A STUDY OF THE DERMAL AND INHALATION EXPOSURE OF LOADERS, PILOTS AND FLAGGERS TO ORDRAM IN COLUSA COUNTY IN MAY 1981

by

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Summary

Potential inhalation and dermal exposure of loaders, pilots, and flaggers to a granular formulation of Ordram during rice field applications were measured in Colusa County in May 1981. Exposure to Ordram was measured during two 2-hour work periods. It was estimated that loaders were exposed to 20.9 to 24.5 milligrams; exposure to pilots was estimated to be 0.03 to 0.29. milligrams; exposure to flaggers was estimated to be 0.01 to 0.44 milligrams. There is no Federal or State occupational exposure standard for Ordram. It appears there would be an adequate margin of safety from potential adverse reproductive effects for male pilots and flaggers for a 2-hour period of exposure daily. There may not be an adequate margin of safety for loaders from excessive dust released from the granules of Ordram, the data on adverse reproductive effects on male rats can be extrapolated directly to man on a milligram per kilogram basis. New data under development, however, suggests that rats are much more sensitive to this effect than primates. Data developed in studies with primates may be more applicable to humans. Until this is resolved, the exposure to pesticide loaders of Ordram should be considerably reduced.

Introduction

Ordram is a Toxicity Category 3 selective herbicide which contains the active ingredient, molinate (S-ethyl hexahydro-1-H-azepine carbothioate, CAS 2212-67-1), and is used on rice for the control of watergrass. It is typically applied aerially as 10 percent granular formulation (Ordram 10G) in California. Ordram has not been considered a hazardous product capable of causing significant acute or chronic illness. No illnesses with delayed onset or deaths are known to have occurred from exposure to Ordram. No cases of human cancer or damage to human embryos, due to Ordram exposure, have been documented.

The acute oral LD_{50} of Ordram is reported as 501-720 mg/kg (Ben-Dyke, et al, 1970 and Jones, et al, 1968). The acute dermal LD_{50} in rats is reported as 1167 mg/kg. This author also reported that an inhalation dose of 2 mg/m^3 (duration unspecified) produced no effect (Dyadicheva, 1970).

A subacute inhalation study reported that rats, exposed to 113 mg/m^3 for 1 month, exhibited depressed activity, decreased body weight, increased blood pyruvate levels, transient leukocytosis, and a slight decrease of neutrophilic phagocyte activity. Rats exposed to 4.5 mg/m^3 for 4 months exhibited transient increases in thyroid function and white blood cell counts. An increase in 17-ketosteroid excretion was also noted. Relative organ weights remained unchanged (Dyadicheva, 1971).

Subacute oral exposure in the rat (1/20 of the LD_{50} for 4 months) resulted in slight effects on thyroid and adrenocortical functions (Dyadicheva, 1971), reduced phagocytic activity of the blood and reduced antibody formation although the immunoprotective properties of the blood were considered unaffected (Olefir, 1971, 1973).

A mutagen assay in a microbial system revealed that Ordram exhibits no mutagenic effects (Shirasu, et al, 1976). Studies in rats have revealed that Ordram administered orally at 3.6 mg/kg/day for 2 months decreased the motility and viability of spermatozoids in males and fertility in females (Anina, et al, 1975).

Data on file from the Stauffer Chemical Company reported a reproduction no-effect level of 0.2 mg/kg/day (from a 3-generation reproductive study in rats).

Stauffer Chemical Company toxicology data also reported a chronic no-effect level of 7.2 mg/kg/day in a 93-week feeding study in mice.

Ordram is rapidly metabolized and excreted; excretion is almost complete 48 hours after administration, with metabolites predominantly found in the urine (deBaun, et al, 1978).

Concerns over potential reproductive effects of Ordram led the manufacturer (Stauffer Chemical Company), to initiate studies monitoring pesticide formulation workers and pesticide applicators for potential exposure and potential reduction in sperm counts and motility. The California

Department of Food and Agriculture decided to initiate an exposure study on pesticide applicators for comparison of exposure levels between formulation workers and applicators.

Materials And Methods

The aerial application firm selected for the study had a record of good compliance with the Department's pesticide regulations; this included factors such as being a licensed pest control operator, using licensed pilots and providing clean clothes daily for workers. Ordram 10G came packaged in 50 pound bags and was loaded manually onto the plane. The loading procedure consisted of breaking the bags into a large hopper mounted on a hydraulic lift mounted on a truck. The hopper mounted on the truck has a coarse screen and a large sawtooth blade welded across the top. One loader stood on the flatbed truck that held the palleted bags of material and tossed the bags onto the blade. A second loader stood on the hopper,lifted the ends of bags, discharging the material into the hopper and tossed the bags off to the side for final disposal.

Preparing a hopper-load for the plane required approximately 10 minutes. Each load was approximately 1,600 pounds of material (32 50-pound bags of Ordram 10G).

Loading the material from the truck onto the plane consisted of the loader pulling the canvas neck down over the plane's hopper and pulling a lever mounted on the truck's hopper discharging the material into the plane's hopper The loader stood on the wing of the plane and held open the canvas neck over the hopper, ensuring that the material flowed in the proper direction.

The plane used was a Turbo-Thrush equipped with an air-conditioned closed cockpit. The left cockpit door was opened while the plane was on the ground reloading or refueling, but closed while airborne. The pilot stayed in the cockpit while on the ground except for 1 occasion when he exited to clean the windshield of the plane.

The application firm normally applied Ordram for the first 2 hours in the morning then spent the balance of the day applying fertilizer or seeding rice.

The pilot wore a T-shirt, long pants, socks and street shoes. The flaggers wore short-sleeved shirts, undershirts, long pants, socks, street shoes, and jackets. The loaders wore shirts, undershirts, long pants, socks and street shoes. They were furnished with clean coveralls each day. None of the workers involved wore rubber gloves, boots, or respirators.

Potential inhalation exposure was measured using a DuPont Constant Flow Sampler P-4000 personnel sampling pump with a Tygon air intake hose attached to the lapel of the worker's upper garment, underneath the chin.

In the air intake line, air sampling tubes, containing XAD-4 porous polymer resin (SKC #226-30-11-04), were inserted. The flow rate was 1 liter per minute. Flow rates were calibrated using a Kurz 540S flow calibrator.

Potential dermal exposure was measured using pads according to the method of Durham and Wolfe, 1962. Pads were constructed in the following sequence, from inner to outer layers: (1) 1 sheet of paper, (2) 1 sheet of aluminum foil, (3) a layer of 8 pieces of gauze and (4) a layer of cloth (35% Cotton, 65% Dacron Polyester). The cloth and the gauze were pre-extracted with nanograde hexane and acetone to remove interferences. The pads measured 4 inches on a side and were bound together by taping the perimeter with masking tape. A 49 cm^2 area was marked on the paper layer using a square template to standardize the area of exposure being determined.

The pads were attached to coveralls or clothing with safety pins. Pads were mounted on exposed skin areas by being pinned to athletic sweat bands which were pulled over the exposed skin area.

Pads were located on the back of the neck, on the center of the chest, on the arms above the elbow and on the thighs.

At the end of the work shift, the air sampling tubes were capped and placed in a glass jar. Each day's air samples also contained a blank shipping control tube which was treated identically to exposed tubes. The pads were removed from the workers, the taped edges were cut off and each gauze plus foil backing and cloth pad was carefully separated and placed in separate glass jars. Matched pairs of pads were placed in the same jar (i.e., the cloth from left and right arms were combined in the same jar and the gauze from the left and right arms were combined in the same jar). The scissors used to cut the pads were rinsed with 95 percent ethanol between samples.

Potential exposure to workers' hands was determined by washing the hands with 250 ml of distilled water discharged from a separatory funnel into a steel bowl. The bowl was rinsed between samples with 95 percent ethanol and distilled water. The handwash water was transferred to glass jars. All sample jars were capped with aluminum foil and screw caps, refrigerated with blue-ice packages and brought to California Department of Food and Agriculture's Chemistry Laboratory Services in Sacramento within 48 hours of sampling. All samples were analyzed for Ordram by gas-liquid chromatography.

Blank samples of handwash water and exposure pads were prepared at the time all samples were prepared for shipping. These were handled in a manner identical to all other samples. Analysis of all blank samples revealed no detectable residues.

Results

The results of the various experimental data and information are summarized in the following tables:

Table 1 - Air concentration levels monitored for inhalation exposure of various workers. Inhalation exposure for an average 2-hour workshift was estimated by assuming a 33 liters/minute (1.98 m^3/hour) respiratory rate for male loaders and an average 14 liters/minute (0.84 m^3/hour) for male and female flaggers. Male pilots were considered to have a respiratory rate similar to male flaggers, 18 liters/minute (1.08 m^3/hour) (EPA-600/8-80-038).

Absorption of inhaled molinate by the lung was assumed to be 100 percent.

Tables 2, 3, and 4 - The dermal exposure of workers determined by sampling pads. Column A is the sampling period. Column D is an estimate of the average area of skin of each part of the body in square centimeters according to Berkow (1931) and DuBois and DuBois (1916), assuming an average person weighing 60 kg and standing 170 cm. This average is lower than a commonly used average, 70 kg and 175 cm (HS-676) because the application crew was composed of men and women. Column C is the result of Ordram exposure expressed as micrograms per square centimeter. Column E is an estimate of the dermal exposure to Ordram in micrograms to each body part.

The calculations for the anterior portion of the head and neck use a combination of Ordram residues on the outside cloth and the inside gauze samples placed on the chest to represent exposure of bare skin to airborne Ordram (assuming no face protection from a respirator or dust mask).

Calculations for the posterior portion of the head and neck use a combination of Ordram residues on the outside cloth and inside gauze placed on the back of the neck. Calculations for the anterior portion of the trunk use the gauze portion of the sample taken on the chest to simulate skin covered with clothing.

Similarly, calculations for the posterior portion of the trunk use the gauze portion of the sample taken on the back of the neck.

The arms and forearms use the gauze portions of the sample taken on the forearms. The thighs, legs and feet use the results of the gauze portions of the samples taken on the front of the thigh just above the knee. Column F is the sum of the exposure to the body parts, excluding hands and inhalation exposure.

Table 5 - The exposure to workers' hands determined from handwash sampling.

Table 6 - Total of dermal and inhalation exposures during an average 2-hour work period of loading and appying Ordram.

Discussion

Potential inhalation exposure for each type of worker, during an average 2-hour work period ranged from 5 to 604 micrograms per cubic meter of air inspired. Potential whole body dermal exposure, excluding hands, for flaggers and pilots ranged from none detectable to 282 micrograms; for loaders, these exposures ranged from 17,479 to 22,713 micrograms. Potential exposure to the hands of flaggers and pilots ranged from none detectable to 10 micrograms; exposure to the hands of loaders ranged from 470 to 1077 micrograms.

Potential exposures were not estimated for an average 7-hour workday (HS-676) because the aerial application firms located in rice growing areas do not apply Ordram for an entire workday, but only for a portion ranging from 30 minutes to 4 hours. The 2 applications monitored each lasted 2 hours.

Generally, loading operations proceeded at a rapid rate. The 2 loaders rotated jobs periodically so each spent approximately equivalent amounts of time performing all the various portions of the loading operations.

A cloud of dust would be raised around the loaders during all portions of the loading operations. Inhalation exposure and much of the whole body dermal exposure is believed to be due to this fine dust.

The design of the equipment and precautions taken by the loaders acted to potentially minimize gross exposure to the granular formulation. The worker standing on the truck-mounted hopper actually stood on a screen through which granular material was released from the broken bags.

The loaders took precautions to keep their feet well away from the path of the material spilling into the hopper as they lifted the bags off the funnel screen.

During slack times in the loading operations, the loaders would pile spent bags in preparation for disposal. The workers would clutch a number of bags to their chests and thighs, carrying them to the disposal site. Since the bags are not totally empty, substantial potential for exposure exists from that activity. Greatest exposures were recorded on the loader dermal exposure pads mounted on the arms and thighs.

Some of the higher exposure levels were found on the loaders pads mounted on the back of the neck. These are possibly due to the cloud of dusty fines liberated from loading operations and granular material flying from spent bags being tossed aside.

Substantial inhalation and whole body dermal exposure can potentially result from Ordram granular spilled on the ground that is picked up and blown about from prop-blasts created by the aircraft taking off and landing.

The loaders and pilots occasionally had body contact with the aircraft while performing various operations. Loaders would come in contact with the aircraft while loading or refueling. Normally, they would sit on the fuselage, or stand on the wing, against the fuselage. The pilot exited the cockpit once to clean the windshield, leaning against the fuselage. The pilot flew with the cockpit closed, but opened it when the plane was on the ground refueling or reloading.

Flaggers were not subjected to the types of potential exposures subjected to the loaders (dustiness and prop-blasts). Exposure to flaggers appears to be related to weather conditions. While the first day of work was cool, overcast and moderately windy, the second day was warm, clear, and still. Flaggers were exposed to relatively low levels only on the second day of work. Flaggers were occasionally caught in the spray swath of the plane and lightly showered with granules.

Some distinctly unusual results were obtained from the dermal exposure pads. Any pad that had a residue on the outside cloth portion had an equal or greater residue on the inside gauze portion. This phenomena is possibly due to the dust liberated from loading operations having a greater affinity for the gauze than the cloth. Dust bearing Ordram residues contacts the cloth (35% Cotton and 65% Dacron Polyester) and either falls off or sieves through the pores in the weave of the cloth to adhere to the gauze. This hypothesis is supported by the presence of dustiness during loading operations and aircraft prop-blasts that propel the dust at a high velocity. It is not supported by the pad results obtained from the flaggers, although the discrepancy between the inside and outside layers of these pads are not as great as corresponding results for loaders. Therefore, there is a question as to whether dust bearing Ordram residues is the agent penetrating inside the pads, or Ordram penetrates inside directly. There is also some question as to whether the results of the pads indicate that Ordram can penetrate coveralls and outer clothing.

There is not a great deal of literature on the use of dermal sampling pads for monitoring worker exposure to dusts or granular formulations. More research is needed on the properties of the textiles in relation to the trapping and permeation of dusts to assess their suitability as indicators of worker exposure to these types of formulations.

The relative amounts of dust formed could be due to the hardness or softness of the different granular materials. This could influence the tendency of the granules to fracture and produce dust.

The air sampling technique determining potential inhalation exposure traps vapor-phase Ordram and an extremely wide size distribution of dust particles bearing Ordram residues. The technique makes no differentiation between respirable and non-respirable dust particles. Out of the respirable fraction that is deposited in the lung, only a fraction of the Ordram residues adsorbed to the particles will desorb through the lung membranes into the bloodstream at any given time. The potential net effect is that exposure levels are lower, though duration of exposure is prolonged. Inhalation exposure could also be attenuated further because absorption of molinate either vapor-phase or adsorbed to dust, in the lung is probably less than 100%, though the rate of transport through lung membranes is not known at this time.

Dermal sampling techniques determine pesticide residues that can fall onto exposed skin (predominately the head, neck and hands) and whatever clothing the workers are wearing at the time. Calculations of the margin-of-safety consider that all the residue detected is available for dermal absorption. The levels of Ordram available for dermal absorption would be attenuated by the layers of clothing worn by the workers.

Work practices could also act to attenuate potential exposures. Exposure is continuous for no more than three months each year. A continuous level of Ordram would be present in a worker's body for a limited duration only. Substantial opportunities exist for turnover or repair of receptors (i.e., molecular sites of action for the toxicant) that would mitigate toxicity due to Ordram exposure. Unfortunately, the distribution and fate of Ordram and its metabolites in exposed workers has not been monitored. Data on adverse reproductive effects to male rats if extrapolated on a per kilogram basis do not indicate there is a satisfactory safety factor for loaders of Ordram. New data developed in primates suggests that there may be an adequate safety factor. Until additional studies now underway are completed, exposure of loaders to Ordram should be further reduced.

CONCLUSIONS

Ordram is a herbicide that has presented relatively low acute toxicity hazards to pesticide applicators. It was observed that the loaders would occasionally sacrifice exposure-reducing work habits for speed and efficiency. Such is probably not the case when working with a more acutely toxic granular formulation (e.g. Furadan).

These studies indicate that use of the currently available granular formulation of Ordram can result in substantial exposure to loaders if it is not handled quite carefully. Ordram residues can be found in the breathing zone, on the clothing and the hands of loaders.

Exposure to flaggers and pilots is relatively low.

Results from dermal exposure pads indicate that significant amounts of Ordram residues or dust bearing Ordram residues can penetrate clothing.

Added protective measures that could mitigate the potential hazards due to Ordram exposure, especially to loaders, could include wearing gloves to minimize dermal exposure and using a NIOSH-MSHA approved dust mask or respirator during the operations where dust is present in the workers' breathing zones (these measures are suggested in the product safety information sheet published by the manufacturer). A potential drawback of gloves and boots could be the trapping of granular material inside, maintaining prolonged dermal contact. The measure of protection offered by coveralls must be investigated further, especially in light of the results of dermal sampling conducted in this study.

Workers should always stand upwind when loading Ordram and avoid prop wash from the airplane whenever possible.

The air temperature at the time Ordram is usually applied can be above 85° F. Workers cannot be expected to wear protective clothing and respirators for very many minutes per hour which will overheat the body and result in possible heat stress. This can result in an increased skin absorption rate due to sweating.

It appears that a different formulation may have to be developed. The currently available granular product appears to decay to dust very easily, resulting in excessive skin and inhalation exposure to loaders of pesticide application equipment.

As a result of these various concerns, the Stauffer Chemical Company agreed to provide a training program for Ordram users until the issue concerning the potential for reproductive damage was resolved. An information leaflet to assist in this training program was developed by Stauffer in cooperation with the Departmnt. It is provided as Appendix 2.

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The use of trade names is for purpose of designating a product and does not signify an endorsement of a particular product.

Table 1

Concentration of Ordram found in the Breathing Zone (Ambient) of Employees Applying Ordram

Day Studied	Worker	Hours of Exposure	ppb (v/v)	ug/m^3	Estimated Ordram Inhalation Exposure Over a 2-Hour Work Period (ng)
1	Loader 1	2	18.34	140.24	555
	Loader 2	2	23.18	177.29	702
	Flagger 1	2	0.51	3.87	7
	Flagger 2	2	0.39	2.98	5
	Pilot	2	1.90	14.55	31
2	Loader 1	2	40.20	307.43	1217
	Loader 2	2	78.92	603.64	2390
	Flagger 1	2	28.57	218.48	367
	Flagger 2	2	0.84*	6.41*	11*
	Pilot	2	3.35	25.65	55

*Sample was collected improperly. Data probably not correct.

Table 2

Estimates of Dermal Exposures of Ordram to Loaders

Day Studied	Worker	Column A: Hours of Exposure	Column B: Skin Area Studied	Column C: Amount of Ordram on Cloth Patches (ug/cm^2) Outside Cloth	Column C: Amount of Ordram on Cloth Patches (ug/cm^2) Inside Gauze	Column D: Area of Skin Surface (cm^2) Covered	Column D: Area of Skin Surface (cm^2) Bare	Column E: Estimated Ordram Dermal Exposure Over a 2-Hour Period (ug) Covered Skin	Column E: Estimated Ordram Dermal Exposure Over a 2-Hour Period (ug) Bare Skin	Column F: Total Dermal Ordram Exposure for Average 2-Hour Work Period Excluding Hands (ug)
1	1	2	Head & Neck Anterior	0.28	0.71		500		495	
		2	Head & Neck Posterior	0.17	0.48		500		325	
		2	Trunk, Anterior	0.28	0.71	3,340		2,371		
		2	Trunk, Posterior	0.17	0.48	3,006		1,443		
		2	Arms & Forearms	0.55	1.26	2,254		2,840		
		2	Thighs, Legs & Feet	1.77	2.20	6,346		13,961		
			Total							21,435
	2	2	Head & Neck Anterior	0.11	0.27		500		190	
		2	Head & Neck Posterior	0.71	1.41		500		1,060	
		2	Trunk, Anterior	0.11	0.27	3,340		902		
		2	Trunk, Posterior	0.71	1.41	3,006		4,238		
		2	Arms & Forearms	0.58	1.00	2,254		2,254		
		2	Thighs, Legs & Feet	0.80	1.97	6,346		12,502		
			Total							21,146

(Cont.)

Table 2

Estimates of Dermal Exposures of Ordram to Loaders

Day Studied	Worker	Column A: Hours of Exposure	Column B: Skin Area Studied	Column C: Amount of Ordram on Cloth Patches (ug/cm^2) Outside Cloth	Column C: Amount of Ordram on Cloth Patches (ug/cm^2) Inside Gauze	Column D: Area of Skin Surface (cm^2) Covered	Column D: Area of Skin Surface (cm^2) Bare	Column E: Estimated Ordram Dermal Exposure Over a 2-Hour Period (ug) Covered Skin	Column E: Estimated Ordram Dermal Exposure Over a 2-Hour Period (ug) Bare Skin	Column F: Total Dermal Ordram Exposure for Average 2-Hour Work Period Excluding Hands (ug)
2	1	2	Head & Neck Anterior	0.27	0.43		500		350	
		2	Head & Neck Posterior	0.66	1.06		500		860	
		2	Trunk, Anterior	0.27	0.43	3,340		1,436		
		2	Trunk, Posterior	0.66	1.06	3,006		3,186		
		2	Arms & Forearms	0.30	0.62	2,254		1,397		
		2	Thighs, Legs & Feet	1.47	2.44	6,346		15,484		
			Total							22,713
	2	2	Head & Neck Anterior	0.59	1.29		500		940	
		2	Head & Neck Posterior	0.42	0.87		500		645	
		2	Trunk, Anterior	0.59	1.29	3,340		4,309		
		2	Trunk, Posterior	0.42	0.87	3,006		2,615		
		2	Arms & Forearms	0.85	1.53	2,254		3,449		
		2	Thighs, Legs & Feet	0.47	0.87	6,346		5,521		
			Total							17,479

Table 3

Estimates of Dermal Exposures of Ordram to Flaggers

Day Studied	Worker	Column A: Hours of Exposure	Column B: Skin Area Studied	Column C: Amount of Ordram on Cloth Patches (ug/cm^2) Outside Cloth	Column C: Amount of Ordram on Cloth Patches (ug/cm^2) Inside Gauze	Column D: Area of Skin Surface (cm^2) Covered	Column D: Area of Skin Surface (cm^2) Bare	Column E: Estimated Ordram Dermal Exposure Over a 2-Hour Period (ug) Covered Skin	Column E: Estimated Ordram Dermal Exposure Over a 2-Hour Period (ug) Bare Skin	Column F: Total Dermal Ordram Exposure for Average 2-Hour Work Period Excluding Hands (ug)
1	1	2	Head & Neck Anterior	ND[a]	ND		500			
		2	Head & Neck Posterior	ND	ND		500			
		2	Trunk, Anterior	ND	ND	3,340				
		2	Trunk, Posterior	ND	ND	3,006				
		2	Arms & Forearms	ND	ND	2,254				
		2	Thighs, Legs & Feet	ND	ND	6,346				
			Total							
	2	2	Head & Neck Anterior	ND	ND		500			
		2	Head & Neck Posterior	ND	ND		500			
		2	Trunk, Anterior	ND	ND	3,340				
			Trunk, Posterior	ND	ND	3,006				
		2	Arms & Forearms	ND	ND	2,254				
		2	Thighs, Legs & Feet	ND	ND	6,346				
			Total							

[a] ND means none detected

(Cont.)

Table 3

Estimates of Dermal Exposures of Ordram to Flaggers

Day Studied	Worker	Column A: Hours of Exposure	Column B: Skin Area Studied	Column C: Amount of Ordram on Cloth Patches (ug/cm^2) Outside Cloth	Column C: Inside Gauze	Column D: Area of Skin Surface (cm^2) Covered	Column D: Bare	Column E: Estimated Ordram Dermal Exposure Over a 2-Hour Period (ug) Covered Skin	Column E: Bare Skin	Column F: Total Dermal Ordram Exposure for Average 2-Hour Work Period Excluding Hands (ug)
2	1	2	Head & Neck Anterior	ND	ND		500			
		2	Head & Neck Posterior	ND	ND		500			
		2	Trunk, Anterior	ND	ND	3,340				
		2	Trunk, Posterior	ND	ND	3,006				
		2	Arms & Forearms	ND	ND	2,254				
		2	Thighs, Legs & Feet	ND	0.01	6,346		63		
			Total							63
	2	2	Head & Neck Anterior	ND	ND		500			
		2	Head & Neck Posterior	0.03	0.04		500	35		
		2	Trunk, Anterior	ND	ND	3,340				
		2	Trunk, Posterior	0.03	0.04	3,006		120		
		2	Arms & Forearms	ND	ND	2,254				
		2	Thighs, Legs & Feet	ND	0.02	6,346		127		
			Total							282

Table 4

Estimates of Dermal Exposures of Ordram to Pilots

Day Studied	Worker	Column A: Hours of Exposure	Column B: Skin Area Studied	Column C: Amount of Ordram on Cloth Patches (ug/cm^2) Outside Cloth	Column C: Amount of Ordram on Cloth Patches (ug/cm^2) Inside Gauze	Column D: Area of Skin Surface (cm^2) Covered	Column D: Area of Skin Surface (cm^2) Bare	Column E: Estimated Ordram Dermal Exposure Over a 2-Hour Period (ug) Covered Skin	Column E: Estimated Ordram Dermal Exposure Over a 2-Hour Period (ug) Bare Skin	Column F: Total Dermal Ordram Exposure for Average 2-Hour Work Period Excluding Hands (ug)
1	1	2	Head & Neck Anterior	ND	ND		500			
		2	Head & Neck Posterior	ND	ND		500			
		2	Trunk, Anterior	ND	ND	3,340				
		2	Trunk, Posterior	ND	ND	3,006				
		2	Arms & Forearms	ND	ND	2,254				
		2	Thighs, Legs & Feet	ND	ND	6,346				
			Total							
2	1	2	Head & Neck Anterior	ND	ND		500			
		2	Head & Neck Posterior	ND	ND		500			
		2	Trunk, Anterior	ND	ND	3,340				
		2	Trunk, Posterior	ND	ND	3,006				
		2	Arms & Forearms	ND	0.02	2,254		45		
		2	Thighs, Legs & Feet	0.02	0.03	6,346		190		
			Total							235

Table 5

Amount of Ordram Found on the
Hands of Employees Applying Ordram

Day Studied	Worker	Hours of Exposure	Ordram Found (micrograms)
1	Loader 1	2	700
	Loader 2	2	470
	Flagger 1	2	4.5
	Flagger 2	2	5.4
	Pilot	2	3.8
2	Loader 1	2	603
	Loader 2	2	1077
	Flagger 1	2	9.9
	Flagger 2	2	ND
	Pilot	2	ND

Table 6

Total Exposure to Employees Applying Ordram
During an Average 2-Hour Work Period

Day Studied	Worker	Estimated Ordram Dermal Exposure (Excluding Hands) (milligrams)	Estimated Ordram Exposure to Hands (milligrams)	Estimated Inhalation Exposure to Ordram (milligrams)	Estimated Total Exposure to Ordram (milligrams)
1	Loader 1	21.435	0.700	0.555	22.690
	Loader 2	21.146	0.470	0.702	22.318
	Flagger 1		0.005	0.007	0.012
	Flagger 2		0.005	0.005	0.010
	Pilot		0.004	0.031	0.034
2	Loader 1	22.713	0.603	1.217	24.533
	Loader 2	17.479	1.077	2.390	20.946
	Flagger 1	0.063	0.010	0.367	0.440
	Flagger 2	0.282		0.011	0.293
	Pilot	0.235		0.055	0.290

Appendix I
Analytical Methods

Date: 6-3-81
Supersedes: New

ORDRAM ON XAD-4 AIR SAMPLE TUBES

SCOPE: This method is for the desorption and analysis of Ordram from commercially prepared XAD-4 resin tubes.

PRINCIPLE: Ordram will be collected from the air onto XAD-4 resin in the air sample tubes by means of a low volume air sample pump. The Ordram is desorbed from the resin with acetone, diluted or concentrated as necessary and analytically determined by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Acetone, nanograde.
2. Analytical grade Ordram.
3. Approved and calibrated personal-sampling pump.
4. XAD-4 resin tubes, SKC or equivalent.
5. Developing vials with teflon septum caps, SKC #226-02 or equivalent.
6. Tube breaking kit, triangular file, tweezers, paper clip, etc.
7. Assorted volumetric glassware and pipets as needed for standards and samples.
8. Hewlett Packard 5880 gas chromatograph with NPD detector.
9. Six foot x 2mm glass column containing 10 percent SP-2100 on 100/120 mesh Chromosorb WHP.
10. Suggested starting GC parameters with the above column are:

    a. injector = 220 deg. C.
    b. column = 160 deg. C. and 35 ml/min helium.
    c. detector = 300 deg. C.

ANALYSIS:

Interferences: High humidity may affect trapping efficiency.

1. Score each sample tube with a file in front of the first section of the resin.
2. Break the tube open.
3. Remove and dispose of the wire.
4. Transfer the glass wool and the first (larger) section of resin into a desorption vial containing 3 ml of acetone and label as front section.
5. Transfer the central foam plus and the backup portion of the resin into a second desorption vial containing 3 ml of acetone and label as back portion.

6. Place the filled and labeled desorption vials on a sample rotator and rotate for 1 hour.
7. If more then several hours is to elapse before the chromatography will take place transfer an aliquot of each sample into a second vial. Label the vial and store in the freezer until assayed.

8. Determine the amount of Ordram present by gas chromatography.

DETERMINATION OF DESORPTION EFFICIENCY:

1. Remove the foam and second (small) portion of resin from an XAD-4 tube of the same lot number to be used for the sampling.
2. Inject a known and reasonable amount (calculate the amount required from the anticipated level of Ordram expected in the field or the desired sensitivity) of Ordram standard into the remaining section of resin in the tube with a microsyringe. Cap the tube and store as the tube will be stored during sample shipment. The storage time should be the same as the time expected to elapse between taking the sample and analyzing the sample.
3. At least 5 tubes should be run in this manner and the mean determined by the analytical procedure.
4. Desorption efficiency = (Area Sample-Area blank)/Area Standard), where the standard is the same amount as injected into the tube.
5. In like manner a check should be made on the adsorption coefficient. Follow steps 1 and 2 above, but before storage place the spiked sample tube on an air pump and draw a representative volume of air through the tube at a representative sampling rate (it helps to leave the back portion of resin in the tube for this determination).

CALCULATIONS:

1. Determine the weight of Ordram present on tube section from gas chromatographic analysis in nanograms.
2. Correct this total weight by subtracting any weight value from the blank or control tube.
3. The corrected weight is then divided by the determined desorption efficiency (and adsorption efficiency if needed) to obtain the final corrected weight or Ordram present.
4. The volumne of air sampled is converted to standard conditions of 25 deg. C and 760mm Hs.

$$VS = (V * P * 298)/(760 * (T+273))$$

where;

VS = volume of air as measured
V = barometric pressure in mm Hg
T = temperature of the air in degrees C.

5. Calculate ppb vapor phase in the air from the above data.

$$\text{ppb v/v} = (ng * 24.45)/(VS * 187)$$

where;

ng = corrected nanograms (#3)
VS = Corrected air volume in liters (#4)
187 = molecular weight of Ordram

for Ordram at 25 deg. C.

$$\text{ppb v/v} = (ng * 0.13075)/VS$$

REFERENCE:

1. DBCP on Charcoal Tubes, T. Jackson, CDFA Worker Safety Method, 7-27-78.
2. Analysis of XAD-4 Resin, T. Jackson, CDFA Worker Safety Method, 2-5-76.

Written by:

Scott Fredrickson
Agricultural Chemist II

Date: 6-4-81
Supersedes: New

ORDRAM IN WATER HANDWASHES

SCOPE: This method is for the analysis of Ordram as collected water handwashes from workers.

PRINCIPLE: Ordram adhering to the hands of workers is washed off with water. The solution is collected, extracted with ethyl acetate and analyzed by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Ethyl acetate, nanograde.
2. Sodium sulfate.
3. 500 ml graduated cylinder.
4. Assorted volumetric glasware and pipets as needed for samples and standards.
5. Gas chromatography.
   Instrument: Hewlett Packard 5880 with NPD detector
   Column: 6' x 2 mm glass column containing 10% SP-2100 coated on 100/120 mesh Chromosorb W-HP operating at 160 C and 35 ml/min helium carrier gas
   Temperatures: Detector at 300 C
   Injector at 220 C
   Under these conditions, Ordram elutes in about 5.0 minutes.

ANALYSIS:

Measure and record the amount of solution. Place a 100 ml aliquot in a 250 ml separatory funnel, add 10 ml saturated NaCl solution, and extract with 50 ml ethyl acetate. Drain the water layer and place the ethyl acetate in a 100 ml glass-stoppered graduate. Re-extract the water layer twice more with 20 ml ethyl acetate, combining the extracts in the graduate. Bring to volume, add sufficient sodium sulfate to dry the solvent, and analyze by GC.

Calculations must reflect the fact that only an aliquot was analyzed. Results have been reported in micrograms/total sample, and the total amount of handwash solution should be noted.

Recoveries are in excess of 95 percent.

A. Scott Fredrickson
Agricultural Chemist II

Date: 6-3-81
Supersedes: New

The Extraction of Ordram from Cloth Patches

Twenty-five ml of acetone was added to the patches (49 sq. cm), the sample containers were sealed with aluminum foil and rotated 15 minutes on a jar roller at 30 rpm. Gauze was treated in a similar manner. A portion of the extract was analyzed by gas chromatography without further treatment.

GC conditions:

Instrument: Hewlett Packard 5880 with NPD detector at 250 deg. C

Column: 6 ft. x 2 mm glass packed with 10% SP-2100 coated on 100/120 mesh chromosorb W-HP operating at 160 deg. C and 35 mL/min helium carrier gas

Injector: On column injection, 220 deg. C

Under these conditions, Ordram eluted in 5.00 minutes. There were no interfering materials, and recovery was >95%.

A. Scott Fredrickson
Agricultural Chemist II
6-3-81

Appendix II

Field Information, Ordram Exposure Study,
Colusa County, May 1981

	Day 1	Day 2
Pesticide used	Ordram 10G	Ordram 10G
Application rate	40 lbs. per acre	40 lbs. per acre
Carrier used	Granular	Granular
Type of aircraft	Turbo-Thrush	Turbo-Thrush
Aircraft height above crop	30 feet	30 feet
Average hours spent spraying	2	2
Average number of acres treated	130	130
Aircraft capacity	1700 lbs.	1700 lbs.
Refill time	1-1 1/2 minutes	1-1 1/2 minutes
Climatic conditions	Cool, overcast, windy	Warm, calm

Stauffer CHEMICALS

ORDRAM® 10-G

SELECTIVE HERBICIDE

PRODUCT SAFETY INFORMATION FOR AIRCRAFT LOADERS

Ordram® 10-G has been used for more than 18 years in California, other parts of the United States and the world for control of watergrass in rice fields.

Tests show that feeding Ordram to male rats reduces the number of off-spring when they mate. This effect disappears after the Ordram feeding is stopped. Tests on monkeys have shown no effect on their sperm.

A study of the sperm of male workers in several plants involved in the manufacture of Ordram was started in 1980 at the request of Stauffer. The study is being done by the University of Rochester in New York and will not be completed until 1983.

Studies of aerial application procedures show that "loaders" have a risk of exposure to Ordram dusts. The California Department of Food and Agriculture and the California Department of Health Services have expressed concern over the possibility of adverse reproductive effects occurring in workers exposed to Ordram in California. Until the human study is complete, the following extra precautions are recommended to reduce exposure while loading Ordram 10-G or handling empty bags:

- Avoid prop wash from the aircraft.
- Work up-wind while loading.
- Avoid skin contact with dust while handling bags.
- Wear protective clothing and NBR-nitrile or rubber gloves.
- Wear dust mask or respirator when loading Ordram or handling empty bags.

CDFA suggests that handling of this product should be in a manner consistent with precautions for handling any toxic product regardless of its immediate toxicity. Additional information is contained in the following paragraphs.

ANIMAL TESTING:

Like all of Stauffer's products, Ordram has been tested extensively in laboratory animals. Those tests have shown that Ordram does not produce cancer and that it does not produce birth defects. Ordram is not considered a hazardous product capable of causing significant acute illness. Animal tests, however, have shown that when male laboratory rats are fed Ordram, a decrease in fertility is seen. When the effect was first observed, Stauffer initiated one of the most extensive investigations of an agricultural chemical ever undertaken.

That investigation showed that Ordram in laboratory animals:

- Affects only the male rat. Females are unaffected.
- The loss of fertility is apparently caused by damage to the sperm of the male rats.
- The effect is reversible. When the male rats are no longer fed Ordram, their fertility returns to normal.
- Additional tests showed that although the effect occurred in male mice, it did so only at high doses of Ordram.
- Reduced fertility did not occur in rabbits at even higher dose levels.
- When Ordram was fed to male monkeys, no effects on sperm were found.

HUMAN STUDIES:

Stauffer has engaged specialists, experts in human male fertility at the University of Rochester, New York, to conduct an extensive study of Stauffer plant workers exposed to Ordram. This study began in 1980. Though no major adverse effects have been seen, this study will not be completed until June 1983.

WORK PRACTICES:

As the information about the effect in rats was being developed, Stauffer and the California Department of Food and Agriculture conducted studies to determine exposure levels of aerial applicators to Ordram.

Those studies showed that during aerial application, "loaders" received the highest exposure to Ordram 10-G dust. It was observed that the loader's exposure was high because of work practices which did not conform to the label instructions to "avoid contact with skin and clothing". In addition, Stauffer and CDFA studies showed that contamination of the hands by Ordram granular material was a major source of exposure. Therefore it is recommended that:

- Empty Ordram bags should be held away from the body.
- Workers should also avoid prop wash and always work upwind.
- Loaders should wear NBR-nitrile or rubber gloves while loading aircraft or handling empty bags. The gloves should be washed inside and out at the end of each work day.
- Loaders should wear clean coveralls each day and remove them before leaving work.
- Dust masks or dust filtering respirators should be worn during hopper loading and filling of the aircraft.
- Workers should always stand upwind while burning empty bags.
- Loaders should wash their hands thoroughly prior to smoking or eating food.
- Loaders should shower thoroughly at the end of each work shift.

Both the California Department of Food and Agriculture and Stauffer Chemical Company urge all Ordram users to carefully follow these recommendations.