

WORKER EXPOSURE DURING CAPTAN
APPLICATIONS TO GRAPES

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HS-1511 April 11, 1990

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SUMMARY

Two ground rig mixer/loader applicators were monitored during captan dusting treatments to grapes. Total urine was collected for three days, followed by one day of dermal and inhalation monitoring. Urine samples were analyzed for cis-1,2-dicarboximide-4-cyclohexene (THPI). Dermal and inhalation samples were analyzed for captan.

Breathing zone values for the two workers monitored were 0.05 mg and 0.02 mg for an eight hour workday. The eight hour time-weighted average values are 0.06 mg/m³ and 0.02 mg/m³, well below the American Conference of Governmental Industrial Hygienists Threshold Limit Value- Time Weighted Average Value of 5 mg/m³. Dermal dosimetry from the two monitored workers yielded eight hour dermal exposure values of 22 mg and 10 mg.

All urine collected during the three day sampling period had detectable levels of THPI present, ranging from 20 ug to 147 ug. However, creatinine levels for all urines were below the analytical laboratory's normal range, indicating incomplete collection of 24-hour urines. To estimate THPI levels for a complete 24 hour sample, urinary THPI levels were adjusted, using 1400 mL/24 hours as an average urinary output rate. The calculated values of THPI range from 47 ug to 158 ug. From this range of THPI levels, the daily dermal captan dose is calculated to be from 12 to 41 mg.

The Environmental Protection Agency (EPA) currently uses a generic data base to estimate worker exposure during captan applications. For the work situation during our study, EPA estimates 504 mg dermal exposure, and 48.4 mg inhalation exposure. These estimates are substantially higher than the values obtained from actual exposure monitoring.

INTRODUCTION

Captan is the accepted common name for N-trichloromethyl-thio-4-cyclohexene-1,2-dicarboximide. It is a broad-spectrum fungicide registered since the early 1950's and used on a number of fruit and vegetable crops, plant seeds, and non-food products. The Environmental Protection Agency (EPA) records show registrations for approximately 600 federally registered pesticide products containing captan as an active ingredient (EPA, 1985). There are 124 captan-containing registered products in California, with approximately 761,245 pounds used each year (CDFA, 1987).

A special review process for captan was initiated in 1980, following identification of possible mutagenic and oncogenic effects in several studies (EPA, 1989). Captan has been shown to be mutagenic in in vitro experiments in bacteria, eukaryotic microorganisms, and mammalian cells in culture, but the results are ambiguous in the in vivo experiments. EPA concluded that the risk to humans of heritable mutagenicity is extremely low or non-existent and is not quantitatively extrapolating mutagenic risk to humans in the case of captan. However, EPA has classified captan as a probable human carcinogen based on evidence that it produces oncogenic effects in mice and male rats and therefore may pose a potential risk of cancer to consumers and handlers of treated commodities (EPA, 1989).

Captan is also under review by the California Department of Food and Agriculture (CDFA) risk assessment process due to its inclusion on the list of chemicals of concern generated by Senate Bill 950 (The Birth Defect Prevention Act of 1984).

Also of concern was the potential dermal and inhalation exposure to agricultural workers. EPA used a generic data base to estimate applicator exposure during their review of captan. During the summer of 1988, CDFA conducted a mixer/loader and applicator exposure study to more accurately assess exposure during a captan application to grapes.

MATERIALS AND METHODS

Application:

Captan sulfur 15-40 Dust (EPA # 239-1678 279 AA) was applied at a rate of 25 lb/acre (3.75 lb a.i./acre) by two applicators using duster rigs. These ground rigs are designed with a hopper into which the dust pesticide formulation is added. The dust is blown upward through two vents (located behind the driver) which open approximately seven feet above the ground. Monitored applications began between midnight and 4:00 A.M., and continued until 10:00 A.M.. Applications ended before the daily temperature became too warm in an attempt to prevent foliar damage.

Urine Monitoring:

Seasonal captan applications had begun prior to the investigators' arrival at the site, so no pre-application urine samples were collected. Total 24-hour urines were collected from each applicator for three consecutive days. Several one liter brown Nalgene^R bottles were provided to each applicator. Each day's sample collection began at 7:00 A.M., and ended the following morning at 7:00. The sample schedule did not mimic the application schedule, but the investigators felt that this would not adversely affect the study outcome. At the end of each 24-hour sampling period, each day's output was combined, the volume was recorded, and an aliquot was stored on dry ice. Urine was analyzed for cis-1,2-dicarboximide-4-cyclohexene (THPI), identified by EPA as a metabolite of oncogenic potential (EPA Position Document 4, 1989).

Inhalation Monitoring:

Operator breathing zone (OBZ) samples were collected using an MSA Fixt-Flo^R Model 1 personal air sampler, connected by a length of Tygon tubing to plastic filter cassettes loaded with glass fiber filters, type AE (SKC 225-7). The air pumps were calibrated to draw one liter/minute using a Kurz 540S Mass Flow Calibrator. One pump was attached to each tractor cab, with the filter pointing down, drawing air from the OBZ during the application. After exposure, the cassettes were capped, placed in Ziploc^R bags, and stored on dry ice.

Dermal Monitoring:

Each applicator was monitored for dermal exposure for one day, conducted at the completion of the urine monitoring. Long-sleeve 100 percent cotton T-shirts were given to each worker to wear beneath a pair of clean one-piece cloth coveralls, next to his skin. One hundred percent nylon tube socks, worn beneath the coveralls, served as lower leg dosimeters. Bi-layer patch dosimeters were attached to the front and rear of the coveralls at thigh level. Thigh dosimeters were constructed of an outer layer of polyester/cotton twill, a middle layer of 12-ply 100 percent cotton gauze, and an inner layer of aluminum foil. Dosimeters were encased in a foil-backed holder which allowed an exposed surface area of 23.75 cm².

At the end of the monitored work period, each applicator was given a Chubb's^R brand wipe to clean his hands. He was asked to use the wipe to clean both hands until the wipe was visibly dirty. He then placed the used wipe into a four-ounce glass jar, and repeated the procedure with a clean wipe. Both wipes were analyzed as one sample. After the handwiping procedure was concluded, each worker was given a wipe to clean his face and neck. The procedure was repeated a second time, following the same criteria as outlined for cleaning hands.

Thigh patches were removed and the layers of each dosimeter were separated, with the twill layer considered as one sample, and the gauze and foil layers considered as another. Matched layers from each worker's front thigh dosimeters were combined into one four-ounce glass jar, to be analyzed as one sample. Back thigh dosimeters were treated in an identical manner.

Next, each worker removed his socks and placed them into a one-gallon size Ziploc^R bag. The worker then removed his T-shirt. The sleeves were cut off at the shoulder seam, and placed into a one-gallon Ziploc^R bag. The torso was placed in a separate Ziploc^R bag and submitted as a separate sample.

Using EPA's value of 3820 cm² for the surface area of the thighs, the residue levels from the gauze and foil layers were extrapolated to give a thigh exposure estimate. Values obtained from the T-shirt, handwipe, and face and neck wipe dosimetry were used to estimate the upper body.

All glass sample jars were sealed with aluminum foil, capped, and stored on dry ice. All Ziploc^R bags and Nalgene^R bottles were also stored on dry ice. Each evening, samples were shipped by Greyhound bus to GDFA's laboratory in Sacramento. All samples, with the exception of the urine, were extracted within 24-hours of collection. Urines were stored frozen until analysis. Blanks were submitted for all sample types along with the dermal field samples. The blanks were stored, shipped, and analyzed in the same manner as the actual field samples.

Extraction, Cleanup and Analysis:

The initial captan residue extract was prepared by separately tumbling T-shirt dosimetry with ethyl acetate. Captan residues were extracted from glass fiber filters and hand, face and neck wipes with ethyl acetate. The extract of all media types was then analyzed using a Hewlett-Packard 5880A gas chromatograph with an electron capture detector. The minimum detectable level of captan in all cloth dosimetry was 0.10 ug/mL and recoveries were 98 percent. The minimum detectable level for hand, face and neck wipes was 0.001 ug/sample with recoveries of 99 percent.

Urinary THPI was determined as reported by Winterlin et al., 1984. Twenty-five mL aliquots were extracted with methylene chloride. The methylene chloride extract was passed through a solid phase extraction cartridge (Sep-Pak, Waters Associates), filtered, dried, and taken up in benzene. The extract was analyzed using a Hewlett-Packard 5880A gas chromatograph with a N/P ionization detector. The minimum detectable level of THPI in urine was 0.03 ug/mL and recoveries ranged from 80 to 89 percent.

RESULTS

Operator breathing zone inhalation values for the two workers monitored were 0.19 mg and 0.05 mg. When these five hour results were adjusted to an eight hour workday, the resulting values were 0.32 mg and 0.08 mg, respectively. The eight hour time-weighted average values are 0.06 mg/m³ and 0.02 mg/m³ (Table 2).

Total dermal exposure values for the monitored period (4.75 hours) were 13 mg and 6 mg, adjusted to eight hour values of 22 mg and 10 mg, respectively (Table 2).

All urine collected during the study had detectable levels of THPI present, ranging from 0.034 ppm to 0.113 ppm (20 ug to 147 ug). After adjusting urinary THPI values to an average daily output of 1400 mL hours, THPI values ranged from 47 ug to 158 ug.

DISCUSSION

Although application and mixing/loading are dusty procedures, inhalation contributed very little to the overall exposure. The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value-Time Weighted Average value is 5 mg/m³ (American Conference of Governmental Industrial Hygienists, 1987-1988). The inhalation exposures measured during this study were well below the ACGIH standard.

The majority of worker exposure during the applications monitored was to the legs, especially the lower leg and front thigh. A large part of the lower leg exposure probably occurs during the loading procedure. The applicator cuts open several bags of the captan-sulfur dust and empties them into the hopper. This usually results in spillage around the worker's feet. Also, the application itself is a very dusty process, with a visible cloud of dust billowing above the duster rig. Since the applicator is seated in an open cab, he is likely to come into contact with the settling dust.

All urine collected had creatinine levels below the analytical laboratory's normal range, indicating incomplete collection of 24-hour volume. To estimate THPI levels for complete samples, urinary THPI levels were estimated using two different methods. The first method adjusted the measured creatinine level to an average value of 1500 mg/24 hours, adjusting the measured THPI level accordingly. The second method adjusted the daily urine output to 1400 mL/24 hours, with the THPI level likewise adjusted. In order to check the feasibility of the first method's estimates, the urine volumes necessary to excrete 1500 mL of creatinine within a 24 hour period were calculated (Table 3). These volumes ranged from 3.1 to 18.7 L/24 hours. Because these volumes are not reasonable, THPI estimates based on the second method were used for dermal exposure estimates.

Based upon rat metabolic studies, 85 percent of a captan oral dose would be eliminated within 96 hours, with 15 percent of the urinary metabolites eliminated as THPI (Hoffman et al., 1973 and Maddy et al., 1989). Dermal absorption of captan is fairly rapid, with two percent of an administered dose absorbed per hour. After adjusting for the molecular weight difference between captan (300.61) and THPI (151.18), an estimate of worker exposure can be calculated using the amount of THPI detected from our sampling and assuming an absorption rate of six percent per 24 hours. From the range of THPI levels detected in our sampling (from 20 ug adjusted to 47 ug, to 147 ug adjusted to 158 ug), and assuming a 24 hour absorbed dose, the dermal captan dose is calculated as 12 to 41 mg (Figure 1).

$$\begin{array}{l} 158 \text{ ug THPI in urine} \\ \times \text{ molecular weight (captan/THPI) factor} \\ 316 \text{ ug captan equivalents} \\ \quad / 0.15 \text{ (eliminated dose present as THPI)} \\ 2107 \text{ ug captan equivalent metabolized to THPI} \\ \quad / 0.85 \text{ (percent of absorbed does eliminated)} \\ 2478 \text{ ug captan equivalent absorbed dose} \\ \quad / 0.06 \text{ (absorption rate - 6\% per 24 hours)} \\ 41 \text{ mg dermal exposure - captan equivalents} \end{array}$$

Figure 1. Estimates of dermal captan exposure using THPI urine levels

Our dermal monitoring results estimated dermal exposure to be 22 mg and 10 mg for eight hours of mixing/loading and applying captan. A previous study of dermal exposure to Captan 50W during applications to strawberries estimated the absorbed captan dose at 2.5 mg per day (O'Connell et al, 1989).

The EPA currently uses a generic data base (EPA, 1985) to obtain estimates for worker exposure during captan applications to grapes. For the eight-hour work day, EPA estimates 504 mg dermal exposure, and 48.4 mg inhalation exposure (Table 1).

During our study, the two workers loaded their own rigs in addition to applying. The loading procedure took approximately 15 minutes of every hour of application, for a total of two hours each day. Dermal monitoring was done during an application which lasted just under five hours. In order to compare our results with EPA estimates, the five hour values were extrapolated to eight hour figures. The highest extrapolated dermal and inhalation values are 22 mg and 0.32 mg, respectively (Table 1). Clearly, the data which EPA uses to estimate captan applicator exposure yields higher values than those obtained from dermal dosimetry monitoring. Biological monitoring yielded results very close to those obtained from dermal monitoring.

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TABLE 1
 Applicator Exposure: Surrogate Data vs. Measured Values

EPA estimates of exposure*:

	mixer/loader (mg/2 hr work period)	applicator (mg/6 hr work period)
dermal	360	144
inhalation	12	0.4
total (mg/8 hr work period)		
dermal	504	
inhalation	12.4	

CDFA measures exposure:

mixer/loader and applicator (mg/8 hour work period)		
	applicator #1	applicator #2
dermal	22	10
inhalation	0.32	0.08

* - EPA estimates hourly exposure as follows: mixer/loader - 180 mg/hr dermal, 12 mg/hr inhalation. Applicator - 24 mg/hr dermal, 0.06 mg/hr inhalation. Data from the monitored application, extrapolated to an eight hour day consisted of 2 hours mixing/loading and 6 hour application.

TABLE 2

Captan Mixer/Loader Applicator Exposure
(all results in mg unless noted)

	Applicator #1	Applicator #2
(4.75 Hour Application)		
Shirt:		
torso	0.8	0.7
sleeves	0.7	0.4
Socks:	7.8	2.6
Thigh:		
front	2.4	0.6
rear	0.2	0.1
Neck/face wipe:	0.3	0.1
Hand wipe:	1.1	1.1
Total dermal:	13.3	5.6
Inhalation ^{a)} (mg)	0.19	0.05
TWA value (mg/m ³)	0.06	0.02
Adjusted estimates for eight-hour application:		
Total dermal	22 mg	10 mg
Inhalation	0.32 mg	0.03 mg

a) Calculations assume a ventilation rate of 29 L per minute.

TABLE 3

Urinary THPI Values

	Day 2		Day 3	
	applicator #1	applicator #2	applicator #1	applicator #2
creatinine(mg)	104	128	224	288
actual urine volume (mL)	1300	800	700	600
measured THPI (ug/mL)	0.113	0.079	0.048	0.034
adjusted THPI ^{a)} (ug/24 hours)	2120	738	228	104
adjusted urine ^{b)} volume (mL)	18748	9371	4694	3120
THPI adjusted to 1400 mL/24 hour urine volume (ug/24 hours)	158	110	68	47

a) THPI value was adjusted, using 1500 mg/24 hours as an average creatinine excretion rate

b) Urine volume was adjusted to indicate 24 hour urine volume needed to excrete 1500 mg/24 hours