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Dissipation of Herbicide Residues in the Soil of a Citrus Orchard (*Citrus sinensis* L. Osbeck) after the Ninth Consecutive Annual Application

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In the State of São Paulo, weeds in citrus groves must be controlled between December and March or from August to November (Blanco and Oliveira 1978). Residual herbicides such as terbacyl, bromacyl and diuron are applied annually for this purpose separately or in combination (Rodriguez 1960; Gregory and Roessing 1964; Donadio and Moreira 1969; Hertwig 1970). These herbicides persist a long time in soil, with bromacyl controlling up to 95% of weeds and diuron, with a shorter residual effect, controlling up to 60%, 225 days after application (Gregory and Roessing 1964). Bromacyl and terbacyl were effective for 150 days and the combination of bromacyl + diuron was effective for 180 days following application (Hertwig and Leiderman 1972).

On the other hand, the bioactivity and resistance to degradation of herbicides may present problems of damage to non-target organisms (fungi, actinomycetes, bacteria, and microarthropods) and movement outside the area of application, with consequent contamination of other segments of the environment, as surface waters or groundwater (Jacques and Harvey 1979). Herbicide degradation in soil depends on several edaphic and climatic factors. Since these factors vary from one location to another, it is clear that herbicide persistence in soil may vary widely (Tena et al. 1982).
The persistence and leaching of terbacyl, bromacyl and diuron applied to citrus and peach groves over consecutive years have been evaluated in some investigations (Tucker and Phillips 1969; Marriage et al. 1975; Khan et al. 1976; Marriage et al. 1977; Majka and Lavy 1977; Tucker 1978).

The presence of the herbicides in soil may be evaluated by bioassay or by chemical analysis. One of the objectives of bioassay is the qualitative evaluation of the presence of herbicides in soil (Locatelli 1977). Thus, indicator plant species with susceptibility proporcional to the increase in herbicide concentration are used (Jacques and Harvey 1979).

The objective of the present study was to evaluate the degradation and leaching of

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herbicide residues in the soil of citrus grove after the ninth consecutive annual application.

MATERIAL AND METHODS

The field experiment was conducted in a orchard of Pera orange grafted onto Cravo lemon, planted in 1975 in the municipality of Conchal-SP on a red-yellow "Latosol" soil (Comissão de Solos 1960). On a sample in layer of 20.0 cm depth, the soil contained 32.3% clay, 25.0% silt, 31.5% fine sand, 11.1% coarse sand, 1.75% organic matter with a pH of 4.9. This pH is typical of citrus groves soil in the State of São Paulo, . The herbicides terbacyl, bromacyl and diuron were applied annually between October and November at the dose of 3.2 kg/ha, and the bromacyl + diuron mixture was applied at the dose of 2.1 + 1.1 kg/ha. The plots were weeded with a hoe 3 to 5 days before the pre-emergence applications, and the material cut was removed. The experimental design used was randomized blocks with three replications on 54 m^2 plots with four plants separated by a distance of 4.5 m.

The soil samples from the plots were collected into thick-walled PVC tubes 10 cm in diameter one day before and 36, 63, 96, 129 and 216 days after the ninth consecutive annual application in 1985. Forty cm long tubes with one sharp edge were prepared in order to facilitate penetration into the soil; they also had a centralized longitudinal opening of 2.0 x 30.0 cm. The opening was sealed with adhesive tape and the tubes were driven vertically into the soil up to the upper end of the opening. The tubes were then placed horizontally on a table in a greenhouse, with the opening looking up. Cucumber seeds (Cucumis sativus) cv. Aodai SH 191 were sown at 1.0 cm intervals in the opening and 1 cm depth. Fluorescent lamps (40 W) spaced 25 cm apart were placed over the table at a height of 50 cm and were left on from 8:00 to 18:00 hours every day. Temperature was 23 ± 2 °C.

After sowing, the tubes were irrigated daily with distilled water, and Hoagland nutrient solution (Epstein 1975) at 3 day intervals, after seedling emergence. Fourteen days after sowing, the above ground portion of seedlings in each 5.0 cm portion of the opening was cut and immediately weighed. These data were used to estimate percent reduction in weight compared that of the seedlings grown in soil which received no herbicide. The criterion used to determine the presence of herbicide in the soil layer was the occurrence of 50% or more reduction in material weight compared to the seedlings grown in soil which received no herbicide, as proposed by Santelmann (1978).

RESULTS AND DISCUSSION

The reductions in weight of the above ground portions of the cucumber seedlings in the 5.0 cm depth layers in relation to that grown in soil which received no herbicide are presented in Table 1. On the basis of the criterion adopted, the presence of terbacyl and bromacyl residues in the soil at a depth of 5.0 to 15.0 cm was detected in the first sampling, immediately before the ninth annual application. This prolonged presence is comparable to that observed at 216 days for bromacyl,

dispersed in the layer between 5.0 and 30.0 cm. The absence of terbacyl 216 days after application may have been due the climatic differences (temperatures, distribution and intensity of rain, rate of solar energy) after the applications,

Table 1. Mean reductions (%) in weight of above ground portion of cucumber seedling immediately before and at different times after the ninth consecutive annual herbicide application in the soil of a citrus orchard.

Depth	Days after the ninth consecutive application					
(cm)	immed. before	36	63	96	129	216
			TERBACYL			
0.0 - 5.0	11.8	100.0	100.0	6.8	15.3	30.7
5.0 - 10.0	54.4	100.0	100.0	94.4	34.2	0.0
10.0 - 15.0	53.1	99.0	100.0	74.2	17.4	25.0
15.0 - 20.0	25.4	50.5	100.0	0.0	63.9	0.8
20.0 - 25.0	0.0	1.2	100.0	35.0	0.0	0.0
25.0 - 30.0	50.8	9.8	66.7	0.0	42.3	31.1
			DIURON			
0.0 - 5.0	67.1	100.0	100.0	85.5	82.0	61.0
5.0 - 10.0	43.7	17.6	30.4	46.0	0.0	39.6
10.0 - 15.0	49.0	0.0	8.9	0.0	33.0	37.2
15.0 - 20.0	20.3	4.2	3.9	40.6	9.2	0.0
20.0 - 25.0	36.7	17.9	0.0	39.3	21.4	0.0
25.0 - 30.0	47.7	21.6	45.2	14.0	0.0	20.5
			BROMACYL			
0.0 - 5.0	38.8	100.0	97.1	47.3	20.0	0.0
5.0 - 10.0	80.6	100.0	100.0	84.5	61.8	41.7
10.0 - 15.0	69.4	100.0	100.0	95.5	89.9	68.6
15.0 - 20.0	42.4	96.9	81.8	92.2	81.5	21.0
20.0 - 25.0	43.3	17.9	56.4	62.4	63.3	6.3
25.0 - 30.0	50.8	5.9	0.0	12.9	73.2	10.6
			BROMACYL + DIURON			
0.0 - 5.0	0.0	100.0	100,0	58.0	61.3	0.0
5.0 - 10.0	0.0	100.0	97,5	69.0	56.6	1.9
10.0 - 15.0	0.0	58.8	87,8	69.0	73.4	38.7
15.0 - 20.0	0.0	23.7	83,1	17.2	63.9	19.3
20.0 - 25.0	0.0	0.0	53,2	19.7	45.9	0.0
25.0 - 30.0	9.2	0.0	0,0	0.0	0.0	0.0

Herbicide present if reduction > 50% (Santelmann 1978).

occurring between the two years after the eighth and ninth application, affecting the leaching and degradation of the herbicides.

Thirty-six days after application, terbacyl was found to be present at a depth ranging from 0.0 to 20.0 cm, at 63 days it had moved down to 30.0 cm, at 96 it was concentrated between 5.0 and 15.0 cm, and at 129 days between 15.0 and 20.0 cm. On the others layers may be ocurred leaching and degradation of the terbacyl. These results agree with those obtained by Marriage et al. (1977), when they applied terbacyl (4.5 kg/ha) to a peach orchard for seven consecutive years. They observed losses of terbacyl by degradation and leaching, and 50% of the dissipation from the soil surface occurred between 150 and 210 days. Most of the terbacyl moved into the soil to a depth of 15.0 cm and only small amounts reached 60.0 cm.

At 36 days, bromacyl was detected in the 0.0 to 15.0 cm layer, at 63 days it had moved to 25.0 cm, and at 96 days it was no longer detected on the surface (0.0 to 5.0 cm) but was present at a depth of 5.0 to 25.0 cm. Bromacyl leached to 30.0 cm by 129 days, but on 216 days, it was still present at 10.0 to 15.0 cm. In the sandy soil of a citrus orchard, Tucker and Phillips (1969) detected concentrations of 0.22 kg/ha terbacyl and bromacyl in the first 45 cm from the surface as residues of 11.2 kg/ha amounts applied over a period of five consecutive years. They also noted that the factors that most affected the dissipation of these herbicides in soil were: biodegradation, rain, absorption by plants, level of organic matter and ion-exchange capacity of the soil.

Diuron persisted in the superficial layer (0.0 to 5.0 cm) throughout the collection period. Marriage et al. (1975), after the third consecutive annual application of diuron at 4.5 kg/ha on a peach orchard, found leaching of the herbicide until 15.0 cm depth, but 92% of the total was concentrated in the 0.0 to 5.0 cm layer. Khan et al. (1976) studied the movement and persistence of diuron in the soil of a peach orchard which received an annual application of 4.5 kg/ha for seven years. Khan et al. (1976) observed no significant accumulation of the herbicide, which moved to a depth of 15.0 cm from the surface. Majka and Lavy (1977) applied diuron to a soil with 28% clay, 2.9% organic matter and pH 6.5 and observed that the herbicide persisted in the 0.0 to 5.0 cm layer for 54 days after four irrigations of 50 mm at 12 day intervals.

In contrast to the applications of each herbicide separately, no herbicides were detected in soils treated with the bromacyl + diuron mixture before the ninth annual application. This difference is due to the smaller doses applied in the mixture. However, herbicide residues were present in the 0.0 to 15.0 cm layer at 36 days and to a depth of 25.0 cm at 63 days. At 96 days, the herbicides were concentrated in the 0.0 to 15.0 cm layer, at 129 days had reached a depth of 20.0 cm. But at 216 days herbicide residues were not detected. It can be seen that this mixture had a complementary effect when compared to the application of each agent separately, although the effect was less intense due to the smaller doses. When the herbicides were applied separately, diuron was concentrated in the 0.0 to 5.0 cm layer in all soils collected, and bromacyl was concentrated in the 5.0 to 30.0 cm layer starting at 96 days. These results agree with those reported by Tucker (1978). That

investigator evaluated bromacyl and diuron residues in the soil of commercial citrus groves which received seven and eight years of consecutive annual applications. The levels detected ranged from 0.3 and 3.9% of the bromacyl applied throughout the period and from 0.7 to 3.1% of diuron. Diuron was also found to concentrate more in the surface layer due to its low water solubility, and bromacyl was distributed more uniformly in the soil profile.

The present soil residue dissipation data for terbacyl, bromacyl and diuron can explain the long periods of weed control achieved by these herbicides in citrus orchards, reported by others (Rodriguez 1960; Gregory and Roessing 1964; Donadio and Moreira 1969; Hertwig 1970; Hertwig and Leiderman 1972), in the same region where the present study was carried out.

On the basis of these results, it can be seen that the bioassay method in a greenhouse using cucumbers as test plants was efficient in evaluating the degradation and leaching of bromacyl and diuron in the surface layer of the soil between 0 and 30 cm of depth.

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