

# Surface-to-food pesticide transfer as a function of moisture and fat content

ANNE P. VONDERHEIDE<sup>a</sup>, CRAIG E. BERNARD<sup>a</sup>, THOMAS E. HIEBER<sup>b</sup>, PETER E. KAUFFMAN<sup>b</sup>,  
JEFFREY N. MORGAN<sup>a</sup> AND LISA JO MELNYK<sup>a</sup>

<sup>a</sup>United States Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Microbiological and Chemical Exposure Assessment Research Division, Chemical Exposure Research Branch, Cincinnati, Ohio 45268, USA

<sup>b</sup>National Council on the Aging

Transfer of pesticides from household surfaces to foods may result in excess dietary exposure in children (i.e., beyond that inherent in foods due to agricultural application). In this study, transfer was evaluated as a function of the moisture and fat content of various foods. Surfaces chosen for investigation were those commonly found in homes and included Formica<sup>®</sup>, ceramic tile, plastic, carpet, and upholstery fabric. Each surface type was sprayed with an aqueous emulsion of organophosphates, fipronil, and synthetic pyrethroids. In the first phase of the study, multiple foods (apples, watermelon, wheat crackers, graham crackers, white bread, flour tortillas, bologna, fat-free bologna, sugar cookies, ham, Fruit Roll-ups<sup>®</sup>, pancakes, and processed American cheese) were categorized with respect to moisture and fat content. All were evaluated for potential removal of applied pesticides from a Formica surface. In the second phase of the study, representative foods from each classification were investigated for their potential for pesticide transfer with an additional four surfaces: ceramic tile, plastic, upholstery, and carpet. Moisture content, not fat, was found to be a determining factor in most transfers. For nearly all surfaces, more efficient transfer occurred with increased hardness (Formica and ceramic tile). Comparatively, the polymer composition of the plastic delivered overall lower transfer efficiencies, presumably due to an attraction between it and the organic pesticides of interest. *Journal of Exposure Science and Environmental Epidemiology* (2009) **19**, 97–106; doi:10.1038/jes.2008.6; published online 16 April 2008

**Keywords:** children, excess dietary exposure, pesticides, surface transfer, transfer efficiency.

## Introduction

Traditional dietary pesticide exposure assessments have focused on contamination during production (e.g., pesticides in agriculture for both field and post-harvest protection) ([www.ams.usda.gov/science/pdp/](http://www.ams.usda.gov/science/pdp/); [www.cfsan.fda.gov/~comm/tds-toc.html](http://www.cfsan.fda.gov/~comm/tds-toc.html)). However, recent residential monitoring studies (in which duplicate diets were collected) have demonstrated that a significant portion of total human exposure can result from food contamination in homes following residential pesticide usage (Hu et al., 2004). Children consuming food in a contaminated environment are susceptible to dietary exposures not traditionally measured with duplicate diets. Such exposures, termed excess dietary exposures, are derived from contact between foods and contaminated surfaces (Melnik et al., 2000). Limited data exist concerning these transfers, but they are thought to be a critical element in

predicting total dietary exposure (Akland et al., 2000; Melnyk et al., 2000; Hu et al., 2004).

Children are particularly susceptible to such added exposures due to unstructured eating behaviors (Goldman, 1995; Landrigan et al., 1999; Hubal et al., 2000) and as a result, these activities can become an important factor in determining total dietary intakes (Akland et al., 2000; Melnyk et al., 2000; Freeman et al., 2001). In an effort to account for all routes of intake, a Children's Dietary Intake Model (CDIM) was developed (Akland et al., 2000). In addition to the pesticide residue on the food, contamination introduced from two activity-based parameters are measured and included in the CDIM. One parameter encompasses surface-to-food contamination resulting from food placed in contact with contaminated surfaces (Rohrer et al., 2003) before ingestion. The other concerns surface-to-hand contamination occurring when a child touches a contaminated surface (Freeman et al., 2005; Auyeung et al., 2006) and then handles food (Black et al., 2005). Both activity factors have been found to be important in determining a child's total dietary intake; however, current data are insufficient for adequate assessment of the impact of these parameters. Consequently, default assumptions are included (Hubal et al., 2000), resulting in poor model estimation of dietary exposure (Akland et al., 2000).

Laboratory experiments have been conducted to determine these transfer efficiencies for a variety of food items (Rohrer

1. Address all correspondence to: Dr Lisa Jo Melnyk, United States Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Microbiological and Chemical Exposure Assessment Research Division, Chemical Exposure Research Branch, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, USA. Tel.: +513 569 7494. Fax: +513 569 7757.

E-mail: [Melnik.lisa@epa.gov](mailto:Melnik.lisa@epa.gov)

Received 27 September 2007; accepted 24 January 2008; published online 16 April 2008

et al., 2003), although to date none have investigated underlying food characteristics that might influence pesticide transfer. Moisture and fat content are attributes that seemingly would have an influence on pesticide transfer depending on the nature of the compound. Therefore, this study quantified the influence using a variety of foods at the high and low ends of the spectrums for these two attributes. Categorizing foods by these attributes will allow for the creation of distributions of transfer efficiencies to assist in strengthening the CDIM and subsequently improve assessments of children's dietary exposure in the context of aggregate exposure evaluation.

## Experimental

### Study Design

This study was conducted in two phases. In the initial phase, foods most commonly eaten by children 1- to 6-years-old were determined using the Dietary Exposure Potential Model (DEPM) (Tomerlin et al., 1997). Within DEPM, the consumption database CSFI 1994–1996, 1998 (Continuing Survey of Food Intakes by Individuals) was used (population consisted of citizens of the US). The identified food groups were apples, watermelon, crackers, white bread, flour tortillas, cold cuts (lunchmeats), cookies, pancakes, and sliced cheese. From this list, 13 foods were chosen with a range of moisture and fat contents, namely, apples, watermelon, wheat crackers, graham crackers, white bread, flour tortillas, bologna, fat-free bologna, sugar cookies, ham, Fruit Roll-ups<sup>®</sup>, pancakes, and processed American cheese. All foods were investigated for transfer of pesticides from Formica<sup>®</sup> treated with an aqueous emulsion of organophosphates (malathion and chlorpyrifos), fipronil, and synthetic pyrethroids (bifenthrin, permethrin, cyfluthrin, cypermethrin, and deltamethrin). Specifically, each food was placed in contact with pesticide-treated Formica (Akland et al., 2000; Rohrer et al., 2003). Wipes (isopropanol-moistened gauze pads) were used to determine available pesticide levels on the Formica surface (Bernard et al., 2008). In addition, an aluminum foil deposition coupon was placed

on the surface and sprayed. Aluminum foil was considered inert and allowed for the determination of pesticide concentrations without surface impact. Foods, foils, and wipes were extracted with a pressurized fluid extractor (Accelerated Solvent Extraction system (ASE)) (Ahmed, 2001; Rosenblum et al., 2002) and analyzed by gas chromatography-micro electron capture detection (GC- $\mu$ ECD) (Bernard et al., 2008).

In the second phase of the study, representative foods from each classification were chosen for investigation with additional household surfaces including ceramic tile, ABS (acrylonitrile/butadiene/styrene) plastic, carpet (Queen Carpet, low-level pile), and a generic upholstery-type fabric. These were chosen because they are commonly found in homes or associated with children's possessions. Identical procedures were employed in both phases. Specific experimental and analytical schemes are outlined below.

### Pesticide Disbursement

The pesticides were combined in one mixture to achieve target pesticide deposition levels ( $0.5 \mu\text{g cm}^{-2}$  of each pesticide) on the sprayed surface(s). These were established to mimic concentrations typical of residential homes (Krieger et al., 2001). However, the viscosity and lack of homogeneity of the commercial pesticides resulted in some variability of deposition level as shown in the results displayed later. Foil coupons were therefore sprayed and analyzed with every batch to determine actual pesticide deposition.

The pesticide mixture was prepared on the day of use to ensure stability of the compounds and to avoid concentration changes due to evaporation, volatilization and/or hydrolysis. Table 1 lists the commercial components used in the preparation. Following thorough mixing using a magnetic stir bar, the spray mixture was transferred to a 2 quart reservoir pressurized under nitrogen gas (20 psi) for delivery in a custom spray chamber (Bernard et al., 2008). The chamber ( $4' \times 4' \times 3'$ , L  $\times$  H  $\times$  W) was composed of galvanized steel and contained a Full Cone spray nozzle (TeeJet<sup>®</sup>, Wheaton, IL, USA) located at the center of the chamber and positioned approximately 20" above the chamber floor. Spray delivery was regulated through a Plast-O-Matic

**Table 1.** Commercial components of pesticide spray mixture

Pesticide	Tradename	Percentage <sup>a</sup> (%)	Manufacturer
Fipronil	Termidor SC	9.1	BASF, Research Triangle Park, NC, USA
Chlorpyrifos	Ortho borer and leaf miner spray	12.6	Monsanto Company, San Ramon, CA, USA
Malathion	Ortho malathion 50 plus	50	Monsanto Company, San Ramon, CA, USA
Deltamethrin	Suspend SC	4.75	Aventis Environmental Science, Montvale, NJ, USA
Cypermethrin	Demon EC	25.3	Syngenta Group Company, Greensboro, NC, USA
Bifenthrin	Talstar I	7.9	FMC Corporation, Philadelphia, PA, USA
Cyfluthrin	Cy-kick CS	6.0	Whitmire Micro-Gen Research Laboratories Inc., St Louis, MO, USA
Permethrin	Dragnet SFR	36.8	FMC Corporation, Philadelphia, PA, USA

<sup>a</sup>Percentage of active ingredient in commercial product.

continuous duty solenoid valve (Plast-O-Matic Valves, Cedar Grove, NJ, USA) that was controlled with a GraLab-451 timer (GraLab, Centerville, OH, USA).

The reservoir pressure (20 psi) and spray duration (0.5 s) were maintained to enable a uniform layer of solvent across the surface. Four replicates of each surface type, which were precut into coupons ( $20 \times 20$  cm or  $400$  cm<sup>2</sup>), could be sprayed simultaneously. Sprayed surfaces were transferred to a glove box (Fisher Scientific, Pittsburgh, PA, USA) for drying. Temperature and humidity within the glove box were monitored throughout the study and were maintained at 25°C and <25%, respectively, to allow for complete dryness after 1 h.

#### *Food Classification*

Food samples were purchased from local grocery stores specific to the Cincinnati area. The following brands were utilized: Oscar Mayer (both types of bologna and ham), Kraft (processed American cheese), Wonder (white bread), Betty Crocker (Fruit Roll-ups), Mission (flour tortillas), and Pillsbury (pancakes). Crackers and cookies were store brand. Apples of the Red Delicious variety and watermelon with seeds were purchased just before sampling. Sample preparation before surface exposure was established to mimic the treatment of food before it would be given to a small child. Most foods were simply removed from their packaging. Apples and watermelon were thinly sliced to approximately 2 mm with a conventional food-slicing machine (Geka, Germany).

Moisture content was measured by a Denver Instruments IR-30 moisture analyzer (Arvada, CO, USA). Approximately 5 g of sample was either ground or used "as is," placed in the instrument and dried at 130°C. Percent moisture was calculated as one minus the ratio of dry weight to wet weight. Fat content was determined from the information listed on the Nutrition Facts label. Percent fat was equal to the total fat per serving (g) divided by serving size (g). Fat content for apples and watermelon were obtained from nutrition information found on the internet ([www.nutri-facts.com](http://www.nutri-facts.com)).

Four food groupings were established as follows: high moisture/low fat, high moisture/high fat, low moisture/low fat, and low moisture/high fat. A value of 50% was set for moisture classification and foods with percentages lower than this were classified as low moisture. Conversely, foods with moisture contents greater than 50% were labeled as high moisture. In a similar manner, a value of 10% was used for the classification of foods based on fat content. Foods were identified as possessing low (<10%) or high (>10%) fat content.

#### *Food Exposure and Surface Wiping*

Geometrically regular food surface areas were mathematically calculated. Geometrically irregular food surface areas

were measured by weight. Specifically, actual food items were traced and their shapes cut out of regular white printer paper. A standard piece of paper of known dimension was weighed and used as the standard to determine the surface area of irregularly shaped food items.

Food surface areas ranged from 31 to 97 cm<sup>2</sup>. Individual items were in contact with the treated surface for 10 min. Immediately after exposure, the food items were carried through the extraction procedure detailed below.

Surface pesticide loadings were determined using a standard wiping method for the household surfaces (Bernard et al., 2008). An identical procedure was employed for all surface types and required a total of four gauze pads (nonsterile  $10 \times 10$  cm 12-ply 100% cotton gauze pads) (Fisherbrand, Fisher Scientific, Pittsburgh, PA, USA). The first gauze pad was wetted with 8 ml isopropanol and was wiped horizontally, sequentially using fresh portions of the pad, until the entire surface area ( $20 \times 20$  cm) had been wiped. The second wipe was used dry and was also sampled in the horizontal direction. Sampling in the vertical direction was performed using a second isopropanol-moistened gauze pad followed by a second dry pad.

#### *Sample Analysis*

Foods, foils, and wipes were fortified with 50  $\mu$ l of a surrogate, 4,4'-dibromobiphenyl ( $10 \mu\text{g ml}^{-1}$ ). Foods were ground with a mortar and pestle with 1:1 ratio of diatomaceous earth (Hydromatrix, Varian, Palo Alto, CA, USA). Fruit Roll-ups, tortillas, and bread were not ground. Ground foods, tortillas, bread, and wipes were transferred to a Dionex 300 ASE 100 ml cell (Sunnyvale, CA, USA), which was prepacked with 5 g of hydromatrix. The extraction solvent was a 50:50 mixture of hexane and acetone and a 50% flush volume was employed. Nitrogen (99.999%) was used at a pressure of 1,500 psi. Specific preparation times were 5, 10 min and 60 s for heat, static, and purge times, respectively. The extraction temperature was 75°C and the samples were put through two extraction cycles.

Fruit Roll-ups were shaken with water-acetonitrile (3:2, v:v) on a Burrell Scientific Wrist Action Shaker (Pittsburgh, PA, USA) at high speed for 15 min in a 500 ml flat-bottomed round flask. Organic solvent was added ((50 ml ethyl acetate/hexane (1:1, v/v)) and shaken at a medium setting for 5 min. The organic layer was decanted into a concentrator tube. The extraction was repeated two more times with organic solvent and the fractions were combined.

All food sample, foil, and wipe extracts were concentrated using a Zymark Turbo Vap II (Hopkinton, MA, USA) to a volume of 0.5 ml. Concentrates were "cleaned" by passing through chromatography columns containing hydromatrix (ASE extracted foods) or hydromatrix and anhydrous sodium sulfate (Fruit Roll-ups). Each concentrate was left on the column for 30 min. Pesticides were eluted with 40 ml ( $\times 2$ ) acetonitrile/acetone (7:3, v/v) and collected in

concentrator tubes. Each volume was reduced to 0.5 ml in the Turbo Vap. Concentrates were further “cleaned” by passing through columns containing 5 g partially deactivated alumina (10%) in excess hexane. These columns were eluted with 10 ml of ethyl acetate/hexane (1:1, v/v) and the eluent collected. The eluent was concentrated to 0.5 ml and then solvent exchanged from hexane to ethyl acetate to a final volume of 1 ml. Suspended particulates were removed by passing the extract through a disposable 13 mm filter (0.2  $\mu\text{m}$  PTFE, Whatman, Clifton, NJ, USA). The 1 ml final sample extract was fortified with 10  $\mu\text{l}$  of an internal standard, pentachlorobenzene (100  $\mu\text{g ml}^{-1}$ ).

#### Instrumentation

One microliter of sample was analyzed by an HP 6890 GC- $\mu\text{ECD}$  (Agilent Technologies, Palo Alto, CA, USA) equipped with a 30 m  $\times$  0.25 mm (RTX-5 crosslinked 95% dimethyl and 5% diphenylpolysiloxane) chromatography column with a film thickness of 0.25  $\mu\text{m}$  (Restek Corporation, State College, PA, USA). The GC oven was held at an initial temperature of 100°C for 2 min, and increased at a rate of 25°C  $\text{min}^{-1}$  to 215°C and held for 1 min. The temperature was then increased at a rate of 15°C  $\text{min}^{-1}$  to 290°C and held for 1 min followed by an increase at a rate of 5°C  $\text{min}^{-1}$  to 315°C and held for 3 min. A post-run program was applied with an oven temperature of 100°C held for 5 min. The flow rate for helium gas was 1.4 ml  $\text{min}^{-1}$ , which was maintained at a constant flow throughout the run. The make-up gas was 5% methane/95% argon, 99.999% purity.

Injection was split 5:1. The injection port temperature was maintained at 260°C as a result of the possibility of isomerization for the pyrethroids with cyano substituents at the asymmetric  $\alpha$ -carbon atom, such as cypermethrin and

cyfluthrin (Wong, 2006). The detector temperature was set to 340°C. Instrument concentrations were translated to pesticide levels by using individual food surface areas.

#### Surface Transfer Efficiency

Surface transfer efficiency (TE) was calculated as a percentage of the measured pesticide surface loading:

$$\text{TE} = C_f/C_s \times 100\% \quad (1)$$

where,  $C_f$ , level of pesticide transferred to the food sample ( $\text{ng cm}^{-2}$ );  $C_s$ , loading of pesticide on surface as determined from surface wiping ( $\text{ng cm}^{-2}$ ).

Pesticide availability from each of the surfaces examined was calculated by comparing surface levels with levels simultaneously collected on aluminum foil deposition coupons.

#### Quality Control

Both blank and fortified foods and wipes were analyzed with each experimental set. The blank foods and wipes were below detectable limits for all pesticides. Recoveries of fortified samples are tabulated in Table 2 (relative standard deviation (RSD) shown in parentheses). Acceptable limits for surrogate recoveries were established as 50–150% for the food samples and 70–130% for the wipe samples. All calculated values fell within these ranges.

## Results and discussion

#### Phase 1

Values for both moisture and fat content of the 13 foods are listed in Table 3. They were classified into one of four groups based on these values. High-moisture/low-fat foods included apples, watermelon, ham, and fat-free bologna. Bologna and

**Table 2.** Percent recoveries for fortified samples (% RSD)

	Percent recovery				
	Wipe <sup>a</sup>	Apple <sup>b</sup> High moisture/low fat	Bologna <sup>b</sup> High moisture/high fat	Bread <sup>b</sup> Low moisture/low fat	Cookie <sup>b</sup> Low moisture/high fat
Malathion	100 (19)	80 (13)	120 (14)	110 (16)	83 (9.6)
Chlorpyrifos	95 (12)	76 (18)	120 (21)	100 (16)	81 (14)
Fipronil	100 (20)	110 (14)	110 (38)	100 (6.8)	110 (17)
Bifenthrin	86 (16)	82 (14)	97 (26)	64 (19)	81 (14)
Permethrin	100 (15)	89 (18)	120 (9.0)	120 (9.2)	88 (16)
Cyfluthrin	86 (14)	74 (18)	77 (22)	95 (20)	63 (16)
Cypermethrin	85 (15)	77 (13)	75 (7.7)	91 (23)	68 (19)
Deltamethrin	82 (14)	76 (8.6)	67 (20)	64 (11)	72 (15)

<sup>a</sup> $n = 16$ .

<sup>b</sup> $n = 4$ .

cheese constituted the high-moisture/high-fat foods. White bread, fruit roll-ups, flour tortillas, and pancakes were classified as low-moisture/low-fat foods. Finally, sugar cookies, graham crackers, and wheat crackers made up the low-moisture/high-fat group.

Pesticide levels were calculated for each food type and these are shown in Table 4. Values ranged from 150 to 700 ng cm<sup>-2</sup> for the high-moisture/low-fat foods and from 150 to 660 ng cm<sup>-2</sup> for the high-moisture/high-fat foods. For the foods with low-moisture content, numbers ranged from 16 to 370 ng cm<sup>-2</sup> for the low-fat foods and from less than

the limit of detection (<LOD) to 146 ng cm<sup>-2</sup> for the high-fat foods. An additional Formica surface was sprayed and wiped for each experimental set and average pesticide loadings ranged from 200 to 870 ng cm<sup>-2</sup> as shown in Table 4. Availability of the pesticides for transfer from the Formica was determined to be 89% (RSD 12%, *n* = 4) by comparison of the surface pesticide loadings with known pesticide application (aluminum foil deposition coupon).

Pesticide levels for each food type were used to calculate transfer efficiencies and results are shown graphically in Figure 1. Analysis of variance (ANOVA) was used to determine whether the mean TE for the eight pesticides could be considered identical for all foods within the given food group and a Tukey–Kramer multiple comparison procedure was employed to identify significant differences between each pair of foods within food groups. Statistical analysis showed TE was consistent with classification groups except for Fruit Roll-ups. Multiple comparisons by the Tukey–Kramer test indicated the TE of Fruit Roll-ups to be significantly higher than that of any other low-moisture, low-fat food (*P* < 0.01), suggesting that the TE of Fruit Roll-ups was not representative of this group.

The average TE was calculated for the representative foods within each classification (results for Fruit Roll-ups were not included). The mean TE for the high-moisture/low-fat foods was 76 ± 6% and for the high-moisture/high-fat foods, 76 ± 9%. For the low-moisture foods, those with a low fat content showed an average TE of 12 ± 5% and for the

**Table 3.** Moisture and fat content of foodstuffs

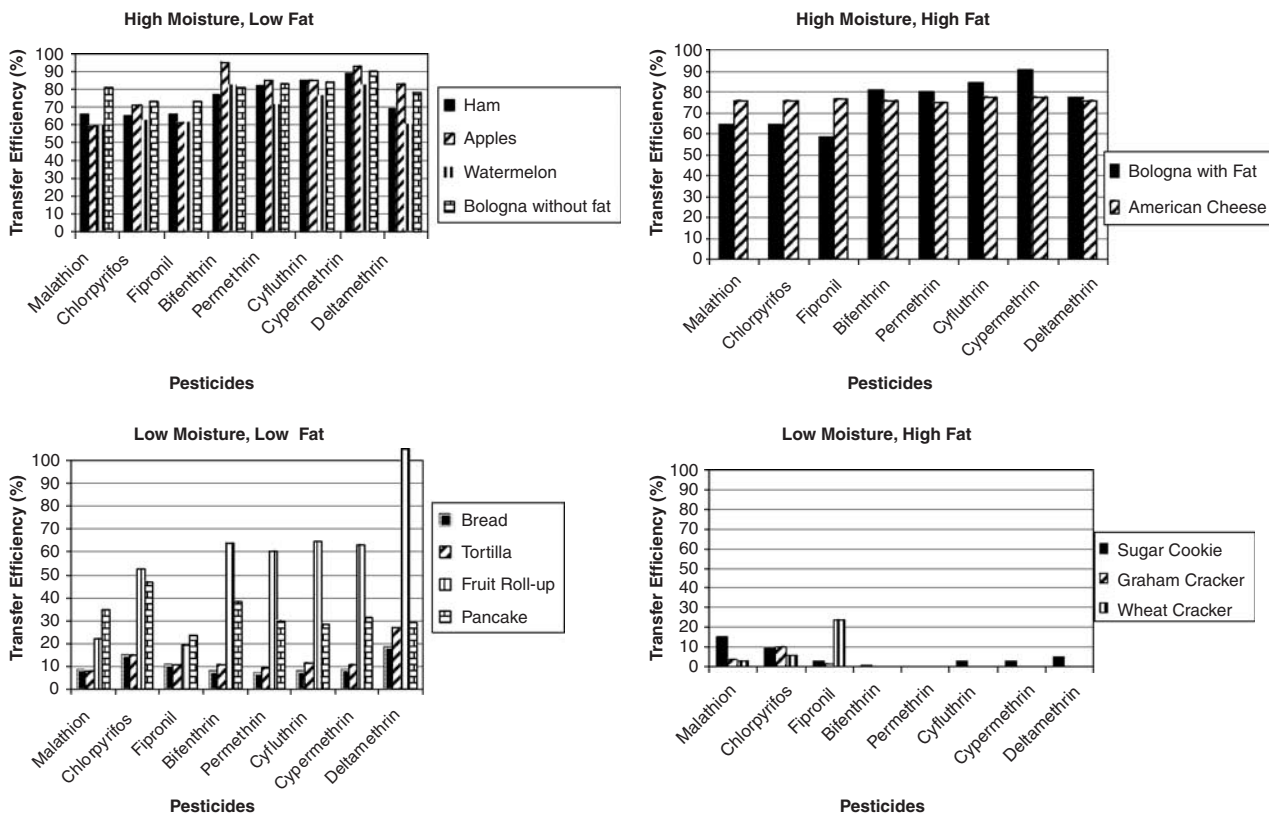
Food item	Moisture (%)		Fat (%)	
Ham	High	71	Low	3.2
Apples		85		0.36
Watermelon		88		0.43
Fat-free bologna		75	High	0
Processed American cheese		53		12
Bologna		69		14
Fruit Roll-ups	Low	10	Low	7.1
Bread		40		3.7
Tortillas		32		8.2
Pancakes		43		3.4
Wheat crackers		2.8	High	20
Graham crackers		7.8		10
Sugar cookies		11		12

**Table 4.** Average transfer of pesticides to foods contacting Formica, ng cm<sup>-2</sup> (*n* = 4)

		Malathion	Chlorpyrifos	Fipronil	Bifenthrin	Permethrin	Cyfluthrin	Cypermethrin	Deltamethrin
High moisture, low fat	Ham	570 ± 220	240 ± 86	410 ± 170	170 ± 76	200 ± 97	170 ± 92	260 ± 130	240 ± 120
	Apples	520 ± 240	250 ± 120	380 ± 220	210 ± 110	200 ± 130	170 ± 120	270 ± 170	290 ± 230
	Watermelon	520 ± 220	220 ± 120	380 ± 150	180 ± 85	170 ± 100	150 ± 94	240 ± 140	210 ± 150
	Fat-free bologna	700 ± 47	260 ± 11	450 ± 38	180 ± 14	200 ± 16	170 ± 22	260 ± 25	270 ± 26
High moisture, high fat	Bologna	560 ± 140	230 ± 45	360 ± 67	180 ± 34	190 ± 48	170 ± 35	260 ± 59	270 ± 45
	Cheese	660 ± 150	270 ± 50	470 ± 96	170 ± 37	180 ± 42	150 ± 33	220 ± 49	270 ± 37
Low moisture, low fat	Bread	74 ± 10	54 ± 7	66 ± 7	18 ± 3	18 ± 2	16 ± 2	24 ± 3	65 ± 4
	Tortillas	65 ± 9	55 ± 6	67 ± 7	24 ± 4	21 ± 5	22 ± 4	31 ± 6	94 ± 14
	Fruit Roll-ups	190 ± 110	190 ± 60	120 ± 100	140 ± 56	140 ± 64	130 ± 49	180 ± 80	370 ± 130
	Pancakes	300 ± 68	170 ± 29	150 ± 41	85 ± 25	71 ± 21	57 ± 18	91 ± 30	100 ± 25
Low moisture, high fat	Sugar cookies	129 ± 7	34 ± 3	18 ± 4	1 ± 1	<LOD	5 ± 1	8 ± 2	17 ± 9
	Graham crackers	34 ± 2	36 ± 4	10 ± 1	1 ± 1	<LOD	<LOD	<LOD	<LOD
	Wheat crackers	22 ± 1	20 ± 2	146 ± 6	<LOD	<LOD	<LOD	<LOD	<LOD
Wipe <sup>a</sup>		870 ± 140	360 ± 44	620 ± 81	220 ± 30	240 ± 40	200 ± 24	290 ± 34	350 ± 35

Limit of detection (LOD) = 1 ng cm<sup>-2</sup>.

<sup>a</sup>Wipe of an additional Formica surface.



**Figure 1.** Pesticide transfer from Formica to all foods.

low-moisture/high-fat foods, a mean TE of  $3.6 \pm 7\%$  was calculated. These values demonstrate that the high-moisture foods transferred the pesticides from Formica more efficiently, regardless of fat content.

As moisture content proved to be a determining factor in pesticide transfer from Formica, the criteria for moisture content (low,  $<50\%$  and high  $>50\%$ ) was examined for accuracy by considering the classification made for pancakes, a food with a borderline moisture content of  $43\%$ . Results indicated the TE of pancakes to be lower than any of the high-moisture, low-fat foods ( $P < 0.01$ ) and therefore this food had been properly classified.

### Phase 2

In the second phase of the study, one representative food was chosen for each category based on the previous ANOVA evaluation. These foods were exposed to the additional treated surfaces. Representative foods included apple (high-moisture/low-fat), bologna (high-moisture/high-fat), bread (low-moisture/low-fat), and sugar cookie (low-moisture/high-fat).

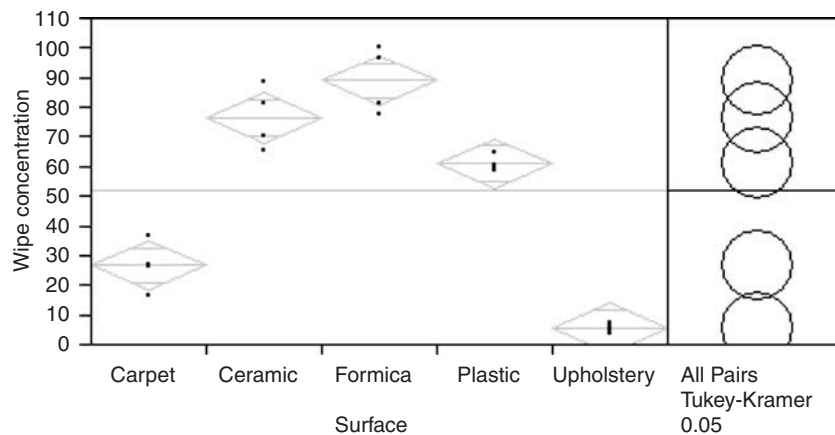
Alternate hard surfaces of ceramic tile and plastic were examined. Pesticide levels for each of the four foods are listed in Table 5. Pesticide levels for the apple brought into contact with the treated ceramic tile ranged from  $190$  to  $750 \text{ ng cm}^{-2}$ .

Bologna demonstrated levels ranging from  $180$  to  $940 \text{ ng cm}^{-2}$ . For the low-moisture foods, levels ranged from  $2$  to  $20 \text{ ng cm}^{-2}$  for the bread samples and from  $3$  to  $39 \text{ ng cm}^{-2}$  for the sugar cookies samples. Food samples brought into contact with plastic showed decreased pesticide levels as compared to the other hard surfaces. The levels on apple samples ranged from  $88$  to  $340 \text{ ng cm}^{-2}$  and values for bologna varied from  $100$  to  $630 \text{ ng cm}^{-2}$ . Bread samples showed levels of  $2$ – $16 \text{ ng cm}^{-2}$  and the range for the sugar cookie samples was  $< \text{LOD}$  to  $31 \text{ ng cm}^{-2}$ .

An additional ceramic tile surface was wiped for each experimental set and average pesticide loadings ranged from  $270$  to  $1,500 \text{ ng cm}^{-2}$  (Table 5). With the ceramic tile samples,  $76\%$  (RSD  $11\%$ ,  $n = 4$ ) of the pesticides sprayed were available for transfer, as compared to the pesticide loading on an aluminum foil deposition coupon sprayed simultaneously. The wipes taken from the ceramic tile samples were additionally investigated to determine any differences in wiping efficiency of individual pesticides. The wiping average of each compound ( $n = 4$ ) was analyzed using a Tukey–Kramer multiple comparison procedure. Results indicated that the averages were not significantly different from each other and wiping efficiency could be calculated as the average efficiency of all eight pesticides.

**Table 5.** Average transfer of pesticides to foods contacting additional hard surfaces,  $\text{ng cm}^{-2}$  ( $n = 4$ )

	High moisture/low fat		High moisture/high fat		Low moisture/low fat		Low moisture/high fat	
	Apple		Bologna		Bread		Sugar cookie	
	Ceramic	Plastic	Ceramic	Plastic	Ceramic	Plastic	Ceramic	Plastic
Malathion	530 ± 86	340 ± 110	940 ± 96	630 ± 160	20 ± 3	12 ± 2	26 ± 4	23 ± 7
Chlorpyrifos	340 ± 61	195 ± 48	400 ± 31	250 ± 62	20 ± 4	16 ± 1	39 ± 6	31 ± 8
Fipronil	440 ± 81	250 ± 84	670 ± 67	270 ± 78	8 ± 1	8 ± 3	4 ± 1	<LOD
Bifenthrin	190 ± 44	170 ± 54	190 ± 15	140 ± 35	2 ± 0.4	2 ± 1	4 ± 1	<LOD
Permethrin	750 ± 180	320 ± 86	430 ± 29	350 ± 80	6 ± 1	8 ± 2	4 ± 1	<LOD
Cyfluthrin	220 ± 55	120 ± 34	240 ± 25	141 ± 23	8 ± 2	5 ± 1	4 ± 1	<LOD
Cypermethrin	270 ± 65	170 ± 47	280 ± 21	160 ± 42	4 ± 1	2 ± 1	3 ± 1	<LOD
Deltamethrin	240 ± 72	88 ± 28	180 ± 18	100 ± 31	5 ± 1	3 ± 1	11 ± 1	<LOD
	Wipe <sup>a</sup>		Wipe <sup>a</sup>		Wipe <sup>a</sup>		Wipe <sup>a</sup>	
Malathion	740	2,800	1,300	890	1,400	2,600	1,100	3,600
Chlorpyrifos	540	1,800	1,000	390	880	1,600	720	1,500
Fipronil	450	1,500	1,500	420	1,200	1,700	970	1,400
Bifenthrin	300	1,500	460	370	420	1,100	310	1,300
Permethrin	1,200	3,500	870	1,700	1,000	2,200	1,100	4,000
Cyfluthrin	310	950	320	470	600	560	380	1,300
Cypermethrin	400	1,600	520	710	550	1,100	380	1,800
Deltamethrin	370	1,100	270	480	620	720	360	1,700

Limit of detection (LOD) =  $1 \text{ ng cm}^{-2}$ .<sup>a</sup> $n = 1$ .**Figure 2.** Visual depiction of statistical comparison of wipe concentrations for five surfaces. Points surrounding and within diamonds represent actual measurements. Horizontal middle of diamond shape represents average of four surface wipes. Y-axis measured in units of  $\mu\text{g cm}^{-2}$ .

Average pesticide loadings on the ABS plastic ranged from 370 to  $4,000 \text{ ng cm}^{-2}$  (Table 5). Analysis of pesticides sprayed on the surface of plastic showed that 61% (RSD 4.4%,  $n = 4$ ) of the pesticides were available. The lower amount may be due to an adsorption of the organic pesticides for this plastic that was not observed with either the Formica or the ceramic tile. In considering the hard surfaces investigated to this point (Formica, ceramic tile, and plastic), multiple comparisons by a Tukey–Kramer test indicated Formica was not significantly different than ceramic tile,

which was not significantly different from plastic (Figure 2). However, plastic was significantly different than Formica.

Transfer efficiencies were calculated for the foods contacting the treated ceramic tile and plastic in the same manner as previously employed. Transfer of pesticides from treated ceramic tile to the four foods followed the same pattern as the Formica (Figure 3). Again, high-moisture foods removed a substantial amount of the pesticides from the treated ceramic tile. However, pesticide transfers were slightly lower than those exposed to the Formica. Presumably, this is due to the

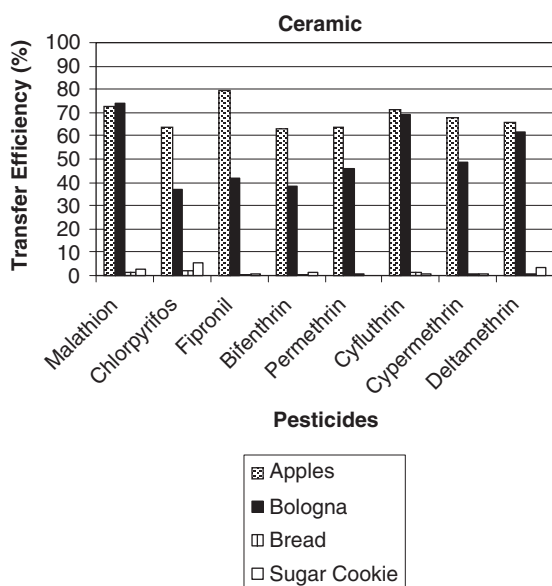


Figure 3. Pesticide transfer from ceramic tile.

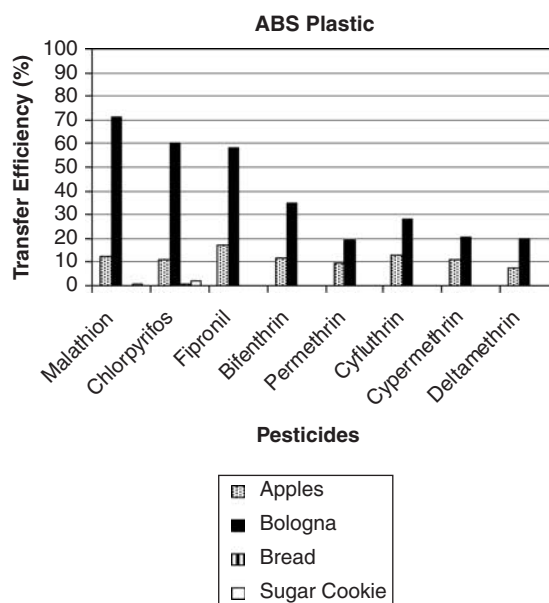


Figure 4. Pesticide transfer from ABS plastic.

somewhat uneven surface area of the tile. Pesticides may be deposited in the pores and be unavailable for transfer when contacted by foods.

Transfer efficiencies for the four foods from treated plastic surfaces are graphically depicted in Figure 4. Apples (high-moisture/low-fat food) showed relatively low TE (approximately 10%). Bologna (high-moisture/high-fat food) also showed diminished transfer when compared to other hard surfaces, particularly for the compounds with low water solubility (pyrethroids). Between the two, it is apparent that enhanced transfer from plastic only occurs in foods with both a high fat content and high moisture content. The pesticides' lipid attraction may improve the transfer. With respect to the low-moisture foods, with both high and low fat content, negligible transfer was demonstrated.

Pesticide loadings on soft surfaces were considerably lower than those for the hard surfaces as measured by wiping (Table 6). For experiments conducted on the upholstery surface, apples showed levels ranging from 8 to 21 ng cm<sup>-2</sup>. Pesticide levels for bologna were in the same range and varied from 4 to 38 ng cm<sup>-2</sup>. For the low-moisture foods, bread levels ranged from 2 to 16 ng cm<sup>-2</sup> and those for sugar cookies ranged from <LOD to 13 ng cm<sup>-2</sup>.

With respect to transfer experiments performed on carpet, apples demonstrated levels of <LOD to 16 ng cm<sup>-2</sup> after contact (Table 6). For the bologna with high moisture and a high fat content, levels varied from 2 to 27 ng cm<sup>-2</sup>. Pesticide levels for bread samples ranged from 1 to 13 ng cm<sup>-2</sup> and those for sugar cookies ranged from <LOD to 25 ng cm<sup>-2</sup>.

Pesticides on softer surfaces (i.e., upholstery and carpet) were transferred to the wipes significantly less than the harder surfaces. Average pesticide loadings for the upholstery

samples ranged from 28 to 140 ng cm<sup>-2</sup> and those for the carpet samples ranged from 140 to 1,800 ng cm<sup>-2</sup> (Table 6). These surfaces appeared to demonstrate absorptive characteristics beyond simple surface irregularities seen with ceramic tile; others have reported less than 1% chlorpyrifos recovered by wiping carpet after pesticide application (Lu and Fenske, 1998). Calculation of availability to wipes by comparison with deposition on the aluminum foil coupon showed that 5.4% (RSD 27%, n=4) of the pesticides were available from the upholstery samples and 26% (RSD 32%, n=4) of the pesticides were available from the carpet samples. Overall, pesticide availability from the soft surfaces, upholstery, and carpet, were significantly different (P<0.01), not only from each other, but from any other studied surface (Figure 2).

Transfer of pesticides to food items from the "soft" surfaces showed considerably less efficiency when compared to transfers from "hard" surfaces, similar to the findings of Rohrer et al. (2003), regardless of moisture content. Overall, transfer from upholstery to the four foods ranged from 5% to 20%. Percent transfer for the foods exposed to carpet were significantly lower (P<0.01) at approximately 5%. However, the levels of transfer to food from the two soft surfaces were quite similar, as shown in the pesticide levels in Table 6. For example, the absolute transfer of malathion from upholstery to an apple slice (21 ng cm<sup>-2</sup>) was not significantly different from the absolute transfer of malathion from carpeting to an apple slice (14 ng cm<sup>-2</sup>). Transfer from upholstery appears to be more efficient by comparison because the wiping procedure was less efficient at removal of the pesticides from the surface; consequently, the divisor of the TE calculation was smaller. Alternatively, to evaluate the

**Table 6.** Average transfer of pesticides to foods contacting soft surfaces,  $\text{ng cm}^{-2}$  ( $n = 4$ )

	High moisture/low fat		High moisture/high fat		Low moisture/low fat		Low moisture/high fat	
	Apple		Bologna		Bread		Sugar cookie	
	Upholstery	Carpet	Upholstery	Carpet	Upholstery	Carpet	Upholstery	Carpet
Malathion	21 ± 6	14 ± 5	35 ± 11	27 ± 6	16 ± 3	13 ± 3	9 ± 2	15 ± 4
Chlorpyrifos	16 ± 5	16 ± 5	38 ± 9	19 ± 3	11 ± 3	10 ± 3	13 ± 3	25 ± 2
Fipronil	15 ± 4	7 ± 4	10 ± 3	6 ± 2	6 ± 1	4 ± 1	< LOD	< LOD
Bifenthrin	8 ± 2	< LOD	6 ± 1	4 ± 1	3 ± 1	2 ± 0.5	5 ± 1	< LOD
Permethrin	20 ± 3	10 ± 5	12 ± 2	7 ± 2	3 ± 1	3 ± 1	< LOD	< LOD
Cyfluthrin	13 ± 3	< LOD	5 ± 1	3 ± 0.4	4 ± 1	5 ± 1	< LOD	< LOD
Cypermethrin	10 ± 1	< LOD	4 ± 1	3 ± 0.4	2 ± 1	2 ± 0.5	< LOD	< LOD
Deltamethrin	9 ± 2	< LOD	4 ± 1	2 ± 1	2 ± 1	1 ± 0.1	5 ± 1	< LOD
	Wipe <sup>a</sup>		Wipe <sup>a</sup>		Wipe <sup>a</sup>		Wipe <sup>a</sup>	
Malathion	100	660	140	780	80	1,800	96	620
Chlorpyrifos	71	460	71	250	57	1,000	76	460
Fipronil	95	390	69	500	64	1,100	72	350
Bifenthrin	55	220	32	290	33	550	43	170
Permethrin	100	400	78	670	79	1,200	87	400
Cyfluthrin	73	140	34	360	40	720	49	140
Cypermethrin	54	170	35	360	42	600	37	160
Deltamethrin	58	260	28	420	38	510	42	220

Limit of detection (LOD) = 1  $\text{ng cm}^{-2}$ .<sup>a</sup> $n = 1$ .

transfer based on the applied loadings, the transfer efficiencies were calculated using the applied pesticide levels. Replacement of the divisor of the TE equation allowed the comparison of the soft surfaces, ignoring the differences in wiping efficiency. By this manner of calculation, transfers from the upholstery and carpet were 2.6% or less and 1.0% or less, respectively. Regardless of the calculation, pesticide transfer from these surfaces was quite low. Furthermore, moisture and fat content of foods did not enhance or influence the transfer of pesticides from soft surfaces.

## Conclusions

Transfer of pesticides from Formica and ceramic surfaces to foods was enhanced with high moisture content; however, fat content had little effect on the TE from these hard surfaces for all pesticides investigated. With the ABS plastic surface, high moisture content alone did not result in enhanced transfer, although high moisture in conjunction with high fat yielded greater transfers. The pyrethroids demonstrated a greater affinity for the ABS plastic surface compared to the other pesticides studied. Overall, low transfer efficiencies from soft surfaces showed negligible differences when comparing foods of different moisture/fat contents. Although moisture and fat were the only variables considered in this study, future studies will investigate actual contact area of specific food items as well as their sorptive characteristics.

In summary, transfer of pesticides from treated surfaces to foods was more likely to occur to a greater extent with denser surfaces. Conversely, transfers from carpet and upholstery fabric to food samples were far less efficient. This indicates that hard surfaces can be grouped together (which may aid in field studies) but carpet and upholstery cannot. During residential monitoring, sample collection to determine the transfer of pesticides from soft surface to foods should take this into account. This study recommends that surface concentration be used to compute TE.

Finally, results demonstrated that the extent of pesticide transfer to foods (for a 10 min contact duration) was less than the total availability as determined by surface wiping. Thus, surface wipes of hard surfaces collected in residences, using the method employed herein, will overestimate the amount of pesticide transferred to foods. Within the CDIM, surface loading is impacted by transfer of pesticides. Therefore, the values determined here will assist in establishing a representative distribution of transfers to impact the residential loadings in a realistic way. This will ultimately allow more accurate predictions of dietary exposures for humans in their homes.

## Disclaimer

The United States Environmental Protection Agency, through its Office of Research and Development, funded and managed the research described here. It has been subjected to the Agency's administrative review and approved for

publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

## References

- Ahmed F.E. Analyses of pesticides and their metabolites in foods and drink. *Trends Analyt Chem* 2001; 20: 649–661.
- Akland G.G., Pellizzari E.D., Hu Y., Roberds M., Rohrer C.A., Leckie J.O., and Berry M.R. Factors influencing total dietary exposures of young children. *J Expo Anal Environ Epidemiol* 2000; 10: 710–722.
- Auyeung W., Canales R.A., Beamer P., Ferguson A.C., and Leckie J.O. Young children's hand contact activities: an observational study via videotaping in primarily outdoor residential settings. *J Expo Anal Environ Epidemiol* 2006; 16: 434–446.
- Bernard C.E., Berry M.R., Wymer L.J., and Melnyk L.J. Sampling household surfaces for pesticide residues: comparison between a press sampler and solvent-moistened wipes. *Sci Total Environ* 2008; 389: 514–521.
- Black K., Shalat S.L., Freeman N.C.G., Jimenez M., Donnelly K.C., and Calvin J.A. Children's mouthing and food-handling behavior in an agricultural community on the US/Mexico border. *J Expo Anal Environ Epidemiol* 2005; 15: 244–251.
- Freeman N.C.G., Hore P., Black K., Jimenez M., Sheldon L., Tulve N., and Lioy P.J. Contributions of children's activities to pesticide hand loadings following residential pesticide application. *J Expo Anal Environ Epidemiol* 2005; 15: 81–88.
- Freeman N.C.G., Sheldon L., Jimenez M., Melnyk L., Pellizzari E., and Berry M. Contribution of children's activities to lead contamination of food. *J Expo Anal Environ Epidemiol* 2001; 11: 407–413.
- Goldman L.R. Environmental health issues. *Environ Health Perspect* 1995; 103(Supplement 6): 13–18.
- Hu Y., Ackland G.G., Pellizzari E.D., Berry M.R., and Melnyk L.J. Use of pharmacokinetic modeling to design studies for pathway-specific exposure of model evaluation. *Environ Health Perspect* 2004; 112: 1697–1703.
- Hubal E.A.C., Sheldon L.S., Burke J.M., McCurdy T.R., Berry M.R., Rigas M.L., Zartarian V.G., and Freeman N.C.G. Children's exposure assessment: a review of factors influencing children's exposure, and the data available to characterize and assess that exposure. *Environ Health Perspect* 2000; 108: 475–486.
- Krieger R.I., Bernard C.E., Dinoff T.M., Ross J.H., and Williams R.L. Biomonitoring of persons exposed to insecticides used in residences. *Ann Occup Hyg* 2001; 45: S143–S153.
- Landrigan P.J., Claudio L., Markowitz S.B., Berkowitz G.S., Romero H., Wetmur J.G., Matte T.D., Gore A.C., Godbold J.H., and Wolff M.S. Pesticides and inner-city children: exposures, risks, and prevention. *Environ Health Perspect* 1999; 107(Supplement 3): 431–437.
- Lu C., and Fenske R.A. Air and surface chlorpyrifos residues following residential broadcast and aerosol pesticide applications. *Environ Sci Technol* 1998; 32: 1386–1390.
- Melnyk L.J., Berry M.R., Sheldon L.S., Freeman N.C.F., Pellizzari E.D., and Kinman R.N. Dietary exposure of children in lead-laden environments. *J Expo Anal Environ Epidemiol* 2000; 10: 723–731.
- Rohrer C.A., Hieber T.E., Melnyk L.J., and Berry M.R. Transfer efficiencies of pesticides from household flooring surfaces to foods. *J Expos Anal Environ Epidemiol* 2003; 13: 454–464.
- Rosenblum L., Garris S.T., and Morgan J.N. Comparison of five extraction methods for determination of incurred and added pesticides in dietary composites. *JAOAC Int* 2002; 85: 1167–1176.
- Tomerlin J.R., Berry M.R., Tran N.L., Chew S., Peterson B.J., Tucker K.D., and Flemming K.H. Development of a dietary exposure potential model for evaluating dietary exposure to chemical residues in foods. *J Expo Anal Environ Epidemiol* 1997; 7: 81–101.
- Wong C.S. Environmental fate processes and biochemical transformations of chiral emerging organic pollutants. *Anal Bioanal Chem* 2006; 386: 544–558.