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Distributions and Determinants of Pre-Emergent Herbicide Exposures Among Custom Applicators

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Custom applicators intensively apply herbicides to corn and soybean fields each spring. The primary objective of this study was to characterize the exposure distributions of the herbicides alachlor, atrazine, 2,4-D 2-ethylhexyl ester (2,4-D EH), and metolachlor among a group of applicators during the spring pre-emergent spray season. A secondary objective was to evaluate determinants of exposure and to estimate within- and between-worker variance components. Fifteen applicators were sampled using a systematic design that included spray and non-spray days and multiple measurements (five to seven) on each applicator. Air, patch, and handwash samples were collected on 89 applicator-days. Applicator-days were classified into three categories: target herbicide sprayed, non-target herbicide sprayed, and no herbicide sprayed. Mixed-model regression analysis was used. For all exposure metrics, adjusted mean herbicide exposures were significantly higher on days when target herbicides were sprayed as compared to non-spray days. For 2,4-D EH only, adjusted mean exposures on non-target herbicide spray days were significantly higher than on non-spray days. Wearing gloves significantly reduced adjusted mean hand exposure for all herbicides (4–20 fold) and adjusted mean thigh exposure for three herbicides (8–53 fold) on days the herbicides were sprayed; however, wearing gloves significantly increased adjusted mean atrazine hand and thigh exposures (9 and 7 fold, respectively) on days that non-atrazine herbicides were sprayed. Few of the other covariates were consistent determinants of exposure. For all exposure metrics, the within-worker variability (GSD_W 2.1–5.6) was greater than the between-worker variability (GSD_B 1.2–2.7). Published by Elsevier Science Ltd on behalf of British Occupational Hygiene Society

Keywords: atrazine; 2,4-D; metolachlor; alachlor; exposure assessment; variance components; mixed-models; determinants of exposure

INTRODUCTION

Custom (or commercial) applicators apply pre-emergent herbicides to corn and soybean fields during spring planting, after which these herbicides are used minimally for the remainder of the year. Thus, most of an applicator's yearly exposure to these herbicides may occur during a short season of 4–6 weeks. Field and weather conditions, weed species, and customer specifications influence the timing and type of herbicide application. Because of these factors, it is difficult for applicators to predict day-to-day spraying activities. During planting season, work hours are long and variable, including work on Saturdays and Sundays.

Pre-emergent herbicides are generally applied by custom applicators using three- or four-wheel flotation vehicles with an enclosed cab, a large tank behind the cab for the mixed chemical, and a 15–18 m spray boom, usually mounted at the rear of the tank. Cabs may be equipped with air conditioning, dust filters and/or charcoal filters. A tank mix usually contains multiple herbicides, occasional spray additives, and a diluent, either 28% liquid urea ammonium fertilizer or water. The number of spray

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jobs varies by day and applicators may spray several different tank mixes within a day. In addition to spraying herbicides, applicators perform other tasks with potential herbicide exposure, such as mixing, loading, rinsing herbicide containers, and doing maintenance on spray rigs (especially during non-spray periods). Other tasks during non-spray periods include *field-station tasks*, such as blending fertilizer, doing paperwork, selling seed and helping customers, and *off-site tasks* such as scouting fields, delivering chemicals or feed, and running errands.

Exposure data for four herbicides, alachlor, atrazine, metolachlor, and the 2-ethylhexyl ester of 2,4-dichlorophenoxyacetic acid (2,4-D EH) are reported in this paper. These herbicides were selected based on their potential chronic toxicity and heavy use on corn and soybean fields (USDA, 1997). By 1996, alachlor use was declining in the US (US EPA, 1999). The US Environmental Protection Agency (EPA) initiated special reviews of alachlor and the triazine herbicides after concerns about possible human carcinogenicity were raised (US EPA 1985, 1994). EPA has classified alachlor as likely to be a human carcinogen at high doses, but not likely at low doses, and has classified the three triazine herbicides as Group C (possible human) carcinogens (US EPA, 1998). The International Agency for Research on Cancer has classified atrazine and 2,4-D as Group 2B carcinogens (limited evidence for carcinogenicity to humans) (IARC 1977, 1991).

Previous exposure studies involving the selected herbicides and ground boom application have been conducted for alachlor (Lauer and Arras, 1982; Cowell *et al*., 1987; Dubelman and Cowell, 1989; Sanderson *et al*., 1995), atrazine (Ciba-Geigy, 1981), and 2,4-D (Kolmodin-Hedman *et al*., 1983; Abbott *et al*., 1987; Grover *et al*., 1986a, 1986b); however, the sampling strategies, exposure metrics, protective measures and/or amount of herbicide used in these studies differ from the study reported here.

The primary objective of this study was to characterize the distributions of the selected or 'target' herbicide exposures among custom applicators during the approximately 6-week spring pre-emergent spray season. Underlying this objective was a hypothesis that applicators are exposed to these herbicides on both 'spray' and 'non-spray' days. Exposure on non-spray days has typically not been measured. Thus, to more adequately describe the exposure distribution, non-spray days were included in the sampling design. Replicate measurements on workers were also obtained so that within- and between-worker variance components could be estimated. A secondary objective was to identify determinants of exposure. The ability to meet the second objective would depend on the distribution of spray and non-spray days in the study period. Exposure measures included personal air, handwash, patch, urine and saliva samples. This paper will report only the results of the air, handwash, and patch sampling.

METHODS

Sampling strategy

Full-time applicators were recruited during visits to companies in a four-county area in Ohio. Participation was voluntary and informed consent was obtained. Companies may have had one or more field stations in the study area. Demographic data, such as age and years of experience as an applicator, were obtained. This study was approved by the NIOSH Human Subjects Review Board.

In order to have a workable arrangement for applicators and their companies, a systematic sampling strategy where each applicator was sampled at roughly 4-day intervals over six consecutive weeks in 1996 was used as the next-best alternative to random sampling. Since herbicide spraying did not occur on a predictable or systematic schedule, this approximation seemed reasonable. Applicators were assigned to 1 day in a 4-day period called a 'cycle' and sampled during multiple cycles over the 6-week period. Each cycle was tied to a fixed set of dates. Thus, samples were collected on a sub-set of applicators each day in a cycle, on both weekdays and weekends, and whether the applicator sprayed or not. Due to an unusually wet spring, sampling was interrupted for two 4-day cycles and then resumed for a total of eight cycles over 6 weeks. If the applicator was not at work on a scheduled sampling day, no sample was collected. Separate samples for application and mixing tasks were not practical due to multiple spray jobs per day and the mixing of chemicals in remote fields. For each spray job, data were collected on several variables, including herbicides applied, application rate, duration of application, glove use, and spray equipment features. For each unsampled day in the 6-week period, information on all herbicides applied, including application rate, duration of application, and number of acres sprayed, was obtained for each applicator by interview and from records. In this paper, the term 'herbicide' refers to the active ingredient. The amount of active ingredient was computed using the product application rate provided by the applicators, the amount of active ingredient in the product, and the number of acres sprayed.

Sample collection and analysis

Samples were collected and analyzed according to NIOSH Methods 9200 (handwash), 9201 (patch), and 5602 (air) for chlorinated and organonitrogen herbicides (NIOSH, 1994). These methods are briefly described below. All samples were stored at 5°C.

Hand sampling. Both hands were sampled separately at the end of the work day at the field station. Hands were checked for cuts or abrasions before sam-

pling and all applicators were asked about allergies to alcohol. To collect a sample, the hand was inserted into a polyethylene bag (30.5 cm×20.3 cm×0.01 cm thickness, Fisher Scientific, Pittsburgh, PA) containing 150 ml of 100% isopropanol (IPA). The bag was secured around the wrist and the hand was shaken at a constant rate for 30 s. An aliquot of the sample was poured into a 125-ml glass jar with a polytetrafluoroethylene-lined (PTFE) cap. Field blanks were collected after the applicators were sampled by pouring 150 ml of IPA into a clean bag and shaking for 30 s. Field staff wore disposable gloves throughout sampling to minimize sample contamination. Although a handwash sample at the beginning of the day would have been desirable to check for pre-work herbicide hand contamination (NIOSH, 1988), sampling was limited to once per day to minimize the drying effects of IPA and to minimize interference with the biological monitoring component of the study.

Air sampling. Full-shift breathing zone air samples were collected on OVS-2 samplers with 11-mm quartz pre-filters (SKC, Inc., Eighty Four, PA) at a nominal flow rate of 1 lpm. Sampling pumps were pre- and post-calibrated using a Gilibrator flow meter (Sensidyne Inc., Clearwater, FL). Samplers were attached to the applicator's left shoulder (driver's window side). Field blanks were prepared in a manner similar to the air samples, except no air was pulled through the blanks.

Patch sampling. Patch samplers were attached (using tape) to clothing at seven locations (right thigh, left thigh, chest, right upper arm, left upper arm, back, and on a cap) so as not to cover exposed skin (to minimize interference with biological monitoring). Observations of work activities suggested that exposure to the lower legs was unlikely. Attaching patches to the lower arms, although desirable, was problematic because applicators often wore short-sleeved shirts. A patch sampler consisted of a 10 cm×10 cm piece of black polyurethane foam (PUF), 6 mm in thickness (SKC, Inc., Eighty Four, PA) inserted into a lightweight chipboard holder with an aluminized interior surface and a 7.6-cm diameter circle cut in one side (45.4-cm^2 sampling area). Patch samplers were attached at the start of the work day and removed at the end of the work day in order of predicted least contamination (hat) to most contamination (thighs). The PUF was transferred to a 125-ml glass jar with a PTFE-lined cap using clean, IPA-rinsed forceps. Field blanks were taken after field samples had been removed and were prepared in a manner similar to the field samples, except blanks were not attached to clothing.

Laboratory analysis. For handwash samples, diazomethane in IPA (0.5 ml) was added to a 10-ml aliquot of the wash solution and the solution allowed to stand for 1 h. For patch samples, IPA (20 ml) and diazomethane in IPA (20 ml) were added to the PUF and the solution rotated at 5–10 rpm for 1.5 h. For air samples, the quartz filter plus front XAD-2 resin and the PUF separator plus back XAD-2 resin were transferred to two separate 4-ml vials. Diazomethane in 2 ml of 10:90 methanol:methyl *t*-butyl ether was added to each vial and the solutions rotated at 5–10 rpm for 1 h. Silicic acid (approx. 10 mg) was then added to all solutions to quench excess diazomethane and the solutions were allowed to stand for 1 h. An aliquot of the solution was filtered through a 0.45-μm PTFE filter into a 2-ml vial. Samples were analyzed by gas chromatography using a 30−m×0.53−mm fused silica capillary column, internally coated with 1.0 μm of DB-1701, and a ^{63}Ni electron-capture detector. Actual sample limits of detection (LOD) are reported in Table 1.

Quality control. Quality control samples included: (1) laboratory-spiked samples run blind by the analyst, (2) field-spiked samples submitted blind with field samples, and (3) laboratory-spiked samples (air and patches only) exposed to ambient field conditions in a herbicide-free area and submitted blind with field samples. Spiking levels were based on the range of results found in preliminary sampling.

Data analysis

A chi-square goodness of fit test was run to assess how well the distribution of acres sprayed in the sampled applicator-days represented the distribution of acres sprayed in the entire study period. The herbicides atrazine, 2,4-D EH and metolachlor were tested using two categories, 0 acres and greater than 0 acres sprayed. Sample size was insufficient to test alachlor. The number of applicator-days in each category for both the sampled days and the entire study period was determined for each herbicide.

Mixed-effects regression models were used to evaluate determinants of exposure and within- and between-worker variance components. Air, handwash, and thigh patch variables with at least 50% of the data above the LOD were used as dependent variables in the analysis. The data were highly skewed and a natural log transformation was applied to all dependent variables. Values below the LOD were estimated by dividing the LOD by two (Hornung and Reed, 1990). Since actual LODs varied by herbicide and by type of media, using LOD/2 did not result in imputing a single constant value into the models. Cycle number (1–8) was included in the model as a fixed effect to adjust for any time-of-sampling effect on exposure. The actual date of sampling was also evaluated as either a fixed or random effect. While model estimates shifted slightly, use of date (either fixed or random) did not change the overall results. Therefore, cycle number was used in all final models.

Each applicator-day was assigned to one of three spray categories: (1) no herbicide sprayed, (2) non-target herbicide sprayed, and (3) target herbicide

Table 1. Herbicide detection limits by sample matrix

Matrix	LOD range (μg/sample)[a]			
	Alachlor	Atrazine	2,4-D EH	Metolachlor
Air	0.08–0.4	0.5–4	0.03–0.2	0.04–0.3
Handwash	2–5	20–50	0.8–2	2–4
Patch	0.5–2	5–10	0.3–0.8	0.4–1

[a]Detection limit varied by analytical batch due to matrix background.

sprayed. The analysis was done in several stages. The initial model included spray category and cycle number as fixed effects, and subject as a random effect. Both the handwash and patch models included a term for left and right. Glove use ('yes' or 'no'), plus an interaction term for glove use and spray category, were then added to the model as fixed effects. Finally, other covariates were tested one-at-a-time after adjusting for spray category and glove use. Continuous covariates included age, years worked as an applicator, years worked for current company, kilograms of target herbicide applied, duration of target herbicide application, acres of target herbicide sprayed, duration of work day, number of spray jobs during the day (all herbicides combined), number of nozzle changes during the day (all herbicides combined), and number of spray jobs during the day with a cab window open (all herbicides combined). Categorical covariates included certified applicator status (yes/no), glove use (yes/no), smoking and chewing tobacco (hand wash model only; yes/no for each), and four spray rig variables (air model only): charcoal filter (yes/no), dust filter (yes/no), air conditioning in cab (yes/no), and boom location (front/back).

Analyses were done using PROC MIXED in SAS v. 6.12 (SAS Institute, Inc., Cary, NC). Compound symmetry was assumed for the correlation of measurements within subjects and the estimation method was restricted maximum likelihood. These procedures were also used to compute the within- and between-worker variance components after adjusting for spray category, glove use and cycle number. A first-order autogressive covariate structure was tried; however, the models did not converge. When comparing geometric mean (GM) levels for the three spray categories, *P*-values were adjusted using the Tukey–Kramer adjustment for multiple comparisons. All significance testing was done at the 0.05 level.

RESULTS

Applicator and work environment characteristics

Of 19 applicators from nine field stations asked to participate in the study, 15 applicators from seven field stations enrolled (79%). All applicators were male and right-handed. Each applicator was sampled for 5–7 days over a 6-week period during May and June, 1996, for a total of 89 applicator-days. Air, patch, and handwash samples were collected from each applicator on each day. The median age for applicators was 40 years (range 23–58), the median number of years of experience as an applicator was 8 (range 1–22), and the median number of years applicators had worked for their current company was 5 (range 1–28). Of the 15 applicators, nine were certified (60%), five smoked cigarettes (33%), and five chewed tobacco (33%). Of the 89 applicator-days, herbicide spraying was done on 30 days; 23 of these days included use of one or more of the target herbicides. Typical application rates were: atrazine, 0.45–0.91 kg/acre; alachlor, 1.1 kg/acre; metolachlor 0.91 kg/acre; 2,4-D EH, 0.23 kg/acre. Over the study period (sampled and non-sampled days), the target herbicides were tank-mixed with other herbicides on 99% or more of the spray jobs. For atrazine, metolachlor, and alachlor, applicators used products that contained a mixture of the target herbicide plus another herbicide on 90, 89 and 48% of the spray jobs, respectively, while all 2,4-D EH usage came from products containing only 2,4-D EH as the active ingredient.

The 89 applicator-days were sampled from 547 applicator-days in the study period. The distribution of the number of acres sprayed in the sample was not significantly different than in the entire study period for the individual herbicides atrazine ($\chi^2 = 0.92$, $df = 1$, $P = 0.34$), 2,4-D EH ($\chi^2 = 0.073$, $df = 1$, $P = 0.79$), and metolachlor ($\chi^2 = 0.29$, $df = 1$, $P = 0.59$). Application characteristics during the 30 days herbicides were sprayed are given in Table 2. The amount of herbicide sprayed, duration of application, and number of acres sprayed for each herbicide are summarized in Table 3. Duration estimates may have included time spent on short interruptions in the field, such as minor spray rig repairs and evaluating field conditions.

Sampling results

Hand sampling. In total, 174 handwash samples were collected. The percentage of handwash samples above the LOD was greater than 50 for all four herbicides (Table 4). Full-shift GM handwash levels for the four herbicides by spray category are given in Table 5. Of 46 handwash field blanks collected, 10

Table 2. Application characteristics—spray days only

Characteristic	*n*	AM[a]	SD[b]	Range
No. of spray jobs per applicator				
Any herbicide	30	2.9	2.5	1–10
Alachlor	3	4.3	4.9	1–10
Atrazine	20	3.3	2.9	1–10
2,4-D EH	12	4.2	3.3	1–10
Metolachlor	10	5.0	3.2	1–10
Duration of spraying, min. per day				
Any herbicide	30	223	177	15–640
Alachlor	3	125	97.6	30–225
Atrazine	20	202	185	25–640
2,4-D EH	12	118	74.2	50–265
Metolachlor	10	207	149	60–505
Duration of work day, h per day	30	12.3	2.9	6.8–17.8

	Frequency (No. of applicator-days)				
	Any Herbicide (*n* = 30)	Alachlor (*n* = 3)	Atrazine (*n* = 20)	2,4-D EH (*n* = 12)	Metolachlor (*n* = 10)
Glove use					
None	8	2	5	3	3
Flock-lined rubber	14	1	11	7	4
Nitrile	5	0	2	2	1
Neoprene	2	0	2	0	2
Polyvinyl chloride	1	0	0	0	0
Type of shirt worn					
Short-sleeve	21	3	13	6	6
Long-sleeve	9	0	7	6	4
No. times spray nozzles changed					
0	13	1	7	2	2
1	12	1	9	6	5
2	3	1	2	3	1
4	2	0	2	1	2
No. of spray jobs with cab window open					
0	21	1	14	8	7
1	3	0	1	0	0
2	4	1	3	2	1
8 or 10	2	1	2	2	2
Type of spray rig (all enclosed cab)					
Four-wheel floater	7	1	6	4	2
Three-wheel floater	13	2	11	7	6
High-clearance	8	0	3	1	2
Pick-up truck	2	0	0	0	0
Boom location					
Behind spray rig	27	3	17	12	8
In front of cab	3	0	3	0	2
Air conditioning in cab	19	1	13	6	7
Dust filter in cab	21	3	15	8	8
Charcoal filter in cab	16	2	11	4	6

[a]AM=arithmetic mean.
[b]SD=standard deviation.

(22%) had detectable levels of at least one of the four herbicides. Four of these 10 blanks were collected on non-spray days. The percentages of field blanks with detectable levels of atrazine, alachlor, metolachlor, and 2,4-D EH were 0, 2, 13, and 17%, respectively. Herbicides detected in a high percentage of worker samples (2,4-D EH and metolachlor) were also detected in a high percentage of field blanks. In nearly all cases where field blanks had detectable levels of a given herbicide, worker samples collected at the same time had substantial levels of the herbicide, suggesting that any contribution due to sampling contamination would be small. Indeed, for all blanks analyzed, the estimated 'worst-case' mean percent

Table 3. Target herbicide usage

Herbicide	Days target herbicide sprayed[a]			
	AM[b]	SD[c]	Median	Range
Alachlor				
kg	33	26	28	10–61
min	125	98	120	30–225
acres	33	28	25	11–64
Atrazine				
kg	98	113	53	9–464
min	202	185	120	25–640
acres	147	147	93	14–548
2,4-D EH				
kg	15	7	17	3–24
min	118	74	85	50–265
acres	60	35	51	15–122
Metolachlor				
kg	166	155	112	34–544
min	207	149	150	60–505
acres	171	154	113	38–527

[a]Alachlor, $n = 3$; Atrazine, $n = 20$; 2,4-D EH, $n = 12$; metolachlor, $n = 10$.
[b]AM=arithmetic mean.
[c]SD=standard deviation.

contamination was 0 (atrazine), <0.1 (alachlor), 1.4 (metolachlor), and 3.7 (2,4-D EH). Since a consistent level of contamination was not seen in the field blanks and the contamination level of an individual sample would be difficult to estimate, handwash data have not been adjusted for field blanks; however, the results indicate the potential for field contamination and the need for careful precautions when taking samples.

Air sampling. Full-shift air sample data were available for 88 out of 89 applicator-days. Herbicides with at least 50% of the samples above the LOD were metolachlor (77%) and 2,4-D EH (55%). Only the range of detected values is reported for atrazine and alachlor (Table 4). Full-shift GM air levels for 2,4-D EH and metolachlor by spray category are given in Table 6. The four herbicides were not detected in the 13 field blanks.

Patch sampling. In total, 623 patch samples were collected. The percentage of samples above the LOD and the range of detected values for each herbicide varied substantially by location (Table 4). For four of seven patch locations (back, right arm, left arm, and hat), this percentage was less than 50 and for chest patches, the percentage marginally exceeded 50 for 2,4-D EH and metolachlor. For thigh patches, all four herbicides had at least 50% of the samples above the LOD. Full-shift GM thigh patch levels of alachlor, atrazine, 2,4-D EH, and metolachlor by spray category are given in Table 7. Only metolachlor was detected in one of 46 patch field blanks; therefore, adjustments for field blanks were not made.

Quality control. Results of laboratory and field recovery studies for the four herbicides in air, patch, and handwash media are given in Appendix A. Across studies, mean recovery ranged from 89 to 123%. Results for ambient-exposed field QC samples were generally comparable to unexposed laboratory and field QC samples, suggesting that significant loss of analyte due to environmental conditions was unlikely. Pooled relative standard deviations (RSDs) ranged from 1 to 16%, with 26 of 34 pooled RSDs below 10%. Precision in laboratory QC samples was generally better than in field QC samples. Results have not been corrected for either laboratory or field recovery.

Table 4. Percent and range of samples greater than or equal to the limit of detection

Exposure measure		Alachlor		Atrazine		2,4-D EH		Metolachlor	
	n	%≥LOD	Range[a]	%≥LOD	Range	%≥LOD	Range	%≥LOD[c]	Range
Air	88	41	0.14–3.2[b]	27	1.3–75	55	0.06–2.4	77	0.17–14
Hands									
right	88	73	2.3–3700	77	24–6900	97	2.5–3400	95	3–4000
left	86	70	2.4–15 000	69	40–18 000	98	1.3–4300	93	3.6–7200
Patches									
hat	89	11	0.72–440	19	7.5–7800	30	0.34–34	38	0.44–1000
back	89	17	0.55–55	15	5.4–310	39	0.32–160	46	0.44–170
right arm	89	21	0.53–380	20	5.8–810	44	0.31–160	48	0.49–750
left arm	89	18	0.57–230	17	5.4–160	51	0.3–74	49	0.42–400
chest	89	24	0.65–580	27	5.4–3700	56	0.38–31	56	0.55–93
right thigh	89	60	0.55–500	65	8.2–3900	84	0.34–6200	79	0.51–2200
left thigh	89	62	0.52–1900	61	7.4–13 000	84	0.33–3800	83	0.61–1200

[a]Range of samples greater than or equal to the LOD (μg/sample).
[b]Units for air samples (μg m^{-3}).
[c]LOD=limit of detection.

Table 5. Handwash samples: spray effect analysis

Herbicide	Spray category	n[a]	GM[b]	GSD[c]	Adjusted GM[d]	95% CI[e]
Alachlor	No herbicide sprayed	114	7.0	3.7	6.8	5.2, 9.0
	Other herbicide sprayed	54	12	5.8	9.9	6.6, 15
	Alachlor sprayed	6	660	11	820**,++f	250, 2700
Atrazine	No herbicide sprayed	114	100	5.0	120	76, 190
	Other herbicide sprayed	20	88	4.1	100	50, 210
	Atrazine sprayed	40	1100	3.3	550**,++	300, 1000
2,4-D EH	No herbicide sprayed	114	29	4.7	33	23, 47
	Other herbicide sprayed	36	100	3.9	77§	44, 140
	2,4-D EH sprayed	24	210	6.7	160**	80, 310
Metolachlor	No herbicide sprayed	114	30	5.8	34	22, 53
	Other herbicide sprayed	40	36	3.3	33	19, 60
	Metolachlor sprayed	20	400	4.2	190**,++	90, 410

[a]Includes right and left hands.
[b]GM=geometric mean (μg/sample).
[c]GSD=geometric standard deviation.
[d]GM adjusted for cycle number (μg/sample).
[e]CI=confidence interval (μg/sample).
[f]Tukey–Kramer adjusted P-values: **target herbicide vs. no herbicide, $P<0.01$; ++target herbicide vs. other herbicide, $P<0.01$; §other herbicide vs. no herbicide, $P<0.05$.

Table 6. Air samples: spray effect analysis

Herbicide	Spray category	n	GM[a]	GSD[b]	Adjusted GM[c]	95% CI[d]
2,4-D EH	No herbicide sprayed	59	0.088	2.3	0.089	0.066, 0.12
	Other herbicide sprayed	18	0.23	2.7	0.21§§e	0.13, 0.33
	2,4-D EH sprayed	11	0.33	2.2	0.36**	0.21, 0.63
Metolachlor	No herbicide sprayed	59	0.44	3.4	0.47	0.31, 0.72
	Other herbicide sprayed	20	0.45	2.7	0.52	0.29, 0.91
	Metolachlor sprayed	9	1.6	1.9	1.2*	0.58, 2.7

[a]GM=geometric mean (μg m^{-3}).
[b]GSD=geometric standard deviation.
[c]GM adjusted for cycle number (μg m^{-3}).
[d]CI=confidence interval (μg m^{-3}).
[e]Tukey–Kramer adjusted P-values: *target herbicide vs. no herbicide, $P<0.05$; **target herbicide vs. no herbicide, $P<0.01$; §§other herbicide vs. no herbicide, $P<0.01$.

Table 7. Thigh-patch samples: spray effect analysis

Herbicide	Spray category	n[a]	GM[b]	GSD[c]	Adjusted GM[d]	95% CI[e]
Alachlor	No herbicide sprayed	118	1.4	4.4	1.5	1.0, 2.4
	Other herbicide sprayed	54	2.1	5.6	2.0	1.1, 3.5
	Alachlor sprayed	6	180	6.6	150**,++f	37, 580
Atrazine	No herbicide sprayed	118	15	4.9	18	11, 30
	Other herbicide sprayed	20	23	6.5	29	13, 65
	Atrazine sprayed	40	240	4.7	150**,++	78, 290
2,4-D EH	No herbicide sprayed	118	2.0	7.0	2.2	1.3, 3.9
	Other herbicide sprayed	36	9.1	5.1	7.4§§	3.4, 16
	2,4-D EH sprayed	24	65	13	48**,++	19, 120
Metolachlor	No herbicide sprayed	118	3.5	8.7	3.7	2.0, 6.9
	Other herbicide sprayed	40	5.7	7.0	6.1	2.7, 14
	Metolachlor sprayed	20	63	3.8	37**,++	13, 100

[a]Includes right and left thighs.
[b]GM=geometric mean (μg/sample).
[c]GSD=geometric standard deviation.
[d]GM adjusted for cycle number (μg/sample).
[e]CI=confidence interval (μg/sample).
[f]Tukey–Kramer adjusted P-values: **target herbicide vs. no herbicide, $P<0.01$; ++target herbicide vs. other herbicide, $P<0.01$; §§other herbicide vs. no herbicide, $P<0.01$.

Exposure determinants

For all target herbicides tested in the handwash, patch, and air models, adjusted mean exposures on days when target herbicides were sprayed were significantly higher than on days when no herbicides were sprayed (Tables 5–7). With the exception of 2,4-D EH in handwashes and in air, and metolachlor in air, adjusted mean exposure on days when a target herbicide was sprayed was also significantly higher than on days when non-target herbicides were sprayed (Tables 5 and 7). For 2,4-D EH in all three media, adjusted mean exposures were significantly higher on days when other, non-target herbicides were sprayed, than on days when no herbicide was sprayed (Tables 5–7).

A significant interaction between glove use and spray category was found for atrazine, 2,4-D EH and metolachlor in the handwash model ($P<0.001$, $P<0.001$, $P<0.01$, respectively), and a borderline-significant interaction was found for alachlor ($P = 0.06$) (Table 8). This interaction was also significant for all four herbicides in the thigh patch model (alachlor, $P<0.05$; atrazine, $P<0.001$; 2,4-D EH, $P<0.001$; metolachlor, $P<0.05$) (Table 9), but not significant for the four herbicides in the air model.

Of the other covariates tested, the number of years worked as an applicator was significantly associated with *decreased* alachlor ($\beta=-0.0607$, $P<0.05$) and metolachlor ($\beta=-0.0864$, $P<0.05$) thigh-patch exposure, the duration of the workday was significantly associated with *increased* atrazine hand exposure ($\beta=1.645$, $P<0.01$), and the number of spray jobs during the day with a cab window open was significantly associated with *increased* alachlor hand ($\beta=0.3384$, $P<0.01$) and thigh patch ($\beta=0.418$, $P<0.001$) exposure. Right or left was not significant in the hand or thigh patch models, except marginal significance ($\beta=0.418$, $P=0.0445$) was found for atrazine hand exposure, with the right hand higher than the left hand. Other covariates tested were not significant.

Exposure variability

The within-worker (GSD_W) and between-worker (GSD_B) variance components expressed as geometric standard deviations for the various exposure metrics are given in Table 10. The GSD_W ranges were: 3.1–4.0 (handwash), 3.6–5.6 (thigh patch), and 2.1–2.5 (air). The GSD_B ranges were: 1.2–2.3 (handwash), 2.0–2.7 (thigh patch), and 1.6–1.9 (air). For all exposure metrics, the within-worker variability was greater than the between-worker variability and accounted for more than 50% of the random effects variability. On average, both the within- and between-worker variance components were higher for thigh-patch samples than for handwash samples and both sources of variability were higher for dermal samples than for air samples.

DISCUSSION

By using a systematic sampling design as an approximation to random sampling, the exposure distributions of a small group of custom applicators to the herbicides alachlor, atrazine, 2,4-D EH, and metolachlor have been described for the principal period of use during the year. Estimates of the geometric

Table 8. Handwash samples: glove effect analysis—spray days only

Analyte	Herbicide sprayed	Glove status	*n*	GM[a]	GSD[b]	Adjusted GM[c]	95% CI[d]
Alachlor	Other	No gloves	12	15	8.7	14	5.8, 31
		Gloves	42	11	5.2	9.0	6.0, 15
	Alachlor	No gloves	4	2600	3.9	2200	510, 9600
		Gloves	2	44	1.9	110*[e]	14, 900
Atrazine	Other	No gloves	6	15	1.5	21	6.7, 63
		Gloves	14	190	2.4	180++	83, 390
	Atrazine	No gloves	10	2800	2.7	1800	710, 4600
		Gloves	30	820	3.0	420**	220, 790
2,4-D EH	Other	No gloves	10	80	1.8	66	27, 160
		Gloves	26	110	4.8	82	45, 150
	2,4-D EH	No gloves	6	2000	1.5	1500	460, 5200
		Gloves	18	98	4.8	81**	40, 160
Metolachlor	Other	No gloves	10	25	3.9	24	9.3, 61
		Gloves	30	41	3.1	39	21, 73
	Metolachlor	No gloves	6	1800	2.8	790	230, 2600
		Gloves	14	210	2.9	110**	46, 250

[a]GM=geometric mean (μg/sample).
[b]GSD=geometric standard deviation.
[c]GM adjusted for cycle number (μg/sample).
[d]CI=confidence interval (μg/sample).
[e]*Target herbicide and gloves vs. target herbicide and no gloves, $P<0.05$; **target herbicide and gloves vs. target herbicide and no gloves, $P<0.01$; ++other herbicide and gloves vs. other herbicide and no gloves, $P<0.01$.

Table 9. Thigh patch samples: glove effect analysis—spray days only

Analyte	Herbicide sprayed	Glove status	*n*	GM[a]	GSD[b]	Adjusted GM[c]	95% CI[d]
Alachlor	Other	No gloves	12	3.8	15	4.2	1.6–11
		Gloves	42	1.8	3.7	1.6	0.91–3.0
	Alachlor	No gloves	4	420	2.9	580	110–3100
		Gloves	2	34	12	11**[e]	1.2–100
Atrazine	Other	No gloves	6	3.6	1.3	7.1	2.1–25
		Gloves	14	51	5.4	47++	20–110
	Atrazine	No gloves	10	810	4.9	760	270–2200
		Gloves	30	160	3.7	100**	53–210
2,4-D EH	Other	No gloves	10	3.3	4.4	3.7	1.2–12
		Gloves	26	13	4.7	9.6	4.4–21
	2,4-D EH	No gloves	6	1500	2.8	780	170–3500
		Gloves	18	23	7.2	21**	8.3–51
Metolachlor	Other	No gloves	10	2.9	8.4	3.4	0.91–13
		Gloves	30	7.0	6.4	7.8	3.2–19
	Metolachlor	No gloves	6	200	4.7	130	24–710
		Gloves	14	39	2.5	22	6.7–70

[a]GM=geometric mean (μg/sample).
[b]GSD=geometric standard deviation.
[c]GM adjusted for cycle number (μg/sample).
[d]CI=confidence interval (μg/sample).
[e]**Target herbicide and gloves vs. target herbicide and no gloves, $P<0.01$; ++other herbicide and gloves vs. other herbicide and no gloves, $P<0.01$.

Table 10. Within- and between-worker variance components

Exposure measure	GSD_W[a] (within-worker)	Within-worker variance %[b]	GSD_B[c] (between-worker)	Between-worker variance %	$\hat{R}_{0.95B}$[d]
Handwash[e]					
Alachlor	4.0	98	1.2	2	2.2
Atrazine	3.1	65	2.3	35	25
2,4-D EH	3.5	89	1.6	11	5.7
Metolachlor	3.6	77	2.0	23	15
Thigh patches[e]					
Alachlor	4.1	80	2.0	20	16
Atrazine	3.6	71	2.3	29	25
2,4-D EH	4.5	78	2.2	22	22
Metolachlor	5.8	75	2.7	25	51
Air					
2,4-D EH	2.1	73	1.6	27	5.8
Metolachlor	2.5	67	1.9	33	13

[a]GSD_W=estimated geometric standard deviation of the within-worker distribution.
[b]Percent of the random effect variance attributable to that source.
[c]GSD_B=estimated geometric standard deviation of the between-worker distribution.
[d]$\hat{R}_{0.95B} = \exp(3.92 \ln(GSD_B))$ = ratio of the 97.5th and 2.5th percentiles of the between-worker distribution.
[e]Variance components were computed after adjusting for spray category, cycle number, and glove use.

means and standard deviations for the significant main effects and for the within- and between-worker variance components were obtained. Censoring in the dependent variables (range 2–45%) may have affected these estimates, particularly at higher levels of censoring. The presence of multiple limits of detection may have offset this effect somewhat. The exact bias introduced by censoring, especially in the presence of multiple detection limits, when using mixed-models is unknown. Further research is needed to understand the effect of censoring on mixed-model results.

Although the level of censoring varied in the data, results were generally consistent across all four herbicides. For all exposure metrics, adjusted mean herbicide exposures were significantly higher on days when the target herbicide was sprayed as compared to days when no herbicide was sprayed; however, adjusted mean herbicide exposures on days non-target herbicides were sprayed as compared to days when

no herbicide was sprayed were not significantly different, with the exception of 2,4-D EH in handwash, air, and thigh-patch samples. The consistency of this finding for 2,4-D EH is intriguing and suggests that 2,4-D EH exposure on days that non-2,4-D EH herbicides are sprayed should be classified separately from non-spray and 2,4-D EH spray days.

Wearing gloves was a consistent determinant of significantly reduced adjusted mean hand (4–20 fold) and thigh (8–53 fold) exposures when the target herbicide was sprayed. Alachlor results are based on very small sample sizes and should be interpreted with caution. The reduction in thigh exposures with the use of gloves suggests that contaminated hands may be a source of exposure to the thighs. The association between glove use and significantly increased atrazine hand and thigh exposure on days when herbicides other than atrazine were sprayed suggests that gloves may be a source of exposure. Applicators may don and remove the same pair of gloves several times per day and do not necessarily wear new gloves every day. As a result, herbicide-contaminated hands may contact the inside of gloves, the hands may contact the outside of previously-contaminated gloves or the outside of contaminated gloves may contact the thighs. Flock-lined gloves, worn frequently in this study, may be especially absorbent for pesticides. The presence of pesticides, including alachlor, on the inside of gloves worn by applicators, has been shown previously using glove rinses (Sanderson *et al*., 1995; NIOSH, 1988). Our results illustrate that glove use can simultaneously offer protective exposure reduction benefits for the herbicide being sprayed, while potentially increasing exposure to herbicides not being sprayed. More frequent hand-cleaning and wearing of new gloves would likely improve the overall protective benefit of glove use.

These results also indicate that herbicide exposure on non-spray days, although much less than on spray days, cannot be assumed to be zero. Contamination of equipment and surfaces may be a major source of exposure on non-spray days and a contributing source of exposure on spray days. Even though alachlor, metolachlor, 2,4-D EH, and atrazine were sprayed on only 3, 11, 13 and 22% of the applicator-days, respectively, these herbicides were detected in 72, 98, 98, and 73%, respectively, of handwash samples and in 61, 81, 84, and 63%, respectively, of thigh patch samples. This suggests that tasks and activities not related to direct herbicide application contribute to exposure. Preliminary surface wipe samples ($n = 24$) taken on food and beverage related-items, in the spray rig, in the office, and on other frequently touched objects showed detectable levels of atrazine, 2,4-D EH, metolachlor, and alachlor in 83, 79, 71, and 67% of samples, respectively (data not shown). Sanderson *et al*. (1995) also found alachlor on 29 (94%) of 31 wipe samples taken inside spray rig cabs (steering wheels, arm rests/door handles, and gear shifts/control switches). Applicators in this study and in Sanderson *et al*. (1995) did not wear gloves while driving spray rigs. These findings, although crude, suggest that surface contamination is a plausible dermal exposure route.

Few of the other covariates tested were associated with significant increases or decreases in mean exposure and none consistently enough across all herbicides or exposure metrics to clearly establish the predictive value of the factor. The lower than expected proportion of spray days in the sample may have affected the power to detect other effects. The amount of target herbicide applied, the duration of target herbicide application, and the number of acres of target herbicide sprayed were not predictive of exposure. This lack of association, which may be related to the method of application in which applicators sit in enclosed cabs away from the spray boom, has been previously reported (Sanderson *et al*., 1995).

The high within-worker variability relative to the between-worker variability for all exposure metrics suggests that factors that vary from day-to-day (other than spraying and glove use) influence the remaining variability more than individual work practices. When day-to-day variability in exposure within-workers is greater than between-workers, control strategies to reduce overall group exposure should focus on high-exposure days and the group as a whole. The relatively high between-worker variability (GSD_B>2.0) for some exposure metrics, however, suggests that some focus on reducing exposures among high-exposure workers would also be desirable. The factors contributing to high within-worker variability, even after adjusting for spray category and glove use, are not readily apparent. Spraying and other tasks performed on non-sampled days may influence exposure through residual contamination in the work environment.

The within- and between-worker variance components for the air samples are similar in magnitude to previously reported values for sodium borate dust (Woskie *et al*., 1994), cobalt aerosol (Kumagai *et al*., 1996), and a variety of other airborne exposures (Kromhout *et al*., 1993). Minimal data have been published on within- and between-worker variability for dermal exposures. Our estimates of within-worker variability for dermal measures (handwashes and patches) are greater than those reported for chemicals in the rubber industry (Kromhout *et al*., 1993) and for captan during re-entry work in fruit growing (de Cock *et al*., 1998); however, our between-worker variability estimates are similar to the values reported in these studies. As in this study, Kromhout *et al*. (1993) found that between-worker variability was greater for dermal exposures than for exposure to gases and vapours. Within-worker variability has also been reported to exceed between-worker variability for job groups where the work is done outdoors, the process is intermittent, or the workers are highly

mobile (Kromhout *et al*., 1993; Woskie *et al*., 1994), all characteristics of custom applicator work. Rappaport (1991) has defined a 'uniformly exposed group' as having a ratio ($\hat{R}_{0.95B}$) of the 97.5th percentile to the 2.5th percentile of the between-worker distribution no greater than two. $\hat{R}_{0.95B}$ ratios for all herbicide exposure metrics exceeded this criterion (Table 10), indicating that for most herbicides and exposure metrics, applicators were not a uniformly exposed group using Rappaport's definition. The low ratio (2.2) for alachlor hand exposure (suggesting uniform group exposure) may be related to the few alachlor spray days in the study ($n = 3$) and the common experience among applicators of being exposed to 'background' or non-spraying sources of alachlor.

Sanderson *et al*. (1995) also collected air, patch, and handwash samples to estimate full-shift alachlor exposures among custom applicators, but only on spray days. On days alachlor was sprayed, mean alachlor air and patch exposures were similar to those found in this study, although our estimates are based on very small numbers. Our hand exposure results (GM = 660 μg, $n = 6$), however, are 30-fold higher than Sanderson *et al*. (1995) (GM = 21 μg, $n = 11$), most likely due to improved recovery of alachlor from 100% IPA (99% recovery) as compared to 10% ethanol (<5% recovery). Both studies found exposure to the thighs to be the highest of any patch location. Exposures to the front of the thighs may be related to leaning against contaminated equipment, chemical splashes, or to possible contact of contaminated objects or hands with the thighs. After the thighs, the chest was the next most exposed body area. Protection to the front of the torso and thighs, as by a chemically-resistant apron, may be beneficial (applicators did not use aprons in this study). All 2,4-D EH air exposures were below the OSHA, ACGIH and NIOSH 2,4-D exposure limits of 10 mg m^{-3} (TWA) and all atrazine air exposures were below the ACGIH and NIOSH exposure limits of 5 mg m^{-3} (TWA) (CFR, 1999; ACGIH, 2000; NIOSH, 1992)

The sampling methods used in this study have limitations. An end-of-the-day handwash may not capture all herbicide exposure to the hands. An unknown amount of herbicide may have been lost due to skin absorption or during routine handwashing. Also, the removal efficiency of these herbicides from the skin by this method is not known. Patch data only represent potential exposure as clothing influences availability for skin absorption. Patch data were not extrapolated to the entire body surface area to estimate total dermal exposure, since this extrapolation assumes uniform exposure over the area represented by the patch. In this setting, herbicide contamination of the skin and clothing was likely to be highly non-uniform as suggested by differences in exposure by patch location and from observations of work activities. Non-uniform deposition of pesticides on the body has been previously described (Fenske, 1990).

Applicators were not selected by a strictly random process, so these results may not apply to all custom applicators. We expect, however, that the results are fairly representative of exposed applicators with similar equipment, herbicide usage, and work practices. Due to unusually wet weather, herbicide spraying was done on only one-third of the applicator-days in the study compared to approximately two-thirds of the days in a more typical pre-emergent season. The amount of herbicide used in the study season was probably less than normal (based on limited data from sampled spray days in pilot studies conducted in 1993, 1994, and 1995) as farmers switched to other crops or to post-emergent herbicides.

CONCLUSION

The characterization of the exposure distributions of the herbicides alachlor, atrazine, 2,4-D EH, and metolachlor among custom applicators during the spring pre-emergent spray season was optimized by including both spray and non-spray days in the study design and by collecting multiple measurements on applicators. This characterization included estimates of the geometric mean and standard deviation for the significant main effects in the analysis and the within- and between-worker variance components after adjustment for the main effects and cycle number. For all herbicides, spraying a target herbicide was a significant determinant of increased exposure. Wearing gloves was a significant determinant of reduced hand exposure (four herbicides) and thigh exposure (three herbicides) when the target herbicide was sprayed; however, wearing gloves was significantly associated with increased atrazine hand and thigh exposure on days that non-atrazine herbicides were sprayed. This glove finding should be confirmed in additional studies and attention should be given to glove use practices. Within-worker variability was greater than between-worker variability, suggesting that factors, not yet identified, that vary day-to-day influence total variability more than individual work practices. The percentage of handwash and thigh-patch samples with detectable levels of target herbicides was much higher than the percentage of target herbicide spray days in the study period, indicating exposure on non-target spray days. Therefore, a complete assessment of an applicator's cumulative exposure should consider all days in the season. The distribution of exposures outside the pre-emergent spray season has not been determined.

Disclaimer—Mention of any company or product does not constitute endorsement by the National Institute for Occupational Safety and Health.

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Appendix A Laboratory and field recovery studies

Sample type		*n*	Fortification range (μg)	Mean recovery (%)	Pooled RSD (%)
Laboratory QC					
Air	Alachlor	21	0.72–3.58	105	3.11
	Atrazine	31	3.75–35.7	104	4.08 (*n*=29)[a]
	2,4-D EH	21	0.35–1.74	104	3.96
	Metolachlor	21	0.65–3.24	99.6	3.32
Hand	Alachlor	15	108–239	99.0	1.11
	Atrazine	13	225–1190	107	2.00 (*n*=13)
	2,4-D EH	9	15.6–261	101	3.19 (*n*=8)
	Metolachlor	17	18.2–486	101	4.39
Patch	Alachlor	21	7.18–59.7	101	3.68 (*n*=20)
	Atrazine	15	19.8–298	99.5	5.49 (*n*=13)
	2,4-D EH	27	3.47–52.1	93.0	4.56 (*n*=26)
	Metolachlor	23	4.05–130	100	3.89 (*n*=19)
Field QC—not exposed to ambient conditions					
Air	Alachlor	20	1–5	108	10.6
	Atrazine	18	2–6	103	15.9
	2,4-D EH	20	1.5–5	103	8.20
	Metolachlor	20	0.5–2.5	111	7.62
Hand	Alachlor	20	22.5–150	120	3.65
	Atrazine	10	60–150	123	7.68
	2,4-D EH	20	15–150	115	5.76
	Metolachlor	20	7.5–15	125	8.21
Patch	Alachlor	22	10–30	108	8.50
	Atrazine	23	25–75	118	7.46
	2,4-D EH	23	10–100	104	5.00
	Metolachlor	22	20–80	104	8.21
Field QC—exposed to ambient conditions					
Air	Alachlor	53	0.24–4.5	113	7.17
	Atrazine	53	2.5–46.8	111	11.8
	2,4-D EH	53	0.128–2.4	111	11.2
	Metolachlor	53	0.208–3.9	108	7.47
Patch	Alachlor	51	1.5–60	98.6	9.99
	Atrazine	54	15.6–312	106	9.38
	2,4-D EH	54	0.8–80	105	11.3
	Metolachlor	54	1.3–130	98.6	10.6

[a]One or more fortification levels had only one sample.