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Residues of Aldicarb and Fenamiphos in Soil, Leaves, and Fruit from a Treated Vineyard

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Residues of aldicarb and fenamiphos [parent compound, sulfoxide, and sulfone metabolites analyzed as sulfone and expressed as total aldicarb (TA) or total fenamiphos (TF)] in the roots, soil, leaves, and fruit from vineyards were determined with a gas chromatograph equipped with packed columns. Temik (aldicarb) granules at 5 kg/ha and Nemacur (fenamiphos) granules at 20 kg/ha were applied either in scatter over the entire area (broadcast) or in 20-cm bands on either side of the rows of vines. No residues of TA or TF were present in any of the samples taken before application, showing that there were no residues from previous treatments. Twenty-eight days after application no TA residues were present in any soil samples at the depths sampled; TF residues were, however, still present in the 30–60-cm layer. In spite of residues of TA and TF in the soil, all fruit samples contained less than 0.01 mg/kg of TA and less than 0.02 mg/kg of TF at harvesting. Band application in contrast to broadcast application gave rise to a lower maximum leaf concentration of TA and a higher maximum leaf concentration of TF. The control samples were without any TA or TF residues.

No nematicide has as yet been registered specifically for use on wine grapes, although research on residues and persistence of aldicarb [2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime] and fenamiphos [ethyl 4-(methylthio)-3-methylphenyl isopropylphosphoramidate] has been done in vineyards in the U.S. (Raski, 1955; Raski and Schmitt, 1964; Hafez and Raski, 1981; Hafez et al., 1981). As there is a nematode problem in vineyards of the Vaalharts area in South Africa, several compounds are being tested there as soil systemic nematicides. This paper describes the total residues (parent compound, sulfoxide, and sulfone analyzed as sulfone) of aldicarb and fenamiphos found in soil, root, leaf, and fruit samples at various times after application. The objectives were to determine whether unacceptably high concentrations of total aldicarb or fenamiphos were present in harvested fruit after applications at dosages used on other crops and to compare the leaching and persistence of the two compounds in the soil.

In soil and plants, aldicarb and fenamiphos are converted into many metabolites of which the sulfoxide and the sulfone are highly toxic to man (Waggoner, 1972); oral LD_{50} (rats) of aldicarb, i.e. the sum of aldicarb and its sulfoxide and sulfone expressed as aldicarb, is 0.5–1 mg/kg and that of fenamiphos, i.e. the sum of fenamiphos and its sulfoxide and sulfone expressed as fenamiphos, is 15–19 mg/kg. A soil or plant sample contains many of the aldicarb or fenamiphos metabolites. The extraction process oxidizes any residues of the parent compound as well as the sulfoxide to sulfone. All the results of aldicarb or fenamiphos in this paper therefore signify the total residues of the parent compound, the sulfoxide metabolite, and the sulfone metabolite analyzed, determined together, and expressed as total aldicarb or total fenamiphos. Aldicarb is registered in South Africa for use on tobacco,

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potatoes, bananas, cotton seed, sugarcane, and green maize. Fenamiphos is registered for use on potatoes, pineapples, tomatoes, bananas, citrus, cotton seed, and papaya (Bot et al., 1985).

MATERIALS AND METHODS

Experimental Design. Vineyards at the Vaalharts Research Station were treated by the Oenological and Viticultural Research Institute; analyses were done at the Plant Protection Research Institute, Pretoria. Granular formulations of aldicarb (Temik) (15% active ingredient) and fenamiphos (Nemacur) (10% active ingredient) were used. The nematicides were applied broadcast on both sides of the vine rows, worked slightly into the soil with a disk, and flood-irrigated immediately afterward. Some randomly chosen (untreated) rows of vines in between the broadcast application plots were treated in strips 20 cm wide on either side of the rows and prepared in the same way as the broadcast application plots. This was done merely to investigate the influence of different application methods on the residues. Only one sample from the band application plot was taken every sampling day, and only leaf samples were used in the comparison; all the other samples (root, soil, fruit) were taken from the broadcast application only. Dosages were as follows: Temik granules, 5 kg/ha; Nemacur granules, 20 kg/ha. Applications were made at the end of September, just before blossom time, in 1982 and again in 1983. There were three plots (replicates) per compound and five vines per plot. Samples were taken 1 day before application and 1, 7, 14, 28, 42, 70, and 105 days after application as well as during harvesting (119 days after application) during the 1982/1983 season. During the 1983/1984 season samples were taken 1 day before application and 1, 3, 7, 10, 14, 28, 42, 70, 112, 126, 133, and 141 (during harvesting) days after application. The samples taken per replicate consisted of three soil samples taken 0–30, 30–60, and 60–90 cm deep (and a control sample), a leaf sample composed of approximately 40 leaves (and a control sample), and a fruit sample toward the end of the season. Soil samples were taken from holes (approximately 45 cm × 45 cm × 90 cm deep) dug each sampling day, by scraping approximately 1 kg of soil from the sides of the holes from 30 cm deep upward, between 30 and 60 cm, and between 60 and 90 cm deep. For the 1983/1984 season, soil samples were taken only 0–30 and 30–60 cm deep because J.T.L. had shown that only a small percentage of roots were found deeper than 60 cm. Root samples were gathered only twice, 1 day before and 1 day after application during the 1983/1984 season because the removal of too many roots affected the vines adversely. During the 1982/1983 season only aldicarb was analyzed for, as no working extraction method or quantitative method for determining fenamiphos was available in this laboratory.

The variation in recoveries for the aldicarb (65–87%) as well as the fenamiphos (62–88%) methods necessitated the use of a processed standard; i.e. a sample consisting of the matrix, the solvents, and a known concentration of a usable standard prepared through the extraction method and used as a direct standard. Even with an external standard and eventual calculation by using percentage recovery, the aldicarb method worked successfully as proved by the results obtained in the interlaboratory calibration exercise (ICE 4/81) in which chopped and ground potato samples, previously treated with granular aldicarb, were supplied to three independent laboratories for analysis; the standard deviation was only 0.01 (Van Dyk et al., 1983). The fenamiphos method was investigated by Krause (1985) and proved successful.

Extraction of Total Aldicarb. The extraction method developed by Carey and Helrich (1970) formed the basis of this method but was eventually changed to such an extent that the full modified method is reported in this paper.

Finely chopped leaves, fruit, or roots (25 g) were placed in 1-L glass jars, homogenized with 100 mL of acetone, transferred to Büchner funnels fitted with Whatman No. 41 paper, and vacuum-filtered into 1-L glass flasks. The extraction was repeated by pouring acetone over the contents in the Büchner funnels, and the extract was transferred to 500-mL Erlenmeyer flasks. Soil samples (50 g) were shaken in 75 mL of acetone and 25 mL of distilled water in 500-mL Erlenmeyer flasks for 3 min, transferred to 150-mL glass centrifuge tubes, and spun for 10 min at 4500 rpm, and the aqueous extract was decanted through Whatman No. 41 filter paper into other Erlenmeyer flasks. Extraction was repeated by rinsing out the original Erlenmeyer flask with acetone and shaking the contents in the centrifuge tubes with this acetone. Further treatments of samples were the same for leaf, soil, root, and fruit samples. All the acetone in the samples were evaporated on rotary vacuum evaporators at 40 °C; the aqueous solution was extracted three times with 50 mL of chloroform in a separating funnel and filtered through Whatman No. 1 PS filter paper.

Oxidation. Combined chloroform extracts were evaporated to near dryness, 2.5 mL of glacial acetic acid (100%) and 2.5 mL of hydrogen peroxide (30%) were added to the flasks, which were placed in a 75 °C water bath for 45 min, cooled to room temperature, and neutralized with 50 mL of 10% aqueous sodium bicarbonate solution. (Flasks were shaken gently while sodium bicarbonate was added to ensure proper mixing.) The aqueous solution was extracted three times with 50 mL of chloroform and filtered through Whatman No. 1 PS filter paper, and the combined chloroform extracts were evaporated to near dryness.

Cleanup. Glass columns (approximately 24-mm i.d.) fitted with sintered-glass frits and Teflon taps were filled with 10 g of Florisil (Supelco, Inc., 60/100 mesh), and approximately 1 g of anhydrous sodium sulfate was added. The columns were prewetted with 30 mL of diethyl ether–benzene (1:1) with the taps left open; the taps were closed when the sodium sulfate was just covered by the mixture. The sample flasks were rinsed with 3 × 5 mL portions of diethyl ether–benzene and transferred to the columns; flow-through was allowed until the sodium sulfate was again just covered by the mixture. Extracts were eluted with 100 mL of 5% acetone–diethyl ether and the eluates discarded and then eluted with 80 mL of acetone, which was collected in 150-mL Erlenmeyer flasks, evaporated to near dryness, and diluted to 10 mL with acetone.

Extraction of Total Fenamiphos. Published residue methods determine thio ethers, sulfoxides, and sulfones of organophosphorus pesticides in general (Hild and Thier, 1978) and not fenamiphos specifically or they determine the parent compound and its sulfoxide and sulfone individually (Brown, 1981). We were interested in total residues; therefore, a method was used in which the parent compound as well as the sulfoxide was oxidized to the sulfone (Thornton, 1971). The method, specifically the one for extraction of peanut vines, pineapple bran, and pineapple forage, was used for leaf and fruit samples, with slight modifications. Smaller amounts of methanol mixture (100 mL) were used, and no Hyflo Super-Cel layer was necessary; a Büchner funnel fitted with Whatman No. 1 filter paper sufficed. Soil samples (50 g) were shaken in 100 mL of methanol for 3 min, left standing for 3 min to

Table I. Residues of Total Aldicarb[a] (mg/kg) in Soil, Leaf, and Fruit Samples from a Vineyard (Wine Grapes) Treated Broadcast with Aldicarb Granules (15% Active Ingredient) at 5 kg/ha in September 1982

	days after application									
	−1	1	7	14	28	42	70	105	112	119
soil										
A[b]	c	1.57 (0.80)[d]		0.59 (0.23)						
B		0.22 (0.08)	0.38 (0.18)	1.31 (0.66)						
C			0.64 (0.27)	0.39 (0.14)	0.09 (0.04)					
leaves		0.13 (0.03)	8.75 (3.01)	2.57 (0.72)	2.83 (0.92)	6.15 (1.56)	2.92 (0.78)	2.04 (0.68)		1.22 (0.42)
fruit								<0.01	<0.01	<0.01

[a] I.e., the parent compound, the sulfoxide metabolite, and the sulfone metabolite analyzed and determined together as sulfone. [b] Key: A, 0–30 cm; B, 30–60 cm; C, 60–90 cm. [c] Nondetectable concentrations. [d] Standard deviation.

Table II. Residues of Total Aldicarb[a] (mg/kg) in Root, Soil, Leaf, and Fruit Samples from a Vineyard (Wine Grapes) Treated Broadcast with Aldicarb Granules (15% Active Ingredient) at 5 kg/ha in September 1983 (Influence of Different Applications (Broadcast vs. Band) Investigated Using Only Leaf Samples for the Comparison)

		days after application											
		−1	1	3	7	10	14	28	42	70	112	126	133	141
roots	A[b]	c	1.88 (0.66)[d]											
	B		1.09 (0.17)											
soil	A		0.42 (0.01)	0.28 (0.12)	0.19 (0.09)		0.39 (0.17)	0.24 (0.12)	0.16 (0.03)					
	B		0.13 (0.01)	0.26 (0.05)	0.35 (0.11)		0.54 (0.63)	0.42 (0.20)	0.37 (0.17)	0.03 (0.02)				
leaves	D			0.29 (0.09)	0.97 (0.33)	1.28 (0.08)	1.06 (0.11)	9.03 (1.68)	11.82 (1.84)	0.91 (0.31)	0.36 (0.12)			
	E			0.67	7.14	6.11	5.97	5.93			0.22			
fruit											0.04 (0.01)	0.03 (0.01)	<0.01	<0.01

[a] I.e., the parent compound, the sulfoxide metabolite, and the sulfone metabolite analyzed and determined together as sulfone. [b] Key: A, 0–30 cm; B, 30–60 cm; D, broadcast application; E, band application. [c] Nondetectable concentrations. [d] Standard deviation.

Table III. Residues of Total Fenamiphos[a] (mg/kg) in Root, Soil, Leaf, and Fruit Samples from a Vineyard (Wine Grapes) Treated Broadcast with Fenamiphos Granules (10% Active Ingredient) at 20 kg/ha in September 1983 (Influence of Different Applications (Broadcast and Band) Investigated Using Only Leaf Samples for the Comparison)

		days after application												
		−1	1	3	7	10	14	28	42	70	112	126	133	141
roots	A[b]	c	9.19 (2.64)[d]											
	B		1.92 (0.87)											
soil	A		0.38 (0.19)	1.24 (0.63)	1.39 (0.66)		2.12 (0.49)	2.71 (0.17)	2.89 (0.80)	2.24 (1.07)				
	B		2.75 (1.22)	0.79 (0.33)	0.28 (0.11)		0.19 (0.09)	0.07 (0.02)	0.35 (0.04)	2.04 (0.58)				
leaves	D					0.05 (0.02)	0.09 (0.00)	1.45 (0.45)	0.80 (0.04)	0.93 (0.19)	0.54 (0.19)			
	E						0.07	2.93						
fruit											0.03 (0.01)	<0.02	<0.01	<0.02

[a] I.e., the parent compound, the sulfoxide metabolite, and the sulfone metabolite analyzed and determined together as sulfone. [b] Key: A, 0–30 cm; B, 30–60 cm; D, broadcast application; E, band application. [c] Nondetectable concentrations. [d] Standard deviation.

allow sludge to settle, and decanted through Whatman No. 1 filter paper. This was repeated (Krause, 1985). Further treatment of samples was as described by Thornton and was the same for leaf, soil, root, and fruit samples. Smaller amounts of chloroform (3 × 100 mL) were, however, used, and filtering was done through Whatman No. 1 PS filter paper or anhydrous sodium sulfate.

Gas Chromatographic Requirements. The aldicarb samples were analyzed on a Mikro Tek MT 220 gas chromatograph with flame photometric detector in the sulfur mode and equipped with a 190 cm × 3 mm i.d. 5% Carbowax 20 M on Gas Chrom Q 80/100-mesh glass column. Detector and column temperatures were 210 and 180 °C, respectively, and nitrogen gas flow was 60 mL/min. The fenamiphos samples were analyzed on a Varian 6000 gas chromatograph with a nitrogen phosphorus detector (NPD), or alkali flame detector, operating at 280 °C. The 50 × 3 mm i.d. column was packed with 5% Dexsil 300 on Gas Chrom Q 80/100 mesh and operated at a temperature of 220 °C, and the nitrogen carrier gas flow was 40 mL/min (Krause, 1985).

RESULTS AND DISCUSSION

The results given in Tables I–III are each the average value of three replicates, except for the band application values, which are from a single sample each. No residues

of aldicarb or fenamiphos [parent compound, sulfoxide, and sulfone metabolites analyzed as sulfone and expressed as total aldicarb (TA) or total fenamiphos (TF)] were present in any of the samples taken before application, showing that there were no residues from previous treatments. The control samples were also without any TA or TF residues. The minimum detectable amount based on the mass of matrix extracted was 0.01 mg/kg for both gas chromatographs. From soil samples taken 1 day after application in 1982 (a broadcast application only), it was evident that the highest concentration of TA (1.57 mg/kg) was still located in the upper 0–30-cm layer with only a slight downward movement probably because of irrigation (Table I). Six days later the highest concentration of TA (0.64 mg/klg) was at a depth of 60–90 cm, and 28 days after application no TA was present in any of the soil samples at the depths sampled.

The TA concentration in the leaves reached a maximum of 8.75 mg/kg between 1 and 14 days after application, decreased rapidly thereafter, and maintained an average of 2.70 mg/kg (3.15–2.04 mg/kg) over the next 13 weeks. At harvesting TA was still present (1.22 mg/kg) in leaf samples. All fruit samples had less than 0.01 mg/kg of TA (Table I).

The TA concentration in the soil samples of the 1983/1984 season progressively decreased in the upper 0–30-cm layer and at the same time increased in the deeper 30–60-cm layer, no doubt as a result of downward movement. By day 70 none was left in the upper layer and only 0.03 mg/kg in the lower layer (Table II); sampling was done only from broadcast application rows. TA in leaf samples taken from the broadcast application plots increased during the first 14 days after application, then rose to very high levels 28 and 42 days after application (see day 42, Table II), but fell to only 0.36 mg/kg 112 days after application. This great increase in translocation from soil to leaves 4–6 weeks after blossom time is evident in both Tables I and II.

Band application in contrast to broadcast application gave rise to a lower maximum leaf concentration of TA (7.14, 11.85 mg/kg) (Table II).

Fruit samples again contained less than 0.01 mg/kg of TA at harvesting.

During the 1983/1984 season the TF residues in the soil translocated rapidly to the deeper 30–60-cm layer 1 day after application and then decreased slowly over the following 28 days, possibly because of migration back to the dry upper layer with soil moisture (Table III). The simultaneous increase in concentration in the 0–30-cm layer during the same period confirmed this. On day 28 the TF concentration in the 30–60-cm layer had increased again, possibly because of rain (17.9 mm) that had fallen on day 21; sampling was done from broadcast application rows.

In leaves the TF concentration reached a maximum of 1.45 mg/kg on day 28 in samples from the broadcast application rows, in contrast to the higher maximum (2.93 mg/kg) reached in samples from the band application rows on day 28 (Table III). Due to unforeseen circumstances, no further leaf samples from the band applications were taken after day 28.

In spite of the higher concentrations of TF in the soil, all fruit samples taken contained less than 0.02 mg/kg of TF.

Too few root samples were taken during the 1983/1984 season for any deductions to be made, although very high concentrations of TA and TF were present in the only samples taken 1 day after the broadcast application (Table II and III).

Standard deviation between the residues of the soil samples is up to 50%, which is quite acceptable because of the many variables that occur in soil sampling such as representative sampling, sloping of the ground surface, water migration, translocation, biodegradation, etc. Standard deviation occurring between residues of leaf and fruit samples is also acceptable.

CONCLUSIONS

At the dosages of aldicarb [5 kg (15% active ingredient)/ha] and fenamiphos [20 kg (10% active ingredient)/ha] tested, there were acceptably low concentrations (<0.02 mg/kg) of metabolites in the grapes at harvest. If it should turn out that treatment with these compounds suppressed nematodes, then they would be acceptable for use in vineyards. The Oenological and Viticultural Research Institute's participation in these trials was specifically for that purpose.

It was evident that the method of application used (band or broadcast) had little effect on the eventual concentration of either TA or TF, because both applications led to very low concentrations in the harvested grapes.

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