Department of Pesticide Regulation

Mary-Ann Warmerdam
Director

MEMORANDUM

Arnold Schwarzenegger
Governor

TO: Joseph P. Frank, Senior Toxicologist **HSM-06002**
Worker Health and Safety Branch

FROM: Sheryl Beauvais, Staff Toxicologist (Specialist) *(original signed by S. Beauvais)*
Worker Health and Safety Branch
(916) 445-4268

DATE: February 24, 2006

SUBJECT: REVIEW OF CARBARYL AIRBLAST EXPOSURE MONITORING AND SOCK DOSIMETRY ANALYTICAL METHOD VALIDATION STUDIES, REGISTRATION DATA PACKAGES 210452 AND 213826

I reviewed worker exposure monitoring data from Registration Data Package 210452, which was submitted by the Agricultural Handlers Exposure Task Force (AHETF). This data package contains two study reports, "Determination of Dermal and Inhalation Exposure to Workers During Application of a Liquid Pesticide Product by Open Cab Airblast Application to Orchard Crops," and "Validation of AHETF Method AHETF-AM-006, Determination of Carbaryl in Sock Samples." These studies (Smith, 2004 and Brookey, 2004, respectively) were submitted by the AHETF in support of AHETF's generic handler exposure database. The first report (Smith, 2004) was subsequently re-issued by AHETF because an error had been discovered in normalized exposure estimates: inhalation exposures had been normalized for sample pump rate rather than default human respiratory rates (Smith, 2005). The re-issued report is one of six reports, including another analytical method validation study (Reed, 2004), submitted to DPR by AHETF; these reports are in Registration Data Package 213826. In the interval between the original and re-issued reports, AHETF decided not to provide normalized exposure estimates; thus, Smith (2005) contains only a summary of residues found in sample matrices.

Airblast Exposure Monitoring Study

Worker exposure monitoring, with 25 male worker replicates, was done during airblast applications to mature, commercial orchard crops in 2003. Applications of Sevin XLR Plus liquid formulation of carbaryl were made to peaches in Georgia (8 worker replicates); to apples in Idaho (8 worker replicates); and to citrus in Florida (9 worker replicates). Application rates were 3.0 lbs active ingredient (AI)/acre to peaches and citrus, and 2.0 lbs AI/acre to apples. This study had two main goals: to fill a data gap by monitoring exposure to airblast applicators in orchards driving open-cab tractors, and to determine a protection factor for rain gear (rain hats and hooded rain jackets) that are considered "chemical-resistant" (CR) under the Worker Protection Standard (WPS).

After reviewing Smith (2005), I consider the study acceptable for use in exposure assessment. It was performed in accordance with the protocol reviewed by regulatory representatives at the

AHETF Joint Regulatory Committee, and the quality assurance results were generally acceptable (discussed below). Results were reported in a way that differs from DPR practice: AHETF reported geometric means, and DPR practice is to use the arithmetic mean rather than the geometric mean as a central tendency estimate, with logarithmic distributions used to calculate upper bound estimates for short-term exposure (Powell, 2003). In this memo, I have summarized the results in ways that are consistent with DPR practice.

Preliminary data from this study, reported to U.S. EPA by AHETF, were incorporated in the Interim Registration Eligibility Decision (IRED) for carbaryl (U.S. EPA, 2004). U.S. EPA (2004) determined that requiring "WPS-compliant headgear" (i.e., rain hats or hoods) would partially mitigate head and neck exposure for open-cab airblast applicators.

Site Descriptions

The sites were described as follows:

Georgia (replicates 1 –8): Peach orchards containing several varieties of peaches were used in the study. Heights of the trees were reported as "varied, and were approximately 10 to 11 feet tall." Tree spacing ranged from 10 to 15 feet.

Idaho (replicates 9 –17): Apple orchards containing several varieties were used. Tree heights ranged between 7 and 15 feet, and spacing ranged from 10 to 15 feet.

Florida (replicates 19 –27): Citrus groves containing several varieties were used. Tree heights ranged between 10 and 15 feet, and spacing ranged from 15 to 24 feet.

Row widths are similar to those reported as typical for California for these crops (UCCE, 2005).

However, it should be noted that the presence or absence of an enclosed cab has little effect on the wheel width of the tractor and only slight effect on the effective zone of operation for the seated worker. It's also possible that tree limbs close enough to hit the enclosed cab might also strike an un-enclosed tractor operator (personal communication, Harvard Fong, Senior Industrial Hygienist, Worker Health and Safety Branch, August 2, 2005).

Rainfall occurred during some applications in Florida and Georgia. Rainfall of approximately 0.1 inch was reported during monitoring of replicates 1 – 5 (Georgia), and trace amounts of rainfall were reported during monitoring of replicates 22 – 24 (Florida). These rainfall amounts were not considered excessive by Smith (2005), nor were exposures of replicates 1 – 5 or 22 – 24 generally lower than exposures than other replicates.

Airblast Applications

Applicators were monitored for 5 – 8 hours each, which is about the length of a typical workday for them. Actual spray times ranged 3.3 – 5.7 hours; applicators handled 24 – 90 pounds AI (11 – 41 kg), and treated 12 – 30 acres (5 – 12 ha). All applicators had open-cab tractors; however, replicates 19 and 21 – 27 were reported to have "open cab with roof." That is, all but one of the Florida replicates had a roof above the applicator. The potential effect of an open-cab tractor with a roof on an applicator's exposure is discussed below, after results are presented.

The normal work clothing worn by workers was summarized in Table 2 of the Field Phase Report (Belcher, 2004). All clothing was described as being in "good" condition. A statement below the table said, "Clothing with holes, tears, and excessive wear were not approved; and the worker was provided an acceptable article of outer clothing." Long-sleeved shirts were supplied for the following replicates: 2, 3, 12, 21, and 25. Replicate 2 had a shirt button missing; no reason is given for the replacement of shirts for the other four replicates. Replicate 12 also had a shirt replaced during the study, as it was torn by a tree branch about 5.5 hours into the application. Long pants were provided for replicates 12 and 25. The rationale for allowing workers to supply clothing, and potential effects of decisions to provide clothing for some workers, are discussed below.

Applicators wore personal protective equipment (PPE) specified by the product label over their normal work clothing. The PPE worn by each applicator was summarized in Table 3 of the Field Phase Report (Belcher, 2004). In general, PPE included CR gloves, either leather or rubber boots, and either a Sou'wester style wide-brimmed rain hat or a hooded rain jacket. Sou'wester hats were made of a "3-ply chemical-resistant material," with "a 5-inch rear brim, inside flaps for the ears, and an elastic chin strap." Waist-length hooded jackets were made of "polylaminated Tyvek® material," with a zipper front, snap over-flap and an elastic band around the hood. Both the rain hat and jacket were considered to be "chemical-resistant," although this has not been verified. In this study, both the rain hat and the hood on the hooded jacket were referred to as "headgear."

Exposure Monitoring

Dermal exposure monitoring was done according to the AHETF standard operating procedure (SOP), with cotton inner whole-body dosimeter (WBD), inner socks, face/neck wipes and hand washes. To estimate a protection factor for the rain hat and rain hood, both inner and outer head patches were used. There was no outer dosimeter on the body, only an inner dosimeter under long-sleeved shirt and long pants or coverall. Applicators wore a single layer of clothing, except for those wearing a hooded rain jacket. The hooded rain jacket gives an additional layer, in addition to the long-sleeved shirt, over the arms and torso. This fact was considered in interpreting dermal exposure monitoring results, as discussed below.

Inhalation exposure monitoring was also done according to the AHETF SOP. Breathing zone monitoring was done using OSHA Versatile Sampler (OVS) tubes, each containing glass fiber filter and XAD-2 sorbent and connected to a sampler pump calibrated to 2 liters per minute.

Analytical Method

Each sample matrix (OVS tubes, WBD, socks, face/neck wipes, hand wash solution, and inner and outer head patches) was analyzed according to methods previously validated and documented by the Agricultural Reentry Task Force. Table 1 lists the limit of quantification (LOQ), the number of samples below the LOQ (<LOQ), and the total number of samples for each matrix. Most matrices had no samples <LOQ; the exceptions were inner head patches (four out of 25 samples, or 16%) and hand wash solutions (one out of 54 samples, or 1.9%).

Table 1. Summary of Exposure Monitoring Samples Below the LOQ of Carbaryl [a]

Matrix	LOQ [b]	No. Samples <LOQ	Total No. Samples	% Samples <LOQ
Inner Whole Body Dosimeters [c]	0.25 [d]	0	150	0
Socks	0.25	0	25	0
Inner Head Patches	0.25 [d]	4	25	16
Outer Head Patches	0.25 [d]	0	25	0
Face/Neck Wipes	1.0	0	25	0
Hand Wash Solutions [e]	1.0	1	54	1.9
Air Sampling Tubes	0.01 [f]	0	25	0

[a] Summary of data from open-cab airblast exposure monitoring study (Smith, 2004), Table 15 – Table 21 of analytical report.
[b] LOQ = limit of quantification, expressed as (µg/sample).
[c] Each whole body dosimeter was divided into six sections: front torso, rear torso, lower leg, upper leg, lower arm, and upper arm. Each section was analyzed separately; thus, there are six times as many samples than for other matrices.
[d] For samples containing more than 500 µg/sample, the LOQ was 20 µg/sample (Florisil cleanup was omitted).
[e] Multiple hand wash samples were collected from each worker, resulting in more than 25 samples.
[f] For samples collected on the last day of the field study, the LOQ was 0.05µg/sample due to matrix interference.

Carbaryl was extracted from cloth matrices (WBD, socks, face/neck wipes, and patches) with acetone. If necessary because of anticipated or demonstrated low residues in the matrix (<50 µg/sample), an aliquot of the extract was subjected to Florisil cleanup prior to dilution and analyzed with high performance liquid chromatography (HPLC). Hand wash samples were extracted using dichloromethane. An aliquot of the extract was evaporated to dryness, then reconstituted in acetonitrile:water (1:1 v:v) for HPLC analysis. Sorbent in each air sampling tube was extracted using acetonitrile. An aliquot of the extract was evaporated to dryness, then reconstituted in acetonitrile:water (1:1 v:v) for HPLC analysis.

Quality Assurance

Quality assurance samples consisted of laboratory control samples of each matrix, laboratory-fortified samples of each matrix, and field fortified samples of each matrix. Travel spikes were prepared for WBDs and OVS air sampling tubes, but not analyzed.

Field fortifications (FFs) consisted of each sample matrix spiked with formulated product. Fortification suspensions for all matrices except air sampling tubes were prepared in the laboratory. Air sampling tubes were fortified in the laboratory, then frozen until monitoring began in the field, when they were attached to sample pumps that were running throughout exposure monitoring. FFs were done daily. Mean overall FF recoveries and coefficients of variation (CVs) are reported in Table 2.

Table 2. Summary of Field Fortification Recoveries for Carbaryl [a]

Matrix	Level [b]	Mean Recovery (%)	SD	CV
Inner Whole Body Dosimeters	5.0	84.5	13	15
	100	97.7	4.8	4.9
	500	98.0	4.6	4.7
	5,000	107	5.2	4.9
Socks	5.0	69.2	14	20
	100	77.5	9.6	12
	500	92.5	10	11
Inner Head Patches	5.0	83.7	11	13
	100	98.1	13	13
Outer Head Patches	100	86.9	8.4	9.7
	5,000	102	5.7	5.6
Face/Neck Wipes	5.0	84.9	7.3	8.6
	100	95.5	8.2	8.6
Hand Wash Solutions	5.0	99.6	6.6	6.6
	100	96.6	9.4	9.7
Air Sampling Tubes	0.05 [c]	109	14	13
	50	101	9.0	8.9

[a] Summary of data from open-cab airblast exposure monitoring study (Smith, 2005), Table 8 – Table 14 of analytical report. Mean and standard deviation (SD) calculations reported by Smith (2005) were spot-checked, and coefficient of variation (CV) was calculated from reported mean and SD (CV = 100*SD/mean).
[b] Fortification level in µg/sample, except for air sampling tubes, where level is µg/tube.
[c] One sample had a recovery of 196% (probably double-spiked), and was omitted from statistical calculations as an outlier.

Mean FFs for each matrix, except socks, ranged 84.5 – 107%. Mean FF recoveries for socks at the low, medium and high levels (5.0, 100, and 500 µg) were 69.2%, 77.5% and 92.5%, respectively. All matrices except socks at the low fortification level had mean FF recoveries within a range considered acceptable to DPR (70 – 120%). However, for airblast applicators the feet are not anticipated to be a substantial part of dermal exposure, and unacceptable FF

recoveries from socks do not affect the evaluation of this study. Data from socks were used to estimate exposure to feet.

Smith (2005) adjusted sample residues for FF recovery, with residue range intervals defined by mid-points between FF levels. These adjustments are reported in Table 10 of Smith (2005). For example, WBD samples with residues ≤ 52.5 µg were divided by 0.845, as the mean FF recovery for dosimeters fortified at the 5 µg level was 84.5%. WBD samples with residues in the range of 52.5 – 300 µg were adjusted by dividing by 0.977, and so on. DPR policy is in general agreement with U.S. EPA policy, in which samples are corrected for field fortification recoveries below 90% (U.S. EPA, 1992; U.S. EPA, 1998). Adjustment factors used by Smith (2005) and in estimating exposures reported in this memo are summarized in Table 3.

Table 3. Field Fortification Recovery Adjustment Factors for Samples [a]

Matrix	Residue Range [b]	Smith (2005) Adjustment Factor [c]	DPR Adjustment Factor [d]	Residues from Table No. in Smith (2005) [e]
Inner Whole Body Dosimeters	≤ 52.5	0.845	0.845	11
	52.5 - 300	0.977	1.0	15
	300 – 2,750	0.980	1.0	15
	> 2,750	1.07	1.0	15
Socks	≤ 52.5	0.692	0.692	12
	52.5 - 300	0.775	0.775	12
	> 300	0.925	1.0	16
Inner Head Patches	≤ 52.5	0.837	0.837	12
	> 52.5	0.981	1.0	16
Outer Head Patches	≤ 2,550	0.869	0.869	12
	> 2,550	1.02	1.0	16
Face/Neck Wipes	≤ 52.5	0.849	0.849	12
	> 52.5	0.955	1.0	16
Hand Wash Solutions	≤ 52.5	0.996	1.0	16
	> 52.5	0.966	1.0	16
Air Sampling Tubes	≤ 25.025	1.09	1.0	17
	> 25.025	1.01	1.0	17

[a] Summary of data from open-cab airblast exposure monitoring study (Smith, 2005), Table 8 – Table 14 of analytical report.
[b] Residue in µg/sample, except for air sampling tubes, where level is µg/tube. Ranges are selected using midpoints between successive field fortification levels.
[c] Smith (2005) adjusted all samples for field fortification recoveries. Values from Table 10 in Smith (2005).
[d] Department of Pesticide Regulation (DPR) policy is to adjust residues for samples with corresponding field fortification recoveries of less than 90%.
[e] Sample residues used to estimate exposure. Tables 11 and 12 in Smith (2005) summarize adjusted residues, and Tables 15, 16, and 17 summarize unadjusted residues.

Results

Data were reported for a total of 25 replicates, numbered between 1 and 27. Two replicates were omitted: Replicate 11 was omitted because the application was unsuccessful, and Replicate 18 changed headgear during work period. With the exception of Replicates 14 and 16, which were performed by the same individual, each replicate corresponded to a different applicator.

The application rates used in this study were all lower than the maximum carbaryl application rates currently allowed in California, which are 5 lbs AI/acre to peaches, 16 lbs AI/acre to citrus, and 3 lbs AI/acre to apples (rates in the study were 3.0, 3.0, and 2.0, respectively). Thus, exposure estimates for airblast applicators in California could be greater than exposures determined by Smith (2005). However, mitigation measures proposed by U.S. EPA in the carbaryl IRED (U.S. EPA, 2004) will reduce some exposure estimates if implemented. For citrus, the maximum application rate in California would be reduced to 12 lbs AI/acre, and airblast applications to citrus in California would require closed cabs. For stone fruit including peaches, U.S. EPA (2004) assumed a maximum application rate of 4 lbs AI/acre (not listed as a handler mitigation measure, but this is the maximum considered in extending Restricted Entry Intervals in California). No mitigation measures were proposed by U.S. EPA (2004) for pome fruits, including apples.

Dermal and inhalation exposure estimates for replicates with and without headgear, summed from whole body dosimeters, hand washes, socks, face/neck wipes, and head patches, are summarized in Table 4. Exposure estimates are reported in micrograms per pound active ingredient handled (µg/lb AI handled). Table 4 is organized such that exposures from workers wearing Sou'wester rain hats are presented first (N = 15), and workers wearing hooded rain jackets are presented last (N = 10). Table 4 also includes total exposure estimates, which are the sum of dermal and inhalation exposure estimates, for each replicate.

Applicators wearing headgear had dermal exposures ranging from 4.66 to 232 µg/lb AI handled, a 50-fold difference. Applicators not wearing headgear would be estimated to have dermal exposures ranging from 49.1 to 1,840 µg/lb AI handled, a 37-fold difference. The ranges of exposures reported in this study are not extraordinarily large in comparison to other handler exposure monitoring studies.

Because the WBDs were worn under work clothing, including rain jackets for ten replicates, a difference in overall exposure between applicators wearing the two types of headgear might be anticipated, and this was indeed the case. For applicators wearing Sou'westers, the arithmetic mean $\pm$ standard deviation (SD) total exposure including the headgear (i.e., omitting outer head patches) was 73.7 $\pm$ 68.5 µg/lb AI handled; the corresponding arithmetic mean $\pm$ SD total exposure for applicators wearing hooded rain jackets was 54.8 $\pm$ 63.4 µg/lb AI handled. For applicators not wearing headgear, arithmetic mean exposures were 696 $\pm$ 612 µg/lb AI handled and 454 $\pm$ 409 µg/lb AI handled, respectively.

Table 4. Exposure to Carbaryl Estimated for Each Airblast Applicator [a]

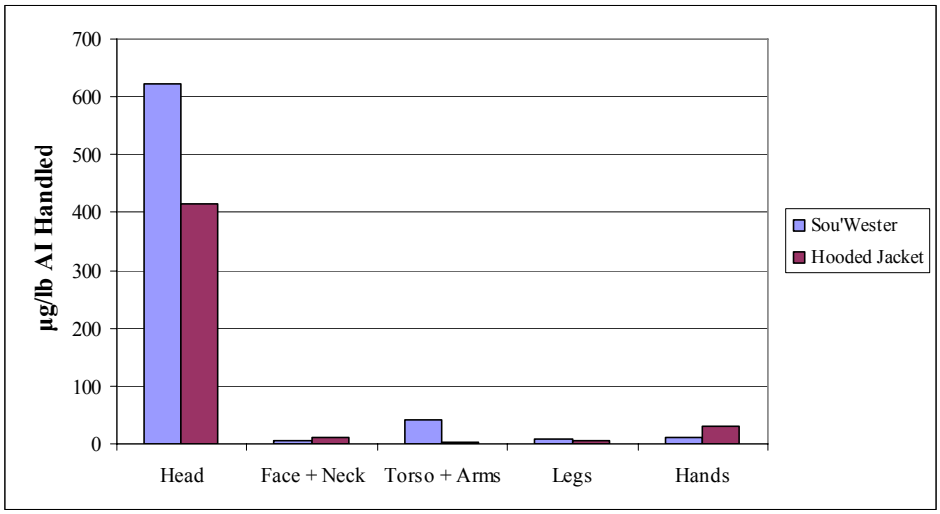
Replicate	Dermal Exposure with Headgear [b]	Dermal Exposure without Headgear [b]	Inhalation Exposure [c]	Total Exposure with Headgear [d]	Total Exposure without Headgear [d]
Sou'wester Rain Hat					
1	10.4	137	0.668	11.1	138
3	90.8	1,170	3.18	93.9	1,180
4	8.70	55.3	0.752	9.45	56.1
6	18.3	352	1.74	20.1	354
8	143	1,830	11.1	154	1,840
10	135	600	2.46	138	602
12	19.7	245	2.85	22.5	248
13	36.9	1,610	2.94	39.9	1,610
15	136	1,460	3.61	136	1,470
16	39.8	537	2.08	41.9	539
17	5.55	125	1.55	7.10	126
22	68.6	433	3.15	71.7	436
23	62.3	356	0.993	63.3	358
26	46.2	159	1.11	47.4	160
27	232	1,320	13.0	245	1,330
Applicators Wearing Hooded Rain Jacket					
2	70.7	583	1.33	72.1	586
5	115	788	3.29	118	791
7	13.1	454	1.31	13.1	455
9	4.66	51.4	0.952	4.66	52.4
14	20.9	169	1.24	20.9	170
19	23.0	123	0.842	23.0	124
20	64.6	658	0.765	64.6	658
21	203	1,340	3.80	203	1,350
24	5.50	48.9	0.251	5.50	49.2
25	22.5	303	0.898	22.7	304

[a] Summary of data from open-cab airblast exposure monitoring study (Smith, 2005). Dermal exposure rate estimates summed from data in Tables 11, 12, 15 and 16 of Smith (2005), rounded to three significant figures.
[b] Headgear consisted of rain hat or hooded rain jacket. Dermal exposure in micrograms per pound active ingredient handled (µg/lb AI handled), summed from whole body dosimeters, hand washes, face/neck wipes, and head patches. Exposure under headgear estimated with a patch placed under hat or hood. Head exposure without headgear was summed from inner and outer head patches.
[c] Inhalation exposure (µg/lb AI handled) calculated from data in Table 17 of Smith (2005), assuming a breathing rate of 16.7 L/min.
[d] Sum of dermal and inhalation exposures.

Figure 1 shows mean dermal exposure estimates based on these data, for workers not wearing CR headgear; the head contributed about 90% of dermal exposure. The mean ± SD head exposure for applicators not wearing headgear (calculated as the sum of adjusted residues from inner and outer hat patches) is 623 ± 566 µg/lb AI handled for Sou'wester and 414 ± 358 µg/lb

AI handled for hooded jacket. The difference in exposure is unexpected, and is perhaps due to the acute slope of the patch on the peaked hoods in contrast to the rounder top of the Sou'wester hats, which allowed the head patches to lay nearly flat. Alternately, some replicates were recorded as pushing hoods back at times because of difficulty with peripheral vision. It's possible that hoods were not in place as consistently as rain hats.

Figure 1. Dermal Exposure Estimates of Open-Cab Airblast Applicators Without Chemical-Resistant Headgear [a]

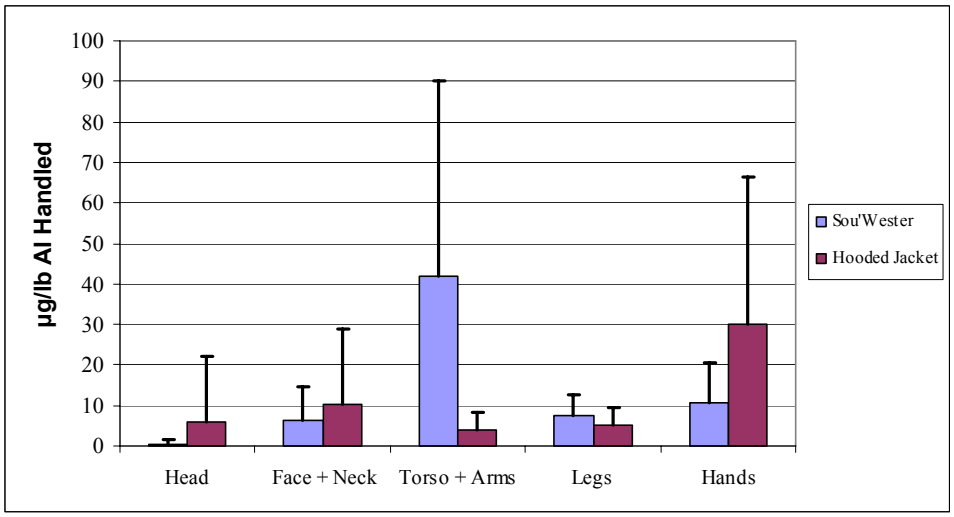


[a] Data from Smith (2005). Each bar is the group mean of either 15 replicates wearing Sou'wester rain hat (light bars) or ten replicates wearing hooded rain jacket (dark bars). Head exposure estimate includes patches attached to outside of headgear and strapped to head below headgear.

Figure 2 shows mean ± SD exposures for applicators wearing CR headgear. Figure 2 suggests that head exposure is substantially decreased by the headgear, and the torso, arms and hands dominate dermal exposure for workers wearing CR headgear.

As hooded rain jackets provide a second layer of clothing on arms and torso, exposures of applicators wearing jackets might be expected to be lower than exposures of applicators wearing Sou'wester rain hats. Examination of Figure 2 suggests that this was indeed the case. For applicators wearing Sou'wester rain hats, mean ± SD exposure of the torso and arms was 41.7 ± 48.3 µg/lb AI handled; for applicators wearing hooded jackets, exposure of the torso and arms was more than an order of magnitude lower, at 4.03 ± 4.43 µg/lb AI handled.

Figure 2. Dermal Exposure for Open-Cab Airblast Applicators Wearing Headgear [a]



[a] Data from Smith (2005). Each bar is the group mean of either 15 replicates wearing Sou'wester rain hat (light bars) or ten replicates wearing hooded rain jacket (dark bars). Error bars represent standard deviations.

An analysis of variance (ANOVA) was done in SAS (2003), to see if exposure monitoring data from applicators wearing the two types of headgear should be pooled; the ANOVA compared combined arm and torso exposures for applicators in both groups (i.e., body parts covered by the jacket). Table 5 summarizes the results of this ANOVA, which showed that the difference in torso and arm exposure between applicators wearing the two types of CR headgear is significant ($P = 0.023$). Because of this significant difference, when estimating exposure it is not appropriate to pool the data from both types of headgear, as was done by Smith (2005). Nor is it possible from these data to calculate a protection factor for the torso and arms from wearing the hooded jacket, as only an inner dosimeter was used in these body regions (inner and outer patches were only placed on the head to estimate penetration through rain hat/hood).

Figure 2 also shows an unexpected difference in hand exposure, which is higher for individuals wearing hooded jackets than for those wearing Sou'westers, 30.0 ± 36.4 µg/lb AI handled and 10.7 ± 9.93 µg/lb AI handled, respectively (however, an ANOVA suggests that hand exposures did not significantly differ between the two groups; $P = 0.220$). Smith (2005) provided example photographs of an applicator wearing each type of headgear. In the photo of the applicator wearing a hooded rain jacket, gloves were worn outside of sleeves. Harvard Fong suggested that if all of the applicators in hooded jackets wore gloves outside of sleeves, then it's possible that pesticide solution could have run down the sleeves and into gloves. For this reason, the proper way to wear gloves over chemical-resistant clothing is to tuck gloves inside sleeves or to tape gloves to sleeves.

Table 5. Analysis of Variance Table for Arm and Torso Carbaryl Exposure of Applicators Wearing Sou'wester Rain Hats or Hooded Rain Jackets [a]

Source	DF [b]	Sums of Squares	Mean Square	F Value	P
Type of Headgear [c]	1	8499	8499	5.95	0.023 [d]
Error	23	32837	1428		
Corrected Total	24	41336			

[a] Data from open-cab airblast exposure monitoring study (Smith, 2005).
[b] Degrees of freedom (DF) totaled 24, as 25 replicates were monitored in the study.
[c] Headgear consisted of either a Sou'wester hat (15 replicates wore this) or a hooded rain jacket (ten replicates wore this).
[d] Difference in arm and torso exposure between workers wearing two types of headgear is significant at an ∀ level of 0.05.

Figure 2 shows that little difference was detected in face/neck exposure or leg exposure between applicators wearing Sou'wester rain hats and those wearing hooded rain jackets. Face/neck exposure, as determined by face/neck wipes, was considerably lower than exposure determined by outer head patches (see Figure 1), in spite of the fact that the face and neck areas were not covered by clothing. Possibly, the lower exposures were due to shading from headgear. However, the efficiency of face/neck wipes have not been compared to patches. Just as hand wipes often result in lower exposure estimates than gloves (Fenske *et al.*, 1999), it is possible that face/neck wipes are more likely to provide lower exposure estimates than head patches.

Exposure Estimates for Open-Cab Airblast, with and without Chemical-Resistant Headgear

Table 6 summarizes mean and standard deviation exposure estimates for applicators with and without the two types of headgear. Table 6 includes dermal, inhalation, and total exposure estimates for the fifteen applicators wearing Sou'westers and the ten wearing hooded rain jackets. Because applicators wearing a hooded rain jacket had an additional layer on arms and torso, only applicators wearing Sou'wester rain hats should be considered when determining the exposure of applicators during open-cab airblast. These values are reported in bold in Table 7.

Comparison of the values in Table 4 with the means in Table 6 provides support for using upper-bound estimates for short-term exposure scenarios. For applicators wearing either type of headgear, ten of the 25 replicates had exposures above the arithmetic mean, while 14 had exposures greater than the geometric mean. For applicators not wearing headgear, nine and 13 replicates, respectively, had exposures greater than the arithmetic and geometric means. This suggests that 40% of the applicators would not be protected by a level based on the arithmetic mean, and more than half would not be protected by a level based on the geometric mean.

Table 6. Mean and Standard Deviation Exposure to Carbaryl of Airblast Applicators [a]

	Sou'wester Rain Hat	Hooded Rain Jacket [b]
Number of Replicates	15	10
Dermal Exposure with Headgear		
Arithmetic Mean	70.2	53.5
Standard Deviation	65.4	62.6
95th Percentile [c]	276	233
Dermal Exposure without Headgear [d]		
Arithmetic Mean	693	452
Standard Deviation	609	408
95th Percentile [c]	2,570	1,850
Inhalation Exposure		
Arithmetic Mean	3.41	1.47
Standard Deviation	3.65	1.15
95th Percentile [c]	9.54	3.18
Total Exposure with Headgear [e]		
Arithmetic Mean	73.7	54.8
Standard Deviation	68.5	63.4
95th Percentile [c]	277	228
Total Exposure without Headgear [d,e]		
Arithmetic Mean	696	454
Standard Deviation	612	410
95th Percentile [c]	2,580	1,850

[a] Summary of data from open-cab airblast exposure monitoring study (Smith, 2005). Exposures were normalized by lbs AI handled (µg/lb AI handled). Data used to calculate means, standard deviations, and 95th percentiles are listed in Table 4. All estimates were rounded to three significant figures.
[b] Statistics for applicators wearing hooded rain jacket are provided for comparison purposes only. These would rarely, if ever, be used in an exposure assessment.
[c] 95th percentile estimates calculated in Excel, assuming a lognormal distribution. First the natural logarithm (ln) was calculated for each value using the LN function; arithmetic mean and standard deviation was then calculated for the natural logarithms (am(lns) and asd(lns), respectively). The NORMSINV function, with a probability of 0.95, was used to get the inverse of the standard normal cumulative distribution, which was multiplied by asd(lns). This result was added to am(lns), and the sum taken as the power of e with the EXP function.
[d] Statistics for applicators without headgear are provided for comparison and possibly for later use if it is determined that this study best represents exposures for all airblast applicators.
[e] Total exposures were calculated by adding dermal and inhalation exposures for each replicate; for this reason, dermal and inhalation mean exposures might not sum to mean total exposure.

Statistics for total exposures reported in Table 6 were calculated after first adding dermal and inhalation exposure for each replicate to give a total exposure for that replicate. Because of this approach, mean and 95th percentile for total exposure might not be equivalent to the sum of these statistics for dermal and inhalation exposure. For example, applicators wearing Sou'wester rain

hats have a 95th percentile dermal exposure of 276 µg/lb AI handled, a 95th percentile inhalation exposure of 9.54 µg/lb AI handled, but a 95th percentile total exposure of 277 µg/lb AI handled; clearly, in this case the total statistic is not equivalent to the sum of dermal plus inhalation statistics. When using values from Table 6, exposure assessors will generally use the statistics for total exposure. In cases where route-specific exposure estimates are needed, then the statistics for total exposure will not be reported.

Table 7. Comparison of Open-Cab Airblast Applicator Total Exposure Estimates Based on Exposure Monitoring Study (Smith, 2005) with Estimates Based on PHED [a]

According to DPR Policy (arithmetic mean)	Study [b]	PHED
Short-Term Exposure, no headgear [c]	2,580	4,100
Short-Term Exposure, with headgear	**277** [d]	2,660 [e]
Long-Term Exposure, no headgear	696	1,030
Long-Term Exposure, with headgear	**73.7**	665 [e]
According to U.S. EPA Policy (geometric mean) [f]		
Exposure, no headgear	442	240
Exposure, with headgear	45.9	165 [e]

[a] Total exposures (µg/lb AI handled). All estimates rounded to three significant figures. PHED: Pesticide Handlers Exposure Database (PHED, 1995).
[b] Based on data from applicators wearing Sou'westers (Smith, 2005).
[c] Department of Pesticide Regulation (DPR) policy for estimating exposures in PHED is described in Powell (2002). Short-term exposures are estimated with a 95th percentile, and long-term exposure estimates are based on the arithmetic mean.
[d] Values in bold should be used in DPR exposure assessments. If route-specific exposure estimates are required, use values in Table 6 for applicators wearing Sou'wester rain hats. DPR should continue to use PHED-based estimates for applicators without chemical-resistant headgear, until studies in PHED are reviewed.
[e] Headgear is assumed to cover about half of head. To calculate exposure with headgear from PHED data, half of mean head exposure is multiplied by 0.1 (assuming a 90% protection factor). Neither DPR nor U.S. EPA (Sandvig, 2002) has had default protection factors for chemical-resistant headgear. The values reported in this table for PHED-based estimates for applicators wearing chemical-resistant headgear were calculated for comparison with estimates previously used and with estimates calculated from Smith (2005), and have not been used in any exposure assessment.
[f] U.S. EPA does not generally provide separate estimates for short-term and long-term exposure for this scenario. Study-based estimates use the geometric mean. PHED-based estimates are from U.S. EPA (1998), Scenario 11. To estimate exposure with headgear from PHED, an assumed 90% protection factor was applied to half of the geometric mean head exposure reported for this scenario (176 µg/lb AI handled).

Table 7 compares exposure estimates from Smith (2005) to estimates generated from existing data in the Pesticide Handlers Exposure Database (PHED, 1995). Exposure estimates were calculated according to policies of DPR and U.S. EPA. In all cases, estimates from Smith (2005) are lower than those DPR would calculate based on PHED. For comparison purposes, Table 7 includes some specially-calculated estimates (PHED-based estimates for applicators wearing headgear) that have not been used in exposure assessments. Exposure estimates based on the 15 replicates wearing a Sou'wester are shown in bold in Table 7.

Both Table 6 and Table 7 report statistics based on data from Smith (2005) for exposure monitoring of applicators wearing CR headgear, as well as estimated exposures of applicators not wearing CR headgear. However, I recommend that a thorough review of data in PHED be conducted before this study is used to replace data from PHED for applicators without CR headgear. Exposure estimates in PHED are based on studies involving applications to grapes in addition to tree crops (apples, apricots and citrus), in which applicators were not wearing CR headgear. The present study was conducted by AHETF to meet a data gap in PHED for airblast applicators wearing CR headgear. Before expanding use of Smith (2005) beyond that purpose, the studies in PHED should be reviewed to determine whether they meet quality criteria and to ascertain whether there are differences in applicator exposure between crop types. Depending on the results of this review, data from multiple studies might be combined to estimate applicator exposure. Additional exposure monitoring might be indicated during applications in grapes, to supplement the exposure monitoring done by Smith (2005) in tree crops. Thus, it makes sense for DPR to continue to use PHED-based estimates for applicators without chemical-resistant headgear.

Protection Factor for Chemical-Resistant Headgear

The purpose of inner and outer head patches was to provide an estimate of the level of protection given by the headgear. Based on total exposure estimates reported in Table 13 of the study report, Smith (2005) concluded that total worker exposure was decreased 10-fold by wearing either type of headgear. Ratios of total exposures with and without headgear (i.e., omitting and including outer head patch data), ranged between 3.6 and 41.9. Smith (2005) relied on this ratio to conclude that exposure over the entire body, rather than just the head, is reduced (pp. 21-22): "Total dermal exposure (TDE) was calculated from the sum of all adjusted dermal matrices (inner WBD, sock, appropriate head patch, face/neck wipe, and hand wash) for each replicate. Calculated Total Dermal Exposures were reduced for workers wearing CR headgear by a factor of 10 over workers not wearing CR headgear." This conclusion seems to imply that a 90% protection factor should be applied to the applicator's entire body, not just the head. However, protection factors from protective clothing and PPE are properly applied only to the portion of the body covered. In the case of CR headgear, approximately half of the head is covered (the face is not covered).

The protection factor (PF) is calculated as follows (Thongsinthusak *et al.*, 1991):

> PF = 100% – percent penetration, where the percent penetration is
> [Dermal exposure]/[Potential dermal exposure] x 100%

Percent penetration and protection factors are summarized in Table 8.

Table 8. Percent Penetration and Protection Factors for Applicators Wearing Sou'wester Rain Hats or Hooded Rain Jackets [a]

Type of Headgear	N [b]	Penetration (%) [c]		Protection Factor (%) [d]	
		Range	Mean	Range	Mean
Sou'wester hat	15	0.005 – 1.4	0.13	98.59 – 99.995	99.87
Hood on rain jacket	10	0.03 – 7.3	0.90	92.77 – 99.97	99.10
Overall (both)	25	0.005 – 7.3	0.43	92.59 – 99.995	99.57

[a] Data from open-cab airblast exposure monitoring study (Smith, 2005).
[b] Number of replicates.
[c] Percent Penetration = [Dermal exposure]/[Potential dermal exposure] x 100%
[d] Protection Factor (PF) = 100% – Percent Penetration

An overview of this study was presented at the July 26, 2005, meeting of the Human Health Assessment Program (HAP). HAP agreed that a protection factor of 90% can be supported based on these data. While it could be argued data in Table 8 suggest that the mean protection factor was generally above 99% for applicators wearing each type of headgear (as well as overall), HAP had several reasons for not finding a protection factor of 99% to be sufficiently protective. These reasons are listed below.

1. There is much overlap in exposure ranges between workers wearing and not wearing headgear.
2. Two applicators out of 25 had < 99% protection from headgear. One of these was wearing a Sou'wester, and one was wearing a hooded jacket. This suggests that nearly one in ten applicators might be anticipated to achieve less than 99% protection from headgear, based on these data.
3. Conditions of study were more controlled than in real-world use. Less careful positioning of hats might result in less protection.
4. Other types of hats (e.g., bump caps) might be allowed on labels. These might have different levels of protection than the hats tested.

The recommended protection factor for CR headgear is 90%, applied to half of the head. For example, if head exposure without CR headgear were 100 µg/lb AI handled, then the estimated head exposure with CR headgear would be calculated by taking half that amount (because headgear is assumed to cover about half of the head) and multiplying that by 0.1:

Half of head: 100 µg/lb AI handled x (0.5) = 50 µg/lb AI handled
Applying PF: 50 µg/lb AI handled x (0.1) = 5 µg/lb AI handled
Total: 50 µg/lb AI handled + 5 µg/lb AI handled = 55 µg/lb AI handled

In this example, the head exposure with CR headgear would be 55 µg/lb AI handled.

Applying Other Protection Factors

Table 7 gives recommended estimates for short-term and long-term exposure for airblast applicators wearing long-sleeved shirt, long pants, CR gloves, and CR headgear. Applicators might also wear other types of protective clothing and PPE, such as coveralls or respirators. No exposure estimates have been provided for workers wearing such additional protection. When appropriate, protection factors may be applied at the time of the assessment. Table 9 summarizes exposure components, including regions of the body that might be covered by protective clothing and PPE, to allow application of protection factors.

Effect of Open Cab with Roof on Exposure

All applicators drove open-cab tractors. Although the tractor cabs were not enclosed, which would substantially reduce the applicator's pesticide exposure (Heitbrink *et al*., 2003), eight of the nine applicators at the Florida site used tractors having a roof above the applicator (Smith, 2005). Because only one Florida replicate used a tractor without a roof, there is no replication of that condition that would allow a statistical comparison within the Florida replicates. However, examination of the range of total exposure estimates suggests that exposures of the eight applicators using tractors having a roof were not lower than that of the applicator driving the roofless tractor.

Of the nine Florida replicates, four wore Sou'wester rain hats and five (including replicate 20, with the roofless tractor) wore hooded rain jackets. Total exposure of these nine replicates without headgear ranged from 49.9 µg/lb AI handled to 1,350 µg/lb AI handled. The highest total exposure among the Florida replicates occurred in replicate 21, who drove a tractor with a roof. The mean $\pm$ SD exposure of the Florida replicates was 530 $\pm$ 494 µg/lb AI handled. This compares with 675 $\pm$ 592 µg/lb AI handled for Georgia replicates and 602 $\pm$ 611 µg/lb AI handled for Idaho replicates.

However, if there is an effect of a roof on applicator exposure, the most likely effect would be to decrease residues collected by the outer head patches, as these are closest to the roof. Comparisons of head patch residues, normalized by amount AI handled, might better establish whether a roof would affect exposure. Figure 3 shows normalized outer head patch residues (µg/lb AI handled) for the nine Florida replicates. Figure 3 suggests that the single replicate driving a roofless tractor had outer head patch residues in the range of the applicators driving tractors with roofs.

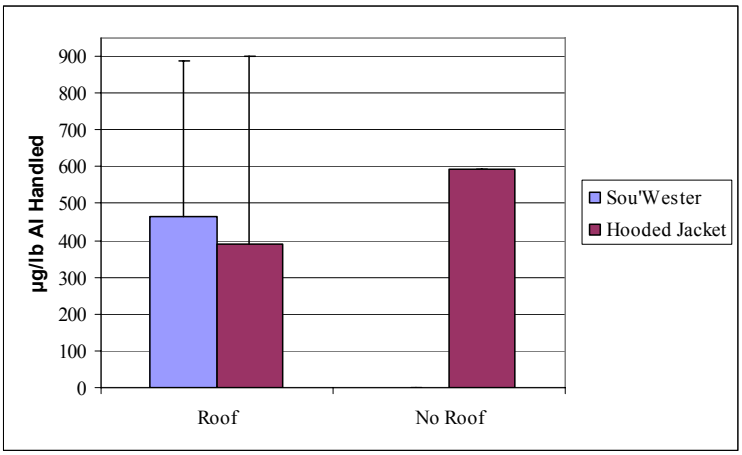
Table 9. Summary of Exposure Components for Open-Cab Airblast Applicators [a]

Exposure Route and Body Region	Mean [b]	Standard Deviation
Inhalation Route	3.41	3.65
Dermal Route		
Head [c]	34.5	96.2
Face/neck	5.94	7.57
Front torso (chest)	8.80	11.2
Rear torso (back)	6.77	8.09
Upper arm	10.2	15.9
Lower arm (forearm)	15.9	17.0
Upper leg (thigh)	5.02	4.42
Lower leg	1.37	1.19
Feet	0.166	0.132
Hands [d]	15.6	20.6

[a] Summary of data from open-cab airblast applicators wearing Sou'westers (Smith, 2005). Dermal exposure rate estimates summed from data in Tables 11, 12, 15 and 16 of Smith (2005), rounded to three significant figures.
[b] Arithmetic mean (µg/lb AI handled).
[c] Exposure with chemical-resistant headgear, based on adjusted residues from inner hat patches. Patch residues were adjusted to extrapolate residues recovered from 100-cm^2 patch to size of area represented by patch (half of head = 650 cm^2).
[d] Hand exposure for applicators wearing chemical-resistant gloves.

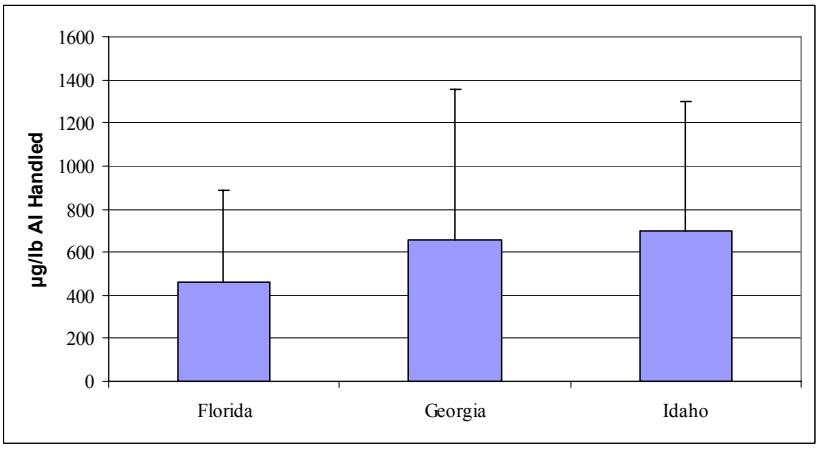
Although statistical comparisons are not appropriate for Florida replicates because only one applicator in Florida drove a tractor without a roof, the four Sou'wester replicates in Florida driving roofed tractors can be compared to Sou'wester replicates in Georgia and Idaho (total 11 replicates), none of whom was reported to drive a tractor with a roof. Figure 4 shows this comparison. An ANOVA was done comparing the replicates graphed in Figure 4. The ANOVA showed that the difference between applicators driving tractors with and without a roof is not significant (P = 0.532). An ANOVA including all 25 replicates was also not significant (P = 0.477). Thus, presence or absence of a roof on each tractor apparently did not affect exposure (of course, other factors might also differ between the study sites). The apparent lack of effect suggests that it is appropriate to pool data for applicators driving tractors with roofs with those driving roofless tractors, and this was done.

Figure 3. Normalized Outer Head Patch Residues for Florida Replicates of Open-Cab Airblast Applicators [a]



[a] Data from Smith (2005). Each bar marked "Roof" is the group mean of 4 replicates wearing Sou'wester rain hat (light bars) or hooded rain jacket (dark bars), and error bars represent standard deviations. The bar marked "No Roof" represents the normalized residue recovered from the outer head patch of the single applicator wearing a hooded rain jacket; all replicates in Florida wearing Sou'wester rain hats drove open-cab tractors having a roof.

Figure 4. Normalized Outer Head Patch Residues for Replicates of Open-Cab Airblast Applicators Wearing Sou'wester Rain Hats [a]



[a] Data from Smith (2005). Each bar is the group mean of replicates wearing a Sou'wester rain hat. Error bars represent standard deviations. Florida replicates: bar represents 4 replicates, each of which drove a tractor with a roof. Georgia and Idaho replicates, bars represent 5 and 6 replicates, respectively, each of which drove a tractor with no roof.

Potential Effect of Clothing Replacement in Study on Exposure

Applicators supplied their own clothing; however, at the start of each study day, replacement of some clothing was done at the discretion of the study director. Long-sleeved shirts were replaced for five replicates, and pants were replaced for two of these replicates. Specific criteria used to determine whether to replace clothing were not reported. Because no reasons were given in the study report for replacing specific items of clothing prior to the study (with the exception of a missing shirt button for one replicate), no comparison can be made between worker-supplied clothing that was replaced and worker-supplied clothing that was not replaced.

The WPS specifies that PPE must be free of "leaks, holes, tears, or worn places" (Title 40 Code of Federal Regulations (40 CFR), Section 170.240(e)(2)); however, clothing such as long sleeved shirts and long pants are specifically exempted from this requirement, "although pesticide labeling may require that such work clothing be worn during some activities" (40 CFR 170.240(b)(2)). Employers are required to train employees handling pesticides on specific safety needs, one of which is "[w]earing work clothing that protects the body from pesticide residues" (40 CFR 170.130(c)(2)(iii)). The most specific statement made by the WPS with respect to work clothing is that a pesticide safety poster must be displayed at agricultural worksites where pesticides have been used within the previous 30 days; among the specific information, required to be on this poster is the following: "Wear work clothing that protects the body from pesticide residues (long-sleeved shirts, long pants, shoes and socks, and a hat or scarf)" (40 CFR 170.135(b)(1)(iii)).

As the WPS provides no specific guidance on how worn clothing may be and still be considered sufficiently protective, the possibility exists that handlers could wear clothing that has some holes, tears, or thinning fabric. Past exposure monitoring studies used by U.S. EPA for exposure estimates have often featured standardized clothing, such as cloth coveralls, that were provided by the researcher. This practice is in agreement with the fundamental research principle that controlling extraneous variables (i.e., factors not being studied) allows better estimation of potential effects of experimental variables (i.e., factors that are varied in a controlled way in the experiment). Because handlers and fieldworkers may wear clothing that is old and subject to wear and a certain amount of damage, U.S. EPA has been criticized for not providing exposure estimates for workers wearing clothing that reflects a range of such conditions. Thus, some recent exposure monitoring studies, including Smith (2005), have allowed workers to supply their own clothing.

Numerous studies have shown that clothing affords some protection against exposure to pesticides (e.g., Staiff *et al*., 1982; Stamper *et al.*, 1989; Nigg *et al*., 1992; Fenske *et al*., 2002). The amount of protection afforded by clothing is partly dependent on the fabric, with heavier fabric such as denim affording greater protection than lighter-weight fabrics (Nigg et al., 1992; Obendorf *et al*., 2003). Other factors include coatings on the fabric (Staiff *et al*., 1982) and pesticide compounds (Stamper *et al.*, 1989). However, openings in the clothing such as sleeves

and neck holes, as well as holes in the fabric itself, can substantially contribute to pesticide exposure (Stamper *et al.*, 1989; Fenske *et al.*, 2002).

One-fifth (five of twenty-five) of applicator replicates came to work on study days wearing clothing that the study director deemed in need of replacement. Presumably, the clothing worn on study days was the same as clothing worn on other workdays. This raises the concern that allowing workers to wear their own clothing resulted in an increase in this extraneous variable, without certainty of capturing the full range of variability that might exist.

Comments for Exposure Appraisal

Some matrix samples were adjusted for mean recoveries of FF. The adjustments were summarized in Table 3. A total of 56 inner dosimeter samples were adjusted for 84.5% recovery; 24 sock samples were adjusted for 69.2% recovery, while the 25th sock sample was adjusted for 77.5% recovery; 20 inner head patch samples were adjusted for 83.7% recovery; 18 outer head patches were adjusted for 86.9% recovery; and eight face/neck wipe samples were adjusted for 84.9% recovery. DPR policy is to adjust sample results when FF recovery is below 90%. The effect of the adjustment is to increase exposure estimates above what they would be if sample results were not adjusted; in addition, because samples are never adjusted for FF recoveries above 100%, exposures of some samples are also greater than what they would be if they were adjusted for FF recoveries. Thus, DPR policy could cause exposures to be overestimated if residue recoveries from adjusted samples were greater than FF recoveries or if residue recoveries from unadjusted samples were identical to FF recoveries (the FF recoveries are a surrogate measure of the true recovery of residues from samples). However, not adjusting sample results for FF recoveries below 90% or adjusting sample results for FF recoveries above 100% could result in exposures being underestimated. It is more health-protective to choose an approach that could result in overexposure rather than an approach that could result in underexposure.

Hand exposure was estimated using hand washes; however, the efficiency of the surfactant solution in removing residues of carbaryl (or any other pesticide) from hands is unknown. Brouwer *et al.* (2000) summarized results of hand wash sampling efficiency studies, and reported that mean efficiency ranged from 23% to 96%. Hand washes supposedly measure the amount of pesticide loaded onto the skin of a worker during a given period of time. This is an operational definition in that only the amount of pesticide that can be washed off the skin is considered for exposure calculations. However, radiolabelled pesticide, applied experimentally to hands that were then washed at various later times, could not be fully recovered even after a few seconds of time (Wester *et al.*, 1992). Thus, hand washing may underestimate dermal exposure, as not all of the pesticide loaded onto hands during occupational activities can be recovered by hand washes. Dermal exposure estimated by face/neck wipes was considerably lower than dermal exposure determined by outer head patches, in spite of the fact that the face and neck areas were not covered by clothing. Possibly, the lower exposures were due to shading from headgear. It is

also possible that the difference is at least partly due to the fact that the head patches were relatively horizontal compared to the face and neck surfaces, which might result in greater residue trapping of the patches than the skin of the face and neck. However, the efficiency of face/neck wipes have not been compared to patches. Just as hand wipes often result in lower exposure estimates than gloves (Fenske *et al.*, 1999), it is possible that face/neck wipes are more likely to provide lower exposure estimates than head patches. If this is the case, then face/neck wipes may underestimate dermal exposure, as not all of the pesticide loaded onto the face and neck during occupational activities can be recovered by the wipe samples.

Eight replicates in the study, all at one site (Florida) drove tractors having a roof above the applicator. These tractors were not enclosed, and are also considered to be open-cab tractors. Based on the available data, applicators driving tractors with roofs did not have significantly lower exposure than applicators driving roofless tractors. Because the roof apparently did not affect exposures, it is considered appropriate to pool data for applicators driving tractors with roofs with those driving roofless tractors. However, it is possible that exposures were slightly lower (although not reaching the level of statistical significance with these samples) than they would have been had all of the tractors been roofless.

One-fifth of the applicator replicates came to work on study days wearing clothing that the study director deemed in need of replacement. There is no evidence to suggest that clothing worn on study days was in worse shape than clothing worn on other workdays. This raises the concern that allowing workers to wear their own clothing probably resulted in increased variability of residues recovered from the inner dosimeters, while perhaps only capturing some of the variability that might exist in residues that penetrate work clothing.

Conclusions

The exposure monitoring study reported by Smith (2005) provided data that are appropriate for use in estimating exposure of airblast applicators driving tractors without enclosed cabs (open-cab tractors). Exposure monitoring of applicators wearing CR headgear was done to fill a data gap in PHED. Because exposure was also monitored outside the CR headgear, exposures can also be estimated for applicators not wearing CR-headgear. However, as PHED contains multiple exposure monitoring studies for airblast applicators not wearing CR headgear, that is not a data gap. It is appropriate to use this study to fill the data gap for applicators wearing CR headgear, but until further review has been completed of open-cab airblast applicator studies included in PHED, I recommend that exposure estimates for applicators not wearing CR-headgear continue to be based on PHED rather than on data from this study.

Because the difference in torso and arm exposure between applicators wearing the two types of CR headgear is significant ($P = 0.023$), when estimating exposure it is not appropriate to pool the data from both types of headgear, as was done by Smith (2005).

For estimating total exposure of open-cab airblast applicators, exposure assessors should use values shown in bold in Table 7. In cases where route-specific exposure estimates are needed, exposure assessors should use the dermal and inhalation estimates reported in Table 6 for Sou'wester replicates, and the statistics for total exposure will not be reported. In general, data from workers wearing hooded rain jackets will not be used in exposure assessment, although there might be occasions when these data would be appropriate (e.g., in evaluating potential mitigation measures).

The recommended protection factor for CR headgear is 90%, applied to half of the head. The protection factor is applied to half of the head on the assumption that approximately that much is covered by the CR headgear (i.e., the face is not covered).

Validation of Sock Analytical Method

Two method validation reports were included in data packages 210452 and 213826; both reports are reviewed here for convenience. Brookey (2004) reported on the method validation for carbaryl analysis in socks. Reed (2004) reported on the method validation for analysis of diazinon and malathion in socks. Both methods involve extraction of the analyte from 100% cotton sock material with acetone. Carbaryl was quantified using high performance liquid chromatography with a water-acetonitrile gradient and post column derivatization/fluorescence detection, following clean-up in a Fluorisil SPE cartridge (Brookey, 2004). Malathion and diazinon were quantified using gas chromatography with a flame photometric detector, following filtering of the extract. The limit of quantification (LOQ) for all three analytes was reported to be 0.25 µg/sample.

Both methods yielded results that all met the following criteria:

- U.S. EPA guideline requirements: Spike recoveries must be between 70% and 120%, with standard deviations (SDs) < 20%.
- AHETF requirements: For each spike level, mean recovery minus one SD must be ≥ 70% and mean recovery plus one SD must be ≤ 120%.
- AHETF requirements: No detectable residues (no detectable responses > 30% of the LOQ) were found in control samples.
- AHETF requirements: Back calculation of standards against the standard curve must give values ± 15% for all but the lowest standard, which must be ± 20%.

Table 10 summarizes mean recoveries and SDs for all three compounds in these method validations. The results of the method validations suggest that the compounds can be readily analyzed in socks. The FF recoveries reported by Smith (2005), however, were lower than the method validation recoveries reported by Brookey (2004); the difference is particularly striking in light of the fact that the low level during method validation (0.25 µg/sample) was considerably less than the low FF level (5.0 µg/sample). The reason for low FF recoveries from socks is not

immediately apparent. Two differences are noted, however, and either or both of these might have contributed to the differences in recoveries. First, FF spiking solutions used the formulated product, whereas diluted analytical standards were used to prepare method validation spiking solutions. Second, FFs were spiked during the time that exposure monitoring samples were collected, and analysis occurred up to 82 days later, while the method validation protocol calls for spikes to occur at least 10 minutes prior to extraction. Some loss of material might have occurred during storage of samples.

Table 10. Summary of Method Validation Recoveries for Carbaryl, Diazinon and Malathion [a]

Compound		Level [b]	Mean Recovery (%)	SD	N
Carbaryl:	Low level	0.25	106	3.1	6
	High level	500	108	3.6	6
	Overall	- -	107	3.4	12
Diazinon:	Low level	0.25	88.6	5.7	6
	High level	100	89.2	5.9	6
	Overall	- -	88.9	5.5	12
Malathion:	Low level	0.25	89.7	5.4	6
	High level	100	96.4	7.0	6
	Overall	- -	93.1	6.9	12

[a] Summary of data from reports of Brookey (2004) for carbaryl and Reed (2004) for diazinon and malathion.
[b] Fortification level in µg/sample.
[c] Mean and standard deviation (SD). N is the number of replicate samples analyzed during validation.

In conclusion, the method validation studies of Brookey (2004) and Reed (2004), like the open-cab airblast exposure monitoring study of Smith (2005), are considered acceptable. Results support the use of AHETF data in exposure assessment.

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