6-trichloro-2-pyridinyl)phosphorothioate] (Figure 1), a broad spectrum insecticidal active ingredient registered for application to more than 40 different food commodities, in several commodities. The method used in the current study was designed to provide more realistic residue data than had been previously available from the field residue studies.

EXPERIMENTAL PROCEDURES

The Chlorpyrifos Market Basket Study (CMBS) was conducted by Dow AgroSciences from 1993 to 1994 in grocery stores across the United States. Sample collection was initiated in November 1993 with the collection of food items in ~200 locations throughout the continental United States and continued at ~2-week intervals for 1 year. The primary difference between the CMBS and typical field residue studies is the point where samples are collected. Field residue studies are conducted according to EPA guidelines designed to measure the maximum residue profile according to pesticide application, and samples are obtained directly from the field to measure residue values prior to distribution in interstate commerce (U.S. EPA, 1996). The CMBS was designed to measure values at the point of consumer purchase.

The food items to be sampled were determined by conducting a chronic dietary exposure analysis of each food item consumed by the U.S. population and subgroups that might contain residues of chlorpyrifos. Estimates of exposure were calculated by multiplying the anticipated residue values or tolerances in the food by the amount of food consumed. The model included a critical commodity contribution assessment that identified individual food items that contributed >1% to the theoretical dietary exposure from chlorpyrifos. The food items selected in the critical commodity analysis were then prioritized on the basis of the pesticide use patterns for chlorpyrifos. The percent of crop treated with chlorpyrifos was also given consideration in the final selection of foods for analysis (Gianessi et al., 1992).

As a result of the analysis, apples, babyfood applesauce, apple juice, fresh orange juice, tomatoes, peanut butter, whole milk, ground beef, and pork sausage were selected for collection. Babyfood applesauce was selected as an opportunity to focus on food in children's diets. The EPA recommended collection of applesauce as an estimate of babyfood applesauce because it is generally known that babyfood manufacturers monitor raw fruits and vegetables for pesticide residues prior to processing (Knizner and Clifford, 1994), and the likelihood of detecting chlorpyrifos in babyfood was very low. Peanut butter was selected because use on peanuts is a significant market for chlorpyrifos, residues tend to concentrate in oils (chlorpyrifos is highly lipophilic), and the food is often consumed by children. Because other animal parts such as fat are incorporated into the processing of these items, ground beef and pork sausage were selected rather than lean beef or pork. Whole milk was selected because it includes the fat component of milk, where the chlorpyrifos residue would be expected to concentrate. The other food commodities selected represent important food items in the diets of children.

Sampling Scheme. The CMBS used implicit stratified systematic sampling to ensure that the foods selected for purchase were representative of the foods purchased in stores by typical U.S. consumers. The study was also designed to be self-weighting with respect to the all commodity volume (ACV), an indicator of the store's total sales. Using this technique, high sales volume stores had a higher probability for inclusion in the study than low sales volume stores. Chlorpyrifos is registered for use on tomatoes only in Florida within the United States; therefore, tomatoes were collected only in that state and only during the months when tomatoes are typically harvested (October through June) to maximize the likelihood of sampling tomatoes with chlorpyrifos residues. The sampling procedure for the CMBS used the proposed guidelines of the U.S. EPA for the use of anticipated residues in dietary exposure assessment as the basic framework (U.S. EPA, 1992).

The CMBS design used a two-stage, implicit stratified systematic sampling method for sampling food items at the retail level. The retail outlets were selected from a database (PGDB) maintained by the Progressive Grocers' Data Center (Progressive Grocers' Trade Dimensions, Inc.). The PDGB contains records for >95000 retail grocery outlets in virtually every urban and rural area in the United States and represents a total of 84% of all grocery sales in 1991. Supermarkets were the only type of grocery outlet sampled because many of the target food items were not available in convenience stores.

Stratification was the first step in the design to partition the population of stores into relatively homogeneous cells to reduce variability. The following variables were used to partition the population: census region, ACV category, geographical region, and urban−rural nature of the community in which the store was located. All stores were cross-classified by these four variables simultaneously to produce a table of 360 cells (10 geographical regions × 4 urbanization status categories × 9 ACV categories = 360 cells). Each cell contained the number of stores with the given combination of stratification codes and the total ACV accounted for by those stores. The purpose of creating the cells was not to create explicit strata but to introduce implicit stratification through the ordering of key variables.

The cells were ordered first by census region, second by ACV category within a census region, then by geographical area, and finally by urban−rural category. Selection of the stores was determined by using systematic sampling across cells by using probability proportional size sampling to draw the sample from the entire database such that the allocation of the total sample size was proportional to the distribution of the total ACV over all cells. A sample of 200 stores was selected and divided into subsamples of 8 stores with each subsample randomly assigned to one of 25 sampling dates (approximately every 2 weeks over the course of a year) to ensure representation of residue profiles throughout the year. One primary store and two additional alternate stores were selected from the sampling stratum. All three stores were in the same zip code to ensure that they were in the same geographical area.

The sampling of tomatoes from Florida was treated as an independent subset of the market basket study, with separate randomization and sample allocation. Stratification was necessary only for the ACV and urban−rural nature of the community. The sample set of 54 stores was divided into subsamples of 3 stores that were each assigned to one of 18 sampling dates.

Because the sample of food was allocated to strata on the distribution of total ACV over strata, this is referred to as proportionate allocation with respect to ACV. This allows the simple arithmetic mean determined for the samples to be used as an estimator of the population mean. This estimator is unbiased and involves no weights as a result of the self-weighting aspect of the design. Weighting would only be required to adjust for nonresponses caused by failure to collect, deliver, or analyze samples.

Sample Size. Using the absolute standard error (ASE) as a measure of precision of a study, the minimum sample size needed to ensure that the ASE derived from the study was at most some preset value, A_0, was obtained as

$$n \geq (\mathrm{SD}/A_0)^2$$

The absolute standard error is the ratio of the standard deviation (SD) to the square root of the sample size, and it is used to measure the variability of the means. An estimate of the minimum sample size can be derived by substituting the values for the SD and $A_0 = 0.01$ ppm [the maximum limit of quantitation (LOQ) desired] in the above formula. The maximum allowable LOQ was set at 0.01 ppm; however, target LOQs were up to 4 times lower than this to enable more realistic values for subsequent use in dietary risk assessment. The SD for calculating sample size for apples (SD = 0.031) and oranges (SD = 0.057) was calculated from monitoring data from the California EPA Pesticide Monitoring Program. The SD for tomatoes was determined from Dow AgroSciences field trial data for tomatoes (SD = 0.06). The SD for tomatoes based on field trial data is expected to be less than the SD based on monitoring data, which would potentially increase the sample size; however, because samples were drawn from only the state of Florida, application patterns of chlorpyrifos should be similar so there would be less variability in the distribution of residue values. The sample size calculated from this analysis was increased to 200 to adjust for the design effect of the CMBS, to ensure that enough samples were drawn from each stratum to allow estimation of the variability in the sample and provide adequate geographical distribution of samples. The sample size for tomatoes was 54, though 36 would have been adequate on the basis of the formula above. Because processing was expected to reduce variability, the minimum sample sizes needed for the processed food items (apple juice, applesauce, orange juice, and animal products) would, at most, be equal to those derived for the raw food items. Therefore, a sample size of 200 was also used for the processed food items.

Field Sampling Procedures. Collection of food samples began on November 29, 1993, and continued biweekly through November 7, 1994. The samples were collected according to accepted Good Laboratory Practices (U.S. EPA, 1989). Mondays were scheduled as the primary day for sampling because a survey of grocery stores indicated that high sales volumes on weekends necessitated the restocking of stores late Sunday or early Monday. Sampling was not conducted during Thanksgiving week or during the Christmas holiday season. The schedules, shopping, and recording instructions were designed to ensure the collection of representative samples and to increase the probability that chlorpyrifos residues in the samples properly reflected those in the commercial supply of the test food items. Food items were collected from a given store only once, unless resampling was necessary because of collection problems, such as sample damage during shipment, or samples not meeting protocol specifications. Duplicate samples were collected for all food items, except apples and tomatoes; for these food items a sample consisted of four to six individual fruits. The primary sample was subjected to analysis, and the duplicate served as the backup, if needed.

Food samplers collected the food items, recorded the required sampling information on standardized data entry forms, and enclosed the forms and food items in the shipping container. The information collected included the size of the sample, brand of sample (other than apples and tomatoes), lot or date code imprinted on the container, date of sample collection, and country of origin for the apples and tomatoes. This information was collected to provide a basis for possible geographical or seasonal analysis. The shoppers did not distinguish between domestic and imported food samples because the market basket study was designed to obtain samples representative of U.S. consumption patterns. Foods stored in the grocery store at ambient temperature, such as peanut butter, were shipped under ambient conditions. Fruits and refrigerated items were shipped chilled with sufficient ice packs to keep samples cool for 48 h. All items were shipped by overnight express to the Dow AgroSciences Global Environmental Chemistry Laboratory—Indianapolis Laboratory for analysis.

Sample Tracking, Storage, and Bulk Preparation. All samples were received at Dow AgroSciences the day after purchase from the grocery store. Upon receipt, all samples were inspected for proper labeling and condition and logged into the in-house tracking system as being received. Chain-of-custody forms were completed, and all samples were transferred to short-term refrigerated storage. 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 containers suitable for long-term frozen storage. Samples of apples, tomatoes, ground beef, and pork sausage were frozen with liquid nitrogen and ground through an Agvise model 2001 hammer mill fitted with a $^3/_{16}$ in. screen. The ground samples were transferred to glass jars with foil-lined lids. In the case of the tomatoes and apples, the fruits were ground as a single sample and then split and transferred to two containers, generating the duplicate samples. Following preparation, the samples were transferred to frozen storage until the time of analysis.

All analyses for chlorpyrifos were completed within 140 days of sample collection, between December 10, 1993, and January 11, 1995. Extensive frozen storage stability data support the stability of chlorpyrifos in the above matrixes for the period of frozen storage incurred by the samples between collection and analysis in this study (U.S. EPA, 1984).

Analytical Method. The analytical methods varied in the sample processing procedures, which are briefly described below, but in all cases the chlorpyrifos present was measured using capillary column (DB-17 or DB-5 from J&W Scientific) gas chromatography and a flame photometric detector (FPD). A Hewlett-Packard (HP) 5890 gas chromatograph (GC) was equipped with an HP 7673A autosampler, and chromatographic data were collected and peaks were integrated using a chromatography data system.

Apples, Applesauce, Fresh Orange Juice, and Tomatoes. Aliquots of juice or finely ground fruit were weighed into glass vials. Acetone was added to the preweighed aliquots as the extraction solvent, and the samples were briefly sonicated and shaken on a flat-bed shaker for ~30 min. An aliquot of the extract was evaporated to reduce its volume and diluted with water. A carbon-18 (C18) solid-phase extraction (SPE) cleanup followed, with final extraction into hexane. An aliquot of the hexane extract was transferred to a GC autosampler vial and analyzed by capillary GC as described above.

Apple Juice. An aliquot of each juice sample was weighed into a glass vial, and 1% phosphoric acid was added to the sample. An aliquot of hexane was added to each sample and the sample shaken on a flat-bed shaker for a minimum of 10 min. Following centrifugation, an aliquot of the hexane was transferred to a GC autosampler vial for analysis by capillary GC.

Ground Beef and Pork Sausage. Aliquots of finely ground tissue were weighed into glass vials. Hexane/*tert*-butyl methyl ether (90:10) was added as the extraction solvent, and the sample was shaken for a minimum of 2 h. Following centrifu-

gation, the sample was chilled at ~−20 °C for a minimum of 2 h (typically overnight) to solidify the fat. An aliquot of the liquid extract was then reduced in volume slightly by evaporation and partitioned three times with acetonitrile. The acetonitrile extracts were combined and evaporated just to dryness. The residue was dissolved in acetone, water was added, and the sample was further cleaned up using a C18 SPE, with final extraction into hexane. An aliquot of the hexane extract was transferred to a GC autosampler vial and analyzed by capillary GC.

Peanut Butter. Samples of peanut butter were analyzed as described above for ground meat, with the exception of modifying the initial extraction solvent to hexane/*tert*-butyl methyl ether, 50:50 (rather than 90:10).

Whole Milk. Aliquots of whole milk were weighed into glass vials. Before analysis, the sample aliquots were heated briefly in a 45 °C water bath to liquefy any solid fats. Acetone and NaCl were added to the samples and then shaken for a minimum of 15 min. The samples were centrifuged, and an aliquot of the extract was transferred to a clean vial. One percent phosphoric acid was added to the samples, which were then extracted twice with hexane. The hexane fractions were combined and evaporated to reduce the volume. The hexane was then extracted three times with acetonitrile. The acetonitrile fractions were combined and evaporated to dryness. The residue was dissolved in acetone, water was added, and the samples were further cleaned up using a C18 SPE, with final extraction into hexane. An aliquot of the hexane extract was transferred to a GC autosampler vial and analyzed by capillary GC as described above.

Gas Chromatograph Calibration. Instrumental sequences were typically set up with a series of five chlorpyrifos standards in hexane at the beginning of the run, followed by samples with a standard interspersed every five or six injections. Following the completion of the sequence, the chromatograms were viewed, baselines identified by the analyst using the manual baseline capability of the data system, and hard copies of the chromatograms printed, indicating the peak area and retention time of the chlorpyrifos peak. A spreadsheet was used to perform power regression analysis using the concentration and corresponding peak area of the chlorpyrifos standards in a given sequence. The results of the regression analysis were then used in a spreadsheet to complete the calculations for the samples contained in the set. The presence of chlorpyrifos in selected sample extracts was confirmed by comparing ion ratios of samples and chlorpyrifos standards using GC with an HP5971 mass selective detection (MSD).

Quality Assurance. The efficiency of the analytical methods was determined at the time of analysis of each set of samples by fortifying aliquots (typically five) of control matrix with spiking solutions of chlorpyrifos in acetone and analyzing them along with the field samples. At the initiation of the study, control samples were purchased from grocery stores in the Indianapolis area, analyzed, and shown to be free of chromatographic interferences. As the study progressed and controls were depleted, field samples that had been analyzed and shown to be free of contamination were also used as controls in the preparation of recovery samples. An unfortified control and a reagent blank (sample containing no matrix, carried through the method) was included in each sample set. Typically, one sample in each analytical set was analyzed in duplicate, to demonstrate consistency of method performance for actual field samples. The mean percent recovery of chlorpyrifos from each matrix ranged from 79 to 101%, which shows that the analytical methods were sufficient for extracting residues of chlorpyrifos.

Limits of Detection (LOD) and Quantitation (LOQ). For each food item, a target LOQ was defined before sample analysis. With each analytical set, recovery samples were analyzed at the target LOQ, at half the LOQ (to demonstrate ability to detect residues below the quantitative limit), and at levels above the LOQ. The recovery data generated during the first 6 months of sample analysis indicated that acceptable recovery was obtained at half the LOQ for all matrixes. At this point, with the data indicating the ability to quantitate down to the original target LOD, the number of recovery samples analyzed at this lower, revised target LOQ was increased, and a recovery sample at half of this level was included with each analytical set.

Table 1. LOQs and LODs for Chlorpyrifos in Selected Food Items

matrix	target LOQ[a] (ppm)	calcd LOQ (ppm)	calcd LOD (ppm)	study LOQ/LOD (ppm)
apples	0.005	0.0066	0.0020	0.007/0.002
applesauce	0.005	0.0076	0.0022	0.008/0.002
apple juice	0.0025	0.0026	0.00079	0.003/0.0008
orange juice	0.005	0.0070	0.0021	0.007/0.002
tomatoes	0.005	0.0051	0.0015	0.005/0.002
peanut butter	0.005	0.0052	0.0016	0.005/0.002
whole milk	0.005	0.0062	0.0019	0.006/0.002
ground beef	0.005	0.0054	0.0016	0.005/0.002
pork sausage	0.005	0.0069	0.0021	0.007/0.002

[a] The revised target LOQ.

Following established guidelines (Keith et al., 1983), the study LOQ and LOD for the analyses described above were calculated using the method recovery data generated over the course of the entire study. For each matrix, the LOQ was calculated as 10 times the standard deviation, and the LOD was calculated as 3 times the standard deviation of the results obtained from the analysis of the recovery samples fortified at the revised target LOQ. The calculated LOQ was equal to or slightly above the revised target LOQ for each matrix. The calculated values, rounded to a single significant figure, were used in the interpretation of the study results. These data are summarized in Table 1.

All field samples with detections less than the study LOQ but greater than or equal to the study LOD are reported as <LOQ, indicating that a detectable residue was found; however, the residue was at a level too low to quantitate. All field samples with detections less than the study LOD are reported as nondetects (ND), indicating that the peak detected (if any) was too small to distinguish from baseline noise.

RESULTS AND DISCUSSION

The design was self-weighted with respect to the ACV of the grocery stores so that each store's probability of selection is proportional to its volume of sales. Tables 2, 3, and 4 show the distribution of stores in the survey and those of the PGDB with respect to the three variables used to define the strata, namely, ACV, geographical region, and urbanization status, respectively. The distribution of sampled stores in each strata is similar to that of the ACV distribution in the database (Table 2). Thus, the sample was self-weighted with respect to the dollar sales volume (Cochran, 1977). The study design and statistical sampling procedures resulted in proper stratification with respect to geographical region and urbanization status, as well (Tables 3 and 4). Therefore, the residues of chlorpyrifos measured in food items sampled in the CMBS are statistically representative of 84% of the food sales in the United States sold in supermarkets.

Residue values less than the LOQ were found in the applesauce, apple juice, whole milk, beef, or pork samples. Only one fresh orange juice sample contained residues greater than the LOQ, at 0.015 ppm. Approximately 20% of the apples contained residues at levels greater than the LOQ, with the highest value being 0.052 ppm. Approximately 20% of the tomato samples contained residues at levels greater than the LOQ, with the highest value being 0.058 ppm. Approximately 50% of the peanut butter samples contained residues at levels greater than the LOQ, with the

Table 2. Distribution of ACV Category in the PGDB and the CMBS

		PGDB		CMBS	
ACV category	ACV[a] ($ × 1000)	no. of stores	% of total ACV[b]	no. of stores	% of total stores in CMBS[c]
4	1500	4377	2.1	3	1.5
5	3000	6562	6.4	12	6.0
6	5000	4512	7.4	21	10.5
7	7000	4045	9.2	16	8.0
8	10000	5957	19.5	38	19.0
A	14000	5454	24.9	52	26.0
B	23000	2539	19.1	37	18.5
C	33000	1052	11.3	21	10.5
total		34498		200	

[a] Midpoint of ACV category. [b] For each ACV category, the ACV was multiplied by the number of stores. These are summed to yield the total ACV. The percent of total ACV is the contribution of each ACV category to the total ACV. [c] CMBS was designed to be self-weighting with respect to ACV.

Table 3. Distribution of Geographical Regions in the PGDB and the CMBS

	PGDB		CMBS	
region	ACV ($ × 1000)	region ACV as % of total ACV	no. of stores	% of total stores in CMBS[a]
northeast	57037	18.6	35	17.5
north central	70338	23.0	48	24.0
west	64970	21.2	43	21.5
south	113820	37.2	74	37.0
total	306165		200	

[a] CMBS was designed to be self-weighting with respect to ACV.

Table 4. Distribution of Urbanization Status in the PGDB and the CMBS

	PGDB		CMBs	
Nielsen class[a]	ACV ($ × 1000)	Nielsen ACV as % of total ACV	no. of stores	% of total stores in CMBS
A	118242	38.6	77	38.5
B	98944	32.3	68	34.0
C	50612	16.5	30	15.0
D	38368	12.5	25	12.5
total	306166		200	

[a] A, all counties belonging to the 26 largest metropolitan areas; B, counties not included above having populations >120000; C, counties not included above having populations >32000; D, remaining counties.

highest level being 0.021 ppm. All detectable residues were at levels well below the corresponding established U.S. tolerance for that commodity. The results are summarized in Table 5.

Table 6 summarizes the observed means, absolute standard errors (ASEs), 95th percentiles, and the 95% confidence intervals around these percentiles for each of the food items in the study. Confidence intervals were estimated using the methods outlined in Hansen et al. (1953) and Campbell and Gardner (1988). Values less than the LOD were assigned a value of the LOD, and values greater than the LOD and less than the LOQ were assigned the LOQ to give the maximum residue values. The small standard deviations indicate that there is little variability in residues for all of the

Table 5. Summary of Analytical Results from CMBS

	U.S. tolerance (ppm)	anticipated residue[a] (ppm)	CMBS			
matrix			no. of samples	no. > LOQ	no. < LOQ, > LOD[b]	no. of ND[c]
apple	1.5	0.39	200	39	29	132
applesauce	1.5	0.18	200	0	4	196
apple juice	1.5	0.18	200	0	2	198
orange juice	1.0	0.28	195	1	0	194
tomatoes	0.5	0.14	54	10	6	38
peanut butter	0.2	0.018	200	92	77	31
whole milk	0.01	0.015	200	0	0	200
ground beef	0.05	0.0057	200	0	1	199
pork sausage	0.05	0.001	200	0	1	199

[a] Average residue value from field trials. [b] <LOQ = less than the LOQ and greater than the LOD. Residue detectable, but not quantifiable. [c] ND, not detected at levels greater than the LOD.

Table 6. Summary Statistics and Error Estimates for Residue Data from the CMBS

food item	sample mean[a] (ppm)	sample SD[b] (ppm)	sample ASE[c] (ppm)	sample 95th percentile	95% CI[d] around 95th percentile
apples	0.0048	0.0086	0.00061	0.023	0.016−0.038
applesauce	0.001	0.0003	2.12E−05	0.001	0.001−0.001
apple juice	0.00041	0.0001	7.76E−06	0.0004	0.0004−0.0004
orange juice	0.001	0.0011	7.96E−05	0.001	0.001−0.001
tomatoes	0.0044	0.0090	0.0012	0.014	0.013−NC[e]
peanut butter	0.0049	0.0037	0.00026	0.012	0.011−0.014
whole milk	0.001	0	0	0.001	0.001−0.001
ground beef	0.001	0.0001	7.5E−06	0.001	0.001−0.001
pork sausage	0.001	0.0002	1.25E−05	0.001	0.001−0.001

[a] Calculated by assigning the LOD to the samples with nondetectable residues and the LOQ to values unable to be measured between the LOD and LOQ. [b] Standard deviation. [c] Absolute standard error ($SD/\sqrt{n}$). [d] Confidence interval. [e] Not calculable with the sample size for tomatoes.

processed commodities. Because the observed ASEs were lower than those assumed for calculating the sample size, the 200 samples (195 for fresh orange juice because targeted grocery stores did not have fresh orange juice in stock and 54 for tomatoes) collected in the CMBS were adequate to maintain the desired level of precision.

The recovery data for each analysis demonstrated acceptable performance of the analytical method for all food items over the course of the study. The sensitivity of the residue methodology was better than expected, which allowed for validation of lower LOQ values than were targeted at the initiation of the study (Table 1). The sensitivity of the flame photometric detector for compounds containing phosphorus resulted in easily interpreted chromatograms. Contamination was not present in any control or reagent blank samples, and chromatographic performance in general was high throughout the study. In all cases where sample extracts were analyzed by MSD to confirm the presence of chlorpyrifos, the analyte was confirmed.

No measured residue levels of chlorpyrifos exceeded established U.S. food tolerances. Indeed, 90% of the commodities sampled and analyzed in the market basket study did not contain quantifiable levels of chlorpyrifos. This is slightly less than the results from the 1993 PDP in which 95% of the samples did not contain detectable levels of chlorpyrifos (USDA, 1995). Although it is difficult to compare these results because different food items were sampled and different residue methods were used, the results indicate that chlorpyrifos is rarely found in food items sampled closer to

consumer purchase than reported in registration field residue studies. These data allow for a more realistic understanding of the exposure to consumers. The limitation of this study is that it is resource intensive, which limits the number of food items that can be collected for measurement.

The CMBS and PDP results demonstrate the impact of several factors in reducing both the frequency of occurrence and the level of residues reaching the consumer. This reduction in commodity residues compared to registration-based field residue studies is due in part to dissipation with time from treatment in the field to processing and finally to consumer purchase. The frequent use of lower chlorpyrifos application rates by growers compared to the maximum application rates employed in field residue studies is also reflected in the decline (U.S. EPA, 1998b; Gianessi, 1998). In commerce, some food items are also typically trimmed and washed before being made available in the market for consumer purchase, which further reduces chlorpyrifos residue levels. For example, apples may be washed in a bleach and water solution immediately after harvest.

Apples illustrate the reduction in residues of chlorpyrifos as commodities more from the field to market. The highest value for apples (0.052 ppm) in the CMBS was 29 times less than the U.S. tolerance (1.5 ppm), 8 times less than the average residue (0.399 ppm) from field residue studies, and 7 times less than the highest PDP value (0.36 ppm) that was reported in 1993 (USDA, 1995).

The results show that chlorpyrifos is rarely detected on food items purchased by the consumer, and, when detected, levels are well below the tolerance. Furthermore, residue levels in the survey were much lower than residues typically observed in field residue studies. The residues of chlorpyrifos obtained in this study are more accurate for refined dietary exposure estimates of chlorpyrifos in the U.S. population, including infants and children. Because dietary exposure is a key element in calculating overall dietary risk, the chlorpyrifos market basket study may be used to refine dietary risk assessment.

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