

The Persistence of Methidathion and Its Effect on the Chemical Composition of Grapes

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ABSTRACT. The persistence of methidathion and its effect on the chemical composition of grapes was studied under field conditions during August 1982. Methidathion 40% EC was sprayed on grapes at 0.2% concentration. Samplings of grape fruits were done at 0 hr, 1, 3, 4, 7, 9, and 15 days after application. GLC method was used for residue analysis of grapes prior and after washing with water. The data indicated that the half life time of methidathion was less than one day. The residue in grapes after washing with water was still high and ranged from 47.9 to 92.1% of the total residue. The safe period for harvesting the grapes was found to be 15 days after spray. Methidathion application had positive effect on the total soluble solids (T.S.S.) and reducing sugars, while Ca, Mg, K, Na and pH did not show any change due to methidathion application.

Methidathion, S-2, 3-dihydro-5-methoxy-2-oxo-1, 3, 4-thiadiazol-3-yl methyl 0, 0-dimethyl phosphorodithioate (supracide), is an organophosphorus insecticide used on grapes, citrus and several other crops for the control of sucking and leaf-eating insects. Like other pesticides, the residues of methidathion are found in the marketed agricultural commodities.

Esser and Muller (1966) and Esser *et al.* (1968) studied the persistence of methidathion in plants and animals. They found that it is rapidly metabolized. Thompson *et al.* (1979) observed a rapid decrease of methidathion and its oxygen analog on citrus leaves. The metabolism of methidathion in higher plants has been investigated by several workers (Simoneaux *et al.* 1978 and 1980, Chopade *et al.* 1981).

The objectives of the present study were:

1. To examine the dislodgable residue and the remaining extractable residue of methidathion in grapes at different intervals following the application of

methidathion. This will help in determining the safe period of harvesting grapes.

2. To study the effect of methidathion on the chemical composition of grapes.

Material and Methods

A field experiment was conducted at Al-Kharj Agricultural Research Station, Kingdom of Saudi Arabia, during August 1982. The weather conditions in this area were as follows: Temperature minimum 24.2°C maximum 44.4°C, relative humidity minimum 9% and maximum 18%, precipitation 0 mm. Methidathion 40% EC was sprayed on grape trees at 0.2% concentration until a complete coverage of plants was ensured. A row of grape trees was left as control. The experimental plants were sampled by taking two kg of fruits at 0 hr (after drying out of spray deposits), 1, 3, 4, 7, 10 and 15 days after application. Samples were kept at freezing temperature for analysis.

Preparation of Samples

For the determination of methidathion total residue in grape fruits, samples of 50 g each were well macerated and blended with 100 ml aqueous acetone (1:1) at high speed 2-3 min. The aqueous acetone extracts were filtered through glass wool on porcelain Buchner Funnel. Transferred filtrates to separatory funnel and extracted further with chloroform three times 30 ml each. The layers were allowed to separate and the organic solvent layer was dried over anhydrous sodium sulphate and the solvent was evaporated to give dry residues.

Another set of samples, 50 g each, was taken to determine the dislodgable residue in grapes. The grape fruits were washed three times with water 100 ml each. The water washings were collected in separatory funnel and extracted three times with chloroform 50 ml each. The chloroform layers were received through anhydrous sodium sulphate and evaporated to dryness. For the determination of the remaining extractable residue in grapes after washing, the previous procedure as for total residue was followed.

GLC

Gas liquid chromatograph (Hewlett-Packard 5830A) equipped with Ni⁶³ electron capture detector (ECD) was used for methidathion analysis. A 1.8 m × 4 mm (i.d.) column packed with 3% ov-17 on 100/120 mesh chromosorb W; Ar/methane (95:5) at 33 ml/min was used. The temperature conditions: injection 250, column 220 and detector 300°C. The retention time (Rt) of methidathion under these conditions was 5.40 min. Through this procedure of extraction and analysis 81% recovery of methidathion was obtained. The results were adjusted for the recovery.

Total soluble solids (TSS) and reducing sugars were determined by taking 250 g of fruit sample and making it into paste. Half of the paste was filtered and read

on Refractometer (Karl Kolb) for TSS. A portion (5g) of the remaining paste was used for the determination of reducing sugars by Lane and Eynon method (1929). Another 5g of the pasted sample was digested with H_2SO_4 and H_2O_2 , diluted, adjusted to pH 6.5 and run on Autoanalyzer (Techincon SMA-9) for Ca and Mg determination. Samples for Na and K were analysed on a Beckman (KLINA) Flame Photometer.

Results and Discussion

The amount of methidathion residue in grape fruits prior and after washing with water is shown in Table 1. In order to show clearly the effect of time and washing with water on the status of methidathion residue in grapes, the data are represented in Fig. 1. The data showed that the amount of methidathion at 0 hr (21.0 mg/kg) dropped rapidly to 2.0 mg/kg after one day of application. However, the later on decrease with time was gradual. This showed that the half-life time of methidathion is less than one day. This trend is reasonable in the views of Esser and Muller (1966) and Esser *et al.* (1968) findings that methidathion is rapidly metabolized in plants and animals. In a similar study, Thompson *et al.* (1979) noticed a rapid decrease of methidathion and monoxone metabolite during the first week after application on citrus leaves.

The amount of methidathion residue in washed grapes was slightly lower than unwashed (Table 1). The residue in washings (dislodgable residue 'b') was 1.33 mg/kg at 0 hr and decreased further with time to the level of 0.03 mg/kg by following the same pattern as shown by total residue. However, this decrease was

Table 1. The persistence of methidathion in grapes at different intervals after application.

Days after application	The amount of methidathion (mg/kg) recovered from:					
	grapes without washing	remaining extractable residue 'a'	dislodgable residue 'b'	total a + b	$\frac{a}{a+b} \times 100$	$\frac{b}{a+b} \times 100$
0	21.00	15.50	1.33	16.83	92.1	7.9
1	2.00	1.57	0.48	2.05	76.6	23.4
3	1.32	0.91	0.58	1.49	61.1	38.9
4	0.57	0.56	0.07	0.63	88.9	11.1
7	0.42	0.34	0.37	0.71	47.9	52.1
10	0.29	0.22	0.16	0.38	57.9	42.1
15	0.09	0.14	0.03	0.17	82.3	17.7

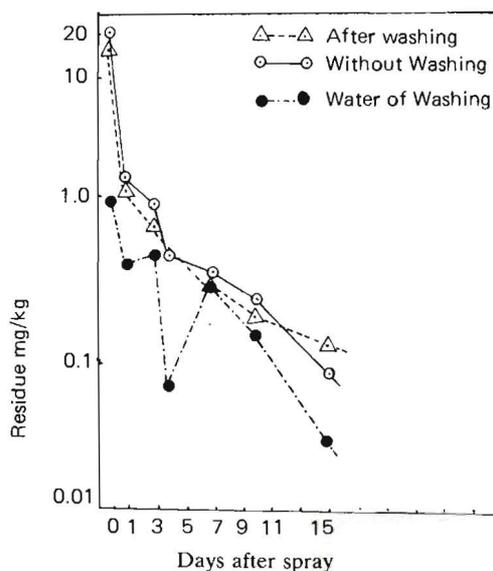


Fig. 1. Methidathion residue in grapes and washing.

more rapid at 1 day after spray. The total residue calculated from dislodgable residue and the remaining extractable residue (a) in washed grapes closely paralleled the total residue obtained from grapes without washing with water.

The average percent contribution of methidathion dislodgable residue to the total residue $\left(\frac{b}{a+b} \times 100\right)$ was low. On the other hand, the contribution of the remaining extractable residue $\left(\frac{a}{a+b} \times 100\right)$ was high and ranged from 47.9 to 92.1%.

This showed that washing of grapes even at 0 hr after application of methidathion did not remove a reasonable quantity of residues. This clearly demonstrated that soon after the application of methidathion insecticide to grapes, it is either absorbed or bound to the surface so tightly that it cannot be removed by simple washings. Thompson *et al.* (1979) observed, in a study on methidathion application to citrus leaves, that the dislodgable residue comprised about 20% of the total residue, 80% being either absorbed or bound to the leaf surface.

The maximum residue limit for methidathion residue in grapes is 0.2 mg/kg as mentioned in 'Recommended International Maximum Limits for Pesticide Residues', 1978. The results in this study clearly demonstrate that the methidathion residue in washed and unwashed grapes remained more than 0.2 mg/kg level for 10 days after application, which later on tended to drop below the maximum limit (0.2 mg/kg) from 10 through 15 days. It can be recommended to local growers to elapse 15 days after methidathion application to grapes as the safe period for harvesting.

The effect of methidathion on the chemical composition of grapes is shown in Table 2. Data indicated that there was no difference for many parameters between treated and untreated fruits at different intervals from 0-15 days after methidathion application. However, TSS and reducing sugars were increased with methidathion treatment.

Statistical analysis of this data was conducted by a Radio Shack computer (TRS-80), using T-test program. The percentage of Ca increased from 0.07 to 0.12% by methidathion application as compared to an increase of 0.06 to 0.12% in untreated grapes. This shows that there is no significant difference between the treated and untreated grapes for all the periods of samplings. The same trend was observed for Mg also. The percentage of Na and K did not show any correlation which may be due to non-detectable levels of sodium in many samples. The changes in pH with time and methidathion application varied from 3.88 to 4.18, while that of untreated grapes were 4.00 to 4.21. This indicates that methidathion application to grapes has no effect on the pH but the observed little changes in both treated and untreated grapes may be due to time effect.

Table 2. The influence of methidathion on the chemical composition of grapes.

Parameters	Treatment	Days After Spray						
		0	1	3	4	7	9	15
pH	C	4.07	4.02	4.01	4.00	4.04	4.19	4.21
	T	4.01	3.99	3.88	4.09	4.05	4.18	4.16
TSS%	C	12.15	14.00	12.50	12.75	12.00	13.75	13.50
	T	12.50	12.00	12.00	12.75	13.50	15.50	15.00
R. Sugars%	C	8.03	10.68	10.54	9.54	9.22	11.06	7.10
	T	8.47	10.33	9.43	10.50	11.57	12.56	11.31
Ca%	C	0.06	0.08	0.08	0.08	0.09	0.10	0.12
	T	0.07	0.08	0.09	0.09	0.11	0.12	0.12
Mg%	C	0.12	0.02	0.02	0.02	0.03	0.02	0.01
	T	0.06	0.04	0.02	0.02	0.01	0.01	0.01
Na%	C	ND	ND	ND	0.26	ND	ND	0.28
	T	ND	ND	0.28	ND	ND	0.27	ND
K%	C	0.27	ND	0.18	0.18	0.05	ND	0.34
	T	0.24	0.23	0.09	0.05	0.10	0.23	0.24

C - Control

T - Treated

ND - Not Detectable

Detection Limit For Na = 1 meq/L = 0.0023%

Detection Limit For K = 0.1 meq/L = 0.00039%

The effect of methidathion on TSS and reducing sugars is presented in Fig. 2 and 3. Figure 2 showed that the amount of TSS in both treated and untreated grapes from 0 to 4 days after application significantly did not change, but from 4 to 15 days a significant increase at 1% level between treated and untreated was noticed. The percent increase was 17.6 and 5.8 for treated and untreated grapes, respectively.

Figure 3, representing the amount of reducing sugars in treated and untreated grapes with time, clearly signified at 5% level that the amount of reducing sugars was higher in treated than untreated grapes, especially from 4 to 15 days after methidathion application.

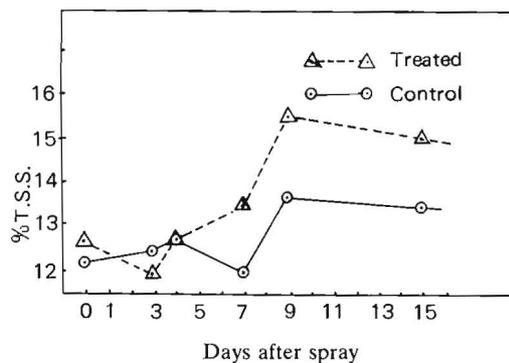


Fig. 2. Effect of methidathion on T.S.S. % in grapes.

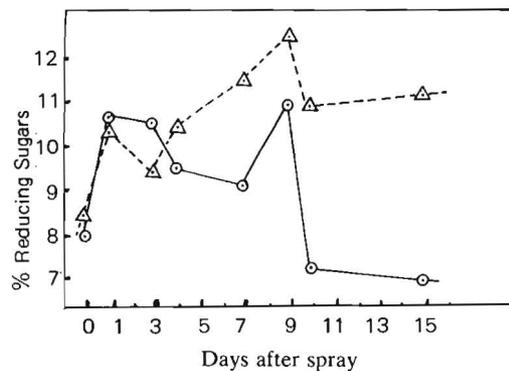


Fig. 3. Effect of methidathion on reducing sugars % in grapes.

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مدة بقاء المثيداتيون (سوبراسيد) وتأثيره على المكونات الكيميائية للعنب

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قسم التحاليل الكيميائية وزارة الزراعة والمياه - المركز الإقليمي
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درست مدة بقاء مبيد المثيداتيون (سوبراسيد) وكذلك تأثيره على التركيب الكيميائي للعنب تحت الظروف الحقلية خلال أغسطس ١٩٨٢. رش المثيداتيون ٤٠٪ على نباتات العنب بتركيز ٢، ٠٪. أخذت عينات من ثمار العنب على فترات صفر، ١، ٣، ٤، ٧، ٩، ١٥ يوماً بعد الرش. استخدمت كروماتوجرافية الغاز في تحليل المتبقي من المبيد على ثمار العنب وذلك قبل وبعد غسله بالماء. وأوضحت النتائج أن نصف مدة بقاء المبيد كانت أقل من يوم واحد. وكانت كمية المبيد المتبقية داخل الثمار بعد غسلها بالماء كبيرة وتراوح من ٩، ٤٧-١، ٩٢٪ من كمية المبيد الكلية. وحددت فترة الأمان لجمع محصول العنب بعد الرش بمبيد السوبراسيد هي ١٥ يوماً من تاريخ الرش.

وجد أن لهذا المبيد تأثيراً إيجابياً على مجموع المواد الصلبة والسكر في ثمار العنب بينما لم يحدث أى تأثير على المكونات التي درست مثل الكالسيوم، المغنسيوم، البوتاسيوم، الصوديوم، والأس الهيدروجيني.