Persistence of Parathion and its Oxidation to Paraoxon on the Soil Surface as Related to Worker Reentry into Treated Crops[1]

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The considerable interest in establishing safe reentry times for personnel working in fields treated with insecticides, particularly parathion, is due to a number of unexplainable poisonings that have occurred in recent years. QUINBY and LEMMON (1958) reported cases of parathion poisoning among farm workers, sometimes at relatively long intervals after spraying, when the parathion, presumably, had reached safe levels. MILBY et al. (1964) reported parathion poisoning from 16 orchards in California in which an average of 23 days elapsed between the last application and the poisoning. They found paraoxon on the foliage of trees that had been sprayed with parathion and implied that paraoxon may have caused the poisoning of farm workers.

The route and the extent of exposure of farm workers to pesticide residues have not been ascertained. Most research related to worker reentry has concerned concentrations or persistence of organophosphate insecticides, or their toxic degradation products, on foliage, fruit, or dust associated with the foliage (QUINBY and LEMMON, 1958; MILBY et al., 1964; BAILEY 1972; WESTLAKE et al., 1973; SERAT 1973; POPENDORF and SPEAR, 1974; SPEAR et al., 1974; LEFFINGWELL et al., 1975). POPENDORF and SPEAR (1974) concluded that harvest workers in the central valley of California are exposed to pesticide residues primarily because the pesticide-containing dust is dislodged from the foliage during crop harvesting. SPEAR et al. (1974) found that the dislodgable residues in citrus groves three weeks

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after parathion application were mainly paraoxon. Other workers have identified paraoxon as a photodegradation product of parathion on foliage (JOINER and BAETCKE, 1973; GRUNWELL and ERICKSON, 1973). The formation of paraoxon, or its persistence, is apparently enhanced by the presence of dust on the foliage (WESTLAKE et al., 1973; SPEAR et al., 1974; POPENDORF et al., in press). WARE et al. (1972, 1973) reported very low concentrations of paraoxon and a relatively low persistence of parathion sprayed on clean cotton leaves in Arizona.

Considerable quantities of insecticides ultimately reach the soil surface, either by direct application or by wash-off from crops in excess water applied with the insecticide. Pesticides are much more persistent in dry soil than moist soil, mainly because they are less volatile (SPENCER et al., 1969, 1973) and microbiological activity is lower in dry soil (LICHTENSTEIN and SCHULZ, 1964). Essentially, all the episodes of worker poisoning with organophosphate insecticides have occurred during the hot, dry summer months in California while workers were harvesting tree fruits or grapes. These crops are often furrow or drip irrigated, which results in a relatively high percentage of the soil remaining dry during the summer irrigation season. In this study, we determined the persistence of parathion and its oxidation to paraoxon on dry soil under treated citrus trees in relation to the hazard to workers reentering the grove to pick fruits.

MATERIALS AND METHODS

Test plots were in a furrow-irrigated citrus grove near Lindcove, California. Furrows were on each side of the tree row and in the row middle. The grove was irrigated at 10- to 14-day intervals, with less than 40% of the grove floor being wetted during irrigations. Thus, approximately 60% of the grove floor remained dry during the experiment. The soil was San Joaquin loam (pH 7.2; organic matter 1.2%; clay 9.7%, predominately kaolinite and illite).

Ethyl parathion (wettable powder) was sprayed on three plots of about 250 trees each at the rates of 2 lb/A in 500 gallons of water/A, 4 lb/A in 1000 gallons of water/A, and 8 lb/A in 1500 gallons of water/A in early June 1974. Periodic sampling after application of parathion included several types of foliar samples and samples of soil and dust beneath the sprayed citrus trees. Fruit pickers reentered the grove at 14, 21, and 25 days after application of 2, 4, and 8 lb parathion/A, respectively. The relationship between their blood cholinesterase response and exposure to parathion and paraoxon on foliage or soil will be reported elsewhere. This report is limited to the soil and dust sampling phase of the study.

Dust samples were taken periodically from dry soil at the dripline of the tree and in the row middle between irrigation furrows. Soil samples were taken from the dripline in the dry area between irrigation furrows, from the row middle in the dry area between furrows, and from the dripline within the wetted furrow area. Soil and dust samples from each position were obtained before parathion was applied and at various times after application, beginning 2 days after spraying at 2 and 4 lb/A, and 4 days after spraying at the 8-lb/A rate. Samples of loose dust were obtained by vacuuming through a 100-mesh screen installed on the bottom of a 17.7- x 25-cm wooden frame. The frame was held on the soil surface and a stainless steel nozzle attached to a portable vacuum cleaner was passed over the screen. Soil samples were obtained with a 3-cm-diameter stainless steel tube closed off with a stainless steel plate at 1 cm from the sampling end to ensure sampling to only the 1-cm depth. Except during the fruit picking period, individual samples consisted of 48 soil cores, or dust sampling sites, obtained from 12 trees in each plot during each sampling day. Thus, each composite sample of 48 sites represented either the loose dust passing through a 100-mesh screen in an area of 2.2 m^2 or soil from 339 cm^2 to a depth of 1 cm. During the picking period, the plots were subdivided into thirds and each type of sample was taken from 8 trees instead of 12 trees, resulting in 32 individual sampling sites rather than 48 for each composite sample.

Samples were frozen immediately with dry ice and kept frozen until processed in the laboratory. Samples taken from the known sampling areas were weighed to enable calculation of parathion and paraoxon concentrations on a unit area basis. Dust and soil samples were extracted with an azotropic mixture of hexane and acetone for 5 and 4 hours, respectively, in a Soxhlet extractor. Concentrations of parathion and paraoxon in the extracts were determined by gas chromatography using a flame-photometric detector sensitive to phosphorus-containing compounds.

The gas chromatograph was equipped with a 1.83-m x 4-mm I.D. Pyrex glass column packed with 3% OV-1 on chromosorb W-HP (80-90 mesh). The operating parameters were: nitrogen carrier flow, 100 ml/min; burner flow rates, 74 ml hydrogen/min and 100 ml air/min; and inlet, column, and detector temperatures of 200°, 190°, and 205°C, respectively. Minimum detectable limits were 0.02 and 0.07 µg/g parathion and 0.07 and 0.25 µg/g paraoxon in soil and dust, respectively.

RESULTS AND DISCUSSION

Parathion and paraoxon concentrations in dust obtained at the dripline of trees treated at the rates of 2, 4 and 8 lb parathion/A are shown in Figure 1. Parathion concentrations in dust were very high and its rapid oxidation to paraoxon was apparent even at the first sampling dates, i.e., 2 and 4 days after application at the 2-, 4-, and 8-lb/A rates, respectively. With 8 lb parathion/A, paraoxon concentration reached a maximum of 157 μg/g (ppm) at 11 days and decreased very slowly thereafter. Paraoxon concentrations remained above 100 μg/g for at least 46 days after application. At 4 lb parathion/A, concentrations of parathion and paraoxon were lower, with the paraoxon concentrations being slightly higher than the parathion concentrations after 8 days following application. At 2 lb parathion/A, concentrations of parathion and paraoxon were similar to the 4-lb/A rate on day 2, but concentrations decreased more rapidly at 2 lb/A. Figure 2 shows the total parathion and paraoxon concentrations per unit area in dry soil samples obtained from the first centimeter of soil at the dripline and middle of the row at various times after the application of 8 lb parathion/A. These values are assumed to represent the total amount of parathion or paraoxon in the soil, since movement below 1 cm would be negligible in the dry soil.

Table 1 illustrates comparative concentrations of parathion and paraoxon in each type of dust and soil sample. The residue concentrations on a weight basis (μg/g) were much higher in dust than in soil samples, but the reverse was true when concentrations were expressed on an area basis ($\mu g/cm^2$). This would be expected since the soil represented the 0- to 1-cm depth, whereas the dust was only the loose material at the soil surface. The ratio of paraoxon to parathion increased with time. The percent of the total soil paraoxon in dust was much greater than the percent of the total parathion. The ratio of paraoxon to parathion was greater in dust than in soil. These results indicate that sampling only the bulk soil may not be adequate for evaluating the potential hazards from paraoxon and parathion in loose dust at the soil surface.

The depth of dust required to account for the total paraoxon residue indicated that paraoxon was being produced only at the soil surface, most likely by photolysis. For example, at day 4 the total amount of paraoxon in the soil could be contained in dust only 0.009 cm deep at the paraoxon concentration measured in dust (114 μg/g) that day (Table 1). The calculated depth of dust required to contain the total residue was greater for parathion than for paraoxon, and this depth increased with time for both, probably because paraoxon and parathion slowly diffused into the dry soil.

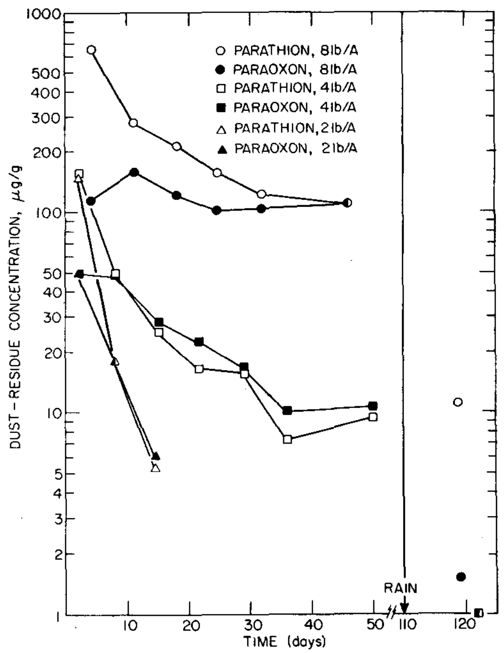

FIG. 1. Concentrations of parathion and paraoxon in dust obtained at the dripline of citrus trees at various times after the application of 2, 4, and 8 lb parathion/A.

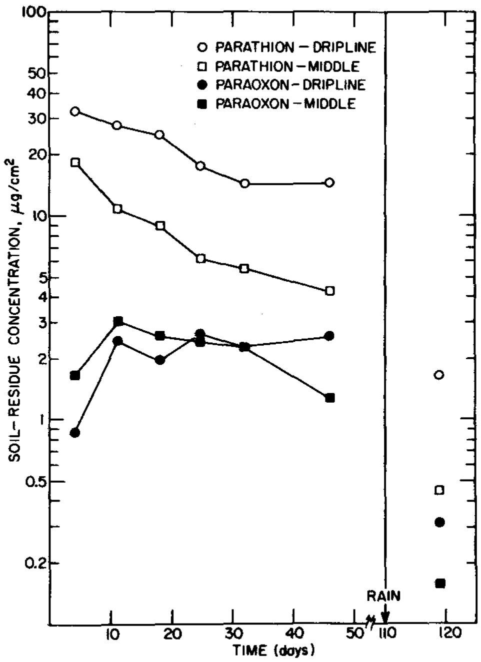

FIG. 2. Concentrations of parathion and paraoxon in the 0- to 1-cm layer of dry soil obtained at the dripline and row middle at various times after the application of 8 lb parathion/A.

TABLE 1

Paraoxon (oxon) and parathion (thion) in soil and dust obtained from beneath citrus trees at 4, 11, and 25 days after spraying with 8 lb parathion per acre.

Days	Sample Location	Type of Sample	Residue concentration				Ratio	% of total residue in dust[1]		Dust depth for total residue[2]	
			oxon		thion		$\frac{\text{oxon}}{\text{thion}}$	oxon	thion	oxon	thion
			$\mu g/g$	$\mu g/cm^2$	$\mu g/g$	$\mu g/cm^2$				cm	cm
4	Drip, dry	Dust	114	0.183	657	1.06	0.173	21.0	3.2	0.009	0.057
	Drip, dry	Soil	1.63	0.870	35.2	32.6	0.026	-	-	-	-
	Drip, wet[3]	Soil	No sample, irrigation water in furrows.								
	Middle, dry	Dust	64	0.117	257	0.475	0.246	7.0	2.6	0.023	0.063
	Middle, dry	Soil	1.56	1.66	16.4	18.2	0.091	-	-	-	-
11	Drip, dry	Dust	157	0.252	277	0.444	0.567	10.3	1.6	0.018	0.114
	Drip, dry	Soil	2.69	2.44	30.4	27.6	0.088	-	-	-	-
	Drip, wet[3]	Soil	0.24	0.323	5.0	6.54	0.049	-	-	-	-
	Middle, dry	Dust	59	0.128	106	0.237	0.540	4.2	2.2	0.046	0.088
	Middle, dry	Soil	3.13	3.06	11.2	10.9	0.279	-	-	-	-
25	Drip, dry	Dust	101	0.190	156	0.288	0.702	7.3	1.6	0.026	0.120
	Drip, dry	Soil	2.84	2.60	19.6	17.7	0.158	-	-	-	-
	Drip, wet[3]	Soil	0.09	0.126	1.0	1.34	0.088	-	-	-	-
	Middle, dry	Dust	36	0.136	40	0.150	0.908	5.6	2.6	0.061	0.137
	Middle, dry	Soil	2.0	2.42	5.3	6.2	0.400	-	-	-	-

[1] The total residue is the amount of parathion or paraoxon contained in the 0- to 1-cm soil samples.

[2] Calculated depth of dust required to contain the total residue assuming the same bulk density as the soil.

[3] Sampled within irrigation furrows wetted at 10- to 14-day intervals.

Paraoxon and parathion concentrations were higher in dust from the dripline than in dust from the middle of the row. However, the ratio of paraoxon to parathion was greater from the row middle and the total amount of soil paraoxon ($\mu g/cm^2$) was greater at the row middle than at the dripline for the first 18 days. The higher ratio of paraoxon to parathion and the greater total paraoxon at the row middle than at the dripline was most likely caused by the greater amount of sunlight reaching the soil surface at the row middle.

The concentrations of parathion and paraoxon were much lower in soil from the irrigation furrows than from the "dry" sampling sites. Parathion did not persist and paraoxon did not accumulate in irrigation furrows, probably because they were hydrolyzed in the wet soil or volatilized from the surface of the wet soil after irrigation. Also, parathion and paraoxon concentrations in dust and soil were extremely low following a rain that fell 110 days after parathion application (Fig. 1 and 2). This response in wet soil indicates that wetting the soil likely would lessen the hazards to pickers from parathion and paraoxon on the soil surface or in dust.

The importance of these relatively high paraoxon levels in dust on the grove floor will depend on the amount of dust as well as the concentration of paraoxon. The dust, containing residues, can be blown onto foliage which later comes in contact with workers, or workers reentering groves can be contaminated by direct contact with the soil surface or by stirring up dust as they move through the grove. The amount of dust sampled in this study averaged 2.0 and 3.0 mg/cm^2 from the dripline and row middle, respectively. This difference was due to the presence of leaves and other trash at the dripline. Even though these amounts of dust are relatively small, they are considerably larger than occur on foliage (POPENDORF et al., in press). Also, the amount of dust on the grove floor may vary widely and is often considerably more than was found in this test grove.

SUMMARY

Soil and dust samples from beneath citrus trees contained relatively high concentrations of paraoxon and parathion for at least 45 days after parathion was applied at normal rates. These data indicate that parathion dripping on dry soil from sprayed crops, or sprayed directly on the soil surface, can persist for long periods and be oxidized to the highly toxic paraoxon. The residue concentrations are much higher on the loose dust particles than in the bulk soil. The data indicate that the soil or

grove floor should be considered as a possible contributing source of toxicant along with foliage, or dust on foliage, to workers reentering treated fields. In any event, the data confirmed the high rates of oxidation of parathion to paraoxon on particulate matter, whether on foliage (SPEAR et al., 1974) or at the soil surface. The particulate matter appears to contribute to the accumulation of paraoxon, either by enhancing oxidation of parathion to paraoxon or by decreasing dissipation of paraoxon.

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REFERENCES

BAILEY, J. B.: Agrichem Age 15, 6 (1972).
GRUNWELL, J. R., and R. H. ERICKSON: J. Agr. Food Chem. 21, 929 (1973).
JOINER, R. L., and K. P. BAETCKE: J. Agr. Food Chem. 21, 391 (1973).
LEFFINGWELL, J. T., R. C. SPEAR, and D. JENKINS: Arch. Environ. Contam. Toxicol. 3, 40 (1975).
LICHTENSTEIN, E. P., and K. R. SCHULZ: J. Econ. Entomol. 57, 618 (1964).
MILBY, T. H., F. OTTOBONI, and H. MITCHELL: J. Am. Med. Assoc. 189, 351 (1964).
POPENDORF, W. J., and R. C. SPEAR: Am. Ind. Hyg. Assoc. J. 35, 374 (1974).
POPENDORF, W. J., R. C. SPEAR, and S. SELVIN: Environ. Sci. Tech. (in press).
QUINBY, G. E., and A. B. LEMMON. J. Am. Med. Assoc. 166, 740 (1958).
SERAT, W. F.: Arch. Environ. Contam. Toxicol. 1, 170 (1973).
SPEAR, R. C., T. H. MILBY, and J. T. LEFFINGWELL: Abstracts, 167th ACS Meeting, Los Angeles (1974).
SPENCER, W. F., M. M. CLIATH, and W. J. FARMER: Soil Sci. Soc. Am. Proc. 33, 509 (1969).
SPENCER, W. F., W. J. FARMER, and M. M. CLIATH: Residue Reviews 49, 1 (1973).
WARE, G. W., B. ESTESEN, and W. P. CAHILL: Bull. Environ. Contam. Toxicol. 8, 361 (1972).
WARE, G. W., D. P. MORGAN, B. ESTESEN, W. P. CAHILL, and D. M. WHITACRE: Arch. Environ. Contam. Toxicol. 1, 48 (1973).
WESTLAKE, W. E., F. A. GUNTHER, and G. E. CARMAN: Arch. Environ. Contam. Toxicol. 1, 60 (1973).