Residues of 2-Methyl-2-(methylthio)propionaldehyde *O*-(Methylcarbamoyl)-oxime (Temik) in Citrus Following Soil Applications

Rudolph Hendrickson and W. R. Meagher[1]

Temik residues in component parts of citrus following soil applications were investigated by colorimetric analysis (modification of the Griess test for nitrites). Maximum concentration of Temik in Temple oranges occurred 33 weeks after application and possibly sooner in Marsh grapefruit. In both grapefruit and oranges, more residue was found in the juice than in the peel of the fruit, prior to full maturity. Greatest concentrations of residue accumulated in the fruit and, respectively, less in leaves, roots, and corresponding components of adjacent trees. Heavy applications of irrigation water greatly increased uptake of Temik in Pineapple oranges, but only a negligible portion penetrated beyond 4 feet in sandy acid soil.

In Florida, a 10% granular formulation of 2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)-oxime (registered as Temik by Union Carbide Corp. and known also as UC-21149) was recently tested as a potential aphicide, broad-spectrum insecticide, and nematocide for citrus. Although the systemic translocation and metabolism of C^{14}-labeled Temik in cotton plants have been investigated (Metcalf *et al.*, 1966), only limited information is available on Temik residues in field crops. This pesticide is not registered or cleared for use on citrus, nor have any results been previously reported for citrus.

The analytical procedure of Johnson and Stansbury (1966) was used in this investigation with certain modifications to improve sensitivity and to remove some interfering substances (Meagher *et al.*, 1967). The technique releases the nitrogen of Temik compounds as nitrous acid to allow stoichiometric diazotization of sulfanilic acid, which in turn couples to form a related quantity of dye in solution that is measured spectrophotometrically. This analytical method is equally sensitive (on a molecular weight basis) to Temik, Temik-oxime, and their sulfone and sulfoxide derivatives. The latter compounds were found as major and minor metabolites in cotton by Metcalf *et al.* (1966) and they presumably also occur in citrus. Therefore, all subsequent data are discussed as Temik residues or Temik and its metabolites.

This report deals with Temik residues found in the soil, leaves, roots, fruit tissue, and juice of citrus after soil applications of this systemic carbamate pesticide at rates approximating 14 to 30 pounds of active material per acre (0.25 to 0.6 pound per tree). Method of application and variety of citrus treated were additional variables in these trials.

EXPERIMENTAL

Type of Citrus, Soil, and Application Rate. One application of Temik 10G was applied March 8, 1966, at the rate of 0.25 pound (active) per Temple orange tree. The experiment was arranged in a randomized block design having four replicates of 15 to 20 trees each. Earlier freeze damage had reduced the size of these 10-year-old trees to that equivalent to 5-year-old trees. The granules were spread uniformly under the tree canopy and then raked into the sandy acid soil.

In a mature Marsh grapefruit grove, also having a sandy acid soil, Temik 10G was applied on May 19 and July 27, 1966, at the rate of 0.2 pound (active) per tree per application. The granules were again raked into the soil underlying the tree canopies. The experimental design consisted of single-tree plots arranged in a 9 × 9 Latin square.

At a third location, Temik was broadcast and evenly raked into soil surrounding four nine-tree plots of 16-year-old Pineapple orange trees infected with burrowing nematodes, *Radopholus similis* (Cobb) Thorne. One pair of plots received a total of 15 pounds (active) per acre in three equal applications spaced a month apart (June 23, July 25, and August 22, 1966); the other pair received twice as much. These application rates were equivalent to 0.3 and 0.6 pound (active) per tree, respectively. Four inches of irrigation water were applied by perforated sprinkler pipe to the area after each application.

Sampling and Analytical Procedure. At regular intervals, composite field samples of fruit were picked to represent the Temple orange blocks, the individual Marsh grapefruit trees, or the nine-tree plots of Pineapple oranges. Each sample consisted of at least nine mature grapefruit, 18 mature oranges, or an equivalent of 4000 grams of whole fruit which was macerated and mixed in a Hobart food chopper prior to subsampling. Composite samples of leaves, roots, and soil were taken at irregular intervals and the latter was representative of the top 12 inches of treated soil unless otherwise noted. Temik residues were extracted either from the samples immediately or after storage at −8° F. The sample size and the analytical procedure for Temik in citrus have been described by Meagher *et al.* (1967). All analyses were replicated at least twice, more often three times, and their average result is presented in the tables.

RESULTS

Temple Orange Studies. Table I presents data on the parts per billion of Temik that accumulated in Temple

Institute of Food and Agricultural Sciences, University of Florida Citrus Experiment Station, Lake Alfred, Fla. 33850

[1] Deceased

oranges at various intervals after a soil application of this pesticide. When the concentrations of Temik residue were recalculated as micrograms of residue per fruit to compensate for the dilution brought about by fruit growth, the maximum occurred at the same 33-week interval, but was more peaked.

The peel and juice of these fruits were separately analyzed in the final months. Temik concentrations, which were 10 to 20% higher in the juice of immature fruit, were equally distributed in the juice and peel by the thirty-sixth week. After 40 weeks, the residue concentrations were from 10 to 20% higher in the peel than in the juice.

The relative concentrations of residue in the whole fruit, leaves, and soil of Temple trees 38 weeks after a Temik application are seen in Table II. Components of the trees adjacent to those treated absorbed sizable and proportionate fractions of that found in treated trees. After processing the peel fraction of fruit from treated trees into dried citrus pulp (cattle food), no significant loss of residue occurred, but only the 3.5-fold concentration increase expected from water loss.

Marsh Grapefruit Studies. Residue information accumulated from five grapefruit plots is presented in Table III. Unlike the preceding study, concentration of Temik in this fruit reached a maximum 17 weeks after the initial soil application and remained at this level for the next 13 weeks. Additional Temik was applied in this experiment approximately 10 weeks after the first treatment and possibly prevented the occurrence of a sharp maximum at a subsequent interval as with Temple oranges. When micrograms of residue per fruit were calculated for each interval, it was more clearly seen that residue per fruit was still increasing at the 30-week interval, and it seemed likely that a maximum would soon occur. The relationship between concentrations of residue in peel and juice was similar to that for Temple oranges.

Table IV shows the relative concentrations of Temik in fruit, leaves, soil, and dried pulp 32 weeks after the first application. Other than a surprisingly high concentration of Temik still found in the treated soil at this interval, the distribution of residues was similar to that found for Temple oranges. All of these concentrations, however, were considerably higher than those of the preceding orange study.

Pineapple Orange Studies. Important differences between this experiment and the previous ones were: The treatment was divided into three equal portions applied monthly, each application was heavily watered (4 inches) into the soil, granules were evenly broadcast underneath tree foliage as well as between trees, and one of the two dosage levels was 50% greater than in the Marsh grapefruit study. Residue analyses of the fruit, leaves, and roots at 13-, 25-, 26-, and 31-week intervals are shown in Table V.

Soil analyses are presented in Figure 1. These analyses can be erroneously inflated, at times, by application of fertilizer to the soil prior to sampling. The analytical technique was again discriminatory of this interference, however, if the soil pH was initially adjusted to 4. Fractional quantities of nitrite salts from the fertilizer were presumed responsible, and were liberated as nitrous oxide gas by the pH adjustment.

Table I. Temik Residues in Temple Oranges (Whole Fruit Basis) Following a 0.25-Pound (Active) Soil Application per Tree on March 8, 1966

(Expressed in parts per billion)

	Weeks after Application				
Block	25	29	33	36	40
A	31.6	31.0	43.1	21.9	16.0
B	35.7	37.0	47.5	21.4	15.9
C	33.9	36.8	48.0	22.0	17.2
D	35.8	36.8	47.3	23.7	16.7
Control	0.3	0.3	0.1	0.6	0.2

Table II. Concentration of Temik Residues in Treated and Adjacent Temple Orange Blocks 38 Weeks after 0.25-Pound (Active) Soil Treatment per Tree on March 8, 1966

(Expressed in parts per billion)

	Treated Trees				Adjacent Trees		
Block	Whole fruit	Leaves	Soil	Dried pulp	Whole fruit	Leaves	Soil
A	19.0	7.6	4.8	72.1	1.7	1.3	0.2
B	18.8	7.1	5.5	65.4	1.5	1.2	0.2
C	18.9	7.2	4.9	70.6	1.4	1.4	0.3
D	18.5	7.4	5.2	66.3	1.6	1.5	0.2
Control	0.2	0.1	0.2	...	0.1	0.1	0.1

Table III. Temik Residues in Marsh Grapefuit (Whole Fruit Basis) Following Two 0.2-Pound (Active) Soil Applications per Tree, Made on May 19 and July 27, 1966

(Expressed in parts per billion)

	Weeks after First Application				
Plot	8	13	17	25	30
1–23	57.6	75.0	287	324	303
3–25	57.6	70.8	299	297	294
5–21	57.1	75.3	292	285	288
7–21	58.9	89.1	289	288	290
9–20	55.2	79.7	292	290	288
Control	0.5	0.6	0.6	0.6	0.5

Table IV. Temik Residues in Treated and Adjacent Marsh Grapefruit Plots 32 Weeks Following Two 0.2-Pound (Active) Soil Applications per Tree on May 19 and July 27, 1966

(Expressed as parts per billion)

	Treated Trees				Adjacent Trees		
Plot	Whole fruit	Leaves	Soil	Dried pulp	Whole fruit	Leaves	Soil
1–23	294	189	1970	1065	30.7	24.7	1.2
3–25	290	204	1980	1080	30.8	24.9	1.1
5–21	292	210	1940	...	31.3	26.6	1.0
7–21	293	208	1940	1100	30.9	27.7	1.4
9–20	284	206	1950	1092	37.9	28.1	1.2
Control	0.1	0.1	0.2	...	1.1	0.3	0.1

DISCUSSION

In the earlier trials, grapefruit accumulated higher concentrations of Temik than oranges per unit of applied pesticide. Uptake of Temik was influenced by either a more extensive root system or a difference in rainfall, although other alternatives were possible. The vastly greater uptake of Temik in the irrigated plots of Pineapple oranges demonstrated the importance of this variable.

Table V. Temik Residues in Pineapple Oranges Following Three Soil Applications of 5 or 10 Pounds (Active) per Acre on June 23, July 25, and August 22, 1966

(Expressed in parts per billion)

	Weeks after First Application				
		25			
Treatment, Lb./Acre	13, whole fruit	Whole fruit	Leaves	26, roots	31, leaves
15	990	1870	1210	147	546
30	2660	3740	2500	297	1060
Control	0.9	0.3	0.1	...	0.2

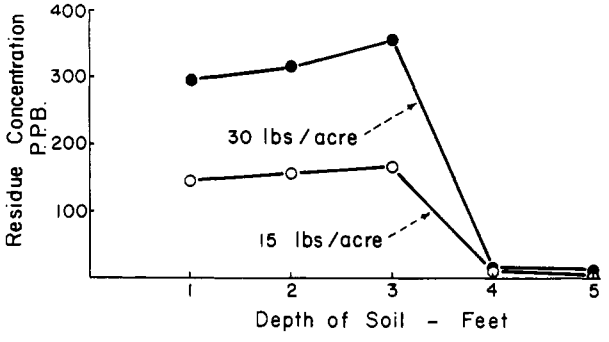

Figure 1. Temik residues at various soil depths 31 weeks after application

Expressed in parts per billion

An eight- to 30-fold increase in Temik residue was noted in citrus fruit, leaves, and roots of heavily irrigated trees, when only 40% of the treatment was applied to the under-tree area.

The mobility of Temik and the extent of its penetration into sandy soils are important factors in the treatment of nematodes; toxic concentrations must reach the nematodes, which primarily are in the roots. In the heavily irrigated applications of Temik, however, only minute quantities of the chemical had reached 4 feet or below, even though 4 inches of irrigation water are usually expected to penetrate 4 feet of sandy soil. Figure 1 illustrates the difficulty of obtaining deep movement of Temik and this is probably related to the solubility of Temik, 6000 p.p.m. in water (Union Carbide Corp., 1965).

The Temik residue found in the leaves and fruit of trees adjacent to treated trees suggested either lateral movement of the pesticide through the soil or intergrowth of the root systems. Detectable quantities of Temik were found at least a year after application and appeared to be more persistent in the tree than in the soil.

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Received for review June 24, 1968. Accepted September 3, 1968. Florida Agricultural Experiment Stations Journal Series No. 3012.