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Degradation of Captan Under Laboratory Conditions

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Captan, N-[(trichloromethyl)-thio] cyclohex-4-ene-1, 2-dicarboximide, is a protective, non-systemic fungicide used for the treatment of foliar, soilborne and seed-borne diseases. It is widely used on fruit, vegetables and ornamental plants.

The pesticide is generally assumed to undergo rapid biological transformations (Knackmuss, 1981). Reactions of a hydrolytic nature or with cellular thiols result in N-S bond cleavage, releasing tetrahydrophthalimide, tetrahydrophthalamic acid and o-aminotetrahydrophthalic acid. Epoxides of captan and tetrahydrophthalimide are possible alteration products which may form under conditions of weathering or degradative metabolism (Lukens and Sisler, 1958; FAO/PL, 1969; Pomerantz and Ross, 1968).

Captan residues may remain in soil from one day to several months depending on soil type, temperature or moisture content (Agnihotri, 1970; Burchfield, 1960; Griffith and Mathews, 1969; Edwards and Thomson, 1973; Li and Nelson, 1985).

There are no data on the degradation of captan in soils with high clay content and low pH which are widely cropped to corn and soybeans in Missouri and surrounding states. A laboratory respirometry experiment using these soils amended with carbonyl-^{14}C-labeled captan was carried out. The experiment was designed to evaluate initial microbial decomposition of captan, to identify pesticide residues and degradative intermediates, and to access the effect of captan on the respiratory activity of soil microorganisms.

MATERIALS AND METHODS

Carbonyl-^{14}C labeled captan was obtained from Chevron Chemical Company and purified using preparative thin layer chromatography

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by ABC-Laboratories (Columbia, Missouri). The chromatogram exhibited three zones which were desorbed using dichloromethane. The parent compound (Captan) TLC zone, after further analysis for radiochemical purity, was found to be 99.3% pure and was used for the experiment.

A Mexico-Putnam silt loam representative of upland claypan soils commonly cultivated to row crops (corn and soybeans) in north Missouri was selected for the experiment. Soil from the plow layer (0-15 cm) was air-dried and passed through 1 mm sieve.

A solution of radioactive captan in methylene chloride (1.9 mg of captan with a total activity 72.5 μCi) was amended with 34 mg of non-labeled captan (chemical standard). Small amounts of soil were treated with the solution and allowed to dry. Aliquots of this soil later were added to duplicate units of the soil prepared for incubation to provide a rate of captan at about 50 ppm.

Incubation was carried out in a system with a constant flow of CO_2-free humidified air similar to that described by Chahal and Wagner (1965) with minor modifications. Each flask had a separate scrubbing tower with glass beads filled with 1.0 N NaOH. Several times during incubation the total amount of evolved CO_2 was measured by titration after addition of $BaCl_2$. The standard error of measurement for use in comparing differences between residue amended and non-amended units of soil was never greater than 8 mg of carbon per 100 g of soil. After titration, $BaCO_3$ was collected, washed, dried, and specific activity of carbon was measured using liquid scintillation counting.

The following treatments were used in the experiment: control (soil with no residues and no captan); soil with ground plant residues (corn or soybeans, 0.5% by weight); soil + captan and soil + residues + captan (each in two replicates). After all ingredients were mixed, water was added (50% of water holding capacity). After incubation at 22-24°C, soil was air-dried and extracted with acetone three times. Acetone extracts were combined, evaporated to small volume and cleaned up on silica gel columns (Onley, 1976) which separated captan from metabolites. After separation, captan was directly determined by GLC equipped with an EC-detector. Metabolite fractions were assayed by the TLC method of Pomerantz and Ross (1968). Tetrahydrophthalimide, the most common breakdown product, was derivatized in an acetone solution of pentafluorobenzylbromide. The resultant derivative was purified on an aluminum oxide column and quantitated by GLC equipped with an EC-detector (Onley, 1976). Recoveries of 84 - 87% were obtained from soil spiked with 0.03-1.00 ppm captan and 85-91% from 0.05-1.00 ppm tetrahydrophthalimide.

Residue analyses employed a Tracer MT 220 gas chromatograph equipped with a radioactive nickel electron capture detector operated at 270°C. The glass column (2 m x 2 mm i.d.) was packed

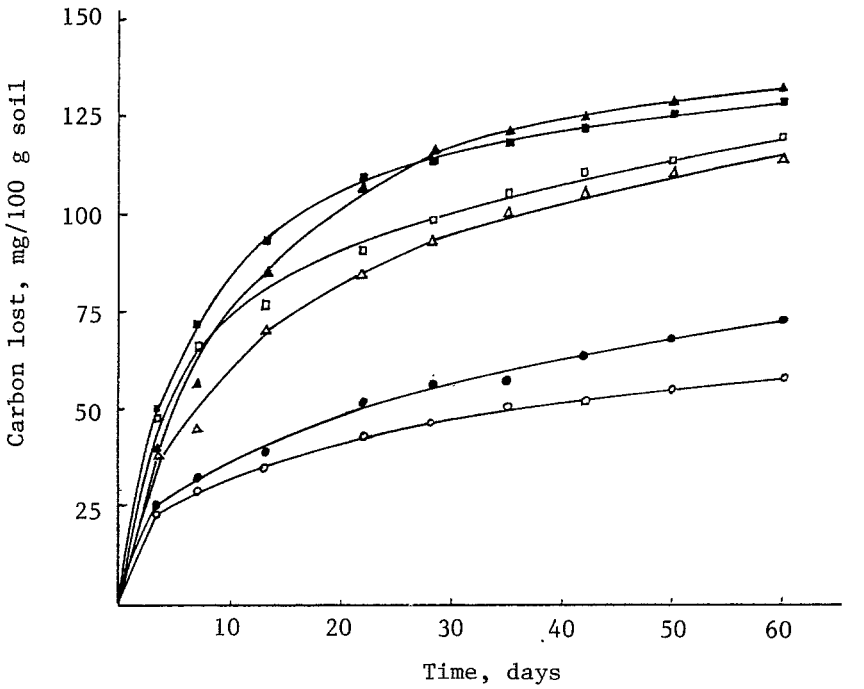

Figure 1. Cumulative curves of carbon evolution from soils treated with captan (o, unamended soil; ●, soil with captan, 50 ppm; △ , soil with corn residues; ▲ , soil with corn residues and captan; □ , soil with soybean residues; ■ , soil with soybean residues and captan).

with 1.5% SP-2250/1.95% SP-2401 on 100/120 Supelcoport . The carrier gas was argon/methane with a flow rate of 20 ml/min and a column temperature of 220°C. The retention time for captan and the tetrahydrophthalimide derivative was 5.7 min and 3.2 min, respectively.

Radioactivity of extracts before and after silica gel separation were also examined. Part of the extract was evaporated to dryness in scintillation vials, and its radioactivity was measured in a scintillation cocktail.

Radioactivity of soil before and after incubation and after organic extraction was measured using a Packard Tri-Carbon liquid scintillation counter and Aquasol II scintillation cocktail.

RESULTS AND DISCUSSION

Captan demonstrated a stimulatory effect on total soil biological activity as measured by soil respiration (Fig. 1). During the first 3 days of incubation this effect was negligible. Although captan may have suppressed some groups of microorganisms, soil respiration was not changed due likely to the availability of

fresh organic material for other groups. Soils treated with captan lost more carbon than non-treated soils, especially during the second and third weeks of incubation. Soil with corn residue lost 107 mg and soil with soybean residues lost 111 mg, captan treatment increased these losses about 20% and 10%, respectively. The results support the finding of other workers who reported that captan accelerates soil biological activity (Agnihotri, 1970; Li and Nelson, 1985).

Decomposition of captan started at a very early stage of incubation and continued at an exponential rate through the first 35 days after which it practically stopped (Fig. 2).

Figure 3 represents the relative daily rates of carbon losses from soil and captan (as percent of the total respective losses) each shown separately. Soil respiration which reflects availability of energy sources for general microbial populations, was highest during first week of incubation. More than half of total carbon lost through respiration was evolved during the first week. In contrast, captan degradation occurred at a very low rate during this time, and reached a maximum only during the second week. A comparison of the rates of carbon evolution from soil organic matter and from captan showed that general microbial populations presumably do not use the pesticide as an energy source. Any organisms capable of degrading captan probably had a low capacity in the beginning. Their activity reached a maximum during the second week of incubation and then slowed although 2/3 of the captan was still present. After 40 days of incubation radioactivity of evolved CO_2 was negligible.

During two months of incubation, 25% of the captan-C was released from the soil amended with no additional plant residues. About 30% of ^{14}C from captan was released from soil amended with soybean residues and 28% from the soil with corn residues. Agnihotri (1970) found that after 35 days of captan application the bacterial population achieved a certain degree of stability but he assumed that all captan applied had been degraded by this time.

Our experiment revealed that after 60 days of incubation, 57 to 64% of initial captan was extractable and found to have undergone no significant chemical transformation (Table 1). Crop residues slightly increased degradation of the pesticide. A total of 4-5% of the radioactivity was extracted from soils as a mixture of three compounds, and one was identified as tetrahydrophthalimide. Less than 8% of initial radioactivity was not extracted from soil by acetone, and probably belongs to bound captan. Unextractable, or bound residues of various pesticides are associated chiefly with organic fraction of soil (Lichtenstein, 1980; Bollag et al., 1980), and their consequent release is of concern because of the toxicity of some of the residues. Amounts of captan transformed to soil-bound residues are very small as compared with other pesticides. For example, ^{14}C-fenitrothion has been shown by Mac Rae (1986) to be bound by up to 74% after 65 day incubation.

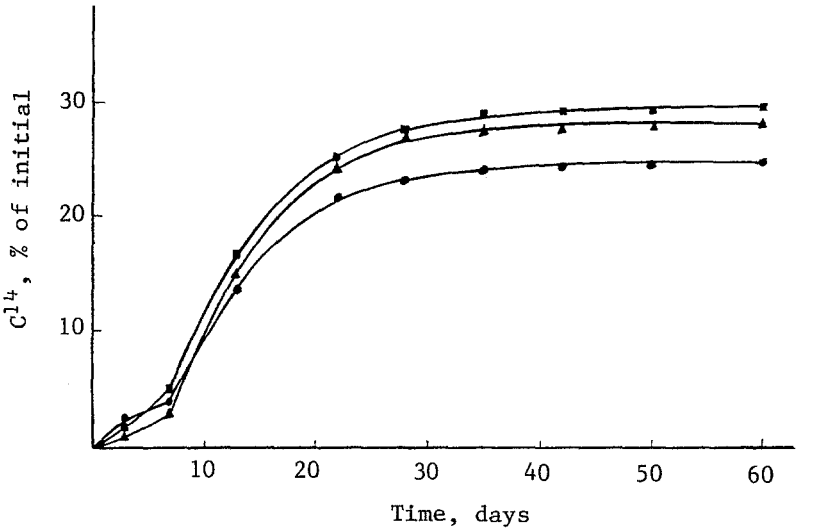

Figure 2.Cumulative curves of ^{14}C evolution from captan during incubation (for legend, see Fig. 1).

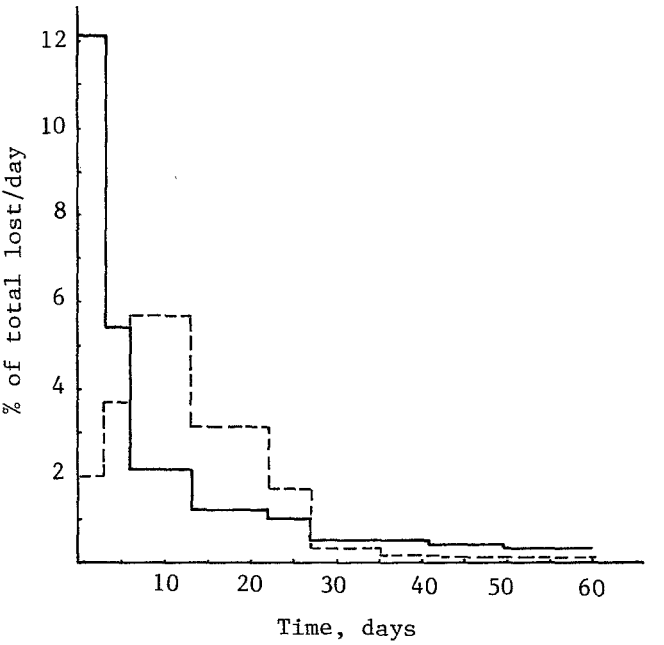

Figure 3. Relative daily rates of carbon loss from soybean residue (bold line) and captan (dotted line). Rates for the corn residues treatment are essentially the same.

Table 1. Distribution of ^{14}C-captan in laboratory incubation experiment.

Soil Treatment	% of Initial Radioactivity			
	Released as $^{14}CO_2$	Extracted as captan	Extracted as metabolites	Non Extracted Residues
Captan	25	64	4	7
Captan + corn residue	28	61	5	6
Captan + soybean residue	30	57	5	8

Degradation of captan in a strictly controlled laboratory environment may not give a true indication of the overall field persistence. It is obvious, however, that biological processes in Mexico-Putnam silt loam soils are responsible for no more than 30% of captan degradation. The rest can persist much longer than 2 months. It should be mentioned that Agnihotri (1970) found under laboratory conditions that captan in fine sandy soil in concentrations comparable with that used in our experiment, did not show fungicidal effect for more than 3-5 days. However, Munnecke (1958), working with a synthetic soil of low pH, reported that captan was very stable in soil. Soil properties probably have a decisive effect on captan persistence.

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