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Potential Exposure of Apple Thinners to Phosalone

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Apple thinning results in considerable human contact with foliage, fruit, and limbs. This work often occurs during that portion of the growing season when trees are most frequently being sprayed for insect control. Therefore, of all workers exposed to pesticide residues upon reentry into sprayed crops, apple thinners probably receive some of the heaviest exposure.

The present study was undertaken to determine the potential dermal and respiratory exposures that experienced apple thinners received while working in orchards shortly after the Federal reentry interval for phosalone {s[(6-chloro-2-oxo-3-benzooxazolinyl)methyl]O,O-diethyl phosphorodithioate}.

MATERIALS AND METHODS

The trees thinned were mature Red and Golden Delicious. They had received their first seasonal cover spray of phosalone for codling moth control. This was an airblast application of a spray prepared by mixing 15 lb (6.8 kg) of 25% wettable powder (WP) phosalone and 5 lb (2.3 kg) of 85% WP succinic acid 2,2-dimethylhydrazide with 500 gal (1,890 L) of water. The spray was applied at a rate of 200 gal/A (1,870 L/ha). The same three male and seven female workers were monitored during exposure at approximately 24 and 48 h after application of the spray. All were experienced thinners whose primary occupation was orchard worker. They were monitored for approximately 2 h during the period between lunch and their afternoon break. The normal daily exposure for these thinners was approximately 7.5 h, and their normal yearly exposure was approximately 30 days.

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Residues that could potentially result in dermal exposure to areas other than hands were collected on multilayered gauze pads (DURHAM & WOLFE 1962; DAVIS 1980). The most common attire for apple thinners in the Pacific Northwest is a cap or head scarf, short-sleeved shirt, long trousers, and shoes. Therefore, it was assumed that only the face, neck, forearms, and hands were exposed. Pads were attached to the shoulders, upper center of the chest and back, and the outside of the forearms of the thinners. Exposed pads were stored in protective envelopes inside unwaxed sandwich bags (DAVIS 1980). All monitoring media were transported to the laboratory in an ice chest containing a frozen-gel refrigerant and were stored in a freezer until extracted. A 25-cm^2 portion was cut from the center of each pad, along with those portions of the protective envelope that had been in contact with the excised portion of the pad. The portions of pad and envelope were extracted by shaking at the maximum setting of a wrist-action shaker for 15 min. This was done in 4-oz (118 mL) powder jars containing 25 mL of an azeotropic mixture of hexane:acetone (41:59), which was also used for extraction of other monitoring media in Soxhlets. After the extract was decanted, the process was repeated with a second 25-mL portion of solvent and the extracts were combined. All extracts were stored in a refrigerator until analyzed. Hourly exposure rates were calculated according to the procedure described by DAVIS (1980).

Hand exposures were estimated from residues collected on thin cotton or nylon gloves. The female thinners usually wore medium-weight cotton gloves, so did not object to wearing our monitoring gloves. The male thinners felt that gloves interfered with their work, so their hand exposures were not monitored. Exposed gloves were stored in 4-oz (118-mL) powder jars and were Soxhlet extracted for approximately 3 h using the hexane:acetone mixture.

Residues that could potentially produce respiratory exposure were collected on polyurethane foam plugs 3.8 cm in length and 2.5 cm in diameter. The foam plugs were placed inside samplers made from sections of aluminum pipe 5.1 cm in length with a 2.5-cm inside diameter. One end of each sampler was sealed with a 0.64-cm-thick aluminum disc, which had a hose connector threaded into its center. The samplers were attached at the workers' lapels with the open end down. Air was drawn through the plugs by battery-operated personal air sampling pumps attached to the workers' belts (Du Pont Model P 4000 High-Flow Samplers, Du Pont Co., Applied Technology Div., Wilmington, DE 19898). Airflow through the plugs was maintained at approximately 3 L/min and was measured before and after the monitoring period. The mean of these two measurements was used to calculate the volume of air sampled. Exposed plugs were processed in the same manner as gloves. Subjective estimates of respiratory rates for pesticide workers were used to calculate potential respiratory exposures. These rates are 30 L/min for male and 16 L/min for female thinners (LEWIS et al. 1980).

To determine dislodgeable residues on foliage, six leaf-punch samples were taken on each of the 2 days the workers were monitored. The samples were collected at approximately the middle of the workers' exposure period and were taken from trees that were about to be thinned. Each sample consisted of 30 punches, 10 from each of 3 trees. Samples were taken to reflect the ratio of varieties being thinned, i.e., on each day, 2 Golden and 4 Red. Dislodgeable residues were extracted from the leaf-punch samples by the following modification of the procedure of IWATA et al. (1977). After dislodgement of residues into Sur-Ten solutions, the residues were partitioned twice into 50-mL portions of hexane. To determine total foliar residues, the leaf-punch samples that had been treated with Sur-Ten solutions were reextracted by shaking 10 min with 60-mL portions of hexane. Total foliar residues were the sum of residues found by both extraction procedures. Foliar residue levels were calculated using the surface area of both sides of the 2.2-cm-diameter punches.

All residues were quantified by gas chromatography through a 1.8-m x 4-mm (inside diameter) glass column packed with 3% SP-2100 on 80/100-mesh Supelcon AW-DMCS (Supelco, Inc., Bellefonte, PA 16823). The carrier gas was nitrogen with a flow of 80 mL/min; the oven temperature was 210°C; and the temperature of the ^{63}Ni electron capture detector was 350°C.

Since gauze pads, polyurethane foam plugs, gloves, leaf punches, and extracts were stored for various periods of time, it was necessary to investigate storage losses. It was also necessary to determine recoveries from the various sampling media. For these investigations, all storage conditions and extraction procedures were the same as those used for field samples. All samples for these laboratory investigations were prepared using a portion of the 25% WP phosalone that had been used to prepare the orchard spray. To determine the stability of phosalone during freezer storage, small alpha-cellulose pads were fortified with a simulated spray and were extracted after various periods of storage. To determine the stability of phosalone in extracts, the initial extracts from the alpha-cellulose pads were reanalyzed after various periods of storage. Recovery of dry phosalone residues from multilayered gauze pads was determined using pads that had from 0.8 to 12 mg of the 25% WP phosalone sandwiched within the gauze. This procedure was described in detail elsewhere (STEVENS & DAVIS 1981). To produce dry residues in other media, fortification was done with an acetone extract of the WP. This was prepared by mixing 4 g of WP with 100 mL of acetone, stirring 1 h, and filtering. Gloves (four cotton and four nylon) were fortified by placing each in a Soxhlet receiver with the cuff outside, distributing 1 mL of the acetone filtrate inside each glove [10 mg active ingredient (AI)/glove], and allowing the gloves to air dry for 1 h prior to extraction. Polyurethane foam plugs were fortified with a 1:100 dilution of the acetone filtrate. A gas chromatography syringe was used to inject 100 µL of the diluted filtrate into the center of each three plugs (10 µg AI/plug) and the plugs were air dried for 30 min prior to

extraction. Recovery from the Sur-Ten solution used to dislodge foliar residues was determined using a portion of the acetone filtrate, which had been diluted at 1:50. Four 100-mL portions of Sur-Ten solution were each fortified with 1 mL of the diluted filtrate (200 µg AI/sample).

RESULTS AND DISCUSSION

Investigation of the stability of phosalone in frozen media and in extracts indicated no losses after 2 mo of storage. Recoveries from various monitoring media are shown in Table 1. Since the only significant losses occurred in the extraction of dislodgeable residues, only these data were corrected for losses.

Table 1. Recovery of Phosalone from Fortified Monitoring Media

Medium	Approximate Amount of Phosalone Added	Extraction Method	Recovery[a] %
Gauze pads	0.2-3 mg	Shaking[b]	99 ± 6 (8)
Polyurethane foam plugs	10 µg	Soxhlet[b]	110 ± 6 (3)
Cotton gloves	10 mg	Soxhlet[b]	100 ± 5 (4)
Nylon gloves	10 mg	Soxhlet[b]	95 ± 15 (4)
Sur-Ten solution	200 µg	Dislodgeable residue[c]	66 ± 2 (4)

[a]Mean ± standard deviation for the number of replicates indicated in parentheses.
[b]Solvent was hexane:acetone (41:59).
[c]Solvent was hexane.

Dislodgeable and total phosalone residues found at approximately 24 and 48 h after application are shown in Table 2. Comparison of the dislodgeable residue data by Student's t-distribution indicated no significant differences at the 95% confidence level between the following: Red at 24 h vs Golden at 24 h, Red at 48 h vs Golden at 48 h, or Red and Golden at 24 h vs Red and Golden at 48 h.

Table 2. Phosalone Residues Found on Apple Foliage[a]

Delicious Apple Type	Hours After Application	Foliage Residue ($\mu g/cm^2$)[b]	
		Dislodgeable	Total
Red	24	1.7 ± 0.1 (4)	2.3 ± 0.2
Golden	24	1.4 ± 0.1 (2)	1.8 ± 0.1
Red	48	1.6 ± 0.3 (4)	2.0 ± 0.3
Golden	48	1.7 ± 0.3 (2)	2.2 ± 0.3
Red and Golden	24	1.6 ± 0.2 (6)	2.1 ± 0.3
Red and Golden	48	1.6 ± 0.3 (6)	2.1 ± 0.3

[a]After application of a spray containing 1.5 lb phosalone/200 gal water to each acre of orchard (1.7 kg/1,870 L/ha).
[b]Mean ± standard deviation for the number of replicates indicated in parentheses.

Potential dermal and respiratory exposures received by the thinners are shown in Table 3. These data were also examined for significant differences at the 95% confidence level using Student's t-distribution. When data from either day's monitoring were compared, there were no significant differences between men and women in dermal exposure to areas other than hands. This indicated that men and women would have received approximately the same total dermal exposure. Therefore, to arrive at the total dermal exposures indicated in the last two lines of Table 3, the mean hand exposure received by men was assumed to be the same as that received by women. There was an apparent difference in respiratory exposures received by men and women, but comparison of the amounts of phosalone collected during a given time on their air samplers indicated that this difference was due to the different respiratory rates used to calculate their exposures. To obtain a single respiratory exposure value that could be used to estimate the hazard due to exposure at 24 or 48 h after phosalone application, all respiratory exposures were recalculated assuming that both men and women had a respiratory rate of 23 L/min. These recalculated respiratory exposures are also shown in the last two lines of Table 3. Total dermal exposures to areas other than hands and recalculated respiratory exposures were both significantly lower at 48 h than at 24 h, in spite of the fact that the dislodgeable residue levels were not different. Apparently the residues had become more resistant to dislodgement by contact with workers' clothing, but not to dislodgement by Sur-Ten solutions or workers' hands. Finally, there was no significant difference in the amounts of residue collected on the two types of gloves used for the monitoring.

Table 3. Potential Exposure of Apple Thinners to Phosalone

Sex of Thinners	Time to Reentry (h)	Exposure (µg/h)[a]						
		Face	Neck	Forearms	Total Dermal Other Than to Hands	Hands	Total Dermal	Respiratory
Male (3)	24	340 ± 150	110 ± 28	3,300 ± 160	3,800 ± 230	--	--	150 ± 38
Female (7)	24	300 ± 78	120 ± 33	3,100 ± 430	3,500 ± 510	5,500 ± 950[b]	9,000 ± 1,400	89 ± 25
Male (3)	48	270 ± 130	70 ± 35	2,000 ± 320	2,400 ± 180	--	--	90 ± 15
Female (7)	48	260 ± 130	75 ± 29	2,400 ± 670	2,700 ± 800	5,500 ± 990[c]	8,200 ± 1,500	60 ± 17
Male and Female (10)	24	310 ± 97	120 ± 31	3,100 ± 380	3,600 ± 450	--	9,100[d,e]	130 ± 32[d,f]
Male and Female (10)	48	260 ± 120	74 ± 29	2,300 ± 590	2,600 ± 680	--	7,100[d,e]	81 ± 22[d,f]

[a]Mean ± standard deviation for the number of workers indicated in parentheses.
[b]Monitored using cotton gloves.
[c]Monitored using nylon gloves.
[d]Typical exposures for all workers thinning phosalone-treated apples.
[e]Sum of mean total dermal exposure to areas other than hands for 10 workers and mean hand exposures for seven workers.
[f]Calculated assuming a respiratory rate of 23 L/min for all workers.

The exposures found in this study can be compared with those found after application of WP parathion (WOLFE et al. 1975). The total foliar residues found in the present study were 2.1 $\mu g/cm^2$ on both days. Wolfe reported the same total foliar residue at 24 h for his "Series 3" experiment. He also reported potential dermal and respiratory exposures of 9.9 and 0.11 mg/h, respectively, at 24 h. The same respective exposures obtained in the present study were 9.0 and 0.13 mg/h at 24 h and 8.2 and 0.081 mg/h at 48 h. Considering the relatively large variations encountered when monitoring potential exposure, these two studies are in excellent agreement.

To estimate the acute toxic hazard due to the potential exposures observed, one must make two assumptions. Since the inhalation toxicity of phosalone has not been reported (NIOSH 1980), one must assume that its acute inhalation toxicity is equal to its acute oral toxicity. Also, one must assume that the acute toxicity of phosalone is the same for rats and humans. The dermal and oral LD_{50}s for phosalone in rats have been reported to be 390 and 120 mg/kg, respectively (NIOSH 1980). Therefore, the same respective LD_{50}s for a 70-kg human are assumed to be 27 and 8.4 g. The potential dermal and respiratory exposures for thinners at 24 h after application of phosalone were found to be 9.1×10^{-3} and 1.3×10^{-4} g/h, respectively. Thus, the thinners were assumed to have received 0.034% of a lethal dose/h by the dermal route and 0.0015% of a lethal dose/h by the respiratory route. While working their normal 7.5-h day, they would receive a total of 0.27% of a lethal dose. It is apparent that the acute toxic hazard for apple thinners entering phosalone-treated orchards at more than 24 h after application is very small.

REFERENCES

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

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

IWATA, Y., J.B. KNAAK, R.C. SPEAR, and R.J. FOSTER: Bull. Environ. Contam. Toxicol. 18, 649 (1977).

LEWIS, R.G., M.D. JACKSON, and K.E. MACLEOD: Protocol for Assessment of Human Exposure to Airborne Pesticides, EPA-600/2-80-180. U.S. Environmental Protection Agency, Research Triangle Park, NC (1980).

NIOSH: Registry of Toxic Effects of Chemical Substances, Quarterly Microfiche Update, National Institute for Occupational Safety and Health, Cincinnati, OH (Oct. 1980).

STEVENS, E.R., and J.E. DAVIS: Bull. Environ. Contam. Toxicol. 26, 681 (1981).

WOLFE, H.R., J.F. ARMSTRONG, D.C. STAIFF, S.W. COMER, and W.F. DURHAM: Arch. Environ. Contam. Toxicol. 3, 257 (1975).