Residue Dynamics and Persistence of Aldicarb and Its Biologically Similar Active Metabolites in Grapevines

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Abstract: Residue dynamics in grapevine of the nematicide aldicarb (2-methyl-(methylthio) propionaldehyde-O-(Methylcarbamoyl) oxime) and its biologically similar active metabolites, aldicarb sulfoxide and aldicarb sulfone, were determined by gas chromatographic techniques. Residues were found in the roots, trunks, stems, and leaves of grapevine 120 d after application. Residues in leaves as high as 1.40 and 8.89 ppm resulted from 4.5 and 9 kg ai/ha respectively. In roots, trunks, and stems the residues had also declined after 180 d. No residues were detected in the newly forming immature fruit. Residues in roots, trunks, young branches, and leaves declined further after 270 d, but residues in mature fruit at harvest time were 0.03 and 0.05 ppm from application of 4.5 and 9 kg ai/ha, respectively. In other trials the amount of aldicarb toxic residues found in mature fruit at harvest time varied with grape varieties, time and rate of application, total amount of rainfall, irrigation water, and soil type. *Key words:* systemic nematicides.

The need for effective controls to reduce plant parasitic nematodes in established vineyard soils is urgent. The use of post-planting fumigation with 1,2-dibromo-3-chloropropane (DBCP) to control nematodes had become a common practice in California vineyards and in vineyards of many countries (4,8,13,14,15,16,18) when use of DBCP was suspended because of associated health hazards. Several systemic nematicides are now used commercially on a wide range of crops (1,2,5,6,9,10,11,12,17, 19). There are, however, few observations of the way in which these nematicides move in the plant (7,17).

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The insecticide-nematicide, aldicarb (2-methyl-2-(methylthio) propionaldehyde-O-(methylcarbamoyl) oxime), is a broad-spectrum, soil-applied systemic nematicide, rapidly absorbed by plant roots and translocated to the plant shoot. Nematode control may begin within 25 h after application and afford residual protection against many phytophagous pests for up to 10 wk (17).

The fate and persistence of aldicarb in plants, insects, mammals, and soil has been studied extensively (3). Few chemical studies have been reported on the movement of aldicarb in plant parts, none on grapevine.

The present work investigated (i) the movement and persistence of aldicarb and its biologically similar active metabolites, aldicarb sulfoxide and aldicarb sulfone, in roots, trunks, young branches, and leaves of

Vitis vinifera cv. Thompson Seedless grape; and (ii) the persistence of aldicarb, aldicarb sulfoxide, and aldicarb sulfone in the fruit under different circumstances.

MATERIALS AND METHODS

Field trials: These were conducted in eight different vineyards. The residue dynamics of aldicarb and its biologically similar active metabolites in grapevine parts were studied using a vineyard at the University of California at Davis. Trials to determine the effects of grape cultivars, rates, times, methods of application, and soil type on the persistence of aldicarb toxic residues in fruits were conducted on grapes collected from vineyards at Lodi, Escalon, and Delano, California.

At Davis, 8-yr-old vines planted in loam soil with ph 7.2 and spaced 2.4 × 3.6 m were treated with aldicarb 15 G at two rates, 4.5 and 9 kg ai/ha. The chemical was applied by hand broadcasting over 100% of the area. Sprinkler irrigation for 13 h over a 3-d period followed the application. Each treatment was replicated three times in a completely randomized block design with two vines per replicate. Condition of trials at other locations are described with the tabulated results for each experiment.

Plant samples: At Davis root, trunk, young branch, and leaf samples were taken 120, 180, and 270 d after application. Fruit was sampled when immature (at 180 d) and again when mature (at 270 d). In trials at other locations only mature fruit was sampled. Small feeder roots were obtained 50 cm from the trunk. Two samples were taken in the trunk of each vine 90 cm above ground using a brace and 25-mm bit. Holes were 15 cm apart and drilled as deep as the xylem. Medium-sized young branches and leaves were sampled randomly from different locations on the vine. Grapes were separated from stems and then mixed together for uniformity. Three samples of each plant part were composited and mixed. Then a 50-g aliquot weight was taken for residue analysis.

Extraction and analysis of aldicarb toxic residues in grape plant material: The amount of aldicarb and its toxic derivatives, aldicarb sulfoxide and aldicarb sulfone, were determined by a modification of a method (17) supplied by the Agricultural Products Division of the Union Carbide Corporation, Jacksonville, Florida. The modification used no oxidizing agent and allowed the separate determination of each residue component. Some fruit samples were sent to a commercial laboratory which used the unmodified Union Carbide method to determine the total amount of toxic residues expressed as aldicarb sulfone.

Sample preparation and extraction: Composite samples were cut with scissors into small pieces and mixed. The 50-g aliquots used for analysis were placed in a homogenizer jar, and 200 ml of acetone: water (3:1) solvent was added. Jar contents were blended 10 min at high speed and 20 min at medium speed, allowed to settle, and then decanted into a 500-ml Erlenmeyer flask through 150 g anhydrous Na_2SO_4 held in a funnel with a cotton plug. Another 100 ml of extraction solution was added to the homogenizer jar, blended 20 min at medium speed, allowed to settle, and then decanted through Na_2SO_4. This last step was then repeated, and the cake was washed with 50 ml of additional solvent. The combined filtrates and washing were measured, and one-half was discarded. The other half was transferred to a 500-ml separatory funnel and extracted four times by shaking 30 s with 75 ml of chloroform. Extracts were drained through a bed of anhydrous granular Na_2SO_4 into a 500-ml rotary evaporator flask. The combined filtrate was evaporated to near dryness using a rotary evaporator at 40 C. For cleanup a glass chromatography column containing Florisol, 60/100 mesh, PR grade was used. The second fraction from the chromatography column contained the aldicarb and its metabolites, aldicarb sulfoxide and aldicarb sulfone, in a mixture of acetone and ethyl ether (1:1). The mixture was evaporated to dryness under vacuum at 40 C. The residue was dissolved in acetone, transferred to screw-capped test tubes, and stored at −10 C until analysis.

Chromatograph analysis: A Beckman G. C. 45 gas chromatograph equipped with a flame-photometric detector specific for sulfur-containing compounds (394-mm filter) was used. A standard curve for aldicarb, aldicarb sulfoxide, and aldicarb sulfone determination was obtained by using technical

materials provided by the Union Carbide Company. A series of dilutions were made to obtain different concentrations, and an appropriate volume from each was injected into the gas chromatograph. The resulting peak heights were plotted on a log-log scale which resulted in a straight line from which aldicarb, aldicarb sulfoxide, and aldicarb sulfone were calculated.

The concentration of aldicarb and its toxic metabolites from different parts of the grapevine were measured as a ppm of aldicarb, aldicarb sulfoxide, and aldicarb sulfone per gram fresh weight at 120, 180, and 270 d after application.

RESULTS AND DISCUSSION

The residue dynamics of aldicarb and its biologically similar active metabolites in grapevine: Residues were found in roots, trunks, young branches, and leaves of grapevine 120 d after application (Table 1). Residues in roots were mostly in the aldicarb sulfoxide form with some aldicarb sulfone but none in aldicarb form. This indicates that aldicarb in the root tissues is broken down to sulfoxide and sulfone. After 180 d residues in roots had declined from 3.3 to 2.0 ppm at 9.0 kg ai/ha and from 1.9 to 0.45 ppm at 4.5 kg ai/ha. After 270 d there was further decline, and residues were mostly in the form of sulfone. The total amount of aldicarb and its metabolites, aldicarb sulfoxide and aldicarb sulfone, at 9.0 kg ai/ha was almost four times that at 4.5 kg ai/ha. This may be due to the increased growth of the root system at the higher rate resulting in increased rate of aldicarb uptake from the soil solution. Residues in trunk tissues 120 d after application were aldicarb, aldicarb sulfoxide, and aldicarb sulfone, with the sulfoxide form the highest. After 180 d residues in trunk tissues had declined more sharply than in root tissues which may be due to movement to the young branches and leaves. We conclude that the trunk tissues do not store aldicarb or its metabolites. Residues in young branches 120 d after application contained only two forms, aldicarb and aldicarb sulfoxide, but 60 d later the aldicarb disappeared and aldicarb sulfone was detected. Residues in the young branches had also declined after 180 d with a further decline after 270 d in young branches and leaf tissues. At 9.0 kg ai/ha 180 d after application, the aldicarb form disappeared from the young branches but not from the leaves. Samples containing combined young branches and leaves taken 270 d after application showed some aldicarb, indicating that the aldicarb form came from the leaf tissues and not from the young branch tissues. On the other hand, at 4.5 kg ai/ha rate the aldicarb form had disappeared from both young branches and leaf tissues 180 d after application.

Residues in leaves 120 d after application were as high as 1.4 and 8.89 ppm following 4.5 and 9.0 kg ai/ha aldicarb, respectively. Most residues were in sulfoxide form, with some aldicarb form but none in sulfone form. After 180 d the residues had declined to 0.55 and 1.1 ppm, respectively. This decline was mostly in the sulfoxide form which dropped from 7.2 to 2.6 ppm. After 270 d the residues in leaves declined to traces of sulfone.

No residues were detected at either rate in the immature fruit taken 180 d after application. This may be due to the nature of the chemical structure of the immature fruit, which may cause breakdown of the toxic forms to nontoxic forms not detected by the analytical technique used. In mature fruit at harvest time, 270 d after application, total toxic residues resulting from application of 4.5 and 9 kg ai/ha were 0.03 and 0.05 ppm. These residues in fruit were much lower than those in other plant parts. In conclusion, aldicarb and its toxic metabolite residues 120 d after application were concentrated in the leaves, particularly at the higher rate, but after 270 d the residues had declined and started to show in mature fruit.

Persistence of aldicarb and its toxic metabolites in the fruit at harvest: The 'Cardinal' variety treated once with aldicarb 11.25 kg ai/ha 191 d before harvest contained 0.75 ppm residues. But with the lower 4.5 and 9 kg ai/ha rates, or the split application, the toxic residues were 0.60 ppm or less (Table 2). The total amount of toxic residues of aldicarb and its toxic metabolites varied with different varieties (Table 2). Greater amounts of toxic residues were detected in 'Muscat,' 'Cardinal,' and

Table 1. Distribution of aldicarb and its toxic metabolites in grapevine.

Treatment	Plant part	Total toxic residues of aldicarb and its metabolites in ppm											
		120 d after application				180 d after application				270 d after application			
		Aldicarb	Aldicarb sulfoxide	Aldicarb sulfone	Total	Aldicarb	Aldicarb sulfoxide	Aldicarb sulfone	Total	Aldicarb	Aldicarb sulfoxide	Aldicarb sulfone	Total
Aldicarb 9 kg ai/ha	Root	0.00	3.00	0.30	3.30	0.00	1.10	0.90	2.00	0.0	0.2	0.31	0.51
	Trunk	0.78	1.90	0.20	2.88	0.00	0.90	0.09	0.99	0.0	0.018	0.004	0.002
	Stem	1.50	0.60	0.00	2.10	0.00	0.35	0.31	0.66	0.013*	0.04*	0.005*	0.058*
	Leaf	1.65	7.20	0.00	8.85	0.40	2.60	0.10	1.10				
	Fruit					0.00	0.00	0.00	0.00	0.03	0.02	0.005	0.055
Aldicarb 4.5 kg ai/ha	Root	0.00	1.80	0.10	1.90	0.00	0.35	0.10	0.45	0.00	0.02	0.10	0.12
	Trunk	0.20	0.45	0.00	0.65	0.00	0.00	0.10	0.10	0.00	0.00	0.01	0.01
	Stem	1.50	0.00	0.00	1.50	0.00	0.15	0.102	0.252	0.00*	0.02*	0.01*	0.03*
	Leaf	0.60	0.80	0.00	1.40	0.00	0.40	0.15	0.55				
	Fruit					0.00	0.00	0.00	0.00	0.00	0.004	0.023	0.027

*Sample is a composite of stem and leaf.

Table 2. Toxic residues in grape varieties after 1 yr of treatment with aldicarb or sulfocarb using different rates, timing, and application methods.

Location and soil texture	Grape variety	Application: Method	Application: Rate in kg ai/ha	Time in days from application to sampling	Toxic residues in ppm
Lodi, sandy loam	'Cardinal'			First season	
		Two furrows, one on each side of the vine row	Aldicarb 4.5	191	0.31
			Aldicarb 9.0	191	0.60
			Aldicarb 11.25	191	0.75
			Aldicarb 4.5	216	0.26
			Aldicarb 9.0	216	0.53
			Aldicarb 4.5 + 4.5	133	0.55
			Aldicarb 4.5 + DBCP 2 gal.	216	0.37
			Sulfocarb 3.4	191	0.15
			Sulfocarb 5.6	191	0.27
				Second season	
			Aldicarb 4.5	581	0.00
			Aldicarb 9.00	581	0.00
			Aldicarb 11.25	581	0.04
	'Tokay'			First season	
		Brodacast 50% coverage area	Aldicarb 9.0	272	0.00
		Broadcast 100% coverage area	Aldicarb 4.5	272	0.00
		Brodacast 50% coverage area	Aldicarb 9.0	180	0.297
		Brodacast 50% coverage area	Aldicarb 4.5	180	0.077
Escalon, sand	'Mission'			First season	
		Six furrows, two on each side and two cross furrows	Aldicarb 4.5	187	0.530
			Aldicarb 4.5 + 4.5	124	0.730
			Aldicarb 4.5 + 4.5 + 4.5	124	1.100
				Second season	
			Aldicarb 4.5	545	0.000
			Aldicarb 4.5 + 4.5	482	0.037
			Aldicarb 4.5 + 4.5 + 4.5	482	0.040
Delano, sandy loam	'Alicante'			First season	
		5′ band spanning both sides of the vine row	Aldicarb 4.5	219	0.020
			Aldicarb 4.5 + 4.5	136	0.050
			Aldicarb 9.0	219	0.130
			Aldicarb 4.5	136	0.040

Table 2. (Continued)

Location and soil texture	Grape variety	Application: Method	Application: Rate in kg ai/ha	Time in days from application to sampling	Toxic residues in ppm
				Second season	
			Aldicarb 4.5	580	0.004
			Aldicarb 4.5	512	0.008
			Aldicarb 4.5 + 4.5	512	0.022
			Aldicarb 9.0	580	0.005
	'Muscat'			First season	
		5′ band spanning both sides of the vine row	Aldicarb 4.5	219	0.140
			Aldicarb 4.5 + 4.5	136	0.750
			Aldicarb 9.0	219	0.330
			Aldicarb 4.5	136	0.820
				Second season	
			Aldicarb 4.5	580	0.005
			Aldicarb 4.5	512	0.005
			Aldicarb 4.5 + 4.5	512	0.023
			Aldicarb 9.0	580	0.005
Davis, loam	'Thompson Seedless'			First season	
		Broadcast 100% coverage area	Aldicarb 4.5	270	0.027
			Aldicarb 9.0	270	0.054
Lodi, sandy loam	'Tokay'			First season	
		Brodacast 50% coverage area	Aldicarb 9.0	206	0.066
				First season	
		Brodacast 50% coverage area	Aldicarb 9.0	270	0.012
		Broadcast 100% coverage area	Aldicarb 9.0	270	0.014

Table 3. Toxic residues in different grape varieties after 2 yr of treatment with aldicarb using different rates, timing, and application methods.

Location and soil texture	Grape variety	Nematode genera	Application		Time in days from 2nd yr application to sampling	Toxic residues in ppm
			Method	Rate in kg ai/ha		
Lodi, sandy loam	'Cardinal'	*Meloidogyne* and *Xiphinema*	Two furrows, one on each side of the vine row	4.5	216	0.17
				9.0	216	0.29
				11.25	216	0.38
Escalon, sand	'Mission'	*Meloidogyne* and *Xiphinema*	Six furrows, two on each side and two cross furrows	4.5	247	0.051
				4.5 + 4.5	247	0.105
				4.5 + 4.5 + 4.5	247	0.153
Delano, sandy loam	'Muscat'	*Meloidogyne*	5′ band spanning both sides of the vine row	4.5	215	0.040
				4.5 + 4.5	147	0.090
				9.0	215	0.070
				4.5	147	0.075
	'Alicante'	*Meloidogyne*	5′ band spanning both sides of the vine row	4.5	215	0.007
				4.5 + 4.5	147	0.045
				9.0	215	0.005
				4.5	147	0.020

'Mission' than in 'Alicante,' 'Tokay,' and 'Thompson Seedless.' Different degrees of persistence for aldicarb residues in different varieties may result from differences in rates of uptake, root or foliar growth, rates of metabolism, chemical composition of fruit juice, or times of fruit maturity. To avoid high toxic residues in the fruit, early treatments of 'Muscat,' 'Cardinal,' and 'Mission' would be helpful. Sulfocarb treatments had lower toxic residues due to less stability of this compound compared with aldicarb. This correlates with poor nematode control and lesser improvement of yields with sulfocarb.

Total amounts of toxic residues in the second season varied with different varieties also. Some residues were detected at high rates (11.25 kg ai/ha or 4.5 ai/ha applied three times), but single applications of 4.5 and 9.0 and 4.5 kg ai/ha applied twice produced no residues (Table 2).

The total amounts of aldicarb toxic residues resulting from 2 yr of application varied with different varieties. Greater amounts were detected in 'Cardinal' and 'Muscat' than in 'Mission' and 'Alicante' (Table 3). No accumulation of aldicarb toxic residues resulted from 2 yr of application.

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