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Potential Exposure of Apple Thinners to Azinphosmethyl and Comparison of Two Methods for Assessment of Hand Exposure

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To establish the time that must be allowed to elapse before workers can safely re-enter a crop that has been sprayed with a pesticide, one must be able to estimate the hazard associated with working in the crop at any particular time after application of the pesticide. The acute hazard for such re-entry can be estimated by monitoring workers to determine the potential dermal and respiratory exposures they receive. Then, using toxicity data from laboratory animal studies, one can arrive at an estimate for the percent of an acute lethal dose of the pesticide that a worker can be expected to receive during a normal day's work (DURHAM & WOLFE 1962, DAVIS et al. 1982a). A recently postulated system also allows one to determine whether or not it is safe for a worker to receive the observed level of exposure for an entire working season (POPENDORF & LEFFINGWELL 1982).

Exposure of the hands is often found to be the largest component of a worker's total potential exposure to pesticides. Hand exposures contributed 20 to 50% of the total potential exposure of workers who mixed and applied insecticides by airblast sprayer to orchards (WOLFE et al. 1966) and nearly 50% of the total for workers who filled seed potato dusting machines with fungicide (STEVENS & DAVIS 1981). It has also been observed to account for more than 85% of the total exposure received during the spraying of lawns by homeowners (DAVIS et al. 1982a). Hand exposures have been monitored by swabbing or rinsing the hands with solvents (DURHAM & WOLFE 1962, WARE et al. 1973), extrapolating from residues trapped in pads attached to the forearms (BATCHELOR & WALKER 1954), or trapping residues in absorbent gloves (QUINBY et al. 1958). The advantages and disadvantages of these methods have been discussed elsewhere (DAVIS 1983).

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The hand rinse procedure of DURHAM & WOLFE (1962) has become somewhat of a standard procedure through extensive use. However, it is not entirely satisfactory for several reasons. Occasionally, one cannot find a solvent that will remove residues without injuring the skin. Some solvents cause decomposition of residues or interfere with analysis. Residues that penetrate the skin during the exposure period will not be included in the exposure estimate. Finally, hand rinsing requires that workers stop their labors for several minutes after each exposure period, so the operation being studied may be slowed to the extent that further monitoring becomes objectionable to the workers or their supervisor.

Trapping residues with absorbent gloves eliminates most of the problems associated with other methods for monitoring hand exposures. However, gloves may absorb more pesticide than would be retained on the skin. Since hand exposure is often such a large proportion of total exposure, excessive retention of residues by gloves may result in the gross overestimation of total potential exposure.

The present study had two primary objectives. The first was determination of potential dermal and respiratory exposures that occurred while thinning apples at various times after application of azinphosmethyl (O,O-dimethyl S(4-oxo-1,2,3-benzotriazin-3(4H)-ylmethyl) phosphorodithioate). The second was to compare hand exposures assessed using hand rinses and two types of absorbent gloves.

MATERIALS AND METHODS

Potential dermal and respiratory exposures received by professional agricultural workers were monitored using multi-layered gauze pads, ethanol hand rinses, absorbent gloves, and battery-operated personal air pumps fitted with polyurethane foam plug samplers. Detailed descriptions of the fabrication and use of these monitoring media as well as calculation of hourly exposure rates have been presented elsewhere (DURHAM & WOLFE 1962, LEWIS et al. 1980, DAVIS 1980). Gauze pads were attached to the worker's forearms which are often uncovered during thinning. Facial exposure is normally assessed using pads attached to the shoulders, chest and back. However, this was not possible during the present study. The workers complained that pad-holding harnesses might become snagged on branches, light-weight protective jackets with pads attached in advance were cumbersome, and taping the 4 extra pads to their clothing took too long. Polyurethane foam plug air samplers in aluminum holders (DAVIS et al. 1982b) were attached to the workers' collars with the open end down. The personal pumps used to draw air through the samplers were adjusted to flow rates of approximately 3 l/min. Monitoring media were changed and hands were rinsed at the midmorning, lunch and midafternoon breaks, so all exposure periods were approximately 2 h.

The workers were monitored while thinning apples at 1,2,6 and 9 days after the airblast application of azinphosmethyl at 1 lb/A (1.1 kg/ha). The spray contained 10 lbs of a 50% wettable powder formulation per 400 gal (3 g/l) and was applied at a rate of 80 gal/A (750 l/ha). Leafpunch samples, which were shaken with a Sur-Ten detergent solution for the determination of dislodgable residues, were taken at midmorning. Each of these samples consisted of 30 punches, 5 from each of 6 trees, and foliar dislodgable residues were calculated using the surface area of both sides of the punches. Dislodgable residues were extracted from leaf-punch samples, exposed monitoring media were processed, and extraction and storage losses were determined essentially as described elsewhere (DAVIS et al. 1982b). The following are modifications of that earlier description: Media were fortified, as shown in Table 1, using a filtrate from the extraction of 2 g of 50% wettable powder formulation of azinphosmethyl with 100 ml of acetone. Losses of azinphosmethyl during freezer storage were assessed using fortified miniature gauze pads. Finally, gauze pads were extracted in Soxhlets in the same manner as gloves.

Table 1. Fortification of Monitoring Media for Determination of Storage Losses.

Type of Monitoring Media	Approximate Amount of Azinphosmethyl Added	Pre-extraction Treatment
Gauze pads	100µg/pad	Air dried for 1 h
Simulated hand rinses	25µg/ml of ethanol	Not extracted
Polyurethane foam plugs	100µg/plug	Air dried for 1 h
Cotton and nylon gloves	5mg/glove	Air dried for 1 h
Sur-Ten solutions	250µg/sample	None

Residues were quantified by gas chromatography through a 76 cm x 4 mm (inside diameter) glass column packed with 4% SE-30/6% OV-210 on 80/100 mesh Gas Chrom Q. The carrier gas was nitrogen at a flow of 120 cc/min. The column temperature was 200°C and the temperature of the ^{63}Ni electron capture detector was 350°C.

RESULTS AND DISCUSSION

Gauze pads were stored in a freezer for approximately 2 weeks pending extraction. Hand rinses and extracts from other monitoring media were stored in a refrigerator for up to 3 mo. pending analysis. Analysis of residues recovered from the fortified media shown in Table 1 indicated that extraction losses only occured during the extraction of Sur-Ten solutions with hexane to determine dislogable foliar residues. The mean $\pm$ standard deviation for recovery of azinphosmethyl from these solutions was 95 $\pm$ 2% (4 replicates). Stability studies indicated that significant losses of residues occured in 3 types of samples during storage. These losses occured during freezer

storage of gauze dermal exposure pads and refrigerator storage of ethanol hand rinses and hexane extracts of dislodgable foliar residues. The following 3 equations were generated by regression analysis of the storage stability data to correct for these losses. The percentage of initial azinphosmethyl remaining after n days of storage is indicated as x.

1. Storage of gauze pads in a freezer: $X = 100 - 2.1 \ln n$

2. Storage of ethanol hand rinses in a refrigerator: $x = 100 - 2.7 \ln n$

3. Storage of hexane extracts in a refrigerator: $x = 100 - 4.1 \ln n$

No losses occurred when air was drawn at a flow of 3 L/h for 2 h through fortified polyurethane foam plugs. Data presented in the balance of this report were corrected for extraction and storage losses.

To compare hand exposures monitored by using either ethanol rinses or absorbent gloves, both methods were employed at 2 and 9 days after application of the azinphosmethyl. Results of this investigation are shown in Table 2. When compared at the 95% confidence level by t-distribution, hand exposures obtained by rinsing were significantly lower than those obtained by using either type of glove. However, there was no significant differences between exposures obtained by using the different types of gloves. When mean exposures were compared, those obtained by using cotton and nylon gloves were approximately 5 and 4 times larger, respectively, than those obtained by using hand rinses.

Table 2. Comparision of Apple Thinners' Hand Exposures Monitored with Ethanol Rinses or Absorbent Gloves.

Days After Application	Rate of Exposure to Azinphosmethyl (µg/h)[a]		
	Ethanol Rinses	Cotton Gloves	Nylon Gloves
2	1,800±300 (6)	8,500±1,700 (5)	7,000±2,000 (5)
9	960±340 (6)	5,200±2,200 (11)	3,900± 900 (11)
	Ratio of Exposure Means		
	Cotton Gloves/Ethanol Rinses	Nylon Gloves/Ethanol Rinses	
2	4.7	3.8	
9	5.5	4.1	

[a]Mean ± standard deviation for the number of replicates indicated in parenthesis.

Potential dermal and respiratory exposures received by apple thinners working in an orchard at various times after it had been sprayed with azinphosmethyl are shown in Table 3. Foliar dislodgable residues at the various times are also shown in Table 3. The dermal exposures given in the first 4 lines are based on hand exposures obtained with ethanol rinses and calculated exposures for the face and neck. An earlier study indicated that exposure to the face and neck received while thinning apples that had been treated with a spray prepared from a wettable powder formulation of phosalone averaged approximately 14% of exposure to the forearm (DAVIS et al. 1982b). Since it was not possible to directly monitor exposures to the face and neck in the present study, each worker's exposure in these areas was assumed to have been 14% of his forearm exposure. The exposures shown in the last 4 lines of Table 3 were calculated using hand exposures that were 5 times those obtained by hand rinsing. These would correspond to exposures monitored by using cotton gloves.

To estimate the hazard associated with the highest mean exposures indicated in Table 3, one may estimate the respiratory and dermal exposure hazards separately then combine them for the total hazard. NEWELL & DILLEY (1978) estimated the respiratory LD_{50} for an aerosol produced from a solution of azinphosmethyl in 20% dimethylsulfoxide to be 0.33 mg/kg when administered to male rats. However, their value is probably not applicable to the present study. NIGG (1977) and POPENDORF & SPEAR (1974) reported that the pesticide containing particulate material which becomes airborne during orchard work is of such a large size that more than 95% of it would be deposited in a worker's naso-pharynx (POPENDORF & LEFFINGWELL 1982). Such material would subsequently be swallowed, so exposure contributed by this material should be considered as oral rather than respiratory. The oral LD_{50} for azinphosmethyl administered to male rats is 13 mg/kg and to female rats is 11 mg/kg (GAINES 1969). Assuming a LD_{50} of 12 mg/kg and that humans are equally sensitive, the oral LD_{50} for a 70 kg worker would be 840 mg. Also assuming that 100% of the pesticide collected on the polyurethane foam plugs would have been deposited in the naso-pharynx then swallowed, workers receiving the maximum mean "respiratory" exposure of 78 µg/h would swallow 0.62 mg/day or 0.074% of a lethal dose per day. The dermal LD_{50} for azinphosmethyl administered to rats is 220 µg/kg (GAINES 1969). This would correspond to 15,400 µg for a 70 kg worker. The maximum mean dermal exposures received by the thinners were 5,400 µg/h, if hand exposures were monitored by ethanol rinses, and 13,00 µg/h, if gloves were used. These values correspond, respectively, to daily exposures of 43 and 100 mg or 0.28 and 0.68% of a lethal dermal dose per day. Therefore, depending on which hand exposure monitoring method was assumed to be "correct", the thinners received a total of either 0.35 or 0.75% of a lethal dose of azinphosmethyl per day by the dermal and "respiratory" routes.

Table 3. Potential Exposures Received by Apple Thinners Working in an Orchard at Various Times After Application of Azinphosmethyl

Days After Application	Rate of Exposure (µg/h)[a]					Dislodgable Residues (µg/cm^2)
	Face & Neck[b]	Forearms	Hands	Total Dermal	Respiratory	
1	270±170(5)	1,900±1,200(5)	1,300±200(5)[c]	3,400±1,500(5)	49±22(5)	1.7 ± 0.4 (3)
2	440±150(6)	3,100±1,000(6)	1,800±300(6)[c]	5,400±1,300(6)	78±34(6)	1.9 ± 0.2 (4)
6	190± 70(5)	1,300± 500(5)	830±400(5)[c]	2,400±1,000(5)	31± 9(5)	1.4 ± 0.4 (5)
9	140± 80(6)	980± 540(6)	960±340(6)[c]	2,100± 600(6)	18±10(6)	1.4 ± 0.2 (5)
1			6,500[d]	8,700		
2			9,000[d]	13,000		
6			4,200[d]	5,700		
9			4,800[d]	5,900		

[a]Mean ± standard deviation for the number of replicates indicated in parentheses.
[b]Assumed to be 14% of each forearm exposure.
[c]Monitored by ethanol rinse.
[d]Estimation of value that would have been obtained using cotton glvoes (5X mean value obtained by ethanol rinse).

The recently published work of POPENDORF & LEFFINGWELL (1982) allows one to estimate the effect of dermal exposure to selected organophosphorus compounds on acetylcholinesterase inhibition. They postulated that daily acetylcholinesterase inhibition of 2 to 4% is acceptable from the standpoint of seasonal exposure. Also, that 2 and 4% inhibition would occur in 70 Kg workers dermally exposed, respectively, to 52 and 105 mg of azinphosmethyl. These "safe" exposures correspond quite closely to either the 43 or 100 mg daily dermal exposures received in the present study by workers thinning apples during the period of maximum exposure.

The total dermal and respiratory exposure rates and foliar dislodgable residues shown in Table 3 were compared by t-distribution to detect significant differences at the 95% confidence level at various times after application. There were no significant differences when data from day 1 were compared to data from either day 2 or day 6. When data from day 1 were compared to data from day 9, only the respiratory exposure rate had become significantly lower by day 9. These results indicated that, under the conditions that existed during the present study, increasing the time required before reentry by less than 1 week over the present Federal reentry interval of 24 h would not significantly decrease the exposure of apple thinners to azinphosmethyl residues.

This study indicated that there is little acute or semi-acute toxic hazard associated with exposures received while thinning apples at any time in excess of 24 h after application of azinphosmethyl according to the conditions employed. One must also conclude that use of absorbent gloves to monitor hand exposures may lead to grossly exaggerated estimates for total potential dermal exposure.

REFERENCES

BATCHELOR, G.S. and K.C. WALKER: Arch. Ind. Hyg. Occup. Med. 10, 522 (1954).

DAVIS, J.E.: Residue Reviews 75, 33 (1980).

DAVIS, J.E.: Proceedings of the Conference on Determination and Assessment of Pesticide Exposure, Hershey, PA, Oct. 29-31, 1980, In press (1983).

DAVIS, J.E., E.R. STEVENS, D.C. STAIFF, and L.C. BUTLER: Environ. Monit. Assess., In press (1982a).

DAVIS, J.E., E.R. STEVENS, D.C. STAIFF, and L.C. BUTLER: Bull. Environ. Contam. Toxicol., 29, 592 (1982b).

DURHAM, W.F. and H.R. WOLFE: Bull. WHO 26, 75 (1962).

GAINES, T.B.: Toxicol. Appl. Pharmacol. 14, 515 (1969).

LEWIS, R.G., M.D. JACKSON, and K.E. MACLEOD: U.S. EPA Publication EPA-600/2-80-180, Research Triangle Park, N.C. (1980).

NEWELL, G.W. and J.V. DILLEY: U.S. EPA Publication EPA-600/1 78-003, Research Triangle Park, N.C. (1978).

NIGG, H.N.: Proc. Fla. State Hort. Soc. 90, 21 (1977).

POPENDORF, W.J. AND J.T. LEFFINGWELL: Residue Review 82, 125 (1982).

POPENDORF, W.J. and R.C. SPEAR: Amer. Ind. Hyg. Assoc. J. 35, 374 (1974).

QUINBY, G.E., K.C. WALKER, and W.F. DURHAM: J. Econ. Entomol. 51, 831 (1958).

STEVENS, E.R. and J.E. DAVIS: Bull. Enviorn. Contam. Toxicol. 26, 618 (1981).

WARE, G.W., D.P. MORGAN, B.J. ESTESEN, W.P. CAHILL and D.M. WHITACRE: Arch. Environ. Contam. Toxicol. 1, 48 (1973).

WOLFE, H.R., J.F. ARMSTRONG, and W.F. DURHAM: Arch. Environ. Health 13, 340 (1966).

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