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Potential Exposure of Commercial Seed-treating Applicators to the Pesticides Carboxin-Thiram and Lindane

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Small grain cereals, primarily wheat. barley and oats, have been treated with various fungicidal compounds to control smuts and other seed and seedling pathogens for most of the 20th century. Until 1970 the most widely used compounds were organic mercurials applied primarily by commercial seed treaters. However, since 1978 the interstate shipment of organic mercurials has been banned requiring that non-mercury compounds be used for seed treatment (MATHRE et al. 1982). Lindane seed treatment of small grains is used to decrease stand loss attributable to seedling-damaging insects.

The use of commercial seed treating stations has been and continues to be a common practice. Some equipment is available which can treat over 50,000 kg of grain/h. There is little, if any, data available on the exposure of the personnel working in commercial seed facilities, though STEVENS & DAVIS (1981) have reported on exposure to captan during the conditioning of seed potatoes.

Our purpose was to determine the dermal and respiratory exposure of personnel operating commercial seed treating equipment in facilities ranging from newly constructed modern buildings to treating stations in older grain elevators. The fungicides applied were liquid-flowable formulations containing thiram (tetramethylthioperoxydicarbonic diamide) and carboxin (5,6-dihydro-2-methyl-N-phenyl-1,4-oxathiin-3-carboxamide). The use of a maneb (manganese ethylenebisdithiocarbamate) plus the insecticide lindane (gamma isomer of 1,2,3,4,5.6-hexachlorocyclohexane) dust treatment was monitored in two situations.

MATERIALS AND METHODS

Eight different commercial seed conditioning operations were visited in Montana during 1981-82. Since each individual operation tested was unique, a site by site description of each is presented.

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TABLE 1. Dermal and respiratory exposure to carboxin and thiram during commercial cereal seed treating operations using liquid formulations.

		Dermal Exposure (mg/h)			Respiratory Exposure (mg/h)
Site#	Fungicide	Chest	Arm	Hands	
1.	Thiram	ND*	ND	3.70	ND
	Carboxin	ND	ND	8.20	ND
2.	Thiram	ND	ND	1.34	--**
	Carboxin	ND	ND	2.40	--**
3.	Thiram	ND	ND	ND	--**
	Carboxin	ND	ND	ND	--**
4.	Thiram	ND	ND	ND	ND
	Carboxin	ND	ND	ND	ND
5.	Thiram	ND	ND	2.24	0.75
	Carboxin	ND	ND	2.24	0.88
6.	Thiram	ND	ND	ND	ND
	Carboxin	ND	ND	ND	ND
7.	Thiram	ND	ND	ND	ND
	Carboxin	ND	ND	.90	ND
8.	Thiram	ND	ND	2.52	ND
	Carboxin	ND	ND	8.62	ND

*ND = not detectable, i.e., below 0.5 mg.
** = not tested

TABLE 2. Dermal and respiratory exposure to lindane during commercial seed treating operations using a dust formulation of maneb plus lindane.

	Dermal Exposure (mg/h)			Respiratory Exposure (mg/h)
Site #	Chest	Arm	Hands	
9	ND*	ND	81.42	0.36
10	ND	ND	54.80	0.54

* ND = Not detectable, i.e., below 0.1 mg.

Site #1 was a small one-man operation involved with cleaning, treating and weighing of grain. A liquid formulation of carboxin-thiram was applied with a Panogen trip lever barrel treater at a rate of 3666 kg grain/h. A major exposure occurred when the operator used his bare hand to remove excess treated grain from the barrel of the treater.

Site #2 was a small operation involved with cleaning, conditioning and storing grain. A Panogen trip lever barrel treater was used to apply carboxin-thiram. Approximately 2,200 kg of barley were treated/h. The operator wore gloves when cleaning out the barrel of the treater.

Site #3 was a small elevator which stores grain and sells seed in addition to cleaning and treating grain. A Panogen trip lever barrel treater was used to apply carboxin-thiram, conditioning about 3,200 kg grain/h. The operator wore gloves although he was asked to remove his gloves afterwards for the ethanol handshake (DURHAM & WOLFE 1962).

Site #4 was a small operation involved with grain storage in addition to cleaning and treating. A four year old Gustafson S-1000 treater was used to apply carboxin-thiram. Approximately 5,500 kg of barley was conditioned/h. The operator only wore rubber gloves during the transfer of fungicide from a new barrel to the existing pump system.

Site #5 was an Experiment Station involved in bagging treated grain. This was in contrast to the first four sites where the treated grain was placed unbagged directly into the truck box. A Gustafson Mist-o-Matic treater was used to apply carboxin-thiram at the rate of 100 27 kg bags/h. During the bagging operation, the applicator stood directly below a discharge chute holding open a bag which received the grain . The treated grain fell at a high speed and as it hit the bottom of the bag, the dust and residual fungicide blew back out of the bag and into the applicator's face. The applicator did not normally wear a respirator or gloves but did wear a respirator with the exposure pads for purposes of this study.

Site #6 was a one year old seed cleaning and treating plant. A Gustafson S-1000 treater was used to apply carboxin-thiram at the rate of 58,000 kg/h.

Site #7 was a new cleaning and treating plant which used a Gustafson S-1000 treater to apply carboxin-thiram. The wheat was treated at a rate of 17,000 kg/h.

Site #8 was a large cleaning and treating plant utilizing a Gustafson S-1000 treater to apply Cargill RTU-1010 (10% carboxin-10% thiram) formulation. A total of 13,800 kg of wheat was treated in one h. Two commercial seed cleaning machines were utilized and allowed the S-1000 treater to be operated at high speed thereby shortening the total exposure to fungicides. The applicator constantly checked the grain with bare hands to determine the application uniformity of red pigmented fungicide on the seed. However, he did wear rubbber gloves when changing fungicide barrels.

Sites #9 and #10 both used a dust formulation of maneb-lindane. Site #9 was a large seed cleaning and treating operation which utilized a hopper box attached to a Gustafson auger treater. Approximately 19,411 kg/h of wheat were processed. The applicator, when opening the 4.5 kg bag of seed treatment formulation, was exposed to fungicide dust when it was emptied into the hopper of the treater, during the mixing and discharge of treated grain into the truck box.

Site #10 was a large modern seed cleaning and treating plant. A dust formulation of maneb plus lindane was applied with a hopper box attached to a Gustafson S-1000 treater at a rate of 17,800 kg of wheat/h. The operator wore a paper respirator because of the nasal irritation experienced with the dust formulation. However, he checked the uniformity of application using his bare hands.

Dermal exposure was measured by methods similar to those described by DAVIS (1980) and DURHAM & WOLFE (1962). Dermal exposure pads were constructed as follows: Brown wrapping paper was cut in square pieces, with dimensions of 17.5 x 17.5 cm. On top of each square was placed a square piece of Whatman B-2 analytical weighing paper cut to 100 cm^2 followed by a 100 cm^2 piece of commercially washed chromatography filter paper. The chromatography filter paper was free of any interfering products which might be extracted during the chemical analysis. Twelve single layers of alpha-cellulose were cut into a 12.5cm square pad and were placed on the filter paper. The brown wrapping paper was folded and sealed with masking tape. The finished exposed area of the gauze was approximately 25 cm^2.

A dermal exposure pad was fixed to the outside of the upper shirt sleeve with masking tape. A second pad was placed on the chest portion of the applicator's shirt opposite the arm which carried an exposure pad. Immediately after the applicator had completed his normal application, the 25 cm^2 exposure area of the pads was removed and the gauze, filter paper, and weighing paper were placed in a 500 ml Erlenmeyer flask. The wrapping paper was discarded. Each flask was labelled according to the body location, the site where the sample was taken, and the fungicide used during application.

Exposure to hands was determined using the handshake technique (DURHAM & WOLFE 1962). The applicator's hand was shaken in 95% ethanol for one min to extract the residues. The ethanol-residue solution was then placed immediately into a 500 ml Erlenmeyer flask, sealed with aluminum foil and taped for transport to the analytical laboratory .

A Comfo II custom respirator, type F-Part #359440 (Mine Safety Appliances Co., Pittsburgh, PA) was used to sample respiratory air during the treating operation. Respirator pads were prepared as follows: An 8 cm diameter circular Whatman 1 filter paper was placed in the filter holder closest to the mouth of the applicator. Next an alpha cellulose pad 8 cm in diameter with 12 single gauze layers was placed on the filter paper in the respirator. The operators did not complain of any difficulties in breathing through this respirator. Following exposure, the two respirator pads were removed and placed together in one Erlenmeyer flask.

No sample cleanup was necessary due to the freedom from extraneous materials. The 500 ml Erlenmeyer flasks with the exposure pads were taken to the laboratory where 100 ml of CH_3CN were added, and then shaken for 30 min on a wrist-action shaker. The solvent was decanted into a Kuderna-Danish (KD) Evaporative Concentrator flask and the pad extracted once again by repeating the above procedure. The combined extracts were concentrated to 5-10 ml on a steam bath, cooled, and the final volume recorded.

The procedure for analyzing the handshake sample was similar to that described above except that the ethanol rinse was added directly to a K.D. flask and reduced in volume to 5-10 mls, cooled and final volume recorded.

Analyses for carboxin and thiram were performed on a Waters Associates High Pressure Liquid Chromatograph (HPLC), with a model 450 UV detector. Sample solutions and appropriate standards were injected into the HPLC using the following instrument parameters: Injection volume - 10 ul; flow rate - 1.0 ml min^{-1}; chart speed - 0.5 cm min^{-1}; attenuation - 1.0 AUFS;mobile phase - 55% methanol, 5% acetonitrile, 40% deionized water; temperature - ambient; detector wavelength - 254 nm. The column used was a Zorbax C-18, 4.6 m x 25 cm, 5-6 um. A Waters Assoc. Model 730 Data Module was programmed for quantitation by external standard calculation using peak area. The detection limit of carboxin and thiram was 0.5 mg/pad and ethanol handshake.

For lindane analysis the exposed pads were extracted with 100 ml of petroleum ether for fifteen minutes on a wrist action shaker. The liquid was decanted into a K.D. flask and the extraction process repeated. The extracts were combined, concentrated to a 5-6 ml and the volume adjusted to exactly 10 ml with petroleum ether. The ethanol hand wash solutions with lindane were transferred to a K.D. flask, reduced to a 5-6 ml volume and made up to 10 ml volume with ethanol.

Lindane residues were analyzed by gas liquid chromatography. Varian Model 3700, using a flame ionization detector. The column dimensions were 2 mm inside diameter by 1.8 m length glass packed with 3% OV-101 on Gas Chrom Q 100 - 120 mesh. Column, inlet and detector temperatures were 160°, 220° and 330° C, respectively; carrier, 30 ml/min. N_2. The detection limit for lindane was 0.1 mg per pad or ethanol handshake.

Recoveries of standard materials from ethanol solutions fortified with 7.5 mg thiram and 3.4 mg carboxin were 99.7 and 100.6%, respectively. Accuracy and reliability of analytical procedures for each site were determined by using a fortified pad. This involved placement of a known quantity of the formulation used at a given site on an exposed pad. This pad ws carried to the analytical lab along with the pads exposed in the treating stations. Recovery from the fortified pads from eight testing sites was 73 ± 14% and 78 ± 11% for carboxin and thiram, respectively. Detection limits were 0.5 mg/25 cm^2 pad for both carboxin and thiram. All pads were analyzed within 4 days after their exposure at a treating site. For lindane, the detection limit was 0.1 mg/25 cm^2 pad with a recovery of 101 ± 5% from fortified pads.

RESULTS AND DISCUSSION

For those sites where a liquid formulation of carboxin-thiram was used, the dermal exposure on the chest and arms was below the detectable limit of 0.5 mg (Table 1). For sites #1, 2, 5 and 8 where both thiram and carboxin were detectable on the hands, all of the operators had handled treated grain with their bare hands. Respiratory exposure could be documented only in the case where the treated grain was being caught in individual bags (site #5). For two sites (#1 and #4) where fungicide dust from the treatment operation could be seen, no measurable amount of either carboxin or thiram was detected on the respirator pads.

For the two situations involving lindane, no exposure was detectable on the chest and arm pads (Table 2). However, lindane was detected on the hands and on the respirator pads. Workers involved with lindane did complain of nasal irritation if they did not wear a respirator or mask.

Our study suggests that, overall, the application of pesticides as seed treatments in commercial treating operations is a relatively safe operation. Minimal exposure to the operator will result if two simple precautions are observed: (1) wearing of gloves and (2) wearing a respirator when the operator is near the treating operation. We suggest that this operation can continue with minimal pesticide exposure to the operator of a seed treating facility.

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