

POTENTIAL EXPOSURE OF LOADER/APPLICATORS TO METHIDATHION
(SUPRACIDE) DURING APPLICATIONS TO CITRUS
IN RIVERSIDE COUNTY, CALIFORNIA IN 1982

BY

Keith T. Maddy, Staff Toxicologist
Dennis Gibbons, Environmental Hazards Specialist III
Donald M. Richmond, Environmental Hazards Specialist
Scott A. Fredrickson, Agricultural Chemist

HS-1062 December 9, 1983

California Department of Food and Agriculture
Division of Pest Management, Environmental
Protection and Worker Safety
Worker Health and Safety Unit
1220 N Street, Sacramento, California 95814

SUMMARY

Potential exposure of loader/applicators to methidathion (Supracide) was monitored for two days during applications to citrus in Riverside County, California in August 1982. The application equipment used during this study was developed by the grower specifically for his citrus orchards. This equipment consisted of an oscillating boom sprayer mounted on a truck with an enclosed air-conditioned cab. Monitoring showed that most of the methidathion was on the worker's coveralls and gloves. A small amount of methidathion was found in the samples from the worker's breathing zone. We were unable to evaluate fully the effectiveness of the application equipment in providing worker protection for several reasons. These include methidathion being present in the pre-application samples, measurable amounts of parathion contamination in all of the samples, and the lack of a comparable application with typical equipment being used.

INTRODUCTION

Methidathion (the active ingredient in Supracide 2E) is an organophosphate pesticide used widely in agriculture. In 1982, 305,292 lbs. of the material was applied to various crops (including citrus, nuts, cotton and stone fruits) throughout California (1). The chemical properties of this material include a melting point of 39-40°C. Solubility in water is less than 0.1%, but it is readily soluble in methanol, acetone and benzene (5). The material is slightly volatile.

Methidathion is one of the more toxic organophosphate pesticides. It is highly toxic to mammals because of its capacity to interfere with enzymes related to proper functioning of the nervous system. Oral LD₅₀ values for the rat have been reported at 25 - 48 mg/kg for the technical material (5,6) and 65 mg/kg for the Supracide 2E formulation (2). Oral LD₅₀ values in the mouse have been reported at 25 - 68 mg/kg for the technical material (6). Dermal LD₅₀ values in the rat have been reported at 150 - 400 mg/kg for pure and technical formulations (5). Dermal LD₅₀ values in the rabbit have been reported at 375 mg/kg for the technical material (6) and 640 mg/kg for the Supracide 2E formulation (2). Symptoms of methidathion poisoning, is common with other anti-cholinesterase agents, including headache, nausea, dizziness, sweating, weakness, muscular tremors, miosis and impairment of visual acuity.

MATERIALS AND METHODS

The cooperator using Supracide 2E (EPA Registration # 100-501-ZA) was located in Riverside County. The application equipment developed by the grower consisted of an oscillating boom sprayer mounted on a truck with an air-conditioned cab. The application rate was 1-1/2 gallons of Supracide 2E and 2 ounces of 2,4-D per 100 gallons of water per acre. A fertilizer, zinc manganese sulfate, was also added. Supracide 2E was loaded through a closed system, while the 2,4-D and the fertilizer were added through the top of the tank by hand. The pesticides and fertilizer were loaded and applied by one man.

The applicator/loader was monitored for inhalation and dermal exposure. The inhalation exposure was measured as spray mist and vapor in the worker's breathing zone. Dermal exposure was measured by taking handwash, cotton glove and coverall samples. Monitoring urinary metabolites was discussed, but was not possible at the time because the analytical standards for the metabolites were not readily available.

The inhalation exposure was measured with either an XAD-4 resin tube (SKC #226-30-11-4, Lot 126) or a sampling train consisting of a glass fiber filter and an XAD-4 resin tube. The glass fiber filter was used to trap spray mist. The XAD-4 resin tube was used to trap vapors and any spray mist not trapped by the glass fiber filter. The collecting medium was connected to a Dupont Constant Flow pump (model P-4000). A Kurz 540S Mass Flow Calibrator was used to calibrate the flow rate of each pump to 1-1/2 liters of air per minute at the start of the sampling period and to determine the flow rate at the end of the sampling period. The inhalation monitoring was divided into two periods. The first lasted from the start of the first load of the day until the start of the lunch break and the second lasted from the end of the lunch break until quitting time.

Handwash and cotton glove samples were used to measure the potential dermal exposure to the hands. A handwash sample was collected by dribbling 250 ml. of water from a separatory funnel onto the worker's hands while he washed them. The water was collected in a stainless steel basin. A handwash sample was collected prior to the first loading, before and after the lunch break, and at the end of the work day. The (pre-extracted) cotton gloves were worn at all times during the loading operation and while applying. The worker put on cotton gloves after the pre-exposure handwash and removed them before the post-exposure handwash. A new pair of cotton gloves were worn after each break. The worker wore neoprene gloves over the cotton gloves only while loading. The neoprene gloves were not pre-extracted.

Pre-extracted coveralls were used to measure the potential dermal exposure to the body (excluding the hands, feet and head). New coveralls were provided to the loader/applicator at the beginning of each work day. The coveralls were removed from him after the potential for exposure had passed.

Wipe samples were taken from inside the truck cab at the beginning and end of each day of exposure. Two locations were measured and their borders were taped. One site was a 1/2 square foot area on the door panel of the driver's door, the other was a 1 square foot area on the passenger seat. A piece of cotton gauze soaked with methanol was wiped across the area. A second piece of methanol soaked cotton gauze was wiped across the same area in a perpendicular direction to the first gauze.

All samples were sealed in glass jars and placed on ice immediately after collection. They were then shipped to Sacramento for analysis by the Department's laboratory. See Appendices 1 to 3 for the analytical methods for Supracide on glass fiber filters, XAD-4 resin tubes, handwashes, coveralls and gloves.

Results

The results of the data are summarized in the following tables:

Table 1 - The amount of methidathion found in the breathing zone of the loader/applicator. Hourly and daily exposure was estimated by assuming an air inhalation volume of $1.08 \text{ m}^3/\text{hour}$ and 100% absorption by the lungs (4).

Table 2 - The amount of methidathion found in handwash, cotton glove and coverall samples on the loader/applicator and wipe samples taken inside the truck cab. The relationship to exposure and length of exposure are also given.

Table 3 - The amount of parathion contamination found in each of the samples taken during Supracide 2E applications.

Discussion

This study was done under typical operating conditions. The application equipment involved was not cleaned (decontaminated) before the monitored applications. The data from the pre-application wipe samples showed small amounts of methidathion and parathion were present in the truck cab. The pre-exposure handwashes also showed measurable Supracide and parathion. The

worker's personal pickup truck could also have been responsible for contributing to the concentrations found in the pre-exposure handwash measurements.

Although the coveralls contained the largest amount of methidathion (see Table 2), this does not mean the worker was exposed to all of it. If the worker wore a clean pair of coveralls each day, the amount of pesticide penetrating to clothing or skin underneath the coveralls would be kept to a minimum. In a similar study, measurements taken underneath the coveralls of workers applying parathion showed less than 10% of the parathion penetrated through the coveralls (7). If methidathion is similar to parathion, methidathion penetration through the coveralls would be expected to occur at a comparable rate to parathion. A worker not changing his coveralls every day would be exposed to an increasing amount of the methidathion migrating through the coveralls over a period of days.

The cotton gloves contained most of the remaining methidathion found on the loader/applicator (See Table 2). There has been concern that the use of cotton gloves to determine potential hand exposure would greatly overestimate the actual exposure (3). This would be due to the pesticides being adsorbed by the cotton gloves much more readily than it would be by the skin. The data obtained during this study may then reflect the maximum potential hand exposure to the worker.

The handwash samples show relatively small amounts of methidathion (See Table 2). There is some doubt whether washing the hands in water removes all of the pesticide (3). This is probably the case with methidathion which is only slightly soluble in water (5). The amounts of methidathion found in pre- and post-exposure samples indicate this also. The data shows the pre-exposure handwash sample taken after the lunch break to contain more methidathion than the post-exposure handwash sample taken before the lunch break. Possible contamination from the worker's personal vehicle could have contributed to part of this.

The inhalation exposure to the worker was very small (See Table 1). Assuming a respiratory rate of 18 L of air/minute or 1.08 m³ of air/hour (4) and 100% absorption to the lungs, the calculated inhalation exposure to the worker was 21 ug for the first day and 13 ug for the second day.

The wipe samples obtained from inside the truck cab showed small amounts of residue present before the study began and higher levels present after the application (See Table 2). This shows that some methidathion does get into the truck during the application.

In addition, parathion contamination was noticeable in all of the samples obtained (See Table 3). Although the data shows levels of parathion much lower than the levels of methidathion present, they were found throughout the study. These data also indicate a residue problem within the truck cab.

CONCLUSIONS

The special application equipment developed by this cooperator and used during this study appeared to help reduce exposure to the loader/applicator. The data collected from coveralls and patches in 2 previous studies of parathion applications seem to bear this out (7,8). However, any

conclusions about the real effectiveness of this equipment in reducing exposure will have to wait for a further study because of the limited amount of data and the contamination measured in this study. The results of this limited study show most of the potential exposure to the loader/applicator is by the dermal route. More applications need to be monitored to fully characterize methidathion exposure during applications of Supracide 2E. Some changes in the protocol should be made. First, T-shirts and leggings should be worn underneath the coveralls to determine how much material would penetrate through the coveralls to the body surfaces (except face, neck, hands and feet). Second, the exposure monitoring of the hands should be revised. The hands should be washed in a solvent in distilled water with surten solution added. This would eliminate some of the problems mentioned above, although the probability of over-estimation would still be present. Third, collection of total urine through at least 24 hours after application should be done as long as analysis for the breakdown products is possible. Fourth, the differences in potential exposure in contaminated and clean equipment can be studied. The contaminated equipment would be used in the first half of the study. The equipment would then be thoroughly cleaned before proceeding with the second half of the study.

TABLE 1

THE AMOUNT OF METHIDATHION FOUND IN THE
BREATHING ZONE OF THE LOADER/APPLICATOR

Appl. #	AM/ PM	Trapping Medium	Length of Exposure (Minutes)	PPB (V.V)	ug/m ³	Estimated Exposure ^(a)	
						ug/hr.	ug/Exposure Period
1(b)	AM	XAD-4	305	0.20	2.5	2.7	13.7
	PM	XAD-4	180	0.18	2.2	2.4	7.2
2(c)	AM	Glass Fiber Filter	160	0.28	3.5	3.8	10.1
	AM	XAD-4	160	0.09	1.1	1.2	3.2

Estimated Inhalation Exposure Per Day

	<u>Exposure Time</u>	<u>ug/day</u>
Day 1:	485 min.	20.9
Day 2:	160 min.	13.3

(a) Estimate based on an air inhalation volume of 1.08 m³/hr. and 100% absorption by lungs (4).

(b) Application #1 was monitored on 8/24/82.

(c) Application #2 was monitored on 8/25/82.

(d) Limit of Detection: 0.01 ug/sample.

TABLE 2

The Amount of Methidathion Found in Handwash, Gloves, Coveralls, and Area Wipe Samples Taken During Supracide 2E Applications in Riverside County

Appli- cation No.	AM/PM/ Total	Pre/Post Application Sample	Length of Exposure (Minutes)	Handwashes (c)/ (ug/Sample)	Gloves (d)/ (mg/Sample)	Coveralls (d)/ (mg/Sample)	Wipe Samples (ug/Sample)	
							Door Panel 1/2 Foot ² (e)/	Passenger Seat: 1 Foot ² (e)/
1 (a)/	AM	Pre-	---	1,500	---	---	1.4	0.7
		Post-	305	560	10.3	---	---	---
	PM	Pre-	---	754	---	---	---	---
		Post-	180	750	14.9	---	---	---
	Total	Post-	485	---	---	62	11.7	8.2
2 (b)/	AM	Pre-	---	603	---	---	---	---
		Post	160	667	12.9	47.7	19.4	6.2

(a)/ Application No. 1 was monitored on August 24, 1982.

(b)/ Application No. 2 was monitored on August 25, 1982.

(c)/ Limit of detection for handwashes: 1 ug/sample.

(d)/ Limit of detection for gloves and coveralls at 2L of solvent/sample: 40 ug/sample.

(e)/ Limit of detection for wipe samples: 0.25 ug/sample.

TABLE 3

The Amount of Parathion Contamination Found in Samples Taken During Supracide 2E Applications in Riverside County

Appli- cation No.	AM/PM/ Total	Pre/Post Application Sample	Length of Exposure (Minutes)	Air Samples (ppb)		Handwashes (ug/Sample)	Gloves (mg/Sample)	Coveralls (mg/Sample)	Wipe Samples (ug/Sample)		
				Resin (c)/	Glass Fiber Filter (c)/				Door Panel; 1/2 Foot	Passenger Seat: 1 Foot ²	
1 (a)/	AM	Pre-	---	---	---	233	---	---	1.82	1.27	
		Post-	305	0.09	---	196	13.2	---	---	---	
	PM	Pre-	---	---	---	55	---	---	---	---	
		Post-	180	0.11	---	69	4.8	---	---	---	
	Total	Post-	485	---	---	---	---	---	4.2	2.74	2.36
		AM	Pre-	---	---	---	90	---	---	---	---
2 (b)/	AM	Post-	160	0.01	0.04	71	4.0	1.8	3.88	3.89	

(a) Application No. 1 was monitored on August 24, 1982.

(b) Application No. 2 was monitored on August 25, 1982.

(c) Limit of Detection for air samples: 0.01 ppb.

REFERENCES

1. California Department of Food and Agriculture. Pesticide Use Report Annual 1982, pg.145. Sacramento (1982).
2. Ciba-Geigy Corporation, Agricultural Division. Supracide Insecticide Technical Bulletin. Ardslye, New York (1972).
3. Davis, J.E.: Minimizing Occupational Exposure to Pesticides: Personnel Monitoring. Residue Reviews 75: 33-50 (1980).
4. Environmental Protection Agency. Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples. Section 8A, pg. 14-18. Pub. No. EPA-600/8-80-038 (1980).
5. Grob, H., R. Gasser, and M.A. Ruzette: Further Investigations With "Supracide" for use in Orchards and Vineyards (Activity, Metabolism, Residues, Toxicology). Proc. 3rd Brit. Insecticide Fungicide Conf., pg. 451-477 (1965).
6. Kenaga, E.E. and W.E. Allison: Commercial and Experimental Organic Insecticides (1969 Revision). Bulletin Entomological Society of America 15: 85-148 (1969).
7. Maddy, K.T., D. Gibbons, S. Kilgore and S. Margetich: Potential Exposure of Applicators to Parathion When Treating Citrus in Riverside County. California Department of Food and Agriculture Report No. HS-1059 (1983).
8. Maddy, K.T., C. Winter, N. Saini and V. Quan: A Study of Potential Occupational Exposure of a Ground Applicator During Mixing, Loading, and Application of Parathion in Tulare County in June 1981. California Department of Food and Agriculture Report No. HS-888 (1982).

Appendix 1

SUPRACIDE ON GLASS FIBER AIR FILTERS AND XAD-4 AIR TUBES

SCOPE:

This method is for the analysis of Supracide collected on glass fiber air filters and in XAD-4 resin tubes.

PRINCIPLE:

Supracide is collected from the air onto XAD-4 resin in the air sample tubes or glass fiber filters by means of a low volume air sample pump. The Supracide is desorbed from the resin with ethyl acetate, diluted or concentrated as necessary and analytically determined by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Ethyl Acetate, nanograde.
2. Analytical grade Supracide and Supracide oxygen analog.
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. Gas chromatography
Instrument: Perkin Elmer Sigma 2 with NPD detector
Column: Hewlett-Packard 25M x .21 mm fused silica column coated with SE-54, operated at 230 C, psi He, and 100:1 split ratio. Split flow 40 ml/min.
Temperatures: Detector at 300 C
 Injector at 220 C
Under these conditions, Supracide elutes in about 5.3 minutes, Supracide oxon in 4.3 minutes.

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 4 ml of ethyl acetate and label as front section.
5. Transfer the central foam plug and the backup portion of the resin into a second desorption vial containing 4 ml of ethyl acetate 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 than 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 Supracide 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 determinations.
2. Inject a known and reasonable amount (calculate the amount required to add from the anticipated level of analyte expected in the field or the desired sensitivity) of Supracide 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:

The concentration of analyte in the air sampled can be expressed in mg per cu m, which is numerically equivalent to micrograms per liter of air.

$$\text{mg/cu m} = \frac{\text{mg analyte/sample} \times 1000}{\text{liters of air sampled}}$$

The concentration in ppb can be expressed as follows:

$$\text{ppb} = \text{mg/cu m} \times \frac{24.45 \times 760 \times (T+273) \times 10^3}{\text{MW} \times P \times 298}$$

where:

- P = air pressure in mm Hg
- T = air temperature in degrees C
- 24.45 = molar volume (L/mole) at 25 C and 760 mm Hg
- MW = molecular weight (g/mole) of analyte
- 760 = NIOSH standard pressure in mm Hg
- 298 = NIOSH standard temperature -- degrees Kelvin

The molecular weight of Supracide is 302.

DISCUSSION:

Recovery data at the 1 mcgm/spl level is as follows:

XAD-4

Supracide	91%
Supracide-OA	81%

Glass Fiber Filters

Supracide	94%
Supracide-OA	90%

Severe problems were encountered trying to analyze Supraxone using packed columns. Capillary GLC appeared to be superior because of the ease of getting it to chromatograph, and relatively minor problems with response variation.

REFERENCES:

Fredrickson, S.: The Extraction of Supracide and Supraxone from Citrus Leaves, Worker Health and Safety paper (1975).
Sheila Margetich, CDEFA chemist, personal communication.

Appendix 2

SUPRACIDE IN SOAP AND WATER HANDWASHES

SCOPE:

This method is for the analysis of Supracide as collected in soap and water handwashes from workers.

PRINCIPLE:

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

REAGENTS AND EQUIPMENT:

1. Ethyl acetate, nanograde.
2. Sodium sulfate, granular anhydrous.
3. 500 ml graduated cylinder.
4. Assorted volumetric glassware and pipets as needed for samples and standards.
5. Gas chromatography
Instrument: Perkin Elmer Sigma 2 with NPD detector
Column: Hewlett-Packard 25M x .21 mm fused silica column coated with SE-54, operated at 230 C, 20 psi He, and 100:1 split ratio. Split flow 40 ml/min.
Temperatures: Detector at 300 C
 Injector at 220 C
Under these conditions, Supracide elutes in about 5.3 minutes, Supracide oxon in 4.3 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 GLC.

CALCULATIONS:

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.

DISCUSSION:

Recoveries are 85% at 100 mcgms/spl for Supracide, 72% for the oxon. Minimum detectable levels are better than 1.0 microgram/sample.

Severe difficulties were encountered trying to run Supraxone on packed GLC columns. Capillary GLC was superior because of the ease of chromatography, and the relatively minor response changes.

The concentration and type of soap solution will probably affect recoveries. 0.05% Sur-Ten solution has been successfully used.

REFERENCES:

Fredrickson, S.: The Extraction of Supracide and Supraxone from Citrus Leaves, Worker Health and Safety paper (1975).

Appendix 3

SUPRACIDE IN COVERALLS AND GLOVES

SCOPE:

This method is for the analysis of Supracide collected on coveralls and gloves of workers.

PRINCIPLE:

Supracide adhering to the gloves and coveralls of workers is extracted with ethyl acetate and analyzed by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Ethyl acetate, nanograde.
2. Sodium sulfate, granular anhydrous.
3. 500 ml graduated cylinder.
4. Assorted volumetric glassware and pipets as needed for samples and standards.
5. Gas chromatography
Instrument: Perkin Elmer Sigma 2 with NPD detector
Column: Hewlett-Packard 25M x .21 mm fused silica column coated with SE-54, operated at 230 C, 20 psi He, and 100:1 split ratio.
Split flow 40 ml/min.
Temperatures: Detector at 300 C
 Injector at 220 C
Under these conditions, Supracide elutes in about 5.3 minutes,
Supracide oxon in 4.3 minutes.

ANALYSIS:

Coveralls used by workers are placed in a one gallon wide-mouth jar, 2 liters of ethyl acetate are added, and the sample is sealed with foil and placed on a roller for 30 minutes.

Gloves are treated similarly, except that the sample jar is only 500 - 1000 ml, and 200 - 500 ml solvent is used.

The extracts may be concentrated or diluted as required, and are run by GLC without further treatment.

CALCULATIONS:

Results have been reported in micrograms/total sample.

DISCUSSION:

Recoveries are 100% at 1 mg/sp1 for Supracide, 107% for the oxon. Minimum detectable levels were not determined.

Severe problems were encountered trying to analyze Supraxone using packed columns. Capillary GLC appeared to be superior because of the ease of getting it to chromatograph, and relatively minor problems with response variation.

Suitable concentration techniques were not studied, but normal procedures should be satisfactory.

REFERENCES:

Fredrickson, S.: The Extraction of Supracide and Supraxone from Citrus Leaves, Worker Health and Safety paper (1975).
Sheila Margetich, CDFA chemist, personal communication.