

## FENTHION (039)

### EXPLANATION

Fenthion was first evaluated in 1971 and has been reviewed several times since, most recently in 1989. It was proposed for periodic review by the CCPR in 1991 (ALINORM 91/24A, Appendix VI para 18).

The 1992 CCPR was informed that fenthion was still used in many countries on a variety of crops and that substantial data could be made available in time for review by the 1995 Joint Meeting (ALINORM 93/24, para 241 and Appendix V).

New information was made available to the Meeting on residues of fenthion from supervised trials on cherries in Germany, peaches in South Africa and Spain, mandarins and oranges in Spain, olives in Spain, Greece and Italy, rice in Japan and mangoes, rockmelons, cucumbers, zucchini, capsicum peppers and tomatoes in Australia. Data were also supplied from supervised trials on cattle (lactating and non-lactating), pigs and sheep, on animal and plant metabolism, environmental fate, analytical methods, and the stability of fenthion residues in stored analytical samples.

Information on registered use patterns was received from Australia, Canada, New Zealand, The Netherlands, Peru and the sponsor. A summary of world-wide GAP was provided by the sponsor.

### IDENTITY

ISO common name: fenthion

Chemical name:

IUPAC: *O,O*-dimethyl *O*-4-methylthio-*m*-tolyl phosphorothioate

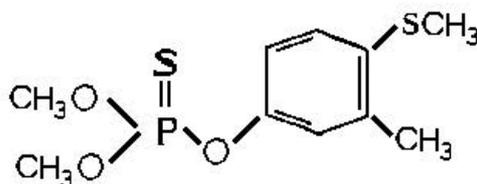
CA: *O,O*-dimethyl *O*-[3-methyl-4-(methylthio)phenyl] phosphorothioate

CAS No: 55-38-9

CIPAC No: 79

Synonyms: MPP; mercaptophos; OMS 2; ENT 25540

Structural formula:



Molecular formula: C<sub>10</sub>H<sub>15</sub>O<sub>3</sub>PS<sub>2</sub>

Molecular weight: 278.3

Structural formulae of the principal metabolites and degradation products of fenthion are shown in

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Figure 1. The structures of fenthion phenol sulfoxide  $\hat{\alpha}$ -glycoside, fenthion phenol sulfone  $\hat{\alpha}$ -glycoside, *O*-methylfenthion phenol sulfone, fenthion phenol sulfonic acid, and 3-methylphenol are not shown.

### Physical and chemical properties

#### Pure active ingredient

Vapour pressure:  $3.7 \times 10^{-4}$  Pa at 20°C (extrapolated)  
 $7.4 \times 10^{-4}$  Pa at 25°C (extrapolated)

Octanol/water partition coefficient:  $\log P_{OW} = 4.84$

Solubility at 20°C:

water	4.2 mg/l
n-hexane	100 g/l
xylene	>250 g/l
1,2-dichloroethane	>250 g/l
2-propanol	>250 g/l
1-octanol	>250 g/l
polyethylene glycol (lutrol)	>250 g/l
acetone	>250 g/l
acetonitrile	>250 g/l
ethyl acetate	>250 g/l
dimethylsulfoxide	>250 g/l

Relative density:  $D_4^{20} = 1.25$

Hydrolysis: at pH 7 and 25°C half-life >40 days

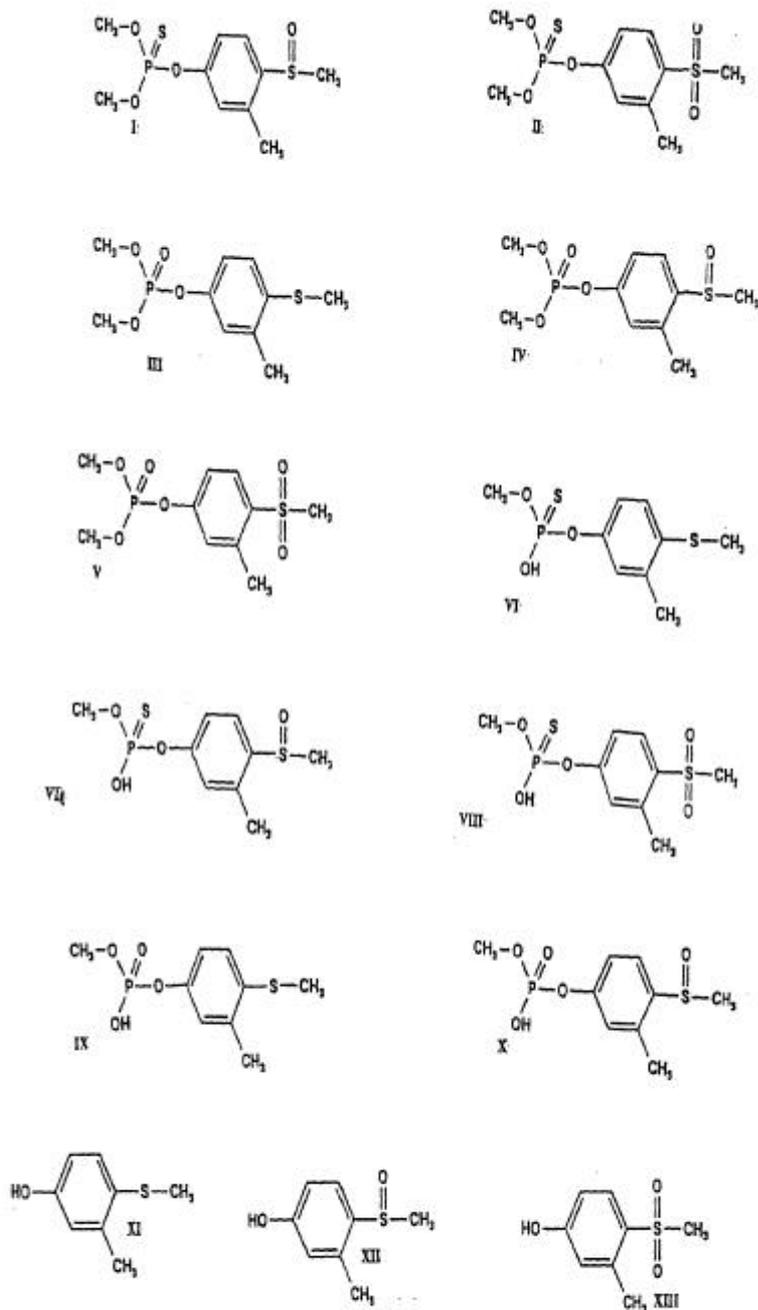
Photolysis: half-lives of 4.5-29 minutes in water at 23-25°C

### Formulations

Fenthion is sold as DP, EC, GR, PO, SA, SO, and WP formulations.

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Figure 1. Structures of principal metabolites and degradation products of fenthion.



- |      |                                   |      |   |
|------|-----------------------------------|------|---|
| I    | Fenthion sulphoxide               | II   | Fenthion sulphone                           |
| III  | Fenthion oxygen analogue          | IV   | Fenthion oxygen analogue sulphoxide         |
| V    | Fenthion oxygen analogue sulphone | VI   | Demethylfenthion                            |
| VII  | Demethylfenthion sulphoxide       | VIII | Demethylfenthion sulphone                   |
| IX   | Demethylfenthion oxygen analogue  | X    | Demethylfenthion oxygen analogue sulphoxide |
| XI   | Fenthion phenol                   | XII  | Fenthion phenol sulphoxide                  |
| XIII | Fenthion phenol sulphone          |      |   |

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## **METABOLISM AND ENVIRONMENTAL FATE**

### **Animal metabolism**

Studies on metabolism by rats, rabbits, cattle, pigs and goats were made available to the Meeting.

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Rats. Male rats were given a single oral or single and multiple peritoneal doses of  $^{32}\text{P}$ -labelled fenthion (Brady and Arthur, 1961). One group (18 rats) was dosed intraperitoneally at 10 mg/kg body weight/day for 10 consecutive days. Urine and faeces were collected over that and the following 10-day period. Animals were killed at 1, 3, 7, 10, 13 and 20 days after beginning the experiment. Liver, kidneys, heart, skin, bone and muscle were analysed for total radioactivity. Acetonitrile-soluble radioactive residues in the tissues were below the limit of determination of the radioassay method ( $<0.05$  mg/kg) after 3 days. Fenthion and its oxidative metabolites were shown not to be stored in tissues. The increasing incorporation of radiolabelled phosphorus into bone showed that ready degradation of fenthion had occurred. Eighty per cent of the administered dose was eliminated by 20 days after the first injection (approximately 60% in the urine, 20% in the faeces).

A second group of 2 rats was given a single intraperitoneal treatment with 200 mg/kg bw of labelled fenthion and killed 1.5 hours later when signs of poisoning were apparent. The concentration of the radiolabel (acetonitrile-soluble, fenthion equivalents) in several tissues was determined. The highest levels were in the liver (29.5 mg/kg), kidneys (26.9 mg/kg), muscle (9.6 mg/kg), heart (9.6 mg/kg) and skin (6.1 mg/kg).

A third group of 4 rats was given a single oral dose by stomach tube of 100 mg/kg bw. Rats were killed on the third and seventh day after treatment. Urine and faeces were collected throughout and both total and chloroform-soluble  $^{32}\text{P}$  were determined. Tissues by the third day contained less than 0.01 mg/kg fenthion equivalents of chloroform-soluble material, except liver which contained 0.2 mg/kg. No acetonitrile-soluble material was detected in the blood, brain or fat. Fenthion was readily oxidized by the rats to give fenthion oxygen analogue (fenthion oxon) and the sulfones and sulfoxides of fenthion and fenthion oxon. The rats excreted 86% of the administered dose by 7 days after treatment (approximately 46% in the urine and 40% in the faeces).

From 96 to 99% of the radiolabel in the urine and faeces was associated with hydrolysis products by 3 days after treatment. *O,O*-dimethyl hydrogen phosphorothioate was the major product in the urine and dimethyl hydrogen phosphate in the faeces. Only a small percentage of the radiolabelled material in the faeces and urine was organosoluble. In the urine, chloroform-soluble radioactivity made up about 4% of the total and contained fenthion oxon sulfoxide and sulfone as the major components (approximately 87% at days 1 and 2 and 57% at day 3). Fenthion, fenthion sulfoxide and fenthion sulfone were present at much lower levels, generally of the order of 5% of the chloroform-soluble radioactivity. Fenthion oxon was present at  $<5\%$  at days 1 and 2 but accounted for 21% of the total chloroform-soluble activity at day 3.

Female rats (24, divided into 3 groups fed different dietary regimes: high energy, high energy plus oil supplement and low energy) were given a single dose of  $^{35}\text{S}$ -labelled fenthion at 25 mg/kg bw, either subcutaneously or orally, and the animals were killed after 30 hours for tissue collection (Begum, 1967). Urine and faeces were collected throughout.

In the orally-treated rats, maximum levels of radioactivity in the blood occurred after 9 hours in the high-energy diet group (54 mg/kg fenthion equivalents) and 1 hour in the low-energy group (59.4 mg/kg). These levels decreased to 9 and 8 mg/kg respectively after 30 hours. In subcutaneously-treated rats, maximum blood levels were after 9 hours (34.3 mg/kg, high-energy diet) and 1 hour (58.7 mg/kg, low-energy diet). After 30 hours, blood levels had declined to about 5 mg/kg in both groups of animals. The presence of an oil supplement had no marked effect on the levels found in the blood.

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In all groups elimination was primarily in the urine, with the average amount of radiolabel eliminated being between 16 and 21% of the oral dose and 22 and 24% of the subcutaneous dose. In the faeces, 1 to 3% of the total dose administered had been eliminated after 30 hours, the route of administration not having a significant effect. The metabolites found in the urine from both the orally and subcutaneously treated rats were mainly water-soluble products (97.5-99% of the <sup>35</sup>S label in the urine after 30 hours), which were not identified. In the urine, fenthion sulfoxide and fenthion oxon sulfoxide and sulfone were the principal chloroform-soluble compounds (approximately 99% of the radioactive material at 30 hours). Smaller amounts of fenthion, fenthion sulfone and fenthion oxon (never more than 10% between 6 and 24 hours and <1% at 30 hours) were also detected. Most of the radiolabel found in the faeces was benzene-soluble and fenthion was the principal component, making up 78% of the total radiolabel present after 30 hours. Fenthion oxon was the other compound of significance found in the faeces (14-16% of the total radiolabel at 30 hours). Fenthion sulfoxide and sulfone and fenthion oxon sulfoxide and sulfone were present in amounts below 5% of the total administered dose at 30 hours.

In the tissues, residues of <sup>35</sup>S-fenthion or its metabolites were detected in the liver (oral 8.6-11.4 mg/kg, subcutaneous 7.6-12.6 mg/kg fenthion equivalents), kidneys (4.2-6.4 and 6.3-9.4 mg/kg respectively) and heart (2-4 and 0.8-3.1 mg/kg). No major difference was noted between the residue levels in orally and subcutaneously treated animals. Fenthion was the predominant radioactive compound identified in all tissues (29.2-33.1% of the radioactive acetonitrile-soluble material isolated). Fenthion oxon and its sulfoxide and sulfone were also major unhydrolysed metabolites in the livers and kidneys, in which fenthion sulfone and, to a lesser extent, fenthion sulfoxide were minor metabolites. In the heart only fenthion and fenthion oxon sulfoxide and sulfone were identified.

Four groups of Wistar laboratory rats (5 male and 5 female rats/group) were treated with fenthion labelled with <sup>14</sup>C at the 1-phenyl position (Puhl and Hurley, 1982). The groups were treated as follows.

Group A: single intravenous dose of 2 mg/kg bw.

Group B: single oral dose of 10 mg/kg bw (low, non-toxic, dose)

Group C: fourteen daily oral doses of unlabelled fenthion followed by one oral dose of radiolabelled fenthion. All doses were 10 mg/kg bw.

Group D: single oral dose of 100 mg/kg bw (toxic level).

Oral doses were administered directly into the stomach. Intravenous doses were injected into the tail vein. The animals were killed 72 hours after the final dose for tissue collection and analysis. Urine and faeces were collected throughout.

Excretion of the radiolabel in all groups was chiefly in the urine (after 72 hours >90% of the <sup>14</sup>C dose was recovered). Faeces contained between 2 and 6% of the recovered <sup>14</sup>C, while tissues had <2%. No radioactivity was detected in expired gases. Total recoveries of the administered radiolabel were between 94 and 110%. Excretion rates in male and female rats had reached plateau values of >90% of the administered dose by 24 hours, except in the high-dose group which took about 48 hours to reach a plateau. The radiolabel remaining in the body after 72 hours was less than 2% of the recovered dose.

Tissue levels were generally low (<0.1 mg/kg as fenthion equivalents) in Groups A, B, and C except in fat (0.12 mg/kg mean) and gonads (0.11 mg/kg mean) from Group C females. In Group D residues were higher, with fat containing the highest levels (mean values of 0.77 mg/kg in males and 3.4 mg/kg in females), but only in proportion to the increased dose.

Male and female rat metabolism was similar with no major differences in distribution. In the urine identified metabolites were found to account for more than 90% of the total recovered <sup>14</sup>C. Fenthion phenol, its sulfoxide and sulfone, including their sulfate and glucuronide conjugates, were the

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major metabolites (approximately 60% of the total <sup>14</sup>C recovered in the urine, faeces, and bodies in groups A-C and 30-40% in group D). Demethyl metabolites made up approximately 30% of the recovered <sup>14</sup>C (30-50% in group D). Fenthion was detected only in the faeces at levels below 1.5% of the total <sup>14</sup>C recovered. Fenthion oxon sulfoxide accounted for 1-4.5% of the <sup>14</sup>C recovered from the urine. The faeces contained less than 3% of the total <sup>14</sup>C recovered: fenthion, the phenol sulfone, and the phenol sulfoxide were all identified, each at levels below 1.5% of the recovered <sup>14</sup>C.

Sprague Dawley Wistar rats were dosed orally or intravenously (i.v.) according to the treatment regimes shown in Table 1 in a study which complied with GLP (Doolittle and Bates, 1993).

Table 1. Regimes for treating rats with radiolabelled fenthion (Doolittle and Bates, 1993).

Group	No. of rats <sup>1</sup>	Dose			Termination (hours)	Purpose
		Route	mg/kg bw	No.		
1	4	oral	0.3	1	72	<sup>14</sup> CO <sub>2</sub> , tissue distribution
2	10	oral	0.3	1	168	tissue distribution
3	10	oral	1.5	1	168	tissue distribution
4	10	iv	0.125	1	24,72,168	tissue distribution
5	10	oral	0.3	15 <sup>2</sup>	168	tissue distribution
6	12	oral	1.5	1	na	cholinesterase

<sup>1</sup> Each group contained an equal number of males and females

<sup>2</sup> Unlabelled fenthion for 14 days, then one dose of [<sup>14</sup>C]fenthion

All the rats eliminated most of the [<sup>14</sup>C]fenthion in the urine, with a little faecal elimination. About 80% of the administered radiolabel was recovered in the urine of the orally treated rats and 100% in that from the i.v. group by 24 hours after dosing. The faeces contained about 2-3% of the administered radiolabel (about 8% in group 3). The cumulative elimination via the urine increased rapidly and had reached constant levels by about 24 hours, except in group 5 which required about 48 hours. The pattern in the faeces was similar. Cage rinses accounted for less than 1% of the total dose in all groups and no <sup>14</sup>CO<sub>2</sub> was found.

Levels of the radiolabel in tissues and organs were below the limit of detection (0.001 mg/kg fenthion equivalents) in groups given single oral doses. Residues in the iv group were also undetectable except in one fat sample containing 0.001 mg/kg. Animals treated orally for 15 days had levels of 0.001 mg/kg in bone, 0.002 mg/kg in fat, 0.004 mg/kg in the spleen, 0.005 mg/kg in the carcass and 0.07 mg/kg in the lung. Tissue and carcass residues on average accounted for less than 1% of the total dose administered. The samples analysed were bone, brain, carcass, fat, heart, kidneys, liver, lung, muscle, ovary, spleen, uterus, testes and whole blood.

The total <sup>14</sup>C recovered in the urine, faeces, cage rinses, tissues, carcass and CO<sub>2</sub> was measured. Most of the administered radiolabel (77-100%) was recovered in the urine in all groups. Levels recovered in the faeces ranged from 2 to 8% of the administered dose. Levels of radiolabel in the tissues were ≤0.01% of the administered dose except in group 5 where approximately 0.2% of the dose was recovered, of which 0.16% was in the lung. More than 98% of the recovered radiolabel was in the urine, faeces and cage washes, showing effective elimination of fenthion in all the treatment groups.

Fenthion phenol and its sulfoxide and sulfone were the major metabolites identified in the urine (pooled by sex) from the orally treated rats 4-24 hours after treatment. Fenthion oxon was tentatively identified. Table 2 shows the results.

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Table 2. Major metabolites found in pooled rat urine (4-24 hours) after oral treatments with [1-<sup>14</sup>C-phenyl]fenthion and their overall average proportions (Doolittle and Bates, 1993).

Metabolite	Mean % of total residue
Ethyl acetate mobile phase	
Fenthion phenol sulfoxide	21.8
Fenthion phenol sulfone	25.9
Fenthion phenol	11.9
Fenthion oxon sulfoxide	4.1
Benzene/methanol mobile phase	
Fenthion phenol sulfoxide	25.4
Fenthion phenol sulfone	21.5
Fenthion phenol	12.1
Fenthion oxon sulfoxide	3.5

The oxon was tentatively identified in group 5 males (11.5% of the total residue) and females (18.7%) in analyses with the benzene/methanol mobile system. An overall average of 63.1% of the total residue was recovered with the ethyl acetate mobile phase and 63.3% with the benzene/methanol.

Serum cholinesterase activities were lower 24 hours after dosing than in the untreated control rats, but were comparable to the controls after 72 and 168 hours.

**Rabbits.** Male and female rabbits fed on low or high calorie diets were dosed by subcutaneous injection (four rabbits) or orally (five rabbits) with [<sup>35</sup>S]fenthion at 25 mg/kg bw and killed after 30 hours for tissue collection (Begum, 1967). Blood, urine and faeces were collected throughout.

In the orally-treated rabbits, maximum levels of <sup>35</sup>S in the blood occurred after 9 hours (57.8 mg/kg fenthion equivalents, high-energy diet) and 3 hours (81.2 mg/kg, low-energy diet) and decreased to 2.8 and 0 mg/kg respectively after 30 hours. In the injected rabbits the maximum blood levels were at 6 hours (77.3 mg/kg, high-energy diet) and 1 hour (78.3 mg/kg, low-energy diet). After 30 hours blood levels had declined to 14.2 and 11.8 mg/kg respectively. The presence of an oil supplement had no marked effect on the levels.

Excretion in the urine was 10.6-25% of the applied radiolabel after 30 hours in the rabbits treated orally and 12.1-17.2% after 24 hours in those injected. At all times after both treatments, approximately 90% or more of the <sup>35</sup>S was water-soluble. Elimination of the <sup>35</sup>S in the faeces was never more than 1%.

The main unhydrolysed metabolites in the urine after 30 hours were fenthion oxon sulfone (approximately 11-22% of the metabolites) and sulfoxide (approximately 70-77%) and fenthion sulfoxide (approximately 7-10%). Fenthion, fenthion sulfone and fenthion oxon were minor components (<7.5% throughout the 30-hour period). In the faeces, fenthion was the principal compound throughout and after 30 hours it accounted for about 70% of the total radiolabel. Fenthion oxon was also a major component (18-20% at 30 hours), with other unhydrolysed metabolites (fenthion sulfone and sulfoxide, and the oxon sulfone and sulfoxide) amounting to less than 6% of the total administered doses.

In tissues, residues of [<sup>35</sup>S]fenthion or its metabolites were detected in the liver (approximately 9-13 mg/kg expressed as fenthion, orally and subcutaneously treated animals), kidneys (approximately 6-10.5 mg/kg) and heart (approximately 2-4.5 mg/kg). No major difference between the residue levels in orally and subcutaneously treated animals was noted. Fenthion was the major residue found in the liver

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and kidneys (approximately 45% and 33%), where fenthion sulfoxide and sulfone and the oxon sulfoxide and sulfone were also detected in varying amounts. In the heart the major compounds were fenthion (28-30%), the oxon sulfone (21-22%) and the oxon sulfoxide (42-50%), but neither fenthion sulfone nor fenthion oxon was detected.

Cattle. [<sup>32</sup>P]fenthion was administered dermally to two lactating Jersey cows (0.5% emulsion, 1 litre/cow, cows about 360 kg each, approximately 14 mg/kg bw), and two other lactating Jersey cows (about 400 kg each) were injected intramuscularly with 3.5 g of the radiolabelled material, equivalent to about 9 mg/kg bw (Knowles and Arthur, 1966). Faeces, milk and urine were collected throughout and the cows were killed 14 days after dermal treatment and 21 days after i.m. treatment. Liver, muscle, fat, skin and injection site samples were collected.

In the urine from both treatment groups, peak concentrations of radioactivity were on the day after treatment. In the i.m. group the total <sup>32</sup>P in the urine decreased from 33 mg/kg fenthion equivalents at day 1 to 1.6 mg/kg at day 21. More than 95% of the radiolabel in the urine was associated with hydrolysis products, with dimethyl phosphorothioate and dimethyl phosphate as major metabolites. The remainder of the label was organosoluble and fenthion sulfone or oxon sulfoxide or sulfone were the major metabolites. Faecal elimination was minor with cumulative levels of 3.7% of the administered dose (dermal) and 4.1% (intramuscular) and peak values of 2.3 mg/kg (dermal) and 5.8 mg/kg (intramuscular) after two days.

In the tissues the highest level of the radiolabel was found in the liver (0.44 mg/kg fenthion equivalents) with the acetonitrile-soluble radioactivity being below 0.001 mg/kg from the dermal treatments and less than 30% of the total radiolabel in the liver from the i.m. Table 3 shows the residues in the tissues.

Approximately 1% of the dermal dose and 2% of the intramuscular dose were eliminated in the milk. Peak levels were at 18 hours after the dermal treatments (0.67 mg/kg fenthion equivalents total, 0.25 mg/kg acetonitrile-soluble) and 8 hours after the intramuscular (1.1 mg/kg total, 0.53 mg/kg acetonitrile-soluble). At 5 days the total radiolabel was 0.32 mg/kg from the dermal and 0.63 mg/kg from the i.m. treatments of which 0.009 and 0.02 mg/kg respectively was acetonitrile-soluble. The residues at day 7 from the dermal treatments were 0.26 mg/kg (total) and <0.001 mg/kg (acetonitrile-soluble). At 14 days after intramuscular treatment the milk contained 0.21 mg/kg fenthion equivalents of which 0.014 mg/kg was acetonitrile-soluble. Fenthion made up approximately half the milk residue with fenthion sulfone and fenthion oxon sulfoxide and sulfone constituting a second major fraction. Fenthion sulfoxide and fenthion oxon were minor metabolites.

Table 3. <sup>32</sup>P in cow tissues at slaughter 14 days after treatment with [<sup>32</sup>P]fenthion (Knowles and Arthur, 1966).

Sample	<sup>32</sup> P as fenthion equivalents, mg/kg			
	Dermal treatment		Intramuscular treatment	
	Total	CH <sub>3</sub> CN-soluble	Total	CH <sub>3</sub> CN-soluble
Muscle	0.03-0.04	<0.001	0.1-1	0.02-0.38
Subcutaneous fat	0.01-0.05		0.16-0.3	0.08-0.2
Omental fat	0.041	<0.001	0.56	0.15
Liver	0.44	<0.001	3.3	0.76
Skin	0.49	0.075		
Injection site			164	76.5

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[<sup>32</sup>P]Fenthion was given to two dairy cows orally by capsule at the rate of approximately 1.5 mg/kg bw for 14 days (Everett, 1963). The animals were killed 7 days after the last dose for tissue analysis. Two other dairy cattle were treated daily by backrubber application for 7 days with 50 ml of a 1% solution of [<sup>32</sup>P]fenthion and killed seven days after the last treatment. Samples of milk were taken throughout both experiments. The amount of fenthion administered was calculated on the basis that all the fenthion used at the rate of 0.1 lb/acre for mosquito control had drifted on to pasture.

The highest residues in the milk (acetonitrile-soluble) in the feeding trial were 0.24 mg/kg after 2 days in one cow and 0.36 mg/kg after 13 days in the other. Within 2 days of stopping treatment they were <0.01 mg/kg in both animals. In the backrubber trials, acetonitrile-soluble residues peaked at 0.15 mg/kg after 4 days in one cow and 0.47 mg/kg after 6 days in the other. Three to five days after the cessation of treatment, residue levels were <0.01 mg/kg in the milk of both cows. Residues in the tissues from both treatments were similar and were reported as total residues of fenthion and metabolites. Subcutaneous fat had the highest levels from the backrubber treatment (0.14 and 0.26 mg/kg). Omental and renal fat levels were <0.1 mg/kg. Residues in the kidneys and liver were approximately 0.02 mg/kg and in muscle ≤0.01 mg/kg. In the feeding study the highest residues were in the kidneys and liver at 0.02-0.04 mg/kg. Levels in the fat were 0.01-0.02 mg/kg and in muscle 0.006-0.01 mg/kg. Eighty-two to ninety-six per cent of the radiolabel was identified as being in fenthion or its metabolites.

A lactating Jersey cow (408 kg) was given a single dermal treatment (backline - top of shoulders to base of tail) with [1-<sup>14</sup>C-*phenyl*]fenthion at 5.08 mg/kg (Krautter, 1990a). Milk, faeces and urine were collected until the animal was killed 18 hours after treatment. Hair, skin, subcutaneous fat, kidneys, liver and muscle were analysed. Milk production and feed and water consumption did not appear to be adversely affected over the trial period.

The mean <sup>14</sup>C residues as fenthion equivalents were treatment site hair 16,200 mg/kg; non-treatment site hair 2.3 mg/kg, treatment site skin 106 mg/kg; non-treatment site skin 0.1 mg/kg; subcutaneous fat at treatment site 6.1 mg/kg, at an untreated site 1.8 mg/kg; peritoneal fat 0.3 mg/kg; liver 0.1 mg/kg; kidneys 0.1 mg/kg; muscle 0.3 mg/kg. The total mean residues in the milk were 0.03 mg/kg 6 and 18 hours after treatment and 0.05 mg/kg 12 hours after treatment. In the urine the mean radiocarbon level was 3.9 mg/kg fenthion equivalents.

Extraction efficiencies from the tissues were all greater than 90% except from skin where an average extraction of 29% was recorded. Recoveries after frozen storage were satisfactory for fat (102%) and muscle (about 70%). Recoveries from kidneys and liver were about 25% (See the section "Stability of pesticide residues in stored analytical samples" for further comments on sample stability).

Fenthion was the major component (typically >90%) of the radiolabel in all tissues except the liver and kidneys where it was 71 and 51% respectively. Fenthion sulfoxide was the source of up to 5% of the radiocarbon in the hair, skin, muscle and fat but was not present in the kidneys or liver, which contained significant amounts of unidentified polar metabolites (44 and 22% respectively). About 5% of the total radioactivity in the liver and about 18% in the kidneys could be extracted into water and was tentatively identified as being from glucuronide conjugates of fenthion phenol sulfoxide and/or sulfone (Krautter, 1990b).

Goat. A lactating goat was dosed orally by capsule once daily for three consecutive days with 1-[<sup>14</sup>C]-phenyl-labelled fenthion at 20 mg/kg bw and slaughtered 3.5 hours after the final dose for tissue analysis (Weber and Ecker, 1992). Milk, plasma and excreta were collected throughout. Approximately 52% of the administered <sup>14</sup>C was recovered: urine 44%, faeces 6.3%, milk 0.2% and edible tissues an estimated 1%. A large part of the final dose remained unquantified in the animal's gastrointestinal tract. Plasma levels peaked within 2-4 hours after dosing. A half-life of about 3 hours in the plasma was calculated for the first dose with the mean residence time being 6.4 hours.

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Levels of <sup>14</sup>C as fenthion equivalents in the tissues and organs were liver 3.3 mg/kg; kidneys 24.1 mg/kg; muscle 0.6 mg/kg; and fat 2.7 mg/kg perirenal, 1.1 mg/kg subcutaneous and 1 mg/kg omental. Residues of fenthion sulfoxide and fenthion sulfone in the fat totalled approximately 0.5 mg/kg (0.3 mg/kg of the sulfoxide, 0.2 mg/kg of the sulfone) supporting a description of the residue as "fat-soluble". In milk the residue level was approximately 3 mg/kg 8 hours after the first and second doses. Detailed results are shown in Table 4.

During storage for an unspecified time at about -20°C further degradation (mainly oxidation and/or hydrolysis) occurred with a consequent increase in the amount of demethylated, oxidized and dephosphorylated residues. Further information on storage stability is provided in the "Stability of pesticide residues in stored analytical samples" section.

In urine, 56% of the radioactivity was associated with fenthion phenol and its sulfoxide and sulfone. Demethylated P=S compounds (demethylfenthion and its sulfoxide and sulfone) made up approximately 29% of the renal radioactivity. Eleven per cent of the radioactivity was associated with demethylated P=O compounds (demethylfenthion oxon and its sulfoxide).

Figs. A male and female Duroc pig (each approximately 15 kg) were given a single oral dose of 5 mg/kg bw of [1-<sup>13,14</sup>C-phenyl]fenthion. One week later, the female pig was dosed with the radiolabelled material at the rate of 10 mg/kg bw per day for two consecutive days and the male pig treated similarly for 3 consecutive days (Pither, 1979). Urine and faeces were collected throughout. Blood samples were taken after the first of the multiple doses. The male pig was killed 6 hours after the last dose (at the residue peak in whole blood) and the female pig 30 hours after the last dose. Tissues were then collected and analysed for radiocarbon.

Table 4. Compounds identified in tissues and milk from a goat dosed with [1-<sup>14</sup>C-phenyl]fenthion(Weber and Ecker, 1992).

Compound <sup>1</sup>	<sup>14</sup> C expressed as mg/kg fenthion equivalents and as % of total <sup>14</sup> C in the sample											
	Liver		Kidneys		Muscle, thigh		Muscle, flank <sup>2</sup>		Fat, composite		Milk, composite <sup>3</sup>	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
FSO	0.8	23	15	64	0.1	15	0.2	26	0.5	33	0.6	21
FPOSODM	0.3	19	2	8	0.2	37	0.2	34	-	-	0.4	16
FSO2	0.3	11	6	24	-	-	<0.1	12	0.2	12	1.4	44
FPSSODM	0.5	8	0.6	3	<0.1	6	<0.1	6	0.1	7	0.1	4
FPSSO2DM	0.4	6	0.3	1	<0.1	6	<0.1	6	0.2	11	0.1	3
FPOSODM	0.2	5	-	-	<0.1	8	<0.1	8	-	-	<0.1	1
FS	<0.1	1	-	-	<0.1	1	-	-	-	-	<0.1	1
FPSSO	<0.1	3	0.1	1	<0.1	1	-	-	0.3	19	<0.1	2
FPSSDM	0.2	6	-	-	<0.1	2	-	-	-	-	<0.1	0.2
FPSSO2	<0.1	1	-	-	<0.1	1	-	-	0.2	16	<0.1	2
FPSS	<0.1	1	-	-	-	-	-	-	-	-	-	-

<sup>1</sup> FSO fenthion phenol sulfoxide, FPOSODM demethylfenthion oxon sulfoxide, FSO2 fenthion phenol sulfone, FPSSODM demethylfenthion sulfoxide, FPSSO2DM demethylfenthion sulfone, FPOSODM demethylfenthion oxon, FS fenthion phenol, FPSSO fenthion sulfoxide, FPSSDM demethylfenthion, FPSSO2 fenthion sulfone, FPSS fenthion

<sup>2</sup> Flank and loin muscles had similar residues

<sup>3</sup> From samples taken after the first, second and third treatments

Blood levels peaked between 5 and 6½ hours after dosing. Excretion in the urine and faeces was rapid in both pigs with about 85% of the first dose eliminated within 30 hours. After 54 hours the totals

## fenthion

recovered in the excreta of the male and female pigs were 95% and 91% respectively. Approximately 86-87% of the administered dose was recovered in the urine, 81-84% within the first 24 hours. Faecal elimination accounted for 9% of the total radiolabel in the male and 4% in the female.

Fenthion phenol sulfoxide (35% of the administered dose in the male and 37% in the female) and fenthion phenol sulfone (27% and 18% respectively) were the major products in the urine; fenthion phenol was also present at 11.6% in the male and 5.8% in the female. In the faeces, fenthion and fenthion oxon were the two identifiable compounds, accounting respectively for 4.1% and 1.8% of the administered activity in the male and 1.8% and 0.4% in the female.

Organosoluble material accounted for less than 10% of the total label and most of the radioactivity (72% in the male and 51% in the female) was in conjugated phenols which were identified after enzymatic hydrolysis.

Total residues in the tissues of the male pig, expressed fenthion, were 8.4 mg/kg kidneys; 8.6 mg/kg liver; 4.7 mg/kg fat; 2.9 mg/kg muscle; 2.4 mg/kg brain and 3.1 mg/kg heart. Residues in the female pig, killed after the longer interval of 30 hours, were substantially lower (1.2 mg/kg kidneys; 0.9 mg/kg liver; 1.6 mg/kg fat; 0.2 mg/kg muscle; 0.2 mg/kg brain; and 0.2 mg/kg heart) indicating effective elimination from the tissues. In the tissues of the male pig fenthion, fenthion oxon, and their sulfoxides and sulfones were found in varying proportions as follows.

Muscle: oxon sulfoxide 47%; oxon sulfone 23%  
Heart: oxon sulfoxide 45%; oxon sulfone 26%  
Fat: fenthion 16%, fenthion sulfone 30%, oxon sulfoxide 14%; oxon sulfone 22%  
Kidneys: oxon sulfoxide 26%; fenthion phenol sulfoxide 14%; fenthion phenol sulfone 12%; fenthion phenol 2%  
Liver: fenthion 20%; fenthion sulfone 11%; fenthion oxon 15%; fenthion phenol sulfoxide plus sulfone 10%

Details of the distribution of metabolites in the female animal were not recorded.

The residues in the skin and tissues after dermal treatment were determined in a two-month old pig, approximately 22 kg, given a backline treatment with [1-<sup>14</sup>C-phenyl]fenthion at 14.4 mg/kg bw and killed after 18 hours (Crosby *et al.*, 1990).

The mean <sup>14</sup>C levels, as mg/kg fenthion equivalents, were as follows.

Treatment site hair	1400
Treatment site skin	134
Treatment site fat	3.9
Non-treatment site hair	94
Non-treatment site skin	0.4
Non-treatment site fat	0.8
Liver	0.2
Kidneys	0.3
Peritoneal fat	0.6
Muscle	0.1

Extraction efficiencies ranged between 85.9 and 119.2% of the radiocarbon for samples except skin, from which 68.5% was extractable. Total recoveries were between 91.7 and 176.3% (skin 68.9%).

Residues were separated by HPLC and showed the following distribution of identified compounds.

Treatment site	
hair	97% fenthion; 1.7% fenthion sulfoxide
skin	99% fenthion; 0.6% fenthion sulfoxide
fat	100% fenthion
Kidneys	26% fenthion; 6.6% fenthion oxon

## fenthion

Liver	69% fenthion
Muscle	88% fenthion; 12% fenthion sulfoxide
Peritoneal fat	81% fenthion; 11% fenthion sulfoxide

Residues in the kidneys and liver included 67 and 31% respectively of an unidentified metabolite, tentatively thought to be a glucuronide conjugate of fenthion phenol sulfoxide or sulfone (Krautter, 1990b).

### Plant metabolism

Data on olives, guavas, cabbage, beans, maize (corn), rice, alfalfa, Bahia grass, Coastal bermuda grass and tea were submitted.

Olives. Two varieties (Leccino and Nocellara del Belice) were given single and double treatments (24-day interval) respectively with 0.5 kg fenthion/ha and olives were picked after 0, 14 and 28 days (Molinari *et al.*, 1992). The residues found in the pulp, oil and pomace after 0 and 28 days are shown in Table 5.

Fenthion and fenthion sulfoxide were the major residue components, with smaller amounts of fenthion sulfone and fenthion oxon.

A half-life of about 11 days was calculated for total fenthion residues under the trial conditions.

Table 5. Distribution of fenthion and its oxidized metabolites in pulp, oil and pomace from olives treated with 1 or 2 applications of fenthion in Italy, 1990 (Molinari, 1992).

Sample	PHI, days	Residue, mg/kg				
		Fenthion	Fenthion oxon	Fenthion sulfoxide	Fenthion sulfone	Total
Leccino variety (single spray)						
Pulp	0	0.62	0.02	0.13	ND	0.76
Oil	0	4.06	1.05	0.10	ND	5.21
Pulp	28	0.11	ND	0.015	ND	0.12
Oil	28	0.50	0.01	ND	ND	0.51
Pomace	28	0.14	0.004	0.07	0.003	0.22
Nocellara del Belice variety (two sprays)						
Pulp	0	1.10	0.04	0.36	ND	1.49
Pulp	28	0.205	0.01	0.04	0.002	0.26
Oil	28	0.93	0.03	ND	ND	0.96
Pomace	28	0.36	0.02	0.26	0.002	0.64

In another series of trials, olive trees were ground-sprayed (with added bait) 3 times (at 8- and 38-day intervals) at approximately 75 g fenthion/ha, or 5 times (at 24-, 8-, 15- and 24-day intervals) at 100 g/ha at a concentration of 0.2 kg ai/hl. Approximately 0.0005 kg fenthion was applied per plant. Samples were taken over a 54-day period after the last sprayings. Residues of fenthion, fenthion oxon and their sulfoxides and sulfones were extracted with chloroform and determined by GLC (Cabras *et al.* 1993).

Fenthion was degraded slowly in both trials with a half-life of about 38 days. Residue levels from 5 treatments were generally higher than from 3. Results are shown in Table 6.

After harvest a 10-kg portion of olives was processed into oil and residues in the oil, oil cake and vegetation water were determined. Details are given in the section "Fate of residues in storage and processing".

fenthion

Table 6. Residues in olives after treatment with fenthion at 3 x 0.075 or 5 x 0.1 kg ai/ha. Trials were conducted in Italy in 1991 (Cabras *et al.*, 1993).

Compound	Residue, mg/kg, mean $\pm$ SD at PHI, days				
	0	11	20	34	54
3 treatments					
Fenthion	0.96 $\pm$ 0.28	0.64 $\pm$ 0.32	0.51 $\pm$ 0.16	0.45 $\pm$ 0.18	0.34 $\pm$ 0.15
Fenthion sulfoxide	0.66 $\pm$ 0.24	0.23 $\pm$ 0.08	0.21 $\pm$ 0.05	0.20 $\pm$ 0.04	0.19 $\pm$ 0.08
Fenthion sulfone	0.02 $\pm$ 0.00	0.06 $\pm$ 0.02	0.05 $\pm$ 0.02	0.05 $\pm$ 0.01	0.04 $\pm$ 0.02
Fenthion oxon	0.02 $\pm$ 0.01	0.03 $\pm$ 0.01	0.03 $\pm$ 0.00	0.02 $\pm$ 0.00	0.02 $\pm$ 0.00
Fenthion oxon sulfoxide	0.29 $\pm$ 0.14	0.25 $\pm$ 0.05	0.33 $\pm$ 0.06	0.24 $\pm$ 0.04	0.07 $\pm$ 0.03
Fenthion oxon sulfone	0.03 $\pm$ 0.02	0.04 $\pm$ 0.00	0.05 $\pm$ 0.02	0.03 $\pm$ 0.01	not detected
5 treatments					
Fenthion	1.93 $\pm$ 0.71	1.43 $\pm$ 0.30	1.34 $\pm$ 0.31	0.87 $\pm$ 0.34	0.72 $\pm$ 0.18
Fenthion sulfoxide	0.76 $\pm$ 0.22	0.58 $\pm$ 0.21	0.56 $\pm$ 0.32	0.58 $\pm$ 0.26	0.51 $\pm$ 0.27
Fenthion sulfone	0.08 $\pm$ 0.04	0.15 $\pm$ 0.04	0.17 $\pm$ 0.06	0.15 $\pm$ 0.05	0.12 $\pm$ 0.02
Fenthion oxon	0.04 $\pm$ 0.01	0.06 $\pm$ 0.01	0.09 $\pm$ 0.01	0.08 $\pm$ 0.01	0.03 $\pm$ 0.01
Fenthion oxon sulfoxide	0.34 $\pm$ 0.11	0.49 $\pm$ 0.06	0.62 $\pm$ 0.19	0.80 $\pm$ 0.15	0.35 $\pm$ 0.09
Fenthion oxon sulfone	0.08 $\pm$ 0.05	0.15 $\pm$ 0.02	0.18 $\pm$ 0.04	0.09 $\pm$ 0.02	0.05 $\pm$ 0.01

Guavas. A guava tree was sprayed once to run-off with a 0.06% solution of [1-<sup>14</sup>C-*phenyl*]fenthion (Fredrickson, 1980). Fruit were sampled after 0, 1, 3, 7, 14, 21, 28 and 32 days and the pulp and peel analysed separately.

Most of the <sup>14</sup>C remained in the peel (88% at day 0, 78% at day 32). In the peel fenthion (59% of the total activity) and fenthion sulfoxide (26%) were the main residues at day 0. Other metabolites at that time accounted for less than 3% of the total radiolabel. At day 32 the residue included demethylfenthion sulfoxide 52%, fenthion phenol sulfoxide about 12%, fenthion <1%, and fenthion sulfoxide 5.6%.

The radiolabel in the pulp was 1% of the total <sup>14</sup>C at day 0, 18% at day 7 and 14% at day 32, with levels of all metabolites <0.1% of the total radiolabel present at day 0. By day 7 the identified residues ranged from 0.1 (fenthion) to 5.4% (demethylfenthion sulfoxide) indicating that some transfer to the pulp had occurred. At day 32, the major pulp metabolite was demethylfenthion sulfoxide (corresponding to 5.5% of the <sup>14</sup>C present at that time) with minor amounts of fenthion (<0.1%), fenthion sulfoxide (1%), fenthion sulfone (0.2%), fenthion oxon sulfoxide (1.1%), fenthion phenol (0.4%), fenthion phenol sulfoxide (1.8%), and fenthion phenol sulfone (0.6%), with 3.5% of unextracted <sup>14</sup>C. Acid reflux of the unextracted material yielded 40% fenthion phenol sulfoxide, 14% fenthion phenol sulfone, 25% fenthion sulfoxide, and 21% demethylfenthion sulfoxide.

On a whole fruit basis, fenthion and its sulfoxide were the major compounds present shortly after spraying, accounting for 95% of the total <sup>14</sup>C. Demethylfenthion sulfoxide was the major compound present at 32 days (60% of the total <sup>14</sup>C content) with fenthion phenol sulfoxide (15.7%), fenthion 0.5%, fenthion sulfoxide 8.3%, fenthion sulfone 1.5%, fenthion oxon sulfoxide 6.3%, fenthion phenol 0.6% and fenthion phenol sulfone 3.7%.

Approximately 11% of the applied radiolabel (9.2% as fenthion sulfoxide, 1% as fenthion) could be rinsed off the guavas at day 0. The level of radiolabel in the rinse decreased gradually but erratically to 7.8% of the total <sup>14</sup>C at day 32. By day 32, fenthion sulfoxide accounted for about 2% of the total <sup>14</sup>C, with similar amounts of fenthion phenol sulfoxide and demethylfenthion sulfoxide.

Cabbage. <sup>32</sup>P-labelled fenthion was sprayed onto cabbage plants as a 0.07% water emulsion at the rate of 9 kg fenthion/ha (Tomizawa *et al.*, 1962). The initial concentration of radiolabel in the leaves was 46 mg/kg fenthion equivalents which rapidly diminished over to 3 days to 20% of the original value. Rainfall or evaporation from the leaf surface soon after application were suggested as possible causes of

## fenthion

the loss. The concentration of the radiolabel was relatively constant between 3 and 12 days.

In samples from days 3 to 12, approximately half the labelled material was soluble in chloroform. Fenthion accounted for 95% of the chloroform-soluble radioactivity initially but for less than 1% of it after 7 days. Fenthion sulfoxide and sulfone were not present at day 0 but made up approximately 50% of the total residue at day 7. About 30% of the labelled material present at day 7 was unidentified and may have been hydrolysis products. An identification of the *S*-methyl isomer (isofenthion) remains tentative as work by Niessen *et al.*, 1962) showed that the isomer was not formed in beans. The isomer was present as an impurity in the radiolabelled fenthion used by Niessen and it appears that the same material was used in Tomizawa's work.

**Beans.** Young bean plants were dipped in a 0.2% emulsion containing [<sup>32</sup>P]fenthion or placed with their roots in an aqueous 0.1% fenthion emulsion (Niessen *et al.*, 1962).

Six hours after the dip treatment most of the radiolabel, about 150 mg/kg fenthion equivalents, was chloroform-soluble and about 20 mg/kg was soluble in water. Over 8 days the chloroform-soluble material decreased to about 15 mg/kg while the water-soluble fraction increased to about 45 mg/kg. Fenthion decreased from about 100 mg/kg at day 0 to about 17 mg/kg after 8 days. Fenthion sulfoxide was the major metabolite identified, with an initial concentration of about 20 mg/kg and a final concentration of about 5 mg/kg, when it made up 52.3% of the residue. Fenthion sulfone and fenthion oxon sulfone and sulfoxide were also detected. The shoots placed in the fenthion emulsion contained about 3 mg/kg of total residue expressed as fenthion, indicative of a slight systemic effect. The *S*-methyl isomer of fenthion was identified as an impurity in the starting material.

**Maize.** Maize plants (0.08 ha blocks, growth stage not stated) were sprayed once with fenthion (0.5 kg/litre EC) at rates of 560, 1120 or 2240 g fenthion/hectare. Samples were taken at 0, 1, 2, 7, 14, and 21 days after treatment (Leuck and Bowman, 1968). The treated maize plants and maize silage prepared from plants sampled one day after treatment were analysed for fenthion and its oxidized metabolites.

The residue distributions from the three treatments were similar, with levels directly related to the application rates. Fenthion sulfoxide and its oxon were the major metabolites at day 0, with fenthion, its sulfone and oxon sulfone as minor residues. Residues decreased over 21 days when fenthion sulfoxide and sulfone were the main metabolites. Residues of fenthion oxon were not detected (<0.002 mg/kg) in any sample. The dry matter content of the maize was 30-31% initially and 45-53% at day 21. Table 7 summarizes the results.

The analytical method used to determine fenthion and its five metabolites was that of Bowman and Beroza (1968) in which fenthion and the metabolites are extracted with chloroform/methanol, chromatographed on silica gel and determined by GLC with a phosphorus-sensitive flame-photometric detector. Recoveries at the 0.1 mg/kg level were 95-100%, the LOD about 0.003 mg/kg.

Table 7. Fenthion and four of its metabolites in maize plants after a single spraying with fenthion at 0.56, 1.12 or 2.24 kg fenthion/hectare (Leuck and Bowman, 1968).

PHI, days	Rate, kg fenthion/ha	Residues, mg/kg wet weight, mean of four replicates				
		Fenthion	Fenthion sulfone	Fenthion oxon sulfone	Fenthion sulfoxide	Fenthion oxon sulfoxide
0	0.56	0.061	0.07	<0.005	6.02	0.16
	1.12	0.22	0.11	<0.005	9.64	0.30
	2.24	0.41	0.22	<0.005	26.4	0.63
1	0.56	0.036	0.24	0.046	2.76	0.39
	1.12	0.068	0.39	0.054	4.56	0.49
	2.24	0.49	0.52	0.068	16.8	0.75

## fenthion

PHI, days	Rate, kg fenthion/ha	Residues, mg/kg wet weight, mean of four replicates				
		Fenthion	Fenthion sulfone	Fenthion oxon sulfone	Fenthion sulfoxide	Fenthion oxon sulfoxide
2	0.56	0.016	0.24	0.084	2.19	0.45
	1.12	0.041	0.52	0.100	4.36	0.70
	2.24	0.32	0.86	0.130	13.9	0.86
7	0.56	<0.002	0.09	0.090	0.26	0.22
	1.12	0.016	0.44	0.125	0.90	0.47
	2.25	0.039	0.68	0.156	2.38	1.03
14	0.56	<0.002	0.04	0.025	0.073	<0.02
	1.12	0.007	0.14	0.036	0.178	<0.02
	2.24	0.011	0.24	0.085	0.42	0.11
21	0.56	<0.002	0.03	0.019	0.41	<0.02
	1.12	<0.002	0.09	0.020	0.082	<0.02
	2.24	<0.002	0.22	0.036	0.34	<0.02

Maize silage was prepared from day 1 maize plants and dried at 29°C for 30 days. The dry matter in the silage was between 25.8 and 30%. Residues were found to be more persistent in the silage than in the field samples, with a reduced degree of oxidation: fenthion and its sulfoxide and sulfone were the major compounds. Fenthion residues showed an approximately tenfold increase in concentration in the silage. Residues at 0 and 30 days respectively from the three treatments were as follows.

### 0.56 kg/ha

Fenthion 0.04, 0.42 mg/kg  
 Fenthion sulfone 0.24, 0.30 mg/kg  
 Fenthion oxon <0.002, 0.034 mg/kg  
 Fenthion oxon sulfone 0.046, 0.031 mg/kg  
 Fenthion sulfoxide 2.70, 0.93 mg/kg; and  
 Fenthion oxon sulfoxide 0.39, 0.02 mg/kg.

### 1.12 kg/ha

Fenthion 0.068, 0.65 mg/kg  
 Fenthion sulfone 0.39, 0.42 mg/kg  
 Fenthion oxon <0.002, <0.002 mg/kg  
 Fenthion oxon sulfone 0.054, 0.010 mg/kg  
 Fenthion sulfoxide 4.56, 3.11 mg/kg  
 Fenthion oxon sulfoxide 0.49, 0.16 mg/kg

### 2.24 kg/ha

Fenthion 0.49, 4.42 mg/kg  
 Fenthion sulfone 0.52, 0.98 mg/kg  
 Fenthion oxon <0.002, 0.070 mg/kg  
 Fenthion oxon sulfone 0.068, 0.025 mg/kg  
 Fenthion sulfoxide 16.8, 7.0 mg/kg  
 Fenthion oxon sulfoxide 0.75, 0.21 mg/kg

The total residues (dry weight) at 0 and 30 days were 12.4 and 6.7 mg/kg at 0.56 kg/ha, 18.5 and 15.9 mg/kg at 1.12 kg/ha, and 64.5 and 46.7 mg/kg at 2.24 kg/ha.

Rice. Rice was sprayed with a 0.07% water emulsion of <sup>32</sup>P-labelled fenthion at 9 kg/ha at 3 and 5 weeks after transplanting, and also a few days before heading (Fukuda *et al.*, 1962). Whole plants or stems were sampled at various intervals. Ears were sampled at 3, 7, and 12 days after application and grains at 14 and 29 days. Radioactivity was determined by a GM counter.

Most of the radiolabel in transplanted plants was initially chloroform-soluble, with virtually no water-soluble material. By day 7, chloroform-soluble material accounted for <10% of the initial radiolabel. Water-soluble radioactivity never exceeded 10% of the initial label.

## fenthion

After spraying the residues were 121 mg/kg expressed as fenthion on the blade and 28 mg/kg on the sheath from the plants sprayed 3 weeks after transplanting and 153 and 18 mg/kg respectively from spraying after 5 weeks. In the rice sprayed before heading the initial value was 110 mg/kg.

In the plants treated at 3 and 5 weeks fenthion was either absent or accounted for about 10% or less of the chloroform-soluble radiolabel. Chloroform-extractable metabolites were detected throughout the experimental period and consisted mainly of fenthion sulfoxide and sulfone. The *S*-methyl isomer of fenthion was tentatively identified as being present throughout the trials but this compound was present in the starting material as a contaminant at a level of about 3.5%. The metabolic patterns in the sheaths and blades were considered equivalent.

The ears of rice plants sampled 12 days after spraying contained fenthion sulfoxide (45% of the radiolabel) and fenthion sulfone (18%) as the major metabolites. Seventeen per cent of the material present had a TLC  $R_f$  value of 0. The *S*-methyl isomer was tentatively identified (19.5% of the  $^{32}\text{P}$ ).

In rice grains sampled 29 days after spraying, the bulk of the radiolabel was in the bran (60 mg/kg fenthion equivalents). Polished rice had 5.7 mg/kg and husks 2.4 mg/kg. The bran and the polished rice contained 0.9 and 0.1 mg/kg of chloroform-soluble material and 30 and 2 mg/kg of water-soluble material respectively. No chloroform-soluble material was found in the husks, which contained 0.8 mg/kg of water-extractable material.

The water-extractable metabolites in rice grains taken 14 days after application contained phosphoric acid and thionophosphoric acid (approximately 4% of the water extractable material identified); dimethyl hydrogen phosphate (4.5%) dimethyl hydrogen thionophosphate (7%) and demethylfenthion (79%).

Alfalfa. Alfalfa was sprayed with [1- $^{13,14}\text{C}$ -phenyl]fenthion at a concentration of 0.42 kg fenthion/ha at a plant height of 15-20 cm. (Dräger *et al.*, 1989). Samples were harvested 7 and 30 days after the application. Aqueous phase extracts and HPLC fractions were treated with  $\alpha$ -glucosidase, cellulase and esterase to release bound metabolites.

Of the applied  $^{14}\text{C}$  radioactivity, 65% was in plant material and 8% in the soil. Loss into the air was considered to account for the remainder.

At 7 days there was a total residue of 13 mg/kg expressed as fenthion, which had dropped to 6.6 mg/kg at 30 days. At 7 days approximately 56% of the radioactivity was organosoluble, at 30 days about 30%. Water-soluble radioactivity was about 40% at day 7 and 62% at day 30. About 8% of the radiolabel at day 30 was unextractable.

Extensive metabolism occurred. The identified compounds at days 7 and/or 30 were fenthion, fenthion sulfoxide, fenthion sulfone, fenthion oxon sulfoxide, fenthion phenol, fenthion phenol sulfoxide, fenthion phenol sulfone, demethylfenthion sulfoxide, demethylfenthion sulfone, demethylfenthion oxon sulfoxide and the glucosides of fenthion phenol sulfoxide and sulfone.

Demethylfenthion sulfoxide was a major metabolite throughout. It accounted for about 21% of the recovered  $^{14}\text{C}$  after 7 days and 30% after 30 days. Fenthion sulfoxide was initially the major metabolite (41.8% of the radiolabel recovered at 7 days) but it was further metabolized to be 19.7% after 30 days. Fenthion was present at 7 and 30 days but at levels representing less than 2.5% of the total radiolabel recovered at those times. The glucosides of fenthion phenol sulfoxide and sulfone corresponded to 13.9% of the recovered radiocarbon at day 7 and 8.7% at day 30. Fenthion phenols and P=O compounds were present in only trace amounts.

Bahia grass. In an evaluation of the uptake by rotational crops from pastures sprayed with fenthion

## fenthion

(Fredrickson and Thornton, 1978), Bahia grass was sprayed (simulated fog) 4 times at 20-day intervals with [ $U\text{-}^{14}\text{C}\text{-phenyl}$ ]fenthion at about 110 g/ha (the total amount of fenthion applied in the trial was about 450 g/ha).

Grass, soil and water were analysed before and one day after each application. After the grass was harvested (day 126, 66 days after the final application), the sod was turned into the soil and the plot allowed to lie fallow for a year after the initial application. Wheat, sugar beets and spinach were then planted and samples of the growing crops, forage and grain were taken over the respective growing periods.

In the grass, residues increased after each spraying. From a concentration of 8.1 mg/kg fenthion equivalents one day after the first application, the levels had reached 16.1 mg/kg one day after the fourth spraying. After 126 days (66 days after the last treatment), the level in the grass was approximately 0.5 mg/kg.

One day after the initial spray fenthion accounted for 13% and fenthion sulfoxide for 65% of the  $^{14}\text{C}$  present, with fenthion sulfone, fenthion phenol sulfoxide and fenthion phenol sulfone each contributing less than 10%. Prior to the third application (day 40) the distribution was fenthion 0.4%, fenthion sulfoxide 20.6%, fenthion sulfone 5%; fenthion phenol sulfoxide 42%; and fenthion phenol sulfone 30%.

One day after the third application fenthion was 2.2% of the residue, fenthion sulfoxide 50.6%, fenthion sulfone 6.4%; fenthion phenol sulfoxide 19.3%; and fenthion phenol sulfone 14.3%. At harvest (day 126) the distribution was fenthion 0.4%, fenthion sulfoxide 2.6%, fenthion sulfone 0.3%; fenthion phenol sulfoxide 62.5%; and fenthion phenol sulfone 27.4%.

Diffuse activity (not associated with any defined TLC  $R_f$  value) made up between 2 and 7.8% of the  $^{14}\text{C}$  during the 126 days.

The decrease of fenthion sulfoxide with time corresponded to the increasing levels of fenthion phenol sulfoxide and sulfone seen over the same periods.

Samples of the crops grown in the treated soil were taken at regular intervals during their growth and at harvest. Residues were all reported as <0.006 mg/kg fenthion equivalents, the limit of detection, except in dry wheat forage where the value reported was <0.02 mg/kg.

Coastal bermudagrass. Coastal bermudagrass, a forage crop, was sprayed once with fenthion (0.5 kg/litre EC) at a rate of 0.56, 1.12 or 2.24 kg fenthion/hectare and sampled at 0, 1, 2, 7, 14, and 21 days after treatment. The grass was sprayed three weeks after cutting for hay (Leuck and Bowman, 1968). The treated grass was analysed for fenthion and its oxidized metabolites. Fenthion sulfoxide and fenthion sulfone were not present in the starting material.

Residues of fenthion, fenthion sulfoxide and sulfone, and fenthion oxon sulfoxide and sulfone were present at varying concentrations at most sampling intervals. Fenthion oxon was not measurable one day after spraying. Residue concentrations were proportional to the treatment rates.

On the day of treatment fenthion and fenthion sulfoxide were the major components. At 21 days fenthion sulfoxide and fenthion sulfone were the main compounds; fenthion was still present but in low concentrations (<0.1 mg/kg). The dry matter content of the grass was about 50-56% at day 0 and about 42-45% at day 21. Table 8 shows the results.

Table 8. Residues of fenthion and five of its metabolites in Coastal bermudagrass sprayed once with fenthion at 0.056, 0.112 or 0.224 kg/ha and sampled over a 21-day period (Leuck and Bowman, 1968).

## fenthion

PHI, days	Rate, kg ai/ha	Residues mg/kg, wet basis, mean values.					
		Fenthion	Fenthion sulfone	Fenthion oxon	Fenthion oxon sulfone	Fenthion sulfoxide	Fenthion oxon sulfoxide
0	0.56	7.67	0.47	0.007	<0.005	19.1	0.33
	0.112	26.1	1.00	0.025	<0.005	38.2	0.58
	0.224	64.3	0.97	0.060	<0.005	71.2	1.84
1	0.56	0.767	1.18	<0.002	0.04	14.0	1.67
	0.112	4.56	2.27	<0.002	0.069	33.0	1.18
	0.224	8.81	3.15	<0.002	0.099	60.0	3.37
2	0.56	0.225	1.54	<0.002	0.116	9.18	0.72
	0.112	1.04	3.13	<0.002	0.217	23.2	1.34
	0.224	4.54	5.04	<0.002	0.198	46.4	3.46
7	0.56	0.056	0.99	<0.002	0.133	1.77	0.38
	0.112	0.102	2.57	<0.002	0.259	4.8	0.75
	0.224	0.308	4.04	<0.002	0.342	10.3	1.98
14	0.56	0.011	0.65	<0.002	0.059	0.45	0.13
	0.112	0.032	1.74	<0.002	0.141	1.07	0.23
	0.224	0.067	2.32	<0.002	0.175	2.12	0.48
21	0.56	0.006	0.32	<0.002	0.033	0.15	0.02
	0.112	0.013	0.80	<0.002<0.002	0.068	0.36	0.05
	0.224	0.034	1.30		0.106	0.59	0.08

**Tea.** The fate of [<sup>32</sup>P]fenthion in tea sprayed at a rate of 9 kg fenthion/ha with a 0.07% emulsion and processed to green tea was reported by Tomizawa *et al.* (1962).

Immediately after spraying levels of <sup>32</sup>P (as fenthion equivalents) were 43 mg/kg in younger tea leaves and 90 mg/kg in older leaves. Three days after spraying the level of <sup>32</sup>P had dropped to 50-60% of the initial value and continued to decline steadily thereafter.

Fenthion was the only compound identified in both old and new leaves at day 0. It rapidly decreased to less than 1% of the chloroform-soluble <sup>32</sup>P present at 7 days. Fenthion sulfoxide and sulfone were the major metabolites from day 3 onwards in both young and old leaves and accounted for approximately 90% of the total <sup>32</sup>P at day 7.

In green tea made from the treated leaves, the radioactivity was 59 and 87% of that in fresh leaves taken 3 hours and 7 days after application respectively. The chloroform-extractable metabolites were distributed as follows in fresh leaves, green tea made from leaves taken 3 h after treatment, and green tea made from leaves taken 7 days after treatment respectively. Fenthion sulfoxide: 56.5%, 33.7% and 53%. Fenthion sulfone 30.3%, 56.3% and 23.5%. The residue in the green tea made from "3-hour" leaves also contained 10% of fenthion.

### Environmental fate in soil

A rotational crop trial with bahia grass in which residues in soil were determined (Fredrickson and Thornton, 1978) was described above. The composition of the soil used was sand 99%, silt 1%, 2.26% organic matter and pH 6.0.

Levels of radiolabel in the soil were low throughout the study (<0.1 mg/kg fenthion equivalents) and only showed small increases after the sprayings. The concentration was 0.033 mg/kg fenthion equivalents one day after the first spraying and 0.087 mg/kg, the highest residue found, on the day after the second application. When the soil was turned after the four sprayings (126 days after the trial started)

## fenthion

the level was 0.021 mg/kg. After rotational crops had been grown (day 530), the level in the soil was <0.006 mg/kg. Leaching water contained no detectable radioactivity. Characterization of the residues was not possible because of the low levels. When a humic and fulvic acid determination was attempted, the sodium hydroxide extract of a soil sample taken 210 days after the initial application and containing 0.015 mg/kg fenthion equivalents could not be assayed in the liquid scintillation counter because the extract was too dark. Combustion of the remaining solids showed that 20% of the radiolabel was associated with the humin and, by difference, approximately 80% was associated with the humic-fulvic acid fraction.

[1-<sup>14</sup>C-*phenyl*]fenthion was added to a sandy loam soil (66% sand, 32% silt, 2% clay, 2.4% organic matter, pH 5.1) at 53 mg/kg and exposed to sunlight (Christopher and Lane, 1987a). Fenthion was rapidly degraded (half-life of 6-7 hours) with the formation of fenthion sulfoxide as the major product. After 30 hours fenthion accounted for 34% of the radiocarbon in the sample and fenthion sulfoxide for 58% (2% initially). Fenthion sulfone, fenthion oxon sulfoxide and fenthion phenol sulfoxide were minor products. Quantitative recovery of the radiolabel was achieved with loss through volatility being less than 0.1%. In dark control soil there was little degradation of fenthion over 30 hours (initially 98% of the radiocarbon and after 30 hours 94%). Fenthion sulfoxide accounted for 6% of the radiocarbon at 30 hours.

Fenthion was one of four thioether pesticides (disulfoton, methiocarb and butocarboxim were the others) added to sterile soils (pH 4.5-7.5, clay 8-15%, silt 17-47%, sand 48-70%) at 50-200 mg/kg and exposed to sunlight to investigate their photo-oxidation (Gohre and Miller, 1986). All the pesticides were converted to their sulfoxides with only trace amounts of the sulfone detected. About 45-80% of the originally added material remained after 4 days. The rate of loss was fastest in the least organic soil.

The effect of soil micro-organisms on the degradation of fenthion was studied by Puhl *et al.* (1979). [1-<sup>14</sup>C-*phenyl*]fenthion was added to non-sterile and sterile loam soil (48% sand, 35% silt, 17% clay, pH 5.5) at 1 mg/kg and aerobically incubated at room temperature (no details provided) for 9 days. Volatile radioactivity was not determined.

Fenthion was degraded more rapidly and extensively in non-sterile than sterile soil. After 9 days fenthion (74% of the total radiocarbon) and fenthion sulfoxide (16%) were the major radioactive species in sterile soil. Fenthion sulfoxide (34%) and fenthion phenol sulfoxide (17%) were the major products in non-sterile soil with lower levels of fenthion sulfone and fenthion phenol sulfone. Fenthion accounted for 12.5% of the total <sup>14</sup>C. In the non-sterile soil 72.9% was organosoluble, 15.3% water-soluble and 11% unextracted. In the sterile soil the respective proportions were 95.8%, 2.3% and 1.9%.

The degradation of [1-<sup>14</sup>C-*phenyl*]fenthion in a silt loam soil (10% sand, 72% silt, 18% clay, pH 5.9) under aerobic and anaerobic conditions has been investigated by Puhl and Hurley (1978a). One or 10 mg/kg of the labelled fenthion was applied to the soil which was then incubated aerobically for 30 days. At this time, several samples treated at 1 mg/kg were flooded with water, the air flushed out with nitrogen and anaerobic conditions maintained for 60 days. Sterilized soil treated at 1 mg/kg was also incubated for 30 days. Light was excluded during the incubations. Aerobic samples at the 1 mg/kg level were sampled over 120 days, and at the 10 mg/kg level over 30 days. Anaerobic samples were taken at 28 and 60 days and sterilized soil samples at 0 to 30 days.

Under aerobic conditions fenthion was rapidly degraded on soil with a half-life of about one day. After 120 days 50% of the radiolabel present was in <sup>14</sup>CO<sub>2</sub>, 8% was organosoluble and 42% was unextractable. The products identified, accounting together for <10% of the total <sup>14</sup>C, were fenthion sulfoxide and sulfone, fenthion phenol sulfoxide and sulfone, and *O*-methyl fenthion phenol sulfone (3-methyl-4-methylsulfonylanisole), which was the main compound and accounted for 3.8% of the <sup>14</sup>C. With 10 mg/kg of fenthion the same compounds were identified in similar proportions over the sampling period of 30 days. The phenol sulfone and carbon dioxide were the main identified products at

## fenthion

30 days.

Under anaerobic conditions degradation was slow with little change in product concentrations between 28 and 60 days, when fenthion phenol sulfone was the major compound. About 42-43% of the radiocarbon was unextractable and 31-34% was due to carbon dioxide.

In the sterile soil, fenthion had a half-life of 14-21 days. Initially it accounted for 94% of the total  $^{14}\text{C}$  and its sulfoxide for 4%. After 30 days the proportions were 33% and 34% respectively. Some fenthion phenol sulfoxide appeared towards the end of the trial (less than 10% of the  $^{14}\text{C}$  present).

Little radiocarbon was found in aqueous fractions at any time.

The total recoveries of radiocarbon were 98% from 1 mg/kg at 120 days, 102% from 10 mg/kg at 30 days, 89% from anaerobic soil at 60 days, and 120% from sterilized soil at 30 days.

The half-life of fenthion on soils containing 2.6 and 0.6% of organically bound carbon (pH 6.8 and 5.2) was determined over a 10-day period at 22°C (Wagner, 1974, revised 1993). The initial fenthion concentration was 200  $\mu\text{g}/100\text{ g}$  soil. Fenthion disappeared rapidly and less than 10% of the original was present at the end of the study. The calculated half-lives were 1.7 and 0.5 days. Fenthion sulfoxide was the main product.

### Mobility

The leaching characteristics of  $^{14}\text{C}$ -labelled fenthion and its degradation products on a sandy loam soil (0.6% organic content, 65% sand, 21% silt, 14% clay) under simulated field conditions have been determined (Tweedy and Houseworth, 1974). [ $^{14}\text{C}$ -*phenyl*]fenthion was incorporated into the soil at a rate of 2 mg/10 g of soil and allowed to age for 30 days under greenhouse conditions in an environment protected from light. The soil was then treated for 45 days with water simulating rain- fall and eluates and soil fractions were analysed daily for the radiolabel.

Approximately 4% of the radiolabel was eluted without significant differences in concentration in any of the water samples. About 87% of the applied radiolabel remained in the soil with 67% found in the top 7.5 cm.

In a similar experiment (Simmons, 1975), [ $^{14}\text{C}$ -*phenyl*]fenthion was added to a loam soil at the rate of 10 mg/kg. The treated soil was aged for 30 days at room temperature, then washed for 45 days with water to simulate rainfall. Leachate and soil were analysed for radiolabel content.

Sixteen per cent of the recovered radiolabel was in the leachate and 55% in the top 4 cm of the soil. A 12% loss of radiolabel occurred during the trial. In the leachate only 1% of the activity was fenthion: fenthion phenol, fenthion phenol sulfoxide and fenthion phenol sulfone were identified as major products (10%). Fenthion sulfoxide and sulfone and fenthion oxon were present as minor components.

In a further study of the mobility of fenthion and its breakdown products in soils, [ $^{13,14}\text{C}$ -*phenyl*]fenthion was added at 1 mg/kg to a sandy loam soil and incubated aerobically at 22-24°C for 4 or 25 days (Christopher and Lane, 1987b). The aged soil was added to sandy loam, silty clay, silt loam and sand soils (sand 66, 4, 13, and 96%, silt 32, 53, 63 and 2%, clay 2, 43, 24 and 2%, organic matter 2.4%, 2.1%, 2.7% and 0.2% and pH 5.1, 6.7, 6.4 and 6.4). The soils were continuously leached with aqueous calcium chloride solution over a two-day period during which time light was excluded.

Leaching was minimal except from sand, with 95-98% of the radiolabel retained in the soils, mainly in the top 6 cm, and 5% or less in all samples of the leachate. In sand 36% of the radiolabel was

## fenthion

leached from the soil aged for 4 days and 46% from the soil aged for 25 days.

Mineralisation to CO<sub>2</sub> was less than 0.5% of the applied radiolabel during the 4-day aerobic incubation and approximately 7% after 25 days.

In the soils (except sand) fenthion sulfoxide was the major compound after 4 days ageing (29-38% of the radiolabel). Fenthion and its sulfone and fenthion phenol sulfoxide and sulfone were minor components. Fenthion sulfoxide and fenthion phenol sulfoxide and sulfone were the main products after 25 days ageing. In sand aged for 4 days, fenthion sulfoxide was again the major product. After 25 days ageing fenthion, fenthion sulfoxide and sulfone, fenthion phenol sulfoxide, and fenthion phenol sulfone were present in amounts below 10% of the total radiocarbon.

Fenthion was not detected in the leachate from the sand. The compounds identified were fenthion sulfoxide (11% of the radiolabel after 4 days ageing and 0.4% after 25 days, fenthion phenol sulfoxide 9% (4 days) and 15% (25 days); fenthion phenol sulfone 3% (4 days) and 20% (25 days); and fenthion sulfone <1% after both 4 and 25 days.

The mobility of radiolabelled fenthion applied to thin-layer plates coated with different soils was investigated with twenty three other pesticides (Thornton *et al.*, 1976). Fenthion was seen to have "low" mobility based on its R<sub>f</sub> value (average 0.16) after development of the plates with water. Pesticides of intermediate and greater mobility had R<sub>f</sub> values >0.4.

In a study of the mobility and persistence of fenthion in soil and water (Flint and Shaw II, 1972), fenthion spray concentrate (about 11 kg/ha) was added to three soils (loam with 40% sand, 42% silt, 18% clay, 1.4% organic matter, pH 7.7; silty clay loam with 8% sand, 54% silt, 38% clay, 2% organic matter, pH 6.3, and silty clay loam with 6% sand, 54% silt, 40% clay, 4% organic matter, pH 6.1) and the treated soils were leached with water. Run-off water and soils were analysed for residues.

Insignificant leaching was reported, with the majority of the fenthion residues remaining in the top centimetre of the soils. Fenthion residues in the run-off water were less than 1% of the amount applied. Fenthion and fenthion sulfoxide were identified in the soils with only limited migration away from the point of application. Freundlich adsorption constants for fenthion on the three soils were calculated (sandy loam 7.7, silty clay loam 12.4 and high organic silty clay loam 67.3) and showed that adsorption was moderate on sandy soil, a little greater on silty soil and high on soil with a high organic content.

An investigation of the adsorption and desorption of [1-<sup>14</sup>C-*phenyl*]fenthion added to three soils (Kansas soil 46% sand, 36% silt, 18% clay, pH 5.5; Hagerstown MD soil 4% sand, 53% silt, 43% clay, pH 6.7 and Florida soil 92% sand, 7% silt, 1% clay, pH 6.9) at concentrations of 0.5 to 10.4 mg/kg indicated that fenthion was strongly adsorbed to the soils (Puhl and Hurley, 1978b).

Freundlich adsorption constants were calculated to be between 19 and 39, of the same order of magnitude as those of 7 to 64 determined by Flint and Shaw II (1972) and similar to those determined by Daly (1988). These values were considered high and suggestive of strong soil adsorption coupled with low mobility. The percentage of fenthion adsorbed in all the soils was high (79 to 91%). Less than 15% of the absorbed fenthion was removed after three or four desorptions, a result consistent with the high adsorption.

A further soil adsorption/desorption study with [1-<sup>13,14</sup>C-*phenyl*]fenthion was conducted on four soils (Daly, 1988). The soil compositions were:

- Sand - 88% sand, 7% silt, 5% clay, pH 4.3;
- Sandy loam - 56% sand, 30% silt, 14% clay, pH 6.6;
- Silt loam - 17% sand, 66% silt, 17% clay, pH 5.9; and

## fenthion

Clay loam - 21% sand, 50% silt, 29% clay and pH 6.4.

The soils were treated with nominal concentrations of 1.0, 5.0, 7.5 and 10 mg/kg and equilibrated with a solution of the radiolabelled fenthion. Adsorption and desorption coefficients were determined with the results shown below.

Soil Type	% organic carbon	Adsorption		Desorption	
		K <sub>d</sub>	K <sub>oc</sub>	K <sub>d</sub>	K <sub>oc</sub>
Sand	0.53	8.62	1638	20.19	3836
Sandy loam	0.58	6.42	1110	12.66	2186
Silt loam	1.53	15.81	1036	33.04	2165
Clay loam	1.16	16.21	1400	28.10	2427

These values confirm that fenthion is resistant to leaching from the soil. The <sup>14</sup>C mass balance was between 91 and 104% for the four soils.

### Environmental fate in water and sediment systems

Because pesticides may enter natural waters by various routes, e.g. control of aquatic weeds, run-off from agricultural uses, uses against mosquitoes and flies, studies on the fate of fenthion in aquatic situations were reviewed.

The half-lives of fenthion in aqueous phosphate buffers and in a simulated field water system were determined by Flint and Shaw II (1972).

Fenthion (10 mg/kg) was incubated with phosphate buffers at pH 5, 7, and 9 at 30° and 50°C and samples were analysed for fenthion and its degradation products over a period of 16 days. Fenthion had half-lives of 23-31 days at 30°C and 2-6.5 days at 50°C. No sulfoxides, sulfones or oxygen analogues were detected.

In the simulated field water system (pond water, stored outside and exposed to full sunlight), fenthion had a half-life of about 1-1.5 days. The faster degradation in pond water was considered to show the importance of micro-organisms in the aquatic breakdown processes. Fenthion sulfone was identified in silt from the pond water, but was not recorded in the absence of silt. No other products were detected.

A second study on the stability of fenthion in sterile phosphate buffers (Simmons and Thornton, 1976) was conducted by adding 5 mg/kg of the [U-<sup>14</sup>C-*phenyl*]fenthion to solutions of buffers at pH 5, 7, and 9 and temperatures of 5, 25 and 40°C.

Half-lives of about 70 to 130 weeks were found at all pH values at 5°C with acid solutions being most stable. At higher temperatures the half-lives were much shorter (2-4 weeks at 40°C). The results are shown in Table 9.

Table 9. Half-lives of fenthion in sterile buffer solutions at varying conditions of pH and temperature (Simmons and Thornton, 1976).

pH	Half-lives (weeks) at		
	5°C	25°C	40°C
5	133	8	4
7	105	6	3
9	69	5	2

## fenthion

The effect of temperature on the stability of fenthion is clearly demonstrated, in agreement with the findings of Flint and Shaw II (1972). Fenthion, its sulfoxide and sulfone, fenthion oxon and its sulfoxide and sulfone, fenthion phenol sulfoxide and fenthion phenol sulfone (but not fenthion phenol) were detected. While the relative proportions of these compounds varied with the pH, temperature and time of sampling, fenthion sulfoxide was the principal product and fenthion sulfone a minor constituent. Fenthion oxon was present in varying amounts with maximum values generally associated with higher temperatures and pH and increasing time. Levels of fenthion oxon sulfoxide and sulfone were generally less than 10% of the total  $^{14}\text{C}$  and occurred mainly at higher temperature and pH, and longer times. Fenthion phenol sulfoxide and sulfone reached maximum values of about 20 to 36% of the total  $^{14}\text{C}$ , also at higher temperatures and pH and longer times.

More than 90% of the radiolabel was initially associated with organosoluble material, which decreased somewhat with time. Less than 10% of the  $^{14}\text{C}$  was generally water-soluble except in the 25°C samples where it accounted for 30% at pH 5, 59% at pH 7, and 60% at pH 9 of the total radiolabel present at 10 weeks. As the pH and temperature increased the amount of material not identified (at the origin of TLC plates) also increased with time, most markedly in the 25° and 40°C samples.

In a further investigation of the fate of fenthion in water (Jensen-Korte, 1983a), fenthion at 3.6 to 5.1 µg/ml was incubated in citrate buffer (pH 4), phosphate buffer (pH 7), and borate buffer (pH 9) at 50, 60 and 70°C. Fenthion concentrations were determined by HPLC and the solutions sampled over times of approximately 30 and 350 hours depending on the buffer system and temperature. The calculated half-lives and those estimated at 22°C by extrapolation are shown in Table 10.

The results confirm that increasing temperature results in faster degradation and show that at 22°C fenthion has a half-life of about 200 days at pH 7. Fenthion phenol was identified in acidic and basic media.

Table 10. Half-lives of fenthion in buffers at pH 4, 7, and 9 at temperatures of 50°C, 70°C, 90°C and, by extrapolation, 22°C (Jensen-Korte,1983a).

pH	°C	Half-life (hours)
4	50	172
4	60	57
4	70	21
7	50	140
7	60	45
7	70	16
9	50	120
9	60	43
9	70	15, 16
4	22 <sup>1</sup>	5348
7	22 <sup>1</sup>	4792
9	22 <sup>1</sup>	3224, 3626

<sup>1</sup> by extrapolation

The fate of fenthion in natural or model aquatic environments, rather than in buffered solutions, was investigated in a number of experiments. Flint and Shaw II (1972, see above) showed

## fenthion

that fenthion in pond water in an outdoor environment was degraded within days.

In a similar situation (Fredrickson, 1976), [U-<sup>14</sup>C-*phenyl*]fenthion was added at 10 mg/l water to a simulated pond prepared from water and lake silt and stored in the open for a period of 7 weeks. The average daytime temperature over the period was about 20°C.

In the water phase, fenthion was not measurable after 35 days and its half-life was less than 2 days. Fenthion sulfoxide was the major identified degradation product. It was present after one day, reached a maximum of 15% of the <sup>14</sup>C content at day 9 and then steadily decreased to 6-7% of the total activity from days 28 to 49. Fenthion phenol was tentatively identified (<2%). Water-soluble activity gradually increased from 2% of the <sup>14</sup>C at day 2 to 24% at day 49.

Fenthion was readily transferred to the silt and reached a maximum equivalent to 37% of the <sup>14</sup>C present (16 mg/kg) at day 5 and then declined to 9% at day 49. Its half-life in the silt was about 20 days. Fenthion sulfoxide levels were between 1 and 4% of the <sup>14</sup>C from day 1 onwards. Low levels (≤2% of the <sup>14</sup>C) of residues thought to be fenthion sulfone and fenthion phenol were detected after 16 and 5 days respectively.

Bound activity in the silt gradually increased to a maximum of 46% of the <sup>14</sup>C present after 49 days with water-soluble activity being constant at about 2-4% from day 2 onwards.

Twenty-one per cent of the bound activity was extractable and of this 3% was associated with humic acids and 18% with fulvic acids.

The total toxic residues (as parent and its sulfoxide and sulfone) were calculated as having a half-life of 16 days in the total system. The stability of fenthion in silt was attributed to the anaerobic conditions which meant that reduction rather than oxidation predominated. The water-soluble activity was not identified.

An investigation of the degradation of pesticides in an aquatic model system (Scholz *et al.*, 1988) examined, *inter alia*, the effect of oxygen concentration on pesticide breakdown using fenthion as a model. [1-<sup>14</sup>C-*phenyl*]fenthion was added to water/sediment samples obtained from The Netherlands, Germany, and the USA at a concentration of 1.5 mg fenthion/litre. The systems were kept at 20-24°C under aerobic and anaerobic conditions and sampled over periods of 66 days (aerobic) and 190 days (anaerobic).

In the aerobic system the proportion of water-soluble activity decreased during the trial from 85% to about 5%. About 75% of the <sup>14</sup>C at the end of the trial was unextractable and approximately 15-20% had been incorporated into carbon dioxide.

Although radiolabelled carbon dioxide was produced continuously in the aerobic system larger amounts were formed in the anaerobic system after a lag time of 60-120 days, and accounted for about 50% of the radiolabel present at 190 days.

In the aerobic system the major products were fenthion sulfoxide and demethylfenthion oxon sulfone. In the anaerobic system, fenthion phenol sulfoxide and fenthion phenol were the major products, with 3-methylphenol and methane detected as minor constituents. The compounds identified are listed in Table 11.

Table 11. Degradation products of radiolabelled fenthion found in model aquatic systems under aerobic and anaerobic conditions (Scholz *et al.*, 1988).

Aerobic conditions	Both aerobic and anaerobic conditions	Anaerobic conditions
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## fenthion

Aerobic conditions	Both aerobic and anaerobic conditions	Anaerobic conditions
Fenthion oxon Fenthion sulfoxide Fenthion oxon sulfoxide Fenthion sulfone Demethyl fenthion sulfone Fenthion oxon sulfone Fenthion phenol sulfone	Demethyl fenthion Demethyl fenthion sulfoxide Fenthion phenol sulfoxide Carbon dioxide	Fenthion phenol 3-Methylphenol Methane

In a study conducted according to the US EPA's guidelines on "Aerobic aquatic metabolism studies", the behaviour and fate of fenthion labelled in the 1-phenyl position with  $^{14}\text{C}$  and  $^{13}\text{C}$  was investigated (Anderson and Wilmes, 1988). Fenthion (1.5 mg/l) was added to pond water and sediment samples obtained from the USA and The Netherlands. The test systems were open to the atmosphere and maintained with shaking in the dark at 20-24°C. Samples were taken over 66 days. The systems were aerobic throughout the course of the trial.

The mass balances were good, with recoveries of 97 and 106% of the applied radioactivity. While the rates were different, most of the radioactivity in the two systems (56% and 74% of that applied at 66 days) was transferred to the sediment and was not extractable with organic solvents. Carbon dioxide was produced in both systems and accounted for 9.5-12.8% of the final radioactivity.

The degradation of fenthion was rapid in both systems with half-lives of about a week and was accompanied by continuous mineralization. Most of the products were in the aqueous phases, with different compounds predominating at various times: initially fenthion sulfoxide, then demethylfenthion oxon sulfone, and finally fenthion phenol sulfoxide and sulfone. Other compounds identified were fenthion sulfone, fenthion oxon, demethylfenthion, demethylfenthion sulfone, demethylfenthion sulfoxide, and demethylfenthion oxon sulfoxide.

The degradation of fenthion under anaerobic conditions in a simulated aquatic system was also reported by Fritz *et al.* (1988). Water and sediment from a pond were incubated anaerobically in the dark at about 22°C for 360 days with [1- $^{14}\text{C}$ -phenyl]fenthion added at the rate of 1.5 mg/l.

The initial pH of the surface water was approximately 5.7-5.8, and over the year of the trial steadily increased to 7.2-7.6. Reducing conditions prevailed throughout the system.

The distribution of the radiolabel varied with the incubation period but its rapid appearance in the sediment was noticeable (28% of the applied  $^{14}\text{C}$ ) after one hour. In water, fenthion decreased from about 72% of the applied radioactivity initially present to about 7% 30 days later and was not detectable after 360 days. In the sediment fenthion was a major component (20% of the applied radioactivity) initially, rose to 60% at 14 days, and then declined to 0.2% at 360 days. Under the anaerobic conditions fenthion was considered to be degraded to methane and carbon dioxide with the system having a first half-life of about 4 to 5 days.

The recovery of radiolabel was >95% up to 60 days and >90% thereafter. The amount of unextracted, bound  $^{14}\text{C}$  in the sediment increased irregularly during the trial from 1.5% to approximately 15.6% of the applied  $^{14}\text{C}$ . Labelled carbon dioxide was at a maximum at 120 and 190 days when it accounted for about 50% of the applied  $^{14}\text{C}$  (in a follow-up experiment). Radiolabelled methane was also detected at these times in the follow-up experiment at about 4% of the total applied radiolabel. No significant amounts of other volatile labelled substances were detected.

Fenthion, fenthion phenol, fenthion phenol sulfoxide, demethylfenthion, demethylfenthion sulfoxide and 3-methylphenol were identified in extracts from the surface water and sediment. Fenthion phenol (maximum values of 30% in the surface water at day 60 and approximately 5% in the

## fenthion

sediment at days 30 and 60) and fenthion phenol sulfoxide (maximum about 24% after 30 days in the surface water and up to 6% in the sediment) were major products at various times. 3-Methylphenol was present at approximately 8.8% and 0.2% in the water at days 60 and 120 and at 0.9% in the sediment at day 60. Only small amounts (<3%) of demethylfenthion and demethylfenthion sulfoxide occurred in the surface water and sediment.

In a model system of salt marsh water and sediment (O'Neill *et al.*, 1989) fenthion was added at a nominal 200  $\mu$ g/litre to three microcosms: one sterilized with formalin and without plants, one non-sterile and without plants and one non-sterile with plants. The systems were maintained in light and darkness at 20°C. Water samples were taken during the following 190 hours, and leaves and sediment were analysed for fenthion at the end of the experiments. The results were used in the validation of a computer modelling system.

Fenthion loss from the water followed first order kinetics with levels of fenthion in the non-sterile systems approaching zero by 200 hours. In the sterile system fenthion was still present in the water after 200 hours at a level between 50 and 100  $\mu$ g/litre.

Half-lives were estimated to be about 4 days in the sterile system and about 33-35 hours in the two non-sterile systems.

The fate of 28 pesticides, including fenthion, in river water has been reported (Eichelberger and Lichtenberg, 1971). Fenthion was added to river water at the rate of 10  $\mu$ g/l and kept for a period of 8 weeks under laboratory conditions in natural and artificial light. Within one week, 50% of the original fenthion was left, at 2 weeks 10% was present and none was detected after 4 weeks. In similarly treated distilled water no fenthion was lost over a three-week period, an indication of the role of biological activity in the degradation of fenthion.

The photolysis of fenthion in distilled water has been investigated by Fredrickson and Nichols (1976). Distilled water containing [U-<sup>14</sup>C-phenyl]fenthion at 5 mg/l was irradiated with artificial light sources approximating the spectral wavelengths of sunlight. The water temperatures were 5°C and 25°C. The effect of acetone as a photosensitizer mimicking the sensitizing effects of dissolved substances in natural water was also investigated at 25°C. Irradiation was for 120 minutes at 25°C and 160 minutes at 5°C.

Rapid breakdown of fenthion was observed in all situations with the half-lives at 5°C and 25°C of 55 and 15 minutes respectively. In the presence of acetone the half-life was 10 minutes. The degradation products identified were fenthion sulfoxide and sulfone, fenthion oxon and its sulfoxide, and fenthion phenol and its sulfoxide and sulfone. At 25°C, the major compounds at 120 minutes were fenthion sulfoxide (18% of the activity) fenthion oxon sulfoxide (15%) and fenthion phenol sulfoxide (12%). Thirty-nine per cent of the <sup>14</sup>C present was associated with unidentified polar metabolites, believed to be polymeric in nature with a high molecular weight (>700).

At 5°C after 160 minutes fenthion (22%), fenthion sulfoxide (12%), fenthion oxon (13%), fenthion phenol (17%), and fenthion phenol sulfoxide (12%) were the major compounds. Polar material accounted for 26% of the activity at that time.

In the sensitized solution after 120 minutes, fenthion sulfoxide (35%) and fenthion phenol sulfoxide (12%) were the main identified compounds, with 36% of polar degradation products.

Irradiation of a 3.5 mg/l solution of fenthion in distilled water for 10 minutes with a high-pressure mercury vapour lamp showed a half-life of 4.5 minutes for fenthion (Jensen-Korte, 1983b). In the same study a solution of fenthion in distilled water exposed to summer sunlight had a half-life

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of four hours. A large number of photoproducts were formed, with the positive identification of fenthion sulfoxide and fenthion phenol.

The photolysis of fenthion at pH 5 in sterile sodium acetate buffer was studied with [1-<sup>13,14</sup>C-*phenyl*]fenthion at a concentration of 7 mg/l (Christopher and Lane, 1987c). Photolysis was by a light source stated to have had a similar spectral distribution to natural sunlight. Irradiation was over a 4-hour period and dark controls were run to check that the products formed were from photochemical processes only. The control solutions contained only fenthion (average 94%) and fenthion sulfoxide (average 3%).

Throughout the irradiation, the buffer temperature was 22-24°C. Recoveries of radioactivity were between 79 and 103%. A half-life of about 30 minutes was calculated, with extensive degradation of the fenthion.

Fenthion phenol, fenthion sulfoxide, fenthion phenol sulfoxide and fenthion phenol sulfonic acid were major photoproducts. Other photoproducts identified included fenthion sulfone and fenthion oxon sulfone. The radioactivity recovered from the HPLC column in these determinations averaged 90% of that injected.

Organosoluble material accounted for 99.8% of the recovered radiocarbon at time 0 and 87.4% at 4 hours, and water-soluble material for 0.2% and 12.6% respectively.

In a study to investigate the direct photodegradation of organic compounds in water under environmental conditions (Wilmes, 1988), fenthion was reported to have had experimental half-lives of 4 hours in the summer and 11 hours in the autumn compared to half-lives of 3 hours in summer and 14 hours in autumn calculated on the basis of the quantum yield of photodegradation in water in monochromatic or polychromatic light.

## METHODS OF RESIDUE ANALYSIS

Methods to determine fenthion and its oxidative metabolites in animal tissues, milk and plant materials were presented. Earlier methods measured total phosphorus, but fenthion and its intact metabolites are now determined by GLC either individually or collectively as fenthion oxon sulfone. The earlier GLC methods required a hydrolysis step to form the fenthion phenols which were brominated and acetylated before determination. This approach was simplified by the omission of the hydrolysis and derivatization steps and the substitution of oxidation to fenthion oxon sulfone which is determined by GLC with appropriate detectors. Fenthion and its metabolites have also been determined by HPLC.

### Clean-up

Permeation chromatography on a polystyrene gel is used to clean up animal and plant extracts for pesticide determination in the DFG method (Thier and Kirchoff (Ed), 1992). Chromatography is on Bio-Beads S-X3 with equal volumes of cyclohexane and ethyl acetate as eluant. Fenthion, fenthion sulfone, fenthion sulfoxide, fenthion oxon sulfoxide and fenthion oxon sulfone are separated and can be individually determined.

### General analytical methods

Fruits and vegetables. The extraction process of Frehse *et al.* for olives (1962a) was developed for plant material in general (Frehse *et al.*, 1962b). The material was extracted with acetone, the extract filtered and the acetone evaporated. The aqueous residue was extracted with chloroform and the

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chloroform evaporated. The resulting residue was dissolved in petroleum ether, extracted with ethanol, and further cleaned up by chromatography on aluminium oxide and activated carbon columns.

Potassium permanganate was used to oxidize fenthion residues to fenthion sulfone and oxon residues to fenthion oxon sulfone. Fenthion sulfone was determined by infra-red spectroscopy using the sulfone band at  $1325\text{ cm}^{-1}$ . Phosphorus determination by wet ashing and the formation of phosphomolybdenum blue could be used to confirm the result. Limits of detection were stated to be 0.01 mg/kg for cherries, 0.03 mg/kg for beets, 0.06 mg/kg for beet leaves, and 0.07 mg/kg for apples and cole crops. Blank values of 0.7-0.8 mg/kg were found on occasion in leaves. Using  $^{32}\text{P}$ -labelled fenthion, recoveries were about 77-83%. In 1984 recoveries using this method were 40-50% from guavas, 75% from olives and olive oil, and 80% from peas (fortification levels not stated). Recoveries from grapes were 130% at 0.23 mg/kg, 80% at 0.45 mg/kg, 70% at 0.9 mg/kg, and 65% at 1.8 mg/kg (Wagner, 1984).

Fenthion was extracted by a simpler process developed for the pesticide disulfoton in crops with lower chlorophyll content, e.g. potatoes or apples (Niessen and Frehse, 1969a,b). The plant material was macerated with acetone, and the filtered solution mixed with water and extracted with chloroform. The residue from the chloroform extract was dissolved in chloroform/carbon tetrachloride (1:1 v/v), cleaned up on an alumina column and determined colorimetrically as total phosphorus. The method was non-specific and identification of the metabolites was by paper chromatography. Details of recoveries were not provided.

Residues of organophosphorus pesticides containing thioether groups when present as the parent compounds and/or sulfoxides and sulfones were determined in fruits and vegetables as the sulfone by Thier and Zeumer (1987). Residues were extracted with acetonitrile, co-extracted water was removed by the addition of dichloromethane, the solvent was evaporated and the residue dissolved in acetone. Fenthion and fenthion sulfoxide were oxidized to fenthion sulfone with potassium permanganate. This step removed most of the interfering plant material and column clean-up was not routinely needed. The residue was extracted into dichloromethane and determined by gas chromatography on a packed column with a phosphorus-specific alkali flame ionisation detector. Recoveries from apples and cherries at the 0.1 mg/kg level were  $\leq 85\%$  and in a variety of vegetables at the same level also acceptable ( $>70\%$ ). At lower levels (0.05 and 0.01 mg/kg) recoveries were  $>70\%$  in most cases. Recoveries from leeks were 66% at 0.01 mg/kg. Recoveries of the oxon were not reported. Recoveries of fenthion sulfoxide and sulfone from carrots and spinach at 0.1 mg/kg were 90-95%. Individual determinations of the parent, sulfoxide and sulfone were possible if the oxidation step was omitted.

In the regulatory method of The Netherlands (Ministry of Welfare, 1988a) fenthion residues are extracted from agricultural products with ethyl acetate in the presence of sodium sulfate. The filtered extract is analysed without further clean-up by gas chromatography with phosphorus-specific detection. Limits of determination are 0.01-0.05 mg/kg, with recoveries of  $>80\%$ . The method measures fenthion only.

Fenthion residues in fruiting vegetables and subtropical and tropical fruits were determined after post-harvest disinfestation with fenthion (Jorgensen *et al.*, 1995). The sample was macerated with acetone and filtered. Water was added and the acetone evaporated. The aqueous phase was extracted with hexane which was dried over sodium sulfate, reduced to 2 ml, and cleaned up by sweep co-distillation. The resulting hexane solution was analysed for fenthion by GLC using a flame-photometric detector. This method was suitable for capsicum peppers, mangoes, tomatoes and zucchini. Cucumbers and rockmelons did not require the sweep co-distillation clean-up. The limits of determination were 0.01-0.02 mg/kg with the following recoveries: capsicums 83% at 0.2 mg/kg; cucumbers 91% at 0.6 mg/kg and 88% at 1.1 mg/kg; mango pulp 97% at 0.1 mg/kg; mango peel 83%

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at 0.7 mg/kg; rockmelon 91% at 0.6 mg/kg and 99% at 1.2 mg/kg; tomatoes 83% at 0.9 mg/kg; zucchini 87% at 0.5 mg/kg.

**Animal products.** A method to determine fenthion and its unhydrolysed metabolites in animal tissues was reported in the mid-1960s (Anderson and Katague, 1965). The sample was successively extracted with acetone and chloroform. After evaporation of the combined solvents, the residue was partitioned between n-hexane and acetonitrile. The acetonitrile was evaporated and the fenthion residues oxidized with *m*-chloroperbenzoic acid to fenthion oxon sulfone. Hydrochloric acid was used to extract the sulfone which was in turn extracted into chloroform. After washing with an alkaline solution, the chloroform was evaporated and the resulting residue hydrolysed with sodium hydroxide. The phenol formed was extracted from the acidified solution with chloroform, then brominated and acetylated and determined by gas chromatography with an electron-capture detector. The LOD was 0.1 mg/kg. Satisfactory recoveries (means of 71-108%) were generally reported for fenthion, fenthion oxon sulfoxide and fenthion oxon sulfone from cattle brain, fat, heart, kidneys, liver, and muscle after spiking at 0.1 mg/kg. The report noted that owing to the complexity of the process and the number of reactions, results for standards varied by  $\pm 20\%$  and a standard had to be included with each set of samples. In a published version of the method (Anderson *et al.*, 1966) it was stated the inherent sensitivity was better than 0.1 mg/kg. Details of the recoveries of fenthion, its oxon sulfoxide, and its oxon sulfone following some small modifications to the method were provided (Chemagro, 1965e). At 0.01 mg/kg, recoveries were 89-114% for fenthion and the oxon sulfoxide, and 93-105% for the oxon sulfone. Control values were  $<0.0025$  mg/kg (average 0.001 mg/kg).

A modification of the alkaline washing of the chloroform extract obtained after the *m*-chloroperbenzoic acid oxidation step, combined with a lower loading of the chromatographic column, improved the sensitivity and resolution of the method (Katague, 1966). This allowed determination of fenthion and its oxon sulfoxide and sulfone in milk at the 0.01 mg/kg level. Reported average recoveries of fenthion and its oxon sulfoxide and sulfone from animal tissues at 0.1 mg/kg were between 71 and 108%.

In a further development of the Anderson and Katague method, the hydrolysis and derivatization steps were omitted and the fenthion oxon sulfone was determined directly (Thornton, 1967). After the *m*-chloroperbenzoic acid oxidation the oxon sulfone was extracted successively with acid and chloroform, and the chloroform evaporated from the washed extract as before. The residue was dissolved in acetone and determined by gas chromatography with thermionic detection. The LOD was 0.05 mg/kg. Recoveries of fenthion and its oxon sulfoxide and sulfone from cattle brain, heart, kidneys, and muscle were more than 80% at 0.1 mg/kg, but that of fenthion from bovine liver was only 64%. Recoveries of the three compounds from chicken giblets and muscle were in the range 87 to 118% at 0.1 mg/kg. Forty-two other organophosphorus pesticides registered in the USA for use on meat, fish and poultry at that time were stated not to have interfered with the determination when they were added at the 5 mg/kg level.

In the regulatory method used for veterinary products in The Netherlands fenthion residues are extracted with acetone/acetonitrile, with the addition of filter aid. The filtered extract is evaporated to dryness and the residue dissolved in hexane/acetonitrile. Fenthion is determined by gas chromatography with phosphorus-specific detection. The LOD is 0.01-0.04 mg/kg, with recoveries of 66-102%. The method determines only fenthion (Ministry of Welfare, 1988b).

The Netherlands also uses a qualitative TLC method to detect fenthion residues (Ministry of Welfare, 1988c) after extraction with ethyl acetate in the presence of sodium sulfate. An aliquot is applied to a TLC plate and the developed plate is sprayed with a bromine solution, then with a homogenate of bee heads. After incubation at 37°C, the plate is sprayed with 2-naphthyl acetate and Fast Bleu B. The cholinesterase from the bee heads hydrolyses the acetate to 2-naphthol which causes a coloured dye to form. If fenthion is present, the reaction cannot occur and a white spot is seen on a

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pink-violet background.

The separate determination of fenthion and fenthion sulfone residues in sheep liver, kidneys, muscle and subcutaneous fat has been reported by Cameron *et al.* (1995). The sample is macerated with acetonitrile and the decanted acetonitrile shaken with hydrochloric acid solution and hexane. The hexane layer, containing the fenthion, is partitioned with hexane-saturated acetonitrile and the acetonitrile phase evaporated. The residue is redissolved in hexane, cleaned up on a silica Mega Bond Elut cartridge eluted with acetone/hexane, and the solvent evaporated. The residue is dissolved in acetonitrile/water for HPLC determination. The original acid aqueous layer is partitioned with dichloromethane and the dichloromethane evaporated. The residue, containing the sulfone, is cleaned up and transferred to acetonitrile/water for HPLC determination as before. Fenthion is measured at 253 nm and fenthion sulfone at 205 nm. The LOD was 0.02 mg/kg for both fenthion and the sulfone, and the limit of detection 0.005 mg/kg.

Fenthion recoveries from muscle and subcutaneous fat at 0.1 mg/kg were 68.7 and 73.2% respectively, and from liver, kidneys, muscle, and subcutaneous fat at 0.04 mg/kg 60-96.4%, 60.8-89.2%, 68.2-89.8%, and 68.5-84%.

Recoveries of fenthion sulfone from liver, muscle and subcutaneous fat at 0.1 mg/kg were 86.5, 79.6 and 83.1% respectively, and from liver, kidneys, muscle, and subcutaneous fat at 0.04 mg/kg 76.5-89%, 76.9-110%, 74.5-85.7%, and 67.8-82.8%.

A method for eggs and milk (Olson, 1968) is essentially identical to that of Thornton (1967, see above). Fenthion and its metabolites are oxidized to the oxon sulfone which is determined by GLC with an AFID.

The LOD was 0.005 mg/kg. Recoveries from milk and eggs of fenthion, its oxon sulfoxide and its oxon sulfone at 0.01 and 0.005 mg/kg were between 74 and 128%.

### Specific methods

Rice. Olson (1967) used *m*-chloroperbenzoic acid to oxidize fenthion and its metabolites to the oxon sulfone to determine fenthion residues in rice.

After blending the sample with acetone, chloroform was added to the filtered solution and the water which separated discarded. The organic phase was evaporated and the residue oxidized with *m*-chloroperbenzoic acid. The oxidized mixture was extracted with hydrochloric acid and the fenthion oxon sulfone extracted into chloroform. After evaporation of the chloroform, the residue was dissolved in acetone and the sulfone determined by gas chromatography, using a packed column and a phosphorus-sensitive detector. Recoveries at 0.1 mg/kg of fenthion and its oxon sulfoxide and sulfone were 75% or higher. The LOD was 0.05 or lower. The results were confirmed by the use of a column with a more polar phase.

A TLC clean-up procedure was used to determine fenthion residues in harvested rice grains by Takase *et al.* (1971). The sample was extracted with benzene, cleaned up by TLC on alumina and the residues determined by GLC with a flame-photometric detector. The limit of detection for fenthion was 0.001 mg/kg with a recovery of 97% at 0.1 mg/kg. The LOD was stated to be 0.005 mg/kg or better.

Total residues of fenthion in rice grain were determined by GLC as fenthion sulfone and fenthion oxon sulfone after oxidation with potassium permanganate (Takino and Kurogochi, 1995). The method determined the sum of fenthion and its sulfoxide and sulfone (total thiono compounds, total P=S) and the sum of fenthion oxon and its sulfoxide and sulfone (total oxons, total P=O).

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Omission of the oxidation step allowed the determination of fenthion. Samples were extracted with acetone and the acetone extract partitioned with dichloromethane. The dichloromethane phase was evaporated and the residue partitioned between n-hexane and acetonitrile. The acetonitrile phase was evaporated and the residue dissolved in dichloromethane. An aliquot was cleaned up by Florisil column chromatography and fenthion determined by GLC with a flame-photometric detector. The residue left after evaporation of a second aliquot was dissolved in acetone and oxidized with aqueous potassium permanganate. The sulfones formed were partitioned into dichloromethane. The solvent was evaporated, and the residue dissolved in acetone and analysed for fenthion sulfone and oxon sulfone by GLC with a flame-photometric detector. The limits of detection were 0.005 mg/kg for all three determinations.

When untreated rice grains were fortified with fenthion and 5 metabolites at a level of 0.1 mg/kg recoveries through the complete method including the potassium permanganate oxidation step were fenthion 88%, 90%; fenthion sulfoxide 105%, 106%; fenthion sulfone 95%, 98%; fenthion oxon 99%, 100%; fenthion oxon sulfoxide 96%, 100%; fenthion oxon sulfone 88%, 90%. Then fenthion alone was determined at the same level without the oxidation step the recovery was 103%.

Citrus fruit and peel. A modification of the method of Olson (1967) for rice gave recoveries at a 0.1 mg/kg fortification level of 86% from the fruit and 106% from the peel (Wagner, 1982).

Orange (including peel and marmalade). Fenthion residues were determined as the oxon sulfone by a development of the method of Olson (1967) for rice (Ohs, 1991a). The limit of determination was stated to be 0.01 mg/kg and recoveries at that level were 70 and 73% from fruit and 96% from juice. In a later modification (Ohs, 1991b) orange peel was macerated with an acetone/water mixture and filtered. A portion of the filtrate was evaporated and the aqueous residue extracted with dichloromethane before oxidation. Recoveries at 0.01 mg/kg were reported as 70 and 70%. Using the same modification recoveries from orange marmalade were stated to be between 80 and 121%.

Apples, pears. Residues of fenthion were determined as fenthion oxon sulfone in apples, apple juice, purée and pomace, pears and pear preserve by a development of the method of Olson (1967) for rice (Ohs, 1990, 1991b).

Apples were macerated with acetone, the macerate mixed with water and filtered. A portion of the filtrate was extracted with dichloromethane. The extract was dried with sodium sulfate and concentrated to dryness. In a later modification (Ohs, 1991b) apple pomace was macerated with an acetone/water solution and filtered. A portion of the filtrate was evaporated and the aqueous residue extracted with dichloromethane as for apples. After oxidation with *m*-chloroperbenzoic acid the reaction mixture was added to isopropyl ether and thoroughly extracted with hydrochloric acid solution. The acid solution was extracted with dichloromethane, which was dried over sodium sulfate and evaporated. The residue was dissolved in ethyl acetate and analysed by gas chromatography on a megabore column with a flame-photometric detector optimised for phosphorus.

Apple juice was applied to a Chem-Elut cartridge and allowed to react for several minutes before elution with dichloromethane, evaporation of the solvent, and oxidation with *m*-chloroperbenzoic acid.

The limit of determination was stated to be 0.01 mg/kg with the following recoveries.

Apples	90 and 94% at 0.01 mg/kg 73 and 74% at 0.5 mg/kg
Apple purée	78 and 86% at 0.01 mg/kg
Apple juice	84% at 0.01 mg/kg
Apple pomace	79 and 84% (Ohs, 1990)

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	93-124% at 0.01 mg/kg (Ohs, 1991b).
Pears	65 and 75% at 0.01 mg/kg 84 and 87% at 0.5 mg/kg
Pear preserve	86 and 89% at 0.01 mg/kg 123 and 126% at 0.5 mg/kg

Cherries, peaches. The procedure used for apples and pears was extended to cherries (Wagner, 1985) and peaches (Ohs, 1994a). The limit of determination for cherries was stated to be 0.05 mg/kg with a 78% recovery at 0.1 mg/kg.

Recoveries from peaches fortified with fenthion, its oxon, and their sulfoxides and sulfones were 76-86% at 0.01 mg/kg, 74-81% at 0.1 mg/kg, and 74-87% at 0.5 mg/kg. The limit of determination was 0.01 mg/kg.

Olives and olive oil. A colorimetric method for fenthion and its metabolites in olives and olive oil (Frehse *et al.*, 1962a) depended upon the determination of phosphorus after wet-ashing. It required extensive clean-up and was non-specific. The lower limits of detection were reported as 0.05 mg/kg for olives and 0.1 mg/kg for olive oil. Recoveries of 75-80%, using <sup>32</sup>P-labelled mixtures of fenthion and its metabolites were reported.

A modification of the methods of Olson for the determination of fenthion residues in rice (1967) and eggs and milk (1968) as fenthion oxon sulfone was applied to olive oil and olives by Wagner (1979). Olive oil was extracted with acetonitrile and the residue left after evaporation of the solvent dissolved in petroleum ether. The petroleum ether was shaken with acetonitrile and the acetonitrile phase washed with petroleum ether. The oily residue left after evaporation of the acetonitrile was oxidized to fenthion oxon sulfone according to the method of Olson. Quantification was by gas chromatography. Olives were macerated with petroleum ether in the presence of sodium sulfate. After filtration and removal of the solvent the residue was worked up in the same way as olive oil. Recoveries at 0.1 mg/kg were 74% from olives and 94% from the oil.

Residues of fenthion and its oxidized metabolites in olive oil were determined after oxidation with potassium permanganate to fenthion sulfone or oxon sulfone (Lentza-Rizos and Avramides, 1990).

The oil was mixed with hexane saturated with acetonitrile, 1 ml of deionised water was added and the mixture shaken. The acetonitrile layer was mixed with more hexane saturated with acetonitrile and the extraction procedure repeated twice using 1 and 0.5 ml of water. The acetonitrile was evaporated from the combined extracts, the residue dissolved in acetone, and potassium permanganate solution added. The reaction mixture was extracted with dichloromethane, which was then evaporated and the residue dissolved in acetone. Fenthion sulfone and its oxon were determined by gas chromatography on a packed column with a nitrogen-phosphorus detector.

Fenthion recoveries were highest (>99%) when the volumes of added water were small and only if the water was added after the initial mixing with the hexane and acetonitrile. Recoveries of fenthion, its sulfoxide, sulfone and oxon sulfone from the extraction step at 0.1 and 1 mg/kg fortification levels were all greater than 99%. Fenthion oxon and its sulfoxide were not determined because standards were not available but it was noted in the report that the total concentration of P=O metabolites was an insignificant part of the residues in olive oil. For the whole method, recoveries of standards and from oils were >79%. Limits of determination were 0.005 mg/kg for fenthion sulfone and 0.01 mg/kg for the oxon sulfone. Potassium permanganate was chosen as an oxidant because it left the P=S bond intact. The recovery of the fenthion oxon sulfone was high on occasion, reaching 147% from a 1 mg/kg standard and 198% from an oil at 0.1 mg/kg.

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Residues of fenthion, its sulfoxide, sulfone and oxon in olives, olive paste and olive pulp were determined without prior oxidation (Molinari and Fontana, 1992). Olives (pitted or unpitted) were homogenised with acetonitrile, the filtered acetonitrile extract dried on a sodium sulfate column and then extracted with n-hexane saturated with acetonitrile. The acetonitrile was evaporated and the residue dissolved in acetone and cleaned up on an alumina column with ethyl acetate as eluant. After removal of the solvents, the residue was dissolved in ethyl acetate and analysed by gas chromatography on a capillary column with a nitrogen-phosphorus detector with parathion-methyl as an internal standard. The aqueous phase from the original acetonitrile extraction was extracted with methylene chloride and that extract then treated in the same way as the acetonitrile extract. Olive oil was analysed directly after dilution with ethyl acetate. Recoveries were stated to be about 80% with detection limits of 5 to 10 µg/kg for fenthion and the metabolites.

A development of the method of Olson (1967) for rice was applied to the determination of fenthion residues as the oxon sulfone in olives and olive oil (Olson, 1988; Ohs, 1991b). The methods are essentially those of Ohs (1990, 1991b) for apples and pears.

Olives were extracted by two procedures. In the 1988 work they were homogenised with acetonitrile and filtered and the aqueous remainder, after evaporation of the solvent, extracted with dichloromethane. The dichloromethane was dried with sodium sulfate and evaporated. The residue was taken up in petroleum ether and partitioned into acetonitrile. The residue left after evaporation of the acetonitrile was then oxidized. In the 1991 work, the olives were first shaken and then homogenised with acetone/water, the acetone was evaporated and the aqueous remainder extracted with dichloromethane. After drying with sodium sulfate the solvent was removed and the residue partitioned between acetonitrile and hexane. The acetonitrile phase was concentrated and the residue oxidized according to the method of Olson. Olive oil was extracted in both procedures with acetonitrile and the acetonitrile phase shaken with petroleum ether. After evaporation of the acetonitrile, the residue was oxidized as before. Determination was by GLC on a magabore column with flame-photometric detection.

Recoveries in the 1988 work from olives were 81% at 0.01 mg/kg and 83% at 0.1 mg/kg, and from olive oil 86% at 0.01 mg/kg and 81% at 0.1 mg/kg. The lower practical limit of determination was 0.01 mg/kg. In the 1991 work the recoveries from olives were 73-82% at 1.0 mg/kg and from olive oil 81-85% at 0.01 mg/kg. The limit of determination was 0.01 mg/kg.

Soil. Soil was mixed with water and then macerated with acetone. The macerate was filtered and the filtrate extracted with dichloromethane. The extract was dried with sodium sulfate and concentrated to dryness before oxidation with *m*-chloroperbenzoic acid. The residue was determined by gas chromatography. The limit of determination was stated to be 0.05 mg/kg with a 90% recovery at the 0.5 mg/kg level (Wagner, 1985).

Water. Wagner (1985) determined fenthion residues in leachate water, after direct extraction with dichloromethane, by the procedure described for soil. The limit of determination was 0.05 mg/kg with 80% recovery at 0.5 mg/kg.

Fenthion residues were determined in drinking water by the method used for apple juice (Ohs, 1990). The limit of determination was 0.01 mg/kg with recoveries of 90 and 94% at that level.

Fenthion was determined in water by TLC after solid-phase extraction on alkyl-modified silica gel (Burger, 1988). The extract was desorbed with acetonitrile/methanol and the residues determined by gradient elution on HPTLC silica gel plates with detection by derivatization and UV and quantification by comparison with external and internal standards. The method was suitable for a number of classes of pesticides and had a limit of determination of 0.05 µg active ingredient/litre. Recoveries of fenthion at a fortification level of 0.1 µg/l were in the range 59-69%. A modification

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using dichloromethane for elution of the solid-phase extract gave recoveries of 68-93% at 0.05 µg/l (Burger, 1990). No reference was made to the determination of fenthion oxidation products.

### Stability of pesticide residues in stored analytical samples

Olives and olive oil. Olives and olive oil fortified at 0.2 mg/kg with fenthion, its sulfoxide and sulfone and fenthion oxon sulfoxide and sulfone were stored below -20°C for 380 days. The total level of fenthion and the metabolites was equivalent to 1 mg/kg (Ohs, 1993).

Olives were extracted with acetone or acetone/water and olive oil with acetonitrile. Residues were determined according to Ohs (1991b). At intervals the stored samples and freshly prepared spiked samples were analysed and the results compared. Residues in stored olives and oil were respectively 83-115% and 101-114% of those in the freshly spiked samples. The results are shown in Table 12.

Table 12. Stability of fenthion residues in frozen olives and olive oil.

Olives			Oil		
Day	Residues, found/added, %		Day	Residues, found/added, %	
	Stored	Fresh		Stored	Fresh
0	79.0	83.6	0	90.4	88.1
7	65.5	54.0 <sup>1</sup>	6	87.1	82.8
13	75.0	85.2	12	95.2	89.5
27	83.9	89.8	26	96.9	88.3
71	62.0	61.2 <sup>1</sup>	70	84.9	83.7
91	80.6	72.3	89	88.1	84.9
182	68.8	79.7	181	92.6	81.2
335	77.4	93.5	334	92.6	90.2
380	81.3	70.6	379	86.6	81.0

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<sup>1</sup> Although these recoveries were below 70%, they were not reanalysed because of the relatively short time between these and the next storage intervals

The results show that fenthion, its sulfoxide and sulfone and fenthion oxon sulfoxide and sulfone were stable in olives and olive oil when stored at -20°C for 380 days.

Lentza-Rizos and Avramides (1994) stored refined olive oil fortified with 1 mg/kg fenthion at -22 to -18°C and with 2 mg/kg at 17-23°C for a year. The samples were stored in brown bottles. Additional samples of virgin olive oils containing incurred fenthion residues of  $\geq 0.5$  mg/kg taken during monitoring studies were stored in brown bottles at 17 to 23°C and analysed at various intervals between 1 and 11 months.

Samples were extracted by partitioning between petroleum ether and acetonitrile with water. Fenthion and its sulfoxide were determined by gas chromatography on a packed column with a nitrogen-phosphorus detector. Fenthion sulfone and the three oxons were not determined, since it had been concluded that fenthion sulfoxide was the only metabolite of significance in stored olive oil.

The total fenthion residues were stable in both sets of fortified sample over a year of storage. In the samples with incurred residues there was no decrease in the total residue, but a slow conversion of fenthion to fenthion sulfoxide was reported.

The results show that total fenthion residues were stable for a year of storage at both -22 to -18°C and at 17-23°C.

Orange peel and pulp. The stability of fenthion residues in orange peel and pulp during frozen storage has been reported by Ohs (1993). The peel and pulp were each fortified at 0.2 mg/kg with fenthion, its sulfoxide and sulfone, oxon sulfoxide and oxon sulfone and stored below -20°C for over a year.

Samples were extracted with acetone or acetone/water and residues determined by the methods of Ohs (1990, 1991b). At intervals the stored samples and freshly prepared spiked samples were analysed and the results compared (Table 13).

Table 13. Stability of fenthion residues in frozen orange peel and pulp.

Orange peel			Orange pulp		
Day	Residues, found/added, %		Day	Residues, found/added, %	
	Stored	Fresh		Stored	Fresh
0	94.6	93.5	0	61.5	66.4
128	77.3	91.7	7	96.8	105
260	80.2	85.0	143	79.9	88.6
433	109	94.3	275	71.9	81.6
			448	117	87.2

The residues of fenthion and the four metabolites were stable in orange peel and pulp for at least 14 months when stored below -20°C.

## fenthion

Animal products. The stability of fenthion and its oxon sulfone in the presence of animal tissues was evaluated by Olson (1966). Cattle brain, fat, heart, kidneys, liver and muscle (steak) were separately spiked with [ $^{32}\text{P}$ ]fenthion and [ $^{32}\text{P}$ ]fenthion oxon sulfone at about 1-2 mg/kg and the spiked samples stored at  $-18^{\circ}\text{C}$  for 0, 2, and 4 weeks (fenthion) and 0, 2, 4, and 6 weeks (oxon sulfone). The samples were extracted with chloroform and the chloroform and water phases radioassayed. The recoveries of the radiolabel from tissues freshly spiked with [ $^{32}\text{P}$ ]fenthion at 1.86 mg/kg were brain 86.2%; fat 76.7%; heart 94.7%; kidney 91.2%; liver 82.6%; muscle 91.0%. The corresponding recoveries of from tissues freshly spiked with the oxon sulfone at 1.27 mg/kg were brain 88.2%; fat 91.2%; heart 93.3%; kidney 88.9% liver 87.4%; muscle 89.8%.

In the samples stored at  $-18^{\circ}\text{C}$ , the  $^{32}\text{P}$  found in the chloroform and water phases was expressed as a percentage of the total  $^{32}\text{P}$  recovered from the freshly spiked samples. Fenthion was stable in all tissues for at least a month. More than 83% of the radioactivity remained in the chloroform phase over the trial period in all samples except muscle where 68.8% of the radioactivity was in the chloroform phase and 0.9% in the water phase after 2 weeks, although the respective values were 105.1% and 1.1% after 4 weeks. Less than 2.5% of the radioactivity was found in the water phase from any sample except fat at 4 weeks. At that time the distribution reported in the fat was 116.2% chloroform-soluble, 12.3% water-soluble, total activity 128.5% of the original.

Radioactive assay indicated that fenthion oxon sulfone was stable for 6 weeks in brain, heart, muscle and fat stored at  $-18^{\circ}\text{C}$ , with more than 77% of the radiolabel in the chloroform phase. Between 4 and 9% of the radiolabel was in the water phase from all samples except fat at 6 weeks from which 86% was in the chloroform phase and 14.4% in the water phase, a total activity of 100.4%. In the kidneys and liver the reported distributions were as shown below.

<u>Storage time</u>	<u>Kidneys</u>		<u>Liver</u>	
	<u><math>\text{CHCl}_3</math></u>	<u>water</u>	<u><math>\text{CHCl}_3</math></u>	<u>water</u>
0	95.7%	4.3%	71.8%	28.2%
2 weeks	79.5%	5.2%	47.8%	33.4%
4 weeks	68.6%	5.4%	29.5%	40.3%
6 weeks	68.4%	6.8%	22.3%	48.2%

These results indicate marginal storage stability in the kidneys and instability in the liver.

The short-term stability of residues of fenthion and its oxon sulfone in cattle tissues at room temperature has been investigated (Olson, 1973). Fresh muscle, liver and fat were fortified at 1 mg/kg with fenthion or fenthion oxon sulfone and allowed to stand in darkness at room temperature for 6 hours. Samples were taken during that period and residues extracted and determined according to the method of Thornton (1967). Fenthion was stable in all the tissues: after 6 hours 96% of the original concentration remained in the liver and muscle and 83% in the fat. Fenthion oxon sulfone was stable in muscle and fat (88% and 107% after 6 hours), but was rapidly lost from liver with 25% decomposition after one hour and about 85% loss after 4 hours.

In a goat metabolism study (Weber and Ecker, 1992), it was noted that fenthion and its metabolites in samples stored at about  $-20^{\circ}\text{C}$  for an unspecified time underwent further degradation to form more oxidized, demethylated and dephosphorylated product. Details of the study are provided in the "Metabolism and environmental fate" section.

## fenthion

The stability of fenthion and fenthion sulfone residues in frozen tissues from sheep treated with fenthion by topical application was investigated by Cameron *et al.* (1995). Sheep given single applications at 20 mg fenthion/kg bw were killed at various times to allow the determination of fenthion and fenthion sulfone in the tissues. The percentages of fenthion remaining after storage at approximately -20°C for 51 weeks were quite low, for example 16-38% in liver, kidneys, muscle and subcutaneous fat at 0.04 mg/kg and 9-50% at 0.2 mg/kg. Fenthion was less stable in muscle than in the other tissues. These results suggested substantial instability during frozen storage.

The percentages of fenthion sulfone remaining in tissues fortified at the same levels as fenthion and stored at approximately -20°C for 52 weeks were 76-109% at 0.04 mg/kg and 59-76% at 0.2 mg/kg. Fenthion sulfone is considered to be stable for at least 52 weeks when stored under freezer conditions.

In tissues freshly spiked with 0.02, 0.04, 0.1 and 0.2 mg/kg, recoveries of fenthion and fenthion sulfone at all levels were good, with mean recoveries of 77.4-84% of the added fenthion and 82.1-90.4% of fenthion sulfone.

Because the residues in the tissues fortified with fenthion and stored frozen suggested a lack of stability, the tissues from the residue study which had also been stored would have been expected to show a similar loss. A number of stored samples of each tissue from the fenthion residue study were reanalysed. The maximum time between the original sampling and analysis was 40 weeks and the minimum time between the original analysis and reanalysis was 46 weeks.

The ratios of the fenthion residues found on reanalysis to those found originally were variable (about 62-156%), indicating that excessive loss of fenthion had not occurred.

### **Residue definition**

The studies on animal and plant metabolism and environmental fate indicated that the use of fenthion would be expected to result in the presence of fenthion and fenthion oxon and their sulfoxides and sulfones under various conditions. Methods are available to measure these residues readily and accurately to the desired limits of determination, either individually or as fenthion oxon sulfone, which allows relatively easy determination of compliance with MRLs.

The inclusion of the principal oxidative metabolites of fenthion in the residue definition is clearly important because they are more active cholinesterase inhibitors than is fenthion.

No change is recommended to the current Codex definition of the fenthion residue.

### **USE PATTERN**

Fenthion's insecticidal properties derive from contact, stomach and respiratory action as a cholinesterase inhibitor. Fenthion has been used since 1957 for the control of a wide range of insect pests including fruit flies, leafhoppers, leaf miners, leaf-eating larvae and cereal bugs in fruit, vines, olives, vegetables, cotton, tea, sugar cane, beet, and rice. The use pattern also includes the post-harvest disinfestation of fruit, the control of insect pests (e.g. mosquitoes, fleas) in public health situations and animal houses and for the control of animal ectoparasites.

Information on use patterns in crops (Table 14) was provided by the sponsor and the governments of Australia, Canada, New Zealand, Peru and The Netherlands. Table 15 lists the use patterns on animals and in animal houses provided by the sponsor, Australia, Canada and New Zealand.

Table 14. Registered uses of fenthion on crops.

fenthion

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray concn., kg ai/hl	No.	
Alfalfa	Greece	EC	spray	0.5-0.6		1	14
Alfalfa	Peru				0.3		14
Adzuki beans	Japan	EC	spray		0.034 - 0.05	1-4	21
Adzuki beans	Japan	DP	spray	0.6-0.8		1-4	21
Almonds	Greece	EC	spray	1.25	0.06	1	14
Apple	Australia	EC	spray		0.05	m <sup>1</sup>	7
Apple	Australia	EC	spray		0.083	3	7
Apple	Belgium	EC	spray	1.24	0.082	1	21
Apple	France	EC	spray	0.55	0.055	1	15
Apple	France	EC	spray	0.825	0.0825	1-2	15
Beets ( <i>Beta vulgaris</i> )	Belgium	EC	spray	0.825-2.48		1	21
Beets ( <i>Beta vulgaris</i> )	France	EC	spray	0.55		1	15
Beets ( <i>Beta vulgaris</i> )	Spain	EC	spray		0.05 -0.1	1	30
Beets ( <i>Beta vulgaris</i> )	Spain	WP	spray		0.06-1	1	30
Beet, sugar	Austria	EC	spray	0.375		1-2	35
Beet, sugar	Greece	EC	spray	0.75	0.15	1	14
Capsicums	Australia	EC	spray	0.41	0.041	m	7
Capsicums	Australia	EC	flood spray or dip		0.041		na <sup>2</sup>
Cereals	Greece	EC	spray	0.5-1		1	14
Cereals, stored	Peru	SP		0.2-0.3			
Celery	Belgium	EC	spray	0.5	0.082	1	21
Celery	Peru	EC			0.2		14
Cherries (sweet & sour)	Belgium	EC		1.24	0.082	1	21
Cherries (sweet & sour)	France	EC		0.55		1	15
Cherries (sweet & sour)	Germany	EC		0.79	0.052	1	14
Cherries (sweet & sour)	Italy	EC		0.25-0.5	0.025-0.05	1-2	28
Cherries (sweet & sour)	Northern European <sup>3</sup>	EC		0.79	0.05	1	14
Chicory, Witloof	Belgium	EC	spray	0.5	0.082	1	21
Citrus fruits	Algeria	EC	+ bait	0.16		1-2	21
Citrus fruits	Australia	EC	spray		0.04	2	7
Citrus fruits	Australia				0.083	3	7
Citrus fruits	Brazil	EC	+ bait	0.075		1	21
Citrus fruits	Brazil	EC		0.4	0.05	2-6	21
Citrus fruits	Brazil	EW	+ bait	0.075		1	21
Citrus fruits	Brazil	WP	+ bait	0.05		3-8	21
Citrus fruits	Brazil	WP		0.25	0.05	3-8	21
Citrus fruits	Costa Rica	EC		0.5-1.25	0.05-0.12	1-3	15
Citrus fruits	Cuba	EC		0.75	0.075	1-2	15
Citrus fruits	El Salvador	EC		0.5-1	0.05-0.1	1-2	15
Citrus fruits	Greece	EC	ground + bait	0.18	0.3	3-5	14
Citrus fruits	Greece	EC		1.5	0.05	1-2	14
Citrus fruits	Guatemala	EC		0.5-1.25	0.05-0.12	1-3	15
Citrus fruits	Honduras	EC		0.5-1.25	0.05-0.12	1-3	15
Citrus fruits	Italy	EC		0.25-0.5	0.025-0.05	1-2	28
Citrus fruits	Jordan	EC	+ bait	0.015-0.03		1	21
Citrus fruits	Jordan	EC	full cover	1-1.5	0.05-0.075	1	21
Citrus fruits	Kuwait	EC	+ bait	0.015-0.03		1	14
Citrus fruits	Kuwait	EC	full cover	1-1.5	0.05-0.075	1	14
Citrus fruits	Libya	EC	+ bait	0.015-0.03		1	14
Citrus fruits	Libya	EC	full cover	1-1.5	0.05-0.075	1	14
Citrus fruits	Mexico	EC		0.6	0.06	1-2	21

fenthion

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray concn., kg ai/hl	No.	
	(oranges only)						
Citrus fruits	Southern European <sup>3</sup>	EC	full cover	0.5	0.05	2	28
Citrus fruits	Southern European <sup>3</sup>	EC	aerial + bait	0.06	0.86	2	3
Citrus fruits	Oman	EC	+ bait	0.015-0.03		1	14
Citrus fruits	Oman	EC	full cover	1-1.5	0.05-0.075	1	14
Citrus fruits	Peru	EC	+ bait		0.2-0.3	1-3	21
Citrus fruits	Peru	EC	full cover		0.4	1-3	14
Citrus fruits	Portugal (oranges only)	EC		0.55-0.72	0.055-0.072	1-4	14
Citrus fruits	Saudi Arabia	EC	+ bait	0.15-0.3		1	14
Citrus fruits	Saudi Arabia	EC		1-2	0.05-0.1	1	14
Citrus fruits	Spain	EC	aerial + bait	0.06	0.86	1-2	3
Citrus fruits	Spain	EC	ground + bait	0.3	0.3	1-2	30
Citrus fruits	Spain	WP	spray	0.9-1.5	0.06-0.1	1-2	30
Citrus fruits	Spain	WP	+ bait	-	0.3	1-2	30
Citrus fruits	Sri Lanka	EC		0.5-1		1-2	
Citrus fruits	Taiwan	EC	+ bait on single trees	0.02		2-3	na
Citrus fruits	Tunisia	EC	+ bait	3.4		1-2	14
Citrus fruits	UAR	EC	+ bait	0.015-0.03		1	14
Citrus fruits	UAR	EC	full cover	1-1.5	0.05-0.075	1	14
Citrus fruits	Uruguay	EC		1.05	0.058	1-2	20
Coffee bush	Peru	EC			0.2		14
Common bean <sup>4</sup>	Belgium	EC	spray	0.5	0.082	1	21
Common bean <sup>4</sup>	Peru	EC			0.2		14
Cucurbits	Australia	EC	dip		0.041	1	na <sup>2</sup>
Deciduous fruit	Australia	EC	spray		0.04	2 & 5	7
Deciduous fruit	Australia	EC	spray		0.052	m	7
Egg plant	Australia	EC	spray	0.4	0.04	m	7
Figs	Australia	EC	spray		0.04	2	7
Forage crops & grasses, rangeland (see also Pastures)	Canada	EC		0.055-0.11		as needed, 3 weeks between applns.	3 day withholding period
Fruit	Austria	EC	spray	1.12	0.075	1-2	35
Fruit	Belgium	EC	spray	1.24	0.082	1	21
Fruiting vegetables other than cucurbits	Australia	EC	dip		0.041	1	na <sup>2</sup>
Fruit trees	Australia	EC	spray		0.041		7
Garlic	Peru	EC			0.2		14
Grapes	Australia	EC	spray		0.04	2 & m	7
Grapes	Austria	EC	spray	0.75	.075	1-2	35
Grapes	Spain	EC	spray	0.35-0.7	0.05-0.1	1-2	30
Grapes	Spain	EC	spray	1	0.1	1	14-21
Grapes	Spain	WP	spray	0.3	0.3	1-2	14-21
Grapes	Spain	WP	spray		0.3	1-2	30
Guava	Australia	EC	spray		0.041	m	14
Hops	Belgium	EC	spray	4.12	0.082	1	21
Kiwifruit	Australia	EC	spray		0.041	m	7
Leeks	Belgium	EC	spray GIS	0.5	0.082	1 & 2-3	21
Loquats	Australia	EC	spray		0.04	m	7
Lychees	Australia	EC	spray		0.05	m	7

fenthion

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray concn., kg ai/hl	No.	
Olives	Algeria	EC	+ bait	0.21-0.32		1	21
Olives	Croatia	EC		0.5-0.75	0.05-0.75	3	28
Olives	France	EC	spray	0.55	0.055	1-2	21
Olives	Greece	EC	ground + bait	0.07	0.3	3-5	21
Olives	Greece	EC	aerial + bait	0.09	0.9	3-5	21
Olives	Greece	EC		0.75	0.05	2	30
Olives	Italy	EC	spray	0.25-0.5	0.025-0.05	2-3	28
Olives	Jordan	EC		0.75-1.5	0.05-0.1	1	30
Olives	Kuwait	EC	+ bait	0.015-0.03		1	21
Olives	Kuwait	EC		0.75-1.5	0.05-0.1	1	21
Olives	Libya	EC	+ bait	0.005-0.03		1	21
Olives	Oman	EC	+ bait	0.015-0.03		1	21
Olives	Oman	EC		0.75-1.5	0.05-0.1	1	21
Olives	Portugal	EC	for cannery	0.55	0.055	1	21
Olives	Portugal	EC	direct consumption	0.55	0.055	1-2	42
Olives	Saudi Arabia	EC	+ bait	0.15-0.3		1	21
Olives	Slovenia	EC		0.5-0.75	0.05-0.075	1-3	28
Olives	Southern European <sup>3</sup>	EC	ground + bait	0.07	0.3	3-5	21
Olives	Southern European <sup>3</sup>	EC	aerial + bait	0.09	0.9	3-5	21
Olives	Southern European <sup>3</sup>	EC	full cover	0.25-0.5	0.025-0.05	3	28
Olives	Southern European <sup>3</sup>	EC	early appln.	1.25	0.08	1-2	90
Olives	Tunesia	EC	+ bait	0.56 - 0.83		1	21
Olives	Turkey	EC		0.52- 0.79	0.05-0.078	1-3	21
Olives	UAR	EC	+ bait	0.015-0.03		1	21
Olives	UAR	EC		0.75-1.5	0.075-0.15	1	21
Olives	Yugoslavia	EC		0.5-0.75	0.05-0.075	1-3	21
Onions, Bulb	Belgium	EC	spray	0.5	0.082	1 and 2-3	21
Onions, Bulb	Peru	EC			0.2		14
Orange	Portugal	EC	spray	0.55-0.72	0.055-0.072	1-4	14
Orange	Mexico	EC		0.6		1-2	21
Papaws	Australia	EC	spray		0.041	m	14
Pastures	Australia	EC	spray	0.28		m	7
Pastures (See also Forage crops)	Australia	EC	spray	0.55		m	7
Pea, garden	Belgium	EC	spray	0.74	0.082	1	21
Peach	Belgium	EC	spray	1.24	0.082	1	21
Peach	Brazil	EC		0.5	0.05	3-8	21
Peach	France	EC	spray	0.55	0.055	1-2	15
Peach	France	EC	spray	0.82	0.082	1-2	15
Peach	Greece	EC	spray	1.25	0.05	1	14
Peach	Israel	EC		0.5 -1.5	0.05-0.15	1	21
Peach	Italy	EC	spray	0.25 -0.5	0.025 -0.05	1-2	28
Peach	Peru	EC		0.5-1	0.05-0.4	1-4	14
Peach	Portugal	EC	spray	0.55	0.055	1-3	14
Peach	South Africa	EC		1.4 -1.75	0.04-0.05	1-3	10
Peach	Southern European <sup>3</sup>	EC		0.5-1.125	0.03-0.075	2	28
Peach	Spain	EC	spray	1 -1.12	0.1-0.112	1-2	14

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Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray concn., kg ai/hl	No.	
Peach	Turkey	EC		2.4	0.08	1-2	21
Peach	Zimbabwe	EC		0.6-0.9	0.03-0.045	1-3	10
Pear	Australia	EC	spray		0.052	m	7
Pear	Australia	EC	spray		0.083	2 & 3	7
Pear	Belgium	EC	spray	1.24	0.082	1	21
Pepinos	Australia	EC	spray		0.041	m	7
Persimmon	Australia	EC	spray		0.04 & 0.05	5 & m	7
Pistachio	Greece	EC	spray	0.75	0.05	1-2	14
Plums (including prunes)	Belgium	EC	spray	1.24	0.082	1	21
Pome fruit	Spain	EC	spray	0.75-1.5	0.05-0.1	1-2	30
Pome fruit	Spain	EC	spray	0.75-1.5	0.05-0.1	1-2	30
Pome fruit	Spain	EC	spray + bait		0.05-0.3	1-2	30
Pome fruit	Spain	WP	spray	0.9-1.5	0.06-0.1	1	30
Pome fruit	Spain	WP	+ bait		0.06-0.1	1	30
Potato	Belgium	EC	spray	0.33	0.082	1	21
Potato	Japan	EC	spray		0.05	1-2	7
Prunus laurocer	Belgium	EC	spray	1.24	0.082	1	21
Quince	Australia	EC	spray		0.083	2 & 3	7
Rape	Austria	EC	spray	0.3		1	35
Rape	Belgium	EC	spray	0.5	0.082	1	21
Rice	Colombia	EC		0.38-0.75		1-3	14
Rice	Costa Rica	EC		0.5-1		2-3	15
Rice	El Salvador	EC		0.3-0.6		1	15
Rice	Guatemala	EC		0.5-1.4		1-2	15
Rice	Japan	EC		0.375-0.75	0.034-0.05	1-2	30
Rice	Japan	WP		0.4-0.75	0.04-0.05	1-2	30
Rice	Japan	GR		1.5-2		1-2	45
Rice	Japan	DP		0.6-0.8		1-2	21
Rice	Kuwait	EC		0.4-0.75		1	14
Rice	Libya	EC		0.4-0.75		1	14
Rice	Malaysia	EC		0.3-0.4		1-3	14
Rice	Mexico	EC		0.6-1		1-2	30
Rice	Panama	EC		0.7-1		1-2	15
Rice	Oman	EC		0.4-0.75		1	14
Rice	Peru	EC	Spray	0.4-0.75	0.2-0.4	1-2	15
Soya bean	Japan	EC	spray		0.034- 0.05	1-3	45
Soya bean	Japan	DP	spray	0.6-0.8		1-3	45
Stone fruit	Australia	EC	spray		0.041	2 & 3	7
Stone fruit	Australia	EC	spray		0.041-0.052	m	7
Stone fruit	Greece	EC	spray	1.25	0.05	1	14
Stone fruit	Spain	EC	spray	0.75-1.5	0.05 -0.1	1-2	30
Stone fruit	Spain	EC	spray	1-1.125	0.05-0.1	1-2	30
Stone fruit	Spain	EC	spray + bait		0.05-0.3	1-2	30
Stone fruit	Spain	WP		1-1.125	0.1	1-2	30
Stone fruit	Spain	WP		0.9-1.5	0.06-0.1	1-2	30
Stone fruit	Spain	WP	+ bait	1-1.12	0.3	1-2	30
Sub-tropical/tropical fruit, inedible peel	Australia	EC	spray		0.041	5	7
Sub-tropical/tropical fruit, inedible peel	Australia	EC	dip		0.041	1	na (5)
Sugar cane	Japan	EC	drench soln.		0.05 -0.1	1-2	200
Sugar cane	Japan	GR	add to soil	4.5		1-2	200
Sweet potato	Japan	GR	add to soil	4.5		1-2	30

fenthion

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray concn., kg ai/hl	No.	
Sweet potato	Japan	DP	spray	0.6-0.8		1-2	45
Tomato	Australia	EC	spray	0.41	0.041	m	7
Tomato	Peru	EC			0.2		14
Useful plants	Belgium	EC	spray		0.082	1	21
Vegetables	Belgium	EC	spray	0.74	0.082	1	21
Yam	Japan	GR	Add to soil	4.5		1-3	45 days

<sup>1</sup> Multiple: repeat as necessary

<sup>2</sup> Not applicable, quarantine treatment only

<sup>3</sup> Use pattern as proposed by sponsor

<sup>4</sup> Pods and/or immature seeds

Information on GAP for uses on ornamental plum, roses, tobacco, and weeping willow was provided but is not included in the Table.

The sponsor advised that the use of fenthion on the following crops would no longer be supported in EU Member States: alfalfa, almonds, beans, beet (fodder and sugar crops), celery, cereals, chicory, grapes, hops, leeks, onions, peas, pistachio, pome fruit, potatoes, rape, stone fruit except cherries and peaches, tobacco and vegetables. Uses on cherries, citrus fruits, olives and peaches (and ornamentals) were the only ones which would to be retained. The use patterns to be proposed are included in Table 14.

Table 15. Registered uses of fenthion on animals, animal houses and other buildings.

Animal or building treated (pest controlled)	Country	Form <sup>1</sup>	Rate, mg ai/kg bw	No. of treatments	Withholding period, days
Cattle (grub)	Algeria	PO	5-10	1 <sup>2</sup>	14 (edible tissues) 5 (milk)
Cattle, non-lactating (lice)	Argentina	SO	8	1 (additional if needed)	28 (edible tissues)
Cattle (lice)	Australia	PO, SA	~ 4-10	1 (additional if needed)	10 (meat) No milk WHP
Cattle (cattle grub, lice)	Belgium	PO, SA	10 (PO) 5 (SA)	1 <sup>2</sup>	14 (edible tissue) 5 (milk)
Cattle, non-lactating (Dermatobia, Myiasis, lice)	Brazil	SO	10.5-15	1 (additional if needed)	14 (edible tissues)
Cattle, beef & non-lactating (lice, cattle grub)	Canada	SN	5-8	1-2	45 days (spot-on) For the PO 35 days for a single treatment, 45 days if two treatments for lice are used.
Cattle (lice)	Chile	SO	8	1 (additional if needed)	14 (edible tissues) 5 (milk)
Cattle (Dermatobia, lice, biting flies)	Colombia	SO	5-16	1 (additional if needed)	Not stated
Cattle, non-lactating (Dermatobia, lice, biting flies)	Costa Rica	SO	5-16	1 (additional if needed)	15 (edible tissues)
Cattle, non-lactating (Dermatobia, lice, biting flies)	Dominican Republic	SO	5-16	1 (additional if needed)	15 (edible tissues)
Cattle (cattle grub, lice)	Eire	SA	8	1 <sup>2</sup>	21 (edible tissue) 5 (milk)
Cattle (cattle grub, lice)	France	PO, SA	5	1 <sup>2</sup>	14 (edible tissue) 5 (milk)
Cattle, non-lactating (Dermatobia, lice, biting flies)	Guatemala	SO	5-16	1 (additional if needed)	15 (edible tissues)

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Animal or building treated (pest controlled)	Country	Form <sup>1</sup>	Rate, mg ai/kg bw	No. of treatments	Withholding period, days
Cattle, non-lactating (Dermatobia, lice, biting flies)	Honduras	SO	5-16	1 (additional if needed)	15 (edible tissues)
Cattle, non-lactating (Dermatobia, lice, grub)	Mexico	SO	5-16	1 (additional if needed) <sup>2</sup>	14 (edible tissues)
Cattle, non-lactating (lice)	New Zealand	PO	Up to 4.5	as needed	21
Cattle, non-lactating (Dermatobia, lice, biting flies)	Nicaragua	SO	5-16	1 (additional if needed)	15 (edible tissues)
Cattle (lice, Myiasis)	South Africa	SO	5	1 (additional if needed)	14 (edible tissues) 7 (milk)
Cattle (grub)	Turkey	SO, PO	5-10	1 <sup>2</sup>	14 (edible tissues) 5 (milk)
Cattle (cattle grub, lice)	UK	PO	10	1 <sup>2</sup>	21 (edible tissues) 5 (milk)
Cattle, non-lactating	Uruguay	SO	8	1 (additional if needed)	28 (edible tissues)
Cattle, beef (grub, lice, biting flies)	USA	SO, PO	5.5-11	1 (additional if needed 35 days later)	45 (edible tissues)
Cattle (Dermatobia, lice, biting flies)	Venezuela	SO	5-16	1 (additional if needed)	not stated
Pigs (lice)	Belgium	SA	5	1 <sup>2</sup>	8 (edible tissue)
Swine (hogs, pigs) (lice)	Canada	SN	9.75	1	14
Sheep (lice, Myiasis)	South Africa	SO	5	1 (additional if needed)	14 (edible tissues) 7 (milk)
Farm buildings, piggeries, poultry houses (insects)	Canada	EC	1.5 kg ai/hl	As necessary	1.5
Rooms & storage sheds	Peru	SP	200-400 kg ai/ha		

<sup>1</sup> PO = pour-on; SA = spot-on; SN = solution; SO = spreading oil; SP = water soluble powder

<sup>2</sup> A repeat treatment may be necessary 10-14 days later to eradicate lice which have hatched from eggs present at first treatment

## RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting was supplied with residue data from supervised trials on various fruits and vegetables, cattle, sheep, and pigs. Data on residues in milk were also provided. Underlined residues in the Tables are from treatments considered to be according to GAP.

### Plant commodities

Data were supplied on pre-harvest applications to cherries, mandarins, olives, oranges, peaches and rice, and on post-harvest trials on capsicums, cucumbers, mangoes, rockmelons, tomatoes and zucchini.

Citrus fruits. Results from 8 residue trials conducted in Spain on mandarins as single ultra-low-volume or low-volume aerial applications with bait were presented. The results are shown in Table 16. Plot sizes, when reported, ranged between 1000 and 10000 sq m. Fruit were sampled at or near maturity.

Residues were not detectable in the pulp (<0.02 mg/kg in 1981, <0.01 mg/kg in 1992). Residues in the whole fruit were calculated from those in the pulp and peel. Blank values on the peel at 3 days PHI were all <0.01 mg/kg.

The 1992 trials were considered to be within Spanish GAP for the aerial application of fenthion with bait to citrus fruits (0.06 kg ai/ha with a 3-day PHI and 1 or 2 applications).

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Table 16. Total residues of fenthion in mandarins from supervised trials in Spain using a single low-volume aerial application of a 500 EC formulation.

Year, variety	Application		PHI, days	Residues, mg/kg, means		Report No., method, LOD
	kg ai/ha	kg ai/hl		Whole fruit	Peel	
1969 Satsuma	0.15 aerial + bait	0.75	0	<0.1	0.25	0329-69 Determined as P 0.1 mg/kg
7			<0.1	<0.1		
14			<0.1	<0.1		
1969 Clementine	0.15 aerial + bait	0.75	0	0.25	0.73	0360-69 GLC 0.05 mg/kg
7			0.22	0.60		
14			0.13	0.29		
28			0.08	0.20		
1969 Satsuma	0.15 aerial + bait	0.75	0	0.39	1.25	0361-69 GLC 0.05 mg/kg
7			0.20	0.34		
14			0.12	0.19		
28			0.04	0.14		
1981 Satsuma	0.19 aerial + bait	0.94	0	0.39	1.31	5000-81 Olson 1982 0.02 mg/kg
14			0.41	1.42		
21			0.26	0.9		
28			0.13	0.48		
35			0.10	0.31		
1981 Satsuma	0.094 aerial + bait	0.47	0	0.35	1.16	5001-81 As for 5000-81
14			0.27	0.96		
21			0.13	0.48		
28			0.15	0.48		
35			0.1	0.31		
1992 <sup>1</sup> Clausellina	0.052 aerial + bait	0.74	0	0.02	0.07	RA-2101/92 205842 Bayer No. 0584/92 Olson 1991 & Ohs 1991 0.01 mg/kg
3			<u>0.02</u>	0.08		
13			<u>0.02</u>	0.11		
1992 <sup>1</sup> Clausellina	0.052 aerial + bait	0.74	0	0.09	0.38	205850 Bayer No.0585-92 As for RA-2101/92
3			<u>0.04</u>	0.20		
13			<u>0.21</u>	1		
1992 <sup>1</sup> Clausellina	0.052 aerial +bait	0.74	0	0.03	0.10	205869 Bayer No. 0586-92 As for RA-2101/92
3			<u>0.04</u>	0.18		
13			<u>&lt;0.01</u>	0.02		

<sup>1</sup> Ohs and Walz-Tylla, 1993. Day 3 was the regular day of harvest

Results from 7 residue trials on oranges in Spain as single low-volume or ultra-low-volume aerial applications with bait were presented (Table 17). Fruit were harvested either at or several weeks before maturity. In the pre-1992 trials the area treated was not recorded or was small (100 sq. m.). In the 1992 trials the treated areas were 4000 sq m.

Table 17. Total residues of fenthion in oranges from supervised trials in Spain following a single treatment with an EC formulation.

Year, variety	Application		PHI, days	Residues, mg/kg, means		Report No., Method, LOD
	kg ai/ha	kg ai/hl		Whole fruit	Peel	
1969 Navel Tompson	0.15 aerial + bait	0.75	0	<0.1	0.20	0328-69 Determined as P, 0.1 mg/kg
7			<0.1	0.15		
14			<0.1	0.20		
1969 Navel	0.15 aerial + bait	0.75	0	0.04	0.12	0357-69 GLC 0.05 mg/kg
7			0.06	0.13		

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Year, variety	Application		PHI, days	Residues, mg/kg, means		Report No., Method, LOD
	kg ai/ha	kg ai/hl		Whole fruit	Peel	
			14	0.02	0.07	
			28	0.02	0.05	
1990 Navelina	0.052 aerial + bait	0.74	0	<0.01	<0.01	0496-90 Olson 19981 & Ohs, 1988 0.01 mg/kg
			14	<u>&lt;0.01</u>	<0.01	
1990 Navelina	0.052 aerial	0.74	0	0.03	0.13	0736-90 As for 0496-90
			14	<u>&lt;0.01</u>	0.02	
1992 <sup>1</sup> Valencia Late	0.052 aerial + bait	0.74	0	0.75	2.8	RA-2101 /92 205818
			3	<u>0.18</u>	0.69	Bayer No. 0581-92 As for
			14	<u>0.10</u>	0.34	496-90
1992 <sup>1</sup> Valencia Late	0.052 aerial + bait	0.74	0	0.98	3.4	205826 Bayer No. 0582-
			3	<u>0.15</u>	0.56	92. As for 496-90
			14	<u>0.11</u>	0.42	
1992 <sup>1</sup> Valencia Late	0.052 aerial + bait	0.74	0	0.09	0.27	205834 Bayer No. 0583-
			3	<u>0.05</u>	0.14	92. As for 496-90.
			14	<u>0.04</u>	0.12	

<sup>1</sup> Ohs and Walz-Tylla, 1993. Day 3 was the regular day of harvest

In the 1990 and 1992 trials the residues in the pulp were all <0.01 mg/kg. In the 1992 trials, residues in the whole fruit were calculated from those in the pulp and peel. Blank values in the 1990 trials were <0.01 mg/kg. In the 1992 trials, the orange peel control values were high (0.80, 0.05, and 0.38 mg/kg at 3 days PHI; 0.19, 0.42, and 0.32 mg/kg at 14 days). These high values were ascribed to the control plots between treated bands being contaminated by aerial drift. Residues in the pulp of control samples were all <0.01 mg/kg. Calculated whole fruit residues in the controls at a 3-day PHI were 0.22, 0.02, and 0.14 mg/kg. Although reported, these control values were not subtracted from the values measured in the treated samples. The 1990 and 1992 trials were again considered to be within Spanish GAP for the aerial application of fenthion to citrus fruit.

Cherries. Ten supervised trials were carried out in Germany. The results are shown in Table 18.

Table 18. Total residues of fenthion in cherries from supervised trials in Germany using single applications of a 500 EC formulation (1968-9) and a 550 EC formulation (1978-9).

Year, variety	Application		PHI, days	Residues, mg/kg, means	Reference, Method, LOD
	kg ai/ha	kg ai/hl			
1968 Sweet cherry	1 <sup>1</sup> (1.25 g/tree)	0.05	0	5.05	89-68
			7	0.95	Determined as P, 0.05 mg/kg
			10	0.55	
			14	<u>1.0</u>	
1968 Sweet cherry	1 <sup>1</sup> (1.25 g/tree)	0.05	0	4.75	90-68
			7	0.95	As for 89-68
			9	0.3	
			14	<u>0.55</u>	
1968 Sour cherry	1 <sup>1</sup> (1.25 g/tree)	0.05	0	4.6	91-68
			7	0.65	As for 89-68
			10	0.5	
			14	<u>0.5</u>	
1968 Sour cherry	1 <sup>1</sup> (1.25 g/tree)	0.05	0	5.4	92-68
			7	1.25	As for 89-68
			10	0.9	
			14	<u>0.6</u>	

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Year, variety	Application		PHI, days	Residues, mg/kg, means	Reference, Method, LOD
	kg ai/ha	kg ai/hl			
1969 Schwarze Knorpel	15 g/tree	30 l/tree (0.05 kg ai/hl)	1	4.8	235-69 As for 89-68
			8	0.6	
			14	<u>0.8</u>	
1969 Schwarze Knorpel	7.5 g/tree	30 l/tree (0.025 kg ai/hl)	1	2.4	236-69 As for 89-68
			8	0.8	
			14	0.35	
1978 Schatten Morelle	1.1	0.05	0	4.2	5000-78 Olson <sup>2</sup> 0.01 mg/kg
			4	1.8	
			7	0.99	
			14	<u>0.32</u>	
			21	<u>0.38</u>	
1978 Schatten-morelle	1	0.05	0	4.0	5001-78 As for 5000-78
			4	1.4	
			7	0.66	
			14	<u>0.65</u>	
			21	<u>0.35</u>	
1978 Heimanns Rubin-weichsel	1	0.1	0	5.6	5002-78 As for 5000-78
			4	4.1	
			7	1.0	
			14	1.1	
			21	0.47	
1979 Schatten-morelle	0.82	0.06	0	0.03	5000-79 Only fenthion oxon sulfone determined
			5	0.02	
			8	<0.01	
			15	<0.01	
			21	<0.01	

<sup>1</sup> Application rates were 1.25 g ai/tree, calculated by sponsor to be approximately 1 kg ai/ha. 2.5 litres were applied per tree so that the concentration was 0.05 kg ai/hl

<sup>2</sup> Method described as: T.J. Olson modified laboratory method (I 127): Chemagro Report Nr 20 417, 1968

The number of trees treated in the trials was between 4 and 8 except in trial number 5000-79 where 0.5 ha was treated.

Single applications were used in all trials. Spray dilutions were 0.05 kg fenthion/hl (7 trials), 0.06 kg/hl (one trial), 0.1 kg/hl (one) and 0.025 kg/hl (one).

Trials at 0.05 kg ai/hl complied with the registered German use pattern of a single application at 0.05 kg fenthion/hl with a 14-day PHI. The 1979 trial (5000-79, conducted at 0.06 kg ai/hl) was excluded as only fenthion oxon sulfone was determined.

In the trials according to German GAP, the initial residues were about 5 mg/kg which decreased to about 0.3-1 mg/kg after 14 days. Residues at 21 days were 0.35 and 0.38 mg/kg. In the 1979 trial (5000-79) in which a normal application rate was used but only the oxon sulfone was determined, residues were low from day 0 and not detectable by day 8. This showed that this metabolite made a negligible contribution to the residue.

Peaches. Supervised trials were carried out in Spain (four trials) and South Africa (one trial). All were according to GAP (0.04-0.05 kg ai/hl, 1-3 sprays, 10-day PHI in South Africa, 0.1-0.112 kg ai/hl, 1-2 sprays, 14-day PHI in Spain, although there were no results at 10 days from South Africa and only one at 14 days from Spain. The results are shown in Table 19.

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In the Spanish trials the areas treated were between 75 and 120 sq m. Spraying was by a power-operated knapsack sprayer. In the 1993 trials control values were all less than 0.01 mg/kg except one of 0.02 mg/kg which was attributed to spray drift on to the control trees. Residues were all calculated from replicate analyses of the pulp and peel. A fenthion half-life of 1.6 days was calculated in 1993.

Table 19. Total residues of fenthion in peaches from supervised trials in Spain and South Africa with one or two applications of a 500 EC formulation.

Country, year, variety	Application			PHI, days	Residues, mg/kg	Report, Method, LOD
	No.	kg ai/ha	kg ai/hl			
South Africa 1986 Variety not stated	1	1.88	0.06	0 7 14 21 29 35	4.8 2.2 1.1 0.44 0.23 0.11	311/ 88946/ C194 Frehse <i>et al.</i> , 1962b 0.05 mg/kg
Spain 1990 Agosto	2	1	0.1	0 20	1.7 b0.40 <u>0.48</u> b0.35	0342-90 Ohs <sup>1</sup> 0.01 mg/kg
1993 July Lady	2 <sup>2</sup>	1.125	0.075	0 0 10 14 21 28	0.30 <sup>3</sup> 0.99 b<0.01 0.20 <u>0.16</u> <u>0.08</u> <u>0.05</u> b<0.01	304301 (Bayer 0430-93) Ohs, 1994b 0.01 mg/kg
1993 Caterine	2 <sup>2</sup>	1.05, 1.125	0.075	0 28	2.3 b<0.01 <u>0.12</u> b<0.01	304328 (Bayer 0432-93) As for 304301
1993 Laura	2 <sup>2</sup>	1.125	0.075	0 24	1.9 b<0.01 <u>0.24</u> b<0.01	304336 (Bayer 0433-93) As for 304301

<sup>1</sup> Method described as Ohs, P. MR 20417, 27 April 1967 (revised: 11 September 1984) which the sponsor advised was the reference Ohs, 1990

<sup>2</sup> 21 days between applications

<sup>3</sup> Before last treatment

b = blank

Olives. The results of supervised trials in Greece, Italy and Spain are shown in Table 20.

In Spain the areas treated were 20 ha in trial 314-69 and 70 ha in trial 196-70, in Greece 600 hectares were sprayed in the 1984 trial and 2000 sq m in the 1988 trials, and in Italy 4000 sq m in trial 279-90, 640 sq m in trial 712-90, and 10 plants in trial 713-90.

Table 20. Total residues of fenthion in olives from supervised trials in Spain, Greece and Italy.

Country, year, form., variety	Application			PHI, days	Residues, mg/kg, means, in fruit	Report no., Method of analysis, LOD
	No.	kg ai/ha	kg ai/hl			
Spain 1968 50 EC Zorzaleno	2	0.3 ULV, ground, full cover + bait	1.5	4 10	0.25 0.1	381A-68 Determined as P 0.1 mg/kg
Spain 1968 50 EC Zorzaleno	3	0.3 ULV, ground, full cover + bait	1.5	14 28	<0.1 <u>&lt;0.1</u>	381A-68-1 As for 381A-68
Spain 1969 50 EC Farga	2	0.15 ULV, aerial + bait	0.75	1 8 15	<0.05 <0.05 <0.05	314/69 Determined as P 0.05 mg/kg

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Country, year, form., variety	Application			PHI, days	Residues, mg/kg, means, in fruit	Report no., Method of analysis, LOD
	No.	kg ai/ha	kg ai/hl			
				30 37 100	<0.05 <0.05 <0.05	
Spain 1970 50 EC Gordal	1	0.19 ULV, aerial + bait	0.75	0 7 30 88	0.2 0.25 <0.05 <0.05	196-70 As for 314/69
Greece 1984 500EC Konservolia Stilidas	4	0.09 ULV, aerial + bait	1.8	0 7 14 21	0.12 0.23 <0.1 <0.1	5000-84 Olson 1967 0.1 mg/kg
Greece 1988 500 EC Amphissis	3	0.09, ULV, aerial	0.97	0 8	0.16 0.05	0032-88 Olson 1988 0.01 mg/kg
Greece 1988 500 EC Amphissis	4	0.09 ULV, aerial	0.97	0 26	0.16 <u>0.04</u>	0033-88 As for 0032-88
Greece 1988 500 EC Amphissis	3	0.09, ULV aerial	0.97	0 27	0.02 <u>0.01</u>	0034-88 As for 0032-88
Italy 1990 250 EC Coratina	2	0.5 ground, full cover	0.05	0 14 28	1.7 0.92 <u>0.87</u>	0279-90 Ohs 1991 0.01 mg/kg
Italy 1990 250 EC Leccino	2	0.5 ground, full cover	0.05	0 14 28	0.86 0.39 <u>0.26</u>	0712-90 As for 0279-90
Italy 1990 250 EC Nocellara del Belice	2	0.5 ground, full cover	0.05	0 14 28	0.93 0.84 <u>0.36</u>	0713-90 As for 279-90

## fenthion

In the 1968 Spanish trials the spray concentration was 1.5 kg ai/hl which is higher than any reported GAP, but since the trials were ULV at 0.3 kg ai/ha they were evaluated against Italian GAP of 0.25-0.5 kg ai/ha with 2-3 applications and a 28-day PHI. However, trial 381A-68 did not include results at 28 days and was not considered further. The aerial applications in Spain in 1969 and 1970 were not considered to meet any European GAP for aerial application as the 0.15 and 0.19 kg ai/ha rates used are approximately twice the registered Greek and proposed Southern European aerial GAP rate of 0.09 kg ai/ha.

The Greek trials were according to Greek GAP for aerial application (3-5 treatments at 0.09 kg ai/ha with a 21-day PHI) except that in trial 0032-88 samples were taken only at 0 and 8 days.

The Italian trials were with ground applications according to Italian GAP (2-3 treatments at 0.025-0.05 kg ai/hl (0.25-0.5 kg ai/ha) with a 28-day PHI).

One of the Spanish, three of the Greek and the three Italian trials were conducted according to relevant GAP.

Blank values were all <0.01 mg/kg in the 1988 Greek trials and the Italian trials 0712-90 and 0713-90. In trial 0279-90 the blank was 0.23 mg/kg at day 0 and 0.11 mg/kg at days 14 and 28.

A published report of a supervised trial in Italy (Cabras *et al.*, 1993) in which olives were sprayed 3 or 5 times at a rate of 0.2 kg ai/hl (approximately equivalent to 0.075 or 0.1 kg ai/ha) was supplied. Olives were sampled at 0, 11, 20,34 and 54 days after the last treatment and analysed for fenthion, fenthion oxon, and their sulfoxides and sulfones by GLC with a nitrogen-phosphorus detector. Limits of determination were between 0.002 and 0.01 mg/kg. The results were presented as means with standard deviations. The trial did not comply with Italian GAP but reflected the current Greek GAP for ground applications with bait (0.3 kg ai/hl (0.07 kg ai/ha), 21-day PHI, 3-5 applications). As the original data were not supplied, the results were not evaluated further. Table 6 shows the means and standard deviations reported. Table 44 gives the residues in processed olive products.

Rice. GAP for rice in Japan requires 1 or 2 applications of 2% DP at 0.6-0.8 kg ai/ha, PHI 21 days; 50% EC at 0.375-0.75 kg ai/ha, PHI 30 days; 5% GR at 1.5-2.0 kg ai/ha, PHI 45 days, or 40% WP at 0.4-0.75 kg ai/ha, PHI 30 days.

Results of trials in Japan between 1969 and 1978, all approximating GAP, are given in Table 21.

Residues were determined in hulled rice. Three of the trials included analyses of polished rice grains and rice bran.

Total residues of fenthion and its oxidative metabolites were determined by GLC with either an AFID or FPD. The limits of determination were  $\leq 0.001$  mg/kg with recoveries of 97% at 0.1 mg/kg and in trial 17/72 91% at 0.02 mg/kg, except in trials 33/79 and 11/71 in which the limits of determination were 0.02 and 0.002 mg/kg and recoveries 90% at 0.25 mg/kg and 89% at 0.02 mg/kg respectively. The plot sizes were not reported.

Table 21. Total fenthion residues found in trials on rice in Japan in 1969, 1971, 1972 and 1978 with DP, EC, and GR formulations.

Year, variety, type <sup>1</sup>	Application	PHI, days	Residues, mg/kg, in hulled rice	Report no.
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	Form.	No.	kg ai/ha	kg ai/hl			
1969 Fujiminori Koshiminori Norin juha-chigo, P	DP 2%	1	0.6	-	15 21 30 31 40	<0.001x2 <u>0.009</u> <u>0.001</u> <u>0.012</u> <0.001	18/69 19/69 23/69
		3	0.6	-	20 40 45	<0.001 <0.001 <0.001	
1969 Chuseishin-senbon, P	DP 2%	1	0.6-0.8	-	14 29	0.014 <u>0.01</u>	20/69
	DP 2%	3	0.6-0.8	-	34	<0.001	
1969 Nihonbare Satchiwatari, P	DP 2%	1	0.8	-	7 15 21 30	<0.001 <0.001 <0.001 <0.001	21/69 22/69
		3	0.8	-	15 21	<0.001 <0.001	
1969 Norin juichigo, U	DP 2%	1	0.8	-	15 30	<0.001 <0.001	26/69
	DP 2%	3	0.8	-	40	<0.001	
1969 Norin nijugo, U	DP 2%	1	0.9	-	14 32	0.016 <0.001	25/69
	2%	3	0.9	-	32	<0.001	
1969 Himehanami, P	50 EC	1	0.5	0.05	12 27	0.034 <0.001 <sup>2</sup> 0.16 <sup>3</sup> <u>0.018</u>	15/69a 15/69b
	50 EC	3	0.5	0.05	43	<0.001	
1969 Kin nanpu, P	50 EC	1	0.7	0.05	15 30	0.022 <u>0.008</u>	25a/69
	50 EC	3	0.7	0.05	47	<0.001	
1969 Hatasangoku, U	50 EC	1	0.7	0.05	14 28	0.035 <0.001 <sup>2</sup> 0.068 <sup>3</sup> <u>0.01</u>	24/69 17/69
	50 EC	3	0.7	0.05	43	<0.001	
1969 Fujiminori, P	50 EC	1	0.5-0.75	0.05	21 40	0.068 <0.001 <sup>2</sup> 0.11 <sup>3</sup> <0.001	16/69
	50 EC	3	0.5-0.75	0.05	40	<0.001	
1971-2 Harebare (17/72) Sasaminori (11/71)	GR 5%	2	2.0	-	43 56	<0.002 <0.002	17/72 11/71
1978 No variety stated	DP Dust 2%	2	0.8	-	23	<0.024 (residues calculated as total P=O and P=S)	33/79
	Dust	2	0.8	-	23	<0.024 (residues calculated as total P=O and P=S)	

<sup>1</sup> P = paddy field rice (rice grown in flooded paddy fields), U = upland rice

<sup>2</sup> polished rice

<sup>3</sup> rice bran

## fenthion

The 1969 trials showed total residues in polished rice from single EC applications of <0.001 mg/kg (three trials) indicating that transfer of residues to the grain was minimal. Residues in rice bran from the same trials were 0.068, 0.11 and 0.16 mg/kg.

Residues were determined in the straw in the 1971-2 and 1978 trials but the results are not shown in Table 21. In trial 17/71 (1971) residues were 0.016 mg/kg at 56 days after two applications of a GR formulation at 2 kg ai/ha and 0.017 mg/kg 37 days after four applications. In trial 17/72 (1972), the total fenthion residue in straw after 4 applications of a GR formulations at 2 kg ai/ha and a 17-day PHI was 0.097 mg/kg. In the 1978 trials with DP formulations, rice straw contained approximately 0.7 mg/kg (P=S + P=O) after two applications at 0.8 kg ai/ha and 23-day PHIs.

Residue data were also supplied from trials in 1994 to support reductions of the PHI from 30 to 21 days for dust formulations and from 45 to 30 days for EC and WP formulations. In most of the trials two applications were made with different formulations: granule and dustable powder, granule and emulsifiable concentrate, or emulsifiable concentrate and dustable powder. Other trials were with two applications of dustable powder. All the trials were according to GAP. Table 22 shows the results.

Residues were determined in the husked rice according to the method of Takino and Kuroguchi (1995). The minimum detectable levels reported were 0.004-0.005 mg/kg. Residues were determined as the sum of the thion (P=S) and oxon (P=O) residues. Recoveries of fenthion, its oxon and their sulfoxides and sulfones at 0.1 and 0.2 mg/kg were 85-103%.

Plot sizes were between 15 and 270 sq m on soils described as volcanic ash (Tochigi), alluvial sandy loam (Chiba), clay (Fukui), loam (Mie), diluvial clay loam (Wakayama), Kochi (clay loam), Miyazaki (grey, lowland), and loam (Kagoshima).

Table 22. Total fenthion residues found in rice grains without husk in Japan in 1994 with DP, EC, and GR formulations. All trials with 2 applications.

Variety	Application		PHI, days	Residues, mg/kg <sup>1</sup>	Trial Reference/remarks
	Form.	kg ai/ha			
Hitomebore	GR,DL <sup>2</sup>	1.6, 0.8	21	<0.015	A-1, Tochigi
Koshihikari	GR,DL	1.6, 0.8	20	<u>&lt;0.014, &lt;0.015</u>	A-2, Chiba
Hana-echizen	GR,DL	1.6, 0.8	21	<0.015	A-3, Fukui
Koshikari	GR,DL	1.6, 0.8	21	<0.014, <0.015	A-4, Mie
Hinohikari	GR,DL	1.6, 0.8	21	<0.019	A-5, Wakayama
Koganenishiki	GR,DL	1.6, 0.8	21	<0.015	A-6, Kochi
Hinohikari	GR,DL	1.6, 0.8	21	<0.015	A-7, Miyazaki
Minamihikari	GR,DL	1.6, 0.8	21	<0.015	A-8, Kagoshima
Hitomebore	GR,EC <sup>3</sup>	1.6, 0.75	29	<0.023	B-1, Tochigi, EC 0.05 kg/hl
Koshihikari	GR,EC	1.6, 0.75	29	<0.014, <0.015	B-2, Chiba, EC 0.05 kg/hl
Hana-echizen	GR,EC	1.6, 0.75	30	<0.015	B-3, Fukui, EC 0.05 kg/hl
Koshikari	GR,EC	1.6, 0.75	30	<0.014, <0.015	B-4, Mie, EC 0.05 kg/hl
Hinohikari	GR,EC	1.6, 0.75	30	<0.019	B-5, Wakayama, EC 0.05 kg/hl
Koganenishiki	GR,EC	1.6, 0.75	30	<0.024	B-6, Kochi, EC 0.05 kg/hl
Hinohikari	GR,EC	1.6, 0.75	30	<0.02	B-7, Miyazaki, EC 0.05 kg/hl
Minamihikari	GR,EC	1.6, 0.75	30	<0.024	B-8, Kagoshima, EC 0.05 kg/hl
Hitomebore	EC,DL <sup>4</sup>	0.75, 0.8	21	<0.028	C-1, Tochigi, EC 0.05 kg/hl

## fenthion

Variety	Application		PHI, days	Residues, mg/kg <sup>1</sup>	Trial Reference/remarks
	Form.	kg ai/ha			
Koshihikari	EC,DL	0.75, 0.8	20	<0.014, <0.015	C-2, Chiba, EC 0.05 kg/hl
Han-echizen	EC,DL	0.75, 0.8	21	<0.015	C-3, Fukui, EC 0.05 kg/hl
Koshihikari	EC,DL	0.75, 0.8	21	<0.014, <0.015	C-4, Mie, EC 0.05 kg/hl
Hinohikari	EC,DL	0.75, 0.8	21	<0.028	C-5, Wakayama, EC 0.05 kg/hl
Koganenishiki	EC,DL	0.75, 0.8	21	<0.025	C-6, Kochi, EC 0.05 kg/hl
Hinohikari	EC,DL	0.75, 0.8	21	<0.024	C-7, Miyazaki, EC 0.05 kg/hl
Minamihikari	EC,DL	0.75, 0.8	21	<0.025	C-8, Kagoshima, EC 0.05 kg/hl
Hitomebore	DL x 2	1.6, 0.8	21	<0.016	D-1, Tochigi, two applications of DP. First application 1.6 kg ai/ha
Koshihikari	DL x 2	0.6	20	<0.014, <0.015	D-2, Chiba, both applications at 0.6 kg ai/ha
Hana-echizen	DL x 2	0.8	21	<0.015	D-3, Fukui, both applications at 0.8 kg ai/ha
Koshihikari	DL x 2	0.6	21	<0.014, <0.015	D-4, Mie, both applications at 0.6 kg ai/ha
Hinohikari	DL x 2	0.6	21	<0.016	D-5, Wakayama, both applications at 0.6 kg ai/ha
Hinohikari	DL x 2	0.8	21	<0.015	D-6, Miyazaki, both applications at 0.8 kg ai/ha
Minamihikari	DL x 2	0.8	21	<0.017	D-7, Kagoshima, both applications at 0.8 kg ai/ha

<sup>1</sup> Sum of thions (P=S) and oxons (P=O)

<sup>2</sup> GR applied 60 days pre-harvest, DL (equivalent to DP) 220-21 days pre-harvest.

<sup>3</sup> GR applied 60 days pre-harvest, EC 29-30 days pre-harvest

<sup>4</sup> EC applied 30 days pre-harvest, DL 20-21 days pre-harvest

### Post-harvest disinfestation

Trials to determine residues after post-harvest disinfestation of fruit and vegetables were carried out in Australia, where fenthion has an important use in allowing horticultural products to meet international quarantine requirements.

Fruit flies cause significant damage, are expensive to control and are easily imported in produce. Consequently many countries apply quarantines against them. Treatment to ensure that quarantine requirements are met must be extremely efficacious (providing virtually 100% mortality). The use of ethylene dibromide and methyl bromide as fumigants is being phased out on environmental grounds and irradiation is not widely accepted. Heat and cold treatments can cause physiological damage to many crops. Post-harvest treatments with insecticides provide simple and effective disinfestation without phytotoxicity and fenthion is effective in this role.

Post-harvest disinfestation with fenthion is a registered use in Australia, and that country has requested the establishment of Codex MRLs to cover the use. Data on fruits and vegetables treated post-harvest are shown in Table 23. Because of the nature of the treatment and the commercial requirements of trading treated material, a 0-day PHI is allowed and GAP for quarantine treatment is a single flood spray or dip at 0.041 kg ai/hl with no PHI. The trials were in the 1980s (tomatoes 1984; mangoes and capsicums 1986; zucchini 1988; rockmelons and cucumbers 1989).

Table 23. Fenthion residues in fruits and vegetables following a single post-harvest dip or spray with an EC formulation. Trials were in Australia between 1984 and 1989.

Commodity	Rate, kg fenthion/hl	Fenthion residues (mg/kg) at 0, 3, and 7 days after treatment		
		0	3	7
Mango	0.037	1.4, 0.98	0.84, 1.5	0.89, 0.9

fenthion

Commodity	Rate, kg fenthion/hl	Fenthion residues (mg/kg) at 0, 3, and 7 days after treatment		
		0	3	7
Rockmelon	0.043	<u>2.1, 1.5</u>	<u>2.1, 1.5</u>	<u>0.9, 1.3</u>
Cucumber	0.043	<u>1.5, 2.0</u>	<u>1.2, 0.7</u>	<u>0.5, 1.2</u>
Zucchini	0.039	<u>1.0, 1.2</u>	<u>0.06, 0.04</u>	<u>0.01, 0.02</u>
Capsicum	0.038	<u>1.7, 2.3</u>	<u>1.6, 1.5</u>	<u>2.6, 2.1</u>
Tomato	0.042	<u>1.2, 1.3</u>	<u>0.8, 1.1</u>	<u>0.59, 1.1</u>
Mango	0.072 <sup>1</sup>	2.2, 1.6	1.6, 1.8	1.3, 1.0
Rockmelon	0.06 <sup>1</sup>	1.7, 2.2	1.1, 1.6	1.5, 1.4
Cucumber	0.06 <sup>1</sup>	4.2, 4.0	1.6, 1.4	1.1, 1.6
Capsicum	0.069 <sup>1</sup>	3.3, 3.0	2.9, 2.8	2.5, 2.5

## fenthion

<sup>1</sup> Excessive concentrations

Residues were extracted with acetone and the acetone extract cleaned up by sweep co-distillation. Fenthion was determined by GLC with an FPD. The method had a limit of determination of 0.01-0.02 mg/kg and determined only fenthion. Recoveries were >80%.

Residues were determined in the whole fruit or vegetable except in mangoes whose peel and pulp were analysed separately and the residue in the whole fruit calculated. In mangoes most of the residue was on the peel (5.7 and 4.8 mg/kg at 0 days, 4.5 and 7.2 mg/kg at 3 days and 3.4 and 3.9 mg/kg at 7 days from 0.037 kg fenthion/hl). In the pulp the corresponding values were 0.21 and 0.06, 0.01 and 0.04, and 0.27 and 0.02 mg/kg.

The residues of fenthion arising from the registered post-harvest uses were generally similar and in the 1-2.5 mg/kg range on the day of treatment. Residues decreased only slowly. Although the treatments were indoors and the extensive formation of fenthion metabolites on the day of treatment may be unlikely, the trials did not conclusively demonstrate that it did not occur.

### Animal residues

#### Residues from use as an ectoparasiticide

Data were supplied on residues in pig and sheep tissues and in cattle tissues and milk after the topical application of fenthion.

Cattle. Registered uses were provided by the sponsor. Dose rates range from 4 to 16 mg/kg bw. A single application is normal practice but redosing is permitted. Withholding periods for edible tissues are 10, 14, 15, 21, 28, 35 or 45 days and for milk 0, 5 or 7 days, depending on the country of registration. In Argentina, Brazil, Canada, Costa Rica, the Dominican Republic, Guatemala, Honduras, Mexico, New Zealand, Nicaragua, Uruguay and the USA the use of fenthion is restricted to non-lactating cattle.

Residues in tissues. Seven trials carried out in the USA from 1965 to 1974 (five back line, one spray and one back rubber. One trial involved two treatments). Dose rates and time intervals (10-45 days) were consistent with the current registered use patterns.

Hereford and Brama steers and females (live weights between about 270 and 420 kg at the beginning of the trial) were slaughtered in groups of 3 at 1, 3, 7, 14 or 28 days after single backline applications of a 2% fenthion pour-on formulation at approximately 6.2 mg ai/kg bw (0.01 oz. ai/100 lbs) (Chemagro, 1965b). Fat, brain, heart, kidneys, liver and muscle were analysed for total fenthion by the method of Anderson and Katague (1965) with a limit of determination of 0.1 mg/kg. The results are shown in Table 24.

Fat contained the highest residues with the maximum value (3.9 mg/kg, 7 days after treatment) found in back fat. By day 28 residues in all fat samples were <0.1 mg/kg. Residues were low in offal, typically <0.1 mg/kg 3 days after treatment, and were all <0.1 mg/kg in muscle after 14 days. treatment.

Table 24. Total fenthion residues in tissues from 15 cattle in the USA in 1965 given a single backline treatment with a 2% fenthion pour-on formulation at 6.3 mg/kg bw (Chemagro, 1965b).

Tissue/organ	Residues, mg/kg, at days after application <sup>1</sup>				
	1	3	7 <sup>2</sup>	14	28

fenthion

Tissue/organ	Residues, mg/kg, at days after application <sup>1</sup>				
	1	3	7 <sup>2</sup>	14	28
Brain	<0.1 x 2, 0.1	<0.1 x 3	<0.1 x 3	<0.1	-
Heart	<0.1 x 2, 0.1	<0.1 x 3	<0.1 x 3	<0.1	-
Liver	0.2 x 3	<0.1 x 3	<0.1 x 3	<0.1	-
Kidneys	<0.1, 0.1 x 2	<0.1 x 3	<0.1 x 3	<0.1	-
Loin muscle	<0.1 x 2, 0.4	<0.1 x 2, 0.2	<0.1, 0.1, 0.2	<0.1 x 3	<0.1 x 3
Round muscle	<0.01 x 2, 0.1	<0.1 x 3	<0.1 x 2, 0.1	<0.1 x 3	<0.1 x 3
Flank muscle	0.1, 0.2, 0.4	<0.1, 0.1, 0.2	<0.1 x 2, 0.1	<0.1 x 3	<0.1 x 3
Omental fat	0.2, 0.8, 1.5	0.3, 0.5, 0.6	0.1, 0.2, 0.3	<0.1 x 2, 0.1	<0.1 x 3
Renal fat	0.3, 0.7, 1.8	0.3, 0.5, 0.6	0.3, 0.5, 2.9	<0.1 x 2, 0.2	<0.1 x 3
Back fat	0.2, 0.8, 1.1	0.1, 0.4, 0.6	0.1, 0.6, 3.9	<0.1 x 3	<0.1 x 3

<sup>1</sup> Control values were <0.01 mg/kg in all tissues

<sup>2</sup> Results after 7 days treated as being after a 10-day withholding period

In a second study 12 cattle (mixed breeds, initial live weights between 300 and 450 kg) were slaughtered in groups of 3 at 1, 3, 7 and 28 days after single backline applications of a 3% pour-on at approximately 9.3 mg ai/kg bw (0.015 oz/100 lbs) (Chemagro, 1968). Brain, heart, fat, kidneys, liver and muscle were analysed for total fenthion residues by the method of Thornton (1967) with a limit of determination of 0.01 mg/kg. The results are shown in Table 25.

Residues were highest after 1, 3, or 7 days, and by day 28 were all <0.1 mg/kg except in two back fat samples (0.12 and 0.13 mg/kg).

Table 25. Total fenthion residues in tissues from 12 cattle given a single backline treatment in the USA in 1968 with a 3% fenthion pour-on formulation at 9.3 mg/kg bw (Chemagro, 1968).

Tissue/organ	Residues, mg/kg, at days after application <sup>1</sup>			
	1	3	7 <sup>2</sup>	28
Brain	0.07, 0.02, 0.15	<0.01 x 3	<0.01 x 2, 0.01	<0.01 x 3
Heart	0.1, 0.12, 0.26	<0.02, 0.02, 0.07	0.06, 0.05, 0.11	<0.02 x 3
Liver <sup>3</sup>	0.12, 0.15 x 2	<0.01, 0.01, 0.02	<0.01, 0.01, 0.02	<0.01 x 3
Kidneys	0.07, 0.08, 0.31	0.05, 0.1, 0.02	0.06, 0.08, 0.15	<0.01 x 2, 0.05
Loin muscle	0.06, 0.15, 0.33	0.03, 0.06 x 2	0.03, 0.07, 0.11	<0.01 x 2, 0.02
Round muscle	0.05, 0.15, 0.16	0.02 x 2, 0.03	0.07, 0.1, 0.13	<0.01 x 3
Flank muscle	0.07, 0.16, 0.34	0.03, 0.08, 0.14	0.06, 0.26, 0.31	<0.01 x 2, 0.02
Omental fat	0.11, 0.17, 0.29	0.12, 0.13, 0.18	0.25, 0.29, 0.4	0.02 x 2, 0.03
Renal fat	0.11, 0.18, 0.26	0.31, 0.33, 0.97	0.29, 0.32, 0.54	0.02, 0.03, 0.04
Back fat	0.13, 0.19, 0.25	0.74, 0.87 x 2	0.41, 0.6, 0.84	0.02, 0.12, 0.13

## fenthion

<sup>1</sup> Control values  $\leq 0.01$  mg/kg in all tissues except heart (0.02 mg/kg)

<sup>2</sup> Results after 7 days were treated as being after a 10-day withholding period

<sup>3</sup> Samples taken on day 3 analysed 1 day later. Samples taken on days 1 and 7 analysed 4 days later

Two mixed breed, male cattle were treated with 12 ml of a 20% fenthion spot-on formulation in the USA (Chemagro, 1970). They weighed 403 and 427 kg at the start of the trial. The dose administered was 0.084 oz ai/animal, approximately 5.6 and 5.9 mg fenthion/kg bw. The animals were killed after 45 days and residues in brain, heart, liver, kidneys, loin muscle, round muscle, flank muscle, treatment site, omental fat, renal fat and back fat were determined by the method of Thornton (1967). The trial complied with the registered US use pattern of a 5.5-11 mg ai/kg application with a 45-day withholding period.

The samples were analysed in duplicate. All residues were at or below the control values (brain 0.01 mg/kg; heart, liver and kidneys  $< 0.01$  mg/kg; muscle and treatment site 0.02 mg/kg; fat 0.05 mg/kg) except one sample of brain at 0.02 mg/kg and one of loin muscle at 0.03 mg/kg.

Two yearling Angus heifers (starting weights 294 and 321 kg) were treated once on the back line with a 20% spot-on formulation at a dose equivalent to 17.7 mg fenthion/kg bw (Cox, 1971). The animals were killed 28 days later and analysed for residues by the method of Thornton (1967). The trial was considered to accord with the registered use patterns of those countries which permit rates up to 16 mg fenthion/kg bw. The results are shown in Table 26.

Table 26. Total fenthion residues in 2 cattle after single back line treatments with a 20% fenthion solution at 17.7 mg/kg bw in the USA (1971) and slaughtered 28 days after treatment (Cox, 1971).

Tissue/organ	Residue, mg/kg
Heart	<u>0.03, 0.06</u>
Liver	<u>0.01, 0.02</u>
Kidneys	<u>0.03, 0.05</u>
Round muscle	<u>0.02, 0.04</u>
Treatment site fat	<u>0.09, 0.47<sup>1</sup></u>
Non-treatment site back fat	<u>0.09, 0.46<sup>1</sup></u>

<sup>1</sup> Confirmed by reanalysis

Six mixed-breed yearling heifers were treated twice with a 20% fenthion solution (spot-on back line) at either 11.8 or 17.7 mg fenthion/kg bw (Chemagro, 1974). The rate used for cattle grub control in the USA is 5.5-11 mg fenthion/kg bw. Samples of back fat were taken after 35 days: the second treatment was then given and samples taken after 45 days. The first samples were taken from the left side of the animals near to the site of application and the second from the right side from the equivalent position. Residues were determined by the method of Thornton (1967).

The residues from the low treatment rate were 0.03, 0.01 and 0.03 mg/kg 35 days after the first treatment and 0.07, 0.02 and 0.03 mg/kg 45 days after the second treatment. Those from the high rate were 0.09, 0.03 and 0.04 mg/kg after 35 days and 0.09,  $< 0.01$  and 0.06 mg/kg after 45 days.

Since treatments up to 16 mg/kg are allowed in some countries, the dosage rates were considered to accord with registered use patterns.

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