CHLORDANE RESIDUES IN FLORIDA CITRUS SOILS[1,4]

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ABSTRACT

Chlordane 10 G applied to the soil surface at 5.6, 8.4, and 11.2 kg AI/ha remained in the 0 to 2.5 cm soil horizon and reached ppb levels after approximately 1 year. Chlordane did not leach below approximately 2.5 cm nor was chlordane detected in irrigation ditch water at or above 1.0 ppb. Chlordane was not found in 'Valencia' and 'Hamlin' orange leaves or fruit at or above 5.0 ppb. Chlordane disappeared in a pseudo-first order fashion with a half-life of 27 to 72 days.

Chlordane was substituted for the control of Fuller rose beetle, *Pantomorus cervinus* (Boh.), in Florida citrus when aldrin and dieldrin were banned by the United States Environmental Protection Agency in 1975. Although chlordane has been used for 25 years to control termites in very young citrus groves, no data are available under Florida conditions regarding its environmental behavior. Studies in other parts of the United States have shown that 15-40% of the applied chlordane may persist up to 14 years in soil (Fleming and Maines 1954, Lichtenstein and Polivka 1959, Nash and Woolson 1967). Chlordane may also penetrate root crops (Stewart 1975) and it has been found in a wide variety of agricultural soils where chlordane had not been used for at least 5 years (Carey et al. 1973). Technical chlordane is a complex mixture of at least 18 chlorinated components (Brooks 1974). It has an ecological magnification of about 100,000 as it moves through the food-web and has a water solubility of 0.056 ppm (Sanborn et al. 1976). In view of the documented environmental persistence and food-web magnification of chlordane, the present study was undertaken to determine the persistence of chlordane and the possible agroecosystem contamination by that chemical after an agricultural application to Florida citrus soils.

MATERIALS AND METHODS

Manual applications of granular 10 G chlordane were made with a Seymour seeder at rates of 5.6, 8.4, and 11.2 kg AI/ha (5.0, 7.0, and 10.0 lb AI/acre). Treatments were replicated 4 times in 0.91 ha plots in a Latin square design. Four no-treatment plots were included as controls.

Two experiments were conducted in 20-year-old 'Hamlin' orange groves near Lake Alfred, Florida (White Clay Pit Road and Shinn Groves) and 1 experiment was conducted in a 'Valencia' orange grove near Ft. Pierce, Florida (Fountain Grove). The Ft. Pierce grove was double-bedded (2 rows between ditches) with 1 m ditches between beds, 2 large feeder ditches at each end of the grove with an additional large feeder irrigation ditch along the road. The Lake Alfred groves were not irrigated.

Soil samples were taken by vacuuming five, 20 cm^2 x 2.5 cm deep volumes

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[1]Florida Agricultural Experiment Stations Journal Series No. 1372. This study supported in part by special funds from the Center for Environmental Programs, Univ. of Fla., Gainesville and by a commercial grant from Velsicol Corporation.
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[4]Use of a specific product does not constitute an endorsement by the University of Florida to the exclusion of similar products.

in each of the plots. A 2.5-10 cm, 10-17.8 cm, 17.8-33 cm and 33-61 cm sample was taken from the center of each vacuumed area with a standard soil sampling tube. The 5 samples from each soil horizon were bulked to obtain 1 sample per plot per soil horizon.

Water samples were taken from the Ft. Pierce grove ditches and lateral ditches in hexane-washed Mason jars. Four water samples from each of 7 irrigation ditches and the 3 supply ditches were taken each sampling day. Eight fruit and 10 leaves constituted a fruit leaf or sample. Samples not extracted immediately were stored a maximum of 15 days at —20°C.

Chlordane was extracted from soil samples by weighing 10 g of air dried soil from each bulked sample into 100-ml beakers and wetting with 2.0 ml of distilled water. Beakers were covered with aluminum foil and held at 4°C for 16 h. Fifty ml of 20:80 benzene:acetone was added to each beaker and the soil was sonicated at 15,000 Hz for 30 sec. The beaker was recovered with foil, the soil allowed to settle and a 5.0 ml aliquot was removed. This aliquot was evaporated almost to dryness in a 50.0-ml volumetric flask under N_2 at 50°C. After cooling, 5.0 ml of benzene was added to the 50.0-ml flask followed by 40.0 ml of 2% sodium sulfate. The flask was capped, shaken, and the layers were allowed to separate. The benzene was moved to the neck of the flask with distilled water and removed to brown glass bottles over a few grams of sodium sulfate for GLC analysis.

Fruit were separated into rind and pulp. The rind was diced, a 10 g subsample was homogenized in 30.0 ml of 1:1 dichloromethane:acetone and a 5.0 ml aliquot taken. Fruit pulp was homogenized and a 10 g subsample extracted as for rind. Leaves were weighed and homogenized in 50.0 ml of 1:1 dichloromethane:acetone and a 5.0 ml aliquot taken. Leaf and fruit extraction aliquots were evaporated to dryness under N_2, taken-up in 5.0 ml of benzene and column chromatographed on a 10 g silica gel column. Elution was with 50.0 ml of benzene.

A 100.0 ml aliquot of each water sample was extracted twice with 20.0 ml of dichloromethane and once with 20.0 ml of benzene. These extractions were combined, taken to dryness, and transferred to 10.0 ml of benzene over a few grams of sodium sulfate for gas-liquid chromatographic (GLC) analysis. All extractions were stored at —20°C prior to analyses.

At the 1 ppm level, recoveries from 8 replications of each fortified substrate were: soil—100.0 ± 4.0%; rind—98.5 ± 3.5%; pulp—98.7 ± 2.0%; and leaves—100.0 ± 3.0%. Chlordane was recovered from water at the 50 ppb level at 95.0 ± 5.5%.

The GLC analysis was done on a 0.8 m x 2 mm glass column packed with 5% SP 2100 on 100/120 mesh Gas Chrom. Q. Operating conditions were: column 190°C, inlet 220°C, Ni^{63} EC detector 300°C, N_2 60 ml/min. All GLC injections were 5 μl. Burdick and Jackson solvents, used for GLC and extractions, were assessed for contaminants by evaporating 500.0 ml to 2.0 ml for GLC.

Quantification was similar to Cochrane et al. (1975) with the quantification of heptachlor, heptachlor epoxide, γ-chlordane and γ chlordane/nonachlor (single peak) in technical chlordane by peak height used for estimation of technical chlordane. Since samples 140 days postapplication generally contained only the γ-chlordane and γ-chlordane/nonachlor GLC peaks, only these GLC peaks were used to estimate technical chlordane for 140 day + samples.

Moisture capacity, pH, and organic matter were measured in composited samples from each grove and soil horizon according to Black (1965) as modified by Anderson et al. (1968). Rainfall was measured with standard fencepost gauges (Weather Measure Corp.[4]). Technical chlordane and individual chlordane component standards were provided by Velsicol Corp. Statistical analyses were performed on a Tektronix 4051 graphic computing system with an interactive digital plotter (Tektronix, Inc.; Beaverton, Oregon 97077[4]).

Results and Discussion

Chlordane was apparently confined only to the upper 2.5 cm soil horizon in all 3 experiments for up to 445 days (Table 1). Only inconsistent and uninterpretable traces of chlordane were detected below 2.5 cm. Consequently only the 2.5 cm results are reported here. No apparent 'disappearance' of chlordane occurred until ca. 150 days postapplication. Tafuri et al. (1977) observed no disappearance of chlordane for ca. 169 days postapplication and confinement of chlordane to the 0-10 cm soil horizon in a clay loam soil.

The data in Table 1 are variable and the levels of chlordane observed on day 139 are consistently higher than those observed on day 48 and in some cases on day 13 postapplication. This variability was probably related to disking and mowing operations which occurred in all 3 experiments just prior to the 3rd sampling. Similarly, Talekar et al. (1977) have attributed variation in dieldrin recovery to rototilling.

TABLE 1. Technical Chlordane (PPM) in Florida Citrus Soils.

Grove name	Treatment (kg AI/ha)	0-2.5 cm residues (mean ± S.D.)			
Fountain	—	13 days*	48 days	139 days	395 days
	5.6	39.5 ± 43.4	2.6 ± 1.9	10.2 ± 12.0	0.49 ± 0.22
	8.4	28.7 ± 25.7	10.9 ± 13.7	19.7 ± 18.9	0.10 ± 0.19
	11.2	21.5 ± 29.2	13.8 ± 6.3	86.1 ± 53.5	0.42 ± 0.25
	No treatment	ND**	ND	ND	ND
White Clay Pit Road	—	14 days	44 days	139 days	445 days
	5.6	4.8 ± 1.8	3.2 ± 1.3	4.0 ± 2.6	ND
	8.4	52.2 ± 50.1	4.0 ± 2.4	6.8 ± 3.8	0.40 ± 0
	11.2	44.9 ± 44.4	7.1 ± 7.2	38.6 ± 40.0	ND
	No treatment	ND	ND	ND	ND
Shinn	—	30 days	65 days	153 days	410 days
	5.6	6.9 ± 1.8	1.8 ± 0.99	11.3 ± 10.9	0.08 ± 0.09
	8.4	3.9 ± 2.6	2.0 ± 1.1	31.6 ± 40.3	0.23 ± 0.27
	11.2	23.8 ± 20.3	10.2 ± 11.4	61.0 ± 32.1	ND
	No treatment	ND	ND	ND	ND

*Days postapplication.
**ND = Not Detected.

The data fit to the standard 1st order kinetic pesticide decay model averaged $R^2 = 0.74 \pm 0.14$ (Fountain Grove); $R^2 = 0.82 \pm 0.13$ (White Clay Pit Road); $R^2 = 0.64 \pm 0.24$ (Shinn Grove) (Table 2). Half-lives in the 3 experiments varied from 23-100 days. The average half-life in each experiment appeared to be related to the moisture capacity of the 0-2.5 cm soil horizon with the higher the moisture capacity, the shorter the half-life (Table 3). Rainfall was about equal among groves: Ft. Pierce 131.06 cm, White Clay Pit Road 150.88 cm, and Shinn Grove 139.45 cm. The half-life for chlordane observed here was about 1/3 that of p,p′-DDT and dieldrin under fall and winter subtropical conditions in Taiwan (Talekar et al. 1977). The high temperature and soil moisture conditions in Florida probably account for this non-persistence of chlordane (Talekar et al. 1977, Williams 1975). Irreversible binding of chlordane to these soils is probably not a factor in either the half-life or 'disappearance' behavior of chlordane (Lichtenstein et al. 1977). The short half-life and rapid disappearance of chlordane in Florida, however, may compromise its use as a residual insecticide for weevil control.

TABLE 2. First-Order Decay Constants for Chlordane in Florida Citrus Soils ($N_t = N_0 e^{-\lambda t}$; N_0 = Initial Mass, N_t = Mass at Time t, λ = Decay Rate).

Grove name	Treatment (kg AI/ha)	λ	Half-life (days)†	(R^2 x 100)
Fountain	5.6	—0.009	77.0	67**
	8.4	—0.01	69.3	90**
	11.2	—0.01	69.3	64*
			Average 71.9	
White Clay Pit Road	5.6	—0.03	23.1	92**
	8.4	—0.02	34.7	90**
	11.2	—0.03	23.1	86**
			Average 26.9	
Shinn	5.6	—0.01	69.3	70**
	8.4	—0.007	99.0	38
	11.2	—0.03	23.1	85**
			Average 63.8	

*$P \leq 0.05$.
**$P \leq 0.01$.
†Half-life = $0.693/\lambda$.

TABLE 3. Physical Characteristics of Experimental Citrus Soils in the 0-2.5 cm Horizon.

Grove	Moisture capacity (%)	pH	Organic matter (%)
Fountain	1.25	6.14	1.7 ± 0.2
White Clay Pit Road	4.90	6.22	2.3 ± 0.6
Shinn	1.31	6.32	2.5 ± 0.8

Chlordane residues were not detected in fruit, leaf, or water samples and consequently chlordane residues, if present, must have been below the detectable level of 5.0 ppb in fruit and leaves and 1.0 ppb in water. Sanborn et al. (1976) found 104 ppm of chlordane in algae when water contained 1.06 ppb of chlordane and Mattraw (1975) detected no chlordane in southern Florida surface waters, yet 33% of southern Florida sediment samples contained chlordane. Biomagnification and low water solubility of chlordane shown in these studies suggest additional experiments designed to determine life-form levels of chlordane after a normal agricultural application of chlordane would be appropriate.

Acknowledgements

The technical assistance of Ms. Roberta Woodruff, Mr. Paul Keene, and Mr. Neil Berger is gratefully acknowledged.

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