

Fate of Benomyl and Its Degradation Compound Methyl 2-Benzimidazolecarbamate on Apple Foliage

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Changes in residues of benomyl and its degradation compound methyl 2-benzimidazolecarbamate (MBC or carbendazim) on apple foliage were determined in experiments conducted in two different years. Benomyl and MBC were simultaneously determined by a rapid high-performance liquid chromatographic method without cleanup using a silica gel column. Benlate fungicide 50% WP at 1.68 kg (3.36 kL)⁻¹ ha⁻¹ was applied as a spray and the original benomyl deposits ranged from 95 to 120 µg/g of leaf (0.95-1.2 µg/cm² of leaf surface). Benomyl dissipated quickly during the first 3-7 days, but the dissipation slowed down thereafter. Twelve days after each application at least 15% of the original deposit existed as intact benomyl. Benomyl gradually converted to MBC, and the MBC concentration in leaves gradually increased after repeated application of Benlate. The MBC concentration remained above 17 µg/g for ~80 days as a result of three applications; the maximum concentration, 55.8 µg/g, occurred 8 days after the third application.

Benomyl, methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, has been one of the most widely used systemic fungicides for more than 10 years. Its mode of action, however, is still not well understood because its natural degradation compound, methyl 2-benzimidazolecarbamate (MBC or carbendazim) is also fungitoxic. Consequently, it was extremely difficult to determine the roles of the two chemicals after spray application. It is generally believed that although the fungicide is applied as benomyl, the actual fungicidal activity derives from MBC. MBC was believed to be produced in aqueous media soon after benomyl is sprayed (Clemons and Sisler, 1969; Peterson and Edgington, 1970).

The persistence of benomyl on plants after spray application has received little attention in the past. Baude et al. (1973) demonstrated by using ¹⁴C-labeled benomyl that it decomposed more slowly than generally believed. Chiba (1975) showed that the rate of decomposition was much slower in water than in common organic solvents; decomposition of benomyl in water, however, was irreversible. It is likely that previous workers failed to recognize that benomyl is rapidly decomposed in organic solvents (Chiba and Cherniak, 1978).

Progress was slow in establishing mode of action and in determining persistence of benomyl because suitable analytical methods were not available to simultaneously determine low concentrations of residues of intact benomyl and MBC in plant tissues. Recently, Chiba and Veres (1980) developed a rapid high-performance liquid chromatographic (LC) method that allows simultaneous determination of residual benomyl and MBC without cleanup.

This paper reports results of studies that trace the fate of benomyl on apple foliage after spray application.

MATERIALS AND METHODS

Field Application. Benlate fungicide 50% WP was applied by spray gun at the rate of 1.68 kg (3.36 kL)⁻¹ ha⁻¹ to dwarf apple trees (cultivars McIntosh and Red Delicious) in an experimental orchard, Agriculture Canada, Vineland Station, Ontario, 3 times during the 1977 growing season. Duplicate 50-g leaf samples were collected before

each spray application. After each application similar samples were taken in duplicate after different intervals for residue analysis.

In 1979 Benlate 50% WP was similarly applied once in the same orchard toward the end of the growing season. This was the only pesticide treatment throughout the entire season. Triplicate 50-g leaf samples were collected before application. After application similar samples were taken in triplicate after different intervals for residue analysis.

Chemicals and Solvents. Analytical standards of benomyl, MBC, and MBC derivative with *n*-propyl isocyanate (MBC-*n*-PIC) were prepared in this laboratory as described previously (Chiba and Veres, 1980).

Chloroform (distilled in glass grade without ethanol preservative for extraction of samples and UV grade with 1% v/v ethanol preservative as the mobile phase for high-performance LC analysis) and *n*-hexane (UV grade) were obtained from Burdick and Jackson Laboratories, Inc., Muskegon, MI. It should be noted that chloroform is on the NIOSH 1976 subfile of suspected carcinogens.

n-Butyl isocyanate (*n*-BIC, Catalog No. P7184, practical) was from Eastman Kodak Co., Rochester, NY, and *n*-propyl isocyanate (*n*-PIC, Catalog No. P5,337-3, 99%) was from Aldrich Chemical Co., Milwaukee, WI. These isocyanates used are both strong lachrymators.

Residue Analysis. The procedures for residue analysis are those described by Chiba and Veres (1980). Samples were analyzed in duplicate in 1977 and in triplicate in 1979.

The molecular weights of MBC and benomyl are not equal. For simplicity, however, throughout this paper MBC concentrations are expressed in values stoichiometrically equivalent to the benomyl concentrations. For example, when benomyl at 10 µg/g decomposes completely to MBC, the actual concentration of MBC is 6.59 µg/g, but it is expressed as 10 µg/g.

RESULTS AND DISCUSSION

1977 Study. The original deposit of benomyl immediately after the first application was 115.7 µg/g. Deposits dissipated gradually; in addition to mechanical abrasion, wash off, and evaporation, the most important avenue of dissipation was the degradation of benomyl to MBC. As a result, the concentration of MBC increased gradually. After 12 days the concentration of benomyl had fallen to 32.7 µg/g, 28.3% of the initial deposit (Figure 1). The

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Table I. Residues of Benomyl and MBC in Apple Foliage at Different Intervals after Application of Benlate in 1977

date	days from first application	days from successive applications	benomyl			MBC		
			av deposit, ppm	SD, ^a ppm	% of total residue	av deposit, ppm	SD, ^b ppm	% of total residue
July 27	0		115.7	4.5	88.4	15.2	2.4	11.6
28	1		111.6	11.0	89.7	12.8	2.9	10.3
30	3		101.9	11.6	85.0	18.1	4.1	15.0
Aug 4	8		43.9	5.3	69.9	18.8	2.0	30.1
8	12		32.7	2.3	55.9	25.8	2.9	44.1
9	13	0	101.8	5.9	75.5	33.1	3.6	24.5
12	16	3	63.0	7.2	60.4	41.5	7.9	39.6
16	20	7	41.5	8.1	52.1	38.0	6.8	47.9
23	27	14	15.2	4.0	33.0	30.8	5.5	67.0
23	27	0	119.4	11.2	73.2	43.7	7.0	26.8
30	34	7	52.1	7.0	48.2	55.8	4.7	51.8
Sept 6	41	14	30.8	6.1	35.5	55.6	6.5	64.5
14	49	22	15.9	2.3	28.5	40.7	8.2	71.5
23	58	31	6.8	0.70	18.4	30.1	1.7	81.6
27	62	35	4.4	0.65	15.1	25.8	7.9	84.9
Oct 4	69	42	4.2	1.9	18.7	19.1	4.3	81.3
18	83	56	2.6	0.96	14.5	17.1	7.6	85.5

^a Average coefficient of variation is 16.0%. ^b Average coefficient of variation is 18.2%.

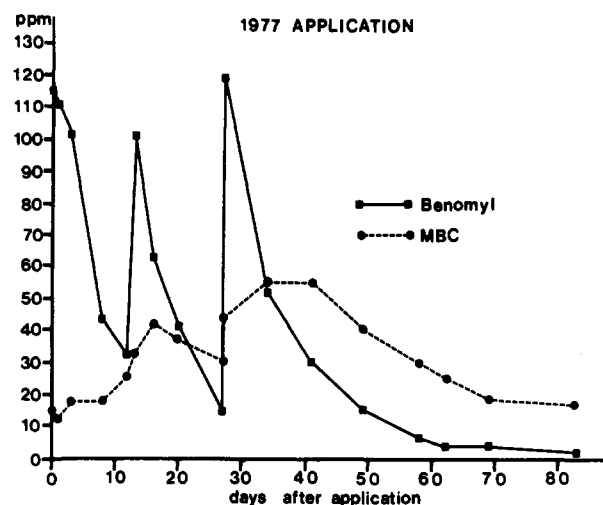


Figure 1. Benomyl residues and formation and dissipation of MBC on apple foliage after Benlate applications in 1977.

MBC concentration, which had been 15.2 $\mu\text{g/g}$ immediately after application, rose to 25.8 $\mu\text{g/g}$ during the same period (Figure 1). The dissipation of benomyl, however, was rather slow. The half-life, judged from Figure 1, is ~ 7 days. This is comparable to the half-life of DDT on grape foliage, when its half-life is based on simple dissipation of DDT rather than on decomposition of DDT to DDE (Chiba, 1970).

After the second application, the concentration of benomyl increased to 101.8 $\mu\text{g/g}$ and subsequently declined to 15.2 $\mu\text{g/g}$, 14.9% of the initial deposit after 14 days. During the same period, the concentration of MBC increased from 33.1 $\mu\text{g/g}$ to 41.5 $\mu\text{g/g}$ and then declined to 30.8 $\mu\text{g/g}$ just prior to the third application (Figure 1).

After the third application, the concentration of benomyl was 119.4 $\mu\text{g/g}$ and that of MBC was 43.7 $\mu\text{g/g}$. The dissipation pattern of benomyl after the third application was similar to that after the previous application; the concentration declined to 30.8 $\mu\text{g/g}$ after 14 days and to 2.6 $\mu\text{g/g}$ after 56 days (Table I).

Results of this study clearly indicate that benomyl is rather stable on plant foliage. Although the levels of MBC residue varied, benomyl formed the major part of the total residues for the first 34 days after application during July

and August, the most important period for protection (Figure 1; Table I).

The highest concentration of MBC, 55.8 $\mu\text{g/g}$, was found 7 days after the third application, and MBC concentrations remained higher than those of benomyl thereafter. The MBC concentration declined to 17.1 $\mu\text{g/g}$ at the end of the season, which was the lowest concentration during the period of 83 days except for the first 3 days immediately after the first application (Figure 1; Table I).

It appears that benomyl degrades faster during tank mixing and spray application than when on the foliage. MBC constituted 4.6% of the total active ingredients of Benlate 50% WP used when determined by the WP method (Chiba, 1979). The corresponding percentage was up to 11.6% when the spray deposit was analyzed immediately after the first application. The corresponding values after the second and third applications were 9.6% and 11.0%, respectively. The percentage of MBC on the average, therefore, increased by 6.1% during tank mixing and application. These values, however, may be higher than real values because a certain amount of MBC might have been produced from benomyl in the leaves during storage at -15°C for a period of more than 2 years before analysis.

The percentage of benomyl in total residues declined consistently with time after application while that of MBC increased (Table I). The table also includes actual values of residues of benomyl and MBC and the values of standard deviations based on analyses of foliage of both McIntosh and Red Delicious apples (two replicates each). Coefficients of variation (standard deviation/mean) averaged 16.0% and 18.2% for benomyl and MBC, respectively. Residue differences were not evident between the cultivars.

1979 Study. The initial benomyl deposit, 88.9 $\mu\text{g/g}$, was slightly lower than that, 115.7 $\mu\text{g/g}$, in 1977. Such variation is common, however, among ordinary spray applications (Chiba, 1970, 1978). The corresponding MBC value of 3.7 $\mu\text{g/g}$, however, was substantially lower than that in 1977, 15.2 $\mu\text{g/g}$. Also, MBC constituted only 4.0% of the total deposit, which was substantially lower than the 1977 value of 11.6%. The percentage of MBC present in the formulated Benlate 50% WP used was 2.6%; the increase in MBC during the tank mixing, spray application, and analytical procedure was only 1.4%. The corresponding value in 1977 was 6.1%; the difference of 4.7% is very

Table II. Residues of Benomyl and MBC in Apple Foliage at Different Intervals after Application of Benlate in 1979

date	days from application	benomyl			MBC		
		av deposit, ppm	SD, ^a ppm	% in total residue	av deposit, ppm	SD, ^b ppm	% in total residue
Aug 24	0	88.9	7.2	96.0	3.7	1.2	4.0
27	3	38.8	2.3	76.8	11.7	1.1	23.2
Sept 4	11	14.2	2.5	51.0	13.7	2.4	49.0
11	18	9.5	0.60	46.2	11.4	2.7	53.8
18	25	3.7	0.94	35.9	6.5	1.4	64.1
25	32	2.7	0.35	33.3	5.3	0.70	66.7
Oct 9	46	0.63	0.20	34.4	1.2	0.30	65.6

^a Average coefficient of variation is 15.4%. ^b Average coefficient of variation is 20.4%.

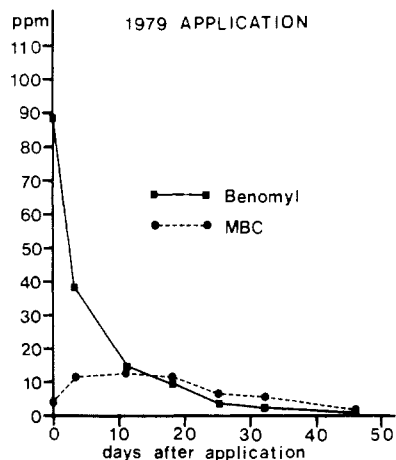


Figure 2. Benomyl residues and formation and dissipation of MBC on apple foliage after Benlate application in 1979.

likely due to the degradation which occurred during the storage as aforementioned.

The low MBC concentration was maintained throughout the 1979 season. Because there was only one application, MBC did not build up to the levels of the previous experiment; the highest MBC concentration in 1979 was 13.7 $\mu\text{g/g}$; the corresponding value in 1977 was 55.8 $\mu\text{g/g}$. The MBC concentration reached that of benomyl on the 11th day after application (Figure 2; Table II).

Benomyl dissipated rather quickly during the first week but slowed substantially thereafter. The half-life of the initial deposit was less than 3 days (Figure 2), which is short compared with corresponding 1977 figures of 7, 5, and 7 days after the first, second, and third applications, respectively. It is probable that the 28.8 mm of rain which fell during the 3-day postspray period eroded some of the initial deposit. No rain fell during the 3 days immediately after either first or third application; 17.4 mm of rain fell after the second application in 1977. Temperature did not seem to be correlated with dissipation; the average temperatures during the 3-day periods were 25.5, 27.5, and 21.3 $^{\circ}\text{C}$ after the first, second and third application, respectively, in 1977 and 23.3 $^{\circ}\text{C}$ in 1979.

Little difference was found in the rate of degradation of benomyl between the two cultivars of apples. Moreover, the basic degradation patterns are similar for the 2 years.

The manufacturer of benomyl now recommends that Benlate be used in conjunction with a companion fungicide. The use of a companion fungicide with a different mode of action may eliminate emerging resistant strains if very few are in the population (Delp, 1980). Delp (1980) also states that sole, long-term exposure of the pathogen to the agent must be avoided.

Results of the present study indicate that although high levels of benomyl residues are obtained even after a single application, they will not last for an extended period. When applications are repeated, however, the fungi will be exposed to relatively high levels of residual benomyl and/or MBC for extended periods (Figure 1; Table I). The concentration of MBC may become even higher if benomyl applications are repeated as was common practice in the past.

If continuous exposure is the cause of the buildup of tolerance to benomyl and/or MBC, repeated applications of benomyl must be avoided. Results of the present study are fully consistent with this view; further work will elucidate the real roles of these two fungicidal chemicals.

LITERATURE CITED

- Baude, F. J.; Gardiner, J. A.; Han, J. C. Y. *J. Agric. Food Chem.* **1973**, *21*, 1084.
 Chiba, M. *Can. J. Plant Sci.* **1970**, *50*, 219.
 Chiba, M. "Abstracts of Papers", 170th National Meeting of the American Chemical Society, Chicago, IL, Aug 24-29, 1975; American Chemical Society: Washington, DC, 1975; PEST 127.
 Chiba, M. *J. Environ. Sci. Health, Part B* **1978**, *B13* (3), 261.
 Chiba, M. *J. Assoc. Off. Anal. Chem.* **1979**, *62*, 488.
 Chiba, M.; Cherniak, E. A. *J. Agric. Food Chem.* **1978**, *26*, 573.
 Chiba, M.; Veres, D. F. *J. Assoc. Off. Anal. Chem.* **1980**, *63*, 1291.
 Clemons, G. P.; Sisler, H. D. *Phytopathology* **1969**, *59*, 705.
 Delp, C. J. *Plant Dis.* **1980**, *64*, 652.
 Peterson, C. A.; Egington, L. V. *Phytopathology* **1970**, *60*, 475.

Received for review October 27, 1980. Accepted January 9, 1981. This paper was presented at the Second Chemical Congress of the North American Continent, Division of Pesticide Chemistry, Las Vegas, NV, Aug 1980.