Movement of Benomyl in Field Soils as Influenced by Acid Surfactants

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ABSTRACT

Benomyl-surfactant mixtures were added to plastic tubes, shallowly inserted into soil of two types in the field. Fungicide movement into soil was detected after 24 hr by bioassaying soil at various depths. A 1% (v/v) concentration of the surfactants Tween 20 (polyoxyethylene sorbitan monolaurate), GAFAC RS-710, and GAFAC RA-600 (General Aniline and Film Corporation, New York, N.Y.), increased the solubility of methyl 2-benzimidazolecarbamate (MBC), the fungicidal breakdown product of benomyl. The GAFAC surfactants contain phosphoric acid moieties. Acidification with either phosphoric acid or GAFAC surfactants increased protonation, and thus, the water solubility of MBC. Greatest movement of the fungicide in soil was found in solutions of GAFAC RA-600 and acidified Tween 20. Thus, movement of the fungicide in soil is dependent upon both water solubility of MBC and surfactant properties.

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Benomyl is a systemic fungicide which has proven particularly effective for controlling fungal diseases when applied as a foliar spray or as a drench applied to soil confined within pots in greenhouse experiments. However, control of disease by the application of benomyl to soil in field experiments has not been so successful.

Benomyl hydrolyzes in aqueous media to form methyl 2-benzimidazolecarbamate (MBC) (5). The cause of poor disease control in field experiments is probably the limited movement of MBC downward through soil, as the solubility of MBC is less than 50 μg/ml. If depth of penetration were restricted to the upper decimeter in field soils, the fungicide would be unavailable to many plant root systems which rapidly grow beyond the area containing the MBC. This lack of movement is exemplified by the research of Leach et al. (8) with Verticillium wilt of cotton, where control of the disease was proportional to the depth of physical incorporation of benomyl into soil.

If movement of MBC in soil could be increased without physical incorporation, its usefulness would be enhanced considerably. Surfactants have been shown to increase the effectiveness of benomyl applied in soil in the control of Verticillium wilt of cotton (12) and potatoes (1). The purpose of this study was to follow the movement of mixtures of benomyl and various surfactants through field soil.

MATERIALS AND METHODS.—*Solubility tests*.—A 1% (v/v) concentration of surfactants Tween 20 (polyoxyethylene sorbitan monolaurate), GAFAC RS-710, and GAFAC RA-600 (General Aniline and Film Corporation, New York, N.Y.), was added to a suspension of benomyl containing 1,000 μg/ml active ingredient in 500 ml water at pH 6.5. The GAFAC surfactants are mixtures of mono- and diphosphate esters having free acid radicals. Tween 20 is a nonionic surfactant without an acid radical. Benomyl was also added to water, pH 2.7, with and without Tween 20. Mixtures were vigorously stirred with a magnetic stirrer for 60 hr.

Aliquots of 100 ml were taken from each flask and centrifuged at 12,100 *g* for 10 min. MBC in the supernatant was then quantitatively determined by bioassay, using a species of the *Penicillium cyclopium* series (11), and spectrophotometrically at 285 nm. Surface tension of the surfactant solutions was determined by a Du Nouy tensiometer.

Movement in soil.—All movement studies were carried on in the field attempting as far as possible to simulate "natural" agricultural practices. The soils used were (I) Guelph loam, pH 7.3, organic matter 4.71%, moisture content 22.1% in 0 to 15 cm and 25.0% in 15 to 30 cm; (II) Vineland silty loam, pH 6.6, organic matter 1.35%, moisture content 5.0% in 0 to 15 cm and 26.0% in 15 to 30 cm.

Plastic tubes, 12 cm long and 5 cm in diam, were inserted into soil in the field to a depth of 5 cm. Twenty-five ml of each benomyl mixture were added to each of three replicate tubes. When drained, 75 ml of water were then added as a drench. The 25-ml aliquot was equivalent to 1.3 cm of liquid or 128,060 liters/hectare containing 42.9 kg active benomyl.

Vertical movement of benomyl was determined after 24 hr, by taking soil cores, 30 cm long and 2 cm in diam, and analyzing each centimeter by a bioassay technique (10), using *Penicillium*. Three ml of spore suspension (0.3 optical density at 450 nm) were added to 200 ml of molten potato-dextrose agar, and 10 ml dispensed into petri plates.

From each centimeter of the soil core, two 0.5-g aliquots of air-dry soil were individually compacted into 9-mm cylinders and placed on the agar. Benomyl was detected by the zones of inhibition and depth of penetration was recorded.

RESULTS AND DISCUSSION.—Bioassay of MBC in the supernatant was in close agreement with the reported spectrophotometric results (Table 1). The amount of MBC in solution is dependent on the protonation of the nitrogen in the imidazole ring. Acidification with either phosphoric acid or GAFAC surfactants increases protonation, and thus, water solubility. Acid alone does not completely solubilize MBC at the pH at which the surfactants will solubilize.

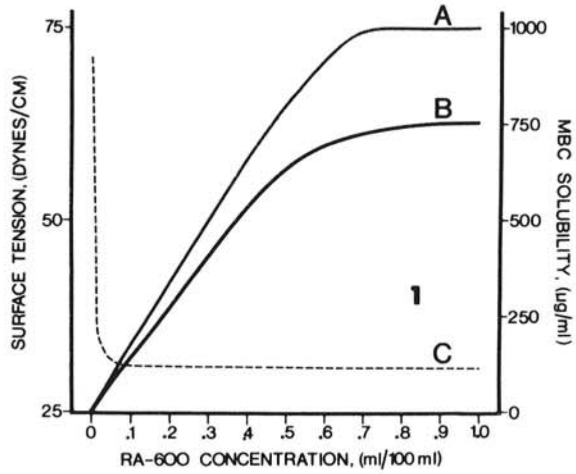
Increasing the concentrations of the surfactant RA-600 increases the amount of MBC in solution (Fig. 1, curve A). Solubilization is partly due to the acidification of the solutions by the varying concentrations of the surfactant. Figure 1, curve B shows the amount of MBC in solution in water adjusted with phosphoric acid to pH values equivalent to those caused by the acid surfactant (Fig. 1, curve A). Acid alone was less effective in solubilizing MBC

TABLE 1. Solubility of methyl 2-benzimidazolecarbamate (MBC) in aqueous solutions

Mixtures[a]	pH	MBC solubility (μg/ml)
A. Water control	6.5	
B. Benomyl	6.5	10
C. Benomyl + 1% Tween 20	6.5	20
D. Benomyl + 1% RS-710	3.1	840
E. Benomyl + 1% RA-600	2.7	1,000
F. Benomyl[b]	2.7	750
G. Benomyl + 1% Tween 20[b]	2.7	950

[a] Tween 20 (polyoxyethylene sorbitan monolaurate) RS-710 and RA-600 mixtures of mono- and diphosphate esters, having free acid radicals.

[b] Water adjusted with H_3PO_4 to pH 2.7.



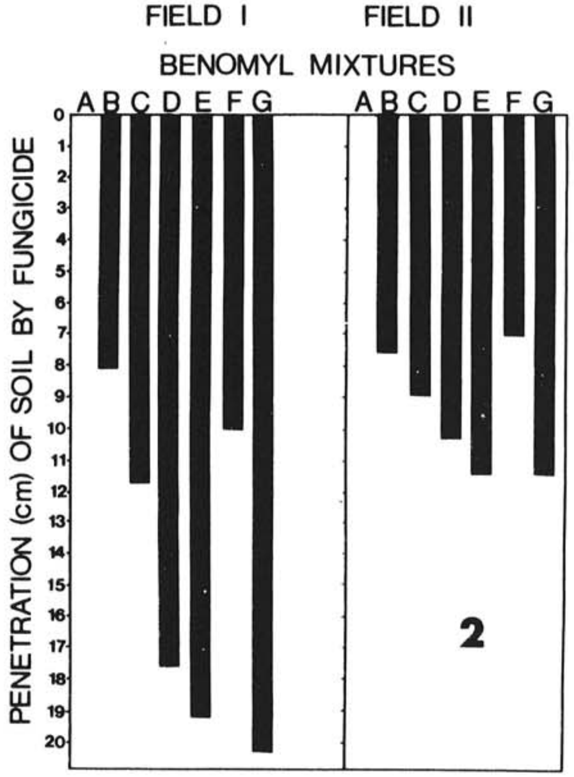


Fig. 1-2. **1)** Influence of surfactant, RA-600 (General Aniline & Film Corporation, New York, N.Y.), on the solubility of methyl 2-benzimidazolecarbamate (MBC) and surface tension of the solutions; A = solubility of MBC as affected by the acidic surfactant RA-600; B = solubility of MBC as affected by acid alone; C = surface tension of aqueous solutions containing varying concentrations of the surfactant RA-600. **2)** Influence of several surfactants on the movement of the fungicide in soil, as determined by *Penicillium* bioassay of soil aliquots at various depths. Field I, Guelph loam; Field II, Vineland silty loam. Benomyl mixtures: Water control (A); benomyl, with no surfactant (B); benomyl, with 1% surfactant; Tween 20 (C); RS-710 (D); RA-600 (E); and benomyl without (F) and with (G) 1% Tween 20 in water pH 2.7. Variance within replicates were within 2.3 cm.

than the surfactant. The difference between curves A and B (Fig. 1) must be due to unique properties of the surfactant.

The lowering of the surface tension might explain this difference. However, surfactant concentrations of 0.01% to 0.05% (Fig. 1, curve C) are sufficient to significantly lower the surface tension, yet higher concentrations of the surfactant are required to create a large increase in MBC solubility.

The difference in the actual solubility of MBC in the surfactant solutions and that caused by the protonation of MBC by the acidifying surfactants, might be attributed to micelle formation. These surfactants form micelles, or surfactant molecular aggregates, into which MBC dissolves. Consequently, the solubility of MBC in the surfactant is a prerequisite. Over 60,000 μg/ml MBC will dissolve in 100% RA-600.

A mixing time of 60 hr is required to completely solubilize the 1,000 μg/ml active benomyl in RA-600. Apparently, benomyl must break down to MBC before extensive solubilization can occur.

In soil penetration studies (Fig. 2), the movement of benomyl, or more precisely its fungicidal breakdown product, MBC, was enhanced by the addition of the surfactant Tween 20. The GAFAC surfactants, which solubilized the MBC to a greater extent than did Tween 20, showed a greater capacity to move the fungicide through soil. From mixture F (Fig. 2), the buffering capacity of the soils was able to raise the pH and precipitate out the MBC before it had moved far into the soil.

Acid plus Tween 20 was as effective as the GAFAC surfactant RA-600 in increasing the movement of MBC in soil.

The addition of the surfactants may have allowed the solutions to wet the soil particles faster, thus allowing greater downward movement (9). The ability of the surfactants to solubilize MBC increased the availability of the fungicide at lower soil levels. MBC could then be washed farther down by the surfactants.

In the dry soil (Field II), MBC did not penetrate so far, yet the relative differences in downward movement between mixtures remained constant. Water will move by gravitational force only when it is greater than the forces of adhesion and cohesion which form the water layers around soil particles (6). Downward movement of water, and thus the MBC in dry soils, is limited for this reason.

One of the primary purposes for adding surfactants to pesticides is to promote wetting and coverage because of their ability to lower surface tension. However, the unique hydrophilic-lipophilic properties of these additives permitted the surfactants to serve in more than this one function.

Booth & Rawlins (2) evaluated various surfactants as adjuvants for the fungicidal action of benomyl on *Verticillium*. They bioassayed the supernatant obtained from mixtures of benomyl and specific surfactants on *Verticillium*-seeded agar. They failed to suggest reasons for the relatively large increases in zones of inhibition using surfactants RS-710 and RA-600 with benomyl. Our data prove that these large zones of inhibition are in proportion to the increase in MBC in solution, as determined spectrophotometically.

Buchenauer & Erwin (4) reported that the addition of HCl to benomyl at high concentrations increased the uptake of MBC and was advantageous as a foliar spray for the control of Verticillium wilt of cotton. Our data show that at least 1,000 μg/ml MBC are soluble in water at pH 2.0, as compared to 10 μg/ml at pH 6.5. Since they used pH values of 1.5 to 1.7, the increased control with a higher concentration of HCl might be due to the higher concentration of soluble fungicide applied to the cotton plants.

Movement of pesticides in soil has been studied for many years. The technique often used is to add the test solutions to air-dry soil in columns, then to assay for the test chemical at various depths (7). Several inherent deficiencies are undefined soil compaction, greater movement of liquids along the sides of the column, and uniform soil moisture to a depth of 40 cm which is not found in undisturbed soils. Results obtained are often unrelated to the natural movement of chemicals in field soils. Our technique has a tremendous advantage in that it can be performed in the field under natural conditions.

It is understood that movement of benomyl-surfactant mixtures will vary from soil to soil due to such factors as the innate buffering capacity of the soil, percentage of organic matter, cation exchange capacity, and soil moisture.

Although depth of penetration of the fungicide in soil (Field I) was increased almost 3-fold with the addition of the acid surfactants, relatively high concentrations of surfactants and fungicide were used. The same phenomena governing penetration into soil should be applicable at lower concentrations. However, further research is needed using lower rates of benomyl and surfactants in different soil types. For example, Booth et al. (3) recently reported significant yield increases in cotton using 9 kg/hectare of benomyl applied in a 30-cm band with 1% surfactant.

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