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Degradation of fenthion and fenthion sulfoxide on grapes on the vines and during refrigerated storage

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Abstract

The degradation of the pesticide fenthion and of the metabolite fenthion sulfoxide were studied on two varieties of *Vitis vinifera*, "Sideritis" and "Opsimo Edessas", grown in the vineyard of the Agricultural University of Athens. Vines were sprayed with fenthion according to manufacturer instructions. One part of the sprayed grapes remained on the vines and another part was harvested, packed according to the recommended trade practices and stored in a refrigerator at $0 \pm 0.5\,^{\circ}\mathrm{C}$ and relative humidity 80%. It was found that, after spraying, fenthion was very quickly transformed on the grapes into fenthion sulfoxide that had a much slower rate of decomposition. Half-lives for the decomposition of fenthion on the trees were found to be 7.6 days for grapes of Sideritis variety and 5.6 days for grapes of Opsimo Edessas variety. Corresponding values for grapes stored in the refrigerator were 42 and 44.7 days. Percentages of fenthion sulfoxide increased up to the 0th day and then decreased steadily due to the decomposition of the pesticide and its metabolite.
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1. Introduction

Fenthion is the common name of *O,O*-dimethyl *O*-4-methylthio-*m*-tolyl phosphorqthroate (Kidd & James, 1991). Trade names of this pesticide are, DMTP, Lebaycid and Fenthion 4E. Fenthion is a moderately toxic compound, belonging to the Environmental Protection Agency (EPA) toxicity class II. Fenthion is a contact and stomach organophosphate insecticide, used against many sucking, biting pests, especially fruit flies, stem borers, mosquitoes, and Eurygaster cereal bugs. In mosquitoes, it is toxic to both the adult and immature forms (larvae). Once used extensively in the US for controlling intestinal worms, fenthion no longer has FDA approval, due to poisoning deaths. Fenthion is available in dust, emulsifiable concentrate, granular, liquid concentrate, spray concentrate, and wettable powder formulations. While it is effective as an insecticide, it is also moderately toxic to mammals, and highly toxic to birds.

Fenthion is moderately toxic via the oral route, with reported oral LD_{50} values of 180–298 mg/kg in rats, 150 mg/kg in rabbits, and 88–145 mg/kg in mice (Kidd & James, 1991; U.S. Public Health Service, 1995). It is moderately toxic via the dermal route as well, with reported dermal LD_{50} values of 330–1000 mg/kg in rats, and 500 mg/kg in mice (Kidd & James, 1991; U.S. Public Health Service, 1995). Other tests on mice and rats did not show teratogenic or mutagenic effects from fenthion (U.S. Public Health Service, 1995).

Fenthion is phytotoxic (or harmful) to linden, hawthorn, sugar maple trees, and to certain rose varieties (U.S. Public Health Service, 1995). It is not considered phytotoxic when used at recommended rates, although injury has occurred in certain varieties of apples and cotton. Plant foliage should not be sprayed when temperatures exceed 32 °C (Thomson, 1982).

Fenthion is of moderate persistence in soil, with an average field half-life of 34 days under most conditions (Wauchope, Buttler, Hornsby, Augustijn-Beckers, & Burt, 1992). Its water solubility is 2 mg/l at 20 °C (Kidd & James, 1991). In soil, residues of fenthion may persist

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for approximately 4–6 weeks (Harding, 1979). It adsorbs fairly strongly on to soil particles, and so is not likely to move (or leach) through the soil (Harding, 1979; Wauchope et al., 1992). In one study of its persistence in water, 50% of applied fenthion remained in river water 2 weeks later, while 10% remained after 4 weeks. It is more rapidly degraded under alkaline conditions (U.S. Public Health Service, 1995).

Fenthion is very easily decomposed into several metabolites. The most abundant metabolite is fenthion sulfoxide, followed by fenthion sulfone, fenthion oxon, fenthion oxon sulfone and fenthion oxon sulfoxide. Fenthion is used for the protection of fruits and vegetables from insect attacks but its transformation to fenthion sulfoxide and its decomposition rates on fruits and vegetables have not been properly studied up to now. Grapes of varieties Opsimo Edessas and Sideritis, both used, for wine making and as table grapes, were sprayed with Lebaycid (trade formulation for fenthion). The transformation of fenthion into fenthion sulfoxide and the decomposition of their residues on the vines and during refrigerated storage were studied.

2. Materials and methods

2.1. Pesticide application and sampling

Applications of pesticide were performed in the vineyard of the Agricultural University of Athens. Six lines, of 24 vines each, were sprayed. Two lines were sprayed with Lebaycid and two were left as controls. Application doses were 80 ml (40 g of active ingredient (a.i.)/100 l water for the Lebaycid 50 EC. The vines were sprayed to run off.

A lot of 15 kg of grapes was collected 2 h after application (EC, 7029/VI/95). The sample was divided into 13 sub-samples. One of these was analysed immediately for pesticide residues. The rest of them were packed into plastic bags, wrapped by a special sodium metabisulfite-impregnated paper and stored in a refrigerated room at 0 ± 0.1 °C. Samples were removed and analysed every 10–15 days and for up to 5 months. Control samples were collected and analysed immediately before spraying, and then every 10 days, from the non-sprayed vine lines.

2.2. Analytical procedures

All samples were analysed by a general method suitable for gas chromatographic analysis with a nitrogen-phosphorus detector (NPD) (Ministry of Welfare, 1988) modified as concerns the timing of the programme. According to the method, the berries of the samples were removed and pulped in a laboratory mixer. Fifty grams of the pulp of each sample were mixed with 100 ml of ethyl acetate and 50 g of sodium sulphate. The mixture was blended for 2 min and the extract was filtered through Whatman No. 1 filter paper, containing 2 g of sodium sulfate, into a conical flask. During filtration all parts were kept under crushed ice to avoid undue evaporation of ethyl acetate. The clear filtrate was injected into the chromatograph.

2.3. Gas chromatographic determination

A Hewlett–Packard gas chromatograph was used, equipped with a splitless injector, an NPD (Garcia-Repetto, Garrido, & Repetto, 1996), and a 30 m × 0.5 mm i.d. × 0.88 μm film thickness, glass capillary column (Hewlett–Packard) coated with cross-linked 5% phenyl methyl silicone (Dorea, Tadeo, & Sanchez-Brunete, 1996). The injection port temperature was 250 °C and the detector temperature 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 to 270 °C a rate of 10 °C/min was used, with a residence time of 2 min. From 270 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 of 2 μl of the extract (in triplicate) were injected, and quantitation of the insecticide was performed by automatic integration of the peak areas (EC, 1999). Certified standards of fenthion and fenthion sulfoxide were used for external calibration. Quantitations of the insecticides in the examined samples were made by comparing the detector responses for the samples to that measured before and after each injection with a calibration standard within the linear range.

2.4. Degradation kinetics

To determine degradation kinetics, plots of concentration against time were constructed for each data set, and the maximum squares of correlation coefficients found were used to determine the equations of best fit curves. For all six cases studied, exponential relations were found to apply, corresponding to first-order rate equations. Confirmations of the first-order rate kinetics were further made, graphically, from the linearity of the plots of ln C against time.

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

$$C_t = C_0 \, e^{-kt}, \tag{1}$$

where C_t represents the concentration of pesticide at any time t, C_0 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, i.e, $t_{1/2} = \ln 2/k$.

3. Results and discussion

3.1. Determination and recovery

The method of analysis was simple and fast. The response of the detector for fenthion and fenthion sulfoxide was linear in the studied range of 0.02–2.0 and 0.02–2.0 mg/kg, respectively ($y = 159.83x - 0.1626$, $R^2 = 0.9998$; $y = 197.59x + 2.1976$, $R^2 = 0.9994$).

The efficiency of the method was evaluated by spiking control samples with fenthion and fenthion sulfoxide at various concentration levels. The results of the recovery studies are presented in Table 1. As seen from this table, average recoveries were from 84% to 105% (RSD: 2.6–5.3%) for fenthion, and for fenthion sulfoxide, from 78% to 102% (RSD: 2.6–5.4%). These values are within the accepted range for residue determination (EC, 1999). The method limit of determination, evaluated as the product of the standard deviation at the lowest validation level with the Student's *t*-test and 99% confidence level, was 0.02 mg/kg for fenthion and 0.04 mg/kg for fenthion sulfoxide. Dorea et al. (1996) determined fenthion in fruits by a multiresidue method. Average recoveries varied from 86% to 104% with relative s.d. 1.4–8.0% for GC-NPD. Detection limit was 0.01 mg/kg.

3.2. Degradation of fenthion and fenthion sulfoxide

Results of degradation of fenthion and fenthion sulfoxide are presented in Table 2 and Figs. 1–4. Fenthion and fenthion sulfoxide were found to follow pseudo-first-order kinetics. Decomposition half-life of total fenthion (fenthion and fenthion sulfoxide) on the vines was 10.3 days, but it was extended to 53.2 days in refrigerated storage for Sideritis and 9.4 and 60.8 days for Opsimo Edessas, respectively. It can be seen that half-lives at 0 °C were 5.2- to 6.5-fold times higher than that on the vines. Other workers have found similar results.

Cabras et al. (1995) studied the fate of fenthion from vine to wine. The influence of clarifying agents (bentonite, charcoal, potassium caseinate, gelatin, polyvinylpolypyrrolidone, and colloidal silicon dioxide) was also studied. Fenthion residues on grapes showed first-order kinetics with high decay rates ranging from 0.97 to 3.3 days.

In this work (Cabras et al., 1995) on grapes, results were expressed as total fenthion. Due to the high toxicity of fenthion sulfoxide and the lack of relevant study we also studied the decomposition of fenthion into fenthion sulfoxide and further degradation products.

From Figs. 1–4 it can be seen that fenthion after spraying is transformed into fenthion sulfoxide and

Table 1
Recovery of fenthion and fenthion sulfoxide in the grapes

Fenthion			Fenthion sulfoxide			Samples
Level (mg/kg)	Recov. %	RSD	Level (mg/kg)	Recov. %	RSD	Nr
0.02	84	5.3	0.02	78	3.45	3
0.05	94	4.8	0.05	91	4.3	3
0.1	89	3.5	0.1	86	5.1	3
0.25	105	4.3	0.25	93	5.4	3
0.5	98	2.8	0.5	95	3.6	3
1	97	3.3	1	98	2.6	3
1.5	95	4.6	1.5	102	3.1	3
2	96	2.6	2	99	4.2	3

Table 2
Decomposition equations and half-lives for fenthion and fenthion sulfoxide in the grapes

| Variety	Pesticide	Equation	R^2	k	Half-life ($t_{1/2}$) (days)
Sideritis	Total fenthion (trees)	$y = 8.3386\,e^{-0.0676t}$	0.968	0.0676	10.3
	Fenthion (trees)	$y = 8.2928\,e^{-0.0913t}$	0.975	0.0913	7.6
	Fenth. sulfoxide (trees)	$y = 1.1699\,e^{-0.0282t}$	0.974	0.0282	24.6
	Total fenthion (refrig.)	$y = 9.9297\,e^{-0.013t}$	0.974	0.013	53.2
	Fenthion (refrig.)	$y = 9.2655\,e^{-0.0165t}$	0.982	0.0165	42.0
	Fenth. sulfoxide (refrig.)	$y = 1.0572\,e^{-0.0021t}$	0.879	0.0021	267
Opsimo Edessas	Total fenthion (trees)	$y = 8.6333\,e^{-0.07371t}$	0.984	0.0737	9.4
	Fenthion (trees)	$y = 8.4375\,e^{-0.1233t}$	0.988	0.1233	5.6
	Fenth. sulfoxide (trees)	$y = 1.6114\,e^{-0.0336t}$	0.970	0.0336	20.6
	Total fenthion (refrig.)	$y = 9.5662\,e^{-0.0114t}$	0.955	0.0101	60.8
	Fenthion (refrig.)	$y = 8.4951\,e^{-0.0155t}$	0.954	0.0167	44.7
	Fenth. sulfoxide (refrig.)	$y = 1.5143\,e^{-0.0027t}$	0.903	0.002	256
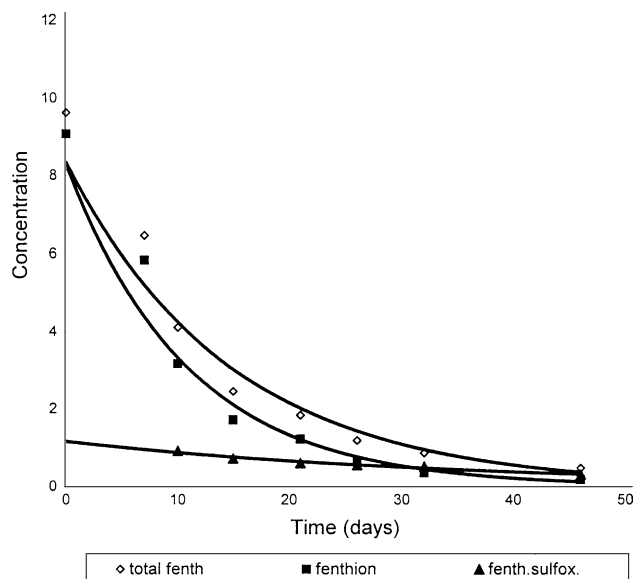
Fig. 1. Degradation of fenthion, fenthion sulfoxide and total fenthion on grapes of Sideritis variety on the vines.

Fig. 2. Degradation of fenthion, fenthion sulfoxide and total fenthion on grapes of Sideritis variety stored in refrigerator.
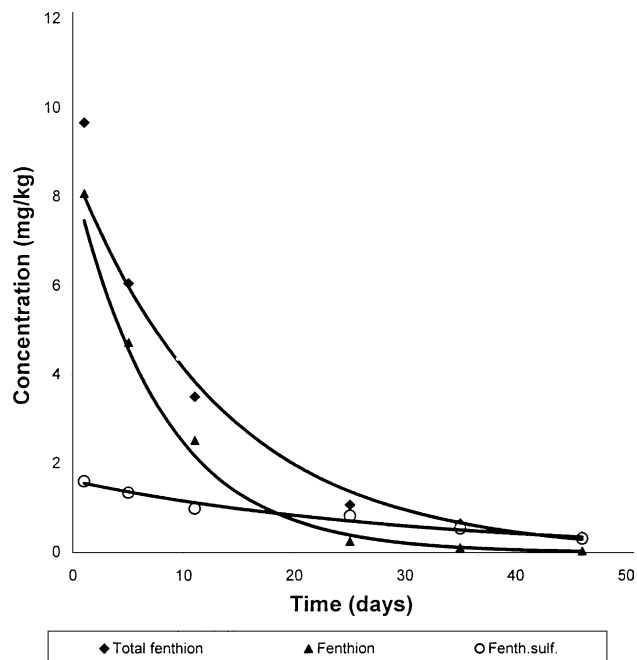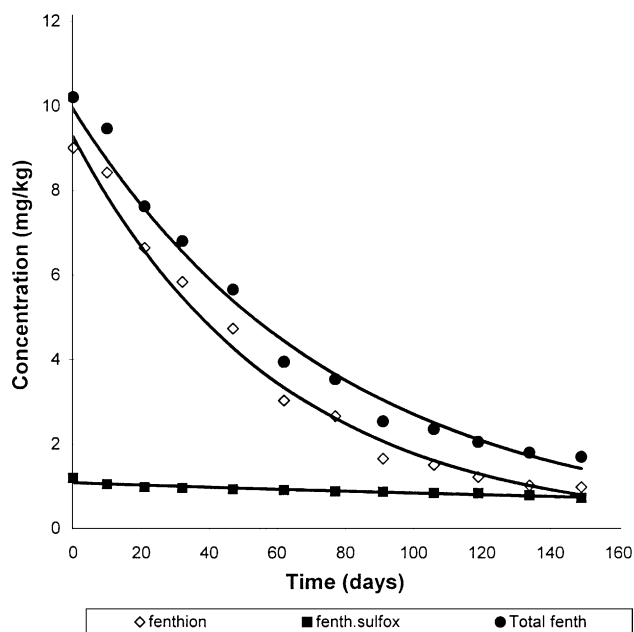

Fig. 3. Degradation of fenthion, fenthion sulfoxide and total fenthion on grapes of Opsimo Edessas variety on the vines.
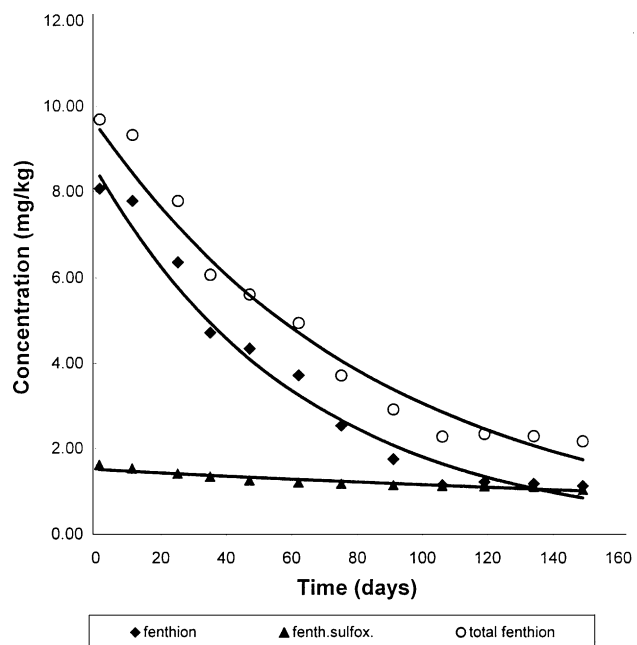

Fig. 4. Degradation of fenthion, fenthion sulfoxide and total fenthion on grapes of Opsimo Edessas variety stored in refrigerator.

these pestcides are subsequently decomposed into other degradation products. For grapes on the vines (variety Opsimo Edessas) fenthion was transformed by 16.5% into fenthion sulfoxide by the first day and 89.2% at day 46. For the same grapes stored in a refrigerator, fenthion was transformed by 16.7% into fenthion sulfoxide on the first day and 47.9% at day 149.

For grapes on the vines (variety Sideritis), fenthion was transformed by 5.8% into fenthion sulfoxide on the first day and 64.6% at day 46. For the same grapes, stored in the refrigerator, fenthion was transformed by 11.8% into fenthion sulfoxide on the first day and 42.4% at day 149.

From Figs. 1 and 3 it can also be seen that, in grapes of the variety Opsimo Edessas, fenthion sulfoxide had its maximum value from the first day (1.6 mg/kg). For grapes of the Sideritis variety, fenthion sulfoxide had a maximum at the 10th day (9.26 mg/kg) and then began to decrease.

From Figs. 1–4 it can also be seen than fenthion sulfoxide, in all cases studied, decomposed at a lower rate than fenthion. In any case, it should be taken into consideration that the degradation rate exhibited by fenthion sulfoxide is the sum of two processes, namely the decomposition of fenthion into fenthion sulfoxide and the decomposition of fenthion sulfoxide into further degradation products.

4. Conclusions

It was found that, on the grape, fenthion, after spraying, immediately begins to be metabolised into fenthion sulfoxide. The percentage of fenthion sulfoxide was relatively low by the first day (5.8–16.5%) and increased to 64.6–89.2% at day 46 on grapes on the vines. Comparative increases were also measured for grapes stored in the refrigerator.

It was also interesting that, during refrigerated storage of grapes, the degradation rate of total fenthion (fenthion + fenthion sulfoxide) was about 5–6 times lower than on the grapes on the vines. Merchants who store grapes in refrigerators should take this into consideration.

References

Cabras, P., Garau, V. L., Pirisi, F. M., Cubeddu, M., Cabitza, F., & Spanedda, L. (1995). Fate of some insecticides from vine to wine. *Journal of Agricultural and Food Chemistry, 43*(10), 2613–2615, 12 Ref.

Dorea, H. S., Tadeo, J. L., & Sanchez-Brunete, C. (1996). Determination of organophosphorus pesticide residues in fruits by gas chromatography with ITD and NPD detection. *Chromatographia, 43*(7/8), 380–386.

EC, 7029/VI/95. Commission of the European communities, Directorate General for Agriculture –VI B II-1. 7029/VI/95 rev. 5, 22/7/97. Appendix B: General recommendations for the design, preparation and realisation of residue trials. Annex 1: Sampling.

EC, Commission Recommendation 99/333/EC of 3 March 1999 concerning a co-ordinated Community monitoring programme for 1999 to ensure compliance with maximum levels of pesticide residues in and on certain products of plant origin, including fruit and vegetables (OJ No L 128/25 of 21-05-1999).

Garcia-Repetto, R., Garrido, I., & Repetto, M. (1996). Determination of organochlorine, organophosphorus, and triazine pesticide residues in wine by gas chromatography with electron capture and nitrogen-phosphorus detection. *Journal of AOAC International USA, 79*(6), 1423–1427.

Harding, W. C. (1979). *Pesticide profiles: insecticides and miticides. Bulletin 267*. College Parks, MD: University of Maryland Cooperative Extension Service.

Kidd, H., & James, D. R. (Eds.). (1991). *The agrochemicals handbook* (3rd ed., pp. 5–14). Cambridge, UK: Royal Society of Chemistry Information Services (as updated).

Ministry of Welfare, Health and Cultural Affairs. (1988). In: Greve P. A. (Ed.), *Analytical methods for residues of pesticides in foodstuffs* (pt 1, p. 3). Rijswijk: The Netherlands.

Thomson, W. T. (1982). *Insecticides, acaricides, and ovicides. Agricultural chemicals. Book I* (pp. 5–23). Fresno, CA: Thomson Publications.

U.S. Public Health Services. (1995). Hazardous Substance Data Bank (pp. 5–9). Washington, DC.

Wauchope, R. D., Buttler, T. M., Hornsby, A. G, Augustijn-Beckers, P. W. M., & Burt, J. P. (1992). SCS/ARS/CES. Pesticide properties database for environmental decision making. *Reviews of Environmental Contamination and Toxicology, 123*, 1–157.