Shaughnessy #: 059101

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To: Dennis Edwards
Product Manager #12
Registration Division (TS-767C)

From: Michael Firestone, Acting Chief
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Hazard Evaluation Division (TS-769C)

Attached, please find the EAB review of...

Reg./File No.: 464-404

Chemical: Chlorpyrifos

Type Product: Insecticide

Product Name: Dursban 4E

Company Name: Dow Chemical USA

Submission Purpose: Support of the existing registration of the Dow turf insecticide line of products

ACTION CODE: 605

Date In: 12 FEB 87 EAB #: 70260

Date Completed: 28 AUG 87 TAIS Code:

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

XX Toxicology Branch

_____ Benefits and Use Division

Monitoring study requested by EAB: /___/

Monitoring study voluntarily conducted by registrant: /XXX/

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1.0 INTRODUCTION

Dow Chemical USA has submitted an exposure assessment for applicators of chlorpyrifos (Dursban 4E) to turf. This submission is in support of the existing registration of the Dow turf insecticide line of products.

2.0 DISCUSSION OF DATA

Dow conducted an exposure assessment measuring both respiratory and dermal exposure to chlorpyrifos. The company used Dursban 4E, a 4 lb/gal emulsifiable concentrate for the study. The application rate was approximately 1.1 lb ai/A. There were a total of six replicates measured in this study and no protective clothing was employed by the applicators. The mean area sprayed by each applicator was 49,000 ft^2/hr. Dow estimates that an applicator will apply 1000 gallons of finished spray solution to 250,000 ft^2 per day. Therefore, an average applicator will be applying chlorpyrifos for 5 hours per day [(250,000 ft^2/day)/(49,000 ft^2/hr) = 5 hr/day]. No data were provided for exposure via mixing/loading. Therefore, surrogate data will be employed to estimate exposure to mixer/loaders. A number of assumptions will be necessary for this assessment. They are:

1. An average worker has a mass of 70 kg.

2. Exposure is not corrected for dermal absorption.

3. Total spray time is five (5) hours per day.

Specific study information is provided below.

2.1 METHODS: RESPIRATORY EXPOSURE

Dow estimated respiratory exposure by calculating short-term time weighted average exposures for six replicates during routine application of chlorpyrifos. Dow employed battery operated DuPont P-200 vacuum pumps which were used to draw air through 150 mg of chromosorb 102 solid sorbent contained in glass tubes. The approximate air flow rates were 200 cc/min. Each sample trial was conducted over 30 minutes of actual spray time. Dow defined spray time to be from the time the hose was uncoiled until the hose was completely recoiled back on the truck. When the initial 30-minute trial was concluded, the tube was removed, capped and stored for future analysis. A new tube was then attached and used for the second trial. The chromosorb 102 was extracted with hexane and analyzed by GC using Electron Capture detection.

2.2 METHODS: DERMAL EXPOSURE

Dow estimated dermal exposure by placing 2" x 2" gauze pads at various locations of the body. Hand exposure was measured by using cotton glove liners. As with the respiratory measurements, two 30-minute trials were conducted. The patches were attached with safety pins to the outside of the uniform. Each pad had a small piece of 2 mil polyethylene behind it to prevent contamination of the patches by the contaminated clothing. The patches were located at the following areas: sternum, fly, back and front of each thigh, and back and front of each calf. No measurements were made of arm, neck, head, or back exposure. After the first 30-minute spray trial, both the gauze pads and the glove liners were removed and replaced. The gauze pads were put into narrow analysis vials with screw tops while the glove liners were placed in dark bottles with polyseal caps. Both were later desorbed with hexane and analyzed by GC. The liners were sufficiently heavy that appreciable absortion into the weave could be obtained. A total of six replicates were employed.

2.3 QUALITY ASSURANCE

The chromosorb 102 tubes, glove liners and gauze patches were all spiked in the field with known amounts of chlorpyrifos using a microliter syringe and stock solutions of 0.094 ug/uL and 0.94 ug/uL of chlorpyrifos. The recovery of chlorpyrifos from fortified samples ranged from 80 to 106% of the spiked value.

2.4 RESULTS: RESPIRATORY EXPOSURE

The short-term time weighted averages (TWAs) are presented in Table 1 of the Dow report. Two sets of values are presented, one for each 30-minute trial. Therefore, for each replicate, the mean of the two values will be used for the TWA. Replicate #3 only had one measured TWA so that given value will be used. Using the standard breathing rates found in Subdivision U of the Pesticide Assessment Guidelines, assuming light work (29 L/min), the following exposures can be calculated:

Replicate	TWA (ug/m^3)	Exposure (ug/hr)
1	2.7	4.7
2	1.7	3.0
3	1.2	2.1
4	2.4	4.2
5	1.1	1.9
6	2.3	4.0

Sample calculation:
$2.7\ ug/m^3 \times 1\ m^3/1000\ L \times 29\ L/min \times 60\ min/hr = 4.7\ ug/hr$

The range of exposures was 1.9-4.7 ug/hr with a mean of 3.3 ug/hr. Assuming a 5 hr workday, applicator exposure would be expected to average 16.5 ug/day. For a 70 kg individual, exposure would be 0.24 ug/kg/day.

2.5 RESULTS: DERMAL EXPOSURE

The values for the residues of chlorpyrifos recovered from the gauze pads and glove liners are presented in Tables 2-4 of the Dow report. Hand exposure was measured directly by the use of cotton glove liners. Therefore, the values presented (in mg) are considered to represent the whole hand. The sum of the values of the two 30-minute trials gives hand exposure in mg/hr. The results are presented below:

Replicate Number	Right Hand (mg/hr)	Left Hand (mg/hr)	Both Hands (mg/hr)
1	10.94	7.57	18.51
2	23.00	2.33	25.33
3	16.30	1.27	17.57
4	14.85	0.67	15.52
5	10.64	2.64	13.28
6	15.41	2.60	18.01
Mean	15	2.8	18

These data indicate that exposure was much greater for the right hand as compared to the left hand (as much as 22 times higher). This disparity can be accounted for by assuming that the applicators were all right-handed and, as such, exposed their right hands to contamination from the spray nozzle due to the close proximity of the hand to the nozzle.

The body exposure was presented as ug/patch/hr. The data are presented below:

Patch Area	Rep 1	Rep 2	Rep 3	Rep 4	Rep 5	Rep 6	Median
Sternum	3.0	0.8	0.5	2.4	0.4	1.9	1.4
Groin	2.4	1.7	5.3	12.5	11.3	16.3	8.3
L thigh	27.5	24.0	10.1	52.6	111.1	242.6	40
L thigh (b)	2.4	97.3	10.6	4.2	37.0	94.1	24
R thigh	24.5	38.5	24.7	114.6	24.7	116.8	39
R thigh (b)	36.5	210.4	12.9	31.3	5.1	34.5	33
L calf	450.2	313.1	247.2	302.2	127.2	175.8	270
L calf (b)	64.5	21.4	45.2	66.5	92.3	34.5	55
R calf	446.5	443.5	296.5	379.8	193.1	472.8	410
R calf (b)	87.3	25.4	34.9	45.3	27.9	11.1	31

One major flaw of this study is the lack of upper body data. No data were presented with which to estimate neck, arm (upper and lower), back or head exposure. Therefore, several assumptions must be made in order to estimate such exposure. These assumptions are as follows: 1) hand exposure values (in ug/cm^2) will be used to estimate forearm exposure; 2) the mean of hand exposure (in ug/cm^2) and the sternum pad will be used to estimate upper arm exposure; 3) back exposure will be calculated as 40% of chest exposure (this is based on the ratio of back to front exposure as seen on the thigh and calf pads); and head and neck exposures will be calculated from the sternum pad and back exposure (in ug/cm^2). These assumptions may grossly overestimate upper body exposure but, in the absence of sufficient data, they will be deemed acceptable.

Where two patches were used to measure exposure, the mean of the two pads will be used to calculate exposure. Each patch was 2" x 2" which is approximately 25.81 cm^2. Using the body surface areas found in Subdivision U of the Pesticide Assessment Guidelines, the following exposures can be calculated:

Body Part	Surface Area (cm^2)	ug/pad/hr	ug/cm^2/hr	ug/body part/hr	ug/body part/day*
Chest	3550	4.9	0.19	670	3.4×10^2
Back	3550	2.0	0.077	270	1.4×10^2
Neck, front	150	1.4	0.054	8.1	4.1×10^1
Neck, back	110	0.56	0.022	2.4	1.2×10^1
Head	1300	0.98	0.038	49	2.5×10^2
Upper arm, R	1455	---	18	26000	1.3×10^5
Upper arm, L	1455	---	3.4	4900	2.5×10^4
Forearm, R	605	---	36	22000	1.1×10^5
Forearm, L	605	---	6.8	4100	2.1×10^4
Hand, R	410	---	36	15000	7.5×10^4
Hand, L	410	---	6.8	2800	1.4×10^4
Thigh, R	1910	36	1.4	2700	1.4×10^4
Thigh, L	1910	32	1.2	2300	1.2×10^4
Calf, R	1190	220	8.5	10000	5.0×10^4
Calf, L	1190	160	6.2	7400	3.7×10^4
TOTAL				98000	4.9×10^5

*Based on a 5 hour workday.

$$\text{Dermal Exposure} = \frac{4.9 \times 10^5 \text{ ug/day}}{70 \text{ kg individual}} = 7.0 \times 10^3 \text{ ug/kg/day}.$$

Converting to mg/hr, the total body exposure is 98 mg/hr or 4900 mg/day. This estimate is based on 100% absorption of

chlorpyrifos by the skin and does not take into account the protective value of clothing. Clothing can be estimated to reduce exposure by roughly 50% to covered areas. EAB will assume that applicators wore short-sleeved shirts and long pants. With this assumption, the exposure to chlorpyrifos is reduced to 71 mg/hr or 360 mg/day; for a 70 kg individual, exposure is estimated to be 5.1 mg/kg/day. Hand exposure accounts for 31% of this exposure. The use of protective gloves could reduce hand exposure by up to 90%. Assuming that such gloves are worn, exposure is reduced to 55 mg/hr or 270 mg/day; for a 70 kg individual, exposure is 3.9 mg/kg/day.

2.5 SURROGATE MIXER/LOADER DATA

The Dow study reflected the use of chlorpyrifos as a 4 lb/gal emulsifiable concentrate (Dursban 4E) mixed as 1 gal + 40 fl oz (1.31 gal) of Dursban into 800 total gallons. A total of 4 gallons of finished spray is needed to cover each 1000 ft^2. Considering the above, the following application rate can be derived:

$$\frac{1.31 \text{ gal Dursban 4E}}{800 \text{ gal solution}} \times \frac{4 \text{ lb ai chlorpyrifos}}{1 \text{ gal Dursban 4E}} = 6.55 \times 10^{-3} \text{ lb ai/ga}$$

$$6.55 \times 10^{-3} \text{ lb ai/gal} \times 4 \text{ gal}/1000 \text{ ft}^2 = 2.62 \times 10^{-5} \text{ lb ai/ft}^2$$

$$2.62 \times 10^{-5} \text{ lb ai/ft}^2 \times 1 \text{ ft}^2/2.295684 \times 10^{-5} \text{ A} = 1.14 \text{ lb ai/A}$$

EAB utilized three articles found in the published literature to estimate mixer/loader exposure. These exposures were calculated assuming that the mixer/loader wore normal work attire consisting of a long-sleeved shirt and long pants as well as protective gloves. If actual hand exposure under the protective gloves was not measured, EAB assumed that exposure to the unprotected hand would be reduced 90% by protective gloves. If actual measurements of exposure under clothing were not measured, EAB assumed that clothing provided 50% protection to covered areas.

The exposure during open pour mixing/loading is 0.93 mg/lb ai based on 18 replicates in a study by Abbott, et al. (1987). The exposure during closed system mixing/loading is 0.015 mg/lb ai based on 9 Dubelman, et al. (1982), and 9 Peoples, et al. (1979), replicates.

Treating 250,000 ft^2 per day at a rate of 2.62×10^{-5} lb ai/ft^2 will require 6.55 lb ai. Therefore, assuming a 70 kg individual, the following exposures can be calculated.

Open Pour Mixing/Loading

$$\frac{0.93 \text{ mg/lb ai} \times 6.55 \text{ lb ai/day}}{70 \text{ kg individual}} = 8.7 \times 10^{-2} \text{ mg/kg/day}$$

Closed System Mixing/Loading

$$\frac{0.015 \text{ mg/lb ai} \times 6.55 \text{ lb ai/day}}{70 \text{ kg individual}} = 1.4 \times 10^{-3} \text{ mg/kg/day}$$

3.0 DISCUSSION

The registrant has recommended that applicators wear permeation resistant gloves (especially when recoiling the hose), impervious pants and permeation resistant footwear such as neoprene boots in an effort to reduce exposure. EAB agrees with this recommendation. However, EAB is concerned that no upper body data were presented in this report. While it may be true that lower body and hand exposure are the major components of dermal exposure in this type of application, without any data to quantify upper body exposure, EAB must assume that such upper body exposure exists and may be significant. The extrapolations to upper body exposure presented in this report may overestimate such exposure but they are needed to provide some sort of exposure estimates for these regions. EAB would rather overestimate than underestimate exposure to these areas. Therefore, the registrant may wish to submit another study that quantifies upper body as well as lower body exposure to show if upper body exposure is negligible compared to lower body exposure. Mixer/loader data should also be presented in such a study. Study guidance can be found in Subdivision U of the Pesticide Assessment Guidelines. A protocol outlining the study should be submitted to the Agency for review and approval by EAB prior to study initiation.

4.0 CONCLUSIONS

EAB has estimated exposure to applicators to be 0.24 ug/kg/day for respiratory and 5.1 mg/kg/day for dermal. The use of protective gloves would reduce dermal exposure to 3.9 mg/kg/day. Mixer/loader exposure is estimated to be 8.7×10^{-2} mg/kg/day for open pour and 1.4×10^{-3} mg/kg/day for closed system.

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REFERENCES

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2. Dubelman, S., et al. 1982. "Operator Exposure Measurements During Application of the Herbicide Diallate." J. Agric. Food Chem. 30:375-381.

3. Peoples, S. A., et al. 1979. Monitoring of Potential Occupational Exposure of Mixer/Loaders, Pilots, and Flaggers During Application of Tributyl Phosphorotrithioate (DEF) and Tributyl Phosphorothioate (Folex) to Cotton Fields in the San Joaquin Valley of California in 1979. Report HS-676, Worker Health and Safety Unit, California Department of Food and Agriculture. 34 pp.