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Assessment of Dermal Exposure to Pesticides Under "Pick Your Own" Harvesting Conditions

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Humans may be exposed to pesticides through several routes, the most common being consumption of pesticide-treated food. This route has been well studied and assessed (Krol, 2000 and references cited therein). A second route, exposure to air-borne pesticides in both enclosed and outdoor environments, has also been well evaluated (Wallace, 1991). The special case of exposure via air or skin of persons, such as agricultural field workers or exterminators, who routinely handle pesticides has been examined and addressed through government regulations (40 CFR 170). In contrast to these cases, very little information is available regarding exposure of the general public who engage in "pick-your-own" (PYO) activities.

Accordingly, in 2001 and 2002 we conducted a study to examine potential dermal exposure to pesticide residues under actual field conditions in commercially operated PYO facilities. This term is loosely defined as an environment in which the consumer may enter a commercial agricultural setting and harvest produce such as strawberries, blueberries, and raspberries (U.S. EPA, 1997). The only information readily available on post-application dermal exposure doses under pick-your-own harvesting conditions is for pesticide residues on PYO strawberries (U.S. EPA, 1997). This evaluation, however, is based purely on mathematical models and does not take into account actual field data.

In the study described here we present an operational approach for assessing transfer of pesticides from treated crops to surfaces used for manual harvest of the crop. The data presented under the conditions and methods specified provide the first assessment of potential dermal exposure to pesticides under realistic PYO field conditions.

MATERIALS AND METHODS

Samples were collected during both the 2001 and 2002 seasons by the same right-handed individual. The collector wore nylon Wells-Lamont glove liners (Style M115, size small, lot #CN357, Morton Grove, IL, 60053) on both hands during harvesting of each produce sample. During method development cotton liners (Protective Industrial Products, Guilderland Center, NY, 12085) were also evaluated; while other researchers have relied on cotton fabric for the determination of residues of the fungicide captan on strawberry leaves (Bissel,

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1990), we noted interferences in the analysis from this fabric which mandated the use of nylon liners.

Primarily strawberries and blueberries were collected, although single samples of raspberries, peaches, and green beans were also harvested. For each berry sample, no less than one and no more than two pint(s) was collected. The produce was picked and placed directly into a brown paper bag as harvested. Upon completion of the harvesting of a single sample, the right-hand glove liner was placed into a separate brown paper bag from the left-hand liner. Two field blanks consisting of gloves brought into the field but not worn for harvesting were included. The gloves and fresh produce were delivered to the laboratory on the same day as their collection.

Produce samples were analyzed by a method developed in our laboratories (Pylypiw, 1993) employing a liquid extraction procedure followed by GC analysis.

As each glove sample was removed from its brown paper bag, the top colored band encircling the glove was removed; during method development it was determined that this band caused interferences with the analysis. Each glove was placed into an individual 250 mL brown glass jar to which 50 mL of 2-propanol and 100 mL petroleum ether were added. The jar was capped, shaken vigorously for approximately 2 minutes and allowed to sit overnight at room temperature. The extracts were transferred to a 500 mL separatory funnel, maximizing solvent transfer from the glove to the funnel. To the liquid in each funnel 200 mL of deionized water was added and 5 mL of a saturated sodium sulfate solution. The funnel was swirled and the aqueous layer drained and discarded. This process was repeated two additional times without the addition of sodium sulfate. The petroleum ether layer was then transferred to a 40 mL clear glass vial containing approximately 5 grams of anhydrous sodium sulfate to remove any residual traces of water.

The samples were quantified and confirmed on an Agilent (Agilent Technologies, Palo Alto, CA) model 6890 gas chromatograph (GC) equipped with dual injector ports and detectors. Quantification was accomplished with an electron capture detector (ECD); confirmation was done using an Agilent 5973 mass selective detector (MSD). For all analyses an Agilent 7683 auto sampler was used. Each injection port was fitted with a Supelco MDN-12 fused capillary column; 30m x 0.25 mm ID x 0.25 µm film thickness (Supleco, St. Louis MO, part no. 24388). Operating conditions were as follows for the GC/ECD analysis: GC inlet set at 250 °C, 1 µL injections made at 30 psi in pulsed splitless mode maintained for one minute; hydrogen carrier gas was supplied by a hydrogen generator (Balston model 75-34) at a flow rate of 1.2 mL/minute; ECD detector set to 325 °C using a make-up gas of P-5 at 60 mL/minute. The initial GC oven temperature was set at 75 °C, ramped at 25 °C/minute to 250 °C, then ramped at 30 °C/minute to a final temperature of 280 °C and held for 16 minutes.

For the GC/MS analysis, a 2 μL splitless injection was made into a Programmable Temperature Vaporization (PTV) inlet, which was ramped from 75 °C to a final temperature of 320 °C at a ramp of 500 °C/min and then held for 2 min at 320 °C. The carrier gas was helium at a flow rate of 1.1 mL/min; the mass spectrometer was operated in full scan mode over the range m/z 70 to m/z 430.

Two mixed calibration standards containing common pesticides (Krol, 1999) at concentrations ranging from 0.05 to 2 ppm were run before the samples, after every six samples, and at the end of the entire run. Quantification was by external standard calibration. To assess recovery, glove liners in triplicate were spiked with a mixed standard containing pesticides found in this study at three concentration levels 0.005μg/glove, 0.010μg/glove, and 0.020μg/glove and extracted using the protocol outlined above.

RESULTS AND DISCUSSION

A total of 50 produce samples and 100 glove liners were analyzed as part of this study. None of the produce samples exceeded EPA tolerance levels. The data from the two-year study are presented in Table 1 for the 2001 harvest and in Table 2 for the 2002 harvest. Recoveries, averaged over the triplicate glove spikes at the three levels of spiking, were as follows for commonly found pesticides: vinclozolin (91%), malathion (114%), DCPA (81%), captan (99%), endosulfan I (79%), endosulfan II (81%), endosulfan sulfate (88%), bifenthrin (99%), iprodione (96%), and fenpropathrin (112%). None of the data in the tables has been corrected for recovery. For quantification on the ECD, the LOD for the glove matrix was 0.005 μg/glove; the LOD for produce was 0.002 μg/g. If an entry in either table is blank, the residue was below the LOD value.

There are some general comments to be made regarding the data in the two tables. First, as stated above, harvesting throughout both seasons was conducted by the same right-handed individual. Although there are some exceptions, the residues detected on the right-hand glove are consistently higher than those detected on the left-hand glove. A paired t-test of the data confirmed that the difference between the right-glove residues was significantly different from the left-glove residues ($p<0.05$). Second, in only five instances is a pesticide found on a glove sample without its being found in the corresponding fruit sample: four strawberry samples for fenhexamid in 2001 and one strawberry sample for captan in 2002. And third, field blanks were negative for pesticide residues. The hypothesis of this study is that pesticides used on field crops are transferred to surfaces in contact with the crops during harvesting under "pick-your-own" conditions. All three of the comments regarding the data from the exposed gloves and the controls are consistent with the hypothesis being correct.

Of the pesticides detected in this study, only iprodione and bifenthrin are identified as systemics (Meister, 2005). It would be reasonable to assume that

Table 1. 2001 Data

		Endosulfan	Fenhexamid	Captan	Malathion	DCPA	Bifenthrin	Vinclozolin	Iprodione	Sulfur
STRAWBERRIES	LG[1]									
	RG[1]	1.86								
	Fruit[2]	0.014	0.11							
	LG		0.5							
	RG		2.4	18.4						
	Fruit		0.12	0.36						
	LG		0.074							
	RG		0.12							
	Fruit	0.006	0.007							
	LG	0.35	0.25	2.3		0.05				
	RG	3.8	68.4	1150	35	0.38				
	Fruit	0.16	0.4	9	0.36	0.16				
	LG	0.6	32.1							
	RG	1.9	1.6							
	Fruit	0.16	0.64							
	LG									
	RG	0.3								
	Fruit	0.15								
	LG									
	RG									
	Fruit	0.088								
	LG									
	RG	5.2		7.4						
	Fruit	0.17								
	LG		5	3.3	0.58					
	RG		174	600	51.7		5.2			
	Fruit		1.1	0.14	0.084		0.06			
	LG	0.2								
	RG	2								
	Fruit	0.15				0.05				
	LG			283	25.9	0.48		0.19		
	RG			484	44.8	2.62		0.73		
	Fruit			0.21	0.1	0.2		0.04		
	LG									
	RG									
	Fruit	0.076								

Table 1. Continued

		Endosulfan	Fenhexamid	Captan	Malathion	DCPA	Bifenthrin	Vinclozolin	Iprodione	Sulfur
STRAWBERRIES	LG		1.26	77.3	9.16					
	RG		9.41	1120	95.6					
	Fruit		0.11	0.52	0.004					0.84
	LG									
	RG	2.6								
	Fruit	0.13								
	LG	0.7	8.5							
	RG	1.5	2.72							
	Fruit	0.15								
	LG		0.74							
	RG	0.8	0.66							
	Fruit	0.14								
	LG	0.7	0.86							
	RG	1.1	2.52	4.84						
	Fruit	0.18		0.058						
	LG	0.7	1.42							
	RG	1.3	7.85							
	Fruit	0.11								
BLUEBERRIES	LG				3.41					
	RG			45.6	9.26					
	Fruit				0.13					
	LG									
	RG									
	Fruit			0.032						
	LG								0.08	
	RG								0.96	
	Fruit	0.048							0.32	
	LG									
	RG									
	Fruit	0.05								
	LG									
	RG									
	Fruit	0.046								

[1]LG=left glove; RG=right glove. Glove values are given in total µg/glove.

[2]Fruit values are given in µg/kg.

During the 2001 season 3 strawberry samples, 5 blueberry samples, and 1 raspberry sample contained no detectable pesticide residues in fruit, LG, and RG for each sample.

Table 2. 2002 Data

		Captan	Endosulfan	Iprodione	Fenpropathrin	DCPA
STRAWBERRIES	LG					
	RG	3.6	3.27			
	Fruit	0.011	0.197			
	LG					
	RG	8.3				
	Fruit					
	LG					
	RG	84.8	3.237			0.5
	Fruit	0.007	0.114			75.7
	LG	10.1	0.361			
	RG					
	Fruit	0.008	0.112			
	LG					
	RG	41.3				
	Fruit	0.046	0.072			
	LG				2.19	
	RG				14.7	
	Fruit				0.070	
BLUEBERRIES	LG	1.8				
	RG	39.7				
	Fruit	0.164				
	LG	292.3				
	RG	846.5				
	Fruit	3.736				
	LG	10.8				
	RG	18.8				
	Fruit	0.258	0.056			
	LG	31.0				
	RG	125.0				
	Fruit	0.724.0				
	LG	22.2	10.688			
	RG	280.0	27.197			
Peaches		3.500	0.823			
	LG					
	RG	98.6		64.996		
Raspberries		2.004		3.418		

During the 2002 season 1 strawberry sample, 4 blueberry samples and 1 green bean sample contained no pesticide residues in fruit, LG, and RG for each sample.Endosulfan value listed is the total of endosulfan I,endosulfan II, and endosulfan sulfate.

systemics are likely found *in* the fruit rather than on the plant surfaces. Conversely, non-systemics, such as endosulfan and captan, would likely be found *on* plant surfaces. Furthermore, no correlation was found between the amount of pesticide in a fruit sample and the amount on the corresponding glove sample. Therefore, it is reasonable to assume that most of the pesticide residues detected on the gloves were dislodged from *all* plant surfaces that came in contact with the collector's hands during harvest, and not solely from the fruit portion.

The surface area of the small size glove liners used during harvesting was determined to be approximately 300 cm^2. Using this number, together with the largest residue found on a glove sample (1197 μg captan for a 2001 strawberry sample), we calculate a value of 4 μg of captan residue/cm^2 of glove surface. It is informative to compare this value to the dislodgeable foliar residue (DFR) calculated from equation 1 (U.S. EPA, 1997), specifically for captan:

$$DFR_t = (AR * F) * (1\text{-}D)^t * CF2 * CF3 = 3.95\ \mu g/cm^2 \qquad (1)$$

where t = postapplication day used in calculation. Since the Maestro 75DF label indicates "DO NOT reenter treated areas within 48 hours of application", we use t = 2.
AR = application rate. Maestro 75DF fungicide is 75% captan; application rate of ai is 2.97lbs/acre as determined from label instructions.
F = fraction of active ingredient retained on foliage. Value suggested in reference is 0.2.
D = fraction of residue dissipating daily. Using a half-life of captan on plants of 3 days (RED, 1999), a reasonable value for D may be computed as 0.23.
CF2 = conversion factor to convert lbs ai to μg (= 4.54E8 μg/lb)
CF3 = conversion factor to convert surface area to cm^2 (= 2.47E-8 acre/cm^2).

The pesticide residue found on gloves in the present study, 4 μg of captan residue/cm^2 of glove surface, compares well with the dislodgeable foliar residue calculated from the EPA approach, 3.95 μg of captan residue/cm^2, using the values specified above. This agreement supports the operational method used here for assessing dermal exposure to pesticide residues under PYO conditions.

This study confirms for the first time the intuitive conclusion that pesticide transfer from the treated crop to the surface used in manual harvesting of the crop does occur under actual pick your own harvesting conditions. Labeling requirements to address PYO operations may be a reasonable consequence of the study.

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REFERENCES

Bissel, S, Graham, E, Marade J, Troiano J, del Valle M (1990) Comparison of sampling methods for determination of pesticide residue on leaf surfaces. State of California, Department of Food and Agriculture, Division of Pest Management, Environmental Protection and Worker Safety Environmental and Pest Management Branch, 1220 N Street, Sacramento, CA 95814.

Code of federal regulations (CFR) (1999) Title 40 part 170, Worker protection standards, U.S. Government Printing Office, Washington, D.C.

Krol WJ, Arsenault, T, Pylipiw, HM Jr., Mattina, MJI (2000) Reduction of pesticide residues on produce by rinsing. J Ag Food Chem 48: 4666-4670.

Krol, WJ, Arsenault, T, Mattina, MJI (1999) Pesticide residues in produce sold in connecticut 1999. Bulletin 964, The Connecticut Agricultural Experiment Station, New Haven, CT.

Meister RT (ed) Crop protection handbook (2005) 37733 Euclid Ave.,Willoughby, OH 44094.

Pylypiw, HM, Jr. (1993) Rapid gas chromatographic method for the multiresidue screening of fruits and vegetables for organochlorine and organophosphate Pesticides. J AOAC Int 76: 1369-1373.

Reregistration eligibility decision (RED): Captan, Document Number EPA-738-R-99-010, U.S. Environmental Protection Agency, Office of Pesticide Programs, U.S. Government Printing Office; Washington, D.C., Nov 1999; 2-49.

U.S. EPA (1997) Standard operating procedures for residential exposure assessments, draft report. Washington D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs. http://www.epa.gov/oscpmont/sop/1997/semptember/sopindex.htm (last accessed 02/16/05).

Wallace, LA (1991) Comparison of risks from outdoor and indoor exposure to toxic chemicals. Env Health Persp 95: 7-13.