FENITROTHION (037)

first draft prepared by Trijntje van der Velde-Koerts and Bernadette C. Ossendorp, National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands

EXPLANATION

Fenitrothion, a contact insecticide originally evaluated by the JMPR in 1969 and re-evaluated for residues several times up to 1989, is included in the CCPR periodic review programme. At the 30th session of the CCPR (ALINORM 99/24), fenitrothion was scheduled for review by the JMPR in 2003. The main manufacturer supplied information on identity; metabolism and environmental fate; residue analysis; use pattern; residues resulting from supervised trials on cereals; and the fate of residues during storage or in processing. In addition, GAP information and/or national MRLs were supplied by the governments of Australia, Germany, The Netherlands and the USA.

IDENTITY

ISO common name: fenitrothion

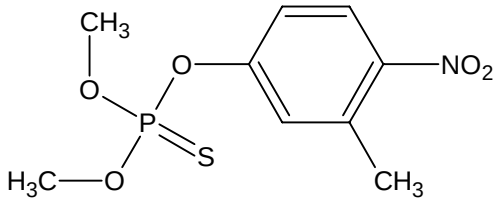
Chemical names
IUPAC: *O*,*O*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate
CA: *O*,*O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate

CAS Registry No: 122-14-5

CIPAC No: 35

Synonyms/trade names: sumithion®

Structural formula: identified by IR (liquid film method using NaCl plate), ^{1}H-NMR (270 MHz) and direct insertion MS (EI at 70 eV) (Kimura, 1987)



Molecular formula: $C_9H_{12}NO_5PS$

Molecular weight: 277.24 (non-GLP, Kimura, 1987)

Physical and chemical properties

Pure active ingredient

Minimum purity:	99% (w/w)	Reference
Appearance:	viscous clear (colourless) liquid	Bates, 2001
	clear light yellow liquid	Kimura, 1988a & 1988b
Vapour pressure:	1.48×10^{-4} Pa (1.11×10^{-6} Torr) at 10°C; 6.76×10^{-4} Pa (5.07×10^{-6} Torr) at 20°C; 1.57×10^{-3} Pa (1.18×10^{-5} Torr) at 25°C (interpolated); 3.39×10^{-3} Pa (2.54×10^{-5} Torr) at 30°C. OECD 104, using the gas saturation method	Schetter, 2000
Melting/freezing point:	A glass transition was observed around –30°C (243°K), then a freezing exotherm between –24°C and –3°C (249-270°K), which probably represented a cold crystallization, and then a final melting between –1°C and +1°C (272-274°K). OECD 102, using differential scanning calorimetry.	Bates, 2001

Octanol/water partition coefficient:	log K_{ow} = 3.319, s.d. 0.080, at pH 6.15-6.24 and 25°C. OECD 107, using the shake flask method.	Schepler and Schick, 2002
Water solubility:	19.0 mg/l at 20 ± 0.5°C. OECD 105, using the column elution method.	Concha, 2000
Relative density:	1.328 g/cm^3 at 20°C. OECD 109, using a liquid density meter	Bates, 2001
Hydrolysis:	pH 5 buffer, stable, half-life 191-200 days, 12% transformation after 30 days, at 25 ± 1°C. pH 7 buffer, stable, half-life 180-186 days, 9% transformation after 30 days, at 25 ± 1°C. pH 9 buffer, relatively unstable, half-life 100-101 days, 21% transformation after 30 days, at 25 ± 1°C	Ito *et al*., 1988
Photolysis:	in pH 5 buffer, rapid photolysis, half-life 3.3–3.6 days, 100% transformation after 30 days at 25 ± 1°C in artificial sunlight.	Katagi *et al*., 1988
Dissociation constant:	not applicable.	

Technical material

Minimum purity	930 g/kg	Reference
Main impurities:	Information on about 10 impurities was made available to the Meeting	Asada, 2000
Appearance:	94.3-95.3% purity, oily liquid with deep yellow-red to reddish yellow colour	Asada, 1996a & 1996b
	94.6% purity, viscous amber liquid	Bates, 2001

Formulations

Fenitrothion is available in the following formulations.

Emulsifiable concentrate (EC) formulations containing 20, 150 (+7.5 g/l esfenvalerate), 218, 200 (+200 g/l 2-*sec*-butylphenyl *N*-methylcarbamate, BPMC or fenobucarb), 250 (+12.5 or 50 g/l esfenvalerate + 50 g/l fenvalerate), 300, 450 (+300 g/l BPMC), 500, 500 (+25 or 75 g/l esfenvalerate), 508, 600, 750, 800, 950 or 1000 g/l fenitrothion.

Ultra-low volume (UL) formulations containing 800, 950, 980, 1270 g/l fenitrothion.

Soluble concentrate (SL) formulations containing 218 g/l fenitrothion.

Dustable powder formulations (DP) containing 20, 20 (+15 or 20 g/kg BPMC), 30, 30 (+20 g/kg BPMC +20 g/kg thiophanate-methyl), 40 or 50 g/kg fenitrothion.

Wettable powder (WP) formulations containing 20, 400 or 500 g/kg fenitrothion.

Microcapsule (CS) formulations containing 150 (+100 BPMC) or 200 g/kg fenitrothion.

List of reference compounds used in various study reports

Abbreviation	Synonyms used in study reports	Trivial and systematic chemical name(s)	Found as or in
-	FNT	fenitrothion (parent)	quails, hens, soil
AA-FNO	-	acetylaminofenitro-oxon; *O*,*O*-dimethyl *O*-(3-methyl-4-acetylaminophenyl) phosphate *O*-(4-acetylamino-3-methylphenyl) *O*,*O*-dimethyl phosphate	metabolite in goat
AA-FNT	-	acetylaminofenitrothion; *O*,*O*-dimethyl *O*-(3-methyl-4-acetylaminophenyl) phosphorothioate; *O*,*O*-dimethyl *O*-(3-methyl-4-aceetamidophenyl) phosphorothioate; *O*,*O*-dimethyl *O*-4-aceetamido-m-tolyl phosphorothioate;	metabolite in goat; metabolite in water/sediment
AAMC	-	3-methyl-4-acetylaminophenol; 4-acetylamino-3-methylphenol	metabolite in goat; metabolite in hens;

Abbreviation	Synonyms used in study reports	Trivial and systematic chemical name(s)	Found as or in
AAMC-sul	-	3-methyl-4-acetylaminophenyl sulfate sulfate of 4-acetylamino-3-methylphenol	metabolite in quails and hens;
AMC	-	4-amino-3-methylphenol; 3-methyl-4-aminophenol	-
AM-FNO	-	aminofenitro-oxon; *O*,*O*-dimethyl *O*-(3-methyl-4-aminophenyl) phosphate; *O*-(4-amino-3-methylphenyl) *O*,*O*-dimethyl phosphate	metabolite in goat
AM-FNO-sul	-	*N*-sulfo aminofenitro-oxon; *O*,*O*-dimethyl *O*-(3-methyl-4-sulfo-aminophenyl) phosphate; sulfate of *O*-(3-methyl-4-aminophenyl) *O*,*O*-dimethyl phosphate	metabolite in goat
AM-FNT	-	aminofenitrothion *O*,*O*-dimethyl *O*-4-amino-m-tolyl phosphorothioate; *O*,*O*-dimethyl *O*-(3-methyl-4-aminophenyl) phosphorothioate;	metabolite in goat; metabolite in water/sediment
AM-FNT-sul	-	N-sulfo aminofenitrothion; *O*,*O*-dimethyl *O*-(3-methyl-4-sulfo-aminophenyl) phosphorothioate; sulfate of *O*-(3-methyl-4-aminophenyl) *O*,*O*-dimethyl phosphorothioate	metabolite in goat
A-NMC	-	*O*-acetyl-3-methyl-4-nitrophenol	metabolite in water/sediment
BIS-FNT	BIS-SMT	*O*-methyl *O*,*O*-bis(4-nitro-*m*-tolyl) phosphorothioate; *O*-methyl *O*,*O*-bis(3-methyl-4-nitrophenyl) phosphorothioate	impurity
CA-FNO	COOH-SMO	fenitro-oxon-3-COOH; *O*,*O*-dimethyl *O*-(3-carboxy-4-nitrophenyl) phosphate;	photolysis product; metabolite in hens;
CA-FNT	COOH-SMT	fenitrothion-3-COOH; *O*,*O*-dimethyl *O*-(3-carboxy-4-nitrophenyl) phosphorothioate	photolysis product
CA-NMC	-	5-hydroxy-2-nitrobenzoic acid; 3-carboxy-4-nitrophenol	metabolite in hens;
DHMN	-	1,2-dihydroxy-4-methyl-5-nitrobenzene	rice storage
DM-AA-FNO	-	*O*-(4-acetylamino-3-methylphenyl) *O*-hydrogen *O*-methyl phosphate	metabolite in goat
DM-AM-FNT	-	desmethylaminofenitrothion; *O*-methyl *O*-hydrogen *O*-(3-methyl-4-aminophenyl) phosphorothioate; *O*-(4-amino-3-methylphenyl) *O*-hydrogen *O*-methyl phosphorothioate	metabolite in goat
DM-FNO	DM-SMO	desmethylfenitro-oxon; *O*-methyl *O*-hydrogen *O*-(3-methyl-4-nitrophenyl) phosphate	photolyis product; metabolite in quails and hens; metabolite in soil; rice storage
DM-FNT	DM-SMT	desmethylfenitrothion; *O*-methyl *O*-hydrogen *O*-(3-methyl-4-nitrophenyl) phosphorothioate	hydrolysis and photolysis product; metabolite in quails and hens; metabolite in grapes; metabolite in soil; rice storage
DM-HM-FNO	-	desmethylfenitro-oxon-3-CH_2OH; *O*-hydrogen *O*-(3-hydroxymethyl-4-nitrophenyl) *O*-methyl phosphate; *O*-methyl *O*-hydrogen *O*-(3-hydroxymethyl-4-nitrophenyl) phosphate	metabolite in quails
DM-HM-FNT	-	desmethylfenitrothion-3-CH_2OH; *O*-hydrogen *O*-(3-hydroxymethyl-4-nitrophenyl) *O*-methyl phosphorothioate; *O*-methyl *O*-hydrogen *O*-(3-hydroxymethyl-4-nitrophenyl) phosphorothioate	metabolite in quails
DMMN	-	1,2-dimethoxy-4-methyl-5-nitrobenzene	rice storage
DMPTA	-	dimethylphosphorothioic acid	wheat storage

Abbreviation	Synonyms used in study reports	Trivial and systematic chemical name(s)	Found as or in
DM-SM-FNT		desmethylfenitrothion *S*-isomer; *S*-methyl *O*-hydrogen *O*-(3-methyl-4-nitrophenyl) phosphorothioate	rice storage
2,4-DN-FNT	2,4-DN-SMT	*O*,*O*-dimethyl *O*-2,4-dinitro-m-tolyl phosphorothioate; *O*,*O*-dimethyl O-(3-methyl-2,4-dinitrophenyl) phosphorothioate	impurity
4,6-DN-FNT	4,6-DN-SMT	*O*,*O*-dimethyl O-4,6-dinitro-*m*-tolyl phosphorothioate; *O*,*O*-dimethyl O-(3-methyl-4,6-dinitrophenyl) phosphorothioate	impurity
FA-FNO	-	formylaminofenitro-oxon; *O*,*O*-dimethyl *O*-(3-methyl-4-formylaminophenyl) phospate *O*-(4-formylamino-3-methylphenyl) *O*,*O*-dimethyl phosphate	metabolite in goat
FA-FNT	-	formylaminofenitrothion; *O*,*O*-dimethyl *O*-(3-methyl-4-formylaminophenyl) phosphorothioate; *O*,*O*-dimethyl *O*-(3-methyl-4-aminoformylphenyl) phosphorothioate	metabolite in goat; metabolite in soil
FNO	SMO	fenitro-oxon; *O*,*O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphate	photolysis product; metabolite in quails; metabolite in soil; rice storage
HM-FNO	-	fenitro-oxon-3-CH_2OH; *O*,*O*-dimethyl *O*-(3-hydroxymethyl-4-nitrophenyl) phosphate	metabolite in quails
HM-FNT	-	fenitrothion-3-CH_2OH; *O*,*O*-dimethyl *O*-(3-hydroxymethyl-4-nitrophenyl) phosphorothioate	-
HM-NMA	-	1-methoxy-3-hydroxymethyl-4-nitrobenzene	-
HM-NMC	-	3-hydroxymethyl-4-nitrophenol; 5-hydroxy-2-nitrobenzylalcohol	metabolite in quails and hens; rice storage
HM-NMC-glu	-	glucuronide of 5-hydroxy-2-nitrobenzylalcohol	metabolite in quails and hens
HM-NMC-sul	-	3-hydroxymethyl-4-nitrophenyl sulfate; sulfate of 5-hydroxy-2-nitrobenzylalcohol	metabolite in quails and hens
NMA	MNA	1-methoxy-3-methyl-4-nitrobenzene; 3-methyl-4-nitroanisole	metabolite in soil; rice storage
NMC	4 NMC; MNP	4-nitro-*m*-cresol 3-methyl-4-nitrophenol	impurity; hydrolysis and photolysis product, metabolite in quails and hens; metabolite in grapes and tomatoes; metabolite in soil and water/sediment; rice storage
NMC-B-glc	-	NMC-ß-glucoside; 3-methyl-4-nitrophenol-beta-glucoside	metabolite in grapes and tomatoes
NMC-B-glc conj	-	conjugates of NMC-ß-glucoside	metabolite in tomatoes
NMC-conj	-	conjugates of 3-methyl-4-nitrophenol	metabolite in grapes and tomatoes
NMC-sul	-	3-methyl-4-nitrophenyl sulfate sulfate of 3-methyl-4-nitrophenol	metabolite in quails and hens
6NMC	6NMC	5-methyl-2-nitrophenol	impurity
2NMC-FNT	2NMC-SMT	*O*,*O*-dimethyl *O*-2-nitro-*m*-tolyl phosphorothioate; *O*,*O*-dimethyl *O*-(3-methyl-2-nitrophenyl) phosphorothioate	impurity
6NMC-FNT	6NMC-SMT	*O*,*O*-dimethyl *O*-6-nitro-*m*-tolyl phosphorothioate; *O*,*O*-dimethyl *O*-(3-methyl-6-nitrophenyl) phosphorothioate	impurity
3NPC-FNT	3NPC-SMT	*O*,*O*-dimethyl *O*-3-nitro-*p*-tolyl phosphorothioate; *O*,*O*-dimethyl *O*-(4-methyl-3-nitrophenyl) phosphorothioate	impurity
SM-BIS-FNT	S-methyl-BIS-SMT	*S*-methyl *O*,*O*-*bis*(4-nitro-*m*-tolyl) phosphorothioate; *S*-methyl *O*,*O*-*bis*(3-methyl-4-nitrophenyl) phosphorothioate	impurity

Abbreviation	Synonyms used in study reports	Trivial and systematic chemical name(s)	Found as or in
SM-FNT	SCH_3-SMT; S-methyl-SMT	fenitrothion *S*-isomer; *O*-methyl *S*-methyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate; *O*,*S*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate; *O*,*S*-dimethyl *O*-4-nitro-*m*-tolyl phosphorothioate	photolysis product; rice storage

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

The Meeting received information on the fate of orally-dosed fenitrothion in lactating goats and in egg-producing quails and hens. Metabolism in laboratory animals (mice, rats, guinea pigs, rabbits and dogs) was summarized and evaluated by the WHO panel of JMPR in 2000.

Lactating goats dosed orally

Six female goats (Japanese Saanen, bodyweights 35 kg) were fed [phenyl-^{14}C]fenitrothion (0.5 mg ai/kg bw), mixed with 200 g of crushed hay, for 7 consecutive days (Mihara *et al*., 1978). The animals were dosed after the morning milking. The goats were also fed 2 kg crushed hay, 0.3 kg bran and 14 g NaCl per day: therefore the dose corresponded to 7.6 ppm in feed. The specific activity of the undiluted radiolabel was 0.20 MBq/mmol and the radiochemical purity was >99%. The goats were milked twice daily and the evening milk samples were combined with the milk collected the following morning. Whole milk was separated into cream and skimmed milk by centrifugation. Urine and faeces were collected separately throughout the experiment. Two goats were each killed at 1, 7 and 18 days after the last dosing. Various tissues were removed for radiochemical analysis but only the results for liver, kidney, omental fat, mesenteric fat, peri-renal fat, quadriceps femoris muscle and abdominal muscle are reported here. All samples were stored at –20 °C (storage time not stated) prior to analysis. The radiochemical content of milk, excreta and tissues was determined by (combustion) LSC.

Approximately 44% and 17% of the daily dose of radioactivity was eliminated in urine and faeces, respectively, during day 1 after the first treatment and the corresponding values at 7 days after the first treatment were 48% and 38% of the cumulative dose. The administered radiocarbon was almost quantitatively excreted during the dosing and 7-day post-treatment periods; 50% of the cumulative dose was recovered in urine, 44% in faeces and 0.1% in milk.

In whole milk, a plateau of 0.011 mg/kg eq was reached on the second day of dosing, with a maximum of 0.012 mg/kg eq on the 5th day of dosing. Residue levels in whole milk declined to 0.003 mg/kg eq within 7 days after treatment (DAT). Tissue residue data are shown in Table 1. At 1 DAT, liver contained the highest content of radiocarbon (0.85-1.5 mg/kg eq) and only low concentrations were present in kidney, muscle and fat (0.002-0.031 mg/kg eq). At 7 DAT, ^{14}C concentrations in the organs and tissues, except liver, had decreased significantly. At 18 DAT, ^{14}C was less than 0.005 mg/kg eq in all organs and tissues analyzed, except liver. In liver, the radiocarbon residue decreased exponentially with time.

Urine was neutralized and extracted with benzene. The aqueous phase was lyophilized and redissolved in methanol. Homogenized faeces were neutralized and subsequently extracted with benzene, methanol, warm methanol, then refluxed with methanol for 2 hours. Homogenized organs and tissues were neutralized, diluted with water and subsequently extracted with ethyl acetate and methanol. In some cases, the extracts were partitioned between *n*-hexane and ACN, and the solids were refluxed with methanol. Cream was partitioned between *n*-hexane and ACN. Skimmed milk was extracted with methanol/ACN (1:2, v/v) and the extract was partitioned into chloroform. The chloroform layer was evaporated to dryness and partitioned between *n*-hexane and ACN. The aqueous layer, remaining after removal of the MeOH/ACN extract, was lyophilized and subsequently extracted with MeOH/ACN and refluxed with methanol for 1 hour. Extracts were analyzed by TLC (silica gel with 8 solvent systems) by comparison with authentic standards: parent, FNO, NMC, AM-FNT, AM-FNO, FA-FNT, FA-FNO, AA-FNT, AA-FNO, AM-FNT-sul, AM-FNO-sul, DM-AM-FNT, and AMC. Metabolites were identified by NMR and MS analysis.

At least 14 components were detected in urine and faeces and 11 of these were identified. The amounts present are shown in Table 2. The major metabolites were AM-FNT, DM-AA-FNO, AM-FNT-sul, and AM-FNO-sul. Parent fenitrothion was not found in any organ or tissue analyzed (<0.001 mg/kg eq); information other minor metabolites is not presented here. The radioactive residue in liver was not extractable with benzene or by refluxing with methanol, although the residue decreased with time (see Table 1). Four radioactive components were detected in milk and these are listed in Table 3 but no parent fenitrothion, FNO or NMC was detected. These findings indicate that fenitrothion does not accumulate in the lactating ruminant. As the major metabolite in urine and faeces was AM-FNT, reduction of the nitro group was presumed to be the first step in the metabolism of fenitrothion. The other metabolites were then derived from AM-FNT by conjugation of the amino group, conversion to the oxon, hydrolysis of a methoxy group or a combination of two or more of these steps.

Table 1. Concentration of radioactivity in tissues of female goats after oral administration of [phenyl-^{14}C]fenitrothion at 0.5 mg/kg bw/day for 7 days (Mihara *et al*., 1978).

Matrix	Concentration of ^{14}C (mg/kg eq)					
	DAT = 1		DAT = 7		DAT = 18	
	Goat A	Goat B	Goat C	Goat D	Goat E	Goat F
Liver	0.85	1.5	0.30	0.31	0.10	0.10
Kidney	0.025	0.031	0.006	0.006	0.003	0.003
Omental fat	0.011	0.008	0.008	0.010	0.002	0.004
Mesenteric fat	0.012	0.008	0.005	0.010	0.002	0.002
Peri-renal fat	0.011	0.010	0.006	0.008	0.004	0.003
Quadriceps femoris muscle	0.003	0.002	0.001	<0.001	0.003	0.002
Abdominal muscle	0.005	0.002	0.001	<0.001	0.002	0.001

DAT = days after treatment.

Table 2. Amounts of metabolites (mean ± s.d.) excreted into urine and faeces during the first 7 days oral administration of [phenyl-^{14}C]fenitrothion (0.5 mg/kg bw/day) to female goats (Mihara *et al*., 1978).

Metabolites	Urine, %TAR	Faeces, %TAR	Total, %TAR
AM-FNT	20.0 ± 1.7	31.1 ± 1.1	51.1
Unknown G2	trace	1.1 ± 0.1	1.1
FA-FNT	1.4 ± 0.2	1.4 ± 0.2	2.8
AA-FNT	trace	1.3 ± 0.1	1.3
Unknown G5	1.0 ± 0.1	0.0 ± 0.0	1.0
AAMC	1.9 ± 0.1	1.9 ± 0.3	3.8
AM-FNO	3.4 ± 0.4	0.0 ± 0.0	3.4
FA-FNO	0.7 ± 0.1	0.0 ± 0.0	0.7
AA-FNO	0.9 ± 0.1	0.0 ± 0.0	0.9
AM-FNT-sul	6.8 ± 0.7	0.0 ± 0.0	6.8
AM-FNO-sul	4.9 ± 0.4	0.0 ± 0.0	4.9
DM-AM-FNT	3.2 ± 0.6	0.0 ± 0.0	3.2
DM-AA-FNO	11.3 ± 1.8	2.1 ± 0.5	13.4
Unknown G14	0.0 ± 0.0	2.6 ± 0.6	2.6
Residues (unextractable)	0.0 ± 0.0	3.0 ± 0.5	3.0
Total	55.5 ± 1.3	44.5 ± 1.3	100.0

TAR = total applied radioactivity.

Table 3. Metabolites in milk and cream 24 hours after the cessation of oral administration of 0.5 mg/kg bw of [phenyl-^{14}C]fenitrothion to female goats (Mihara *et al*., 1978).

Metabolites	Whole milk		Cream	
	mg/kg eq	%TRR	mg/kg eq	%TRR
AA-FNO	<0.001	5	<0.004	<2
AM-FNT-sul	0.004	39	<0.004	<2
AM-FNO-sul	0.002	22	<0.004	<2
DM-AA-FNO	0.002	15	<0.004	<2
Residues (unextractable)	-	14	-	<2
Total		95		5

TRR = total radioactive residue.

Egg-laying quails and hens, dosed orally

[Phenyl-^{14}C]fenitrothion was administered orally to 15 Japanese quails, at a single dose of 5 mg/kg bw, and to six White Leghorn hens, at a dose of 2 mg/kg bw/d, for 7 consecutive days (Mihara *et al*., 1979). The specific activity of the undiluted radiolabel was 0.20 MBq/mmol and the radiochemical purity was >99%. Quails weighed 100-130 g and hens weighed 1.5-2.2 kg. Birds were fed *ad libitum*. Assuming a daily feed intake of 30 g for quails and 120 g for hens, a dose of about 35 ppm feed for hens and about 20 ppm feed for quails was calculated. The dose was administered by gelatin capsule, once daily. Excreta and eggs were collected daily and the eggs were separated into whites and yolks. Quails were sacrificed at 1 hr, 1 and 7 days after the single administration, hens were sacrificed at 1 and 7 days after the final dose. Various tissues were removed for analysis, but only the results for muscle, liver and kidney are reported here. Fat was not investigated. All samples were stored frozen (temperature and time not stated). The radiochemical content of eggs (whites and yolks), excreta and tissues was determined by (combustion) LSC.

Excreta were extracted with MeOH/water (80:20, v/v). Eggs (whites and yolks) were extracted sequentially with acetone, MeOH, warm MeOH and by 2 hrs refluxing with MeOH. Homogenized tissues were diluted with water and extracted with ethyl acetate. After removal of the extraction solvent, ethyl acetate extracts were partitioned between *n*-hexane and ACN. Extracts were analyzed by TLC (silica gel with 7 solvent systems), by comparison with authentic standards for: parent fenitrothion, FNO, DM-FNT, DM-FNO, HM-FNT, HM-FNO, CA-FNT, CA-FNO, DM-HM-FNT, DM-HM-FNO, CA-NMC, NMC, NMC-sul, HM-NMC, HM-NMC-sul, AAMC, AAMC-sul. Polar metabolites were isolated from TLC plates and subjected to enzymatic hydrolysis (*beta*-glucuronidase or arylsulfatase).

Radioactivity was very rapidly excreted by both quails and hens (Table 4). From quails, 93% TAR was recovered in the urine and faeces 6 hrs after dosing and 99% TAR after 24 hrs. Excretion from hens was similar: 94% TAR had been eliminated 6 hrs after the final dose and 100% TAR was recovered within 5 days after the final dose. The radioactivity eliminated into eggs did not exceed 0.2% TAR.

Residues did not reach a plateau in hens eggs, during the dosing period of 7 days. The radioactive residues in the hen egg whites increased as dosing progressed, reaching a maximum of 0.02 mg/kg eq on the 8th day (DAT = 1), while in the yolks it reached a maximum of 0.1 mg/kg eq on the 7th day (last treatment day).

One hour after oral administration of ^{14}C-fenitrothion to female quails, the highest content of radiocarbon was found in kidney and liver (Table 5). Fenitrothion and NMC were present in all edible tissues. Small amounts of FNO and the HM-FNO were present in some tissues. The radiocarbon content of tissues and eggs was very low at 1 day and 7 days after the single or the final administration in both quails and hens (Table 6).

More than 18 metabolites were found in the excreta, among which 14 compounds were identified (Table 7). The major metabolites were NMC and its sulfate conjugate, which accounted for 70% TAR in quails and 51% TAR in hens. DM-FNT and DM-FNO were found as minor metabolites and, in addition, metabolites were detected in which oxidation of the *m*-methyl group had occurred. The major metabolites in hen eggs were NMC and NMC-sul (sulfate conjugate); the fenitrothion content of eggs was 0.005 mg equivalents fenitrothion/kg, if calculated on the basis of whole egg (Table 8).

The major route of metabolism of fenitrothion in birds was by hydrolysis of the P-O-aryl link and oxidation of the *m*-methyl group. Metabolites formed by these routes were also conjugated with sulfate. Hydrolysis of the methoxy group of fenitrothion and reduction of the nitro group of NMC, followed by conjugation, were minor pathways. The proposed pathways of metabolism of fenitrothion in goat, hen and quail are shown in Figure 1.

Table 4. Cumulative excretion of radioactivity after oral administration of [phenyl-^{14}C]fenitrothion to birds, expressed as %TAR (Mihara *et al*., 1979).

Species	Dose mg/kg bw/d	Matrix	Days after final administration				
			6 hrs	1	2	3	5
Quails	5 (single)	Excreta	93%	99%	100%	101%	102%
		Eggs	<0.1%	<0.1%	<0.1%	0.1%	0.2%
		Total	93%	99%	100%	101%	102%
Hens	2 (7 days)	Excreta	94%	97%	99%	99%	100%
		Eggs	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%
		Total	94%	97%	99%	99%	100%

Table 5. Concentration of total ^{14}C, fenitrothion and some metabolites in tissues of female quails, 1 hr after oral administration of 0.5 mg/kg bw of [phenyl-^{14}C]fenitrothion (Mihara *et al*., 1979).

Tissues	Total ^{14}C, mg/kg eq	parent, mg/kg	NMC, mg/kg eq	HM-FNT, mg/kg eq	FNO, mg/kg eq	HM-FNO, mg/kg eq	Others, mg/kg eq	Unextracted, mg/kg eq
Liver	0.81	0.12	0.26	ND	0.036	0.013	0.051	0.32
Kidney	2.2	0.11	0.23	ND	ND	0.019	0.39	1.4
Muscle	0.16	0.055	0.007	ND	ND	ND	ND	0.097

ND = <0.005 mg/kg eq.

Table 6. Total radioactive residues in tissues of female quails and hens after oral administration of fenitrothion (Mihara *et al*., 1979).

Tissues	DAT =1		DAT=7	
	Quails, TRR, mg/kg eq	Hens, TRR, mg/kg eq	Quails, TRR mg/kg eq	Hens TRR mg/kg eq
Liver	0.016	0.098	ND	0.008
Kidney	0.016	0.10	ND	0.007
Muscle	ND	ND	ND	ND
Fat	-	0.016	-	ND

ND = not detected, < 0.005 mg/kg eq.
- = not analyzed.

Table 7. Metabolite distribution in excreta during 24 hours after final oral administration of fenitrothion to birds (Mihara *et al*., 1979).

Metabolite	Quails, %TRR	Hens, %TRR
Parent	0.3%	0.4%
NMC	33%	49%
NMC-sul	38%	2.0%
HM-NMC	1.5%	8.5%
HM-NMC-sul	9.6%	7.1%
HM-NMC-glu	1.4%	2.1%
AAMC	ND	1.0%
AAMC-sul	1.5%	4.6%
CA-NMC	ND	1.2%
CA-FNO	ND	trace
DM- FNT	6.5%	12%
DM-HM-FNT	0.8%	ND
DM-FNO	1.2%	3.1%
DM-HM-FNO	1.0%	ND
Unidentified [1/]	1.6%	2.4%
Unextracted	4.1%	6.6%
Total	100%	100%

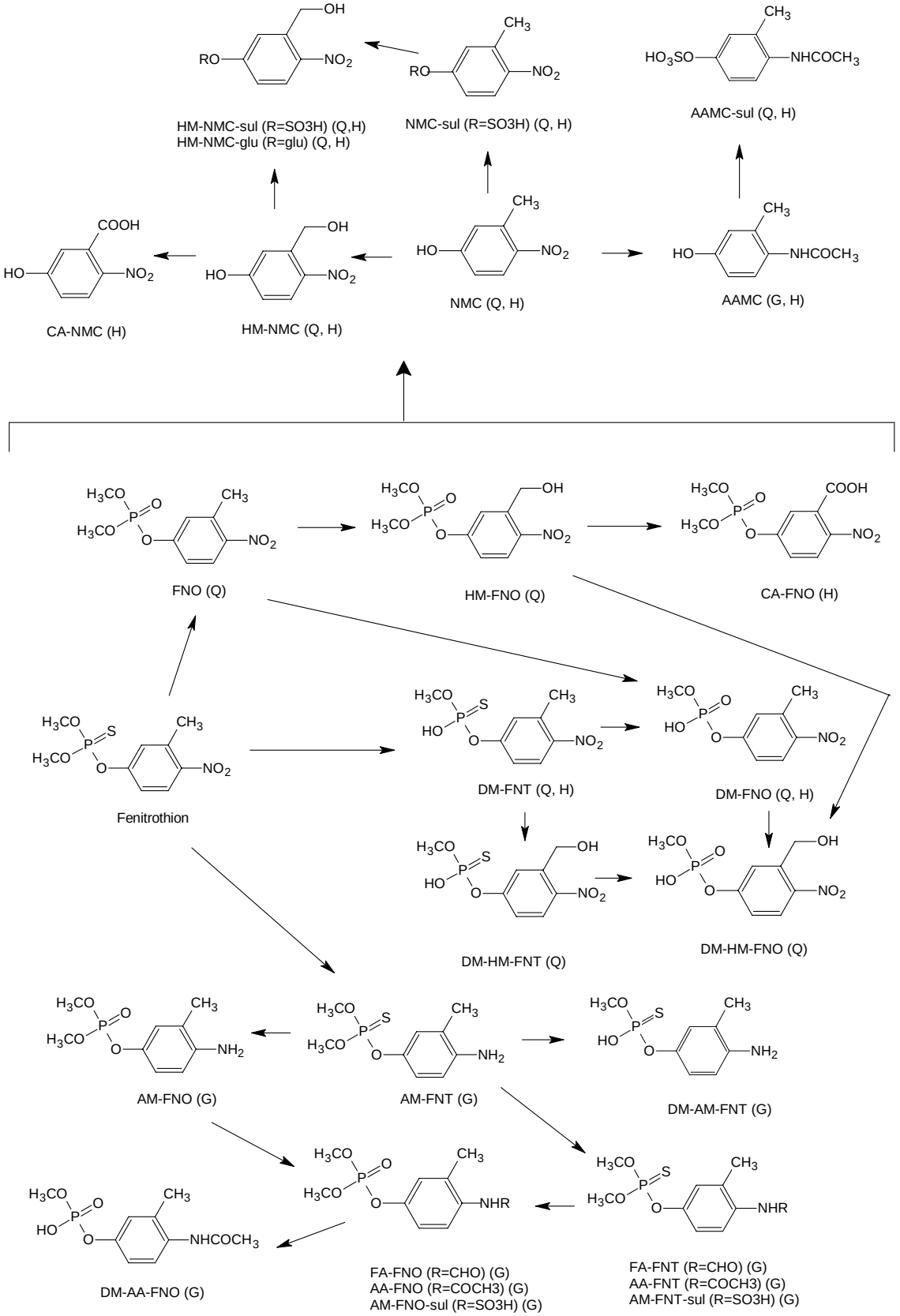
ND: <0.1%.
[1/] Consisted of one compound in quails, at 1.6% TRR, and four compounds in hens, at 0.2, 0.4, 0.7 and 1.1% TRR.

Table 8. Metabolite distribution in hen eggs, at DAT = 1, from hens treated with fenitrothion for 7 days at 2 mg/kg bw/d (Mihara *et al*., 1979).

Metabolite	Whole eggs, TRR, mg/ kg eq	Egg white, % TRR[1/]	Egg yolk, % TRR[1/]
Parent	0.005	4%	4%
NMC	0.012	4%	18%
DM- FNT	0.001	2%	<1%
NMC-sul	0.021	6%	34%
DM-FNO	0.003	1%	4%
HM-NMC-glu	0.004	3%	4%
Unidentified	0.009	7%	9%
Total	0.055	27%	73%

[1/] %TRR in whole eggs.

Figure 1. Proposed metabolic pathways for fenitrothion in animals (G = goat, Q = quail, H = hen).



Plant metabolism

The Meeting received information on the fate of fenitrothion after spray application to grapes and tomatoes and on the fate of fenitrothion in stored rice.

Grapes

Two grape vines (var. Thompson Seedless) were sprayed in the field (Madera County, California, USA), using a handheld CO_2-propelled sprayer, with an EC 500 formulation of [phenyl-^{14}C]fenitrothion (Baker *et al*., 2002). The application rate was 3 times 0.82 kg ai/ha, with 14-day intervals and spray volumes of 1000 l/ha. At the first application, smaller and larger grape bunches were present. At the second application, grape bunches were filling out, while at the third application the berries were increasing in size. During application, the soil was covered with a tarp. During the study there was no rainfall but the vines were drip-irrigated. Grape bunches were collected at mature harvest (35 days after the last treatment).

Recovery of total applied radioactivity was not determined. Of the total recovered radioactive residue (TRR) in grape berries, 97% was extractable (0.72 mg/kg eq): 3.5% TRR could be removed by rinsing with ACN/water; 87% TRR was recovered in subsequent ACN, MeOH and acidified ACN extracts; and 6.0% TRR was recovered from the remaining solids using more rigorous treatments (enzymes, detergents, strong acid, strong base). Rinses, ACN extracts and MeOH extracts were characterized further by HPLC and/or TLC analysis, using co-chromatography against reference compounds (parent fenitrothion, DM-FNT, SM-FNT, DM-FNO, NMC-B-glc and NMC). Grape rinses contained 10 metabolites but each was below 0.01 mg/kg eq (<1.4% TRR). In ACN plus MeOH extracts, a total of 79% TRR was identified or characterized (see Table 9). The major metabolites were NMC conjugate 1, followed by NMC-B-Glc; parent fenitrothion was not detected. During storage (136 days at -20°C), no changes were introduced in the metabolite pattern, nor in the radioactivity levels.

Table 9. Characterization of radioactive residues in grape berries (Baker *et al*., 2002).

Fraction	Component	mg/kg eq	%TRR
Grape rinse	unidentified [1/]	0.025	3.5%
ACN plus MeOH extracts	NMC conj 1	0.19	26%
	NMC-B-glc	0.15	21%
	NMC conj 6	0.053	7.4%
	DM-FNT	0.052	7.2%
	NMC conj 5	0.046	6.4%
	NMC conj 2	0.039	5.4%
	NMC conj 4	0.019	2.6%
	NMC conj 3	0.012	1.7%
	NMC	0.007	0.97%
	Unidentified [2/]	0.056	7.8%
Acidified ACN extracts	Unidentified	0.006	0.83%
Enzyme, acid, base extracts	Unidentified	0.043	6.0%
Unextracted residues (solids)	Unidentified	0.021	2.9%
Total		0.72	100%

[1/] Ten compounds in grape rinses, each <0.01 mg/kg (< 1.4% TRR).

[2/] Four compounds in acetonitrile extracts and 4 compounds in methanol extracts. Seven of these compounds were each <0.01 mg/kg (<1% TRR). On acid hydrolysis, one polar compound in the methanolic extract, at 0.03 mg/kg (4.2% TRR), could be converted to a less polar product with a similar retention time as SM-FNT.

Tomatoes

Tomato plants (var. F1 Shirley) were sprayed in a greenhouse with a solution of [phenyl-^{14}C]fenitrothion (Croucher, 2002). The first application was in May 2001, at growth stage BBCH 85 (ripe fruits present). The foliage and fruit of the plants were sprayed evenly, using a hand sprayer. The actual application rate was 2 x 0.69 kg ai/ha, with 14-day intervals and a spray volume of 4000 l/ha, for the normal application dose, and 2 x 2.1 kg ai/ha, for the 3x exaggerated application dose. At harvest, the mature fruit, immature fruit and foliage were collected (15 days after the last treatment).

Recovery of total applied radioactivity was not determined. Of the total recovered radioactive residue (TRR), 63-70% was recovered in rinses and initial extracts of fruits and foliage (see Table 10). When the post-extraction solids from mature fruit were further extracted with CAN, followed by 1 M HCl and finally with 6 M NaOH, a further 19% TRR was extracted. Metabolites in the rinses, acetone/water and ACN extracts, obtained from mature fruits treated at the normal application rate,

were characterized by HPLC against reference compounds (see Table 11). The main metabolite in the extracts did not correspond to any of the reference compounds available (AM-FNT, FNO, DM-FNO, SM-FNT, FA-FNT, CA-FNT, CA-FNO, AA-FNT, NMC-B-glc, DM-FNT, NMA, NMC). Attempts to identify the main metabolite by LC-MS were inconclusive. The main metabolite could not be hydrolyzed by ß-glucosidase, but could be hydrolyzed with cellulase, resulting in the formation of both NMC (28%) and NMC-B-glc (44%), with 27% remaining as unaltered metabolite. The main metabolite is considered to be a further conjugate of NMC-B-glc. During storage (138 days at -20°C), no changes were introduced in the metabolite pattern, nor in the radioactivity levels. The proposed pathway of fenitrothion metabolism in plants is shown in Figure 2.

Table 10. Recovered radioactivity in extracts of the fruit and foliage from tomato plants and in post-extraction solids (Croucher, 2002).

Fraction	1x application rate (2 x 0.69 kg ai/ha)						3x application rate (2 x 2.1 kg ai/ha)			
	mature fruit		immature fruit		foliage		mature fruit		foliage	
	mg/kg parent eq	%TRR	mg/kg parent eq	%TRR	mg/kg parent eq	%TRR	mg/kg parent eq	%TRR	mg/kg parent eq	%TRR
Surface wash	0.0054	2.6%	0.0037	1.3%	-	-	0.018	5.1%	-	-
Acetone/water	0.13	60%	0.18	63%	1.2	65%	0.21	61%	7.0	70%
ACN extracts	0.011	5.1%	-	-	-	-	-	-	-	-
Hot 1 M HCl extract	0.008	3.8%	-	-	-	-	-	-	-	-
6 M NaOH extract	0.021	9.9%	-	-	-	-	-	-	-	-
Unextracted (solids)	0.037	18%	0.10	36%	0.66	35%	0.12	33%	3.0	30%
Losses	0.0018	0.87%	-	-	-	-	-	-	-	-
Total	0.21	100%	0.29	100%	1.9	100%	0.35	100%	10	100%

- = extraction not conducted.

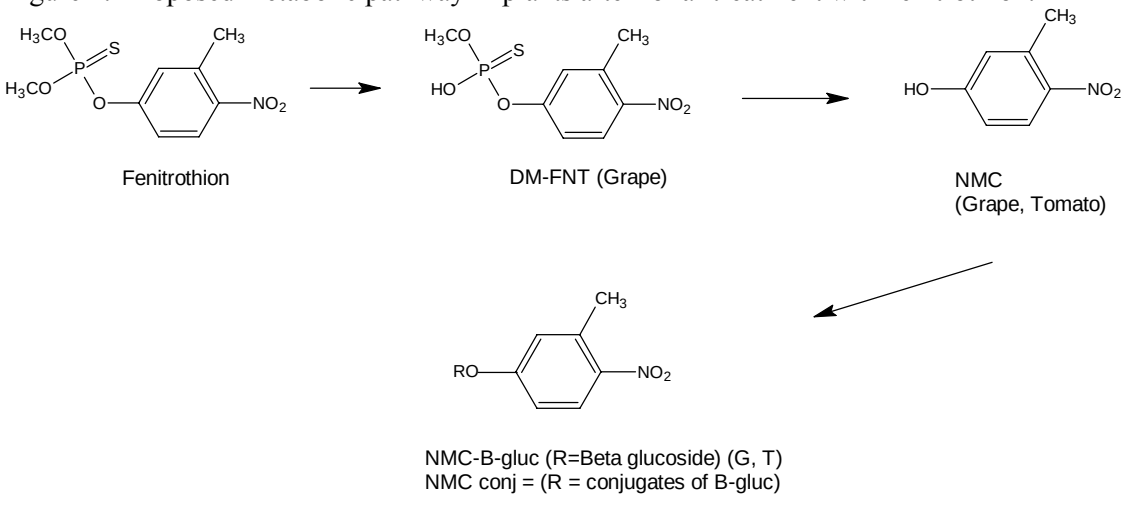
Table 11. Characterization of radioactive residues in mature tomato fruits using HPLC (normal dose) (Croucher, 2002).

Fraction	Component	mg/kg as parent eq	%TRR
Surface wash, acetone/water extracts, ACN extracts	NMC-B-glc conj	0.050	24%
	Fenitrothion (parent)	0.028	13%
	NMC-B-glc	0.015	7.3%
	NMC	0.015	7.0%
	Unidentified [1/]	0.025	12%
1 M HCl extracts	Unidentified, acid-extractable [2/]	0.012	5.7%
6 M NaOH extracts	Unidentified, base-extractable	0.021	9.9%
Unextracted	Solids	0.037	18%
Losses		0.0076	3.6%
Total		0.21	100%

[1/] At least 7 compounds in MeOH rinse, acetone/water and ACN extracts, each <0.008 mg/kg as parent eq (<4% TRR). These compounds were considered to be conjugates of NMC.

[2/] Including 0.004 mg/kg eq acid-extractables from pellets formed during ACN extraction.

Figure 2. Proposed metabolic pathway in plants after foliar treatment with fenitrothion.



Fate of fenitrothion in stored rice

An emulsion containing [*m*-methyl-^{14}C]fenitrothion was applied to unpolished rice grain (variety Nishikaze, 13% moisture content), at dose rates of 6 and 15 g ai/t (Takimoto *et al*., 1978). Rice samples were then stored at 15 or 30°C in the dark, with a KOH trap for acidic volatiles, for 12 months and then analyzed at intervals. The distribution of radioactivity was investigated by autoradiography and by separating treated grain into seed coat, endosperm and germ fractions. Separated and whole-grain samples were extracted with MeOH. Extracts were analyzed by LSC and 2D-TLC (silica gel, with 7 solvent systems). Metabolites were identified by comparison of retention times with those of reference compounds: parent fenitrothion, FNO, SM-FNT, DM-FNT, DM-FNO, DM-SM-FNT, NMC, HM-NMC, NMA, 1,2-dimethoxy-4-methyl-5-nitrobenzene, 1,2-dihydroxy-4-methyl-5-nitrobenzene. Some extracts were treated with diazomethane to generate methylated compounds which could be analyzed by TLC and GC-FTD (flame thermionic detector, KBr single crystal).

Fenitrothion gradually decomposed, with half-lives of about 4 and >12 months at 30°C and 15°C, respectively. The major metabolites were DM-FNT and NMC (Tables 12 and 13). DM-FNT was formed in the early stages of degradation but its concentration remained fairly constant after 3 months. The concentration of NMC increased throughout the storage period. These two products accounted for about 80% of metabolites formed after 12 months storage. Minor metabolites, found particularly at the end of the storage period, were FNO, DM-FNO, SM-FNT, DM-SM-FNT, NMA, HM-NMC, DHMN and DMMN. One reference compound (HM-NMA) was not detected. NMC was the major component in the base trap, no radiolabelled carbon dioxide was present.

Table 12. Degradation of fenitrothion applied to rice grain stored at 15°C (Takimoto *et al*., 1978).

Applied concentration	Month	% of applied radioactivity						
		FNT	DM-FNT	DM-FNO	NMC	Others [1/]	Unextracted	Recovery (%)
6 g ai/t	0	100	0.2	-	0.1	-	0.8	101
	1	92	4.6	0.3	1.0	0.1	1.6	99
	2	85	6.3	0.7	2.3	0.4	2.0	97
	3	77	10	1.3	4.5	0.6	2.4	96
	4.5	76	12	1.7	7.9	0.6	3.4	102
	6	69	12	1.9	9.4	0.5	3.0	96
	9	67	9.7	1.9	13	0.8	3.3	96
	12	65	10	1.7	17	2.4	4.6	101
15 g ai/t	0	100	0.2	-	-	-	0.2	100
	1	93	4.2	0.3	0.9	0.1	1.8	101
	2	89	7.3	0.7	2.4	0.5	2.0	102
	3	84	11	1.2	4.5	0.6	2.4	104
	4.5	78	11	1.3	6.7	0.5	3.3	100
	6	73	14	1.9	9.4	0.6	3.0	102
	9	68	12	1.8	13	1.2	3.5	98
	12	65	11	1.6	16	2.7	4.2	100

- = not detected.
[1/] Others included FNO, SM-FNT, DM-SM-FNT, NMA, DHMN, DMMN and the contents of the KOH trap.

Table 13. Degradation of fenitrothion applied to rice grain stored at 30°C (Takimoto *et al*., 1978).

Applied concentration	Month	% of applied radioactivity								
		FNT	DM-FNT	DM-FNO	NMC	NMA	DHMN	Others [1/]	Unextracted	Recovery (%)
6 g ai/t	0	98	-	-	0.6	-	-	-	0.7	99
	0.25	91	5.8	0.4	2.8	-	-	0.2	2.0	102
	1	67	17	1.4	8.9	-	-	0.6	3.5	99
	2	59	19	2.1	13	-	0.1	0.6	3.3	97
	3	58	17	2.4	18	-	0.2	0.6	4.4	100
	4.5	51	16	2.6	25	-	0.5	0.6	4.7	100
	6	43	17	2.2	29	-	1.0	0.9	4.1	97
	9	32	17	1.7	36	4.0	1.9	4.4	4.5	102
	12	22	19	1.1	38	9.1	2.9	5.0	5.0	102

Applied concentration	Month	% of applied radioactivity								
		FNT	DM-FNT	DM-FNO	NMC	NMA	DHMN	Others [1/]	Unextracted	Recovery (%)
15 g ai/t	0	101	0.3	-	0.6	-	-	-	0.6	103
	0.25	90	7.0	0.5	2.6	-	-	0.3	2.0	103
	1	72	14	1.0	6.9	-	-	0.8	3.3	98
	2	64	18	1.8	12	-	0.1	0.7	4.0	100
	3	57	20	2.2	17	-	0.3	0.8	4.6	101
	4.5	45	21	2.6	26	-	0.6	0.9	4.8	101
	6	41	18	1.1	30	3.0	1.7	1.6	4.2	101
	9	32	21	1.2	33	4.6	3.1	3.6	4.9	104
	12	26	18	1.1	38	6.7	3.2	3.9	5.6	103

- = not detected.
[1/] Others included FNO, SM-FNT, DM-SM-FNT, HM-NMC, DMMN, an unidentified compound and the contents of the KOH trap.

Autoradiography showed that radioactivity was principally located in the aleurone layer (part of the seed coat) but penetrated into the endosperm during storage. Weight ratios of the separated seed coat, germ and endosperm fractions, relative to whole grain, were 3.0, 3.2 and 94%, respectively. Immediately after application, radioactivity was mainly located in the seed coat and the endosperm but, during storage, radioactivity decreased in the seed coat, increased in the germ fraction and remained fairly constant in the endosperm (Table 14). During the first 6 months, fenitrothion concentration decreased significantly in the seed coat and endosperm but increased in the germ cell. The decline in concentration was slower in all fractions during the 6-12 month period. The concentration of fenitrothion in endosperm declined from 4.5 to 3.3 mg/kg at 15°C and to 1.2 mg/kg at 30°C. The amount of fenitrothion in bran (seed coat plus germ) was approximately 40 times that in endosperm at all time points. The major metabolites were found in all three fractions, though the proportions of the metabolites varied.

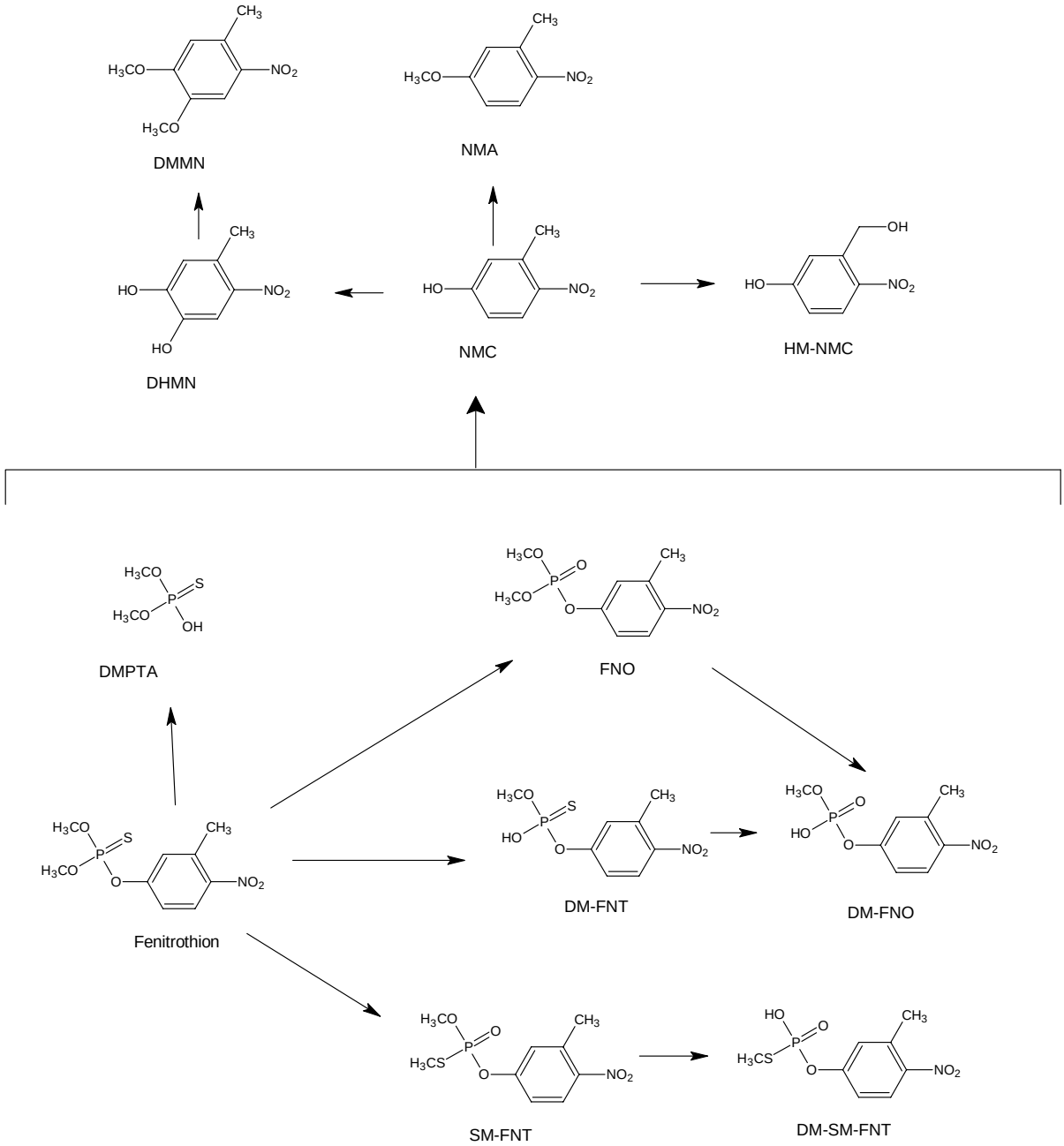
The proposed degradation pathway of fenitrothion applied post-harvest to stored cereal grains (rice) is shown in Figure 3.

Table 14. Distribution of fenitrothion and metabolites in rice grain treated with fenitrothion at 15 g ai/t (Takimoto *et al*., 1978).

Month	Fraction	% of applied radioactivity							
		Total	FNT	DM-FNT	DM-FNO	NMC	NMA	Others [1/]	Unextracted
Stored at 15°C									
0	Seed coat	64	63	0.4	<0.1	0.4	-	0.2	0.6
	Endosperm	28	28	0.1	-	0.2	-	<0.1	0.4
	Germ cell	6.1	6.1	-	-	-	-	-	-
6	Seed coat	49	39	4.3	1.5	3.7	-	0.2	0.4
	Endosperm	36	28	3.8	0.5	4.2	-	<0.1	1.1
	Germ cell	15	12	1.4	0.1	1.1	-	<0.1	<0.1
12	Seed coat	43	30	4.2	1.5	6.0	-	0.6	0.7
	Endosperm	33	21	3.8	0.5	7.9	-	<0.1	1.4
	Germ cell	19	14	1.7	0.2	2.7	-	0.1	0.1
Stored at 30°C									
0	Seed coat	64	62	0.3	0.1	0.8	-	0.1	0.6
	Endosperm	29	28	0.1	-	0.4	-	<0.1	0.3
	Germ cell	5.1	5.0	-	-	0.1	-	-	-
6	Seed coat	35	18	4.8	1.1	9.6	<0.1	0.6	0.7
	Endosperm	39	13	8.5	0.3	15	<0.1	1.0	1.8
	Germ cell	23	13	2.4	0.1	5.5	<0.1	0.9	0.2
12	Seed coat	32	10	5.1	1.1	12	0.2	1.7	1.3
	Endosperm	41	7.7	9.4	0.4	19	0.1	1.9	2.0
	Germ cell	24	10	2.3	0.1	7.3	0.3	2.3	0.7

- = not detected.
[1/] Others included FNO, SM-FNT, DM-SM-FNT, DHMN, DMMN and an unidentified compound.

Figure 3. Proposed degradation pathway of fenitrothion applied post-harvest to stored cereal grains (rice).



Environmental fate in soil

The Meeting received information on aerobic metabolism of fenitrothion in soil. Information on anaerobic metabolism in soil, photo-degradation in/on soil, adsorption-desorption in/on soil, soil leaching and soil dissipation in the field was submitted but was not relevant to this evaluation and therefore was not summarized. Studies on rotational crops were not submitted.

Aerobic soil metabolism

Study 1. The aerobic metabolism of [phenyl-^{14}C]fenitrothion (radiochemical purity >98%, specific activity 6.7 MBq/mg) was studied in a sandy loam soil from Ashland, Nebraska, USA, according to EPA guidelines, for 365 days (Cranor and Daly, 1989; Kodaka *et al*., 2000). Fenitrothion was applied to the soil at a nominal rate of 1 mg ai/kg. The incubation conditions were as follows: aerobic; dark; 75% field moisture capacity (⅓ bar); temperature 25 ± 1°C; moistened CO_2-free air was drawn over

the surface of the soil through a series of traps, to collect organic volatiles (ethylene glycol) and $^{14}CO_2$ (KOH). Duplicate soil samples were taken at 0, 1, 3, 5, 7, 10, 14, 21, 30, 61, 92, 122, 153, 183, 273 and 365 days after treatment. Soils were extracted with 0.2 M HCl/ethyl acetate. Radioactivity in the ethyl acetate and aqueous phases, and in the remaining solids, was quantified by (combustion) LSC. Metabolites were identified by 2D-TLC (silica gel) against reference compounds: parent, FNO, NMC, DM-FNT, DM-FNO, AM-FNT, FA-FNT, AA-FNT, NMA. The presence of parent fenitrothion and NMC was confirmed by HPLC.

Mean recovery was 84-112% TAR. Parent fenitrothion decreased from 88% at 0 DAT, to 0.05% TAR at 365 DAT. Cumulative radioactive volatiles accounted for 71% TAR at the end of the study, the majority of which was $^{14}CO_2$ (67.3% TAR). Six soil metabolites were identified: FNO, NMC, DM-FNT, DM-FNO, FA-FNT and NMA. NMC, the major metabolite, amounted to 20% TAR at day 3, but then decreased to <1% TAR at day 30. The amounts of other metabolites were less than 1% TAR. Non-extractable residues increased to 35% TAR at 21 DAT but then decreased to 20% TAR at 365 DAT. A number of fractions were not identified, however the sum of these did not exceed 4.4% of TAR.

Non-extractable residues from samples taken at 1 and 6 months were fractionated into fulvic acid (9.2% and 7.2% TAR), humic acid (1.7% TAR) and humin (10% TAR). In the fulvic acid fractions, NMC was the predominant metabolite but <0.5% TAR.

On the basis of these results it can be concluded that fenitrothion is mainly degraded via cleavage of the P-O-aryl linkage, cleavage of the P-O-methyl linkage and oxidation of the P=S group to P=O. Moreover, *via* opening of the phenyl ring, these degradation products are finally mineralized to $^{14}CO_2$. Half-lives of both fenitrothion and the major metabolite, NMC, were determined (see Table 15).

Table 15. DT_{50} and DT_{90} values for fenitrothion in soils under aerobic conditions at 25°C (Cranor and Daly, 1989; Kodaka *et al*., 2000).

Report	Substance	Soil type	DT_{50}, days	DT_{90}, days [1/]	Model	r^2
HM-91-0108	Parent fenitrothion	Sandy loam[2/]	2.0	6.6	1st order	0.978
HM-0187	NMC	Sandy loam[2/]	3.3	11	1st order	0.928

[1/] The DT_{90} value was not presented in the report, so it was calculated using the k value from the DT_{50} calculation in the report.

[2/] Soil characteristics: pH 6.2; 1.6% om; CEC 9.5 meq/100 g; 16% clay particles; bulk density 1.18 g/cm^3; ⅓ bar moisture 15.12%.

Study 2. The route and rate of degradation of [phenyl-^{14}C]fenitrothion (radiochemical purity 99.3%, specific activity 7.4 MBq/mg) was studied, according to SETAC guidelines, in four soils over a period of 90 days (Yeomans and Swales, 2001). Flasks containing 50 g soil (see Table 16 for soil characteristics) were incubated in the dark at 20 ± 1°C for 14 days, to establish equilibrium. Following this period, ^{14}C-fenitrothion was applied to the soils at a rate equivalent to 0.75 kg ai/ha. Samples were then incubated under the same conditions, at 45% maximum water-holding capacity, for a further 90 days. Carbon dioxide-free air was drawn through the flasks and passed through a series of traps - paraffin in xylene, ethanediol and NaOH - to collect evolved volatiles. Samples were taken at 1, 3, 7, 14, 29, 59 and 90 days after treatment. Soils were extracted with 0.2 M HCl/ethyl acetate. Radioactivity in the ethyl acetate and aqueous phases, and in the remaining solids, was quantified by (combustion) LSC. Extracts containing >1% TAR were concentrated and analyzed by HPLC-UV (Spherisorb S3 ODS2, with two gradient systems) against reference compounds: parent, NMA, NMC, AM-FNT, FNO, DM-FNO, SM-FNT, FA-FNT, CA-FNT, CA-FNO, AA-FNT, NMC-β-glucoside and DM-FNT. The presence of parent, NMC and NMA was confirmed by 2D-TLC (silica gel).

Table 16. Characteristics of the soils used in study 2 (Yeomans and Swales, 2001).

Soil name	PT102	PT103	SK15556090	SK960087
USDA textural class	Sandy loam	Sandy loam	Silt loam	Clay loam
% organic matter	4.3	2.2	7.8	4.7
pH in 1M KCL	6.9	4.9	6.2	7.2

Soil name	PT102	PT103	SK15556090	SK960087
Clay (<2 μm)	11	12	20	34
CEC mEq/100 g	14.6	11.1	17.8	22.2
Water holding capacity at pF 0, %	62.8	42.3	110.9	73.4
Water holding capacity at pF 2.5, %	21.2	16.6	34.7	29.6

Mean recovery of radioactivity from all four soils was 89-100% TAR. Extractable radioactivity in the aqueous extracts remained less than 4% TAR throughout the study. Unextractable radioactivity increased to maxima of 37-54% TAR after 7 days, declining to 23-43% after 90 days. Trapped $^{14}CO_2$ increased throughout the study, to totals of 51-69% at the end. No radioactivity was retained in the traps for organic volatiles. Fenitrothion was detected at maxima of 91-96% TAR, immediately after application, but declined rapidly to 2.4-5.4% TAR after 7 days. Two metabolites were identified. NMC was detected at maxima of 17-45% TAR at 1 DAT, declining rapidly to less than 7% TAR after 7 days. The metabolite, NMA, was also detected but at quantities below 0.5% TAR. A further unidentified metabolite was detected at a maximum of 3.2% TAR; other unknowns and unresolved radioactive components occurred at maxima of 0.7% and 0.6% TAR, respectively.

Further investigation of the nature of the unextractable residues was performed, using the sample containing the highest level of unextractable radioactivity from each soil type. Extracted soil samples were Soxhlet-extracted for approximately 12 hours with acetone/acetic acid and radioactivity in the extracts was quantified by LSC. Radioactivity remaining in the soil samples after reflux extraction was separated into humin, humic acid and fulvic acid fractions. The Soxhlet extraction and fractionation, of the unextractable residues in the samples from 7 DAT, gave 1.2-3.0% TAR in the Soxhlet fraction and 7.3-12%, 2.9-16% and 8.1-27% TAR in the fulvic acid, humic acid and humin fractions, respectively.

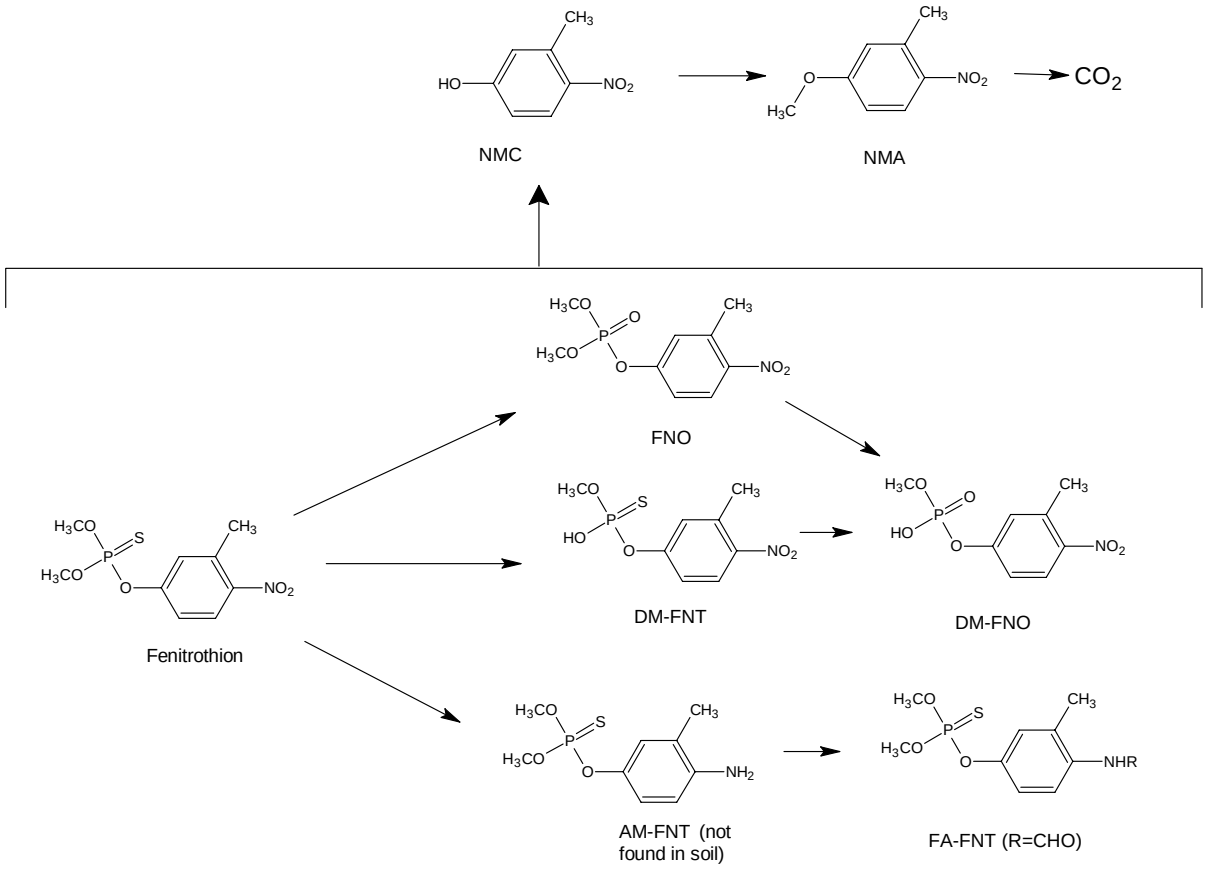
The results of this study indicated that fenitrothion is mainly degraded via cleavage of the P-O-aryl linkage and then further breakdown occurs, *via* opening of the phenyl ring, with eventual mineralization to $^{14}CO_2$. DT_{50} and DT_{90} values for fenitrothion and the major metabolite, NMC, in the four soils were calculated and are presented in Table 17.

Proposed pathways of aerobic soil metabolism of fenitrothion are shown in Figure 4.

Table 17. DT_{50} and DT_{90} values for fenitrothion and NMC in four European soils under aerobic conditions at 20°C (Yeomans and Swales, 2001).

Report	Substance	Soil	DT_{50}, hours	DT_{90}, hours	Model	r^2
HM-0192	Parent	PT102	1	52	2-phase exponential	0.998
	Parent	PT103	33	112	2-phase exponential	0.987
	Parent	SK15556090	17	62	2-phase exponential	0.999
	Parent	SK960087	13	65	2-phase exponential	0.998
HM-0192	NMC	PT102	49	132	2-phase exponential with accumulation phase	1.00
	NMC	PT103	68	171	2-phase exponential with accumulation phase	0.997
	NMC	SK15556090	42	154	2-phase exponential with accumulation phase	1.00
	NMC	SK960087	55	171	2-phase exponential with accumulation phase	1.00

Figure 4. Proposed pathway of fenitrothion metabolism in aerobic soil.



Environmental fate in water/sediment systems

The Meeting received information on the physico-chemical characteristics of fenitrothion, relating to water, and on its metabolism in water-sediment systems. Because rice is grown in water, and rice is a target crop for fenitrothion application, these studies were considered relevant for the present residue assessment. Information on anaerobic aquatic metabolism was submitted but anaerobic conditions are not relevant for residue assessment and these data were not summarized.

Partition characteristics

The octanol/water partition coefficient was determined according OECD 107, using the shake flask method (Schepler and Schick, 2002). Fenitrothion was uniformly ^{14}C-labelled in the phenyl ring, with specific activity of 7.36 MBq/mg and a radiochemical purity of 99.0%. The initial concentrations were 6.13 x 10^{-5} M, 3.06 x 10^{-5} M and 1.53 x 10^{-5} M fenitrothion in the *n*-octanol phase and the respective *n*-octanol:water ratios were 1:6, 2:5 and 4:3. Results were: log K_{ow} = 3.319, s.d. 0.080, at pH 6.2 and 25°C.

Hydrolysis

Hydrolysis in water was determined according to EPA guideline 161-1 (Ito *et al*., 1988). Fenitrothion was uniformly ^{14}C-labelled in the phenyl ring with a specific activity of 2.2 MBq/mmol and a radiochemical purity of 99.9%. Solutions containing fenitrothion at 1 mg/l, at pH 5, 7 and 9 were kept in the dark at 25 ± 1°C for 30 days. Duplicate samples were taken at 0, 3, 5, 7, 14, 21 and 30 days and compounds present were identified by 2D-TLC, followed by HPLC-UV, against reference standards.

At pH 5, fenitrothion was stable, with a half-life of 191-200 days. After 30 days, 12% transformation was observed, with the following degradation products: 9.8% DM-FNT, 1.1% NMC, 0.8% unidentified and 0.4% missing.

At pH 7, fenitrothion was stable, with a half-life of 180-186 days. After 30 days, 9% transformation was observed, with the following degradation products: 6.8% DM-FNT, 1.5% NMC, 0.6% unidentified and 2.4% missing.

At pH 9, fenitrothion was relatively unstable, with a half-life of 100-101 days. After 30 days, 21% transformation was observed, with the following degradation products: 5.1% DM-FNT, 14.4% NMC, 1.2% unidentified and 0.1% missing.

Photolysis

Photolysis in water was determined according to EPA guideline 161-2 (Katagi *et al.*, 1988). Fenitrothion was uniformly ^{14}C-labelled in phenyl ring with a specific activity of 2.2 MBq/mmol and a radiochemical purity of 99.9%. Solutions of fenitrothion (1 mg/l) in acetate buffer (pH 5) were irradiated with artificial sunlight (2 kW Xenon lamp ≥290 nm) at 25 ± 1°C for 30 days, with 10 hours light and 14 hours darkness per day. Duplicate samples were taken at 0, 2, 4, 7, 14, 21 and 30 days and the compounds present were identified by 2D-TLC against reference standards. CA-FNT was also identified by HPLC-UV.

At pH 5, fenitrothion was rapidly photolyzed, with a half-life 3.3-3.6 days (dark control 71-141 days). At 30 days, 100% transformation had occurred. At several time points, the following proportions of degradation products were found: CO_2, <0.1-42.4%; CA-FNT, <0.1-12.4%; CA-FNO, NMC, FNO, SM-FNT, DM-FNO, DM-FNT, each at ≤1.2%; unidentified components, 0.3-48% (<10% each). The degradation product, CA-FNT, amounted to 8.0-12.4% at day 14 but decreased thereafter. Photo-products were further degraded to CO_2 (41.2-42.0%) at 30 days.

Water-sediment systems

The degradation of [phenyl ^{14}C]fenitrothion was examined, according to SETAC guidelines, in two water-sediment systems, over a 59-day period (Swales, 2001). The radiochemical purity of the radiolabel was >99%, the specific activity was 2 GBq/mmol. Samples of sediment and water were collected from two sites in the UK: Millstream Pond (Dorchester, Dorset) and Emperor Lake (Chatsworth, Derbyshire). Their characteristics are described in Table 18. Samples of each water-sediment system were sieved (2 mm mesh) and placed in glass cylinders of 4.5 cm diameter, to give units containing a sediment layer of 2.5 cm and a water layer of 6 cm. Moistened CO_2-free air was drawn over the water surface and the units were incubated in the dark for 61 days (Millstream Pond) or 55 days (Emperor Lake), to equilibrate. Following equilibration, [^{14}C]fenitrothion was applied to each system, at a rate equivalent to 0.750 kg ai/ha, and the systems were incubated in the dark at 20 ± 2°C for 59 days. During this period, moistened CO_2-free air was drawn over the water surface and passed through two traps for volatiles (foam bung, ethanediol/2% paraffin in xylene; NaOH solution). The contents of volatiles traps and samples of each water/sediment system were removed at intervals of 0 and 4 hours and 1, 2, 3, 7, 30 and 59 days. Radioactivity in the water, sediment and extracts was analyzed by (combustion) LSC. Surface water was decanted, filtered and extracted with ethyl acetate. Sediment samples and filter papers, from filtration of the surface water, were extracted once with 0.2 M HCl + ethyl acetate, followed by ethyl acetate. Extracts containing >1% of applied radioactivity were concentrated and analyzed by HPLC, against reference standards for parent fenitrothion, AM-FNT, FNO, DM-FNO, SM-FNT, FA-FNT, CA-FNT, CA-FNO, AA-FNT, NMC-B-glc, DM-FNT, NMA, NMC and A-NMC. Selected extracts were analyzed using TLC, LC-MS or GC-MS, to confirm the identity of degradation products provisionally identified by HPLC. Unextractable radioactivity in the 59-day sediment samples was Soxhlet extracted with acetone. Radioactivity remaining in the sediment after reflux extraction was separated into humin, humic acid and fulvic acid fractions. Radioactivity was determined by (combustion) LSC.

Table 18. Characteristics of two water-sediment systems studied (Swales, 2001).

	System:	Millstream Pond, A	Emperor Lake, B
Sediment	UK textural class	Sandy silt loam	Sandy loam
	Clay (<2 μm)	13	16
	% organic carbon	7.4	3.4
	pH in 1M KCl	6.9	5.7
	CEC mEq/100g	29.8	16.2
	Total N (mg/kg)	210	1939
	Total P (mg/kg)	1948.3	542.3
	Biomass (study start) μg C/g	706.42	389.26
	Biomass (study end) μg C/g	336.42	177.39
Water, initial values	Total N (mg/l)	1.4	<0.05
	Total P (mg/l)	0.1	<0.05
	Dissolved organic carbon (mg/l)	28.9	67.3
	Water hardness (mg/l as $CaCO_3$)	223	60
	Suspended solids (mg/l)	<0.05	16
Water, values at end of study	Total N (mg/l)	1.4	79.8
	Total P (mg/l)	0.6	0.1
	Dissolved organic carbon (mg/l)	14.2	4.7
	Water hardness (mg/l as $CaCO_3$)	262	71
	Suspended solids (mg/l)	44	20

Total recovery of applied radioactivity from systems A and B was 87-100%. Radioactivity in the surface waters declined from 92-93% TAR at 0 hours to 1.5-4.0% TAR at day 59. Total radioactivity in the sediments increased from 5.3-6.2% TAR at 0 hours to 73-81% TAR after 59 days. Unextractable radioactivity in the sediments increased from 0.8% TAR at 0 hours to a maximum of 71-76% TAR at 59 days. Carbon dioxide amounts increased throughout the study, to a maximum of 14-15% TAR at 59 days. Other volatiles remained at less than 0.4-0.5% TAR. However, 1.7% TAR was detected in the ethanediol trap attached to system B, at 30 days. This was attributed, by the author of the report, to 'suck-back' from the sodium hydroxide trap. The further extraction of the initially unextractable residues (day 59) revealed 1.8-3.0% TAR in the Soxhlet extract and 4.8-10%, 6.8-32% and 29-49% TAR in the fulvic acid, humic acid and humin fractions, respectively.

In the Millstream Pond system (system A), parent fenitrothion declined rapidly in the water phase, from 90% TAR at 0 hours to 0.1% TAR at 7 days. There was a concurrent increase of parent fenitrothion in the sediment phase, rising from 4.4% TAR at 0 hours to a maximum of 28% TAR after 1 day, then declining to 0.5% TAR at 30 days. In the water phase, a number of degradation products were found: NMC, A-NMC, AM-FNT, AA-FNT, Unk 1, Unk 2 and other unknowns. Of these, A-NMC, AM-FNT and Unk 2 were found in significant quantities, with respective maxima of 15% TAR (day 2), 18% TAR (day 3) and 17% TAR (day 7). All three compounds declined rapidly, to non-detectable levels, or to 0.2% TAR in the case of AM-FNT, by the end of the study. Other unknowns in the water phase did not exceed 3.5% TAR. In the sediment phase, NMC, AM-FNT, AA-FNT, Unk 1, Unk 3 and other unknowns were found. However, only NMC was found at significant levels, at a maximum of 13% TAR at day 3 and declining to 0.2% TAR by day 7. Other compounds and individual unknowns in the sediment did not exceed 4.7% TAR.

A similar pattern was observed in the Emperor Lake system (system B). Again parent fenitrothion declined rapidly in the water phase, from 92% TAR at o hours to 0.5% TAR on day 7. Its increase in concentration in sediment was not as marked, rising from 5.2% TAR at 0 hours to a maximum of 9.5% TAR on day 3. Levels then declined to 0.3% TAR by day 30. In the water phase, NMC, A-NMC, AM-FNT, AA-FNT, Unk 1, Unk 2 and other unknowns were found, with NMC and A-NMC occurring at significant levels. NMC was found at a maximum of 22% TAR on day 7, then declined to non-detectable levels by day 30. A-NMC occurred at a maximum of 22% TAR at 2 days, then declined to 1.4% TAR by day 3. Other compounds and individual unknowns did not exceed 7.9% TAR. In the sediment phase, NMC, AM-FNT, AA-FNT, Unk 1 and other unknowns were

found. However, NMC was the only metabolite identified which occurred at significant levels, occurring at a maximum of 9.6% TAR on day 3, then declining to 0.3% TAR by day 59. The other identified and unknown metabolites were not found at levels greater than 2.3% TAR.

A-NMC was only found at significant levels in the water phase in the day 2 samples of systems A and B and was not found in either sediment. During freezer storage it was observed that NMC in organic solvent extracts of the surface water samples changed to A-NMC. According to the study author, this suggests that A-NMC is an artefact, produced from NMC, and the extent of its formation is somewhat variable during the work-up procedure or storage. The extraction with ethyl acetate, followed by concentration, could have resulted in transesterification between NMC and ethyl acetate, possibly catalyzed by co-extracted organic components of the sediments. In determining degradation rates, the A-NMC was assumed to have been present originally as NMC and the quantities of the two components were summed.

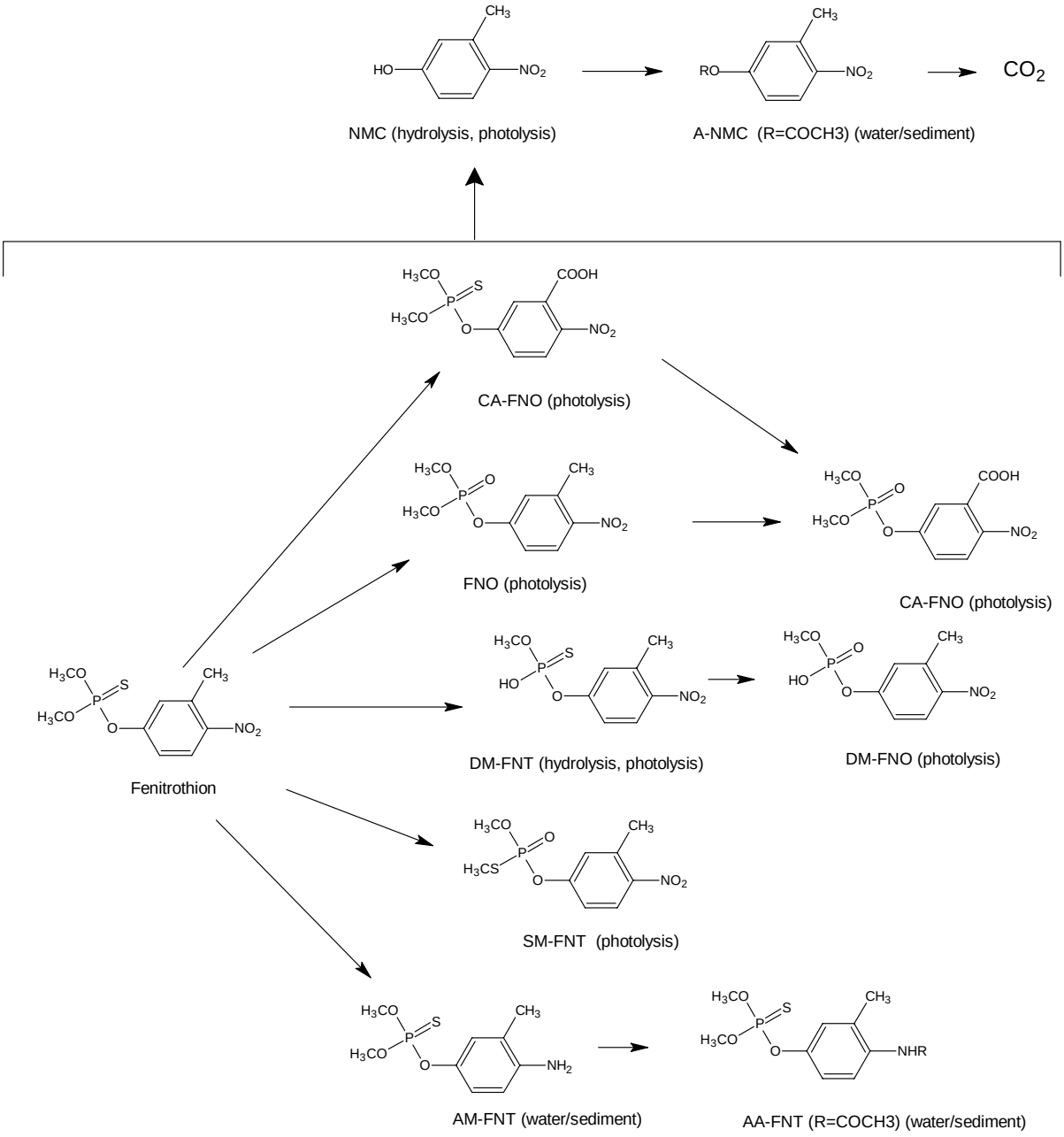
Unk 2 was detected in the water phase of both systems and was detected at significant levels in system A. It was present in the aqueous phase of the surface water after partitioning, indicating that it was polar in nature. Attempts to identify the compound by HPLC and/or TLC were unsuccessful, due to its instability during frozen storage under nitrogen. With LC-MS, ions of low abundance were detected which suggested that Unk 2 may be DM-AM-FNT.

Rates of degradation of fenitrothion and its major degradation products have been calculated where possible and are presented in Table 19. The proposed degradation pathways for fenitrothion in hydrolysis, photolysis and water/sediment systems is presented in Figure 5.

Table 19. Calculated degradation rates of fenitrothion and its major degradation products in two water/sediment systems (Swales, 2001).

Compound	System	Phase	DT_{50} (days)	DT_{90} (days)	r^2	Model
Parent	A	Total system	1.59	5.3	0.99	1st order
	B	Total system	1.56	5.19	0.998	
	A	Water	0.88	2.94	0.997	1st order
	B	Water	1.27	4.2	0.997	
	A	Sediment	1.1	4	0.97	1st order
NMC (+ A-NMC)	A	Total system	3.55	8.28	0.837	Two-phase exponential
	B	Total system	6.99	16.85	0.97	with accumulation phase
	A	Water	1.85	4.28	0.761	Single-phase exponential
	B	Water	7.38	17.19	0.952	with accumulation phase
AM-FNT	A	Total system	7.41	22.83	0.99	Two-phase exponential
	B	Total system	2.56	5.69	0.992	with accumulation phase
	A	Water	6.09	14.19	0.959	Single-phase exponential
	B	Water	3.04	7.06	0.942	with accumulation phase

Figure 5. Proposed pathways of degradation of fenitrothion by hydrolysis, photolysis and in water-sediment systems.



METHODS OF RESIDUE ANALYSIS

Analytical methods

The Meeting received information on several methods for the determination of parent fenitrothion residues in cereal grains and related processed products, and on one method for the determination of DM-FNT residues in wheat grain. Methods for residues in soil, water and air were submitted but were not relevant for the residue assessment and are therefore not summarized here. In some cases, methods used to analyze samples from field trials were not given a unique code and one method, or its minor variants, may be identified by more than one code number in the following summary. In one case, two unrelated determination techniques sharing a common extraction are identified by a single code number.

The government of The Netherlands reported a multi-residue enforcement method for determination of fenitrothion residues in fruit and vegetables, consisting of an extraction technique

generally employed for non-fatty matrices and detection by GC-ITD. LOQs were 0.03-0.05 mg/kg (Netherlands, 1996).

Method ER-70-0014 (Ohnishi *et al*., 1987, non-GLP) was used in a supervised residue study on wheat, treated post-harvest, and in a processing study on wheat. Pulverized samples were extracted with acetone/water followed by partitioning into dichloromethane and clean-up using Florisil. Fenitrothion was quantified by GC with a flame thermionic detector (FTD). The validation data provided are summarized in Table 20.

Table 20. Recoveries and matrix interferences (in untreated controls) associated with the determination of fenitrothion in wheat commodities by method ER-70-0014 (Ohnishi *et al*., 1987).

Commodity	Reported LOQ, mg/kg	Spike level, mg/kg	n	Recovery, %	Recovery range, %	% RSDr	Residues in control samples (mg/kg)
Wheat grain	0.01	0.1	1	92	-	-	<0.01
Bran	0.01	1.0	1	96	-	-	0.02
Pollard	0.01	1.0	1	100	-	-	0.07
Germ	0.01	-	-	-	-	-	-
Flour	0.01	-	-	-	-	-	-
Gluten	0.01	10	1	110	-	-	1.18
White bread	0.01	1.0	1	102	-	-	0.02
Brown bread	0.01	1.0	1	98	-	-	0.03

Method ER-71-0015 (Turnbull and Ardley, 1987, non-GLP) was used in a supervised residue study on wheat, treated post-harvest, and in a processing study on wheat. Pulverized samples were extracted with MeOH for 72 hours, followed by quantification of fenitrothion by GC-ECD. The validation data provided are summarized in Table 21.

Table 21. Validation data for the determination of fenitrothion in wheat commodities by method ER-71-0015 (Turnbull and Ardley, 1987).

Commodity	Reported LOQ, mg/kg	Spike level, mg/kg	n	Recovery, %	Recovery range, %	%RSDr	Residues in control samples (mg/kg)
Wheat grain	0.05	12	1	99	-	-	<0.05
Bran	0.25	25	1	97	-	-	<0.25
Pollard	0.1	-	-	-	-	-	-
Germ	0.25	-	-	-	-	-	-
Flour	0.05	2	1	102	-	-	<0.05
White bread	0.1	1	1	94	-	-	<0.1
Brown bread	0.1	3	1	90	-	-	<0.1

Method HR-0227 was used in supervised trials and storage stability studies on brown rice, conducted in 1993 in Japan (Komatsu and Yabusaki, 1994). Samples of grain (10 g) or straw (5 g) were soaked in water (2-24 hrs) and extracted with acetone. The acetone extract was cleaned up on a Kieselgur column (ChemElut). The grain sample extract was further purified by partitioning between *n*-hexane and acetonitrile. The acetonitrile layer was taken to dryness and re-dissolved in toluene for analysis. Grain and straw extracts were analyzed by GC-FPD in the phosphorus mode, using a DB-17 capillary column. Fenitrothion was quantified using five single standards in acetone/toluene, in the range 0.01-0.4 mg/l (the corresponding mg/kg range was not stated). Linearity and matrix effects were not verified. Validation results are shown in Table 22.

Table 22. Validation data for method HR-0227 for the determination of fenitrothion residues in rice grain and straw (Komatsu and Yabusaki, 1994).

Commodity	Reported LOQ, mg/kg	Spike level, mg/kg	n	Mean % recovery	Recovery range, %	%RSDr	Residues in control samples (mg/kg)
Rice, brown grain	0.01	0.10	2	88	87-89	-	<0.01 (4)
Rice, straw	0.04	1.6	2	95	91-99	-	<0.04 (4)

Method HR-0229 (also known as HR-0230) was used in supervised trials and storage stability studies on wheat (HR-0229) and barley (HR-0230), conducted in 1993 in Japan (Kuroda and Higuchi,

1993a & 1993b). Grain (25 g) was soaked in acetone overnight. Acetone was evaporated from the filtrate and the aqueous residue was partitioned with *n*-hexane after addition of sodium chloride solution. The *n*-hexane layer was then partitioned with acetonitrile and the fenitrothion in the acetonitrile layer was partitioned back into *n*-hexane after the addition of sodium chloride solution. The hexane layer was further cleaned up on Florisil. Grain extracts were analyzed by GC-FPD in the phosphorus mode, using a packed glass column (Ultrabond 20M). Fenitrothion was quantified using six single standards in acetone, in the range 0.025-0.5 mg/l (the corresponding mg/kg range was not stated). Linearity and matrix effects were not verified. Validation results are shown in Table 23.

Table 23. Validation data for the determination of fenitrothion residues in wheat (Kuroda and Higuchi, 1993a) and barley (Kuroda and Higuchi, 1993b) grain by method HR-0229 (or HR-0230).

Commodity	Reported LOQ, mg/kg	Spike level, mg/kg	n	Mean % recovery	Recovery range, %	RSD, %	Residues in control samples (mg/kg)
Wheat, grain	0.01	0.4	4	86	81-90	5.4	<0.01 (4)
Barley, grain	0.01	0.4	4	84	79-86	3.9	<0.01 (4)

Method HR-0228 was used in supervised trials and storage stability studies on brown rice, conducted in 1994 in Japan (Kuroda and Higuchi, 1995). Grain (25 g) was extracted and cleaned-up as for method HR-0229. Grain samples were analyzed by GC-FPD in the phosphorus mode, using a capillary column (G-100). Fenitrothion was quantified using five single standards in acetone, in the range 0.05-1.0 mg/l (the corresponding mg/kg range was not stated). Linearity and matrix effects were not verified. Validation results are shown in Table 24.

Table 24. Validation data for the determination of fenitrothion residues in brown rice by method HR-0228 (Kuroda and Higuchi, 1995).

Commodity	Reported LOQ, mg/kg	Spike level, mg/kg	n	Mean % recovery	Recovery range, %	RSD, %	Residues in control samples (mg/kg)
Rice, brown grain	0.01	0.4	4	85	84-86	0.88	<0.01 (4)

Method HR-0223 (also known as HR-0224, HR-0225 or HR-0226) was used in supervised trials and storage stability studies on brown rice, conducted in 1995 in Japan (Suzuki, 1996a, 1996b, 1996c and 1996d). The same method was used in trials HR-0224, HR-0225 and HR-0226. Grain (20 g) was soaked in water (2 hrs), extracted with acetone and the extract filtered through Celite. The filtrate was rotary evaporated and the aqueous residue was partitioned into *n*-hexane. The *n*-hexane then underwent partition with acetonitrile. The acetonitrile layer was taken to dryness, re-dissolved in hexane/diethyl ether and further cleaned-up on a Florisil mini-column. Grain extracts were analyzed by GC-FPD in the phosphorus mode, using a capillary column (G-100). Fenitrothion was quantified using four replicate standards in acetone, in the range 0.02-0.6 mg/l (the corresponding mg/kg range was not stated). Linearity was verified (one curve, $r > 0.999$). Matrix effects were not verified. Validation results are shown in Table 25.

Table 25. Validation data for the determination of fenitrothion residues in brown rice by method HR-0223 (Suzuki, 1996a, 1996b, 1996c and 1996d).

Commodity	Reported LOQ, mg/kg	Spike level, mg/kg	n	Mean % recovery	Recovery range, %	RSD, %	Residues in control samples (mg/kg)
Rice, brown grain	0.01	0.1	16	98	93-100	2.1	<0.01 (16)
		1.0	16	95	90-99	2.7	

Method HR-0222 was used in supervised trials and storage stability studies on brown rice, conducted in 1996 in Japan (Hidai, 1997). Grain (20 g) was soaked in water (2 hrs), extracted with acetone and filtered through Hyflo Super-Cel. The filtrate was rotary evaporated and the aqueous residue was partitioned into dichloromethane. The dichloromethane extract was taken to dryness and re-dissolved in *n*-hexane, which underwent partition with acetonitrile. The acetonitrile layer was taken to dryness, re-dissolved in hexane and further cleaned up on a silica-gel column. Grain extracts were analyzed by GC-FPD in the phosphorus mode, using a capillary column (5% DC 200). Fenitrothion was quantified using five single standards in acetone, in the range 0.1-2.0 mg/l (the

corresponding mg/kg range was not stated). Linearity was verified (one curve, r >0.999). Matrix effects were not verified. Validation results are shown in Table 26.

Table 26. Validation data for the determination of fenitrothion residues in brown rice by method HR-0222 (Hidai, 1997).

Commodity	Reported LOQ, mg/kg	Spike level, mg/kg	n	Mean % recovery	Recovery range, %	RSD, %	Residues in control samples (mg/kg)
Rice, brown grain	0.01	0.2	8	96	92-102	3.9	<0.01 (8)

Method 152 was described by Westberg (2002, to GLP) as a GC-FPD method for fenitrothion and an HPLC-MS/MS method for DM-FNT in wheat. The method was used in storage stability studies on wheat grain. Homogenized wheat samples (20 g) were extracted with ACN/water (65:35, v/v) and the extract was filtered and divided into two aliquots.

To one aliquot of the filtered extract, salts (NaCl and anhydrous Na_2SO_4) were added to aid removal of the water, followed by a hexane wash to remove fats and oils. The resulting water-free ACN extract was further purified using silica gel column chromatography. The eluate was evaporated to dryness, reconstituted in acetone and the fenitrothion was analyzed by GC-FPD in the phosphorus mode (fused silica column with Rtx-200). Calibration was by a five-point calibration curve using external standards in acetone, in the range 0.006-0.10 mg/l, corresponding to 0.006-0.10 mg/kg. Calibration was verified as linear: r = 0.99966 (1 curve). Further validation results are shown in Table 27.

The second aliquot of the filtered extract was diluted with ACN/water (20:80, v/v) and analyzed for DM-FNT by HPLC-MS/MS (Luna phenyl hexyl column, gradient elution, turbo ion-spray, negative ion mode, MRM acquisition monitoring the transition *m/z* 262 → 152). Calibration was by a five-point calibration curve, using external standards in ACN/water (20:80, v/v) in the range 0.00012-0.0025 mg/l, corresponding to 0.006-0.125 mg/kg. Calibration was verified to be linear: r = 1.0000 (1 curve). Further validation results are shown in Table 28.

Table 27. Validation data for the determination of fenitrothion (parent) residues in wheat by method 152 (GC-FPD) (Westberg, 2002).

Commodity	Reported LOQ, mg/kg	Spike level, mg/kg	n	Mean % recovery	Recovery range, %	RSD, %	Residues in control samples (mg/kg)
Wheat, grain	0.01	0.01 0.10	5 5	106 102	104-109 94-110	2.1 6.1	<0.0033 (2)

Table 28. Validation data for the determination of the fenitrothion metabolite DM-FNT residues in wheat by method 152 (HPLC-MS/MS) (Westberg, 2002).

Commodity	Reported LOQ, mg/kg	Spike level, mg/kg	n	Mean % recovery	Recovery range, %	RSD, %	Residues in control samples (mg/kg)
Wheat, grain	0.01	0.01 0.10	5 5	97 91	84-110 87-93	11 2.9	<0.0033 (2)

Method ER-MT-8802 was originally developed for the determination of fenitrothion and fenitro-oxon in wheat, gluten and biscuits (Ohnishi *et al*., 1988). A modified version of this method was used in supervised trials (HR-0231) on wheat, barley and triticale, conducted in Australia in 2001 (Litzow, 2002).

In the original method, samples were soaked in acetonitrile (overnight) and filtered through Hyflo Super-Cel and the filtrate was washed with *n*-hexane. The acetonitrile layer was concentrated to dryness and the residue redissolved in *n*-hexane/acetone (10:1, v/v) before clean-up on deactivated silica-gel. The eluate was concentrated to dryness and redissolved in acetone before being analyzed by GC-FPD in the phosphorus mode, using a capillary column (CBP-1-W12-100, methyl silicone column).

The method was adapted for the determination of fenitrothion residues in the grain and straw of wheat, barley and triticale (Litzow, 2002). The extraction and clean-up techniques were unchanged, however the final extracts were reconstituted in toluene, rather than acetone, and final

determination was by GC-MS (HP-5MS column), monitoring the ions at *m/z* = 277 (target), 109 and 260 (qualifying). Fenitrothion was quantified using three-level standards in toluene, in the range 0.5-1.5 mg/l (corresponding to 0.05-0.15 mg/kg)m. Linearity was verified (one curve, r^2 >0.99). Matrix effects were not verified. Extracts containing residues at higher concentrations were diluted. Validation results are shown in Table 29.

Table 29. Validation data for the determination of fenitrothion (parent) residues in cereal grains and straw by a modified version of method ER-MT-8802 (Litzow, 2002).

Commodity	Reported LOQ, mg/kg	Spike level, mg/kg	n	Mean % recovery	Recovery range, %	RSD, %	Residues in control samples (mg/kg)
wheat, grain	0.06	0.06	2	102	88-116	-	<0.018 (10)
wheat, straw	0.06	0.06	2	108	106-109	-	<0.018 (10)
barley, grain	0.06	0.06	1	85	-	-	<0.018 (5)
barley, straw	0.06	0.06	1	108	-	-	<0.018-<0.06 (5)
triticale, grain	0.06	0.06 0.6	1 3	98 97	- 92-101	- 4.7	<0.018-<0.06 (5)
triticale, straw	0.06	0.06 0.6	1 3	86 88	- 83-92	- 5.4	<0.018-<0.06 (5)

Stability of pesticide residues in stored analytical samples

Cereal grain and straw

In a first study, untreated samples of wheat grain were fortified with fenitrothion at a concentration of 1.0 mg/kg (Kuroda and Higuchi, 1993a). The amount of fenitrothion was then determined after 34 and 87 days at –20°C. Samples of grain were analyzed in duplicate by GC-FPD, using method HR-0229. The results (Table 30) showed that residues of fenitrothion on wheat grain are stable during storage at about -20°C for up to 87 days. Results were not corrected for concurrent method recovery (81-90%) nor for matrix interference (<0.01 mg/kg).

Table 30. Storage stability of fenitrothion residues on wheat grain (n = 2) stored at –20°C (Kuroda and Higuchi, 1993a).

Matrix	Year of trials	Fortification level (mg/kg)	Storage period (days)	% Remaining
Wheat grain	1993	1.0	34	78–79
	1993	1.0	87	85–86

In a second study on wheat grain, the stability of fenitrothion (parent) and DM-FNT was investigated. Samples were spiked at 0.5 mg/kg and stored at –20 ± 5°C (Willard, 2002a). Duplicate samples were analyzed for residues of parent fenitrothion and DM-FNT, using method 152 (Table 31). Results were not corrected for concurrent method recovery (94-111% for parent, 84-112% for DM-FNT) nor for matrix interference (<0.0033 mg/kg for parent and DM-FNT).

Table 31 Storage stability of parent fenitrothion and DM-FNT residues on wheat grain (n = 2) stored at –20°C (Willard, 2002a).

Analyte	Fortification level (mg/kg)	Storage time (days)	% remaining
Parent	0.5	37 113	95-99 90-91
DM-FNT	0.5	30 113	102-102 91-94

In a third study, untreated samples of barley grain were fortified with fenitrothion at a concentration of 1.0 mg/kg (Kuroda and Higuchi, 1993b, HR-0230). The amount of fenitrothion was then determined after 84 and 105 days at –20°C. Samples of grain were analyzed in duplicate by GC-FPD, using method HR-0229. Results in Table 32 show that the residues of fenitrothion on barley grain are stable after storage at about -20°C for up to 105 days. Results were not corrected for concurrent method recovery (79%-86%) nor for matrix interference (<0.01 mg/kg).

Table 32. Storage stability of fenitrothion residues on barley grain (n = 2) stored at –20°C (Kuroda and Higuchi, 1993b).

Matrix	Year of trials	Fortification level (mg/kg)	Storage period (days)	% Remaining
Barley grain	1993	1.0	84	81-84
	1993	1.0	105	78-80

In a fourth study, untreated samples of rice grain were fortified with fenitrothion at 0.20-1.0 mg/kg (Komatsu and Yabusaki, 1994; Kuroda and Higuchi, 1995; Suzuki, 1996a, 1996b, 1996c and 1996d; Hidai, 1997). The amount of fenitrothion was then determined after 8-149 days at -20°C. Untreated samples of rice straw were also fortified with fenitrothion, at a concentration of 2.0 mg/kg. The amount of fenitrothion was then determined after 45 and 71 days at -20°C.

Samples of grain and straw were analyzed in duplicate by GC-FPD using methods HR-0227, HR-0228, HR-0223 and HR-0222 for the 1993, 1994, 1995 and 1996 trials, respectively. Results from all trials (Table 33) showed that the residues of fenitrothion on rice grain and straw are stable during storage at about -20°C, for up to 149 days on grain and 71 days on straw. Results were not corrected for concurrent method recovery (87-100%) nor for matrix interference (<0.01 mg/kg).

Table 33. Storage stability of fenitrothion residues on rice grain and straw (n = 2) stored at –20°C (Komatsu and Yabusaki, 1994; Kuroda and Higuchi, 1995; Suzuki, 1996a, 1996b, 1996c and 1996d; Hidai, 1997).

Matrix	Year of trials	Fortification level (mg/kg)	Storage period (days)	% remaining	Reference
Brown rice straw	1993	2.0	45	94-95	HR-0227
	1993	2.0	71	85-93	HR-0227
Brown rice grain	1993	1.0	8	94-96	HR-0227
	1993	1.0	34	93-98	HR-0227
	1994	1.0	36	87-89	HR-0228
	1994	1.0	41	88-88	HR-0228
	1996	0.2	77	93-97	HR-0222
	1995	1.0	81	93-96	HR-0225
	1996	0.2	97	95-96	HR-0222
	1995	1.0	99	92-93	HR-0226
	1995	1.0	100	92-93	HR-0223
	1995	1.0	107	91-91	HR-0225
	1995	1.0	110	91-92	HR-0226
	1995	1.0	123	89-92	HR-0224
	1996	0.2	125	93-97	HR-0222
	1995	1.0	129	91-93	HR-0224
	1996	0.2	141	92-94	HR-0222
	1995	1.0	149	90-93	HR-0223

USE PATTERN

Fenitrothion is a broad spectrum contact organophosphorus pesticide for use against chewing, sucking and boring insects in a wide variety of crops. It is useful for controlling weevils, bugs, stem borers, worms, nematodes, chafers, grass grubs, grasshoppers and locusts in orchards, vineyards and various field/forage crops. It is also useful in controlling flour beetles, moths, weevils and grain borers in stored grain and seeds.

Fenitrothion is registered for use in Argentina, Australia, Brazil, Japan, Russia, South Korea and Vietnam for control of insect pests on citrus fruit; pome fruit (apples, pears); stone fruit (plums, peaches, cherries, Japanese apricots); berries and small fruit (strawberries, mulberries, grapes); miscellaneous tropical and sub-tropical fruit (olives, Japanese persimmons); onions; cabbages; fruiting vegetables (tomatoes, egg plant, cucumbers, melons, oriental pickling melons, watermelons, pumpkins); leafy vegetables (lettuce, spinach); legume vegetables (garden peas, green beans, broad beans, green soybeans); pulses (peas, beans, soya beans, azuki beans, kidney beans), both in the field and as stored seeds; root and tuber vegetables (table beet, sugar beet, potatoes, yams, burdock, konjac); stalk and stem vegetables (leeks, udo); cereals (maize, rice, barley, oats, rye, wheat, millet, sorghum), both in the field and as stored grain; oilseeds (cotton, peanuts, hemp); cocoa; sugar cane;

tea; medicinal crops (nalta jute (leaves and shoots), *Murraya paniculata* jack (roots)); forage crops (pasture, lucerne); and pastures for seed production. Fenitrothion is not authorized for use in Germany and The Netherlands.

Because only the registered uses on cereals were supported by supervised residue trials data, these uses are summarized in Table 34 (pre-harvest uses on cereals and cereal forage), Table 35 (uses on stored grains) and Table 36 (surface treatments of bulk stored grain). In addition, fenitrothion can be applied to the surface of structures used for storage of grain (e.g. storage areas on farms, produce stores, feed and flour mills, warehouses and processing plants, transport equipment and animal feed bins) (see Table 37) and it is also used as a seed treatment (Table 38). For all uses, original labels were available, together with an English translation.

Table 34. Registered pre-harvest uses of fenitrothion on field grown cereals.

Crop	Country	Form g ai/l	Application				PHI, days
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	Number (interval, days)	
Barley	Russia	EC 500	foliar spray	0.25	ns	ns	15
Cereals	Argentina	EC 1000	foliar spray	0.10-1.0	0.1-1.4	ns	14
	Argentina	EC 1000	foliar spray by aeroplane	0.10-1.0	max, 0.67-6.7	ns	14
	Australia [1/]	EC 1000	foliar spray	0.27-0.55	ns	max 3 (≥ 14)	14 (WHP = 14)
	Australia [1/]	EC 1000	foliar spray by aeroplane	0.27-0.35	ns	max 3 (≥ 14)	14 (WHP = 14)
	Russia	EC 500	foliar spray	0.30-1.25	ns	ns	15
Corn	Japan	EC 500	ns	ns	0.050	4	7
Rice	Japan	EC 450 [2/]	foliar spray	0.375	0.045-0.15	max 4	21
	Japan	EC 450 [2/]	foliar spray by aeroplane	0.45-0.90	1.5-9.0	max 4	21
	Japan	EC 450 [2/]	foliar spray by unmanned helicopter	0.45	5.6	max 4	21
	Japan	EC 500	ns	ns	0.012-1.5	max 4	21
	Japan	EC 500	foliar spray	0.375	0.15	max 4	21
	Japan	EC 500	foliar spray by aeroplane	0.45-0.60	1.5	max 4	21
	Japan	EC 500	foliar spray by unmanned helicopter	0.45	5.6	max 4	21
	Russia	EC 500	foliar spray	0.50	ns	ns	15
	South-Korea	EC 500	foliar spray	0.4-0.8	0.05	max 3	21
	Vietnam	EC 500	foliar spray	0.50	0.125-0.156	ns	7
Sorghum forage	Australia [1/]	EC 1000	foliar spray	0.27-0.55	ns	max 3 (≥ 14)	NA (WHP = 14)
	Australia [1/]	EC 1000	foliar spray by aeroplane	0.27-0.35	ns	max 3 (≥ 14)	NA (WHP = 14)
Wheat	Japan	EC 450 [2/]	foliar spray by aeroplane	0.45-0.60	1.5-5.6	1	7
	Japan	EC 500	ns	ns	0.050	1	7
	Japan	EC 500	foliar spray by aeroplane	0.45-0.60	1.5-5.6	1	7

NA = Not applicable.
ns = Not specified.
PHI = Pre-harvest interval (for human consumption).
WHP = Graze or feed withholding period.
[1/] GAP information provided by national government.
[2/] Mixed formulation of 450 g/l fenitrothion plus 300 g/l BPMC (2-*sec*-butylphenyl *N*-methylcarbamate).

Table 35. Registered post-harvest uses of fenitrothion on stored cereal grains (for food, fodder and seed purposes).

Crop	Country	Form g ai/l	Application				Waiting period, days
			Method	Rate g ai/t	Spray conc, kg ai/hl	Number (interval, days)	
Barley	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <3 months	6	0.6	ns	1
	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <6 months	12	1.2	ns	91
	Australia [1/]	EC 1000	admixture (spray) for grain stored up to 9 months	6 + methoprene (1 g ai/t)	0.6	ns	1
	Brazil	EC 500	spray	5-10	1.0-3.3	ns	14
Cereal grain	Argentina	EC 1000	spray	6	0.86-2.0	ns	1
	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <3 months	6 [2/]	0.6	ns	ns
	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk, 3-6 months	12 [2/]	1.2	ns	90
	Russia	EC 500	spray	10	ns	ns	ns
Maize	Brazil	DP 20	admixture (powder)	5-10	ns	ns (150)	14
	Brazil	EC 500	spray	5-10	1.0-3.3	ns	14
Millet	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <3 months	6	0.6	ns	1
	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <6 months	12	1.2	ns	91
	Australia [1/]	EC 1000	admixture (spray) for grain stored up to 9 months	6 + methoprene (1 g ai/t)	0.6	ns	1
Oats	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <3 months	6	0.6	ns	1
	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <6 months	12	1.2	ns	91
	Australia [1/]	EC 1000	admixture (spray) for grain stored up to 9 months	6 + methoprene (1 g ai/t)	0.6	ns	1
Rice	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <3 months	6	0.6	ns	1
	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <6 months	12	1.2	ns	91
	Australia [1/]	EC 1000	admixture (spray) for grain stored up to 9 months	6 + methoprene (1 g ai/t)	0.6	ns	1
	Brazil	DP 20	admixture (powder)	5-10	ns	ns (150)	14
Rye	Brazil	DP 20	admixture (powder)	5-10	ns	ns (150)	14
Sorghum	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <3 months	6	0.6	ns	1
	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <6 months	12	1.2	ns	91
	Australia [1/]	EC 1000	admixture (spray) for grain stored up to 9 months	6 + methoprene (1 g ai/t)	0.6	ns	1
Wheat	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <3 months	6	0.6	ns	1
	Australia [1/]	EC 1000	admixture (spray) for grain stored in bulk for <6 months	12	1.2	ns	91
	Australia [1/]	EC 1000	admixture (spray) for grain stored up to 9 months	6 + methoprene (1 g ai/t)	0.6	ns	1
	Brazil	DP 20	admixture (powder)	5-10	ns	ns (150)	14
	Brazil	EC 500	spray	5-10	1.0-3.3	ns	14

[1/] GAP information provided by national government.

[2/] Either alone or in combination with Sumitrin Synergised Grain Protectant.

ns = Not specified.

Table 36. Registered surface treatments of fenitrothion to bulk stored cereal grain (for food, fodder and seed purposes).

Crop	Country	Form g ai/l	Application				waiting period, days
			Method	Rate g ai/m^2	Spray conc, kg ai/hl	Number (interval, days/months)	
Barley	Australia [1/]	EC 1000	surface treatment (spray)	0.5	1	ns (2 months)	ns
Cereal grain	Argentina	EC 1000	surface treatment (spray) for grains in bags	ns	1	ns	1
	Australia [1/]	EC 1000	surface treatment (spray) for grains stored in bulk, stacks of bags etc.	0.5 [2/] or to run-off from bags	1	ns (1 month in summer; 2-3 months in winter)	ns
Maize	Brazil	DP 20	surface treatment (powder)	ns	ns	ns (150 days)	14
Millet	Australia [1/]	EC 1000	surface treatment (spray)	0.5	1	ns (2 months)	ns
Oats	Australia [1/]	EC 1000	surface treatment (spray)	0.5	1	ns (2 months)	ns
Rice	Australia [1/]	EC 1000	surface treatment (spray)	0.5	1	ns (2 months)	ns
	Brazil	DP 20	surface treatment (powder)	ns	ns	ns (150 days)	14
Rye	Brazil	DP 20	surface treatment (powder)	ns	ns	ns (150 days)	14
Sorghum	Australia [1/]	EC 1000	surface treatment (spray)	0.5	1	ns (2 months)	ns
Wheat	Australia [1/]	EC 1000	surface treatment (spray)	0.5	1	ns (2 months)	ns
	Brazil	DP 20	surface treatment (powder)	ns	ns	ns (150 days)	14

[1/] GAP information provided by national government.
[2/] Either alone or in combination with Sumitrin Synergised Grain Protectant.
ns = Not specified.

Table 37. Registered surface treatments of fenitrothion on structural elements used for storage of grain.

Crop	Country	Form g ai/l	Application				waiting period, days
			Method	Rate g ai/m^2	Spray conc, kg ai/hl	Number (interval, months)	
Empty bags	Argentina	EC 1000	surface treatment (spray)	ns	1.0	ns	1
Empty stores, trucks, wagons	Argentina	EC 1000	surface treatment (spray)	1.0	1.0-4.0	ns	1
Structural elements [3/]	Australia [1/]	EC 1000	surface treatment (spray)	0.50 [2/] or to run-off	1.0	ns	ns
Grain storage facilities & equipment [4/]	Australia [1/]	EC 1000	surface treatment (spray)	0.50	1.0	ns (2 months in warm weather; 3 months in winter)	ns
Empty warehouse premises and empty stores	Russia	EC 500	surface treatment (spray)	0.20	ns	ns	7 (warehouse); 1 (store)

[1/] GAP information provided by national government.
[2/] Either alone or in combination with Sumitrin Synergised Grain Protectant.
[3/] Storage areas on farm, produce stores, feed and flour mills, ware-houses and processing plants, transport equipment, animal feed bins.
[4/] Walls, floors, roof structure, machinery, transport vehicles, areas around storage facilities. Treatment should be used as a routine hygienic procedure before grain is stored in any facility.
ns = Not specified.

Table 38. Registered treatments of fenitrothion to rice seed.

Crop	Country	Form g ai/l	Application				Timing
			Method	Rate, g ai/t	Spray conc, kg ai/hl	Number	
Rice	Japan	EC 500	immersion	ns	0.05	ns	6-72 hours before sowing
	Japan	EC 500	spray on dry seed	ns	0.05-0.5	ns	ns
	South Korea	EC 500	ns	800 [1/]	0.05	ns	24 hours before sowing

[1/] The label states 20 l diluted emulsion (20 ml product/20 l water) per 20 l of rice seed. According to the manufacturer, this equates to 800 g ai/t of rice seed, assuming that 1 l of rice seed weighs 0.625 kg.
ns = Not specified.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised trials of pre-harvest treatments of fenitrothion to cereal grains (rice, wheat, barley, triticale) in Japan and Australia. In some trials, pre-harvest treatments were combined with a seed treatment prior to planting.

Rice

Sixteen trials were conducted in locations typical of rice-growing areas in Japan in 1993, 1994, 1995 and 1996 (Komatsu and Yabusaki, 1994; Kuroda and Higuchi, 1995; Suzuki, 1996a, 1996b, 1996c and 1996d; Hidai, 1997). In the 1993-1995 trials, seeds were soaked in a fenitrothion emulsion for 24 hours prior to planting, followed by 4 applications with fenitrothion in the growing season, using a knapsack sprayer. In the 1996 trials, fenitrothion was applied on 4 occasions using an unmanned helicopter, without prior soaking of the seeds.

Mature brown rice and straw were collected 14-30 days after the last application and dried for a period of between 8 to 29 days, before being threshed and hulled. Samples were stored frozen at -20°C for 51-154 days. Residues of fenitrothion in grain were determined by GC-FPD (methods HR-0228, HR-0227, HR-0223 and HR-0222). Samples were not corrected for concurrent method recovery (84-102%) nor for matrix interferences (<LOQ). The reported LOQs for fenitrothion were 0.01 mg/kg for rice grain and 0.04 mg/kg for rice straw. Residue studies are summarized in Table 39. All residue results are on a fresh weight (after the usual air-drying for threshing) basis.

Table 39. Fenitrothion residue data on brown rice grain and straw from pre-harvest treatments (Komatsu and Yabusaki, 1994; Kuroda and Higuchi, 1995; Suzuki, 1996a, 1996b, 1996c and 1996d; Hidai, 1997).

Location, year (variety) reference	Application						DAT	Residues, mg/kg	
	Form.	No.	Interval (days)	kg ai/ha	kg ai/hl	Last treatment		Grain	Straw
Chiba, Japan, 1993 (Hatsuboshi) HR-0227	EC 500	4 [1/]	8-7-6; 10-8-7	0.50	0.050	30/8 [2/] 24/8 [2/]	15 21	0.16 [3/] 0.04 [3/]	1.4 [3/] 0.44 [3/]
Hiroshima, Japan, 1993 (Medium Shin Senbon) HR-0227	EC 500	4 [1/]	9-7-7; 6-7-7; 10-4-7	0.75?	0.050	14/9 [2/] 7/9 [2/] 29/8 [2/]	14 21 30	0.10 [3/] 0.03 [3/] 0.02 [3/]	1.1 [3/] 0.31 [3/] 0.31
Akita, Japan, 1994 (Akita Komachi) HR-0228	EC 500	4 [1/]	7-7-7	0.62	0.062	29/8	21	0.02 [3/]	-
Hiroshima, Japan, 1994 (Medium Shin Senbon) HR-0228	EC 500	4 [1/]	7-7-7	0.94	0.062	6/9	20	0.05 [3/]	-
Mie, Japan, 1995 (Koshihikari) HR-0223	EC 500	4 [1/]	6-7-7	0.62	0.062	9/8	21	<0.01 [3/]	-
Wakayama, Japan 1995 (Hinohikari) HR-0223	EC 500	4 [1/]	10-7-13	0.94	0.062	21/9	21	0.12 [3/]	-
Fukui, Japan, 1995 (Koshihikari) HR-0224	EC 500	4 [1/]	7-7-7	0.62	0.062	28/8	21	0.07 [3/]	-
Gifu, Japan, 1995 (Nihonbare) HR-0224	EC 500	4 [1/]	34-22-11	0.62	0.062	4/9	21	0.01 [3/]	-
Fukushima, Japan, 1995 (Hitomebore) HR-0225	EC 500	4 [1/]	56-21-11	0.62; 0.82 (2x); 0.94	0.062	8/9	21	0.09 [3/]	-
Togichi, Japan, 1995 (Koshihikari) HR-0225	EC 500	4 [1/]	16-20-20	0.94	0.062	4/9	21	0.10 [3/]	-
Akita, Japan, 1995 (Akita Komachi) HR-0226	EC 500	4 [1/]	7-8-6	0.62	0.062	4/9	21	0.06 [3/]	-
Yamagata, Japan, 1995 (Domannaka) HR-0226	EC 500	4 [1/]	6-8-6	0.94	0.062	28/8	21	0.01 [3/]	-
Ibaraki, Japan, 1996 (Koshihikari) HR-0222	EC 500	4	14-14-14	0.53; 0.47; 0.46; 0.48	6.2	22/8	21	<0.01 [3/]	-
Gifu, Japan, 1996 (Hatsushimo) HR-0222	EC 500	4	15-14-13	0.50	6.2	10/7	21	0.08 [3/]	-
Niigata, Japan, 1996 (Koshihikari) HR-0222	EC 500	4	15-15-13	0.50	6.2	30/8	21	<0.01 [3/]	-

Location, year (variety) reference	Application						DAT	Residues, mg/kg	
	Form.	No.	Interval (days)	kg ai/ha	kg ai/hl	Last treatment		Grain	Straw
Fukui, Japan, 1996 (Hanaechizen) HR-0222	EC 500	4	14-14-14	0.50	6.2	8/8	21	<0.01 [3/]	-

[1/] Seeds soaked for 24 hours, in fenitrothion 500 g/l EC diluted 1000 times, prior to planting (49-138 days before first foliar treatment). Treatment of seed by soaking not included in the number of applications.

[2/] Decay trial with different starting dates but the same harvest day for all PHI values.

[3/] Results are the mean of two analytical samples.

HR-0227. Non-GLP. Seed soaked 30 March (Chiba) or 16 April (Hiroshima). Application by motor spray equipment (Chiba) or fully automatic knapsack spray (Hiroshima). Spray volume 1000-1500 l/ha. At Hiroshima, dose rate in kg ai/ha was uncertain, text and field report state 1500 l/ha (= 0.75 kg ai/ha) but summary table states 1000 l/ha (= 0.50 kg ai/ha). No unusual weather conditions. Soil type: alluvial sandy clay (Chiba); sandy loam (Hiroshima). Plot size 13-20 m^2. Field samples: brown rice grain 4-6 kg and 10 bundles of straw. Samples were ground and stored at –20°C for 51-65 days. Results not corrected for concurrent method recovery or matrix interference (see method HR-0227).

HR-0228. Non-GLP. Seed soaked 1 April (Akita) or 14 April (Hiroshima). No unusual weather conditions. Application by knapsack-type accumulator spray (Akita) or semi-automatic knapsack spray (Hiroshima). Spray volume 1000-1500 l/ha. Soil type: fine grey lowland soil (Akita); sandy loam (Hiroshima). Plot size 20-30 m^2. Field samples: brown rice grain 2-6 kg. Laboratory samples were 2.0-2.6 kg. Samples homogenized and stored at –20°C for 59-71 days. Results not corrected for concurrent method recovery or matrix interference (see method HR-0228).

HR-0223. Non-GLP. Seed soaked 29 March (Mie) or 17 May (Wakayama). No unusual weather conditions. Application by small pressure sprayer (Mie) or knapsack power spray (Wakayama). Spray volume 1000-1500 l/ha. Soil type: sand (Mie); clay loam (Wakayama). Plot size 10-64 m^2. Field samples: brown rice grain 2-4 kg. Samples homogenized and stored at –20°C for 110-131 days; Wakayama samples stored at –5°C for 3 days before homogenization. Results not corrected for concurrent method recovery or matrix interference (see method HR-0223).

HR-0224. Non-GLP. Seed soaked 14 April (Fukui) or 11 May (Gifu). No unusual weather conditions. Application by knapsack manual spray (both locations). Spray volume 1000 l/ha. Soil type: loam (Fukui); not stated (Gifu). Plot size 20-150 m^2. Field samples: brown rice grain 2 kg. Samples homogenized and stored at –20°C for 112-127 days. Results not corrected for concurrent method recovery or matrix interference (see method HR-0223).

HR-0225. Non-GLP. Seed soaked 6 April (both locations). No unusual weather conditions. Application not stated (Fukushima) or power spray (Tochigi). Spray volume 1000-1500 l/ha. Soil type: loose granular gley (Fukushima); multi-humus Kuroboku soil (Tochigi). Plot size 100-250 m^2. Field samples: brown rice grain 2 kg. Samples homogenized and stored at –20°C for 123-127 days. Results not corrected for concurrent method recovery or matrix interference (see method HR-0223).

HR-0226. Non-GLP. Seed soaked 29 March (Akita) or 8 May (Yamagata). No unusual weather conditions. Application by knapsack-type accumulator spray (Akita) or knapsack-type power spray (Yamagata). Spray volume 1000-1500 l/ha. Soil type: clay loam (Akita); loam (Yamagata). Plot size 40-50 m^2. Field samples: brown rice grain 2.0-3.5 kg. Samples homogenized and stored at –20°C for 105-134 days. Results not corrected for concurrent method recovery or matrix interference (see method HR-0223).

HR-0222. Non-GLP. No unusual weather conditions. Application by unmanned helicopter (Ibaraki, Niigata, Fukui), Yamaha R-50 (Gifu). Spray volume 7.4-8.5 l/ha. Soil type: sandy loam (Ibaraki, Gifu); clay loam (Niigata, Fukui). Plot size 1000-4000 m^2. Field samples: brown rice grain 2.0 kg or not stated (Ibaraki). Samples homogenized and stored at –20°C for 94-154 days. Results not corrected for concurrent method recovery or matrix interference (see method HR-0222).

Winter wheat

Four trials were conducted in two locations typical of wheat-growing areas in Japan (Kuroda and Higuchi, 1993a) and Australia (Litzow, 2002). In these trials, fenitrothion was applied three times using knapsack or boom sprayers. Mature wheat was harvested 0-14 days after the last application. In the Japanese trials, the wheat was dried for 8-10 days before being threshed. In the Australian trials, wheat was either mechanically threshed immediately after sampling or placed into frozen storage at the analytical facility and then temporarily removed for mechanical threshing to generate grain and straw samples. Samples were stored frozen at about -20°C for 58-128 days. Residues of fenitrothion in grain and straw were determined by GC-FPD, using method HR-0229, or GC-MS, using modified method ER-MT-8802. Results were not corrected for concurrent method recovery (81-116%) or matrix interference (<LOQ). The reported LOQ for fenitrothion was 0.01-0.06 mg/kg for grain and 0.06 mg/kg for straw. Residue studies are summarized in Table 40. All residue results are on a fresh weight (after the usual air-drying for threshing) basis.

Table 40. Summary of fenitrothion residue data on husked winter wheat grain and straw from pre-harvest treatment (Kuroda and Higuchi, 1993a; Litzow, 2002).

Location, year (variety) reference	Application						DAT	Residues, mg/kg	
	Form.	No.	Interval (days)	kg ai/ha	kg ai/hl	Last treatment		Grain	Straw
Hokkaido, Japan, 1993 (Horoshiri Komugi) HR-0229	EC 500	3	7-7-7; 7-7-14	0.50	0.050	20/7 [1/] 13/7 [1/]	7 14	<0.01 [2/] <0.01 [2/]	-
Ushiku, Japan, 1993 (Norin No.61) HR-0229	EC 500	3	7-8-7; 7-7-14	0.75	0.050	10/6 [1/] 2/6 [1/]	7 14	0.30 [2/] 0.04 [2/]	-
Dalby, Queensland, Australia, 2001 (Sunvale) HR-0231	EC 1000	3	14-14	0.55	0.80 (2x) 0.82	11/12 mature	0 1 3 7 14	1.0 0.22 0.20 0.22 0.10	68 22 20 15 4.1
Mallala, South Australia, Australia, 2001 (Janz) HR-0231	EC 1000	3	14-14	0.55	0.73 (2x) 0.75	17/12 mature	0 1 3 7 14	0.98 0.64 0.17 0.20 0.21	22 7.1 3.2 2.2 1.2

[1/] Decay trial with different starting dates but the same harvest day for all PHI values.
[2/] Results are the mean of two analytical samples.

HR-0229. Non-GLP. No unusual weather conditions but 9 hours after spraying there was 1 mm rainfall at Ushiku. Application by knapsack-type power spray (Hokkaido); full automatic knapsack sprayer (Ushiku). Spray volume 1000-1500 l/ha. Soil type: Kuroboku improved half-bog alluvial soil (Hokkaido); light clay (Ushiku). Plot size 28-54 m^2. Field samples: brown rice grain 2-4 kg. Samples homogenized and stored at –20°C for 58-112 days. Results not corrected for concurrent method recovery or matrix interference (see method HR-0229).

HR-0231. GLP. No unusual weather conditions. Application with 2-metre wide hand-held spray booms, involving two different sprayers with hollow-cone nozzles. Spray volume 67-75 l/ha. Soil type: black self-mulching clay (Dalby) or brown clay loam (Mallala). Plot size 400 m^2. Field samples: grain 1 kg; straw 1 kg, hand-harvested. Samples homogenized and stored at –20°C for 92-128 days. Results not corrected for concurrent method recovery or matrix interference (see modified method ER-MT-8802).

Winter barley

Three trials were conducted in locations typical of barley-growing areas in Japan (Kuroda and Higuchi, 1993b) and Australia (Litzow, 2002). In these trials, fenitrothion was applied three times using a knapsack sprayer or a hand-held boom sprayer. Mature barley was harvested 0-14 days after the last application. In the Japanese trials, the barley was dried for 0-7 days before being threshed. In the Australian trial, barley was placed into frozen storage at the analytical facility and then temporarily removed for mechanical threshing to generate grain and straw samples. Samples were stored frozen at about -20°C for 92-138 days. Residues of fenitrothion in grain and straw were determined by GC-FPD, using method HR-0229, or GC-MS, using modified method ER-MT-8802. Results were not corrected for concurrent method recovery (79-108%) or matrix interference (<LOQ). The reported LOQs for fenitrothion were 0.01-0.06 mg/kg for rice grain and 0.06 mg/kg for rice straw. The studies are summarized in Table 41. All residue results are on a fresh weight (after the usual air-drying for threshing) basis.

Table 41. Summary of fenitrothion residue data on husked winter barley grain and straw from pre-harvest treatments (Kuroda and Higuchi, 1993b; Litzow, 2002).

Location, year (variety) reference	Application						DAT	Residues, mg/kg	
	Form.	No.	Interval (days)	kg ai/ha	kg ai/hl	Last treatment		Grain	Straw
Ushiku, Japan, 1993 (Misato Golden) HR-0230	EC 500	3	7-7-7; 7-7-14	0.75	0.050	3/6 [1/] 27/5 [1/]	7 14	1.3 [2/] 0.16 [2/]	-
Tokushima, Japan, 1993 (Tone Nijo) HR-0230	EC 500	3	7-7-7; 7-7-14	0.50-0.75 (3x)	0.050	14/5 [1/] 7/5 [1/]	7 14	0.78 [2/] 0.10 [2/]	-
York, Western Australia, 2001 (Stirling) HR-0231	EC 1000	3	14-14	0.55	1.0	26/11 mature	0 1 3 7 14	4.2 0.57 0.19 <0.06 <0.06	53 8.6 4.5 1.3 0.41

[1/] Decay trial with different starting dates but the same harvest day for all PHI values.
[2/] Results are means obtained from analysis of two analytical samples.

HR-0230. Non-GLP. No unusual weather conditions. Application by fully automatic knapsack sprayer (Ushiku) or knapsack-type power sprayer (Tokushima). Spray volume 1000-1500 l/ha; for Tokushima the exact spray volume was not stated and therefore the kg ai/ha is given as a range. Soil type: light clay (Ushiku); loam (Tokushima). Plot size 28-30 m^2. Field samples: brown rice grain 2-4 kg. Laboratory samples were 2.0-2.5 kg. Samples homogenized and stored at –20°C for 102-138 days. Results not corrected for concurrent method recovery or matrix interference (see method HR-0229).

HR-0231. GLP. No unusual weather conditions. Application with 2-metre wide hand-held spray booms, involving two different sprayers with hollow-cone nozzles. Spray volume 55 l/ha. Soil type: gravel, pH ($CaCl_2$) 4.4. Plot size 384 m^2. Field samples: grain 1 kg; straw 1 kg, mechanically harvested. Samples homogenized and stored at –20°C for 92-128 days. Results not corrected for concurrent method recovery or for matrix interference (see modified method ER-MT-8802).

Winter triticale

One trial on winter triticale was conducted in a location typical of cereal-growing areas in Australia in 2001 (Litzow, 2002). Fenitrothion was applied 3 times, using a hand-held boom sprayer. Mature triticale was harvested 0-14 days after the last application. Samples were placed in frozen storage at the analytical facility and then temporarily removed for mechanical threshing to generate grain and straw samples. Samples were stored at about -20°C for 92-128 days. Residues of fenitrothion in grain and straw were determined by GC-MS, using modified method ER-MT-8802. Results were not corrected for concurrent method recovery (92-101%) or matrix interference (<LOQ). The reported LOQs for fenitrothion were 0.06 mg/kg for grain and straw. Residue studies are summarized in Table 42. All residue results are on a fresh weight (after the usual air-drying for threshing) basis.

Table 42. Summary of fenitrothion residue data on winter triticale from pre-harvest treatments (Litzow, 2002).

Location, year (variety) reference	Application						DAT	Residues, mg/kg	
	Form.	No.	Interval (days)	kg ai/ha	kg ai/hl	Last treatment		Grain	Straw
Tabbita, New South Wales, Australia, 2001 (Abacus) HR-0231	EC 1000	3	14-14	0.55	1.0 (2x); 1.1	26/12 mature	0	2.2	56
							1	1.0	16
							3	0.26	4.8
							7	0.12	2.8
							14	0.08	2.0

HR-0231. GLP. No unusual weather conditions. Application with 2-metre wide hand-held spray booms, involving two different sprayers with hollow-cone nozzles. Spray volume 52-55 l/ha. Soil type: red clay loam, pH ($CaCl_2$) 5.3. Plot size 600 m^2. Field samples: grain 1 kg; straw 1 kg, hand-harvested. Samples homogenized and stored at –20°C for 92-128 days. Results not corrected for concurrent method recovery or matrix interference (see modified method ER-MT-8802).

FATE OF RESIDUES IN STORAGE AND PROCESSING

The Meeting received information on the fate of residues of fenitrothion during storage of wheat, during simulated processing of stored rice (polishing and cooking) and stored wheat (milling and baking) and under pasteurization conditions in sterile buffers.

Fate in storage

Stored wheat (post-harvest treatments)

In a first study, conducted on a laboratory scale in Canada, hard red spring wheat grain (Neepawa variety), with 12% moisture content, was evenly sprayed with a 96% EC formulation of fenitrothion that had been diluted with water (Abdel-Kader and Webster, 1982). The application rate was 1.2 ml/kg, equivalent to 12 g ai/t. After mixing, the wheat samples were stored in screw-capped jars (240 ml), in the dark at 20°C, and were analyzed for fenitrothion, FNO, DM-FNT, SM-FNT, NMC, DMPTA and DM-SM-FNT after 0, 1, 3, 6 and 12 months. The analytical method involved extraction with acidified acetone or MeOH; derivatization with diazoethane to ethylate the metabolites DM-FNT, DMPTA, and DM-SM-FNT; clean-up with silica gel; and quantification by GC-FPD (or GC-ECD for NMC). Where high concentrations of fenitrothion occurred, extraction with acidified acetone was followed by an additional sequential extraction procedure, whereby fractions containing fenitrothion + FNO + SM-FNT, DMF + DM-FNT and DMPTA were produced. Mean recoveries for all compounds at 4 fortification levels of 0.1-5.0 mg/kg were 90-98% (RSD 0.8-3.3%, n = 3).

Data were reported graphically (not as numerical values) and, because it was a laboratory-scale experiment, results from this study are not included in Table 43. The concentration of fenitrothion in stored wheat samples declined to about 5.5 mg/kg after 3 months and to about 2.5 mg/kg after 12 months. The major metabolites were DM-FNT, NMC and DMPTA. Residues of DM-FNT and DMPTA initially increased to 2.0 and 0.55 mg/kg, respectively, after 6 months, then decreased to 0.98 mg/kg and 0.21 mg/kg, respectively, after 12 months. NMC increased throughout the study from 0.38 mg/kg at 1 month to 0.96 mg/kg after 12 months. Neither FNO nor SM-FNT was detected at any time point.

A second study was performed in Australia, involving post-harvest treatment with fenitrothion at 12 g ai/t (Turnbull and Ardley, 1987 and Ohnishi *et al*., 1987). Australian standard white grade wheat grain (612 t) was treated with a combination of two formulations ('Sumithrin Synergised Grain Protectant', containing 50 g/l d-phenothrin plus 425 g/l piperonyl butoxide, and 'Fenitrogard Liquid Insecticide', containing 1000 g/l fenitrothion). After treatment over a period of 3 days at a rate of 12 g ai/t fenitrothion, the wheat was stored in an 800 t capacity vertical silo in Billimari, New South Wales. On loading the silo, the grain averaged 31°C and 12% moisture content. Subsequent temperature and moisture content readings were taken from a neighbouring silo: grain temperature 27-31°C and moisture content 12%. Residues of fenitrothion in whole wheat grain after 1 and 3 months of storage were determined using method ER-71-0015. Residues after 1 month were also determined using method ER-70-0014. Results are summarized in Table 43.

A third study was performed in Argentina, in February 2002, in four wheat storage facilities (Willard 2002b). Wheat at sites AG1 and AG2 was provided by many local growers and the field history of the wheat was not available. At all sites the wheat was treated with a 1000 g/l EC formulation of fenitrothion at 6 g ai/t. The formulation was diluted with water and sprayed onto the wheat during conveyance into the storage units. The actual application rates (listed in Table 43) were calculated from the average of two calculation methods: by spray time and by the amount of spray mixture remaining. Application rates at AG3 and AG4 were higher than nominal. At site AG4, the pump was malfunctioning during treatment, so the exact application rate could not be calculated but it was estimated to be about 5.4-10 g ai/t. Wheat grain samples were collected at intervals, during transfer of the grain from the storage unit to a truck or bin, after which the wheat was returned to the storage unit. On each occasion, 12 sub-samples were collected and mixed and a single sample of 1 kg was analyzed. Storage container air temperatures were 5-40°C during the trial period. Analytical samples were stored frozen (-23 to -12°C), except for the pre-treatment and DAT 1 samples, which reached temperatures of +5°C. Samples were stored for 41-103 days and were analyzed for parent fenitrothion and DM-FNT, using method 152. Results were not corrected for concurrent method recovery (98-105% for parent; 70-101% for DM-FNT) or residue levels in pre-treatment samples. Results are shown in Table 43 and indicate that the level of fenitrothion declined and DM-FNT increased over the field storage period. According to the study authors, the residues detected in pre-treatment samples from sites AG1 and AG2 were field-related but, because the wheat had been provided by many unidentified local growers, the source could not be identified.

Table 43 Residues of parent fenitrothion and a metabolite in stored wheat, after post-harvest treatment (Turnbull and Ardley, 1987; Ohnishi *et al*., 1987; Willard 2002b).

Location, year (variety) reference	Application		Storage time	Residues, mg/kg	
	Form. (g ai/l)	Rate (g ai/t)		Fenitrothion	DM-FNT
Billimari, New South Wales, Australia; 1987 (ns) Turnbull and Ardley 1987 and Ohnishi et al., 1987	liquid 1000 [1/]	12	1 month 3 months	6.8 [2/] 7.6	na na
Ricardone, Santa Fe, Argentina, 2002 (ns) AG1, Willard, 2002b	EC 1000	6.2	pre-treatment 1 day 14 days 58 days	0.11 5.0 3.0 1.7	<0.01 0.12 0.72 1.6
Soldini, Santa Fe, Argentina, 2002 (ns) AG2, Willard, 2002b	EC 1000	6.4	pre-treatment 1 day 14 days 56 days	0.67 5.6 4.2 2.8	0.42 0.58 1.4 2.5

Location, year (variety) reference	Application		Storage time	Residues, mg/kg	
	Form. (g ai/l)	Rate (g ai/t)		Fenitrothion	DM-FNT
Marcos Juarez, Cordoba, Argentina, 2002 (ns) AG3, Willard, 2002b	EC 1000	6.9	pre-treatment	<0.01	<0.01
			1 day	3.5	0.040
			14 days	1.5	0.41
			58 days	1.8	1.0
Salto, Buenos Aires, Argentina, 2002 (ns) AG4, Willard, 2002b	EC 1000	[3/]	pre-treatment	<0.01	<0.01
			1 day	3.1	0.030
			14 days	1.9	0.27
			58 days	1.2	0.50

na: Not determined.
[1/] 1000 g ai/l but formulation not stated.
[2/] Average of 3 laboratory samples, each analyzed in duplicate.
[3/] Estimated to be about 5.4-10 g ai/t.

Fate in processing

Effect on the nature of residues during simulated processing

A study utilizing radio-labelled fenitrothion was conducted to assess the effects of simulated processing by way of pasteurization, baking/brewing/boiling and sterilization (Rosenwald, 2002). The test system consisted of closed glass vials containing radio-labelled fenitrothion in sterile potassium phthalate buffer solutions. The specific activity was 7.4 MBq/mg and the radiochemical purity was >99%. The vials were incubated in thermostatically-controlled oil baths. Pasteurization was simulated by heating at 90°C for 20 min (at pH 4); baking/brewing/boiling by heating at 100°C for 60 min (at pH 5); and sterilization by heating at 120°C for 20 min (at pH 6). Samples were cooled to room temperature and analyzed by LSC and HPLC (Sphere Image 5 ODS2 or Sumipax ODS-A212 columns, both with gradient elution). The resultant compounds were identified on two different HPLC systems, by co-chromatography with reference standards: parent fenitrothion, AA-FNT, AM-FNT, CA-FNO, CA-FNT, DM-FNO, DM-FNT, FA-FNT, FNO, NMA, NMC, NMC-ß-glc and SM-FNT.

Fenitrothion was mostly in solution (>93% TAR) in the buffer solutions of pH 4, 5, and 6. The radioactive balances for the experiment were complete, with 97-102% TAR measured in the buffer solutions after processing. Solutions remained at the correct pH under sterile conditions. The results of this simulated processing are presented in Table 44 and show that fenitrothion is likely to be relatively stable during the process of pasteurization but is likely to be readily degraded to DM-FNT during baking/brewing/boiling and sterilization. No other degradation products were identified as significant.

Table 44. Degradation pattern of fenitrothion during simulated processing (Rosenwald, 2002).

Compound	Average (n =2) present as % TAR		
	Simulated pasteurization	Simulated baking/brewing/boiling	Simulated sterilization
Fenitrothion	81.6	34.6	15.3
DM-FNT	12.2	61.9	82.2
NMC	0.7	0.8	1.3
Total unknown(s)	1.0	1.1	1.3
Total recovery (mean)	95.5	98.4	100.1

Effect of polishing and cooking on residues in stored rice

The effect of cooking of unpolished and polished rice grains, treated post-harvest with 15 g ai/t [*m*-methyl-^{14}C]fenitrothion and stored at 30°C, was studied (Takimoto *et al*., 1978). Rice grain in distilled water was heated at 100°C for 20 minutes. Boiled rice was extracted with a water/EtOH mixture, partitioned into diethyl ether at pH 1-2. Metabolites were determined as described in the plant metabolism study, fate during storage (Takimoto *et al*., 1978).

Results are summarized in Table 45. When unpolished rice grains were cooked immediately after treatment, the amount of fenitrothion decreased to about 60%, with formation of DM-FNT and NMC. When cooked after storage, about 40% of the fenitrothion originally present was lost, with an increase of DM-FNO and NMC. Amounts of other metabolites, NMA and DHMN, decreased. After

polishing and washing, 80% of the applied radioactivity remained in the bran and washings. The concentrations of fenitrothion, DM-FNT and NMC were decreased by about a factor two (relative to unwashed endosperm) by a combination of washing and boiling (Table 45). Processing factors could not be calculated because data in mg/kg were not provided. Nevertheless, the percentage transfer may be calculated as the ratios of %TAR for the corresponding commodities.

Table 45. Effect of cooking on rice grain treated with 15 g ai/t fenitrothion, stored at 30°C (Takimoto *et al*., 1978)

Rice grain	Month	% of applied radioactivity [% before cooking]								
		FNT	DM-FNT	DM-FNO	NMC	Others [1/]	Unextracted	EtOH trap	Other fractions [2/]	Recovery (%)
Unpolished	0	61	18	0.4	12	1.6	2.1	4.4	n.a.	100
		[101]	[0.3]	[-]	[0.6]	[-]				
	6	25	19	8.4	46	3.5	1.6	1.7	n.a.	106
		[41]	[18]	[1.1]	[30]	[6.3]				
	12	18	12	10	52	5.3	2.0	1.0	n.a.	100
		[28]	[18]	[1.1]	[38]	[13.8]				
Polished [3/]	6	6.1	3.2	0.2	8.2	0.5	2.5	0.5	83	104
		[13]	[8.5]	[0.3]	[15]	[1.0]				
	12	5.1	3.8	0.2	8.4	0.4	3.3	0.3	77	99
		[7.7]	[9.4]	[0.4]	[19]	[2.0]				

- = Not detected.
n.a. = Not applicable.
[1/] Others included FNO, SM-FNT, DM-SM-FNT, HM-NMC, NMA, DHMN, DMMN and unidentified compounds.
[2/] Other fractions included seed coat, germ fraction and washings.
[3/] Polished rice grain was washed before cooking.

Effect of milling and baking on residues in stored wheat

A processing study was performed in Australia in 1987 on milling and baking products, generated from wheat that had been stored for about 1 or 3 months following post-harvest treatment with 12 g ai/t fenitrothion (Turnbull and Ardley, 1987 and Ohnishi *et al*., 1987). Following approximately 0.75 and 3.5 months storage, 1 t samples of wheat grain (in jute bags each containing 80 kg) were transported to the Bread Research Institute, Sydney, for milling. Prior to milling, the samples were pallet-stacked before being cleaned and conditioned to 16% moisture content. The conditioned wheat was then allowed to stand for 18 hours before being milled, using a Pilot Sizing Mill with a throughput of 660 kg wheat per hour. The processing occurred approximately 1.1 and 4.25 months post-treatment with fenitrothion. Milling fractions included flour at two extraction rates (75% and 80%), bran, pollard and wheat germ. Where possible, samples were generated from each extraction rate but otherwise they were generated from a blend of the two milling rates. A sample of gluten was generated from a sub-sample of flour that had been washed with clean water to remove all starch. White and brown bread samples were generated at the Bread Research Institute from the milled flour, according to Australian statutory requirements (4.9 kg flour 80% extraction, 0.82 kg bran and 0.27 kg pollard). Brown flour consisted of 90 parts of 100% wholemeal and 10 parts white flour. Bread was baked at 260°C for 32 minutes and was in accordance with Australian standards. Samples of whole wheat, flour, bran, pollard, gluten, germ, white bread and brown bread were stored at approximately –18°C prior to residue analysis, using methods ER-70-0014 and ER-71-0015.

The results showed that fenitrothion residues did not concentrate in the flour or bread products. Most of the residues were found in germ and bran, in which there was a three- to four-fold concentration of the residues. Residues were not significantly different in fractions from different extraction rates, so the results were averaged. Processing factors were calculated and results are summarized in Table 46. Residue transfer based on absolute quantities (% transference) could not be calculated because the fraction weight data of the processed commodities were not provided.

Table 46. Residue results from processing studies on wheat, treated post-harvest with fenitrothion (Turnbull and Ardley, 1987 and Ohnishi *et al*., 1987)

Portion analyzed	Fenitrothion, mg/kg	Processing factor	% Transference
Wheat stored 1 month post-treatment (Ref: ER-70-0014 and ER-71-0015 [1/])			
whole grain	7.0	-	n.a.
bran	28	4.0	
pollard	12	1.7	
germ	26	3.7	
flour	1.5	0.21	
gluten	4.2	0.60	
white bread	0.62	0.089	
brown bread	3.0	0.43	
Wheat stored 3 months post-treatment (Ref: ER-71-0015)			
whole grain	7.6	-	n.a.
bran	30	3.9	
germ	24	3.2	
flour	2.0	0.26	
white bread	0.8	0.11	
brown bread	2.5	0.33	

[1/] Values are average results of analysis by methods ER-71-0015 and ER-70-0014, except gluten which was analyzed only by method ER-70-0014.

n.a. Not available.

Residues in the edible portion of food commodities

No data were available.

RESIDUES IN ANIMAL COMMODITIES

Direct animal treatments

Not required, fenitrothion is not used for direct animal treatments.

Farm animal feeding studies

Information was submitted on cattle grazing on fenitrothion-treated grass and on cattle fed with corn (maize) silage treated with fenitrothion.

Cattle grazing on pastures treated with fenitrothion

Fenitrothion was applied, as an EC formulation, to two pastures at application rates of 0.125 and 0.375 kg ai/ha in Buenos Aires, Argentina (Miyamoto and Sato, 1969). Ten cattle with body weights approximately 300 kg, were confined to each pasture immediately after spraying. Two animals were removed for slaughter from each field, 1, 3, 7 and 10 days after spraying and breast muscle and omental fat were removed for analysis at necropsy. Other tissues were not investigated. Meat was homogenized with water/ethanol and parathion was added as an internal standard. The homogenate was extracted with benzene. The benzene extract was evaporated to dryness, redissolved in *n*-hexane and partitioned into acetonitrile. Fat was homogenized with *n*-hexane and parathion was added as an internal standard. The homogenate was extracted with acetonitrile and the acetonitrile extract then washed with hexane. Final extracts of meat and fat were evaporated to dryness and redissolved in acetone. Fenitrothion was quantified by GC with a phosphorus detector (FTD, KBr crystal). Residues were detected in the meat and fat of the cattle and the results are shown in Table 47.

Table 47. Fenitrothion (parent) concentrations in tissues of cattle that had grazed on treated pastures (Miyamoto and Sato, 1969).

Days feeding on pasture	Pasture sprayed with 0.125 kg ai/ha		Pasture sprayed with 0.375 kg ai/ha	
	Fenitrothion in muscle, mg/kg	Fenitrothion in fat, mg/kg	Fenitrothion in muscle, mg/kg	Fenitrothion in fat, mg/kg
1	0.007	0.002	0.014	0.014
	0.011	<0.001	0.009	0.003
3	<0.001	<0.001	0.001	0.007
	<0.001	<0.001	<0.001	0.004
7	<0.001	<0.001	<0.001	<0.005

Days feeding on pasture	Pasture sprayed with 0.125 kg ai/ha		Pasture sprayed with 0.375 kg ai/ha	
	Fenitrothion in muscle, mg/kg	Fenitrothion in fat, mg/kg	Fenitrothion in muscle, mg/kg	Fenitrothion in fat, mg/kg
7, continued	<0.001	<0.001	<0.001	<0.001
10	Not analyzed	<0.001	Not analyzed	0.001
	Not analyzed	0.001	Not analyzed	0.004
Control	<0.001	0.003	<0.001	0.004

Cattle fed on corn silage treated with fenitrothion

Corn (growing maize) was sprayed in the field with a diluted EC formulation of fenitrothion at 1.1, 2.2 or 3.4 kg ai/ha (Leuck *et al*., 1971). The following night there was 46 mm rain and therefore the same corn was re-sprayed 3 days later at the same rates. During the night, again there was 6 mm rain. On the following day, the corn was cut, placed in tower silos and aged for 76 days, to produce silage. An untreated sample of corn from the same field was used to prepare control silage, over the same period. Four groups of 4 lactating Jersey cattle were fed the treated or control silage, *ad libitum* for 56 days. Each cow was also given a daily allowance of concentrate. The animals were milked twice daily and, at the end of each week, a composite sample was prepared by combining the milk from 2 consecutive morning and evening milkings. Pooled samples of urine and faeces were prepared at 4-week intervals, by combining excreta from 2 consecutive morning and afternoon collections. All samples were stored frozen (temperature and time not stated) until analysis. Organs and tissues were not investigated. Silage, seepage from the silo towers, urine, faeces and milk were analyzed by GC. Parent, FNO and AM-FNT were quantified by GC-FPD in the phosphorus mode and NMC was quantified as its methyl ether derivative, using GC-ECD. Results were presented in the form of fenitrothion equivalents (eq). Full details of the method were not available to the Meeting (references Bowman and Beroza, 1969, and Bowman *et al*., 1968, were not submitted). The method required modification for the quantification of AM-FNT and recoveries for this metabolite were 95% from milk and urine (0.05 mg/kg eq), 68% from faeces (0.1 mg/kg eq) and 78% from corn silage (0.1 mg/kg eq). Values for faeces and corn silage were corrected for method recovery. The identity of AM-FNT was confirmed by comparison with retention times of standards on two different GC columns, by NMR and by IR.

On the day of ensiling, total residues in corn silage from the 1.1, 2.2 and 3.4 kg ai/ha application rates were 4.5, 11 and 17 mg/kg eq, respectively, on a wet product basis consisting of parent fenitrothion (87-91% of the total), FNO and NMC. The total residue in corn silage declined to 3.4, 6.6 and 9.5 mg/kg eq after 128 days in the silos, consisting of parent (68-79% of the total) and NMC. Total residues in the seepage from silos declined from 0.45 mg/kg eq at 2 days after ensiling to 0.008 mg/kg eq at 20-22 weeks after ensiling, at all dose rates. The total residue consisted of AM-FNT (21-89%) and NMC (11-79%); parent fenitrothion was also present, at low levels (4.2-11%), at early time points. Cows fed silage from corn silage treated with 1.1, 2.2 and 3.4 kg ai/ha ingested respective averages of 0.21, 0.41 and 0.66 mg/kg bw/day of fenitrothion and metabolites.

In the milk of cows fed silage treated at 3.4 kg ai/ha, AM-FNT was the only compound detected (0.001-0.005 mg/kg eq). No residues (<0.001 mg/kg eq) were found in the milk of cows consuming silage from corn treated at lower rates. Urine contained 0.53-5.1 mg/kg eq total residues; faeces contained 0.037-0.18 mg/kg eq total residues (see Table 48). AM-FNT was the major metabolite in urine and faeces, although small amounts of parent fenitrothion were also present in both matrices. NMC was only detected in very small amounts in urine, 4 weeks after feeding had started.

Table 48. Residues in urine and faeces from cows fed with silage made from fenitrothion-treated corn (maize) (Leuck *et al*., 1971).

Matrix	Residue component	Cows fed with silage produced from corn treated at:		
		1.1 kg ai/ha	2.2 kg ai/ha	3.3 kg ai/ha
Urine [1/]	Total residue, mg/kg	0.67, 1.1, 0.78	0.53, 1.6, 4.3	4.0, 4.5, 5.1
	Fenitrothion, % total	1.5, 1.5, 2.3	0.7, 1.2, 2.0	1.6, 1.6, 2.1
	AM-FNT, % total	99, 98, 98%	99, 98, 98	98, 98, 98
	FNO, % total	-	-	-

Matrix	Residue component	Cows fed with silage produced from corn treated at:		
		1.1 kg ai/ha	2.2 kg ai/ha	3.3 kg ai/ha
Urine, continued	NMC, % total	-, 0.4, -	-, 0.5, -	-, 0.5, -
Faeces [1/]	Total residue, mg/kg	0.037, 0.044, 0.048	0.038, 0.080, 0.099	0.17, 0.18, 0.17
	Fenitrothion, % total	8.1, 4.5, 4.2	4.5, 5.0, 6.1	8.0, 2.2, 8.4
	AM-FNT, % total	92, 95, 96	95, 95, 94	92, 98, 92
	FNO, % total	-	-	-
	NMC, % total	-	-	-

[1/] Values derived from samples collected 1, 4, and 8 weeks after feeding had started.
- Not found.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Fenitrothion was included in the Australian Total Diet Surveys (ATDS) of 1996 and 2000 (Table 49). Estimated dietary intakes of fenitrothion were 6.5-15.5% of the maximum ADI in ATDS 18 (1996) and 0.59-1.7% of the maximum ADI in ATDS 19 (2000).

In the Australian National Residue Survey of 2001-2002, fenitrothion residues were regularly detected in cereals and their products, in those cases where fenitrothion has uses as a post-harvest grain protectant (Table 50). Residues were also detected in samples of canola and field peas, for which no MRLs have been set, but residues were not detected above the MRL in other crops.

Table 49. Estimated daily dietary exposure for sub-populations in Australia, based on total diet studies conducted in 1996 and 2000 (ANZFA, 2001).

Pesticide	Study	ADI, mg/kg bw	% maximum ADI					
			Adult males 25-34 years	Adult females 25-34 years	Boys 12 years	Girls 12 years	Toddlers 2 years	Infants 9 months
Fenitrothion	ATDS 18	0.002	7.0	6.5	9.4	7	15.5	11.0
	ATDS 19	0.002	0.71	0.59	1.2	0.84	1.7	0.99

Table 50. Residue monitoring data from the Australian National Residue Survey of 2001-2002 (AFFA, 2002).

Commodity	LOR (mg/kg)	MRL (mg/kg)	No. samples	Samples with residues	Samples with residues exceeding MRL
Apple	0.05	0.5	232	0	0
Barley	0.1	10	1170	272	0
Bran	0.1	20	109	45	0
Canola	0.1	not set	265	3	3
Cattle (fat)	0.05	0.05	616	0	0
Chickpea	0.1	not set	36	0	0
Deer (fat)	0.05	0.05	32	0	0
Field pea	0.1	not set	159	1	1
Flour	0.1	10	108	15	0
Game pig (fat)	0.05	0.05	60	0	0
Goat (fat)	0.05	0.05	104	0	0
Honey	0.01	not set	196	0	0
Horse (fat)	0.05	0.05	20	0	0
Kangaroo (fat)	0.05	0.05	67	0	0
Lupin	0.1	not set	172	0	0
Oat	0.1	10	125	15	0
Ostrich (fat)	0.05	0.05	23	0	0
Pear	0.05	0.1	74	0	0
Pecan nut	0.01	0.1	45	0	0
Pig (fat)	0.05	0.05	308	0	0
Poultry (fat)	0.05	0.05	52	0	0
Sheep (fat)	0.05	0.05	469	0	0
Sorghum	0.1	10	352	69	0
Wheat	0.1	10	3428	361	0

LOR: limit of reporting.

NATIONAL MAXIMUM RESIDUE LIMITS

MRLs (Table 51) for Australia and The Netherlands were provided by the national governments. MRLs for the other countries were provided by the manufacturer.

Table 51. National MRLs for food crops and animal commodities. Residue is defined as fenitrothion (no metabolites).

Country	Codex Code	Food Commodity	MRL
Argentina		Apples	0.5
		Cereals	0.5
		Cereals, stored	10
		Citrus	0.5
		Cotton	1
		Pasture	1
		Peaches	0.5
		Pears	0.5
		Soya beans	0.1
Australia	AL 1020	Alfalfa fodder	5 T
	AL 1021	Alfalfa forage (green)	5 T
	FP 0226	Apples	0.5
	VB 0041	Cabbages, Head	0.5
		Canola forage (green)	10 T
	GC 0080	Cereal grains	0.5
	FS 0013	Cherries	0.5
	FB 0269	Grapes	0.5
	AL 0157	Legume animal feeds [except alfalfa forage (green) and peanut fodder and forage (green)]	10 T
	VL 0482	Lettuce, Head	0.5
	VL 0483	Lettuce, Leaf	0.5
	MM 0095	Meat, Mammalian (in the fat)	0.05* T
	ML 0106	Milks (in the fat)	0.05* T
	VD 0541	Soya beans (dry)	0.3
	AS 0161	Straw, fodder (dry) and hay of cereal grains and other grass-like plants	10 T
	VO 0448	Tomatoes	0.5
Austria		Potatoes	0.05
Belgium		Citrus fruits	2
		Fruit and vegetables	0.5
		Herbs	0.02
		Potatoes	0.02
		Spices	0.02
		Tea	0.5
Denmark		Fruit and vegetables	0.5
		Potatoes	0.05
		Tea	0.5
EU (Directive 98/82 EC)		Tea	0.5
Finland		Citrus fruits	2
		Fruit and vegetables	0.5
		Potatoes	0.05
France		Citrus fruits	2
		Fruit and vegetables	0.5
		Potatoes	0.01
		Tea	0.5
Germany		Citrus fruits	2
		Fruit and vegetables	0.5
		Herbs	0.05
		Potatoes	0.05
		Spices	0.5
		Tea	0.5
Italy		Citrus fruits	2
		Fruit and vegetables	0.5
		Herbs	0.5

Country	Codex Code	Food Commodity	MRL
Italy, continued		Potatoes	0.5
		Tea	0.5
Luxembourg		Citrus fruits	2
		Fruit and vegetables	0.5
		Herbs	0.02
		Potatoes	0.02
		Spices	0.02
		Tea	0.5
Netherlands		Cereals	0.5
		Citrus fruits	2
		Cocoa beans	0.1
		Meat	0.05*
		Milk	0.002*
		Other animal oils and fats	0.05*
		Other fruits	0.5
		Others	0.02*
		Potatoes	0.05*
		Soya beans	0.1
		Tea	0.5
		Vegetables	0.5
Russia		Apples	0.1
		Bread, sunflower	0.1
		Cherries	0.1
		Citrus fruits	0.1
		Flour	0.3
		Grain (cereals), rice	0.3
		Pears	0.1
		Plums	0.1
		Sugar and table beet	0.1
		Sunflower (seeds and oil)	0.1
		Tea	0.5
		Tobacco	0.1
South Korea		Almonds	0.1
		Apples	0.5
		Bananas	0.2
		Barley	5
		Buckwheat	5
		Cabbages	0.5
		Cacao beans	0.1
		Carrots	0.2
		Cherries	0.2
		Chestnuts	0.1
		Citrus fruits	2
		Corn	5
		Crown daisy	0.2
		Cucumbers	0.05
		Egg plants	0.1
		Gingko nuts	0.1
		Grapes	0.5
		Indian millet	5
		Lettuce	0.2
		Melons	0.05
		Mush melons	0.05
		Oats	5
		Onions	0.05
		Other cereal grains	5
		Other fruits	0.2
		Other pulses	0.2
		Peas	0.5
		Peanuts	0.2
		Pears	0.2

Country	Codex Code	Food Commodity	MRL
South Korea, continued		Pecans	0.1
		Peppers	0.1
		Peppers	0.2
		Pimentos	0.1
		Pineapples	0.05
		Potatoes	0.05
		Pumpkins	0.2
		Radishes (root)	0.2
		Rice	0.2
		Rye	5
		Soya beans	0.1
		Spinach	0.2
		Strawberries	0.2
		Sweet potatoes	0.05
		Tomatoes	0.2
		Walnuts	0.1
		Water melons	0.2
		Welsh onions	0.02
		Wheat	6
Spain		Fruit and vegetables	0.5
		Herbs	0.05
		Potatoes	0.05
		Spices	0.05
		Tea	0.5
Sweden		Citrus fruit	2
		Fruit and vegetables	0.5
		Potatoes	0.05
		Tea	0.5
United Kingdom		Citrus fruit	2
		Fruit and vegetables	0.5
		Potatoes	0.05
		Tea	0.5

* MRL set at or about the LOQ.
T Temporary MRL.

APPRAISAL

Fenitrothion, a contact insecticide which was first evaluated by the JMPR in 1969 and re-evaluated for residues several times up to 1989, is included under the CCPR Periodic Review Programme. At the 30th Session of the CCPR (ALINORM 99/24) fenitrothion was originally scheduled for periodic residue review by the 2001 JMPR but this was postponed until 2003.

The basic manufacturer supplied information on identity, metabolism and environmental fate, use patterns, residue analysis, residues from supervised trials on cereals, and the fate of residues during storage and processing. In addition, information on GAP and/or national MRLs was reported by the governments of Australia, Germany, The Netherlands and the USA.

Animal metabolism

The Meeting received information on the fate of orally-dosed fenitrothion in lactating goats and in laying quails and hens.

The metabolism of fenitrothion in laboratory animals (mice, rats, guinea pigs, rabbits and dogs) was evaluated by the WHO panel of the 2000 JMPR. It was concluded that, after oral administration, fenitrothion is rapidly and extensively absorbed from the mammalian intestinal tract (about 90-100% of the dose) and eliminated within 24 h. Fenitrothion is rapidly metabolized by mixed-function oxidases to the highly reactive fenitro-oxon, by oxidative desulfuration. The oxon is then further metabolized by demethylation [*sic*] and hydrolysis, to 3-methyl-4-nitrophenol and dimethylphosphate. A minor metabolic pathway involves further oxidation to 5-hydroxy-2-nitrobenzoic acid (3-carboxyl-4-nitrophenol).

Six female Japanese Saanen goats were fed [phenyl-^{14}C]fenitrothion mixed with 200 g of crushed hay for 7 days (0.5 mg ai/kg bw, corresponding to 7.6 ppm in the feed). The goats were milked twice daily and the evening milk samples were combined with the milk collected on the following morning. Whole milk was separated into cream and skimmed milk. Two goats were killed 1, 7 or 18 days after the last dose. The administered radiocarbon was almost quantitatively excreted during the treatment and 7-day post-treatment periods; 50% of the dose was excreted in the urine, 44% in faeces and 0.1% eliminated in milk.

In whole milk, a plateau of 0.011 mg/kg eq was reached on the second day of dosing, with a maximum of 0.012 mg/kg eq on the 5th day of dosing. Residue levels in whole milk declined to 0.003 mg/kg eq within 7 days of the end of treatment. Four radioactive components were detected in milk: acetylaminofenitro-oxon (5% TRR), *N*-sulfoaminofenitrothion (39% TRR), *N*-sulfoaminofenitro-oxon (22% TRR), and *O*-(4-acetylamino-3-methylphenyl) *O*-hydrogen *O*-methyl phosphate (15% TRR). No parent fenitrothion, fenitro-oxon or 3-methyl-4-nitrophenol was detected. In cream, no radioactive residues were detected.

One day after the last dose, liver contained the highest content of radiocarbon (0.85-1.5 mg/kg eq), with lower concentrations in kidneys (0.025 –0.031 mg/kg eq), muscle (0.002 to 0.005 mg/kg eq) and fat (0.008-0.012 mg/kg eq). After 18 days, the radiocarbon was below 0.005 mg/kg eq in all tissues analyzed except liver (0.1 mg/kg eq). The parent compound was not found (<0.001 mg/kg eq) and metabolites were not investigated.

[Phenyl-^{14}C]fenitrothion was administered orally in gelatin capsules to 15 Japanese female quails, as single doses of 5 mg/kg bw (about 20 mg/kg feed), and to six White Leghorn hens, daily for 7 consecutive days at 2 mg/kg bw/day (about 35 mg/kg feed) and eggs were collected daily. Quails were killed 1 h, 1 or 7 days after their single doses and the hens 1 or 7 days after their last doses. Radioactivity was very rapidly excreted by both: 93-94% of the applied radioactivity (AR) was excreted in the faeces 6 h after dosing. The maximum radioactivity in the eggs was 0.2% of the AR.

The radioactive residues in hens' eggs did not reach a plateau during the 7-day dosing period, reaching maxima of 0.02 mg/kg eq on the 8th day in the whites and 0.1 mg/kg eq on the 7th day in the yolks (73% of the TRR in the yolks and 27% in the whites). In whole eggs, fenitrothion constituted 8% of the TRR (0.005 mg/kg eq). The main metabolite was 3-methyl-4-nitrophenyl sulfate (40% of the TRR) and others identified were 3-methyl-4-nitrophenol (22% of the TRR), the glucuronide of 5-hydroxy-2-nitrobenzyl alcohol (7% of the TRR), demethylfenitro-oxon (5% of the TRR) and demethylfenitrothion (2% of the TRR).

In the hens killed one day after treatment, residues were 0.098 mg/kg eq in liver, 0.1 mg/kg eq in kidney, <0.005 mg/kg eq in muscle and 0.016 mg/kg eq in fat.

In a quail killed one h after treatment, 0.81 mg/kg eq radioactive residue was found in the liver (15% parent compound, 32% 3-methyl-4-nitrophenol, 4.4% fenitro-oxon, 1.6% fenitro-oxon-3-CH_2OH and 40% unextracted), 2.2 mg/kg eq in the kidney (5% parent, 10% 3-methyl-4-nitrophenol, 0.9% fenitro-oxon-3-CH_2OH, 64% unextracted and 18% unidentified), and 0.16 mg/kg eq in muscle (34% parent, 4.4% 3-methyl-4-nitrophenol and 61% unextracted). Fat was not investigated.

The metabolism of fenitrothion in laboratory animals was qualitatively similar to that in farm animals.

Plant metabolism

The Meeting received information on the fate of fenitrothion in grapes and tomatoes after spray application and in rice during storage.

Two Thompson Seedless grape vines were sprayed three times at 14-day intervals in the field (Madera County, California, USA), with an EC 500 formulation of [phenyl-^{14}C]fenitrothion at a rate of 0.82 kg ai/ha and a spray volume of 1000 l/ha. Bunches of grapes were collected at mature harvest, 35 days after the last treatment. Of the total recovered radioactive residue (TRR) in the grapes, 97% was extractable (0.72 mg/kg eq). The main metabolites were 3-methyl-4-nitrophenol conjugate 1 (26% of the TRR) and 3-methyl-4-nitrophenol-β-glucuronide (21% of the TRR); the parent was not

detected. Among the minor metabolites, 3-methyl-4-nitrophenol conjugates 2 to 6 constituted 23.5%, demethylfenitrothion 7.2% and 3-methyl-4-nitrophenol 0.97% of the TRR. Parent fenitrothion was not detected.

The foliage and fruit of F1 Shirley tomato plants were sprayed twice at a 14-day interval at normal and threefold rates in a greenhouse with a solution of [phenyl-^{14}C]fenitrothion. The first application was at growth stage BBCH 85 (ripe fruit present). The application rates were 0.69 kg ai/ha with a spray volume of 4000 l/ha for the normal application and 2.1 kg ai/ha for the threefold application. Mature fruit, immature fruit and foliage were collected at harvest 15 days after the last treatment. Of the total recovered radioactive residue 63-70% was recovered in surface rinses and initial extracts of fruit and foliage. The parent was found at 13% of the TRR, 3-methyl-4-nitrophenol β-glucuronide at 7.3% and 3-methyl-4-nitrophenol at 7% in the mature fruit. When the remaining solids from mature fruit were further extracted with acetonitrile (ACN) followed by 1 M HCl and finally with 6 M NaOH, a further 19% of the TRR was extracted. The main metabolite in the combined extracts (24% of the TRR) did not correspond to any of the reference compounds available but could be hydrolyzed with cellulase, resulting in the formation of both 3-methyl-4-nitrophenol (28%) and 3-methyl-4-nitrophenol β-glucuronide (44%), with 27% remaining as the unaltered metabolite. The main metabolite is considered to be a further conjugate of 3-methyl-4-nitrophenol β-glucuronide.

An emulsion of [α-methyl-^{14}C]fenitrothion was applied to unpolished Nishikaze rice grain at rates of 6 and 15 g ai/t and samples were stored at 15° or 30°C in the dark for 12 months for analysis at intervals. Residues of fenitrothion gradually decreased, with half-lives of about 4 and over 12 months at 30°C and 15°C, respectively. The main metabolites were demethylfenitrothion and 3-methyl-4-nitrophenol. Demethylfenitrothion was formed in the early stages of degradation but the concentration remained fairly constant after 3 months. The concentration of 3-methyl-4-nitrophenol increased throughout the storage period. After 12 months at 15°C, 65% of the applied radioactivity was recovered as the parent compound, 10% as demethylfenitrothion and 16% as 3-methyl-4-nitrophenol, and after 12 months at 30°C 24% as parent, 18% as demethylfenitrothion and 38% as 3-methyl-4-nitrophenol. Minor metabolites, found particularly at the end of the storage period, were fenitro-oxon, demethylfenitro-oxon, *S*-methyl-fenitrothion, demethylfenitrothion *S*-isomer, 1-methoxy-3-methyl-4-nitrobenzene, 3-hydroxymethyl-4-nitrophenol, 1,2-dihydroxy-4-methyl-5-nitrobenzene and 1,2-dimethoxy-4-methyl-5-nitrobenzene. These constituted together about 4% of the applied radioactivity at 15°C but, at 30°C, 1-methoxy-3-methyl-4-nitrobenzene constituted about 8%, 1,2-dihydroxy-4-methyl-5-nitrobenzene about 3%, and the remaining minor metabolites about 6%. One reference compound (1-methoxy-3-hydroxymethyl-4-nitrobenzene) was not detected. No radiolabelled carbon dioxide was present. Autoradiography showed that the radioactivity was principally in the aleurone (part of the seed coat) but penetrated into the endosperm during storage. The concentration of fenitrothion in endosperm decreased from 4.5 to 3.3 mg/kg at 15°C and to 1.2 mg/kg at 30°C. The amount of fenitrothion in bran (seed coat plus germ) was approximately 40 times that in endosperm at all sampled intervals.

Although the maian metabolites found in plants were also found in animals, some minor ones were not: *S*-methyl-fenitrothion, demethylfenitrothion *S*-isomer, 1-methoxy-3-methyl-4-nitrobenzene, 1,2-dihydroxy-4-methyl-5-nitrobenzene and 1,2-dimethoxy-4-methyl-5-nitrobenzene.

Environmental fate in soil

The Meeting received information on aerobic degradation in soil.

The aerobic degradation of [phenyl-^{14}C]fenitrothion was studied in a US sandy loam soil for 365 days and in four European soils (two sandy loams, a silt loam and a clay loam) for 90 days.

In the first study, the parent decreased from 88% initially to 0.05% of the total applied radioactivity (TAR) at 365 days. At the end of the study, accumulated volatile radioactivity was 71% of the TAR, most of which was present as $^{14}CO_2$ (67.3% of the TAR). Six degradation products were identified: fenitro-oxon, 3-methyl-4-nitrophenol, demethylfenitrothion, demethylfenitro-oxon, formylaminofenitrothion and 1-methoxy-3-methyl-4-nitrobenzene. The main product, 3-methyl-4-

nitrophenol, amounted to 20% of the TAR at day 3 but decreased to <1% of the TAR at day 30. Other products were below 1% of the TAR. Unextractable residues increased to 35% of the TAR at day 21 but then decreased to 20% of the TAR at day 365. A number of fractions were not identified but the sum of these did not exceed 4.4% of the TAR. Calculated half-lives were 2.0 days and 3.3 days for parent and 3-methyl-4-nitrophenol, respectively.

In the second study, unextracted radioactivity increased to 37%-54% of the TAR after 7 days, decreasing to 23%-43% after 90 days, and trapped ^{14}C as $^{14}CO_2$ increased to 51%-69% by the end of the study. Fenitrothion was detected at 91%-96% of the TAR immediately after application but decreased rapidly to 2.4%-5.4% of the TAR after 7 days. The two products identified were 3-methyl-4-nitrophenol (17%-45% of the TAR at 1 day, decreasing rapidly to below 7% of the TAR after 7 days) and 1-methoxy-3-methyl-4-nitrobenzene (<0.5% of the TAR). A further unidentified compound was detected at a maximum of 3.2% of the TAR and other unknowns and unresolved background radioactivity occurred at maxima of 0.7% and 0.6% of the TAR, respectively. Calculated half-lives were 1-33 h for the parent compound and 42-68 h for 3-methyl-4-nitrophenol.

These results indicate that fenitrothion is mainly degraded via cleavage of the P-O-aryl linkage and further breakdown occurs via opening of the phenyl ring, with eventual mineralization to CO_2. The Meeting decided that studies on residues in succeeding crops were not necessary, as the residues of fenitrothion in soil decrease rapidly.

Environmental fate in water-sediment systems

The Meeting received information on degradation in water and water/sediment systems.

In a 30-day study at 25°C in the dark at pH 5, 7 and 9 in sterile solutions, fenitrothion (uniformly ^{14}C-labelled in the phenyl ring) was hydrolyzed faster at higher pH, with half-lives of 191-200 days at pH 5, 180-186 days at pH 7 and 100-101 days at pH 9. Demethylfenitrothion and 3-methyl-4-nitrophenol were identified as degradation products. Fenitrothion was rapidly photolyzed with a half-life of 3.3-3.6 days. Photoproducts were further degraded to CO_2. In water/sediment systems, the amount of fenitrothion decreased rapidly in the water phase with a concurrent initial increase of parent in the sediment phase. Unextractable radioactivity in the sediment increased to 71%-76% of the TAR at 59 days.

Methods of analysis

Several methods for the determination of fenitrothion in cereal grains and their processed products were reported to the Meeting. Extraction with acetone, acetone/water, methanol, acetonitrile/water or acetonitrile was followed by clean-up, partitioning into a suitable organic solvent and quantification by GC-NPD, GC-ECD, GC with an FPD, or GC-MS. LOQs in grain were 0.01-0.06 mg/kg, in straw 0.04-0.06 mg/kg, in bran 0.01-0.25 mg/kg, in pollard, white and brown bread 0.01-0.1 mg/kg, in germ 0.01–0.25 mg/kg and in flour 0.01-0.05 mg/kg.

The Meeting was informed by the government of The Netherlands of a multi-residue enforcement method for fruit and vegetables, consisting of extraction by a method for non-fatty samples and GC with an ion-trap detector. The LOQ was 0.05 mg/kg.

Methods to determine fenitrothion in animal commodities were not provided.

Stability of residues in stored analytical samples

The Meeting received data on the stability of residues in cereal grain and straw. Information on storage stability in animal products was not available.

Fenitrothion and demethylfenitrothion residues were stable at –20°C for the times tested: wheat grain (113 days), barley grain (105 days), rice grain (149 days) and rice straw (71 days).

Definition of the residue

Fenitrothion was rapidly excreted by goats, quails and hens. In whole goat milk, a maximum of 0.012 mg/kg eq radioactive components was found but the parent compound, fenitro-oxon or 3-methyl-4-nitrophenol were not detected. The radioactivity was attributed to 4 metabolites of which the main

one constituted 39% of the TRR (0.005 mg/kg eq). No radioactive residues could be detected in cream. The parent compound could not be detected in goat liver, kidney, fat or muscle, although maximum ^{14}C levels of 1.5 mg/kg eq were found in liver, 0.031 mg/kg eq in kidney, 0.012 mg/kg eq in fat and 0.005 mg/kg eq in muscle. The nature of these residues was not investigated.

Of the total recovered radioactivity in eggs, 73% was in the yolk and 27% in the white. In whole egg, the parent was found at 8% of the TRR (0.005 mg/kg eq) and the main metabolites were 3-methyl-4-nitrophenyl sulfate (40% of the TRR) and 3-methyl-4-nitrophenol (22% of the TRR).

In a metabolism study on hens, residues were 0.098 mg/kg eq in liver, 0.1 in kidney, <0.005 in muscle and 0.016 in fat. In a study on quails, the parent made up about 15% of the residue in liver, about 5% in kidney and about 34% in muscle; the main metabolite in the tissues was 3-methyl-4-nitrophenol.

The metabolism of fenitrothion in animals has not been fully elucidated, but in general it is expected that the levels of the individual metabolites will be <0.005 mg/kg at the expected exposure levels.

On the basis of the limited information available, the Meeting agreed that fenitrothion is a suitable marker molecule for enforcement in animal commodities and is also the compound of interest for dietary risk assessment.

The log K_{ow} of fenitrothion is 3.32. Taking into account the results of the metabolism studies (no radioactivity in cream but found in yolk, only slightly more in fat than in muscle), the Meeting decided that fenitrothion should not be classified as fat-soluble.

After the pre-harvest treatment of grapes, the main metabolites were 3-methyl-4-nitrophenol conjugate 1 (26% of the TRR) and 3-methyl-4-nitrophenol β-glucuronide (21%); the parent was not detected. The main metabolite in tomatoes (24%) was considered to be a further conjugate of 3-methyl-4-nitrophenol β-glucuronide. The parent constituted 13% of the TRR.

Information on residues in cereal grains after pre-harvest treatments was not reported. After the post-harvest treatment of cereal grains, the residue consisted mainly of parent, demethylfenitrothion and 3-methyl-4-nitrophenol. The key effect that determined the ADI and the acute RfD for fenitrothion was inhibition of brain and/or red cell acetylcholinesterase. The Meeting concluded that 3-methyl-4-nitrophenol does not need to be considered for dietary risk assessment, as it does not inhibit cholinesterase. Demethylfenitrothion was also not considered to be relevant for dietary risk assessment, as it is not metabolized to a more potent oxon and structure-activity considerations indicate that it is likely to be only a weak inhibitor of cholinesterase.

The metabolism of fenitrothion in plants has also not been fully characterized. The supported uses of fenitrothion are pre-harvest applications on cereals and post-harvest on stored cereal grains. The Meeting concluded that the available studies on cereals were adequate only for the post-harvest uses on stored cereal grains. To support the pre-harvest uses on cereals, relevant metabolism studies are required.

Definition of the residue (for compliance with MRLs and for estimations of dietary intake): *fenitrothion*, for both plant and animal commodities.

Results of supervised trials on crops

The Meeting received information on supervised trials on cereal grains (rice, wheat, barley, triticale), with pre-harvest treatments in Japan and Australia. In some trials pre-harvest treatments were combined with a seed treatment before planting. However, as data on metabolism in cereal grains after pre-harvest treatment were lacking, the trials could not be evaluated.

No trials were reported on apples, head cabbages, cacao beans, cauliflowers, cherries, citrus fruits, cucumbers, egg plants, grapes, leeks, head lettuce, bulb onions, peaches, pears, peas, peppers, potatoes, radishes, soya beans, strawberries, tea or tomatoes. The Meeting therefore recommended the withdrawal of the existing CXLs for these commodities.

Cereal grains (group 020). Five trials on stored wheat were carried out in Australia and Argentina. The trial in Australia complied with Australian GAP for post-harvest use on wheat (912 g ai/t with a waiting period of 3 months) and the residue level was 7.6 mg/kg. In Argentina, the trials complied with the Argentine GAP for post-harvest use on cereals (6 g ai/t with a waiting period of 1 day) and residues were 3.1, 3.5, 5.0 and 5.6 mg/kg.

The Meeting estimated a maximum residue level for cereals, based on post-harvest use, confirming the current CXL for cereal grains of 10 mg/kg (Po) and estimated an HR of 7.6 mg/kg and an STMR of 5.0 mg/kg.

Straw, fodder and forage of cereals and grasses (group 051). The Meeting received details of supervised trials on cereals (rice, wheat, barley, triticale) which received pre-harvest treatments in Japan and Australia. However, because details of metabolism were not provided, the trials could not be evaluated.

Fate of residues in storage and during processing

In storage

Hard red spring Neepawa wheat grains were evenly sprayed with fenitrothion at a rate of 12 g ai/t and samples were stored in screw-capped jars (240 ml) in the dark at 20°C, for analysis after 0, 1, 3, 6 and 12 months. The concentration of fenitrothion in the stored samples decreased to about 5.5 mg/kg after 3 months and to about 2.5 mg/kg after 12 months. The main metabolites were demethylfenitrothion, 3-methyl-4-nitrophenol and dimethyl phosphorothioic acid. Residues of the first and the last increased to 2.0 and 0.55 mg/kg after 6 months and, after 12 months, decreased to 0.98 mg/kg and 0.21 mg/kg, respectively. The 3-methyl-4-nitrophenol increased from 0.38 mg/kg at 1 month to 0.96 mg/kg after 12 months. Neither fenitro-oxon nor *S*-methyl-fenitrothion was detected at any time point.

In processing

The Meeting received information on the fate of fenitrothion, during simulated processing, in stored rice during polishing and cooking and in stored wheat during milling and baking.

A study with radiolabelled fenitrothion in sterile buffer solutions showed that fenitrothion is relatively stable during simulated pasteurization (90ºC for 20 min; 82% of the TAR remaining as parent, 12% demethylfenitrothion and 0.7% 3-methyl-4-nitrophenol formed) but is readily degraded to demethylfenitrothion during simulated baking/brewing/boiling (100ºC for 60 min; 35% of the TAR remaining as parent, 62% demethylfenitrothion and 0.8% 3-methyl-4-nitrophenol formed) and sterilization (120ºC for 20 min; 15% of the TAR remaining as parent, 82% demethylfenitrothion and 1.3% 3-methyl-4-nitrophenol formed).

When unpolished rice grains, treated post-harvest with 15 g ai/t [α-methyl-^{14}C]fenitrothion and stored at 30°C, were cooked immediately after treatment, the amount of fenitrothion decreased to about 60%, with the formation of demethylfenitrothion and 3-methyl-4-nitrophenol. When cooked after storage, about 40% of the fenitrothion was lost and residues of demethylfenitro-oxon and 3-methyl-4-nitrophenol increased. Other metabolites, such as 1-methoxy-3-methyl-4-nitrobenzene and 1,2-dihydroxy-4-methyl-5-nitrobenzene, decreased.

After polishing and washing the treated rice, 80% of the applied radioactivity remained in the bran and rinses. The combination of washing and boiling decreased the content of fenitrothion, demethylfenitrothion and 3-methyl-4-nitrophenol by about a factor of 2. Processing factors could not be calculated because actual residue levels were not reported. The Meeting recommended the withdrawal of the existing CXLs for rice, polished, (1 mg/kg PoP) and rice bran, unprocessed, (20 mg/kg PoP).

Wheat, stored for up to 3 months after post-harvest treatment with 12 g ai/t fenitrothion, was milled and baked into white and brown bread. The parent compound was determined in all processed products. Processing factors derived from wheat stored for 1 and 3 months were comparable. Calculated processing factors were 4.0 and 3.9 for bran (mean 3.95), 1.7 for pollard, 3.7 and 3.2 for

germ (mean 3.45), 0.21 and 0.26 for flour (mean 0.235), 0.60 for gluten, 0.089 and 0.11 for white bread (mean 0.10) and 0.43 and 0.33 for brown bread (mean 0.38).

From the highest residue and STMR for cereal grains (7.6 mg/kg and 5 mg/kg respectively) and the processing factors for wheat bran, flour, white bread and brown bread, the Meeting estimated a maximum residue level of 30 mg/kg in bran and estimated STMR-Ps of 19.75 mg/kg in bran, 1.175 mg/kg in flour, 0.50 mg/kg in white bread and 1.9 mg/kg in wholemeal bread.

Farm animal dietary burden

The Meeting estimated the dietary burden of fenitrothion residues in farm animals (Tables 52 and 53) from the diets listed in Appendix IX of the FAO Manual (FAO, 2002). One feed commodity only from each Codex Commodity Group was used, so the calculation included wheat grain but no other cereals. Calculation from the HR values provided the concentrations in feed suitable for estimating MRLs for animal commodities, while calculation from the STMR values for feed was suitable for estimating STMR values for animal commodities. In the case of processed commodities, the STMR-P value was used for both intake calculations.

Table 52. Estimation of maximum farm animal dietary burdens.

Commodity	Codex Code	Residue (mg/kg)	Basis	% Dry matter	Residue, dry wt (mg/kg)	% of diet			Residue contribution (mg/kg)		
						Beef	Dairy	Poultry	Beef	Dairy	Poultry
Wheat grain	GC	10	MRL	89	11.24	50	40	80	5.62	4.50	8.99
					Total				5.62	4.50	8.99
					Feeding levels in goat and hen metabolism studies				7.6	7.6	35

Table 53. Estimation of median farm animal dietary burdens.

Commodity	Codex Code	Residue (mg/kg)	Basis	% Dry matter	Residue, dry wt (mg/kg)	% of diet			Residue contribution (mg/kg)		
						Beef	Dairy	Poultry	Beef	Dairy	Poultry
Wheat grain	GC	5	STMR	89	5.62	50	40	80	2.81	2.25	4.50
					Total				2.81	2.25	4.50
					Feeding levels in goat and hen metabolism studies				7.6	7.6	35

Farm animal feeding studies

The Meeting received information on residues in the tissues of cattle grazing on fenitrothion-treated grass and in cattle fed with fenitrothion-treated maize silage.

Fenitrothion was applied as an EC formulation to two pastures at rates of 0.125 and 0.375 kg ai/ha. Ten cows were confined to each pasture immediately after spraying. Four animals, two from each field, were slaughtered after 1, 3, 7 or 10 days and only breast muscle and omental fat were analyzed. Residues were found in the muscle and fat samples taken 1 day after spraying from cows grazing on both pastures (0.007-0.014 mg/kg in muscle, <0.001-0.014 mg/kg in fat). By day 3 residues were found only in samples from the cows grazing on the pasture treated with 0.375 kg ai/ha (<0.001-0.001 mg/kg in muscle, 0.004-0.007 mg/kg in fat) and after day 3 no residues could be detected.

For the feeding trial, maize was sprayed in the field with 1.1, 2.2 or 3.4 kg ai/ha fenitrothion as an EC formulation, cut the next day and aged for 76 days. Groups of four lactating Jersey cows were fed treated or control silage *ad libitum* for 56 days. Cows fed silage from maize treated with 1.1, 2.2 and 3.4 kg ai/ha ingested averages of 0.21, 0.41 and 0.66 mg/kg bw/day of fenitrothion and its metabolites. Animals were milked twice daily and at the end of each week a composite sample was prepared by combining the milk from 2 consecutive morning and evening milkings. In the milk of cows fed silage from maize treated at 3.4 kg ai/ha, aminofenitrothion was the only compound detected, at 0.001-0.005 mg/kg when expressed as fenitrothion. No residues (<0.001 mg/kg eq) were found in the milk of cows consuming silage from maize treated at lower levels. Tissues were not analyzed.

Animal commodity maximum residue levels

In the metabolism study, where goats were dosed at 7.6 ppm in the feed, the parent compound was undetected in tissues and milk, so no residues are to be expected at the calculated dietary burden of 5.6 mg/kg feed for beef cattle and 4.5 mg/kg for dairy cattle.

The dietary burden for poultry was 9 mg/kg, lower than the feeding level in the metabolism study on hens (approximately 35 ppm in the feed) and therefore the resulting residues in eggs and poultry tissues were calculated by applying the respective transfer factors (transfer factor = residue level in egg or tissue ÷ residue level in metabolism study) to the estimated dietary burden. In the metabolism study there was only one residue result reported per tissue and therefore this value was used, in conjunction with the estimated maximum dietary burden, to calculate the highest likely poultry commodity residue levels (Table 54) and it was also used, in conjunction with the estimated STMR dietary burden, to estimate the poultry commodity STMRs (Table 54).

Table 54. Calculation of MRLs and STMRs for poultry tissues and eggs.

	Feeding level (ppm) actual[2/]	Fenitrothion residues, mg/kg [1/]									
		Muscle		Fat		Liver		Kidney		Eggs	
		High [3/]	Mean [4/]	High [3/]	Mean [4/]	High [3/]	Mean [4/]	High [3/]	Mean [4/]	High [3/]	Mean [4/]
MRL	*9*	*(0.001)*		*(0.004)*		*(0.025)*		*(0.016)*		*(0.001)*	
poultry	35	0.005		0.016		0.098		0.10		0.005	
STMR	*4.5*		*(0.0006)*		*(0.002)*		*(0.013)*		*(0.013)*		*(0.0006)*
poultry	35		0.005		0.016		0.098		0.100		0.005

[1/] Residue values in parentheses in *italics* are extrapolated from residues found at the feeding level in the hen metabolism study.

[2/] Values in *italics* are the estimated dietary burdens. Values in normal font are feeding levels in the hen metabolism study.

[3/] High is the residue level calculated from that found in the feeding study and the estimated maximum dietary burden.

[4/] Mean is the residue level calculated from that found in the feeding study and the estimated STMR dietary burden.

The Meeting concluded that residues above the LOQ are unlikely to arise in poultry commodities, particularly because total radioactive residue levels from the metabolism study were used to calculate the residue levels in poultry. Data from the quail metabolism study showed that, of the total radioactive residues, parent fenitrothion formed 15% in liver, 5% in kidney and 34% in muscle.

However, in the absence of a validated analytical method for the determination of fenitrothion in animal commodities, and in the absence of information on storage stability of fenitrothion in analytical samples from animal commodities, the Meeting decided it could not recommend maximum residue levels for animal commodities.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed in Table 55 are suitable for establishing maximum residue limits and for IEDI and IESTI assessment.

Definition of the residue for compliance with MRL and for estimation of dietary intake: *fenitrothion.*

The definition applies to plant and animal commodities.

Table 55. Summary of recommendations.

CCN	Commodity	MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR (mg/kg)
		New	Previous		
FP 0226	Apples	W	0.5@		
VB 0041	Cabbages, head	W	0.5@		
SB 0715	Cacao beans	W	0.1@		
VB 0404	Cauliflowers	W	0.1@		
GC 0080	Cereal grain	10 Po	10 Po	5	7.6
FS 0013	Cherries	W	0.5@		
FC 0001	Citrus fruits	W	2@		
VC 0424	Cucumbers	W	0.05 (*)@		

CCN	Commodity	MRL (mg/kg)		STMR, STMR-P (mg/kg)	HR (mg/kg)
		New	Previous		
VO 0440	Eggplant	W	0.1@		
FB 0269	Grapes	W	0.5@		
VA 0384	Leeks	W	0.2@		
VL 0482	Lettuce, head	W	0.5@		
MM 0095	Meat (from mammals other than marine mammals)	W	0.05 (*) (fat) E		
ML 0812	Milks	W	0.002 (*) E		
VA 0385	Onions, bulb	W	0.05 (*)@		
FS 0247	Peaches	W	1@		
FP 0230	Pears	W	0.5@		
VP 0063	Peas (pods and succulent [= immature] seeds)	W	0.5@		
VO 0051	Peppers	W	0.1@		
VR 0589	Potatoes	W	0.05 (*)@		
VR 0494	Radishes	W	0.2@		
CF 0649	Rice bran, unprocessed	W	20 PoP		
CM 1205	Rice, polished	W	1 PoP		
VD 0541	Soya beans, dry	W	0.1@		
FB 0275	Strawberries	W	0.5@		
DT 1114	Tea, green, black	W	0.5@		
VO 0448	Tomatoes	W	0.5@		
CF 0654	Wheat bran, processed	W	2 PoP		
CM 0654	Wheat bran, unprocessed	30 PoP	20 PoP	19.75	30.02
CF 1211	Wheat flour	W	2 PoP	1.175	
CF 1212	Wheat wholemeal	W	5 PoP		
CP 1211	White bread	W	0.2 PoP	0.50	
CP 1212	Wholemeal bread			1.9	

@ CXL deleted by the CAC in June 2003.

FURTHER WORK OR INFORMATION

Desirable

1. Metabolism in cereals (including rice) after pre-harvest treatment.
2. Validated analytical method for the determination of fenitrothion in animal commodities.
3. Freezer storage stability in animal commodities.
4. Farm animal transfer studies.
5. Processing study in rice.

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDIs) of fenitrothion, based on the STMRs estimated for three commodities, was 120-640% of the maximum ADI (0.005 mg/kg bw) for the five GEMS/Food regional diets (Table 56). The information provided to the Meeting precludes an estimate that the dietary intake would be below the ADI.

The Meeting noted that the intake calculations were conservative, because they did not take into account the reduction of residue levels obtained by processing of cereal grains, except in the processing of wheat. Further information on the effect of processing on residues in rice would be particularly useful, to refine the intake calculations.

Table 56. International Estimated Dietary Intakes (IEDIs) of fenitrothion for the five GEMS/Food regional diets (ADI = 0-0.005 mg/kg bw/day).

Code	Commodity	STMR or STMR-P mg/kg	Diets: g/person/day. Intake = daily intake: µg/person									
			Mid-East		Far-East		African		Latin American		European	
			diet	intake	diet	intake	diet	intake	diet	intake	diet	intake
GC 0080	Cereal grain (except wheat) [1/]	5	106.9	534.5	336.8	1684.0	290.0	1450.0	140.4	702.0	46.1	230.5
CP 1211	White bread	0.05	215.3	10.8	76.0	3.8	18.9	0.9	37.3	1.9	117.2	5.9

Code	Commodity	STMR or STMR-P mg/kg	Diets: g/person/day. Intake = daily intake: µg/person									
			Mid-East		Far-East		African		Latin American		European	
			diet	intake	diet	intake	diet	intake	diet	intake	diet	intake
CP 1212	Wholemeal bread	1.9	107.7	204.6	38.0	72.2	9.4	17.9	74.7	141.9	58.6	111.3
Total intake (µg/person)=				749.9		1760.0		1468.8		845.8		347.7
Bodyweight per region (kg bw) =				60		55		60		60		60
ADI (µg/person)=				300		275		300		300		300
% ADI=				250.0		640.0		489.6		281.9		115.9
Rounded % ADI=				250		640		490		280		120

[1/] The consumption value for wheat flour is the sum of the consumption of white bread and that of wholemeal bread. The intake of fenitrothion was calculated using the consumption and STMR-P values for white bread and wholemeal bread.

Short-term intake

International Estimated Short Term Intakes (IESTIs) for fenitrothion were calculated for the food commodities (and their processed fractions) for which maximum residue levels were estimated and for which consumption data were available. The results are shown in Tables 57 and 58.

The IESTI represented 1-150% of the acute RfD (0.04 mg/kg bw) for the general population and 2-240% of the acute RfD for children. Estimated short-term intakes from rice (husked) and rice (polished) accounted for 120 and 150% of the acute RfD, respectively, for the general population. Estimated short-term intakes from maize (fresh, flour, oil), husked rice and polished rice account for 160, 240 and 240% of the acute RfD, respectively, for children. The Meeting concluded that the short term intake of residues of fenitrothion from uses, other than on these 3 commodities, that have been considered by the JMPR is unlikely to present a public health concern.

The Meeting noted that the intake calculations were conservative, because they did not take into account the reduction in residue levels obtained by processing of cereal grains, except the processing of wheat. Further information on the effect of processing on residues in rice would be particularly useful, to refine the intake calculations.

Table 57. Assessment of risk to the general population from the short-term dietary intake of residues of fenitrothion (acute RfD = 0.04 mg/kg bw, i.e. 40 µg/kg bw/day).

Codex Code	Commodity	STMR or STMR-P mg/kg	HR or HR-P, mg/kg	Large portion diet			Unit weight			Variability factor	Case	IESTI µg/kg bw/day	% acute RfD rounded
				Country	Body wt (kg)	Large portion, g/person	Unit wt, g	Country	Unit wt, edible portion, g				
GC 0645	Maize (fresh, flour, oil)	-	7.6	FRA	62.3	260	-	-	ND	ND	1	31.69	80
CM 0649	Rice, husked	-	7.6	JPN	52.6	319	-	-	ND	ND	1	46.13	120
CM 1205	Rice, polished	-	7.6	JPN	52.6	402	-	-	ND	ND	1	58.06	150
CF 1211	Wheat flour	1.175	-	USA	65.0	365	-	-	ND	ND	3	6.60	20
CP 1211	White bread	0.05	-	SAF	55.7	479	-	-	ND	ND	3	0.43	1
CP 1212	Wholemeal bread	1.9	-	SAF	55.7	395	-	-	ND	ND	3	13.49	30

Table 58. Assessment of risk to children up to 6 years, from the short-term dietary intake of residues of fenitrothion (acute RfD = 0.04 mg/kg bw, i.e. 40 µg/kg bw/day).

Codex Code	Commodity	STMR or STMR-P mg/kg	HR or HR-P, mg/kg	Large portion diet			Unit weight			Variability factor	Case	IESTI µg/kg bw/day	% acute RfD rounded
				Country	Body wt (kg)	Large portion, g/person	Unit wt, g	Country	Unit wt, edible portion, g				
GC 0645	Maize (fresh, flour, oil)	-	7.6	FRA	17.8	148	-	-	-	-	1	63.31	160

Codex Code	Commodity	STMR or STMR-P mg/kg	HR or HR-P, mg/kg	Large portion diet			Unit weight			Variability factor	Case	IESTI µg/kg bw/day	% acute RfD rounded
				Country	Body wt (kg)	Large portion, g/person	Unit wt, g	Country	Unit wt, edible portion, g				
CM 0649	Rice, husked	-	7.6	FRA	17.8	223	-	-	-	-	1	95.00	240
CM 1205	Rice, polished	-	7.6	JPN	15.9	199	-	-	-	-	1	94.92	240
CF 1211	Wheat flour	1.175	-	AUS	19.0	194	-	-	-	-	3	12.02	30
CP 1211	White bread	0.05	-	SAF	14.2	270	-	-	-	-	3	0.95	2
CP 1212	Wholemeal bread	1.9	-	SAF	14.2	240	-	-	-	-	3	32.11	80

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