Decay of Methidathion on Greek Soultanina Grapes during Storage and on the Vines

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Decomposition of the pesticide methidathion on and in soultanina (Thomson seedless) grapes was studied. Vines, uncovered and covered were sprayed with the pesticide. Samples were collected and analyzed in regular time intervals. Two lots were collected, the first of them, 2 h after spraying and the second 20 days later, and were stored in a commercial refrigerated room. Degradation of the pesticide was studied for about 50 days for the grapes on the vines and 130 days for the grapes stored in the refrigerated room. The half-life of the pesticide methidathion was found to be 5 days for the uncovered vines, 7 days for the covered vines and 64 days for the grapes stored in the refrigerator.

Keywords: *Degradation; grapes; methidathion*

INTRODUCTION

Soultanina (Thomson seedless) table grapes (Vitis vinifera L.) is a significant crop in Greece. The major part of the annual production, about 0.1 million tons, is exported, mostly to the United Kingdom. A significant part of the produce is stored in refrigerated rooms at 0 ± 0.5 °C.

A number of pesticides are used to control insects. Methidathion *S*-2,3-dihydro-5-methoxy-2-oxo-1,3,4,-thiadiazol-3-ylmethyl-*O*,*O*-dimethylphosphorothioate (Kidd and James, 1991) is a nonsystemic insecticide and acaricide with stomach and contact action. The compound is used to control a variety of insects and mites, in crops such as fruits, vegetables, alfalfa, sunflower, and plants in greenhouses. It works by inhibiting cholinesterase activity in the target pests (Gallo and Lawryk, 1991). This compound commonly used in Greece in vine yards to control insects such as Pentatomidae (*Dolycoris baccarum L.*), Lepidoptera (*Clysia ambiguella*, Hb. and *Polychrosis botrana*, Schiff) and Coleoptera (*Rhynchites bacchus*, L. and *Hoplia minuta*, Panz.). Methidathion is highly toxic classified by the EPA as a compound of toxicity class I (U.S. EPA, 1991).

The objectives of this work were to study the rate of methidathion degradation on and in grapes stored in refrigerated rooms and that on and in grapes remained on uncovered and covered vine yards.

MATERIAL AND METHODS

Field Experiment. The field experiment was carried out in 1998 in a vine yard, near Korinthos (southern Greece). The experimental area was comprised of five plots, consisiting four vines each, that received routine agricultural practices. An aqueous emulsion of a dose of methidathion (40%EC) was 40 g of active ingredient (ai) 100 L of water. Four of the experimental plots received the recommended dose (RD) of the pesticide and one was not treated to be used as a control. The emulsion was applied with a motorized mistblower and the vines were sprayed to runoff. Application was performed during October when the grapes were ripe. Half of the cultivar used was covered by means of polyethylene sheet. It has been suggested (Gubler et al., 1987) that covering of the vines would control Botrytis bunch rot of grapes. It is common practice in Greece, for late harvesting grapes, vine yards to be covered by polyethylene sheets to prevent any effect on grapes by rainfall. Most of this crop is stored in refrigerated rooms for future consumption. Sometimes growers apply a pesticide dose somewhat higher than the RD based on the understanding that pesticide degradation takes place during the storage period.

Sampling and Storage Procedures. Sampling intended for stored grapes, was performed by randomly collecting grapes from various places of the plot, according to FAO/WHO (1986) recommendations. Samples of about 25 kg of grapes were collected 2 h following the pesticide application, to allow enough time for the emulsion to dry. An equal amount was collected 20 days later, a time period suggested as being safe for harvesting by insecticide producers.

Each sample was divided into four portions of 6−7 kg each, and packaged into plastic boxes following the common commercial practice for storage of table grapes. A polyethylene bag was fixed inside the plastic box, the grapes were placed in the bag and a special carton sheet containing sodium metabisulfite was put on the top of the grapes to prevent any rot of the product *(Botritis cinerea*). Sulfur dioxide (SO_2) is an effective fungistat (Marois et al., 1985) and is applied by repeated fumigation (Athanasopoulos and Thanos, 1998) of grapes or by means of in package SO_2 generators (Nelson,-1983, Kokkalos,1986). The plastic boxes were stored in a commercial refrigerated room at 0 ± 0.5 °C. Samples of about 2 kg were removed every 10 days either from the vines or from the refrigerator, and sent to our laboratory for analysis.

At the same time samples from the vines were collected on the 22 day after the pesticide application, and then every 10 days thereafter to compare the degradation rate of that pesticide to that on the refrigerated grapes.

The berries of each sample were blended thoroughly. A portion of the homogenized grapes was used for extraction.

Analytical Procedure. All samples were analyzed by a general method suitable for nitrogen containing compounds

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10.1021/jf990831s CCC: $19.00
Published on Web 07/20/2000

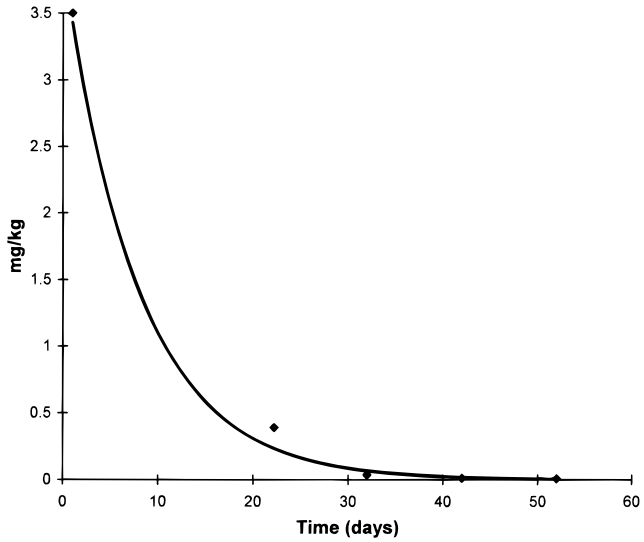

Figure 1. Degradation curve of methidathion on and in grapes from uncovered trees.

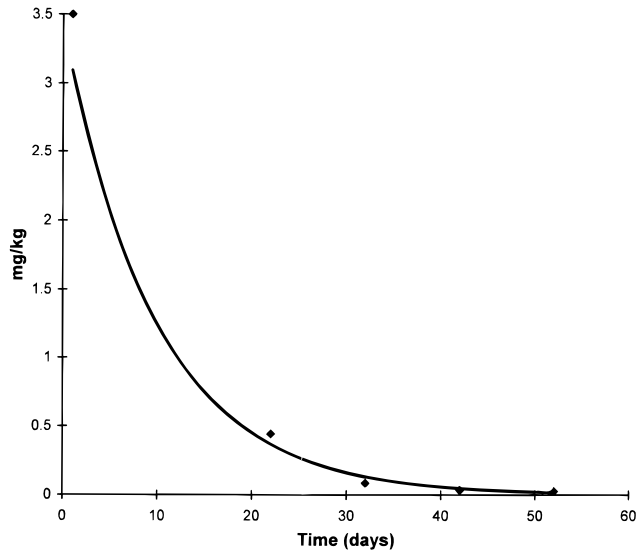

Figure 2. Degradation curve of methidathion on and in grapes from covered trees.

(Ministry of Welfare, Health and Cultural Affairs, 1988) appropriately modified as concern the timing of the heating program. According to the method, 50 g of the homogenized sample was mixed with 100 mL of ethyl acetate and 50 g of anhydrous sodium sulfate. The mixture was blended for 3 min and the extract filtered, through a Whatmann No 1 filter paper containing 3 g anhydrous sodium sulfate, in a volumetric flask. During filtration all parts were kept under crushed ice to avoid undue evaporation of the solvent. The clear filtrate was used for injection.

Gas Chromatographic Determination. A Hewlett-Packard (Model 5890 series II) gas chromatograph was used, equipped with a splitless injector, an NPD, and a 30 m × 0.5 mm i.d x 0.88 ìm film thickness glass capillary column (Hewlett-Packard) coated with 5% phenyl methyl silicone. The injection port temperature was set at 250 °C and the detector temperature was set at 290 °C. The column temperature was programmed as follows: The initial temperature of 120 °C was increased at a rate of 20 °C/min to 210 °C with a residence time of 2 min. From 210 °C to 270 °C a rate of 10 °C/min was used with a residence time of 2 min, and from 270 °C to 285 °C a rate of 13 °C/min was used with a residence time of 5 min at the final temperature. Helium carrier gas at a flow rate of 7 mL/min was used. Samples (in triplicate) of 2 μL of the extract were injected, and quantitation of the pesticide was

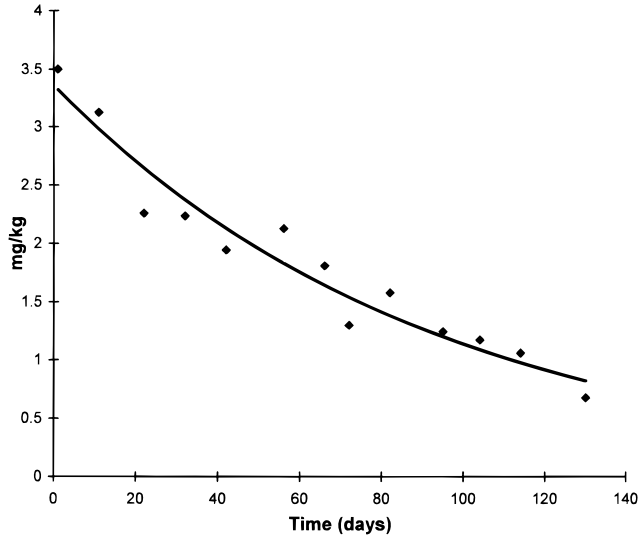

Figure 3. Degradation curves of methidathion on and in grapes stored in a refrigerated room, collected 2 h after spraying.

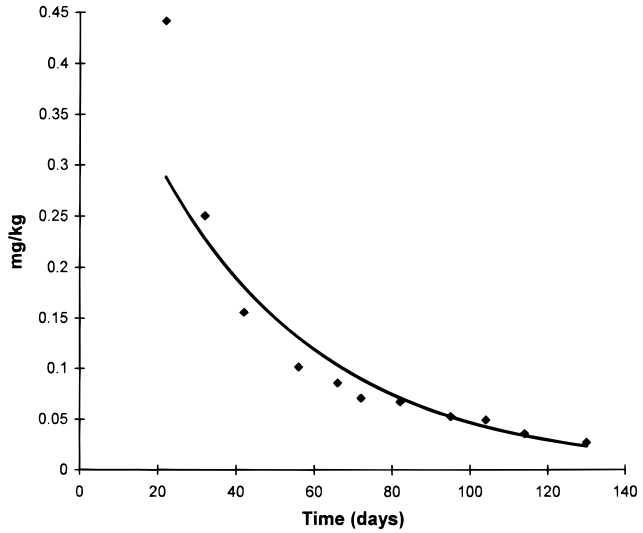

Figure 4. Degradation curves of methidathion on and in grapes stored in a refrigerated room, collected 20 days after spraying.

performed by automatic integration of the peak areas. Certified standards (Chem Service, PA) of the pesticide were used for external calibration. The response of the detector for methidathion was found to be linear in the studied range of 0.02−5 mg/kg. The method limit of detection was found to be 0.004 mg/kg and the limit of quantitation 0.02 mg/kg.

Degradation Kinetics. To determine degradation kinetics, plots of concentration against time were made for each data set, and the maximum square of correlation coefficients found were used to determine the equations of best fit curves. For all twelve cases studied exponential relations were found to apply, corresponding to first-order rate equations. Confirmation of the first-order rate kinetics were further made graphically from the linearity of the plots of lnC against time.

The rate constant k was calculated from the first-order rate equation

$$C_t = C_o e^{-kt} \quad (1)$$

where C_t represents the concentration of pesticide at time t, C_o represents the initial concentration, and k is the rate constant in days^{-1}. The half-life ($t_{1/2}$) was determined from the k value for each experiment, being, $t_{1/2} = \ln 2/k$.

Table 1. Kinetic Parameters for the Degradation of Methidathion on and in Soultanina Grapes

degradation	equation	correl. coeffic. R^2	rate constant k (days^{-1})	half-life $t_{1/2}$ (days)	time to reach legal limit (days)	
methidathion					0.5[a]	0.1[b]
on the vines, ucovered	$C = 1.9046e^{-0.1311t}$	0.905	0.1311	5	10	23
on the vines, covered	$C = 3.426e^{-0.1014}$	0.969	0.1014	7	13	35
refrigerated	$C = 3.358e^{-0.0109t}$	0.948	0.0109	64	174	322
refrigerated (after 20 days)	$C = 0.481e^{-0.0233t}$	0.953	0.0233	30		67

[a] Methidathion MRL = 0.5 mg/kg. [b] Methidathion MRL (after 2000) = 0.1 mg/kg.

RESULTS AND DISCUSSION

The method of analysis was simple and fast. Quantitation of the pesticide in the examined samples was made by comparing the detector response for the sample to that measured before and after each injection with calibration standards.The efficiency of the method used was evaluated by spiking control samples with methidathion at the concentration levels of 0.25, 0.5, 1, 1.3, 1.8, 2, 2.2, and 2.5 mg/kg. Average recoveries were from 95% to 108%. Relative standard deviations for all measured samples of this pesticide were from 1.2% to 11.3%, values being within the accepted range for pesticide residues (Greve, 1984). Results of the study are presented in Figures 1−4 and Table 1. Best-fit curves were calculated according to the highest R^2. In all cases studied degradation followed first-order kinetics. Methidathion is of low persistence in the soil environment; reported field half-lives are 5−23 days, with a representative value of about 7 days (Wauchope et al., 1992). In plants, methidathion is rapidly metabolized (Kidd and James, 1991). Also, over 60% of methidathion sprayed on oranges was removed from the outside of the fruit 2 days after the application. Within 1 week, the residue of the pesticide remaining on the fruit was less than 1% (U.S. EPA, 1988).

The decomposition rate of methidathion (Figure 2, Table 1) on and in the grapes from covered vines was found to be 40% lower than that on and in the grapes from uncovered vines (Figure 1 and Table 1) and further for the stored grapes the decomposition rate was found 1280% lower. Required MRL for this pesticide is 0.5 mg/L (95/39/EC) and for the near future it will be 0.1 mg/L. Time required for the residues to reach MRL was calculated for both levels (Table 1). For both, uncovered and covered cultivars, t_{MRL} is shorter than that suggested by the manufacturers of this pesticide (21 days), but for stored grapes it is much longer (174 days). Even for the lower MRL requirement (0.1 mg/kg) the calculated time was found to be 23 days which is quite close to that suggested (21 days) by the manufacturer. On the other hand in covered cultivars, the rate of degradation was lower (t_{MRL} = 35 days). Finally on the grapes stored in the refrigerated room the rate of degradation was even lower (t_{MRL} = 322 days).

Obtained data indicate that during unusual agricultural practices, such as covering of the vines or storing the grapes, should be taken under consideration when MRL and harvesting times, following the last pesticide application, are specified.

LITERATURE CITED

Athanasopoulos, P.; Thanos, A. Quality characteristics of Soultanina table grapes stored in pilot plant scale. *Fruits* **1998**, *53*, 199−206.

Gallo, M. A.; Lawryk, N. J. Organic phosphorus pesticides. In *Handbook of Pesticides Toxicology*; Hayes, W. J., Laws, E. R., Eds.; Academic Press: New York, 1991.

Greve, P. A. Good Laboratory Practice in Pesticide Residue Analysis. In *Pesticide Residue Analysis*; Ambrus, A., Greenhalgh, R., Eds.; Proceedings of a FAO/WHO Course; FAO/WHO: Rome, 1984; p 281.

Gubler, W. D.; Marois, J. J.; Bledsde, A. M.; Bettigal, L. J. Control of Botrytis bunch rot of grape with canopy management. *Plant Dis.* **1987**, *71*, 599−601.

Kidd, H., James, D. R., Eds. *The Agrochemical Handbook*, 3rd ed.; Royal Society of Chemistry, Information Services: Cambridge, UK, 1991.

Kokkalos, T. J. Post-harvest decay control of grapes by using metabisulphite in cartons enclosed in plastic bags. *Am. J. Enol. Vit. Culture* **1986**, *37*, 149−151.

Nair, N. G.; Emmett, R. W.; Parker, F. E. Programming applications of dicarboximates to control bunch rot of grapes caused by Botrytis cinerea. *Plant Pathol.* **1987**, *36*, 175−179.

Marois, J. J.; Bledsoe, A. M.; Fubler, W. D.; Luvisi, D. A. Control of Botrytis cinerea on grape berries during postharvest storage with reduced levels of sulfur dioxide. *Plant Dis.* **1986**, *70*, 1050−1052.

Ministry of Welfare Health and Cultural Affairs. *Analytical Methods for Residues of Pesticides in Foodstuffs*; Greve, P. A., Ed; Rijswijk: The Netherlands, 1988; Part 1, p 3.

Nelson, K. E. Effects of in-package sulfur dioxide generators, package liners, and temperature on decay and desiccation of table grapes. *Am. J. Enol. Vit.* **1983**, *3*(4), 10−16

Northover, J. Infection sites and fungicide prevention of Botrytis sinerea bunch rot of grapes in Ontario. *Can. J. Planta* **1987**, *9*, 129−136.

U.S. Environmental Protection Agency. Memorandum from the Office of Pesticides and Toxic Substances to Office of Pesticides Programs Division Director, Washington, DC, 1991.

U.S. Environmental Protection Agency. Guidance for the registration of Pesticide products containing methidathion as the active ingredient Washigton, DC, 1988.

Wauchope, R. D.; Buttler, T. M.; Hornsby, A. G.; Augustiln-Beckers, P. W. M.; Burt, J. P. SCS/ARS/CES Pesticide properties database for environmental decision making *Rev. Environ. Contam. Toxicol.* **1989**, *123*, 1-157.

Received for review July 26, 1999. Revised manuscript received April 26, 2000. Accepted May 13, 2000.

JF990831S