

# Health & Safety

# Report

Worker Health and Safety Branch

HS-1769

## Exposure of Hand Applicators to Triclopyr in Forest Settings, 1995

February 29, 2000

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### Study Dates

Study Initiation	May 31, 1995
Field Monitoring Start	July 5, 1995
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Lab Sample Analysis Start	November 6, 1995
Lab Sample Analysis Completion	May 20, 1997
Study Completion	February 29, 2000

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<sup>1</sup> All raw data related to sample collection

<sup>2</sup> All raw data related to sample analyses and test/reference substances

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**QUALITY ASSURANCE STATEMENT: Project Number 9501**

The study was audited at the following intervals:

**Field Activities**

Audit Date	Phase	Study Director Notified	Management Notified
06/06/95	Protocol	06/06/95	06/06/95
07/10/95	Field Monitoring	07/19/95	07/19/95
11/17/99 - 11/30/99	Raw Data	12/07/99	12/07/99
11/17/99 - 11/30/99	Final Report	12/07/99	12/07/99

James R. Sanborn 2/24/00  
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**Laboratory Activities**

Audit Date	Phase	Study Director Notified
04/24/95	Protocol	04/28/95
06/09/95	Standards Audit	11/17/97
07/14/95	Sample Receipt	11/17/97
04/08/96	In-process	04/09/96

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## STUDY COMPLIANCE STATEMENT

Based upon all information supplied to me including the California Department of Food and Agriculture, Center for Analytical Chemistry, (Laboratory Statements of 'Compliance), I hereby confirm that all aspects of this study, Project 9501, were conducted in compliance with the US Environmental Protection Agency, Good Laboratory Practice standards (GLP, 40 CFR 160), with the following exceptions:

The test substance characterization was not documented before its use in the study as required in 40 CFR 160.105(a).

The testing facility did not have procedures established for handling reference substances as required in 40 CFR 160.107 before July, 1995.

Supplemental and support data such as weather data were, not collected in compliance with GLP.

Not all required quality assurance SOPs were in place at the time of study conduct and other required SOPs may not have been in place at the time of study conduct.

Neither analytical reference standards nor reference standards for field fortifications were characterized under GLP before July, 1995.



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Janet R. Spencer, Associate Environmental Research Scientist,  
Study Director

Date

Protocol and SOP deviations were documented and can be found in Appendix 11.

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## Exposure of Hand Applicators to Triclopyr in Forest Settings, 1995

### ***Executive Summary***

***Objectives*** The study objectives were to estimate dermal and inhalation exposure of workers who apply triclopyr to National Forests, and to assess absorbed dose via urinary monitoring. Study estimates were compared to US Department of Agriculture Forest Service (USFS) Environmental Impact Statement (EIS) estimates for realistic, conservative and worst case exposures, which were developed from surrogate data (1).

***Background*** The USFS is responsible for managing over 20 million acres of USFS land in the Pacific Southwest Region (Region 5). Vegetation management, including mechanical, manual, thermal, biological and chemical means, is necessary to control competing plant species and achieve timber yield objectives. The USFS EIS presents the hazard, exposure and risk analyses for the thirteen herbicides used in Region 5 (1). Dosage estimates for worker exposures were based on studies of worker exposure to liquid formulations of 2,4-D and 2,4,5-T applied by backpack sprayer. Realistic, conservative and worst case worker exposures (dosages) were estimated using the 50<sup>th</sup>, 95<sup>th</sup> and 99<sup>th</sup> percentiles, respectively, of the observed distribution of the 2,4-D and 2,4,5-T worker exposure data. Estimates of risk based on a wide range of potential exposure scenarios were then compared to animal toxicity data. The EIS requires that site-specific worker exposure monitoring evaluate at least 10% of the Region's herbicide application projects annually. In 1995, the USFS contracted with the California Environmental Protection Agency, Department of Pesticide Regulation, Worker Health and Safety Branch (WH&S), to conduct exposure monitoring of workers handling and applying triclopyr.

***Methods*** This study evaluated the dermal, inhalation, and urinary exposure of 10 applicators to triclopyr. Monitoring was conducted over two study days. Applicators used backpack sprayers to apply dilute triclopyr and glyphosate together in a tank mix. Applicator exposure to glyphosate was monitored separately; results are available in Schneider, et al., HS-1764 (2). Dermal exposure monitoring was conducted using long-sleeved cotton T-shirts and knee-length socks, which were worn next to the skin for the duration of the workday. Dermal exposures to the hand and face/neck regions were evaluated by wipe samples collected at intervals throughout the workday. Personal air pumps drew air through glass fiber filters to measure triclopyr aerosols. Urinary triclopyr was measured in aliquots sub-sampled from each worker's 24-hour composite urine collections. Daily estimated absorbed dosages (EAD), with standard deviations where appropriate, were calculated and compared to USFS model estimates. WH&S collected additional samples and data to verify the concentration of the test substance, provide quality control and assurance, and to document various study parameters such as the time spent handling triclopyr, amount of triclopyr applied each day, acreage treated, etc.

***Major Findings*** Mean dermal exposure was 18.67 mg (triclopyr acid) per person. Inhalation exposure was low, accounting for less than 2% of the workers' exposure. Overall, dermal exposures varied by less than ten-fold over the two-day study period.

Upper body exposure accounted for 45% of dermal exposure while leg, hand and face/neck exposure accounted for 33%, 19% and 3%, respectively. Hourly dermal exposures to triclopyr acid ranged from 1 - 8 mg (overall mean = 3.1 mg). The mean EADs for triclopyr acid were 0.013 mg/kg bw and 0.058 mg/kg bw as measured by dermal and inhalation monitoring, and in urine, respectively. There was no statistical difference in worker EAD between days as calculated from either urinary triclopyr or dermal and inhalation monitoring ( $p = 0.09$ ,  $p = 0.35$ , respectively; t-test, paired two-sample for means). However, for the two study days overall, EAD from urinary triclopyr was significantly greater than EAD estimated from dermal and inhalation monitoring ( $p < 0.01$ ). Mean EAD from urinary triclopyr (0.058 mg/kg bw) approximated the USFS model for conservative exposure scenarios (0.056 mg/kg bw): 16 exposures (80%) exceeded the predicted realistic estimate (50<sup>th</sup> percentile), 8 exposures (40%) exceeded the conservative estimate (95<sup>th</sup> percentile) and 5 exposures (25%) exceeded the worst case estimate (99<sup>th</sup> percentile). For the dermal and inhalation monitoring, only 10% of EADs exceeded the USFS realistic model estimate and no exposures exceeded either the conservative or worst case estimates. Predicted margins of exposure (MOE) were 86, 45, and 35, respectively, for realistic, conservative, and worst case exposures. The authors calculated observed MOE using models and assumptions provided in the USFS EIS with the following stipulations: 1) DPR currently uses average exposure to calculate MOE for subchronic and chronic toxicity, 2) more recent studies may have different endpoints, and 3) DPR neither reviewed nor approved the USFS EIS endpoints. The observed MOE for both systemic and reproductive effects for workers handling and applying triclopyr acid were 192 and 43, respectively, for mean dermal and inhalation exposure and mean urinary triclopyr. Thus, mean exposure measured by urinary triclopyr was higher than predicted by the EIS models, while mean exposure estimated from dermal and inhalation monitoring was lower than predicted.

*Portions of this paper were taken verbatim from Spencer, et al., Exposure of Hand Applicators to Granular Hexazinone in Forest Settings, 1993 - 1995. (3)*

## **Introduction**

The US Department of Agriculture, Forest Service (USFS), in their 1988 Environmental Impact Statement (EIS) evaluated the potential health, environmental, economic and social effects of the vegetation management practices used in their reforestation program (1). The USFS is responsible for managing over 20 million acres of National Forest Service land in the Pacific Southwest Region (Region 5), of which 30% (6.5 million acres) produces commercial wood products. The Region currently sells between 1.5 and 2 billion board feet of National Forest timber each year. Reforestation activities are conducted to reestablish trees and promote stand growth to maintain a continuous supply of timber. Vegetation management is critical to successful reforestation, as control of competing plant species is necessary to achieve timber yield objectives in the Region. Various methods are used to control competition, including mechanical, manual, thermal, biological and chemical means. Of the various alternatives, herbicide treatments are often the most effective and efficient method for controlling competing vegetation.

Triclopyr is a selective systemic herbicide used extensively in reforestation areas to control woody plants and broadleaf weeds. In 1994, 8,862 pounds of triclopyr were applied to forests in California (4). Triclopyr, formulated as 61.6% of the product Garlon™ 4, is typically mixed with glyphosate and applied during the spring to summer months when the target species have emerged. The applicators walk through a defined area spraying the target foliage from a pressurized backpack sprayer equipped with a hand-held spray gun.

The USFS EIS presents the hazard, exposure and risk analyses of the thirteen herbicides used in Region 5 (1). Dosage estimates for worker exposures were based on studies of worker exposure to liquid formulations of 2,4-D and 2,4,5-T applied by backpack sprayer. Realistic, conservative and worst case worker exposures were estimated using the 50<sup>th</sup>, 95<sup>th</sup> and 99<sup>th</sup> percentiles, respectively, of the observed distribution of the 2,4-D and 2,4,5-T worker exposure data. Estimates of risk based on a range of potential exposure scenarios were then compared to animal toxicity data. The USFS desires to both determine the health effects of herbicides used in their program and to develop techniques and equipment to reduce worker exposures. To accomplish these objectives, the EIS requires that site-specific worker exposure monitoring evaluate at least 10% of the Region's herbicide application projects annually.

In 1995, the USFS contracted with the California Environmental Protection Agency, Department of Pesticide Regulation (Cal/EPA, DPR), Worker Health and Safety Branch (WH&S), to evaluate the exposure of workers applying triclopyr using backpack sprayers. The study was conducted in accordance with US EPA, 40 CFR 160 Good Laboratory Practice Standards (GLP) (5) and applicable DPR and USFS regulations.

This study evaluated the dermal and inhalation exposure and urinary triclopyr (absorbed dosage) of 10 applicators over 2 work days (n = 20). Toxicity endpoints and exposure data referenced in this document were contained in the USFS EIS (1). Estimates of dermal exposure, inhalation exposure and absorbed dosage were calculated according to WH&S guidelines (6) and compared to USFS EIS estimates. Dermal exposure monitoring was conducted using long-sleeved cotton T-shirts and knee-length socks, which were worn next to the skin for the duration of the work day. Hand and face/neck dermal exposures were evaluated by using wipes on these regions at intervals throughout the work day. Personal air pumps drew air through a 37-mm diameter glass fiber filter to measure breathing zone concentrations of triclopyr. Urinary triclopyr was measured in aliquots sub-sampled from each worker's 24-hour composite urine collections.

## ***Materials and Methods***

### **Study Design**

*Herbicide Applications* An average of 50,000 acres, representing less than 1% of the Region 5's timber-producing acreage, are chemically treated with herbicides each year (1). The USFS uses herbicides only after evaluating all treatment alternatives and demonstrating their use is essential to achieving project objectives. Herbicides may be applied up to three times during a forest stand rotation of 50 to 150 years; once if needed to prepare the site for planting, and up to two more times to control competing vegetation. Trees are generally about two years old when planted. Site preparation treatments can be applied from spring through fall. Release treatments are made in the first one to seven years post-planting.

This study was conducted to estimate applicator exposures to triclopyr applied as a conifer release treatment. Triclopyr is the active ingredient in the product Garlon™ 4 and is present as 61.6% (5.56 lb/gal) of the formulated product (3,5,6-trichloro-2-pyridinyloxyacetic acid, butoxyethyl ester, DowElanco, US EPA registration number 62719-40). As is the case for formulations of 2,4-D, Garlon™ 4 is formulated and applied in the ester form, but triclopyr acid is the active moiety once absorbed and hydrolyzed by the target plant. The USFS EIS evaluated triclopyr exposure based on pounds triclopyr acid equivalent applied, an amount calculated as 44.3% of Garlon™ 4 by volume (4 lb/gal). In this study, the dermal and inhalation matrices, tank mix samples and test substance samples underwent analysis for triclopyr butoxyethyl ester. Once in the body, the ester is hydrolyzed to the acid; thus the urine samples underwent analysis for triclopyr acid. In this report, "triclopyr" is used for general references to the herbicide and active ingredient; "triclopyr acid" refers to the acid as an analyte, "(triclopyr) BEE" refers to triclopyr butoxyethyl ester and "(triclopyr) AE" refers to triclopyr acid equivalents, calculated from BEE analyses for comparisons to USFS exposure estimates. Triclopyr BEE and triclopyr AE are toxicologically equivalent (7).

The study was conducted in the Eldorado National Forest, Pacific Ranger District, on two consecutive days, July 10 - 11, 1995. Plantations consisted of Ponderosa, Jeffrey, and Sugar pine, and White and Douglas fir that had been planted about 3 months

earlier. Trees were planted in groups of 3 within a 17-foot radius. Planting density averaged 450 trees/acre. The height of the target foliage was approximately 2 - 3.5 feet; density was low to moderate. Terrain varied from moderately to steeply sloping. Morning low temperatures ranged from 47 - 60 °F and the daily high temperature was 73 °F on both days. A light breeze blew each day, with wind speeds generally less than 5 mph. The workdays began at approximately 0600 and ended between approximately 1500 - 1530 hours. Table I provides site and treatment summary information for the two monitoring days.

Table I. Exposure of Hand Applicators to Triclopyr in Forest Settings: Site and Treatment Information

Site Information			
Location	Eldorado National Forest, Pacific Ranger District		
Elevation	5700 - 5800 feet		
Timber Species	Ponderosa, Jeffrey and Sugar pine, Douglas and White fir		
Target Species	bear clover, ceanothus, gooseberry, manzanita		
Number of Applicators	10		
Application Method	Swath, backpack sprayer		
Acreage Treated		Application Rates	
July 10, 1995	32.6	Batch Mix (Gal/acre)	25.00
July 11, 1995	32.0	Garlon™ 4 (Gal/acre)	0.25
		Triclopyr BEE <sup>/a</sup> (lb/acre)	1.39
		Triclopyr AE <sup>/b</sup> (lb/acre)	1.00

/a triclopyr butoxyethyl ester, the active ingredient in Garlon™ 4

/b Calculated triclopyr AE (4 lb/gal Garlon™ 4). The USFS EIS evaluated triclopyr exposure based on calculated lb triclopyr AE applied.

The USFS contracted with private applicators to conduct the herbicide treatments and were present at each site to ensure that contract obligations were met. The crew was composed of ten male applicators and several baggers. All spoke Spanish as their primary language. The ten applicators were monitored for two consecutive days of loading and applying Garlon™ 4.

Workers reported showering daily after work and wore clean clothing to the work site each day. Typical work clothing consisted of hard hats, leather boots with laces, one shirt layer, socks, jeans and clean coveralls, either commercially laundered cotton/polyester or disposable TYVEK®. They wore no outer clothing over their coveralls. The workers unzipped their coveralls partially or totally to keep cooler as they carried the heavy (approximately 40 lb when full) backpack sprayers while moving up and down hillsides during the warm summer days. Workers wore latex or knit gloves on either the right hand, which held the spray wand, or on both hands.

Prior to treating the first plot each morning, the entire crew placed plastic produce bags over all timber seedlings within the plot to protect them from the herbicide spray.

Stones were used to secure the bags around the seedlings. Once the first plot was bagged, the applicators commenced spraying. The baggers worked ahead of the applicators to bag the next treatment plot. After the applicators sprayed each treatment plot, the baggers removed the bags and re-used them continuously. Throughout the day, the applicators occasionally assisted in placing and removing the plastic bags. At the end of the work day, all applicators usually assisted in removing bags from the last treatment plot.

The applicators used Solo brand 3.5-gallon backpack sprayers equipped with a 30-inch wand, number 4 flat fan nozzle, (regulator set to 1) and 20-inch pressure pumping bar using up to 15 psi. The sprayers were supported on the workers' backs with webbed nylon straps. Some sprayers had a rubber apron to protect the seat and back upper thigh areas from potential contamination. Crew members operated the pressure pumping bar with their left hand and held the spray wand in their right hand. Workers loaded their sprayers by placing the unit on the ground and unscrewing the 5-inch-wide cap, inserting the nozzle from the batch tank and filling using the nozzle trigger.

Each applicator loaded and sprayed at his own pace, with each worker applying the mix to roughly parallel strips in the treatment area. The dye present in the spray mix allowed applicators to gauge their spray swath by the adjacent dyed swath. One worker (not a study subject) functioned as the crew leader, carrying water in a sprayer to wash off any mix accidentally applied to timber species. Throughout the workday, USFS checked spray coverage by repeatedly measuring off one-fiftieth acre, approximately nine trees, and verifying 90% coverage within each quadrant.

The batch tank held about 300 gallons and was mounted on a caterpillar tractor. The tractor moved throughout the treatment plot so the applicators could refill their sprayers on-site. The rig was equipped with both a bypass valve and a 1,000-foot hose reel with a trigger nozzle. For most treatment areas, applicators filled their sprayers using the bypass valve. For plots which were too steep for the caterpillar to access, the driver pressurized the hose via a gas motor and fed layouts to the applicators.

The batch tank was loaded at a central loading site. Typically, 3 batch loads were prepared each day with a full batch containing approximately 300 gallons. The final batch mixed each day was often less than 300 gallons, so all material would be sprayed out before leaving the site for the day. The caterpillar operator (not a study subject) performed all mix and load tasks. For each batch, he filled the batch tank (via a hose connection to a 3,000-gallon water truck) with about 2/3 the total water required. He then measured the formulated herbicide products, dye and adjuvants and poured them into the batch mix by hand. Lastly, he topped off the mix with water to achieve the desired total volume. The batch mix was not agitated. Garlon™ 4 was present in each batch mix at 1% by volume.

Also present in each batch mix were: the herbicide Accord® (N-(phosphonomethyl)glycine, in the form of its isopropylamine salt) EPA # 524-326; 1%, by volume), a surfactant/anti-foaming agent (1%, by volume), a drift retardant

(0.5%, by volume) and a purple marking dye (0.25%, by volume). Batch mix data are presented in Table II.

Table II. Exposure of Hand Applicators to Triclopyr: Daily Batch Mix Data

	July 10, 1995				July 11, 1995			
Batch Number	1	2	3	Daily Total	1	2	3	Daily Total
Gal. Mixed	315	300	200	815	300	300	200	800
Gal. Garlon™ 4	3.15	3	2	8.15	3	3	2	8
Lb. Triclopyr AE	12.6	12	8	32.6	12	12	8	32

## Study Procedures

### Worker Exposure Monitoring

*Informed Consent (8):* The Committee on Human Research, University of California, San Francisco, approved the worker exposure monitoring proposal (number H7420-11293-01). Workers' informed, written consents were obtained on July 5, 1995. WH&S conducted all aspects of the consent process in Spanish, the workers' primary language. The workers were informed they could withdraw from the study at any time and were read the Experimental Subjects Bill of Rights. Each worker was assigned an identification number. Study volunteers were instructed to perform their work tasks in the usual manner, including wearing their normal work clothing and personal protective equipment, and maintaining their customary work habits.

*Dermal Exposure:* Clothing exposure dosimeters, consisting of long-sleeved T-shirts (100% cotton, pre-washed), and knee-length athletic socks (80% cotton/20% polyester), measured triclopyr BEE residues. Clothing dosimetry permits a direct measurement of dermal exposure to the covered regions with fewer extrapolations to body surface area than are required for patch residues (9,10). Shirts and socks were distributed to the workers each morning upon their arrival at the work site. Workers wore the dosimetry clothing next to the skin for the duration of the workday. All workers wore denim jeans, laced leather work boots, and coveralls. On Day 1, worker 8 wore a long-sleeved woven shirt over the study shirt; all other workers wore only the study shirt. The T-shirt covered the torso, arm and hip regions and was tucked into the worker's pants all day. In this report, exposure measured by the shirts is referred to as "torso" exposure. WH&S exposure monitoring studies have previously included either socks or cotton long johns, as appropriate, to measure lower body dermal exposure (11, 12). Socks were selected for this study since private changing facilities were not available. Sock residues were used to measure exposure to the foot and lower leg and to estimate exposure to the thigh. Workers 4 and 7, both days, and worker 8, Day 1, wore a second pair of socks over the study socks.

Exposure to both the face/neck regions and to the hands beneath the gloves was measured by skin wipes (Chubs® baby wipes). Commercial wipes are preferable to hand rinses when sampling in remote field locations as they are widely available, easily transported, and cannot be spilled. A series of two wipes each was used for the hands and the face/neck areas to collect residue samples at lunch, at the end of the workday,

and at any other time the worker wished to wash these regions. At each sampling interval, the two hand wipes were collected prior to the two face/neck wipes, to prevent cross-contamination. Each worker's wipe samples were combined, by body region, in a one-pint glass jar for each day.

At the end of the day, dermal samples were collected in the following order, to prevent cross-contamination: hand wipes, face/neck wipes, T-shirt, and socks. The wipe sample jars were sealed with aluminum foil, capped with canning lid and ring, and placed in sectioned corrugated cardboard boxes. Each clothing sample was sealed into two one-gallon Ziploc<sup>®</sup> bags. All dermal samples were stored in insulated coolers on dry ice.

Inhalation Exposure (13, 14, 15): Inhalation exposure to triclopyr BEE aerosol was measured by a 37-mm glass fiber filter, type AE (1 µm pore size, SKC number 225-7), backed with a support pad (13). The filter was housed in a plastic cassette (SKC number 225-2) and sealed with self-sealing bands (SKC number 225-25-01) (13). It was attached via vinyl tubing to a personal air pump (MSA Fixt-Flo<sup>®</sup>, Model S or Model TD), (14) clipped to a webbed belt. The cassette was secured in the worker's collar region and worn for the duration of the work day. Initial pump flow was set at 2 L/min using a Kurz<sup>®</sup> mass flow meter (15). Study personnel monitored pump performance throughout the day and replaced pumps as necessary. Initial and final flow rates and elapsed time were recorded for each pump. At the end of the work day, study staff removed the cassettes from the sampling train, capped the ends and stored each cassette in a separate one-quart Ziploc<sup>®</sup> bag. All bagged samples were then double-bagged in a second one-gallon Ziploc<sup>®</sup> bag. Samples were stored in insulated coolers on dry ice.

Urine Samples: WH&S staff collected and processed a spot sample from each worker on July 5, 1995, to provide background exposure information. However, these samples had limited value since workers had been continuously exposed for several days up to and including July 5. The crew was off work on July 8 and 9. For July 10 and 11, 1995, workers were instructed to collect all voids in 1-liter wide-mouth polyethylene bottles. Collections began each morning upon arrival at the work site. Study staff provided additional bottles to workers for their use off-duty. Workers brought their overnight bottles to the work site each morning. During the workday, the collection bottles were stored on ice. At the end of the workday, WH&S staff pooled each worker's bottles, recorded the total daily volume, and placed approximately 15 mL of each worker's composite sample into each of three 50-mL polyethylene vials, using a 50-mL glass syringe. The vials were capped, sealed into Ziploc<sup>®</sup> bags and stored on dry ice.

### **Field Quality Control and Assurance**

Test Substance: Using a graduated cylinder, study staff collected a 25-mL sample of Garlon<sup>™</sup> 4 from the single lot number used during the two study days and placed it in a 250-mL polyethylene jar. The jar was capped, labeled, sealed in a Ziploc<sup>®</sup> bag and stored, with dry ice, in a separate cooler from the exposure and field fortification

samples. Study staff also collected tank mix samples of at least 100 mL from each batch load on each study day, from which two one-mL aliquots were sub-sampled using an Eppendorf Digital Pipette (blue tip). All three tank mix samples were then stored immediately on dry ice in a separate cooler from the exposure and field fortification samples. The aliquots were analyzed and the larger fraction maintained in frozen storage in case of loss of the aliquots. Analysis of the smaller aliquots avoided problems with settling of the mix, phase changes and hydrolysis which are common to larger tank mix samples.

Field fortifications and blanks were prepared daily for each sampling medium. The blanks assessed the adequacy of handling and shipping conditions. The blank filter sample, in its cassette, was attached to an air pump via vinyl tubing, which was run the entire work day at 2 L/min. The cassette was removed from the pump, capped, bagged, labeled and stored on dry ice at the end of the work day. Flow rates and elapsed times were recorded. Matrix blanks were prepared at the end of each study day. Study staff provided matrix for urine sample blanks which were prepared in triplicate, each consisting of a 25-mL aliquot delivered using a 50-mL Hamilton glass syringe into a 50-mL polyethylene vial.

Field fortifications served as indicators of the stability of triclopyr BEE during shipping and storage before extraction and analysis. Three samples of each dermal and inhalation exposure matrix were spiked each study day with standards prepared from Garlon™ 4 in acetone. The glass fiber filters (in cassette), and wipes (four per sample) were each spiked at 100 µg triclopyr BEE per sample, the socks (each pair) at 1 mg, and the T-shirts each at 5 mg. All dermal media fortifications were delivered in 1-mL aliquots via an Eppendorf Digital Pipette (blue tip). The dermal media were allowed to air dry in the field before storing. Inhalation exposure media fortifications were delivered in 40-µL aliquots via an Eppendorf Digital Pipette (yellow tip). Each spiked filter cassette was run on an air pump for the duration of the work day.

Urine sample fortification was conducted with standard prepared from triclopyr acid in ethanol. Each day, study staff prepared triplicate samples at three concentrations by placing 24 mL of control urine in each 50-mL polyethylene vial using a 50-mL glass syringe and adding 1 mL of the appropriate standard using an Eppendorf Repeater™ pipette. Sample fortification was conducted from lowest to highest standard concentration. Final triclopyr acid concentrations in the fortified samples were 0.01 ppm, 0.10 ppm and 1.00 ppm.

All field blanks and fortifications were labeled and stored with dry ice in the same manner as the exposure samples. Field fortifications were extracted with exposure samples and thus used to simultaneously evaluate storage stability.

### **Analytical Methods, Quality Control and Assurance**

Analytical Method Validation (16) After estimating the limit of detection (LOD; at least three times the signal to noise ratio), five replicates of each matrix were evaluated for triclopyr BEE recovery at three standard levels over a three-day period: the limit of

quantitation (LOQ; at least 10 times the signal to noise ratio or 3.33 times the LOD), 10 x LOQ and 100 x LOQ. All matrices showed acceptable recoveries. Analytical standards in both solvent and matrix extract were also evaluated at the LOQ, 10 x LOQ and 100 x LOQ levels. Method validation data are summarized in Table III.

Table III. LOQ and Mean Percent Recoveries for Triclopyr from Fifteen Replicates of Matrices

Fortification Level	Matrix Recoveries: % $\pm$ SD				
	T-shirts	Socks	Wipes	Filters	Urine
	Triclopyr BEE				Triclopyr acid
LOQ	102.50 $\pm$ 4.77	102.00 $\pm$ 2.65	102.60 $\pm$ 4.13	86.83 $\pm$ 1.69	117.5 $\pm$ 7.78
10 X LOQ	106.00 $\pm$ 4.36	106.00 $\pm$ 2.00	105.33 $\pm$ 3.79	92.13 $\pm$ 6.83	105.5 $\pm$ 4.95
100 X LOQ	97.87 $\pm$ 5.55	91.03 $\pm$ 4.57	94.83 $\pm$ 2.75	87.23 $\pm$ 2.73	100.55 $\pm$ 9.12
LOQ	150 $\mu$ g	40.1 $\mu$ g	10 $\mu$ g	1.50 $\mu$ g	50 ppb

Analyses of Dermal Matrices and Glass Fiber Filters (16): Triclopyr BEE was extracted from the samples with ethyl acetate. Direct analysis of these extracts was then conducted. Injection volumes of 2  $\mu$ L were analyzed on a Hewlett-Packard HP-5880A gas chromatograph with an EC detector. Matrix spikes, fortified at the LOQ level, were analyzed with every ten exposure samples; at least one confirmation analysis, by MSD, was conducted for every 10 positive exposure samples. Results were reported as  $\mu$ g triclopyr BEE/sample.

The instrument conditions were as follows:

Column: HP-1 25 m x 0.22 mm x 0.33  $\mu$ m, 1 mL/min flow rate

Oven temperature: 210  $^{\circ}$ C

Injector temperature: 250  $^{\circ}$ C

Detector temperature: 370  $^{\circ}$ C

Gas Flow:

Carrier: Helium, 17 psi

Make-up: 5% methane in argon, 72 mL/min

Split flow: 6.1 mL/min

Retention time: 17.5 min.

Urinalyses (17, 18): Samples were diluted 1:100 with water in plastic containers prior to analysis on the Triclopyr RaPID Assay<sup>®</sup> kit by Ohmicron Environmental Diagnostic, Inc. (18). The principal analytical investigator placed 250  $\mu$ L of diluted sample in each tube, then added 250  $\mu$ L of trichloropyridinol enzyme conjugate and 500  $\mu$ L of trichloropyridinol antibody-coupled magnetic particles to facilitate separation. The tubes were vortexed, then incubated for 20 minutes. Washing solution and color reagent were added, the tubes were again vortexed, then incubated for 20 additional minutes. Five hundred  $\mu$ L of stopping solution was then added and the results read at 450 nm within 15 minutes. Results were reported as ppm triclopyr acid. Matrix spikes fortified at the LOQ level were analyzed with every ten exposure samples; at least one confirmation analysis, by GC-MSD, was conducted for every 10 positive exposure samples.

Storage Stability In addition to the field fortifications which served as storage stability samples for longer intervals, multiple samples of dermal matrices and glass fiber filters were fortified with Garlon™ 4 in acetone and then frozen. Five samples were removed and analyzed for triclopyr BEE at intervals between 9 and 31 weeks. Field fortification analyses indicated no significant storage losses (overall recovery = 95 ± 7%, Appendix I, Table 7), and analysis of the remaining storage stability samples was discontinued. Storage stability was not conducted for urine samples; stability was assessed solely by the field fortifications.

**Data Analysis**

Data Recorded

WH&S field staff recorded each worker’s height, body weight (bw (kg)), and years of experience applying herbicides in forest settings (Table IV), and the crew’s pesticide exposure history during the previous week. They recorded the number of loading/application intervals for each worker and attempted to record individual worker times for each loading and application interval. When individual times were not recorded, the mean application or loading time for all other workers for that specific cycle (i.e., load 12) was substituted for the missing time. Application times were recorded to the nearest minute. Load times were recorded to the nearest second. The time spent in walking to and from the load location was considered part of the application time. Loading and application times were summed for each worker each day. Study staff recorded the overall time the crew spent each day in the following categories: loading, applying, or engaged in a variety of non-pesticide handling tasks categorized as “other”, such as bagging seedlings, removing bags, waiting for a new batch load, lunch or other rest break, and putting on and removing study samples. Field staff also noted the types of work clothing and PPE worn by each worker, the time when each worker removed outer clothing and any unusual exposure incidents, such as handling herbicide with bare hands, spills of herbicide, etc. Protocol and SOP deviations are reported in Appendix II.

Table IV. Exposure of Hand Applicators to Triclopyr: Worker Data

Worker ID	Height (in.)	bw (kg)	Yrs.
1	68.0	85.0	4
2	69.5	75.0	1
3	66.0	63.6	1
4	69.0	77.3	1
5	72.0	79.5	1
6	68.0	75.0	1
7	66.0	61.4	2
8	66.0	75.0	2
9	66.5	72.7	3
10	67.0	58.2	1

Exposure Calculations, Statistical and Graphical Analyses Sample results (raw data) were entered into a Microsoft® Access™ Relational Database Management System for Windows™, Version 7 database, as either triclopyr BEE or triclopyr acid (19) (see Appendix I, Tables 1 and 4). Worker exposures are provided in Appendix I, Tables 2, 3, and 4. Triclopyr AE was calculated as  $[0.72 \times \text{triclopyr BEE}]$  based on the molecular weights of triclopyr AE and triclopyr BEE (256.5 and 356.6, respectively) (20). Sample results were not adjusted for field recoveries. Data were analyzed by queries and reports. Descriptive statistics were calculated using Microsoft® Access™, Relational Database Management System for Windows™, Version 7 (19). Means and SDs were based on individual exposures; calculation of means from table values may differ due to rounding. Figures were generated using Harvard Graphics® and Microsoft® Excel software (21, 22). T-tests (paired or two-sample assuming equal variances, two-tailed,  $\alpha = 0.05$ ) and regression analyses (critical  $F = 0.05$ ) were conducted using Microsoft® Excel™ software (22). Individual worker exposures (intraday and interday) were tested for normal vs. (log)normal distribution at the 0.05 significance level using the Shapiro-Wilks  $W$  test (23).

Dermal Exposure (6) Individual raw data ( $\mu\text{g}/\text{sample}$  triclopyr BEE) are provided in Appendix I, Table 1. Individual dermal exposures (mg triclopyr BEE) were calculated by summing face/neck wipe residues, hand wipe residues, T-shirt residues and leg exposure (as calculated below). No adjustments were made for workers wearing either two pair of socks or an extra shirt, or workers with coveralls partially or totally unzipped or torn. While all workers unzipped their coveralls at least partially, we did not attempt to quantify the increased exposure due to a partially open coverall. Hourly exposures were calculated by dividing each worker's dermal exposure by the time each worker spent loading and applying each day. Pounds applied per worker were calculated as percent of total pounds applied per day, based on the number of loads each worker applied.

*Skin Residues:* Exposure to the face, neck and hands was evaluated directly by the skin wipes.

*Torso Exposure:* Since T-shirts were considered covered by the coveralls, the dosimetry shirt was assumed to perform as a skin surrogate. Thus, T-shirt residues were considered dermal residues in exposure calculations.

*Leg Exposure:* The study socks captured the triclopyr residues that the workers' own socks would otherwise have collected. Ten percent of the sock residues were assumed to penetrate the sock to the skin of the lower legs and feet and be available for dermal absorption. The leg was assumed to receive uniform triclopyr deposition. Thus the thighs ( $3663 \text{ cm}^2$ ), whose surface area is similar to lower leg and foot surface area ( $3711 \text{ cm}^2$ ), were assumed to receive exposure equal to the unadjusted sock exposure. No adjustment for clothing penetration was required for thigh exposure, since the thigh, unlike the foot region, was covered by only the pants and coveralls and was not protected by an additional layer of clothing such as a sock. The socks thus performed as skin surrogates for thigh exposure. Leg exposure was equal to the sum of thigh exposure (represented by sock residues) and lower leg exposure (represented by 10% of sock residues), or, a total of 1.1 times the sock residues.

Potential Inhalation Exposure (PIE, µg), Inhalation Exposure (IE, µg) Individual raw data (µg triclopyr BEE on filters) are provided in Appendix I, Table 1. Inhalation exposure calculations, including pump flows and run times are presented in Appendix I, Table 2. PIE was calculated by adjusting filter residues for pump flow, elapsed time and a 26.7 L/min breathing rate for medium work rate (6). IE was calculated by adjusting PIE for 50% uptake and 100% absorption as follows:

$$\text{Inhalation Exposure (IE)} = [((\mu\text{g BEE})/(\text{L/min End} + \text{L/min Begin})/2) \times \text{Min. pumped}) \times \text{Min. exposed} \times 26.7 \text{ L/min}]/(50/100)$$

Where two pumps were used sequentially to measure a worker's inhalation exposure, each pump's begin and end flow rates were averaged and multiplied by the respective minutes run, then summed.

Daily Dose, Estimated Absorbed Dosage (EAD, mg/kg bw) Individual raw data (µg/sample triclopyr BEE) are provided in Appendix I, Table 1. Individual exposures and exposure calculations are presented in Appendix I, Table 3. Individual doses and dosages of triclopyr BEE and triclopyr AE were calculated using each worker's weight (kg) (6). Daily and group means were calculated as the mean of individual values. The USFS EIS assumed 10% dermal absorption for triclopyr based on surrogate studies with 2,4-D (1). DPR uses a dermal absorption value of 4.8% for triclopyr, based on several recent worker exposure studies (24).

Individual daily doses were calculated as follows:

$$\begin{aligned} \text{mg daily dose BEE} &= \\ &= \text{BEE dermal exposure adjusted for dermal absorption} + \text{BEE inhalation exposure} \\ &= [(mg \text{ BEE dermal exposure} * 0.048) + (mg \text{ BEE inhalation exposure})] \\ \text{mg daily dose AE} &= (\text{mg daily dose BEE}) * 0.72 \end{aligned}$$

Individual daily EAD was calculated as follows:

$$\begin{aligned} \text{EAD BEE (mg/kg bw)} &= \\ &= [(mg \text{ BEE dermal exposure} * 0.048) + mg \text{ BEE inhalation exposure}]/kg \text{ bw} \\ &= \text{mg daily dose BEE}/kg \text{ bw} \\ \text{EAD AE (mg/kg bw)} &= \\ &= [((mg \text{ BEE dermal exposure} * 0.048) + mg \text{ BEE inhalation exposure})]/kg \text{ bw} * 0.72 \end{aligned}$$

Comparison with USFS EIS Models (1) All toxicity endpoints and exposure data referenced in this document were contained in the USFS EIS. Study data were compared to EIS estimates (mg/kg bw/day) for workers applying liquid formulations of triclopyr by backpack sprayer during ground applications. The USFS EIS based their models on the 50th, 95th, and 99th percentiles of exposure estimates from 2,4-D and 2,4,5-T applicator exposure studies to generate respective estimates of absorbed dosage for triclopyr AE for realistic (0.1160 mg/kg bw/day), conservative (0.2244 mg/kg bw/day) and worst case (0.5711 mg/kg bw/day) exposures. By defining exposures in this manner, the statistics establish the probability of those exposures occurring, i.e., a worst case exposure would be likely to occur 1% of the time. The

USFS models assumed a body weight of 70 kg; the monitoring study used actual worker weights to calculate individual absorbed dosages in mg/kg bw/day. The EIS models assumed the following triclopyr AE application rates: realistic and conservative models, 4 lb/acre; worst case model, 8 lb/acre. Model estimates were normalized to the observed application rate of 1 lb triclopyr AE/acre, with the following predicted absorbed daily dosages:

Realistic (mean): 0.029 mg/kg bw

Conservative (95<sup>th</sup> percentile): 0.056 mg/kg bw

Worst Case (99<sup>th</sup> percentile): 0.071 mg/kg bw

Individual, daily and overall mean estimated absorbed dosages, with standard deviations where appropriate, were calculated and compared to the normalized USFS absorbed dosages.

Urinalyses: Raw data (ppm triclopyr acid) and individual dosages (mg acid and mg/kg bw/day acid) are provided in Appendix I, Table 4. Results (ppm triclopyr acid) were normalized to 1400 mL (25). Dosages were compared to triclopyr AE dosages estimated from the dermal exposure monitoring. Where reported, triclopyr BEE dosages were calculated as (1.39 x triclopyr AE), based on the molecular weights of the two compounds (20).

Margins of Exposure (MOE); USFS EIS (1) The USFS EIS classifies triclopyr as slightly acutely toxic in rats (LD<sub>50</sub> = 630 mg/kg bw). The no observed effect level (NOEL) was 2.5 mg/kg bw/day for both chronic systemic toxicity (dog) and reproductive effects (rabbit). To evaluate the risks for humans exposed to triclopyr, the USFS computed a reference dosage by dividing the animal NOEL by an uncertainty factor of 100. Thus, human exposures (absorbed dosages) below 0.25 mg/kg bw/day are not expected to carry an excess risk of adverse systemic or reproductive health effects.

MOE (reported as margins of safety or MOS in the USFS EIS) provide indices of relative safety in evaluating human exposures compared to animal NOELs. They are calculated by dividing the animal NOEL for toxicity endpoints by known or estimated absorbed dosages for human exposures. The USFS MOE for systemic and reproductive effects for realistic, conservative and worst case exposures to triclopyr, normalized to mean study triclopyr AE application rate, were 86, 45, and 35, respectively. This report uses the USFS models for the purpose of comparing observed exposures with predicted exposures. The following equations show calculation of 1) the predicted MOE for the USFS realistic estimate for systemic effects, using the predicted daily absorbed dosage provided above in "Comparison with USFS EIS Models", and 2) calculation of mean study MOE based on dermal and inhalation monitoring:

$$\begin{aligned} 1) \text{ USFS MOE} &= \text{NOEL}/[\text{EAD}]_{\text{realistic}} \\ &= 2.5 \text{ mg/kg bw/day}/(0.029 \text{ mg/kg bw/day}) \\ &= 86 \end{aligned}$$

$$2) \text{ Study MOE} = (2.5 \text{ mg/kg bw/day})/(0.013 \text{ mg/kg bw/day}) = 192$$

## Results

Crew exposure on July 10 followed two days off work. The first work day was eight hours, 55 minutes and the second, nine hours, 30 minutes. Table V summarizes the time spent handling pesticides (Load/Apply) and performing other, non-pesticide handling activities each day.

Table V. Time/Task Summary

Date	Time	Time	Load/Apply	Other <sup>a</sup>	Total
			(Minutes)		
July 10, 1995	0555	1450	360	175	535
July 11, 1995	0600	1530	366	204	570

<sup>a</sup> Includes bagging timber seedlings, pulling bags, pulling hose, lunch/rest breaks, donning monitoring clothing and equipment

Table VI presents daily totals for load and apply times, the number of loads completed by each worker each day, and the pounds of triclopyr AE sprayed by each worker. Load times were of very short duration, averaging about 40 seconds per load for all workers over both study days. The overall time to spray one load averaged 10 minutes. Each worker applied an average of 26 ( $\pm$  2) loads each day.

Table VII reports potential inhalation exposure ( $\mu\text{g}$  PIE), inhalation exposure ( $\mu\text{g}$  IE), regional exposure (mg), dermal exposure (mg DE), and estimated absorbed dose (mg) for both BEE and AE for each worker and study day. The data were not strongly log-normally distributed. Overall, exposures for both DE and IE varied far less than is typical for exposure studies, where exposures regularly exceed 100-fold. Individual regional exposures varied by as much as 50-fold within day (leg exposure, Day 1), while the daily CVs for the other regions ranged from about 50% to 132%. IE was the smallest contributor to exposure, accounting for 1.89% of the overall mean daily dose. IE also showed the least between-day variation (overall % CV = 26) with nearly identical exposures each day (overall mean = 50.18  $\mu\text{g}$ ).

Table VI. Daily Individual Accrued Loads<sup>/a</sup> and Total Time (Minutes<sup>/b</sup>) Spent Loading and Applying; Lb Triclopyr AE Applied (Lb AE), Daily and Grand Means  $\pm$  SD

Worker	July 10, 1995				July 11, 1995			
	N Loads	Apply	Load	Lb AE <sup>/a</sup>	N Loads	Apply	Load	Lb AE <sup>/c</sup>
		Minutes				Minutes		
1	25	245	12.15	3.12	29	282	17.90	3.67
2	24	231	10.85	3.00	21	205	12.08	2.66
3	25	265	7.85	3.12	29	287	15.73	3.67
4	27	283	11.20	3.37	23	265	12.05	2.91
5	27	277	10.28	3.37	23	242	9.85	2.91
6	27	287	9.53	3.37	23	230	7.07	2.91
7	26	267	13.77	3.25	27	265	11.02	3.42
8	26	267	9.80	3.25	28	251	14.87	3.54
9	28	281	12.60	3.50	25	253	12.58	3.16
10	26	268	11.53	3.25	25	261	11.73	3.16
<b>Mean</b>	26	267	10.96	3.26	25	254	12.49	3.20
<b>SD</b>	1.2	17.44	1.70	0.15	2.8	24.26	3.07	0.36

<b>Grand Means <math>\pm</math> SD for Both Study Days</b>	
N Loads	25.70 $\pm$ 2.15
Min. Apply	260.60 $\pm$ 21.61
Min. Load	11.72 $\pm$ 2.54
Lb Triclopyr AE <sup>/a</sup> handled	3.23 $\pm$ 0.27

<b>Grand Means per Load</b>	
Min. to Apply	10.14 $\pm$ 2.24
Min. to Load	0.61 $\pm$ 0.18

/a Each load and apply interval was documented; not all were timed. Where individual times were not recorded, the mean application or loading time for all workers with recorded times for that specific cycle (i.e., load 12) was substituted for the missing time(s).

/b Individual apply times recorded to nearest minute; individual load times recorded to nearest second

/c Columns 2 and 6 (N Loads) summed by day and used to calculate individual % of total daily loads Garlon™ 4 applied. Each load was 5 gal; total daily loads x 5 = total daily gal Garlon™ 4 applied. Lb Triclopyr AE Applied = 4 lb/gal Garlon™ 4.

Table VII. Triclopyr Applicator Inhalation Exposures ( $\mu\text{g}$  Triclopyr BEE); Dermal Exposures and Dose (mg Triclopyr BEE, mg Triclopyr AE)

Worker	ug IE	ug PIE	Face/neck	Hands	Torso	Legs <sup>/a</sup>	DE <sup>/b</sup>	Dose <sup>/c</sup>	DE <sup>/d</sup>	Dose <sup>/e</sup>
	$\mu\text{g}$ BEE		mg BEE				mg BEE		mg AE <sup>/f</sup>	
<b>Day 1: July 10, 1995</b>										
1	59.41	118.81	0.46	1.76	4.07	3.10	9.39	0.51	6.76	0.37
2	34.30	68.60	0.56	1.75	5.03	56.22	63.55	3.09	45.76	2.22
3	57.20	114.41	1.29	2.39	6.48	36.27	46.43	2.29	33.43	1.65
4	40.18	80.35	0.59	1.20	38.73	1.03	41.54	2.03	29.91	1.46
5	39.12	78.23	0.95	2.13	9.28	1.42	13.77	0.70	9.92	0.50
6	45.90	91.79	0.67	2.87	5.30	1.02	9.86	0.52	7.10	0.37
7	71.73	143.46	0.75	1.90	5.04	0.87	8.56	0.48	6.17	0.35
8	39.00	77.99	1.09	13.32	2.74	7.83	24.97	1.24	17.98	0.89
9	66.06	132.12	0.37	0.16	61.64	3.96	66.13	3.24	47.61	2.33
10	54.77	109.54	0.39	0.94	6.46	8.03	15.83	0.82	11.40	0.59
<b>Day 2: July 11, 1995</b>										
1	42.92	85.84	0.44	2.73	3.83	3.87	10.87	0.57	7.83	0.41
2	54.40	108.80	1.35	3.78	6.71	9.06	20.91	1.06	15.05	0.76
3	45.52	91.05	1.18	9.00	6.91	21.00	38.08	1.87	27.42	1.35
4	32.56	65.11	0.80	3.06	6.00	1.15	11.00	0.56	7.92	0.40
5	34.71	69.42	1.10	4.47	6.74	1.14	13.45	0.68	9.68	0.49
6	42.19	84.37	0.78	10.68	13.34	3.77	28.56	1.41	20.57	1.02
7	70.09	140.18	0.86	8.00	21.33	1.84	32.04	1.61	23.07	1.16
8	58.60	117.21	1.96	15.88	13.22	0.83	31.89	1.59	22.96	1.14
9	44.29	88.57	0.59	2.51	6.58	1.79	11.47	0.60	8.26	0.43
10	71.42	142.85	0.61	2.96	4.88	11.95	20.40	1.05	14.69	0.76
<b>Summary Statistics</b>										
<b>Day 1: July 10, 1995</b>										
Mean	50.77	101.53	0.71	2.84	14.48	11.97	30.00	1.49	21.60	1.07
SD	12.85	25.71	0.31	3.76	19.65	18.85	22.64	1.09	16.30	0.78
% CV	25	25	44	132	135	157	75	73	75	73
<b>Day 2: July 11, 1997</b>										
Mean	49.67	99.34	0.97	6.31	8.95	5.64	21.87	1.10	15.74	0.79
SD	13.57	27.13	0.45	4.47	5.40	6.56	10.18	0.50	7.33	0.36
% CV	27	27	46	71	60	116	47	45	47	46
<b>All Days</b>										
Mean	50.18	100.44	0.84	4.57	11.71	8.81	25.93	1.30	18.67	0.93
SD	12.87	25.75	0.40	4.39	14.31	14.11	17.59	0.85	12.66	0.61
% CV	26	26	48	96	122	160	68	65	68	66

/a Leg exposure = 1.1 x sock residues

/b mg BEE DE = Face/neck + Hands + Torso + Legs

/c Dose BEE (mg/day) = (DE \* 0.048) + ( $\mu\text{g}$  BEE IE/1000)

/d mg AE DE = (Face/neck + Hands + Torso + Legs) \* 0.72

/e Dose AE (mg/day) = ((BEE DE \* 0.72) \* 0.048) + ( $\mu\text{g}$  BEE IE \* 0.72)/1000

/f mg AE = mg BEE \* 0.72

Observations of workers whose clothing or work habits provided either greater or fewer opportunities for exposure were congruent with some of the highest and lowest measured exposures. For example, most of the workers unzipped their coveralls to the waist and had purple dye stains on the exposed V-shaped section of their T-shirts. However, on Day 1, workers 4 and 9 removed the top part of their coveralls and either tied the top part of their coveralls around their waist or over one shoulder. These workers had the highest torso exposures for the two-day study. Similarly, worker 8 wore a second shirt over the study T-shirt on Day 1 and had the lowest torso exposure for the two-day study. Workers who removed their gloves frequently (worker 8, Day 1; workers 6, 7 and 8, Day 2) had the highest recorded hand exposures for the study while those workers wearing two pair of socks (workers 4 and 7, Day 1; workers 4, 7 and 8, Day 2) had leg exposures among the lowest within each day. Figure 1 presents “Summary Statistics” data from Table VII as pie charts, showing the percent contribution of each dermal region to triclopyr AE DE for each study day). While roughly 32 lb of triclopyr AE were applied each day (study mean =  $3.2 \pm 0.3$  lb/worker/day; Table VI), triclopyr AE DE for Day 2 was about 30% lower than for Day 1 (21.60 mg vs. 15.74 mg, respectively). Day 2 showed less variation in individual regional exposures than did Day 1. On Day 1, the torso and legs were the greatest contributors to DE (48.3% and 39.9%, respectively). On Day 2, the torso was the largest contributor to DE at 40.9%, with the hands and legs contributing approximately equal amounts to DE (28.8% and 25.8%, respectively). The face/neck regions contributed less than 5% to DE on both days.

Figure 1. % Regional Dermal Exposure, Triclopyr AE

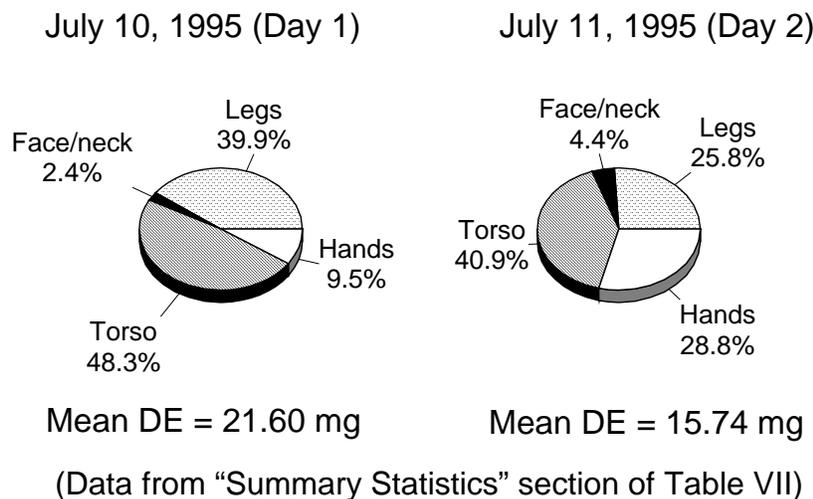


Table VIII gives hourly exposures to triclopyr (mg DE/hr, BEE and AE), based on the total time each worker spent loading and applying triclopyr. Hourly exposures were about 40% greater on Day 1 (3.60 mg AE) and more variable (%CV = 76) compared to Day 2 (2.58 mg AE, %CV = 47). Overall, mean DE was about 3.1 mg/hr (triclopyr AE).

Table IX compares observed daily exposures (EAD, Urine; mg triclopyr acid/kg bw) vs. exposures calculated from dermal and inhalation monitoring and a dermal absorption of 4.8% (EAD, DE + IE; mg triclopyr AE/kg bw). Overall, urinary EAD was significantly greater, averaging 4 times the EAD predicted by DE + IE monitoring ( $p < 0.01$ , t-test, paired two sample for means). DE + IE exposures were greater on Day 1 (mean EAD = 0.015 mg/kg bw, Day 1, vs. 0.011 mg/kg bw, Day 2), while urinary monitoring results were higher for Day 2 (mean EAD = 0.049 mg/kg bw, Day 1, vs. 0.067 mg/kg bw, Day 2). There was no statistical difference in individual between days for either urinary triclopyr or DE + IE EAD ( $p = 0.09$ ,  $p = 0.35$ , respectively; t-tests, paired two sample for means). The urine data reported in Appendix I, Table 4, include pre-study spot samples collected on July 5, which were intended to reflect background levels following

Table VIII. Hourly Exposures to Triclopyr<sup>/a</sup>

Worker	DE (mg/hr)		Worker	DE (mg/hr)	
	BEE	AE		BEE	AE
Day 1, July 10, 1995			Day 2, July 11, 1995		
1	1.57	1.13	1	1.78	1.28
2	10.59	7.63	2	3.42	2.47
3	7.74	5.57	3	6.24	4.49
4	6.92	4.98	4	1.80	1.30
5	2.30	1.65	5	2.20	1.59
6	1.64	1.18	6	4.68	3.37
7	1.43	1.03	7	5.25	3.78
8	4.16	3.00	8	5.23	3.76
9	11.02	7.94	9	1.88	1.35
10	2.64	1.90	10	3.34	2.41
Mean	5.00	3.60	Mean	3.58	2.58
SD	3.77	2.72	SD	1.67	1.20
%CV	75	76	%CV	47	47

	DE (mg/hr)	
	BEE	AE
All Days		
Mean	4.29	3.09
SD	2.93	2.11
%CV	68	68

/a DE from Table VII, time from Table VI

several days without exposure to triclopyr. However, workers had instead been continuously exposed to triclopyr for several days (mean pre-exposure urinary triclopyr =  $30 \pm 18$  mg triclopyr acid). Information on amount of material handled, hours worked, and other pertinent parameters was unavailable. These data were not rigorously investigated but do provide an estimate of steady-state exposure to triclopyr.

Table IX. Urinary Triclopyr (mg triclopyr acid<sup>/a</sup>), Observed Estimated Absorbed Dose (EAD, Urine) vs. EAD from Dermal and Inhalation Monitoring (EAD, DE + IE)

Date	Worker	Urine	EAD, Urine	EAD, DE + IE
		mg triclopyr acid	mg triclopyr acid/kg bw	mg triclopyr AE/kg bw
7/10/95	1	5.75	0.068	0.004
	2	1.96	0.026	0.030
	3	3.53	0.055	0.026
	4	3.12	0.040	0.019
	5	3.57	0.045	0.006
	6	1.12	0.015	0.005
	7	0.81	0.013	0.006
	8	9.45	0.126	0.012
	9	4.12	0.057	0.032
	10	2.86	0.049	0.010
Mean		3.63	0.049	0.015
SD		2.51	0.032	0.011
7/11/95	1	6.16	1.40	0.005
	2	3.89	0.65	0.010
	3	8.81	0.77	0.021
	4	3.81	2.02	0.005
	5	2.49	0.95	0.006
	6	1.57	2.02	0.014
	7	2.70	4.18	0.019
	8	11.05	6.34	0.015
	9	2.65	3.97	0.006
	10	4.66	8.63	0.013
Mean		4.78	0.067	0.011
SD		3.05	0.044	0.006
All Days				
Mean		4.20	0.058	0.013
SD		2.78	0.038	0.009

<sup>/a</sup> mg triclopyr acid = (ppm triclopyr acid x 1400 mL)/1000

Figure 2. Triclopyr Applicator EAD vs. USFS Predicted EAD dermal and inhalation exposure, mg triclopyr AE/kg bw/day

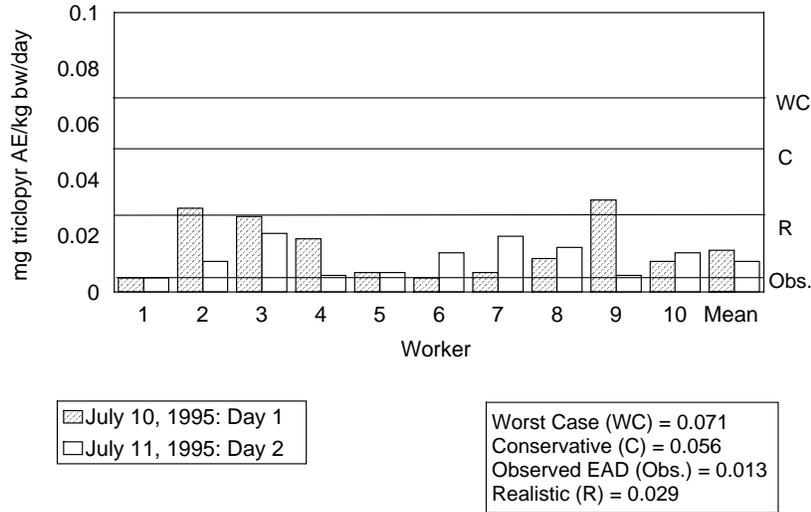
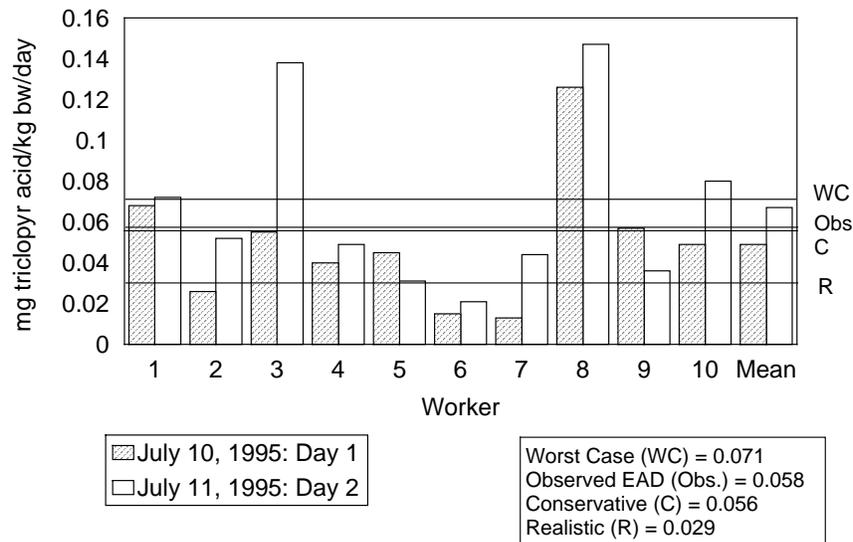


Figure 3. Triclopyr Applicator EAD vs. USFS Predicted EAD mg urinary triclopyr acid/kg bw/day



Figures 2 and 3 show worker triclopyr EAD by day (normalized to observed application rate) for DE + IE monitoring and urinary monitoring, respectively, and the overall mean daily EADs (mean) compared to the predicted USFS realistic, conservative and worst case exposure scenarios. For DE + IE monitoring, mean observed triclopyr AE EAD (0.013 mg/kg bw/day) averaged approximately half the USFS estimate for realistic exposures (0.029 mg/kg bw/day). Only 2 workers on Day 1 (10% of all exposures) had EADs which exceeded the USFS realistic model estimate. No exposures exceeded either the conservative or worst case estimates. For the urinary monitoring, 16 exposures (80%) exceeded the predicted realistic estimate, 8 exposures (40%) exceeded the conservative estimate and 5 exposures (25%) exceeded the worst case

estimate. Mean observed urinary triclopyr EAD (0.058 mg/kg bw/day) approximated the USFS conservative estimate (0.056 mg/kg bw/day).

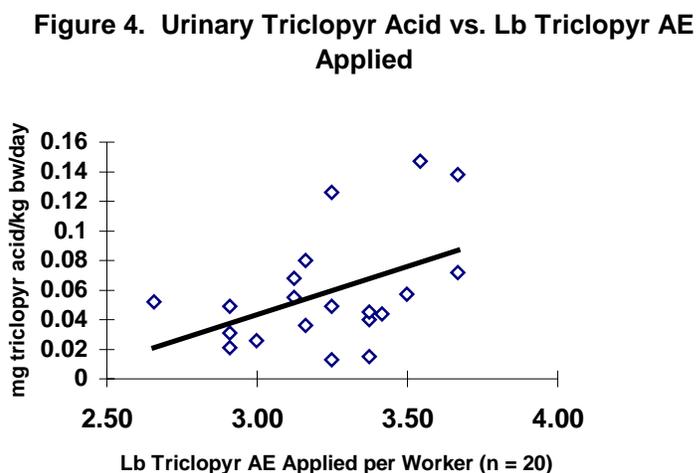
Table X shows the empirical dermal absorption percentages for this study, assuming no contribution from inhalation exposure. Percent dermal absorption varies widely and is higher for Day 2 (34%) than for Day 1 (27.8%); values far exceed the DPR default dermal absorption of 4.8%.

Table X. Empirical % Dermal Absorption ( $[\text{Urine}/\text{DE}]^{\text{a}} \times 100 = \% \text{DA}$ ) for Triclopyr AE (mg)

Worker	DE, mg AE	Urine, mg acid	% DA
<u>July 10, 1995</u>			
1	6.76	5.75	85.1
2	45.76	1.96	4.3
3	33.43	3.53	10.6
4	29.91	3.12	10.4
5	9.92	3.57	36.0
6	7.10	1.12	15.8
7	6.17	0.81	13.2
8	17.98	9.45	52.6
9	47.61	4.12	8.6
10	11.40	2.86	25.1
Mean Day 1	21.60	3.63	27.8
SD Day 1	16.30	2.51	23.4
<u>July 11, 1995</u>			
1	7.83	2.20	78.7
2	15.05	1.95	25.9
3	27.42	6.92	32.1
4	7.92	1.90	48.1
5	9.68	2.49	25.7
6	20.57	0.39	7.6
7	23.07	1.54	11.7
8	22.96	8.28	48.1
9	8.26	1.70	32.1
10	14.69	2.66	31.8
Mean Day 2	15.74	4.78	34.0
SD Day 2	7.33	3.05	23.0
Mean, 2 days	18.67	4.20	30.9
SD, 2 days	12.66	2.78	23.1

<sup>a</sup> mg acid urine from Table IX, DE from Table VII; assuming no contribution from inhalation exposure

Figure 4 depicts the regression of worker urinary triclopyr acid EAD (Table X) on triclopyr AE applied (Table VI). The regression was significant at the 0.05 level ( $r^2 = 0.21$ ,  $F = 0.044$ ).



Test Substance and Tank Mix A single sample of the one lot of Garlon<sup>®</sup> 4 applied during the study was analyzed for triclopyr BEE. Expected recovery was 61.6% by weight; laboratory recovery was 60.02%. Table XI presents the average concentration of triclopyr BEE in the two aliquots analyzed from each batch mix. Expected recovery was 0.616%; most recoveries were lower. Method validation did not include evaluating recovery of triclopyr BEE from tank mix solution; the samples were collected solely to verify the presence of triclopyr. Historically, recovery of target analytes from tank mixes is lower than expected, often due to factors such as hydrolysis or incomplete mixing. Data were not adjusted to tank mix recoveries.

Table XI. Daily % Triclopyr BEE Concentration in Batch Mixes

Batch Mix	Mean % Conc. of Triclopyr BEE	
	July 10, 1995	July 11, 1995
1	0.381	0.446
2	0.493	0.594
3	0.643	0.533
Mean $\pm$ SD	0.485 $\pm$ 0.163	0.524 $\pm$ 0.074
% of expected	79	85

Field Fortifications Raw data for field fortification and blank samples are reported in Appendix I, Tables 5 and 6, respectively. The initial concentration (ppm) and post-field concentrations (ppm and % of initial) of the field spiking solutions are given in Table XII. The post-field concentration of the wipe spiking solution exceeded the study limit of 70 - 120% recovery; all other spiking solutions showed acceptable recoveries.

Table XII. Initial and Post-field Analyses of Field Spiking Solutions

Solution No.	Matrix	Initial ppm	Post-field ppm	% of initial
9501-1	Filter	2300.00	2440.00	106.1
9501-2	Socks	938.00	1000.00	106.6
9501-4	Wipe	97.00	122.00	125.8
9501-5	T-shirt	4602.00	4960.00	107.8
9501-6	Urine	0.222	0.266	119.8
9501-7	Urine	2.68	2.67	99.6
9501-8	Urine	26.40	26.68	101.1

Table XIII. Recovery of Triclopyr Acid (ppm) and Triclopyr BEE ( $\mu\text{g}$ ) from Field Fortifications

Matrix	n	Expected		% of Expected	
		ppm	$\mu\text{g}$	Mean	SD
Urine	6	0.01		NA	NA
Urine	6	0.10		240.00	35.21
Urine	6	1.00		127.00	22.33
Filter	6		100.00	58.98	20.95
Wipes	6		100.00	95.90	8.67
Socks	6		1000.00	85.62	7.98
T-Shirt	6		5000.00	98.23	5.06

NA, not available: LOQ for urine was 0.05 ppm

Field fortification recoveries are shown in Table XIII. Mean recoveries of triclopyr acid from urine were outside the study limits (70 - 120%). The field portion of the study was completed prior to conducting method validation for triclopyr in urine. The 0.01 ppm fortification level samples were not analyzed because the method validation later established the limit of quantitation (LOQ) at 0.05 ppm. No rationale was found for the unusually high recoveries from the 0.10 ppm urine fortifications. Results for 90% of the exposure samples exceeded 1.0 ppm triclopyr acid; urine results were not adjusted for the 127% mean recovery observed for the 1.0 ppm field fortifications.

Wipes, socks and T-shirt fortifications showed acceptable recoveries of triclopyr. Filter recoveries from field fortifications were low (59%). Possible reasons include the behavior of formulated product (field fortifications) vs. analytical standard (method validation, on-going QC), the surface chemistry effects of application in acetone vs. a water solution droplet contained in an aerosol during exposure, and effects from pumping the fortified samples. WH&S plans to conduct a laboratory study to compare pumped vs. unpumped filter fortifications which may increase our understanding of this observation. Exposure samples were not adjusted for field fortification recoveries.

Field Blanks None of the dermal matrices or glass fiber filters had detectable triclopyr. One urine sample had detectable triclopyr acid (0.11 ppm, Day 1). WH&S staff provided the matrix for urine blanks each day. It is possible staff were minimally exposed during monitoring. Future WH&S studies will attempt to avoid potential contamination by collecting voids from staff prior to the monitoring portion of the study.

Storage Stability Average recoveries from stored, fortified samples are presented in Table XIV. All samples showed acceptable recoveries. Raw data are provided in Appendix I, Table 7.

Table XIV. Storage Stability of Triclopyr on Dermal and Inhalation Media  
Mean % Recovery  $\pm$  SD

Matrix	Week	n	Mean $\pm$ SD
Filter	9	5	94.50 $\pm$ 3.17
	15	5	100.32 $\pm$ 4.61
	31	6	81.37 $\pm$ 39.95
Socks	10	5	100.36 $\pm$ 7.44
	16	5	88.00 $\pm$ 7.27
T-shirt	10	5	93.16 $\pm$ 2.65
	16	5	101.14 $\pm$ 2.89
Wipes	10	5	85.88 $\pm$ 3.17
	16	5	93.18 $\pm$ 6.53

## ***Discussion***

Dermal Exposure Dermal exposure was the primary exposure route, accounting for more than 98% of exposure, with the torso region, (arms, wrists, back and front from the hip to the super-sternal notch) receiving the greatest portion of triclopyr dermal residues (41 - 48%). Leg exposure was a large contributor, accounting for 26 - 40% of dermal exposure. Historically, the hands have been the largest contributors to DE for pesticide handlers, even when gloves are worn, and they typically contribute from 30% to more than 90% to dermal exposure (26). Here, hands contributed between approximately 10 - 30% to dermal exposure. Workers in this study used spray wands to broadcast the triclopyr mixture in a sweeping back and forth pattern as they walked. While the majority of the target foliage was no more than three feet tall, applicators were often careless about keeping the spray pattern low. By day's end, all workers were stained purple with dye from head to foot. Workers also unzipped their coveralls to the waist, thereby removing a protective clothing layer from the front of the torso region.

Inhalation Exposure Inhalation exposure was quite low compared to the dermal exposure measurements, representing an average of 1.9% of the daily absorbed dose (mg) for the two study days. This is primarily due to the use of backpack sprayers

operating at low pressures with non-atomizing nozzles. These relatively large droplets and triclopyr's low vapor pressure (0.2 mPa at 25 °C) (20) allow the material to settle rapidly. In a study by Middendorf, et al., (1994) (27), IE contributed an average of approximately 7% to applicator exposures (adjusted to DPR exposure calculation assumptions (6)). Treating denser and taller target foliage, up to 12 feet in height, may have concentrated a greater portion of the spray in the breathing zone and contributed to greater observed IE compared to the current study.

*Estimated Absorbed Dosage* In this study, DE + IE monitoring yielded lower exposure estimates than did urinary monitoring. Mean observed EAD from urinary monitoring was greater than predicted, approximating the USFS EIS conservative exposure model (95<sup>th</sup> percentile). DE + IE EAD was substantially lower than the models, with only 10% of exposures exceeding the realistic model and no exposures exceeding the conservative or worst case models.

Mean urinary EAD was four-fold higher and significantly greater than mean EAD calculated from DE + IE monitoring (Table IX;  $p < 0.01$ , paired t-test). Several factors may have contributed to this observation. Clothing penetration may have been greater than the 10% assumed as a default value (6). Dermal absorption may also have been greater than the 4.8% value DPR currently uses for triclopyr (24); the observed dermal absorption was about six times greater (30.9%; Table X). The crew worked at an aerobic pace and perspired moderately throughout the day. Damp skin and increased blood flow near the skin surface may have increased dermal absorption (28, 29) over that observed in previous studies (24). The dermal monitors also could not capture the portion of the dermal dose that may have penetrated into the body during the workday. Additionally, if actual breathing rates were greater than the DPR default inhalation rate of 26.7 L/min, inhalation exposure may be underestimated (6).

The crew applied similar amounts of triclopyr each day. However, DE + IE EAD was about 30% greater on Day 1 (0.015 mg/kg bw/day, Day 1; 0.011 mg/kg bw/day, Day 2), while urinary EAD was about 50% greater on Day 2 (0.049 mg/kg bw/day, Day1; 0.067 mg/kg bw/day, Day 2) (Table IX). The increase in observed urinary EAD for Day 2 is likely due to continued absorption and excretion of triclopyr from the first day's exposure. The dermal absorption half-life of triclopyr averages 16.8 hours and the subsequent excretion is rapid (half-life = 6 hours, 30); the overall half-life is approximately 23 hours. Residual urinary triclopyr was not a large contributor to observed exposures. Since the crew showered daily after work, well within the first dermal absorption half-life, and wore clean clothes each day, it is likely that no more than 10% remained from the crew's previous exposure 60 hours prior to the study.

Since urinary monitoring encompassed only 12 hours subsequent to Day 2 exposures, estimates based on urinary triclopyr were do not represent actual absorbed dosages for the 2 monitoring days. Absorbed dosages could be characterized in future studies by either monitoring to complete excretion with no subsequent exposures (approximately 4 days post-exposure) or monitoring over a longer continuous exposure period to observe steady state exposures. Since the workers are usually on contract, take minimal time

off and often leave the area immediately after fulfilling contract obligations, observing steady state exposures is the more feasible alternative.

A recent risk assessment completed for the US Department of Agriculture based worker exposure estimates to Garlon™ 4 on 2,4-D exposure rates (7). Application parameters were similar to those in the current study. The central value for estimated daily dosage for backpack sprayer applicators was 0.006 mg AE/kg bw, which is less than that found in the current study by a factor of 2 and 10, respectively, for DE + IE monitoring and urinary monitoring. Middendorf (1992) found mean urinary EAD of 0.004 mg AE/kg bw for backpack sprayer applicators following exposure to Garlon 4™ (31). This is similar to the US Department of Agriculture estimate. Workers in the Middendorf study applied an average of 4.8 lb triclopyr BEE, about 50% more than in the current study.

Exposure databases such as the Pesticide Handlers Exposure Database (PHED) require observed dermal exposures to be normalized to a variable, preferably total lb a.i. handled, before using the model to generate exposure assessments (32). For this study, the regression of urinary triclopyr on lb triclopyr acid applied was significant at the 0.05 level (Figure 4). While urinary exposures varied by only 15-fold, there was a narrow range of application rates. A stronger linear relationship may have been observed had the application rates varied more.

*Margins of Exposure (MOE) (1):* Table XV presents the predicted vs. observed MOE, with the following stipulations: 1) DPR currently uses average exposure to calculate MOE for subchronic and chronic toxicity, 2) more recent studies may have different endpoints, and 3) DPR neither reviewed nor approved the USFS EIS endpoints. The predicted USFS MOE for both systemic and reproductive effects, normalized to triclopyr AE and the application rates in this study, were 86, 45 and 35, respectively, for the realistic, conservative and worst case models. The observed MOE, calculated from mean DE + IE (Table IX, column 5) and mean urinary triclopyr (Table IX, column 4) were 192 and 43, respectively. The MOE estimated from the urine monitoring approximated that for the conservative model, while the MOE estimated from DE + IE monitoring was greater than predicted by all USFS models.

Table XV. Predicted vs. Observed Margins of Exposure (MOE) for Systemic and Reproductive Effects

USFS Predicted MOE <sup>/a</sup>	
Realistic	86
Conservative	45
Worst Case	35
Observed MOE	
EAD, DE + IE <sup>/b</sup>	192
EAD, Urine <sup>/c</sup>	43

/a Reference 1 (Final Environmental Impact Statement, Vegetation for Reforestation, Vol. II and III (1988) USDA Forest Service) normalized to observed triclopyr AE application rate of 1 lb/acre (Table I):

$$\text{example: USFS MOE} = \text{NOEL}/[\text{EAD}_{\text{Realistic (Figure 2)}}] \\ = (2.5 \text{ mg/kg bw/day})/(0.029 \text{ mg/kg bw/day}) = 86$$

$$\text{/b Study MOE}_{\text{EAD, DE + IE}} = \text{NOEL}/\text{EAD}_{\text{EAD, DE + IE; All Days (Table IX)}} \\ = (2.5 \text{ mg/kg bw/day})/(0.013 \text{ mg/kg bw/day}) = 192$$

$$\text{/c Study MOE}_{\text{EAD, Urine}} = \text{NOEL}/\text{EAD, Urine}_{\text{EAD, Urine; All Days (Table IX)}} \\ = (2.5 \text{ mg/kg bw/day})/(0.058 \text{ mg/kg bw/day}) = 43$$

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**Table 1 Dermal and Inhalation Raw Data, µg Triclopyr BEE**

Date	ID	Matrix	ug/spl
10-Jul-95	1	Filter	8.9
10-Jul-95	1	Hand Wipes	1765
10-Jul-95	1	T-Shirt	4074
10-Jul-95	1	Face Wipes	455
10-Jul-95	1	Socks	2816
10-Jul-95	2	Face Wipes	560
10-Jul-95	2	Filter	5.01
10-Jul-95	2	Hand Wipes	1748
10-Jul-95	2	Socks	51105
10-Jul-95	2	T-Shirt	5028
10-Jul-95	3	Hand Wipes	2391
10-Jul-95	3	Socks	32969
10-Jul-95	3	Face Wipes	1295
10-Jul-95	3	T-Shirt	6476
10-Jul-95	3	Filter	7.44
10-Jul-95	4	T-Shirt	38728
10-Jul-95	4	Socks	933
10-Jul-95	4	Hand Wipes	1199
10-Jul-95	4	Filter	3.16
10-Jul-95	4	Face Wipes	588
10-Jul-95	5	Socks	1290
10-Jul-95	5	T-Shirt	9280
10-Jul-95	5	Filter	5.86
10-Jul-95	5	Hand Wipes	2126
10-Jul-95	5	Face Wipes	946
10-Jul-95	6	T-Shirt	5301
10-Jul-95	6	Filter	6.36
10-Jul-95	6	Socks	928
10-Jul-95	6	Hand Wipes	2870
10-Jul-95	6	Face Wipes	668
10-Jul-95	7	Socks	791
10-Jul-95	7	Hand Wipes	1902
10-Jul-95	7	T-Shirt	5042
10-Jul-95	7	Filter	9.94
10-Jul-95	7	Face Wipes	750
10-Jul-95	8	Filter	5.55
10-Jul-95	8	Socks	7115
10-Jul-95	8	Face Wipes	1088
10-Jul-95	8	T-Shirt	2741
10-Jul-95	8	Hand Wipes	13318
10-Jul-95	9	Filter	7.67
10-Jul-95	9	Face Wipes	374
10-Jul-95	9	Hand Wipes	158
10-Jul-95	9	T-Shirt	61640
10-Jul-95	9	Socks	3599

**Table 1, cont. Dermal and Inhalation Raw Data, µg Triclopyr BEE**

Date	ID	Matrix	ug/spl
10-Jul-95	10	Filter	7.59
10-Jul-95	10	Hand Wipes	941
10-Jul-95	10	Face Wipes	393
10-Jul-95	10	Socks	7300
10-Jul-95	10	T-Shirt	6465
11-Jul-95	1	Face Wipes	441
11-Jul-95	1	Hand Wipes	2731
11-Jul-95	1	Socks	3520
11-Jul-95	1	T-Shirt	3827
11-Jul-95	1	Filter	6.43
11-Jul-95	2	Filter	8.15
11-Jul-95	2	T-Shirt	6709
11-Jul-95	2	Hand Wipes	3784
11-Jul-95	2	Face Wipes	1348
11-Jul-95	2	Socks	8240
11-Jul-95	3	Hand Wipes	8996
11-Jul-95	3	Socks	19092
11-Jul-95	3	Filter	6.82
11-Jul-95	3	T-Shirt	6905
11-Jul-95	3	Face Wipes	1175
11-Jul-95	4	Socks	1046
11-Jul-95	4	Hand Wipes	3055
11-Jul-95	4	Filter	3.78
11-Jul-95	4	Face Wipes	799
11-Jul-95	4	T-Shirt	5995
11-Jul-95	5	Filter	4.55
11-Jul-95	5	Socks	1032
11-Jul-95	5	Hand Wipes	4469
11-Jul-95	5	T-Shirt	6740
11-Jul-95	5	Face Wipes	1104
11-Jul-95	6	T-Shirt	13336
11-Jul-95	6	Hand Wipes	10676
11-Jul-95	6	Face Wipes	781
11-Jul-95	6	Socks	3427
11-Jul-95	6	Filter	6.32
11-Jul-95	7	Face Wipes	863
11-Jul-95	7	T-Shirt	21330
11-Jul-95	7	Socks	1677
11-Jul-95	7	Hand Wipes	8000
11-Jul-95	7	Filter	10.5
11-Jul-95	8	Face Wipes	1962
11-Jul-95	8	Socks	751
11-Jul-95	8	Filter	8.67

**Table 1, cont. Dermal and Inhalation Raw Data,  $\mu\text{g}$  Triclopyr BEE**

<b>Date</b>	<b>ID</b>	<b>Matrix</b>	<b>ug/spl</b>
11-Jul-95	8	Hand Wipes	15882
11-Jul-95	8	T-Shirt	13217
11-Jul-95	9	T-Shirt	6575
11-Jul-95	9	Socks	1630
11-Jul-95	9	Hand Wipes	2512
11-Jul-95	9	Face Wipes	588
11-Jul-95	9	Filter	4.81
11-Jul-95	10	Socks	10860
11-Jul-95	10	Hand Wipes	2960
11-Jul-95	10	T-Shirt	4881
11-Jul-95	10	Filter	10.7
11-Jul-95	10	Face Wipes	609

**Table 2 Triclopyr BEE Inhalation Exposure**

Date	ID	µg BEE	L/min End	L/min Begin	Min <sup>a</sup>	µg IE
10-Jul-95	1	8.9	2	2	554	59.41
10-Jul-95	2	5.01	1.9	2	550	34.30
10-Jul-95	3	7.44	Pump 1 1.6	Pump 1 2	Pump 1 382	57.20
10-Jul-95	3	*	Pump 2 1.4	Pump 2 1.6	Pump 2 103	*
10-Jul-95	4	3.16	0.1	2	492	40.18
10-Jul-95	5	5.86	2	2	549	39.12
10-Jul-95	6	6.36	1.7	2	550	45.90
10-Jul-95	7	9.94	1.7	2	542	71.73
10-Jul-95	8	5.55	1.8	2	542	39.00
10-Jul-95	9	7.67	1.1	2	552	66.06
10-Jul-95	10	7.59	1.7	2	545	54.77
11-Jul-95	1	6.43	2	2	621	42.92
11-Jul-95	2	8.15	2	2	618	54.40
11-Jul-95	3	6.82	2	2	615	45.52
11-Jul-95	4	3.78	1.1	2	619	32.56
11-Jul-95	5	4.55	1.5	2	614	34.71
11-Jul-95	6	6.32	2	2	617	42.19
11-Jul-95	7	10.5	2	2	613	70.09
11-Jul-95	8	8.67	1.95	2	612	58.60
11-Jul-95	9	4.81	0.9	2	612	44.29
11-Jul-95	10	10.7	2	2	620	71.42

a Minutes pumped = minutes worker exposed

\* 10-Jul-95: Worker 3 had 2 pumps associated with the single filter sample

Inhalation Exposure (IE) =

$$[(\mu\text{g BEE}) / ((\text{L/min End} + \text{L/min Begin}) / 2) \times \text{Min. pumped}) \times \text{Min. exposed} \times 26.7 \text{ L/min}] / 2$$

The equivalent IE for triclopyr acid = 0.72 x BEE IE based on the ratio of molecular weights of triclopyr AE (256.6) and triclopyr BEE (356.6)

For 2 pumps, each pump's begin and end flow rates are averaged and multiplied by the respective minutes run, then summed as follows for the shaded portion of the above equation:

$$(((\text{L/min End pump 1} + \text{L/min Begin pump 1}) / 2) \times \text{min pump 1}) + (((\text{L/min End pump 2} + \text{L/min Begin pump 2}) / 2) \times \text{min pump 2})$$

26.7 L/min is human breathing rate standard for medium work rate; final division of whole equation by 2 accounts for 50% uptake, 100% absorption (Thongsinthusak et al. (1993)<sup>6</sup>

**Table 3 Triclopyr BEE Dermal Exposure (mg DE), Dermal Dose (DE/kg bw/day) and Estimated Absorbed Dosage (EAD, (mg/kg bw/day))**

Date	ID	µg Triclopyr BEE				mg DE	bw (kg)	DE/kg bw/day	µg IE	EAD (mg/kg bw/day)
		faceneck	hands	legs	torso					
7/10/95	1	455.00	1765.00	3097.60	4074.00	9.39	85.0	0.111	59	0.006
7/10/95	2	560.00	1748.00	56215.50	5028.00	63.55	75.0	0.848	34	0.041
7/10/95	3	1295.00	2391.00	36265.90	6476.00	46.43	63.6	0.730	57	0.036
7/10/95	4	588.00	1199.00	1026.30	38728.00	41.54	77.3	0.538	40	0.026
7/10/95	5	946.00	2126.00	1419.00	9280.00	13.77	79.5	0.174	39	0.009
7/10/95	6	668.00	2870.00	1020.80	5301.00	9.86	75.0	0.132	46	0.007
7/10/95	7	750.00	1902.00	870.10	5042.00	8.56	61.4	0.141	72	0.008
7/10/95	8	1088.00	13318.00	7826.50	2741.00	24.97	75.0	0.333	39	0.017
7/10/95	9	374.00	158.00	3958.90	61640.00	66.13	72.7	0.910	66	0.045
7/10/95	10	393.00	941.00	8030.00	6465.00	15.83	58.2	0.273	55	0.014
7/11/95	1	441.00	2731.00	3872.00	3827.00	10.87	85.0	0.128	43	0.007
7/11/95	2	1348.00	3784.00	9064.00	6709.00	20.91	75.0	0.279	54	0.014
7/11/95	3	1175.00	8996.00	21001.20	6905.00	38.08	63.6	0.599	46	0.029
7/11/95	4	799.00	3055.00	1150.60	5995.00	11.00	77.3	0.143	33	0.007
7/11/95	5	1104.00	4469.00	1135.20	6740.00	13.45	79.5	0.169	35	0.009
7/11/95	6	781.00	10676.00	3769.70	13336.00	28.56	75.0	0.381	42	0.019
7/11/95	7	863.00	8000.00	1844.70	21330.00	32.04	61.4	0.523	70	0.026
7/11/95	8	1962.00	15882.00	826.10	13217.00	31.89	75.0	0.426	59	0.021
7/11/95	9	588.00	2512.00	1793.00	6575.00	11.47	72.7	0.158	44	0.008
7/11/95	10	609.00	2960.00	11946.00	4881.00	20.40	58.2	0.352	71	0.018

µg Triclopyr BEE "legs" = [1.1 \* (Appendix I, Table 2, "µg/spl")] for "Matrix" = "Socks"

µg IE from Appendix I, Table 2, rounded to nearest µg.

mg DE = [µg DE/1000]

= [faceneck + hands + legs + torso]/1000

DE/kg/day = mg DE/(Wt (kg))

EAD = [(mg DE \* 4.8% dermal absorption) + (mg IE)]/kg body wt

= [(mg DE\*0.048) + (µg IE/1000)]/(Wt (kg))

Triclopyr acid equivalents (triclopyr AE) in report = triclopyr BEE \* 0.72 based on the ratio of molecular weights of triclopyr AE (256.6) and triclopyr BEE (356.6)

Appendix I, HS-1769: Exposure of Hand Applicators to Triclopyr in Forest Settings, 1995

**Table 4 Urine Samples**

ID	Date Begin Collection	ppm acid	mg acid	Volume (mL)	bw (kg)	mg acid/kg bw/day
1	7/10/95	4.11	5.75	600	85.0	0.068
2	7/10/95	1.40	1.96	700	75.0	0.026
3	7/10/95	2.52	3.53	450	63.6	0.055
4	7/10/95	2.23	3.12	150	77.3	0.040
5	7/10/95	2.55	3.57	750	79.5	0.045
6	7/10/95	0.80	1.12	600	75.0	0.015
7	7/10/95	0.58	0.81	1400	61.4	0.013
8	7/10/95	6.75	9.45	500	75.0	0.126
9	7/10/95	2.94	4.12	850	72.7	0.057
10	7/10/95	2.04	2.86	1100	58.2	0.049
1	7/11/95	4.40	6.16	500	85.0	0.072
2	7/11/95	2.78	3.89	700	75.0	0.052
3	7/11/95	6.29	8.81	1100	63.6	0.138
4	7/11/95	2.72	3.81	700	77.3	0.049
5	7/11/95	1.78	2.49	1400	79.5	0.031
6	7/11/95	1.12	1.57	350	75.0	0.021
7	7/11/95	1.93	2.70	800	61.4	0.044
8	7/11/95	7.89	11.05	1050	75.0	0.147
9	7/11/95	1.89	2.65	900	72.7	0.036
10	7/11/95	3.33	4.66	800	58.2	0.080
1	7/ 5/95	18.6	1.40	75	85.0	0.016
2	7/ 5/95	21.7	0.65	30	75.0	0.009
3	7/ 5/95	10.3	0.77	75	63.6	0.012
4	7/ 5/95	16.8	2.02	120	77.3	0.026
5	7/ 5/95	15.8	0.95	60	79.5	0.012
6	7/ 5/95	18.4	2.02	110	75.0	0.027
7	7/ 5/95	20.9	4.18	200	61.4	0.068
8	7/ 5/95	52.8	6.34	120	75.0	0.084
9	7/ 5/95	56.7	3.97	70	72.7	0.055
10	7/ 6/95	9.59	8.63	900	58.2	0.148

Data are reported by laboratory as ppm acid ( $\mu\text{g/mL}$ ).

$\text{mg acid} = (\text{ppm acid} \times 1400 \text{ mL})/1000$

$\text{mg/kg bw/day acid} = \text{mg acid}/(\text{Weight (kg)})$ , rounded to three decimal places

In report, urine data expressed as mg BEE and mg/kg bw/day BEE = (acid  $\times$  1.39) based on the ratio of molecular weights of triclopyr acid equivalents (AE, 256.6) and triclopyr BEE (356.6)

**Table 5 Recovery of Triclopyr BEE and Triclopyr Acid from Field Fortifications**

$$\% \text{ Recovery} = (\text{Recovery}/\text{Expected}) * 100$$

Date	WHS No	Matrix	Recovery	Units	Analyte	Expected	% Recovery
7/10/95	JS01-1042	Filter	68.0	µg	BEE	100.00	68
7/10/95	JS01-1040	Filter	28.8	µg	BEE	100.00	28.8
7/10/95	JS01-1041	Filter	81.0	µg	BEE	100.00	81
7/10/95	JS01-1043	Socks	944	µg	BEE	1000.00	94.4
7/10/95	JS01-1044	Socks	943	µg	BEE	1000.00	94.3
7/10/95	JS01-1045	Socks	889	µg	BEE	1000.00	88.9
7/10/95	JS01-1047	T-Shirt	4998	µg	BEE	5000.00	99.96
7/10/95	JS01-1048	T-Shirt	5166	µg	BEE	5000.00	103.32
7/10/95	JS01-1046	T-Shirt	5088	µg	BEE	5000.00	101.76
7/10/95	JS01-1052	Urine	0.28	ppm	Acid	0.10	280
7/10/95	JS01-1053	Urine	0.24	ppm	Acid	0.10	240
7/10/95	JS01-1054	Urine	0.27	ppm	Acid	0.10	270
7/10/95	JS01-1055	Urine	1.12	ppm	Acid	1.00	112
7/10/95	JS01-1056	Urine	1.52	ppm	Acid	1.00	152
7/10/95	JS01-1057	Urine	1.56	ppm	Acid	1.00	156
7/10/95	JS01-1068	Wipes	91.5	µg	BEE	100.00	91.5
7/10/95	JS01-1069	Wipes	90.7	µg	BEE	100.00	90.7
7/10/95	JS01-1067	Wipes	109	µg	BEE	100.00	109
7/11/95	JS02-1042	Filter	60.1	µg	BEE	100.00	60.1
7/11/95	JS02-1041	Filter	76.9	µg	BEE	100.00	76.9
7/11/95	JS02-1040	Filter	39.1	µg	BEE	100.00	39.1
7/11/95	JS02-1043	Socks	798	µg	BEE	1000.00	79.8
7/11/95	JS02-1044	Socks	759	µg	BEE	1000.00	75.9
7/11/95	JS02-1045	Socks	804	µg	BEE	1000.00	80.4
7/11/95	JS02-1047	T-Shirt	4957	µg	BEE	5000.00	99.14
7/11/95	JS02-1046	T-Shirt	4463	µg	BEE	5000.00	89.26
7/11/95	JS02-1048	T-Shirt	4798	µg	BEE	5000.00	95.96
7/11/95	JS02-1052	Urine	0.18	ppm	Acid	0.10	180
7/11/95	JS02-1053	Urine	0.23	ppm	Acid	0.10	230
7/11/95	JS02-1054	Urine	0.24	ppm	Acid	0.10	240
7/11/95	JS02-1055	Urine	1.22	ppm	Acid	1.00	122
7/11/95	JS02-1056	Urine	1.2	ppm	Acid	1.00	120
7/11/95	JS02-1057	Urine	1.0	ppm	Acid	1.00	100
7/11/95	JS02-1069	Wipes	101	µg	BEE	100.00	101
7/11/95	JS02-1068	Wipes	98.5	µg	BEE	100.00	98.5
7/11/95	JS02-1067	Wipes	84.7	µg	BEE	100.00	84.7

**Table 6 Recovery of Triclopyr BEE and Triclopyr Acid from Blank Matrix**

<b>Date</b>	<b>Matrix</b>	<b>Result</b>	<b>Analyte</b>	<b>units</b>
7/10/95	Filter	ND	BEE	ug/spl
7/10/95	Socks	ND	BEE	ug/spl
7/10/95	T-Shirt	ND	BEE	ug/spl
7/10/95	Urine	0.11	Acid	ppm
7/10/95	Urine	ND	Acid	ppm
7/10/95	Wipes	ND	BEE	ug/spl
7/11/95	Filter	ND	BEE	ug/spl
7/11/95	Socks	ND	BEE	ug/spl
7/11/95	T-Shirt	ND	BEE	ug/spl
7/11/95	Urine	ND	Acid	ppm
7/11/95	Wipes	ND	BEE	ug/spl

**Table 7 Storage Stability of Triclopyr BEE on Dermal and Inhalation Matrices**

Week	Matrix	ug Spiked	% Recovery
9	Filter	97.6	93.7
9	Filter	97.6	93
9	Filter	97.6	99.7
9	Filter	97.6	91.3
9	Filter	97.6	94.8
10	Socks	1000	107
10	Wipes	122	83.6
10	T-Shirt	4957	91.9
10	T-Shirt	4957	94.8
10	T-Shirt	4957	96.4
10	T-Shirt	4957	89.5
10	T-Shirt	4957	93.2
10	Socks	1000	102
10	Socks	1000	98.2
10	Socks	1000	88.6
10	Wipes	122	89.3
10	Wipes	122	89.3
10	Wipes	122	82.8
10	Wipes	122	84.4
10	Socks	1000	106
15	Filter	97.6	94.7
15	Filter	97.6	107
15	Filter	97.6	97.9
15	Filter	97.6	102
15	Filter	97.6	100
16	Wipes	122	102
16	T-Shirt	4957	103
16	T-Shirt	4957	104
16	T-Shirt	4957	96.7
16	Wipes	122	88.5
16	T-Shirt	4957	102
16	Wipes	122	85.2
16	Socks	1000	91.7
16	Socks	1000	91.4
16	Socks	1000	93.7
16	Socks	1000	87.6
16	Socks	1000	75.6
16	Wipes	122	95.1
16	Wipes	122	95.1
16	T-Shirt	4957	100
31	Filter	97.6	102
31	Filter	97.6	94.9
31	Filter	97.6	95.4
31	Filter	97.6	99.3
31	Filter	97.6	96.6

**Appendix II: Exposure of Hand Applicators to Triclopyr in Forest Settings, 1995**

**Documentation of Protocol and SOP Deviations**

**Protocol Deviations**

<b>Study ID</b>	<b>Date</b>	<b>Protocol Requirement</b>	<b>Deviation</b>	<b>Effect on Study/Sample(s) Involved</b>
JS01, JS02	07/10/95 07/11/95	I., D., 1. Application activities will abide by the label, California Code of Regulations and USFS regulations.	Some workers wore contaminated gloves from previous day or knit gloves which are not allowed by label; some cleaned contaminated nozzles or loaded bare-handed (CCR violation). USFS regulations were not available to study staff nor were we familiar with them to determine compliance.	No effect on study conduct but increased worker exposures. Since deviations are likely to occur, future study protocols should avoid this stipulation.
JS01, JS02	07/05/95	I., D., 17., b): The QAU will audit the study subject consent process.	The QA, D. Meinders, was present on 7/5/95 as were J. Spencer, B. Hernandez and C. Evans. No QA report is available for this inspection phase.	Likely none, but it indicates a lack of control on the part of the study director, who should have requested such a report.
JS01	07/10/95	I. D., 10. A retention sample of sufficient quantity to afford evaluation of the concentration of the active ingredient will be collected from each lot number used during the study and analyzed for the a. i.	The first tank mix of the day contained 65 gallons of mix from the previous day so the lot numbers involved were unknown.	Likely none: samples were collected for the lot number used in the 250 gallons of mix added to the amount previously in the tank. During the two days, only one lot number was used and it is likely that all material used in the study was from this single lot number.
JS01	07/10/95	I. D., 9., a, (7): Inhalation monitoring will be conducted for the duration of each study day.	Worker 3's pump was disconnected for approximately 66 minutes, as he had mistakenly indicated the work day was over.	Likely none: During this time he was either resting or handling the bags but was not spraying. The 66 minutes will be subtracted from the total inhalation monitoring time for the day for this worker.
JS01	07/10/95	I. D., 9., a, (7): Inhalation monitoring will be conducted for the duration of each study day.	Worker 4's pump failed and could not be replaced due to logistics for approximately one hour.	Minimally Negative: Inhalation exposure to the last 7 loads cannot be evaluated. Filter residues were not adjusted. Inhalation is typically only a small component of total exposure.

**Appendix II: Exposure of Hand Applicators to Triclopyr in Forest Settings, 1995**

**Documentation of Protocol and SOP Deviations**

**Protocol Deviations**

<b>Study ID</b>	<b>Date</b>	<b>Protocol Requirement</b>	<b>Deviation</b>	<b>Effect on Study/Sample(s) Involved</b>
JS01	07/10/95	I., D., 9., b), (3), (c): Hand wipes will be taken at meal breaks, at the end of the day and any time the worker wishes to wash these areas.	Worker 1 washed hands under a faucet at 1005.	Negative: A portion of hand exposure may have been lost. Results were not adjusted. Hands are typically a large component of total exposure.
JS02	07/11/95	I., D., 12., a), (1): Filters prepared as field blanks shall be connected in train to an air pump and pumped for the duration of the monitoring period.	The blank (Sample no. JS02-1026) was not pumped. The original blank was spiked in error and no spares were available at the field site.	Minimally positive: An unpumped blank was submitted to the lab. While deviating from the protocol, this blank will better evaluate potential losses in handling, transport, and storage without the pumping time as a confounder.
JS02	07/11/95	I., D., 9., b), (3), (d): The skin wipes for each region will be combined for each worker each day.	Worker 3 placed an end-of-day hand wipe into his face/neck jar, then transferred it to the proper jar.	Minimally negative: The hand wipe may have contaminated the face/neck wipes, resulting in larger values than actual for the face/neck wipes. The degree of contamination is likely to be minimal, however, based on the brevity of the contact. The results will be examined for this possibility.
JS02	07/11/95	I. D., 9., c): Workers will submit all urine voids during the study.	Worker 5 spilled some of his urine sample	Unknown: Sample still had one of the higher volumes recorded for the day, triclopyr acid content was among the lowest three for the day. Data were not adjusted.

**Appendix II: Exposure of Hand Applicators to Triclopyr in Forest Settings, 1995**

**Documentation of Protocol and SOP Deviations**

**SOP Deviations**

<b>Study ID</b>	<b>Date</b>	<b>SOP Number</b>	<b>SOP Requirement</b>	<b>Deviation</b>	<b>Effect on Study/Sample(s) Involved</b>
JS01, JS02	07/10/95 07/11/95	WHS-AD01	Reviews shall be kept current with the stipulated time frames.	The following WHS SOPs had lapsed review periods during this portion of the study: AD01 - AD05, EQ01, EQ17 - EQ19, FO07 - FO08, PS01, PS03, QA01 - QA03, SA01, TS02	Negative: While all pertinent SOPs were followed, the non-adherence to the required review schedule suggests that the controls for the administrative process of initiating and coordinating the necessary reviews are inadequate.
JS01, JS02	02/02/97	CDFA WHS-ST-2	Record preparation of analytical standard in the Standard Book.	Preparation of the triclopyr acid standard was recorded in computer file.	No effect. Preparation of standard was documented.