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Received for review November 12, 1975. Resubmitted October 6, 1977. Accepted October 19, 1977.

Conversion of Parathion to Paraoxon in Foliar Residues: Effects of Dust Level and Ozone Concentration

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Dwarf Eureka lemon trees were treated with parathion and placed in an environmental chamber for 4 days with the object of determining the effect of foliar dust level and atmospheric ozone concentration on the production of paraoxon in the dislodgeable foliar residues. At low levels of foliar dust little paraoxon was produced regardless of ozone concentration. Compared to production at low dust levels, paraoxon production was increased by a factor of 4 at high dust levels without ozone and by nearly a factor of 30 at high dust levels in the presence of 300 ppb of ozone.

In California there have been at least 29 separate poisoning incidents reported among agricultural fieldworkers exposed to organophosphate pesticide residues since the introduction of these compounds in 1948 (Spear et al., 1975a). Parathion has been implicated in the majority of these incidents, and there is now strong evidence that its oxygen analogue, paraoxon, is the principal toxic constituent of the weathered residue on both foliage and in the soil of orange groves in Central California (Spear et al., 1977a,b). Although paraoxon has been detected in foliar residues in other regions of the United States (Utah Biological Test Laboratory Report, 1976) (UBTL), it appears that the environment of the Central Valley of California is particularly conducive to the formation and persistence of this highly toxic metabolite of parathion.

The sporadic occurrence of the known incidents and the findings of an investigation into a poisoning incident in June 1975 (Spear et al., 1977b) led us to inquire into the nature of unusual environmental circumstances which might lead to an abnormal production of paraoxon in foliar and soil residues. In an attempt to identify these factors, parathion-treated dwarf Eureka lemon trees were exposed to various experimental conditions in an environmental chamber. This report deals with the effects of foliar dust and of atmospheric oxidant concentrations on paraoxon residue levels observed in these chamber experiments. Complementary investigations were carried out with soil

residues and will be reported subsequently.

EQUIPMENT AND METHODS

The experiments described below were carried out in an environmental chamber constructed of enamelled plywood whose interior dimensions are 7.5 ft high by 7.8 ft wide by 14 ft in length. The chamber has both temperature and humidity control and is equipped with Atlas Electric RM-65 xenon arc lamps whose spectrum is quite similar to that of sunlight. The intensity of these lamps in the critical region from 280 to 450 nm results in approximately 75% of the radiant flux at summer noontime in the Central Valley of California.

Ozone was introduced into the chamber from a Wellsbach T-23 laboratory ozonator. Ozone levels were continuously monitored with a Dasibi 1003-AH UV photometer and frequently with a Mast Model 724 Oxidant Monitor. When ozone levels were within the operating ranges for both instruments, no differences were observed in their readings. Although hydrocarbons emanating from the chamber and/or from the trees in confined circumstances might lead to molecular species not normally found in the field, we believe the uniformity of ozone levels indicated by the Mast and Dasibi instruments suggest ozone to have been the only significant oxidizing species present in the chamber and that it was an adequate model oxidant for the purposes of this study.

Prior to pesticide application, the foliage of the trees was washed with a solution of Sur-Ten wetting agent in water to remove the preexisting dust load. The trees were then thoroughly rinsed with distilled water. This procedure was required in order to control the foliar dust level for ex-

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Table I. Foliar Dust Levels and Atmospheric Ozone Concentrations during Chamber Exposures

Experiment and figure number	Mean dust level, $\mu\text{g}/\text{cm}^2$	Ozone concn, ppb
1	35.2	0
2	456.0	0
3	30.5	300
4	280.0	300

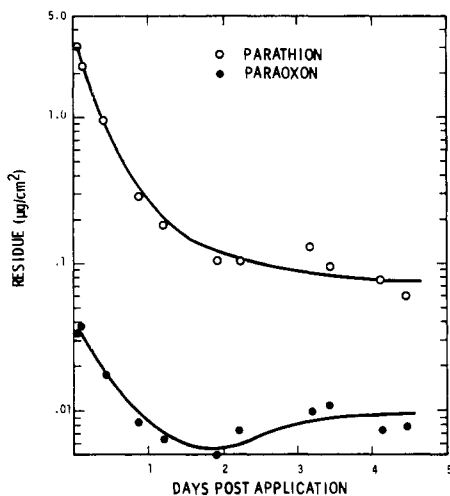


Figure 1. Dislodgeable residues; low dust, zero ozone.

perimental purposes. The desired dust loads were then achieved by adding a standard dust to the spray tank to be applied with the parathion. The standard dust was prepared from soil collected in the citrus growing area of the Central Valley of California and passed through a Denver air classifier prior to use. These dusts have a maximum particle size of $50\ \mu\text{m}$. In all cases, samples of these dusts were analyzed before use to assure that no trace of parathion or paraoxon was present.

An emulsifiable formulation of ethyl parathion was used (Ortho 45% emulsive). Application was by hand sprayer with a tank mix chosen to simulate a field application of 4.5 lb of active ingredient per acre in 300 gal of water. To avoid problems of phytotoxicity, the trees were sprayed out of doors, allowed to dry for 1 to 2 h, and then moved into the chamber.

Dislodgeable residue samples were collected twice on each day of the experiment by the method of Gunther et al. (1974), with modifications to the residue extraction procedure as described by Spear et al. (1975b). Sampling was done with a 1.5 cm diameter punch, and 12 leaf discs were taken from each of three trees, totalling 36 leaf discs/sample. After partitioning the pesticide into chloroform, the pesticide-free aqueous phase was filtered through a Millipore filtration apparatus and the dust collected onto a preweighed 4.25 cm Whatman GF/C filter. Each filter was then oven dried at $105\ ^\circ\text{C}$ for at least 8 h and reweighed in order to quantitate the foliar dust.

Analysis for parathion and paraoxon was performed on a Tracor MT222 gas chromatograph equipped with a Melpar flame photometric detector. Gas flows were as follows: nitrogen carrier, 85 mL/min; hydrogen fuel, 90 mL/min; oxygen, 12 mL/min; and air, 50 mL/min. A 6 ft \times 2 mm i.d., 10% DC200 on Chromosorb WHP 80/100 mesh column was run at $195\ ^\circ\text{C}$. Retention times were 3.8 min for diazoxon, which was used as an internal standard, 5.7 min for paraoxon, and 7.2 min for parathion.

Four experiments were conducted to investigate the effects of ozone and dust level. The conditions for each are given in Table I. On each day of an experiment, the xenon arc lamps were on for 8 h and off for 16 h. When

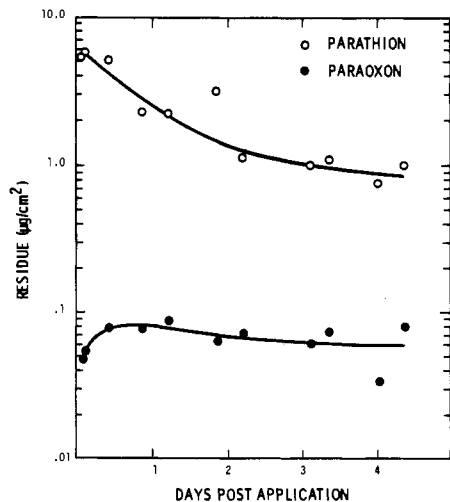


Figure 2. Dislodgeable residues; high dust, zero ozone.

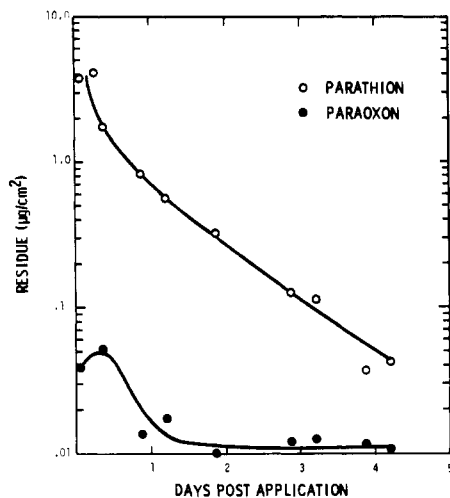


Figure 3. Dislodgeable residues; low dust, high ozone.

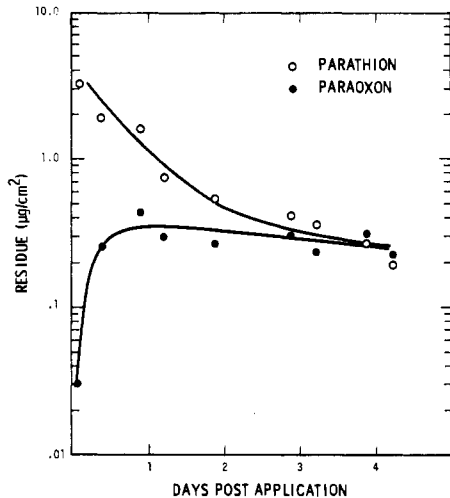


Figure 4. Dislodgeable residues; high dust, high ozone.

ozone was used, it was maintained at 300 ppb for the same 8-h period that the lights were on and dropped to zero for the remaining period. Temperatures and relative humidity were maintained constant at $100\ ^\circ\text{F}$ and 30%, respectively.

RESULTS

The results of the four experiments are shown in Figures 1 to 4. The solid lines indicate the trend of the data and are included for descriptive purposes. The initial deposits of both parathion and paraoxon show considerable vari-

Table II. Paraoxon Production Index as a Function of Dust Level and Ozone Concentration

	Ozone Concentration, ppb	Dust level	
		Low	High
	0	2.74×10^{-3}	11.5×10^{-3}
	300	3.13×10^{-3}	81.8×10^{-3}

ability between experiments, 3.24 to 5.35 $\mu\text{g}/\text{cm}^2$ and 0.030 to 0.047 $\mu\text{g}/\text{cm}^2$, respectively. However, the initial paraoxon/parathion ratios are quite uniform for each dust level. For the "clean" trees (Figures 1 and 3), the oxon/thion ratios were 0.0104 and 0.0105, whereas for the "dusty" trees (Figures 2 and 4), the ratios were 0.0092 and 0.0089, respectively. The mean dislodgeable dust level for the dusty trees is in the range observed in field studies (Popendorf et al., 1975).

From a qualitative point of view, the results depicted in the figures clearly indicate that little paraoxon is produced at low dust levels regardless of the ozone level. At high dust levels and without ozone, relatively low paraoxon residues are produced, whereas in the presence of 300 ppb of ozone, high paraoxon residues are attained. Also, there is a marked effect of dust on the decay rate of parathion, with high dust levels leading to a greater persistence of the parent compound. At the end of the experiments, the parathion residues on the dusty trees were 11 and 18% of the original deposit, whereas the corresponding values for the clean trees were 3.6 and 1.8%. The effect of ozone level on parathion decay is not clear from these experiments.

As an index of the effects of ozone and foliar dust on paraoxon production, we have chosen the "plateau level" of paraoxon divided by the initial parathion deposit. The "plateau level" is defined as the mean paraoxon residue over the last 2 days of each experiment, a period in which the paraoxon residues show little overall change. Dividing the plateau level by the initial parathion residue controls for variations in initial deposit since, for a constant rate of conversion of parathion to paraoxon, it may be expected that higher initial deposits of parathion lead to higher oxon plateaus. This variable will be termed the paraoxon production index.

Table II shows the values of the paraoxon production indices corresponding to the data presented in Figures 1 to 4. These index values demonstrate the interaction between foliar dust levels and atmospheric ozone concentrations on paraoxon production. Foliar dust level and ozone concentration are both very important to paraoxon production. Whereas 300 ppb of ozone led to an eightfold increase in the paraoxon production index at high dust levels, it had little effect at low dust levels.

DISCUSSION

Although it was not our objective to accurately simulate the decay patterns observed in the field, the chamber data

are qualitatively quite similar with a single exception (UBTL Report, 1976; Popendorf et al., 1976; Gunther, 1977). We are not aware of field data indicating a decline in paraoxon levels in the period immediately following application as shown in Figures 1 and 3. Whether this is due to the more frequent sampling schedules typical of the chamber experiments or the very low foliar dust levels present in these experiments is speculative. However, the more normal paraoxon patterns shown in Figures 2 and 4 suggest that dust level is the critical variable in the loss of the initial paraoxon deposit in the chamber.

From a quantitative point of view, the initial deposits of parathion exceed levels typical of field data by as much as a factor of 2. With this fact in mind, the paraoxon plateau of 0.531 $\mu\text{g}/\text{cm}^2$ of the high dust-high ozone experiment is not outside the range of field experience. For example, Popendorf has reported an oxon peak 0.336 $\mu\text{g}/\text{cm}^2$ with the corresponding parathion residue of 2.149 $\mu\text{g}/\text{cm}^2$ 14 h postapplication on citrus foliage in Central California (Popendorf, 1976). Nevertheless, paraoxon residues of 0.600 $\mu\text{g}/\text{cm}^2$ and above must be regarded as being present very rarely in normal field circumstances.

The results presented above show that foliar dust level is a primary determinant of paraoxon production in foliar residues of parathion in the laboratory setting. In addition, at dust levels typical of field conditions, ozone at 300 ppb can substantially increase paraoxon residues. Several of the areas, historically the sites of residue poisoning in California, are known to be troubled by both particulate and oxidant air pollutants. Until studies can be conducted to elucidate the importance of ozone and foliar dust in the field setting, it would be prudent to avoid exposure of workers to residues of parathion applied to dusty groves or orchards during periods of air stagnation.

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Received for review August 23, 1977. Accepted November 18, 1977.