Determining Diuron, Simazine, and Methiocarb Residues in Highbush Blueberries (*Vaccinium corymbosum*)

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Abstract. Two-year-old highbush blueberry bushes (*Vaccinium corymbosum* L. 'Collins') were treated in Mar. 1985 with diuron or simazine at 2.2 or 4.5 kg a.i./ha. No residues were detected by reverse-phase high-performance liquid chromatography-ultraviolet absorbance detection (HPLC-UV) from treated berries that were harvested in June. Methiocarb was applied in May 1986 at 0.84 and 3 kg·ha⁻¹ over the top of 3-year-old 'Collins' when the berries began to ripen. Reverse-phase HPLC-UV of berries treated with methiocarb at 3 kg·ha⁻¹ had combined residues of methiocarb and its sulfone and sulfoxide metabolites of 13.1 ppm from unrinsed and 7 ppm from rinsed berries harvested on the day of treatment; 4.9 ppm from unrinsed and 4 ppm from rinsed berries harvested 4 days after treatment; and 2.4 ppm from unrinsed and 2.5 ppm from rinsed berries harvested 8 days after treatment. Unrinsed berries treated with methiocarb at 0.84 kg·ha⁻¹ had 5.7 ppm residue on the day of treatment and 1 ppm 8 days later. Residues from berries treated with methiocarb at 0.84 or 3 kg·ha⁻¹ were below the legal tolerance level of 5 ppm after the required 7-day waiting period. Chemical names used: n'-(3,4-dichlorophenyl)-N,N'-dimethylurea (diuron); 6-chloro- N,N'-diethyl-1,3,5-triazine-2,4-diamine (simazine); 3,5-dimethyl-4-(methylthio)phenol methylcarbamate (methiocarb).

Blueberry growers must often use chemicals to control pests for efficient production. One of the most costly and time-consuming problems in blueberry culture is weed control (Gupton, 1986). Tilling to control weeds is limited in blueberry orchards because the plants have shallow root systems and mulch is often applied (Eck and Childers, 1966). In addition to weed problems, birds may damage the berries, a problem that can be devastating in some growers' fields. Blueberry loss to birds was ≈5% of the nation's total crop in 1973-74, with a resulting annual loss of \$1.6 to \$2.1 million (Wood, 1977). Using chemicals is the most efficient bird control method in blueberry production. The insecticide methiocarb was used to control birds until it was banned a few years ago. Methiocarb was more effective than fear-provoking techniques (Holland and McFarlane, 1981) and the cost was half as much as netting (Conover, 1982; Holland and McFarlane, 1981). Methiocarb has reduced bird damage to blueberries by 37% to 99% (Conover, 1982; Greenhalgh et al., 1977; Holland and McFarlane, 1981; Holland et al., 1980; Wood, 1977).

The major disadvantage of using pesticides in crop production is the possibility of retaining pesticide residues in the crop. Methiocarb was banned because of questions about residue levels in the fruit (John Fortino, personal communication). In Ontario, blueberries treated in the field with methiocarb at the recommended rate or lower contained 4.2 to 50.7 ppm on the day of treatment and 1.1 to 33.7 ppm 7 days later. Methiocarb's half-life on blueberries was 3 to 7 days (Greenhalgh et al., 1977). Seven days after blueberries were treated with 112 g of methiocarb/100 liters, the residue was 10 to 25 ppm in New Zealand highbush blueberries; total residue half-life was 5 to 10 days (Holland et al., 1980). Blueberries contained 4 to 15 ppm of methiocarb 7 days after being treated with 75 g/100 liters (Holland et al., 1981). Re-registration of methiocarb on blueberries is being considered pending further investigation.

The primary objective of this experiment was to determine the amount of diuron, simazine, or methiocarb residues detected in blueberries from plants treated with these pesticides. Diuron and simazine were analyzed because of their wide use in blueberry production and because of concern about pesticide residues in blueberry fruit. Secondary objectives were to compare the herbicide treatments for weed control, crop yield, and crop injury.

Field plots were established near Fayetteville, Ark., on a blueberry farm planted to 2-year-old 'Collins' highbush blueberry plants in Linker silt loam soil with an organic matter content of 3.3% and pH 5.3. The design was a randomized complete block with four replications. Each experimental unit contained three plants and was 1.6 m wide × 3.6 m long. An

adjacent plot was later added to ensure that there would be enough berries for the methiocarb residue analysis. The plants were mulched with hardwood chips and irrigated with a trickle irrigation system installed under the mulch. The area between the mulched rows (2.3 m) was planted to fescue and mowed as needed.

Diuron and simazine were applied pre-emergence and at the bud-swell stage of the blueberry plants at the recommended rate (2.2 kg·ha⁻¹) and two times the recommended rate (4.5 kg·ha⁻¹) on 25 Mar. 1985, and 18 Mar. 1986, with a CO₂ backpack sprayer in a carrier volume of 300 liters·ha⁻¹. Paraquat (1,1'-dimethyl-4,4'-bipyridinium salts) was applied at 0.56 kg·ha⁻¹ immediately before diuron and simazine to kill the existing weeds. Methiocarb was applied over the top at 0.84 and 3 kg·ha⁻¹ in a water volume of 935 liters·ha⁻¹ on 7 June 1985 and 29 May 1986 when the first berries were ripe. The methiocarb plots were treated for weed control with terbacil [5-chloro-3-(1,1-dimethylethyl)-6-methyl-2,4-(1 H, 3 H)-pyrimidinedione] at 2.2 kg·ha⁻¹ when simazine and diuron were applied elsewhere.

Blueberries from plots treated with diuron and simazine were harvested as they ripened (9 to 11 weeks after treatment), weighed, and stored frozen at -4C in plastic bags for later residue analysis. The methiocarb-treated berries were harvested on the day they were treated and 4 and 8 days after treatment. Half of the berries picked from the methiocarb-treated plots was rinsed with water before being frozen, and the other half was not. The volume of water used for rinsing was three times the berry volume. Rainfall amount was recorded.

To analyze berries for the presence of diuron and simazine, the berries were blended with acetonitrile and partitioned with chloroform, followed by a basic alumina column cleanup step. Samples were analyzed using a Waters (Milford, Mass.) high-pressure liquid chromatograph (HPLC) with a model 6000-A solvent delivery system and a model 440 ultraviolet (UV) absorbance detector. The analysis was by reverse-phase chromatography using a C₁₈ column and 35% acetonitrile-water as the mobile phase. The berries were stored frozen from 1 week to 5 months before being analyzed.

Percent diuron and simazine recovery was determined by fortifying a sample of nontreated berries with a known amount of herbicide. Each fortified control sample consisted of 30 g of berries from control plots to which 100 µl of 100-ppm diuron or 50 µl of 100-ppm simazine, dissolved in methanol, was added before being blended with acetonitrile. Fortification concentrations were 0.33 ppm diuron and 0.17 ppm simazine in the blueberries.

Percent recovery of diuron and simazine was also determined for frozen, stored berries. Each 30-g sample of nontreated blueberries was macerated in a blender and fortified with either 100 or 500 µl of 100-ppm diuron (0.33- and 1.65-ppm concentration) or 50 or 250 µl of 100-ppm simazine (0.17- and 0.85-ppm concentration) dissolved in methanol. Samples

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were swirled, capped, and frozen in glass jars. Diuron and simazine samples were frozen for 6 and 10 months, respectively, before being analyzed.

Procedures for analyzing methiocarb reported by Greenhalgh et al. (1977) and Thornton (1969) were combined and modified for analyzing the methiocarb-treated berries. The resulting procedure consisted of blending the berries with acetone and a buffer, extracting the pesticides with chloroform, oxidizing with potassium permanganate, then cleaning up by silica gel column.

Samples were analyzed using a Waters model 440 HPLC with a UV absorbance detector and a model 6000-A solvent delivery system in a reverse-phase chromatography system using a C_{18} column and acetonitrile-water as a mobile phase. The mobile phase was 40% acetonitrile-water for methiocarb determination and 1% acetonitrile-water for methiocarb's sulfoxide and sulfone. Berries analyzed for their concentration of methiocarb were stored frozen for 6 to 10 months before being analyzed.

Recovery of simazine (application concentration 0.17 ppm) from berries fortified after freezing averaged 94% and recovery of diuron (application concentration 0.33 ppm) from berries fortified after freezing averaged 91%. Recovery of simazine (application concentration 0.17 ppm) from berries fortified before freezing averaged $96\% \pm 8\%$ and recovery of diuron (application concentration 0.33 ppm) from berries fortified before freezing was $103\% \pm 19\%$. Diuron, therefore, remained stable in frozen blueberries for at least 5 months. Simazine persistence data in frozen blueberries were inconsistent, so stability in frozen blueberries could not be verified. Blueberries treated in the field with diuron or simazine at the labeled rate and two times the labeled rate had no detectable herbicide residues. The detection limits using our procedure were 0.17 ppm for diuron and 0.08 ppm for simazine. The legal tolerance level in blueberries is 1 ppm for diuron and 0.25 ppm for simazine (Federal Register). Diuron or simazine residues in the berries, if present, were <0.17 and 0.08 ppm, respectively, and well below the legal tolerance levels. Berries were not analyzed for diuron and simazine in 1986.

The methiocarb recovery rate from blueberries fortified with methiocarb or its sulfone or sulfoxide metabolite averaged 67%. After 17 months of storage at -4°C , 84% to 118% of methiocarb and its metabolites was recovered [except the methiocarb sulfone (50 ppm) sample, the reason for which is unknown]. However, from these results, it seems that methiocarb and its metabolites are stable while frozen for up to 17 months.

The parent compound and residue metabolites in the berries could not be quantified because the methiocarb analysis oxidized methiocarb and methiocarb sulfoxide to the sulfone. Therefore, a residue concentration range was determined from the amount of methiocarb sulfone found in each sample. The lower limit of the range represents the amount of residue detected if the residue were 100%

methiocarb, and the upper limit of the range represents the amount of residue if it were 100% methiocarb sulfone. The original residue concentrations are within this range. Concentrations given in Table 1 are the medians of the concentration ranges for each sample.

These residues are lower than those found in blueberries treated with methiocarb in Ontario (Greenhalgh et al., 1977) and New Zealand (Holland et al., 1981). Berries treated in Ontario contained 50.7 ppm methiocarb residue on the day they were treated with the recommended rate, compared to 13.1 ppm detected in this study. Seven days after treatment, the Ontario berries contained 33.7 ppm; whereas, in the current study, 2.4 ppm was quantified 8 days after treatment. The half-life of the residue in Ontario was 7 days compared to <4 days found by us. Similarly, berries treated in New Zealand at the recommended rate contained 10 to 25 ppm residue 7 days after treatment; half-life was 5 to 10 days. Factors that could account for these differences are variability in environmental conditions, such as amount of UV light, wind velocity, air temperature, rainfall, and amount and type of epicuticular wax.

Methiocarb was applied at three rates: 0, 0.84, and 3 $\text{kg}\cdot\text{ha}^{-1}$. The recommended application rate was 3 $\text{kg}\cdot\text{ha}^{-1}$ in 1985 when our research began. In 1987 the rate recommended on the label was lowered to 2.2 $\text{kg}\cdot\text{ha}^{-1}$. The lowest rate was used by some producers to lower the cost while adequately repelling birds. At the time these studies were conducted, the label required a 7-day waiting period between treatment and harvest, and the legal tolerance level for the combined residues of methiocarb

and its sulfone and sulfoxide metabolites in blueberries was 5 ppm.

Blueberries harvested from control plots seemed to have been contaminated with methiocarb or its metabolites (Table 1). The amount of residue decreased as the preharvest interval increased, indicating that all of the berries were contaminated on the same day, perhaps by sprayer drift. However, residues found in untreated berries harvested on days 1-6 were not significantly different among days, and the amount is reported as an average on the days berries were picked (Table 1).

Berries from treated plots picked on the day of treatment had residues above the legal tolerance level of 5 ppm (Table 1). Rinsing day 0 berries treated with 3 $\text{kg}\cdot\text{ha}^{-1}$ reduced the amount of residue, but it was still above the legal tolerance level. Berries treated with 3 $\text{kg}\cdot\text{ha}^{-1}$ and harvested 4 days after treatment had residues under the legal tolerance level. Rinsing berries with water did not affect the residue level. The residues may have been retained in epicuticular wax or may have penetrated to the inside of the berries; it may have rained (Table 2), or photodecomposition-mediated reduction in easily removable residue could have occurred. Eight days after treatment, the berries contained residues below the legal tolerance level: 2.4 ppm in berries treated with 3 $\text{kg}\cdot\text{ha}^{-1}$ and 1.0 ppm in berries treated with 0.84 $\text{kg}\cdot\text{ha}^{-1}$. Rinsing berries with water did not affect the amount of residue. Reducing the methiocarb application rate from 3 to 0.84 $\text{kg}\cdot\text{ha}^{-1}$ (ratio 3.5) reduced the amount of residue by a factor of 2.5.

Diuron and simazine are suitable for weed control in Arkansas blueberries. Diuron resi-

Table 1. Concentration of methiocarb and/or metabolites found in 1986 blueberries in relation to methiocarb application rate.

Application rate ($\text{kg}\cdot\text{ha}^{-1}$)	Preharvest interval (days)	Washing ^z	Amount found in berries ^y
0.0	1-6 ^x	U	2.9
	7	U	1.1
0.84	0	U	5.7
	8	U	1.0
3.0	0	U	13.1
	0	W	7.0
	4	U	4.9
	4	W	4.0
	8	U	2.4
	8	W	2.5
LSD _{0.05}			1.7

^xBerries not washed (U) or washed (W) before being frozen.

^yDetection limit = 0.2 ppm.

^zBerries from control plots were not harvested when treated berries were harvested.

Table 2. Rainfall measured on methiocarb-treated area from day of treatment to 8 days after treatment.

Date (1986) ^a	Days after treatment	Rainfall duration (hours)	Amount of rain (mm)	Relative rain intensity
31 May	2	0.5	<5	Light
2 June	4	12.0	20	Moderate
3 June	5	0.1	<5	Heavy
5 June	7	1.0	<5	Light

^aRainfall data from 1985 are not shown since only berries harvested in 1986 were analyzed for pesticide residues.

dues were not detected in the fruit. Simazine residues were not detected in berries harvested 9 to 11 weeks after the plants were treated with diuron or simazine. These studies also indicate that methiocarb residues would be <5 ppm when applied at 2.2 kg-ha⁻¹ and harvested after the required 7-day waiting period. The residue can be reduced substantially if only 0.84 kg-ha⁻¹ is applied.

This study indicates that diuron or simazine residues would be below the legal tolerance level when used at the labeled rates on blueberries grown under the environmental conditions of our study. The absence of detectable residues in berries treated with two times the recommended rates also indicates that there is a wide margin of safety in the application rates.

In addition, our study supports further investigation of methiocarb use on blueberries. The residues found on berries grown under the environmental conditions of our study were

below the current tolerance level. Further investigation using the lower 0.84-kg-ha⁻¹ application rate seems particularly justified, since farmers have reported successful bird control using this rate and residues were dramatically reduced.

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