ETHOPROPHOS (149)

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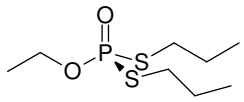
EXPLANATION

Ethoprophos, a nematicide and soil-insecticide, was evaluated for residues in 1984 and in 1987. The toxicology of ethoprophos was periodically reviewed by the 1999 JMPR. Ethoprophos was listed as a priority compound under the periodic re-evaluation programme of the 30th Session of the CCPR (ALINORM 99/24 App VII) for residue review by the 2001 JMPR. The manufacturer requested the postponement of the residue evaluation.

The basic manufacturer supplied information on identity, metabolism and environmental fate, residue analysis, use pattern, residues resulting from supervised trials on strawberry, banana, cucumber, melon, pepper, tomato, potato, sweet potato and sugar cane, fate of residues during storage and in processing, residues in food in commerce or at consumption and national maximum residue limits.

IDENTIT

ISO common name:	ethoprophos
Chemical name	
IUPAC:	*O*-ethyl *S,S*-dipropyl phosphorodithioate
CAS:	*O*-ethyl *S,S*-dipropyl phosphorodithioate
CAS Registry No:	13194-48-4
CIPAC No:	218
Synonyms and trade names:	S,S-dipropyl O-ethyl phosphorodithioate; prophos; ethoprop; Mocap; VC9-104; ENT-27318; AE F034142
Structural formula:	established by IR, ^{1}H-NMR, ^{13}C-NMR, ^{31}P-NMR, APCI-MS (+/-) and UV-VIS (according to OECD 101) (Boeuf *et al.*, 2000)



Molecular formula:	$C_8H_{19}O_2PS_2$ (Boeuf *et al.*, 2000)
Molecular weight:	242.34 (Boeuf *et al.*, 2000)

Physical and chemical properties

Pure active ingredient

Physical and chemical properties were determined with the pure active ingredient, unless specified otherwise.

Property	Description or result	Method(s) (References)
Minimum purity	980 g/kg	(Barriere, 2004a)
Appearance	colourless clear liquid, odour not assessed	(Ristorcelli, 2001a)

Property	Description or result	Method(s) (References)
Vapour pressure	78 mPa at 20°C 123 mPa at 25°C calculated from Clausius-Clapeyron relationship from measurements at 16.0-20.4-24.2-31.4°C	OPPTS 830.7950 92/69/EC A4 OECD 104 Knudsen effusion method (Ristorcelli, 2001b)
Melting/freezing point	below -70°C (203.2 K)	OPPTS 830.7200 92/69/EC A1 differential scanning calorimetry (Ristorcelli, 2001a)
Octanol/water partition coefficient	Log K_{ow} = 2.99 (95% confidence interval 2.9-3.1), temperature not stated K_{ow} is not pH-dependent	OPPTS 830.7570 92/69/EC A8 OECD 117 HPLC method (Ristorcelli, 2001d)
Water solubility	1.3-1.4 g/L (RSD 1.9%-3.8%), 20ºC; solubility not pH-dependent, determined from pH 4 to 9	OPPTS 830.7840 92/69/EC A6 OECD 105 flask method (Ristorcelli, 2001c)
Solubility in organic solvents	purity 94.4% (technical grade) > 500 g/L at 20°C in acetone; acetonitrile; 1,2 dichloroethane; ethyl acetate; n-hexane; methanol; n-octanol; toluene	OPPTS 830.7840 92/69/EC A6 OECD 105 flask method (Ristorcelli, 2001c)
Relative density (D^{20}_4)	1.096, measured at 20.7°C instead of 20°C	OPPTS 830.700 92/69/EC A3 oscillating densitimeter (Ristorcelli, 2001a)
Hydrolysis in aqueous solution, study 1	- Chemical and radiochem. purity >98% - Stability tested over 6 week period at 2 and 200 mg/l at pH 3, 6, 9, in the dark with radio-label on C-1 carbon of the propyl group. Half-life 28-36 weeks at pH3, 20°C 33-39 weeks at pH 6, 20°C 39-44 days at pH 9, 20°C 16-21 weeks at pH 3, 35°C 14-16 weeks at pH 6, 35°C 10-14 days at pH 9, 35°C - Identified degradation product *O*-ethyl *S*-propyl phosphorothioic acid (mP). - Radioactivity was partly lost (up to 40% at 35°C at pH 9 at 7-42 days) as unknown volatile compounds.	Fed. Reg. 43, (132) 29717 (Norris, 1983), non-GLP
Hydrolysis in aqueous solution, study 2	-Radiochem. purity >98%, chemical purity not stated - Stability tested over 30 day period at 10 mg/l at pH 5, 7, 9, in the dark, with 1-ethyl-^{14}C radiolabel at 25 ± 1°C. -Stable at pH5 and 7, 25°C; -Half-life 83 days at pH =9, 25°C; -Identified degradation products ethyl alcohol and S,S-dipropyl phosphorodithioic acid (mK) -Total ^{14}C recovery >99%	US EPA 161-1 (Das, 1989)
Hydrolysis in aqueous solution, study 3	-Radiochem. purity >98%, chemical purity not stated -Stability tested over a 20 day period at 10 mg/l at pH 4, in the dark, with radio-label on C-1 carbon of the propyl group at 60, 70 and 80°C ± 1°C. - Half-life 10 days at 60°C; Half-life 3.5-4.0 days at 70°C Half-life 1.4 days at 80°C Stable at pH 4 at 20°C, half-life >365 days, calculated from Arrhenius plot. - Identified degradation product *S,S*-dipropyl phosphorodithioic acid (mK) - Total ^{14}C recovery >93%.	OECD 111 (Maurer, 2002)

Property	Description or result	Method(s) (References)
Photolysis in aqueous solution; study 1	-Radiochem. purity 98.6%, chemical purity >97.7% - Stability tested over 30 day period at 22 mg/l at pH 7, with 1-ethyl-^{14}C radiolabel at 25 ± 1°C, continuous radiation with xenon-arc lamp at one-half the intensity of sun light. - Stable with or without sensitizer (1% v/v acetone); half-life could not be calculated - Total ^{14}C recovery > 98%.	US EPA 161-2 (Carpenter, 1989)
Photolysis in aqueous solution; study 2	-Radiochem. purity 99.5%, chemical purity not stated - Stability tested over 30 day period at 15 mg/l at pH 7, with 1-ethyl-^{14}C radiolabel at 25 ± 1°C, continuous radiation with xenon-arc lamp at one-half the intensity of sun light. - Half-life 122 days without senzitiser Half-life 104 days with senzitizer (1% v/v acetone). - Total ^{14}C recovery > 98%.	US EPA 161-2 (Gorman, 1995)
Dissociation constant	purity 94.4% (technical grade); pH of a 1% (w/v) suspension in water, at 23°C =3.45 Ethoprophos does not dissociate.	OPPTS 830.7000; (Bascou, 2001)

Technical material

Property	Result	Method(s) (references)
Minimum purity	940 g/kg	(Barriere, 2004a)
Main impurities	no data provided	
Appearance	colourless, clear liquid, odour not assessed	(Ristorcelli, 2001a)
Relative density (D^{20}_4)	1.093, measured at 20.7°C in stead of 20°C	OPPTS 830.700 92/69/EC A3 oscillating densitimeter; (Ristorcelli, 2001a)
Freezing point	below -70°C (203.2 K)	OPPTS 830.7200 92/69/EC A1 differential scanning calorimetry (Ristorcelli, 2001a)
Stability	Techical material was placed in 3 different kind of packaging containers. No significant decrease was observed after a 1 year storage period at ambient temperature (23-25°C) and 50% relative humidity.	EPA 40 CFR 158.175, D 63-17 (Eubanks, 1991)

Formulations

Ethoprophos end-use products are formulated mainly as granulates (GR 50, 100, 150, 200 g ai/kg), or as emulsifiable concentrates (EC, 69.6, 172.9, 200, 720 g ai/l). Ethophrophos can also be formulated as microgranulate (MG, 100, 200 g ai/kg) or as an emulsifiable gel packaged in a water-soluble bag (gel, 720 g ai/l).

FAO specifications for technical and formulated ethoprophos have not been published.

Abbreviations and code names

Table 1. Metabolite and degradation product codes used in the present review.

Code used here	Code used in study reports	Name	Found in
mA	M1 AE0592496	*O*-ethyl *S*-propyl hydrogen phosphorothioate (*O*-ethyl *S*-propyl phosphorothioate)	rat/rabbit; goat?; hen?;

Code used here	Code used in study reports	Name	Found in
			plant; aerobic soil
mB		propanethiol	volatile
mC		dipropyl disulfide	plant; not found in rat; not tested in livestock not found in aerobic soil
mD		ethyl propyl sulfide	plant, not found in rat; not tested in livestock not found in aerobic soil
mE		ethyl propyl sulfoxide	plant, aerobic soil not found in rat, not tested in livestock
mF		ethyl propyl sulfone	plant, aerobic soil not found in rat, not tested in livestock
mG		methyl propyl sulfide	plant?, rat, not tested in livestock
mH		methyl propyl sulfoxide	plant?, rat, not tested in livestock
mI		methyl propyl sulfone	plant?, rat, not tested in livestock
mJ		ethyl dihydrogen phosphate (ethyl phosphate)	plant, rat, goat?; hen?
mK	AE 0712739 RPA 112748	*S,S*-dipropyl hydrogen phosphorodithioate (desethyl ethoprophos)	hydrolysis product in water rat, rabbit; not found in plant, not tested in livestock
mL		*S*-propyl dihydrogen phosphorothioate	plant?; rat; rabbit; not tested in livestock
mM		*S*-ethyl glutathione	rat; rabbit not tested in plant, not tested in livestock
mN	OME	*O*-ethyl *O*-methyl *S*-propyl phosphorothioate	aerobic soil?; plant?; hen? not found in rat; not found in goat
mO	SME	*O*-ethyl *S*-methyl *S*-propyl phosphorodithioate	aerobic soil?; plant?; hen? not found in rat; not found in goat
mP	SH	*O*-ethyl *S*-propyl *S*-hydrogen phosphorodithioate *O*-ethyl *S*-propyl phosphorodithioate	hydrolysis product in water; rat; not tested in plant, livestock or soil

Table 2. Other abbreviations used in the present review.

Code	Abbreviation for:
DAT	days after (last) treatment
ACN	acetonitrile
ai	active ingredient or active substance
CEC	cation exchance capacity
DCM	dichloromethane or methylene chloride
kg dw	kilogram dry weight (feed or soil)
EC	emulsifiable concentrate
EI +/-	electron impact with positive/negative ionisation (for MS)
eq	ethoprophos equivalents
GBq	giga Becquerel
GC-AFID	gas chromatography with alkaline flame ionisation detection
GC-ECD	gas chromatography with electron capture detection

Code	Abbreviation for:
GC-FPD	gas chromatography with flame photometric detection
GC-MC	gas chromatography with microcoulometric detection
GC-MS	gas chromatography with mass spectrometric detection
GC-MS-MS	gas chromatography with tandem mass spectrometric detection
GC-NPD	gas chromotography with nitrogen phosphorus detection
GC-PFPD	gas chromatography with pulsed flame photometric detection
GC-TSD	gas chromatography with thermionic specific detection = GC-NPD
GI tract	gastro intestinal tract
GPC	gel permeation chromatography
HPLC	high performance liquid chromatography
ILV	Independent laboratory validation
LSC	liquid scintillation counting
m/z	mass to charge ratio (mass spectrometry)
om	organic matter
PTVLV injector	programmable temperature vaporizing large volume injector
SIM	single ion monitoring (mass spectrometry)
TLC	thin layer chromatography
TAR	total applied radioactivity or total administered radioactivity
TRR	total recovered radioactivity

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

The Meeting received information on the fate of orally dosed ethoprophos in lactating goats and laying hens. Ethoprophos was labelled at the 1-ethyl position. Metabolism in laboratory rats was summarized and evaluated by the WHO Core Assessment Group of the JMPR in 1999.

Ruminants: lactating goats

[1-ethyl-^{14}C]ethoprophos was administered orally once daily for seven consecutive days by capsule to two lactating goats (Alpine; 46-54 kg; two years old) at an actual (mean) dietary concentration of 32 mg ai/kg dry feed (Byrd, 1993, 1994). The radiochemical purity after repurification was 99.0%, with a specific activity after dilution of 0.11 GBq/mmol. One control goat received capsules containing 100 mg cellulose. Mean feed intake was 632 g/goat/day. Immediately after the sixth dose one goat was enclosed for 24 hours in a plastic gas collection tent with an NaOH trapping solution. The tent was removed immediately before the seventh dose. Urine and faeces were collected once daily; milk was collected twice daily and was pooled for each 24 h period after dosing. Whole blood was collected before termination. The goats were slaughtered 20-21 hours after the final dose and liver, bile, kidney, muscle (from rear leg and lumber spine), fat (omental and peripheral), GI tract tissue and contents were sampled. Samples were homogenised and stored frozen at –15ºC for 1 month. Radioactivity was determined in urine, faeces, milk, blood, tissues, cage rinse and expired volatiles by LSC and combustion-LSC. Tissues and faeces were freeze-dried and sequentially (Soxhlet) extracted with hexane, chloroform and acidic MeOH. Solid residues from muscle were acid- and base-hydrolysed (1 M HCl, 1 M NaOH, each for 1 h at 98ºC), solid residues from liver and kidney were acid- and base-extracted (0.1 M HCl, 0.001 M NaOH) and digested with pronase E and protease (37ºC, overnight) and 6 M HCl. Milk samples were extracted with chloroform/MeOH/water; urine was extracted with ACN/MeOH. Extracts and digests were chromatographed on normal and reverse-phase TLC plates (3 different solvent systems) with detection by LSC. Reference compounds were ethoprophos, mA, mJ, mN, mO, amino-acids (Ala, Arg, Asn, Asp, Cys, Gln, Glu, Gly, His, H-Pro, Ile, Leu, Lys, Met, Phe, Pro, Ser, Thr, Trp, Tyr, Val) and fatty acids (oleic , stearic, myristic, palmitic).

Results. Of the total radioactivity administered 92% and 84% (mean 88%) was recovered from the two goats: 76% in urine, 2.4% in faeces, 2.0% in cage rinse, 0.27% in expired air (24 h period;

extrapolates to 2% for 7 day period), 1.7% in milk, 3.6% in liver, 1.2% in GI tract and contents, 0.27% in the remaining tissues, blood and bile samples.

Residues in milk reached a plateau on the first day of treatment. The following average concentrations were found in edible tissues of the two goats: 0.49 mg/kg eq in milk (average over day 0-7; maximum 0.68 mg/kg eq); 8.8 mg/kg eq in liver; 0.93 mg/kg eq in kidney; 0.095 mg/kg eq in muscle; 0.051 mg/kg eq in fat.

Radioactivity in liver, kidney, muscle, fat and milk was fractionated into extractable, hydrolysable (acid/base) and solid residues (Table 3); the solid residues could be solubilised using protease/acid digestion. A limited set of extracts was characterized. The total extracted radioactivity in liver, kidney, muscle and fat was more than 100%. According to the study author high recoveries in muscle and fat were explained by the low levels of radioactivity.

In tissues almost all the radioactivity in liver and kidney remained in the post-extracted solids. Enzyme/acid digests of these solids co-chromatographed with amino acid standards. According to the study authors the formation of radioactive amino acids occurred via hydrolysis of ethoprophos to ethanol with subsequent conversion to acetaldehyde, acetate, acetyl-coenzyme A, (acetyl-Co A) and amino acids (tricarboxylic acid cycle). The acidic MeOH extract of liver contained three radioactive spots (1.1%, 1.4%, 0.45% of the TRR in liver), the first spot contained mA and/or mJ, but the other two spots did not co-chromatograph with any of the reference compounds used.

In milk 55% was extractable with chloroform. When the radioactivity in the chloroform extract was saponified, the major saponified fraction co-chromatographed with badly-resolved fatty acid standards (palmitic acid, oleic acid and stearic acid). According to the study authors the formation of radioactive fatty acids occurred via hydrolysis of ethoprophos to ethanol with subsequent conversion to acetyl-CoA and fatty acids.

Conclusions. After 7 daily doses of 32 mg ai/kg in the dry feed of dairy goats, the administered radioactivity was mainly excreted in the urine (76% of the TAR). Levels in milk attained a steady state 1 day after the first dose. Radiolabel concentrations were highest in tissues responsible for metabolism and excretion (liver and kidney). The metabolism of ethoprophos was shown to be extensive with most of the radioactivity apparently incorporated into natural products such as fatty acids and amino acids. The parent compound was not found. Primary metabolites tentatively identified were mA and/or mJ.

Table 3. Fractionation of radioactivity in edible tissues of dairy goats, treated for 7 days with 32 mg ai/kg dry feed.

Sample	Mean residue mg/kg eq	extractable		not extractable						Total %
		hexane, chloroform, acidic MeOH		released by acid/base		released by enzyme or 6 M HCl		solids		
		%	mg/kg eq	%	mg/kg eq	%	mg/kg eq	%	mg/kg eq	
Liver	8.8	4.9	0.43	3.6	0.32	103	9.1			111
Kidney	0.93	16	0.15	7.3	0.068	88	0.82			111
Muscle	0.095	24	0.022	132d	0.13	1.6	0.002			158
Fat	0.051	84	0.043	na		73	0.037			157
Milk	0.49	55b 16c	0.27b 0.076c					10a	0.05	81

na: not applicable.
a not treated by enzymes or strong acids.
b chloroform phase.
c MeOH/water phase.
d acid/base hydrolysis.

Poultry: laying hens

Radiolabelled [1-ethyl-^{14}C]ethoprophos was administered orally once daily for seven consecutive days by capsule to two groups of laying hens (3 and 6 hens; Leghorn; weight 1.3-1.8 kg; 102-104 weeks old) (Bates and Byrd, 1993). The radiochemical purity after repurification was 99.0% with a specific activity after dilution of 0.16 GBq/mmol. The hens were originally dosed with 10 mg ai/kg dry feed (2 mg ai per hen per day). Owing to observed toxicity, the study was terminated and restarted with a lower dose. In the final experiment hens were dosed at an actual (mean) dietary concentration of 2.1 mg ai/kg dry feed. Mean feed intake was 96 g/hen/day. One group of three hens was placed in a plastic gas collection tent with an NaOH trapping solution during the whole study. One control group of three hens received gelatine capsules with 100 mg cellulose. Expired volatiles and excreta were collected once daily. Eggs were collected twice daily and pooled for each 24 h period after dosing. Eggs were separated into whites and yolks. Whole blood was collected before termination and separated into red blood cells and plasma. The hens were killed 16-20 hours after the final dose and liver, kidney, muscle (thigh and breast), fat (mesenteric and peripheral), skin with adhering fat, and GI tract tissue and contents were sampled. Samples were homogenised and stored frozen at –15ºC for 1 month. Radioactivity was determined in excreta, eggs, blood, tissues, cage rinse and expired volatiles by LSC and combustion-LSC. Tissues, eggs and excreta from the two groups were pooled, freeze-dried and sequentially (Soxhlet) extracted with hexane, chloroform and acidic MeOH. Solid residues from muscle and egg whites were acid-and base-hydrolysed (1 M HCl, 1 M NaOH, each for 1 h at 98ºC), solid residues from liver and kidney were acid and base extracted (0.1 M HCl, 0.001 M NaOH) and digested with pronase E and protease (37ºC, overnight) and 6 M HCl. Extracts and digests were chromatographed on normal and reverse-phase TLC plates (3 different solvent systems) with detection by LSC. Reference compounds were ethoprophos, mA, mJ, mN, mO, amino-acids (Ala, Arg, Asn, Asp, Cys, Gln, Glu, Gly, His, H-Pro, Ile, Leu, Lys, Met, Phe, Pro, Ser, Thr, Trp, Tyr, Val) and fatty acids (oleic , stearic , palmitic, myristic).

Results. Of the total radioactivity administered 63% (3 hens in gas tent) and 64% (6 hens) was recovered: 44% in excreta, 0.31% in cage rinse, 3.6% in expired volatiles, 1.0% in egg whites, 9.3% in egg yolks, 2.6% in liver, 3.6% in GI tract tissue and contents, 0.62% in the remaining tissues and blood samples.

A plateau was reached in egg whites on the 3rd day of treatment, but not in egg yolks during the treatment period of 7 days. The following average concentrations were found in the edible tissues of the two groups of hens: 0.021 mg/kg eq in egg whites (average over days 3-7; maximum 0.029 mg/kg eq); 0.30 mg/kg eq in egg yolks (average over days 0-7; maximum 0.64 mg/kg eq); 1.2 mg/kg eq in liver; 0.40 mg/kg eq in kidney; 0.010 mg/kg eq in muscle; 0.076 mg/kg eq in fat; 0.021 mg/kg eq in skin with adhering fat.

Radioactivity in liver, kidney, muscle and fat was fractionated into extractable, hydrolysable (acid/base) and solid residues (Table 4); the solid residues could be solubilised using protease/acid digestion. A limited set of extracts was characterized.

Almost all the radioactivity in liver and kidney again remained in the post-extracted solids, and enzyme/acid digests of these solids co-chromatographed with amino acid standards. The study authors concluded that the radioactive amino acids had been formed as in goats. The organic (acidic MeOH) extract of liver contained three radioactive zones (1.9%, 0.95%, 2.0% of the TRR in liver): the first contained mA and/or mJ, the second did not co-chromatograph with any of the reference compounds used and the third co-chromatographed with mN and/or mO.

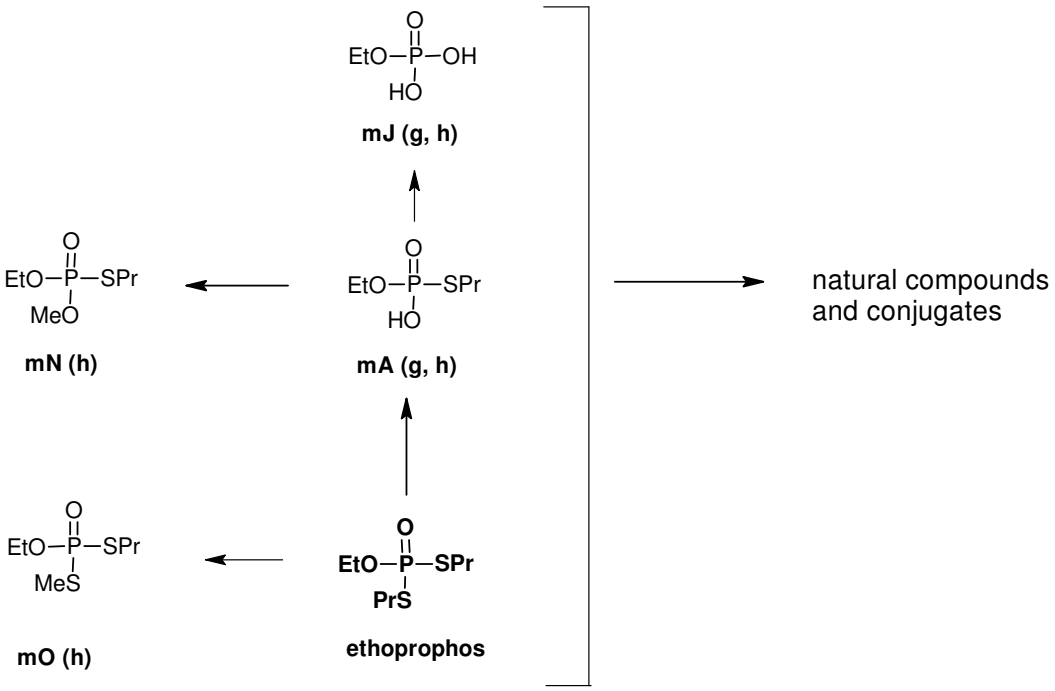
In egg yolks 84% of the TRR was extractable in hexane and 11% in chloroform. The hexane fraction was saponified, and the saponified fraction co-chromatographed with badly resolved palmitic, myristic, oleic and stearic acids. The study authors concluded that radioactive fatty acids had been formed as before.

Conclusion. After 7 daily doses of 2.1 mg ai/kg in the dry feed of laying hens, the administered radioactivity was mainly found in the excreta (44% of the TAR). Radiolabel concentrations were again highest in the liver and kidney. The metabolism of ethoprophos was similar to that in goats, and the parent compound was not found. Metabolites tentatively identified were mA and/or mJ and mN and/or mO.

Table 4. Fractionation of radioactivity in edible tissues of laying hens treated with 2.1 mg ai/kg dry feed.

Sample	Mean residue * mg/kg eq	extractable		not extractable				Total %
		hexane, chloroform, acidic MeOH		released by acid/base		released by enzyme or 6 M HCl		
		%	mg/kg eq	%	mg/kg eq	%	mg/kg eq	
Liver	1.2	14	0.16	3.7	0.043	99	1.2	116
Kidney	0.42	33	0.14	6.4	0.027	102	0.43	142
Muscle	0.010	28	0.003	a23 b53	0.008	1.5	0.000	105
Fat	0.069	97	0.067	na		36	0.024	133
Egg white (day 6)	0.016	12		a14 b95				121
Egg yolk (day 6)	0.30	h84 c11						95

* combined samples from the two groups of hens.
na: not applicable. a: acid hydrolysis b: base hydrolysis h: hexane-extractable c: chloroform-extractable



(Me: methyl; Et: ethyl; Pr: propyl, g: goat, h: hen).
Figure 1. Proposed metabolic pathways of ethoprophos in livestock.

The main route in livestock is incorporation into natural compounds. Metabolites mA, mJ, mN and mO were tentatively identified[1] and mP was inferred from end products.

Plant metabolism

The Meeting received information on the fate of ethoprophos after soil treatment before planting of pulses/oilseeds (French beans), cereals (maize), root and tuber vegetables (potatoes) and leafy crops (cabbage). The ethoprophos was ^{14}C-labelled in the ethyl or propyl group of the molecule.

Crop category: pulses/oilseeds

French beans (snap beans/green beans, Phaseolus vulgaris L.)

French bean bedding plants (variety Contender) were planted in a greenhouse (Maryland, USA, 1968) in clay pots, filled with steam-sterilized soil treated with [1-^{14}C-ethyl]ethoprophos or [1-^{14}C-propyl]ethoprophos (Menzer *et al.*, 1971; non-GLP). The radiochemical purity was not stated; the specific activity (undiluted) was 0.046 GBq/mmol (ethyl label) or 0.10 GBq/mmol (propyl label). Degradation of ethoprophos in steam-sterilized soil was slower than in unsterilized soil because the adsorptive capacity of the soil and the microbial activity was reduced. Hence a maximum amount of ethoprophos was available for uptake by the plants. Ethoprophos was applied as a GR formulation at 14.3 mg ai/kg soil (dosage in kg ai/ha not stated).

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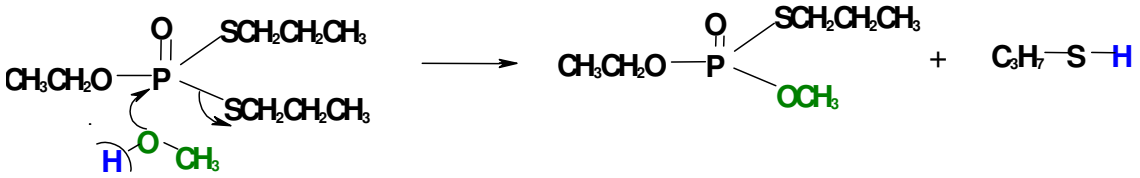
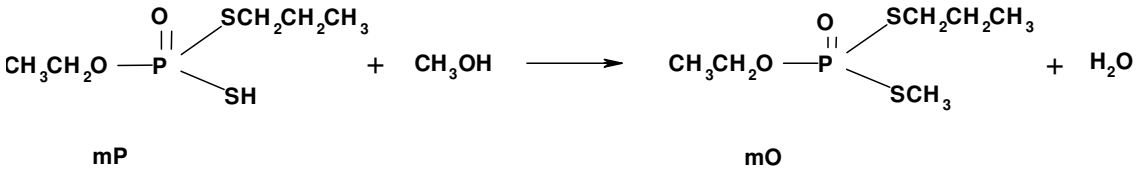
[1] **Formation of metabolites mN and mO**

Trace degradation products mN and mO may be artefacts formed during the extraction with MeOH (Barriere, 2004c). Formation of mN (*O*-ethyl *O*-methyl *S*-propyl phosphorothioate) may be explained by the fact that thiolophosphorous esters can be trans-esterified by alcohols in acidic medium or in the presence of catalysts according to the following reaction scheme:



The degradation product mO (*O*-ethyl *S*-methyl *S*-propyl phosphorodithioate) may be formed by esterification of degradation product mP (*O*-ethyl *S*-propyl phosphorodithioate) with MeOH according to the following reaction scheme:



Although most extractions were done with MeOH without addition of acid, the sample matrix can be acidic itself. Further experiments to confirm this hypothesis are not available.

French bean plants were grown for 63 days and sampled at weekly intervals from day 7 onwards. Storage conditions were not stated. Plant samples were homogenised and successively extracted with MeOH/water (1:1, v/v) and DCM (or vice versa). Extracts were combined and allowed to separate. Soil plus plant roots were homogenised and extracted with MeOH (Soxlet extraction for 16 h). Radioactivity in plant solids and solvent extracts was determined by combustion-LSC and LSC; the soil remaining after extraction was not analysed. Metabolites in the DCM extracts were characterized or identified by silica gel column chromatography with LSC detection, normal-phase TLC (four different solvent systems) with autoradiographic detection, GC-FPD with phosphorus and sulfur detection and IR spectrometry. Metabolites in the MeOH/water extracts were characterized or identified by anion exchange chromatography with identification by co-chromatography with the reference compounds parent, mA, mB, mC, mD, mE, mF, mG, mH, mI, mJ, mK and *S,S,S,S*-tetrapropyl tetrathiopyrophosphate, and dipropyl sulfide.

Results. The total recovered radioactivity in soil extracts and in plants is shown in Table 5. Residues in soil extracts decreased with time; bound residues in soil were not determined. Total residues in bean plants increased with time: 2.2-13% of TAR (ethyl label) and 0.58-8.3% of the TAR (propyl label) at days 7 to 63. Residue concentrations in mg/kg were not given. Extractable residues predominated at first but unextractable residues exceeded them later, >57% from day 21 onwards.

In the DCM extracts of bean plants the major compounds (Table 6) were the parent (maximum 13%) and mD (maximum 9.2%). The parent decreased with time and was less than 10% from day 28 onwards. Minor amounts of mC, mE(+mH), mF(+mI) were present at some sampling points. The identity of mE/mH and mF/mI could not be established with certainty because these metabolites could not be separated on silica gel or TLC. Because both spots were present in ethyl- and propyl-labelled plants, the spots are either mE+mH and mF+mI or the spots consist of mE and mF alone. Metabolite mK was not found, but according to the study authors is not stable and loses mB to form mL, which was found in the plants (not shown in Table 6). Although the presence of mG was suspected in some plant extracts, amounts were too small for confirmatory analyses.

In the MeOH extracts of soil, the major compound was the parent; in the MeOH/water extracts of bean plants the major compounds were mA and mJ (the data were not reported).

Table 5. Percentage recovery of total applied ^{14}C and distribution of radioactivity in extracts of soil and bean plants.

DAT	Percentage recovery in bean and soil						Distribution of radioactivity in bean plant extracts[3]					
	whole bean plant[1]		MeOH extracts of soil		Total recovered[2]		MeOH-water		DCM		Solids	
	Et	Pr	Et	Pr	Et	Pr	Et	Pr	Et	Pr	Et	Pr
	% of TAR						% of TRR					
7	2.2	0.58	111	89	113	89	27	31	54	29	19	40
21	4.2	2.2	73	76	77	78	13	23	23	20	64	57
28	…..	5.5	58	60	…..	65	lost	16	lost	9.2	---	75
35	9.0	6.1	62	57	71	63	7.6	8.4	17	11	76	81
42	9.0	5.9	53	61	62	67	2.6	3.2	18	19	79	78
49	11	8.1	45	39	56	47	10	6.7	23	9.8	67	84
56	14	8.3	37	32	51	40	6.8	3.9	13	11	80	85
63	13	8.3	24	26	36	34	12	6.3	15	10	73	84

DAT: days after treatment (bean bedding plants planted on day of treatment).
Et: ethyl label
Pr: propyl label.
[1] calculated by reviewer (sum of % residues recovered in MeOH/water, DCM and plant solids).
[2] calculated by reviewer (sum of % residues in soil extracts and whole plants (extracts + solids).
[3] calculated by reviewer from % residues recovered in extracts divided by % residues recovered in plants.

Table 6. Characterisation of radioactive compounds in DCM extracts of French bean plants.[1]

DAT	parent		mC		mD		mE(+mH)		mF(+mI)		unknown[2]		missing[3]	
	Et	Pr	Et	Pr	Et	Pr	Et	Pr	Et	Pr	Et	Pr	Et	Pr
	% of TRR													
7	8.3	13.4	na	ND	1.4	ND	ND	ND	ND	ND	4.2	3.9	40.4	12.0
21	8.8	12.3	na	ND	3.2	ND	1.3	0.9	ND	ND	5.0	3.1	4.4	3.3
28	lost	4.7	na	ND	lost	0.2	lost	ND	lost	0.5	lost	3.7	-	0.0
35	6.1	5.4	na	ND	2.6	ND	1.2	0.2	0.6	0.7	3.9	3.1	2.3	1.7
42	12.6[4]	10.4	na	ND	d	1.1	0.5	ND	4.2	ND	1.1	3.3	0.1	3.8
49	1.0	1.5	na	0.5	6.5	1.6	ND	ND	ND	ND	9.5	4.5	5.8	1.6
56	2.8	3.0	na	0.4	5.6	1.2[e]	ND	ND	ND	ND	2.4	4.1	2.2	2.0
63	3.1	3.8	na	0.2	9.2	1.2	ND	ND	0.9	ND	1.7	3.8	0.4	1.1

ND: not detected
DAT: days after treatment (bean bedding plants were planted on the day of treatment)
Et: ethyl label
Pr: propyl label
na: not applicable (mC does not contain the specified label)
[1] calculated by reviewer from % of compound in DCM extract times total % recovered in DCM extract (Table 5).
[2] eluted with MeOH from silica gel column; major compound with ethyl label was mJ (percentage not stated).
[3] calculated by reviewer from % recovered in DCM extract minus the sum of parent and metabolites.
[4] sum of parent and mD.
[5] sum of mD and mG.

In a related study, bean samples from the same experiment were extracted first by DCM then by MeOH/water (Menzer and Iqbal, 1968). The recovered radioactivity was about the same as described above. In the DCM extracts the parent and metabolites mC, mD and mE were identified together with unidentified compound and one unknown metabolite was found in the MeOH extract. In an addendum details of the metabolite identification were explained (Mobil, 1968a). In a second addendum the unknown compound in the DCM extract was identified as the parent and the unknown metabolite in the MeOH extract was identified as mJ (Mobil, 1968b).

In another related study French bean seedlings were planted in soil treated with 100 mg/kg ethoprophos, most likely un[l]abelled (Mobil, 1968a). When the plants were 2 weeks old, the shoots were harvested. Samples were homogenised with hexane and the filtrate was fractionated on a silica gel column using gradient elution with hexane/ether. Three ethoprophos related compounds were found in the fractions: 56 mg/kg mD, 72 mg/kg mC and 3000 mg/kg parent.

Crop category: cereals

Maize (corn, Zea mays L.), study 1

Maize seeds (variety not stated) were planted in a greenhouse (Menzer *et al*., 1971; Menzer and Iqbal, 1968, non-GLP). Experimental methods as in the French bean study (see above). Maize plants were grown for 100 days and sampled at 10-day intervals from day 18 onwards.

Results. The total recovered radioactivity in plant and soil extracts is shown in Table 7. Residues in soil extracts were broadly constant; bound residues in soil were not determined. The total recovered residues exceeded 100% for the ethyl label from day 58 onwards. According to the study authors this could be partially explained by the difficulty of obtaining a homogeneous sample for analysis and the large volume of pulp resulting after extraction of the maize plants, whilt the recovery of the propyl label was generally lower because of the probable release of the extremely volatile propyl-labelled mB.

Residues in maize plants increased with time (Table 7): 0.96-74% of TAR (ethyl label) and 0.26-35%% of TAR (propyl label) at days 18 to 100. Residue concentrations in mg/kg were not given.

Residues were mainly extracted at the early time-points but mainly unextractable later: >67% from day 28 onwards.

In the DCM extracts of maize plants the major compounds (Table 8) were the parent (maximum 40% of the TRR) and mD (maximum 7.6% of the TRR). The parent decreased with time and was less than 10% from day 48 onwards. Minor amounts of mC, mE(+mH) and mF(+mI) were present at some sampling periods; the unknown residues from the ethyl label were mainly mJ (percentage not given). Metabolite mK was not found, but is apparently not stable and loses mB to form mL, which was found (not shown in Table 8). Although the presence of mG was suspected in some plant extracts, amounts were too small for confirmatory analyses.

In the MeOH extracts of the soil, the major compound was the parent; in the MeOH/water extracts of maize plants the major compounds were mA and mJ (the data were not reported).

Table 7. Percentage recovery of total applied ^{14}C and distribution of radioactivity in extracts of soil and maize plants.

DAT	% recovery in maize plants and soil						Distribution of radioactivity in maize plant extracts[3]					
	whole maize plants[1]		MeOH extracts of soil		Total recovered[2]		MeOH-water		DCM		solids	
	Et	Pr	Et	Pr	Et	Pr	Et	Pr	Et	Pr	Et	Pr
	% of TAR						% of TRR					
18	0.96	0.26	65	44	66	45	46	31	48	42	6.3	27
28	2.4	1.6	75	55	77	57	7.5	42	38	53	55	5.0
38	8.4	2.0	59	43	67	45	3.5	9.9	11	23	85	67
48	5.6	2.9	90	41	96	44	---	9.0	22	17	78	74
58	11	8.3	109	59	120	67	3.0	2.1	21	5.3	76	93
68	21	10	104	49	125	59	6.3	5.3	12	5.8	82	89
78	41	12	64	46	106	57	2.2	1.5	4.2	3.9	94	95
88	59	29	70	37	129	66	0.8	1.4	2.6	1.4	97	97
100	74	34	49	27	123	62	1.5	1.1	2.1	1.2	96	98

DAT: days after treatment (maize seeds were planted on the day of treatment).
Et: ethyl label
Pr : propyl label.
[1] calculated by the reviewer (sum of % residues recovered in MeOH/water, DCM and plant solids).
[2] calculated by the reviewer (sum of % residues in soil extracts and whole plants (extracts + solids).
[3] calculated by the reviewer from given % residues recovered in extracts divided by % residues recovered in plants.

Table 8. Characterisation of radioactive compounds in DCM extracts of maize plants.[1]

DAT	parent		mC		mD		mE(+mH)		mF(+mI)		unknown[2]		missing[3]	
	Et	Pr	Et	Pr	Et	Pr	Et	Pr	Et	Pr	Et	Pr	Et	Pr
	% of TRR													
18	39.7	13.4	na	ND	1.4	ND	ND	ND	ND	ND	5.3	28.9	1.1	0
28	27.8	41.2	na	1.0	2.8	0.9	ND	2.4	ND	ND	6.1	7.4	1.1	0
38	3.1	18.9	na	ND	3.8	ND	0.3	ND	ND	ND	3.7	4.4	0.6	0
48	9.6	9.6	na	ND	1.9	0.8[4]	0.4	2.8	ND	ND	9.7	3.7	0.4	0
58	4.0	3.3	na	ND	7.6	ND	ND	ND	1.6	ND	7.6	2.0	0	0
68	4.3	3.1	na	ND	2.1	0.2	ND	ND	ND	ND	5.5	2.5	0	0
78	0.9	1.9	na	ND	1.3	0.0	ND	ND	0.8	0.4	1.1	1.6	0	0
88	0.5	0.3	na	0.1	0.9	0.1	ND	ND	0.2	ND	1.0	0.9	0	0
100	1.2	0.3	na	0.1	0.1	0.3[4]	ND	ND	0.3	0.1	0.5	0.4	0	0

ND: not detected;
DAT: days after treatment (maize seeds planted on day of treatment).
Et: ethyl label
Pr: propyl label
na: not applicable (mC does not contain specified label).
[1] calculated by reviewer from % of compound in DCM extract times total % recovered in DCM extract.

[2] eluted with MeOH from silica gel column; major compound in ethyl-label was mJ (percentage not stated).
[3] calculated by reviewer from % recovered in DCM extract (from Table 7) minus sum of parent and metabolites.
[4] sum of mD and mG.

In a related study, maize samples from the same experiment were extracted first by DCM then by MeOH/water (Menzer and Iqbal, 1968). The same compounds were found as in the corresonding study with French beans (see above for details).

Maize, study 2

Silt loam (pH 5.6, 3.7% om, CEC 21 meq/100g, 7% clay particles was treated with [1-ethyl-^{14}C]ethoprophos (EC formulation; radiochemical purity 98.6%; specific activity after dilution 0.070 GBq/mmol) at a rate of 13 kg ai/ha in plastic-lined wooden boxes in a field in Kentucky, USA (Johnson, 1991a, GLP). The actual concentration in the soil was 10 mg ai/kg. The application mixture was incorporated to a depth of 10 cm. Sweet corn seeds (variety Early extra sweet) were planted 3 days after soil treatment and sampled at the green forage stage (soil, whole plant), at maturity (shanks, husks, silks, grain, empty cobs) and at the fodder stage (soil, senescent stalks without cobs). Plant and soil samples were stored frozen at – 20ºC (storage time not stated). Plant samples were successively extracted with MeOH/water, MeOH and DCM. The remaining solids were extracted first with 0.1 M HCl and then with 0.1 M NaOH. ^{14}C in plants and solvent extracts was determined by (combustion)-LSC. The LOQ was 0.05 mg/kg eq in maize and 0.01 mg/kg eq in solvent extracts. Metabolites in MeOH/water and DCM extracts were identified or characterized by reverse-phase HPLC (one solvent system; detection by UV (220, 230 nm) or beta radioactivity or LSC of collected fractions). The extracts were also subjected to normal-phase TLC-autoradiography (solvent system I for DCM extracts and solvent system II for MeOH/water extracts). Reference compounds used in TLC and HPLC were the parent, mA, mJ, mN and mO.

Results: The total [^{14}C]ethoprophos residue in plants and soil and the distribution of the ^{14}C residue in plants in the various extraction solvents is shown in Table 9. The distribution of metabolites in the MeOH/water and DCM extracts is shown in Table 10.

The total radioactive residue in the samples was very low: in corn forage a TRR of 2.2 mg/kg was detected, in corn cobs 0.27 mg/kg, in grain 0.25 mg/kg, husks 0.79 mg/kg and fodder 1.4 mg/kg. Most of the TRR was solvent-extractable in all samples. Acid or base hydrolysis released a further 6%-14% of the TRR in the forage, grain, cobs and fodder, but in forage 13% and in grain, cobs and fodder more than 40% of the TRR was still bound. During extraction and characterisation 5%-26% of the radioactivity was lost, for which the study author does not give an explanation.

Ethyl phosphate (mJ) was the major metabolite detected in all three plant parts (10%, 35% and 8.9%). The parent ethoprophos and *O*-ethyl *S*-propyl phosphorothioate (mA) were also present in small amounts in forage and fodder. The extracts of forage and fodder also contained small amounts of unidentified components (<6% each). Several of these unidentified components were less polar than ethoprophos.

Conclusions. The proposed metabolic pathways indicate that the primary degradation proceeds from parent ethoprophos to ethyl phosphate through hydrolysis of the two thiopropyl esters. Ethyl phosphate was the predominant metabolite (8.9%-35%). The parent, metabolites mA, mN, mO and several unidentified metabolites were found at minor quantities (<10%).

Table 9. Total-^{14}C residue in maize and soil and distribution of radioactivity (% of the TRR) in maize extracts.

Sample	DAT	Total ^{14}C (mg/kg eq)	Extractable residues, %			Unextractable residues, %			Missing[1]
			MeOH-water	MeOH	DCM	0.1 M HCl	0.1 M NaOH	Solids	
green forage	27	2.2[2]	52	6.2	2.6	3.2	11	13	11%

Sample	DAT	Total ^{14}C (mg/kg eq)	Extractable residues, %			Unextractable residues, %			Missing[1]
			MeOH-water	MeOH	DCM	0.1 M HCl	0.1 M NaOH	Solids	
husks, shanks, silks	69	0.79							
mature grain	69	0.25	26	3.9	9.2	1.8	9.7	44	5.1%
empty cobs	69	0.27	34	12	ND	1.2	7.8	60	none
fodder (stalks)	94	1.4	9.8	14	3.1	1.1	5.1	41	26%
soil	27	4.1 (5.0)[3]							
soil	94	2.1 (2.7)[3]							

DAT: days after treatment (corn planted at DAT 3)
ND: not detected.
[1] calculated by reviewer from 100% minus sum of extractable and unextractable residues (Table 8).
[2] study text and Table 2 say 18 mg/kg, figure in the study summary and appendix 2.02 mg/kg.
[3] mg/kg dry weight

Table 10. Characterisation of radioactive compounds in MeOH, MeOH/water and DCM extracts of maize (% total recovered radioactivity and mg/kg ethoprophos equivalents) at DAT 27 (green forage), 69 (mature grain), 94 (fodder).

Sample	parent		mA		mJ		mN (f)		mO (f)		unknown		total	missing (c)
	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	%
green forage	7.8	0.17	2.3	0.05	10	0.23	0.8	0.02	0.3	0.01	20a	0.42	41	20
mature grain	ND	ND	ND	ND	35	0.09	ND	ND	ND	ND	ND	ND	35	4.6
fodder	0.5	0.01	0.8	0.01	8.9	0.13	1.8	0.03	1.1	0.02d	3.1b	0.06e	16	10

ND: not detected.
a represents at least 9 separate components, each less than 5.5%.
b represents at least 6 separate components, each less than 0.8%.
c calculated by the reviewer:
% total: sum of % metabolites + % parent (Table 9)
% missing: sum of % extractable residues (Table 9) minus % total (Table 10).
d in the study table 0.02 mg/kg; in the study summary 0.01 mg/kg.
e in the study table the summation is 0.06 mg/kg; in the study summary 0.04 mg/kg.
f reference compounds mN and mO could be detected by HPLC but mN could not be detected by TLC solvent system II and retention times for mN and mO in TLC solvent system I were the same. According to the study author confirmation of the identity of extractable components by TLC was marginal owing to sample interferences. Raw TLC data were not reported. Further confirmatory analysis is therefore desirable.

Crop category: root and tuber vegetables

Potatoes, study 1

Silt loam (pH 5.6, 3.7% om, CEC 21 meq/100g, 7% clay particles) was treated with [1-ethyl-^{14}C]ethoprophos (EC formulation; radiochemical purity 98.6%; specific activity after dilution 0.070 GBq/mmol) at a rate of 13 kg ai/ha in plastic-lined, wooden boxes in a field in Kentucky, USA (Johnson, 1991b, GLP). The actual concentration in the soil was 15 mg ai/kg. The application mixture was incorporated to a depth of 10 cm. Potatoes (variety Kenebeck) were planted 3 days after soil treatment. Soil and plants were sampled at the “new potato” stage and at maturity. Potato tubers, vines and soil samples were stored frozen at –20ºC (storage time not stated). Potato tubers were subdivided into three groups: a) soil removed with dry cloth, b) soil removed by thorough washing; c) tubers washed and peeled, and pulp and peel analysed separately. Tubers from group b and vines were successively extracted with MeOH/water, MeOH and DCM. The remaining potato sample was extracted first with 0.1 M HCl and then with 0.1 M NaOH. ^{14}C in potato and solvent extracts was determined by (combustion) LSC. The LOQ was 0.012 mg/kg eq in potato vines and tubers and 0.01 mg/kg eq in solvent extracts. Metabolites in MeOH/water and DCM extracts were identified or characterized by reversed-phase HPLC (one solvent system; UV at 220, 230 nm or beta radioactivity or LSC of collected fractions). The extracts were also subjected to normal-phase TLC with

autoradiography (solvent system I for DCM extracts and solvent system II for MeOH/water extracts). Reference compounds used in TLC and HPLC were the parent, mA, mJ, mN and mO.

Results: The total ^{14}C residue in potatoes and soil and the distribution in the analytical fractons are shown in Tables 11 and 12. The compoundsd identified in the MeOH/water and DCM extracts are shown in Table 13.

Total radioactive residues were 0.24-0.54 mg/kg eq in tubers and 1.1-3.8 mg/kg eq in vines. Most of the TRR was extracted with aqueous MeOH. Acid and base hydrolysis solubilized a further 17% of the radioactivity in the vines, while 31% of the TRR and 23% of the TRR remained fibre-bound in vines and tubers respectively.

Analysis of aqueous and organic extracts of the vines and tubers showed that the most abundant radioactive component in both was mJ (ethyl phosphate 12% and 38% respectively). Parent ethoprophos and mA (*O*-ethyl *S*-propyl phosphorothioate) were also present in small amounts in the vines but were not detected in tubers. Several unidentified radiolabelled compounds were detected (<3% each). Most of these were less polar than the parent compound.

Conclusion. The primary degradation proceeds from ethoprophos to ethyl phosphate (mJ) through loss of the two S-propyl groups, as in maize. Ethyl phosphate was the predominant metabolite in potato tubers (38%). The parent was not found in the tubers, while unidentified metabolites were found in minor quantities (<10%).

Table 11. Total ^{14}C residue in potatoes and soil (expressed as mg/kg ethoprophos).

DAT	growth stage	Vines	Tubers-A	Tubers-B	Tubers-C (pulp)	Tubers-C (peel)	Soil
62	immature	1.1	0.24	0.26	0.24	0.40	2.4
93	mature	3.8	0.33	0.54	0.35	0.51	2.2

DAT: days after treatment (potato tubers were planted at DAT 3)
Tubers-A: soil removed with dry cloth.
Tubers-B: soil removed by thorough washing.
Tubers-C: washed and peeled, pulp and peel were analysed separately.

Table 12. Total ^{14}C residue (expressed as mg/kg ethoprophos) in potato tubers and vines and distribution of radioactivity (% of the TRR) in extracts of potato tubers and vines.

Sample	DAT	Total ^{14}C	Extractable residues, %			Unextractable residues, %			Missing [1]
		mg/kg eq	MeOH-water	MeOH	DCM	0.1 M HCl	0.1 M NaOH	solids	
Vines	62	1.1	29	12	2.6	2.9	14	31	8.5%
Tubers-B	93	0.54	43	12	0.5	0.0	0.0 [2]	23	22%

DAT: days after treatment (potato tubers planted at DAT 3).
tubers-B: soil removed by thorough washing.
[1] calculated by reviewer from 100% minus sum of extractable and unextractable residues.
[2] base hydrolysis produced a thick gel of semi-solubilised starch; this activity was classified as solids.

Table 13. Characterisation of radioactive compounds in MeOH/water and DCM extracts of potato tubers and vines.

Sample	parent		mA		mJ		mN [1]		unknown		total	missing [4]
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	% of TRR
Vines	2.7	0.03	1.5	0.02	12	0.14	1.0	0.01	13[2]	0.14	31	13
Tubers-B	ND	ND	ND	ND	38	0.21	ND	ND	1.2[3]	0.01	39	17

ND: not detected; Tubers-B: soil removed by thorough washing.
[1] mN was only detected by HPLC, not by TLC, so identity uncertain.

[2] represents at least 9 separate components, each less than 3%.
[3] represents at least 3 separate components, each less than 0.6%.
[4] calculated by reviewer: % total: sum of % metabolites + % parent (Table 13);
% missing: sum of % extractable residues (Table 12) minus % total (Table 13).

Potatoes, study 2

This supporting study was conducted to determine the nature of the bound residues in potatoes (O'Neal and Johnson, 1995, GLP). Soil was treated with [1-ethyl-^{14}C]ethoprophos (EC formulation; radiochemical purity 97%; specific activity after dilution 1.84 mCi/mmol) at a dose rate of 13 kg ai/ha in plastic-lined, wooden boxes in a field in Kentucky, USA (1995). The application mixture was incorporated to a depth of 10 cm. The soil was sandy loam (pH 7.0, 2.8% om, CEC 5.8 meq/100g, 8.3% clay particles). The actual concentration in the soil was 5.9 mg ai/kg. Potatoes (minituber variety Kennebec) were planted 3 days after soil treatment and harvested 118 days after treatment (new potato tubers) and 167 days after treatment (mature potatoes). Potato tubers, vines and soil samples were stored frozen at –20ºC (storage time not stated). New potato tubers were extracted with MeOH/water, MeOH and DCM. The total radioactive residue was determined by (combustion) LSC. The LOQ was 0.01 mg/kg eq in potato vines, tubers and solvent extracts. A separate extraction was carried out for characterization of the unextractable residues. New potato tubers were subjected to a sequential extraction scheme using 0.05 M phosphate buffer for isolation of extractable residues (DCM had extracted very little residue), beta-amylase for starch digestion (20 h, 30ºC, pH 7), pronase E (20 h, 25ºC, pH 7.2) for protein digestion, 50 mM EDTA/acetate (pH 4.6, 6 h, 80ºC) for pectin extraction, acetic acid/sodium chlorite (1 h, 70ºC) for lignin extraction, KOH (24 h, 27ºC) plus acetic acid (1 h, ambient) for hemicellulose extraction, sulfuric acid (4 h, ambient) neutralized with KOH to pH 7 for cellulose hydrolysis. The starch isolated from potato tubers by amylase digestion was analysed using reversed and normal-phase radio-HPLC to show whether ^{14}C-labelled glucose was present.

Results: The total ^{14}C residue in potatoes is shown in Table 14. The total radioactive residue was 0.51 mg/kg in new potato tubers harvested 118 days after treatment. This result correlates closely with the TRR determined in the first metabolism study with potatoes (0.54 mg/kg at 90 DAT). The extractability of the TRR was the same as reported in the previous metabolism study: 37% of the TRR was extracted with MeOH/water (80/20), 7% of the TRR with MeOH and a further 1% with DCM. The distribution of the bound radioactive residue in the cell wall fractions is given in Table 15. Normal and reversed-phase radio-HPLC showed the presence of [^{14}C]glucose in the combined phosphate buffer - amylase extract of the starch (47% of the extract).

Conclusion: Supplementary characterisation and fractionation demonstrated that most of the fibre-bound ^{14}C was incorporated into plant structural components. The fibre-bound radioactive residue associated with starch was identified as [^{14}C]glucose.

Table 14. Total ^{14}C residue in potatoes (expressed as mg/kg ethoprophos).

DAT	Growth stage	Vines	Tubers
118	new potato	na	0.51
167	mature potato	2.2	0.97

DAT: days after treatment (potato tubers were planted at DAT 3)

Table 15. Distribution of the fibre-bound residue in potato tubers (as % of the TRR).

TRR mg/kg eq	Phosphate buffer extract	Starch	Protein	Pectin	Lignin	Hemicellulose	Cellulose	Remaining solids	Missing
0.51	41	11	8.5	4.4	3.7	8.2	8.8	6.9	7.8

Crop category: leafy crops

Cabbage

Silt loam (pH 5.6, 3.7% om, CEC 21 meq/100g, 7% clay particles was treated with [1-ethyl-^{14}C]ethoprophos (EC formulation; radiochemical purity 98.5%; specific activity after dilution 0.067 GBq/mmol) at a rate of 11 kg ai/ha in plastic-lined, wooden boxes in a field in Kentucky, USA (Johnson, 1990, GLP). The actual concentration in the soil was 7.6 mg ai/kg. The application mixture was incorporated to a depth of 7.6 cm. Cabbage bedding plants (variety Stonehead) were planted 2 days after soil treatment. Soil and plants were sampled at the leafy stage and at maturity, and stored at –20ºC (storage time not stated). Cabbage was successively extracted with MeOH/water, MeOH and DCM. The remaining solid was extracted first with 0.1 M HCl (30 min) and then with 0.1 M NaOH (30 min). ^{14}C in cabbage and solvent extracts was determined by combustion-LSC and LSC respectively. The LOQ was 0.05 mg/kg eq in cabbage and 0.01 mg/kg eq in solvent extracts. Metabolites in MeOH/water and DCM extracts were identified or characterized by normal-phase TLC with autoradiography (solvent system I for DCM extracts and solvent system II for aqueous extracts). Radioactive bands were scraped from the plates and further analysed by reverse-phase HPLC (one solvent system; detection by UV at 230 nm) or beta radioactivity or LSC of collected fractions). Reference compounds used in TLC and HPLC were the parent, mA, mJ, mN and mO.

Results: The total ^{14}C residue in cabbage and its distribution in the various extraction solvents are shown in Table 16. The compounds identified in the MeOH/water and DCM extracts are shown in Table 17.

The total radioactive residue in leafy cabbage was 15.6 mg/kg eq and in heads 3.1 mg/kg eq. Most of the TRR was extracted with aqueous MeOH. Part of the fibre-bound residue was solubilized by either acid or base hydrolysis; 11% of the TRR or less remained fibre-bound. Ethyl phosphate (mJ) was the major metabolite found in both leafy and head cabbage (21 and 24% respectively). Ethoprophos and mA were also present in small amounts in both. The MeOH/water extracts of immature cabbage also contained significant amounts of three unidentified components (9.3%, 7.6%, 6.4%). These components were present in reduced amounts in mature cabbage heads (4.5%, 0.4%, 1.0%). One of these unidentified components showed relatively polar chromatographic behaviour and accounted for about 9.3% of the TRR in leafy cabbage.

Conclusions: The metabolism in cabbage is essentially the same as in maize and potatoes. The parent, mA, mN and mO and unidentified metabolites were found in minor quantities (<10%).

Table 16. Total-^{14}C residue in cabbage and soil and distribution of radioactivity in extracts of cabbage (% of the TRR).

Sample	DAT	Total ^{14}C mg/kg eq	Extractable residues			Unextractable residues			Missing[1]
			MeOH-water	MeOH	DCM	0.1 M HCl	0.1 M NaOH	solids	
Leaves + heads	33	16	65%	6.8%	3.8%	4.5%	8.6%	11%	1.4%
Mature heads	87	3.1	57%	8.1%	1.2%	3.4%	13%	5.6%	12%
Wrapper leaves	87	8.8							
Soil	33	5.0							
Soil	87	3.3							

DAT: days after treatment (cabbage planted at DAT 2).
[1] calculated by reviewer from 100% minus sum of extractable and unextractable residues.

Table 17. Characterisation of radioactive compounds in MeOH, MeOH/water and DCM extracts of cabbage (expressed as % total recovered radioactivity and mg/kg ethoprophos equivalents) at DAT 33 (immature), 87 (mature).

Sample	parent		mA		mJ		mN[1]		mO[1]		unknown		total	missing [2]
	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	%
Immature leaves + heads	4.0	0.60	2.5	0.5	21	3.3	1.7	0.3[4]	0.6	0.09[4]	26[3]	4.4	55	20
Mature heads	0.8	0.03	0.3	<0.03	24	0.7	1.7	0.05[4]	0.4	0.01[4]	9.6[3]	0.4	37	30

ND: not detected.
[1] only detected by HPLC, not confirmed by TLC, so identity is not certain.
[2] calculated by reviewer % total: sum of % metabolites + % parent;
% missing: sum of % extractable residues (Table 16) minus % total (Table 17).
[3] represents at least 6 separate components; 3 components were less than 1.6%; the other components were 9.3%-7.6%-6.4% in immature leaves/heads and 4.5%, 0.4% and 1.0% in mature heads.
[4] calculated by reviewer from % mN or % mO times 15.6 mg/kg (immature) or 3.1 mg/kg (mature).

Further characterisation of the unextractable and hydrolysable residues is described in an addendum (Wootton and Johnson, 1991). Mature cabbage head from the previous study was successively extracted with DCM and 0.05 M potassium phosphate buffer (pH 7.0) to remove extractable residues. The unextractable residues were subjected to a sequential extraction scheme using beta-amylase for starch digestion (20 h, 30ºC), pronase E (16 h, 30ºC) for protein digestion, 50 mM EDTA/acetate (pH 4.5, 6hr, 80ºC) for pectin extraction, acetic acid/sodium chlorite (4 h, 70ºC) for lignin extraction, KOH (24 h, 27ºC) plus acetic acid (1hr, ambient) for hemicellulose extraction, sulfuric acid (4 h, ambient) and KOH (pH 6.5-7.5) for cellulose hydrolysis.

Results: ^{14}C distribution in the various extracts is shown in Table 18. The extractable residue in the phosphate buffer (34%) was lower than in MeOH/water + MeOH (65%, see previous study). Most of the unextractable ^{14}C in cabbage was incorporated into lignin. According to the study authors, *O*-dealkylation of organophosphate pesticides esters in plants is not uncommon. The subsequent utilisation by a plant of the liberated ethanol as a carbon source is a normal physiological response.

Conclusion: Supplementary characterisation and fractionation demonstrated that most of the fibre-bound residues in cabbage were incorporated into plant structural components, but mainly into lignin.

Table 18. Total ^{14}C residue in cabbage and distribution of radioactivity in extracts of cabbage head (% of the TRR).

Sample	DAT	^{14}C total mg/kg eq	Extractable		Unextractable residues						
			DCM	phosphate buffer	starch	protein	pectin	lignin	hemi-cellulose	cellulose	solids
Mature heads	87	2.7	4.4%	34%	4.9%	5.9%	3.7%	38%	5.5%	8.5%	0.2%

DAT: days after treatment (cabbage planted at DAT 2).

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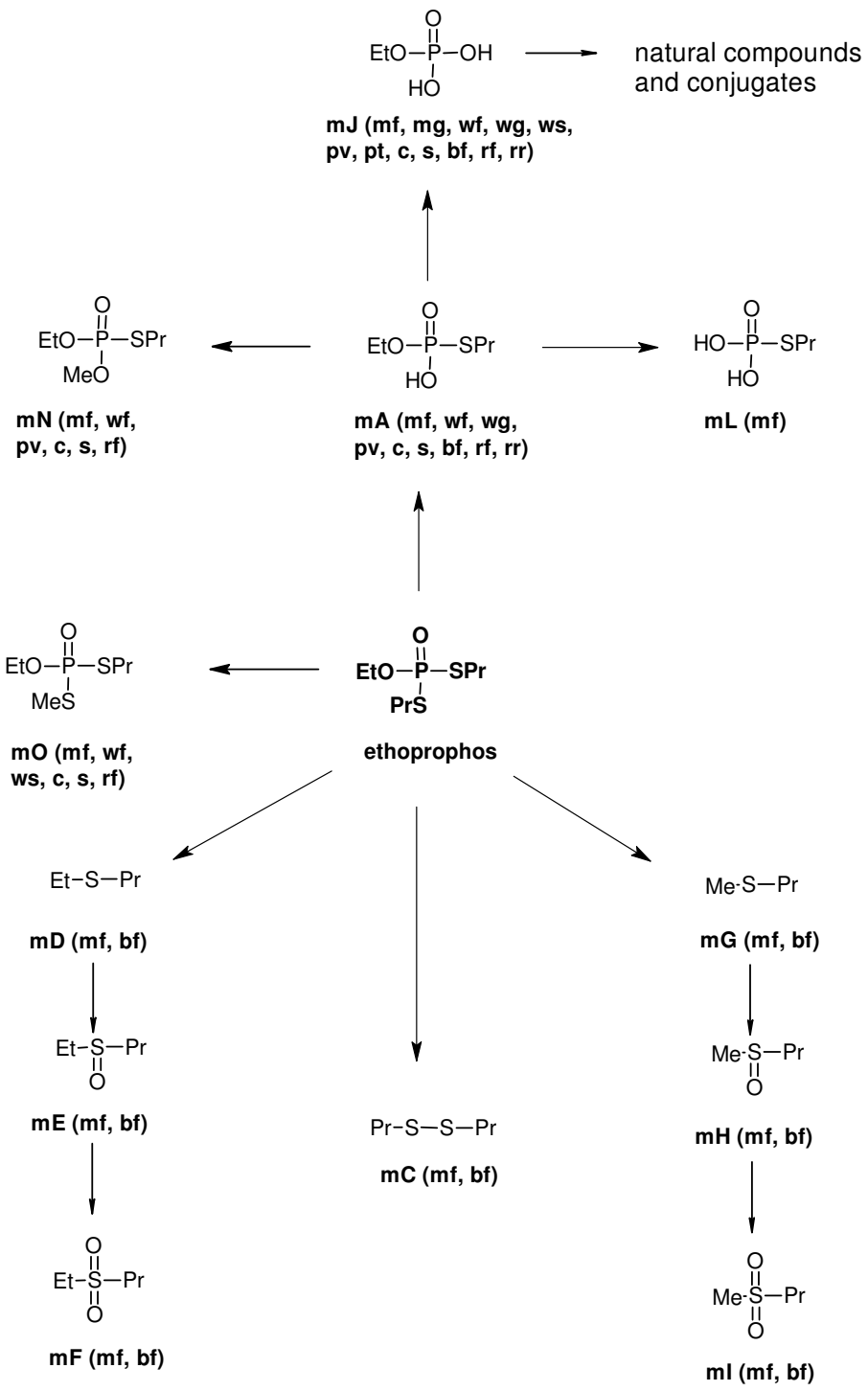

Figure 2 Proposed metabolic pathways of ethoprophos in plants (Me=methyl; Et=ethyl; Pr=propyl, mf=maize forage, mg= maize grain, wf=wheat forage, wg=wheat grain, ws=wheat straw, pv= potato vines, pt= potato tubers, c=cabbage, s=spinach, bf=bean forage, rf=radish forage, rr=radish roots). The major route in plants is ethoprophos – mA - mJ. Metabolites mG, mH, mI, mL, mN and mO were tentatively identified See also footnote to Figure 1.

Environmental fate in soil

The Meeting received information on aerobic degradation in soil and studies on rotational crops (confined and field). Information on anaerobic degradation in soil, photodegradation in or on soil, adsorption-desorption in or on soil, soil leaching, and field dissipation was submitted but was not relevant for this evaluation and was therefore not evaluated.

Degradation in soil under aerobic conditions

Study 1

The route and rate of degradation of propyl-labelled ethoprophos was investigated in a sandy clay loam (SCL) and a sandy loam (SL) under aerobic conditions in the dark at 10 ± 1.5°C and 22 ± 2°C (Greenslade *et al.*, 1984, non-GLP). The specific activity (undiluted) was 22.2 mCi/mmol and radiochemical purity 99.6%. The soils were adjusted to 50% of their maximum water holding capacity (62% and 70% field capacity for SCL and SL respectively). The incubation flasks, containing 100 g fresh soil each, were linked in parallel to a common glass manifold and air was drawn through this system to collect $^{14}CO_2$ in NaOH and other volatile products in a Tenax 15 tube. Based on an application rate of 10.5 kg/ha in the field, the test substance was applied at a nominal concentration of 14 mg ai/kg dw soil. The soils characteristics are summarised in Table 20. Duplicate samples were taken after 0, 1, 3, 7, 14, 27, 41, 60 and 90 days of incubation at 22°C and 0, 1, 3, 7, 14, 27, 41, 70 and 110 days at 10°C. After extraction at ambient temperature with MeOH, diethyl ether, hexane and 0.1N ammonia solution, the MeOH and selected ether extracts was analysed by normal-phase TLC with detection by autoradiography followed by LSC. Reference standards chromatographed with the extracts were the parent, mC, mD, mE and mF. The concentration of ethoprophos was also determined by GC-FPD method 5.

Degradation at 22°C. Overall recoveries of the applied radioactivity at each sampling were similar for both soils at 98%-103% at days 0-3 and 86%-90% at days 14-90. The radiolabelled material applied was almost completely extractable with MeOH, diethyl ether, hexane and ammonia on day 0 (100% and 102% of the TAR for SCL and SL respectively), but only 18% and 14% were extractable on day 90. At day 90, 56% and 60% of the TAR were mineralised as carbon dioxide. Other volatile radioactivity was not detected in the study (<0.007% of the TAR). The unextractable radioactivity amounted to 11% and 14% of the TAR at day 90 and was associated with humic acid, fulvic acid and humin fractions (0.5%-7.9% of the TAR each).

In MeOH and diethyl ether extracts of both soils, most of the radioactivity was associated with unchanged ethoprophos and accounted to 90%/94% (day 0) and 9.0%/7.2% (day 90), see Table 19. Radioactivity associated with polar products retained at the origin of the TLC plates could not be identified but was only in the range of 0.6%-1.5% / 0.5%-1.1% of the TAR. Trace products (0.1%-0.5% of the TAR) corresponding to R_F values of mE and mF were detected. Some very minor less polar products were found, the sum of which accounted for 0.3%-2.1% and 0.2%-1.2% of the TAR.

Degradation at 10°C. The radiolabelled material applied was almost completely extractable by MeOH on day 0 (93% of the TAR for both SCL and SL), while 20% of the TAR was MeOH-extractable at day 110. Contents in other extracts were not reported. At day 110, 50% and 43% of the TAR were found as ^{14}C-carbon dioxide. Other volatile radioactivity was not monitored. Concentrations of ethoprophos fell from 12 and 13 mg/kg (day 0) to 2.1 and 1.8 mg/kg at day 110 (Table 19). Results as % of the TAR were not reported.

Rate of degradation. **The soil moisture content was in line with the level which is generally considered adequate for assessment of degradation rate (40% of the maximum water holding**

capacity or 75% of field capacity is equivalent to ca. pF 3 for the soil types under investigation). Semi-log plots of ethoprop concentrations versus time demonstrated that the degradation was first order. Calculated DT_{50} and DT_{90} values are shown in Table 20.

Conclusion: The main degradation product in soil under aerobic conditions at 10°C and 22°C was $^{14}CO_2$ which accounted for 56%-60% of the TAR (90 days, 22°C) or 43%-50% of the TAR (110 days, 10°C). No other major product could be identified. Most of the radioactivity in the extracts was due to unchanged ethoprophos 90%-94% (day 0, 22°C) and 7.2%-9.0% (day 90, 22°C). The half-life at 22°C was 24-25 days and nearly twice as long at 10°C.

Table 19. Degradation of ethoprophos in soils (% of the TAR and mg/kg dw soil).

Days	sandy clay loam (22°C)		sandy loam (22°C)		sandy clay loam (10°C)		sandy loam (10°C)	
	% of TAR	mg/kg eq[1]	% of TAR	mg/kg eq[1]	% of TAR	mg eq/kg[1]	% of TAR	mg/kg eq[1]
0	90	14	94	14	-	12	-	13
1	90	14	95	15	-	13	-	12
3	82	13	89	14	-	11	-	9.7
7	72	12	77	12	-	11	-	7.3
14	58	8.4	59	9.2	-	8.8	-	8.0
27	38	5.7	40	6.4	-	8.2	-	7.0
41	29	4.3	26	4.1	-	6.7	-	7.0
60	18	2.6	14	2.4	-	-	-	-
70	-	-	-	-	-	4.0	-	4.0
90	9.0	1.2	7.2	1.2	-	-	-	-
110	-	-	-	-	-	2.1	-	1.8

- not sampled or not reported.
[1] determined by GC-NPD method 2.

Table 20. Soil characteristics and degradation times of ethoprophos.

Soil	Temp. (°C)	om (%)	pH (water)	CEC (meq/ 100 g dw soil)	Clay (%)	Moisture pF[1]	DT_{50} (days)	DT_{90} (days)
Sandy clay loam	22	3.2	5.7	19.6	28	3.0	25	82
Sandy loam	22	6.4	7.0	25.1	16	3.0	24	80
Sandy clay loam	10	3.2	5.7	19.6	28	3.0	43	144
Sandy loam	10	6.4	7.0	25.1	16	3.0	42	139

[1] pF values estimated by reviewer, based on pF-curves of representative soils

Study 2
The route and rate of degradation of ethyl-labelled ethoprophos was investigated in a loamy sand soil under aerobic conditions in the dark at 25°C and 80% of the field capacity (1/3 bar moisture) equivalent to a moisture content of 6.1% (Jordan *et al.*, 1986, non-GLP). The specific activity was 3.32 mCi/mmol; the radiochemical purity was >99%. The incubation flasks, containing 50 g fresh soil each, were linked in parallel to a common glass manifold and air was drawn through to collect to collect volatile metabolites in tubes containing XAD-4 resin and active charcoal and $^{14}CO_2$ in a 0.1 M NaOH trap. The test substance was applied at a concentration of 11.9 mg/kg soil. The soil characteristics are summarised in Table 21. Duplicate samples were taken after 0, 1, 3, 7, 14, 28, 56, 84, 112, 168 and 252 days of incubation. After extraction at ambient temperature with MeOH, diethyl ether and ammonium carbonate solution (2%), the combined MeOH and ether extracts were analysed by normal-phase TLC (four different solvent systems) with detection by autoradiography followed by LSC. Reference standards chromatographed with the extracts were parent, mA, mN and mO. Extracts from day 3 and day 112 were also analysed by GC-FPD. Unextractable residues were refluxed with 2% HCl - MeOH for 2 h and extracted with ethyl acetate for TLC analysis.

Table 21. Characteristics of soil.

Texture	Loamy sand
% Clay	7.6
pH	5.3
% om	1.7
CEC (meq/100 g soil)	5.9
% Field capacity (moisture content at 1/3 bar)	7.72

Results: Overall recoveries of the applied radioactivity at each sampling were in a range of 94% to 101% . The radiolabelled material applied was completely extractable with MeOH, diethyl ether and ammonium carbonate on day 0 (100% of the TAR), while 29% of the TAR were extractable on day 252. On day 252, 54% of the TAR was found as $^{14}CO_2$, while other volatile components accounted for up to 2.5% of the TAR. The unextractable radioactivity amounted to 10% of the TAR.

In combined MeOH and ether extracts, most of the radioactivity was associated with unchanged ethoprophos and accounted for 97%-99% of the TAR on day 0 and 24%-25% of the TAR on day 252. One major product was identified as mA (max. 3.6%-7.9% of the TAR) in addition to mO (max. 0.7% of the TAR) and mN (max. 0.3% of the TAR). Unknown compounds of medium polarity were detected amounting to 2.2% and 4.8%, the latter only in two selected samples. Radioactive polar products retained at the origin of the TLC plates could not be identified but were only in the range of 0.1-1.0% of the TAR. The presence of the parent, mA, mO, mN and one unknown compound was confirmed by GC-FPD.

In the ethyl acetate extracts of the HCl-MeOH-hydrolysed soil bound residues, the parent was the major compound identified at 2.8%-3.5% of the TAR on day 252.

Owing to the very low soil moisture of 6.1% degradation was delayed so no information on degradation kinetics could be obtained.

Conclusion. The major degradation product in soil under aerobic conditions at 25°C was $^{14}CO_2$ which accounted for 54% of the TAR after 252 days. Most of the radioactivity in the extracts was from unchanged ethoprophos. The product which accumulated to the greatest extent in the soil was mA.

Study 3
The rate of degradation of unlabelled ethoprophos was investigated in a humic sand (Speyer 2.2), a sandy loam (Speyer 2.3) and a loamy silt soil under aerobic conditions in the dark at 20°C and 40% of the maximum water holding capacity (Fuchsbichler, 1992, **non-GLP**). The incubation flasks, containing 100 g fresh soil each, were closed with a cotton wool plug. The test substance was applied at a concentration of 10 mg/kg soil. The soil characteristics are summarised in Table 23. Samples were taken after 0, 2, 4, 8, 16, 32, 64, 100 and 115 days of incubation and analysed using method 172, version 1991. Results are shown in Table 22. They were not corrected for concurrent recoveries (88%-94%), nor for interferences (<0.01 mg/kg).

Rate of degradation. Half-lifes were calculated using Timme's method. The moisture content of the humic sand may have been too high, whereas the loamy silt soil may have been incubated in relatively dry conditions (based on pF curves of representative soils, 40% of maximum water holding capacity is equivalent to pF <2 for sand and pF 4 for loamy silt). The DT_{50} values, however, do not indicate that degradation has been adversely influenced by the conditions, the value of the humic sand is consistent with DT_{50} values found in other studies. Calculated DT_{50} and DT_{90} values are shown in Table 23.

Conclusion: The half-life at ambient temperature was 10-25 days.

Table 22. Degradation of ethoprophos in soils (expressed as mg/kg).

Days	humic sand Speyer 2.2	sandy loam Speyer 2.3	loamy silt
0	8.6	9.4	8.1
2	8.2	6.9	5.6
4	7.9	6.8	6.2
8	8.0	6.1	3.0
16	4.4	4.8	2.4
32	2.0	2.3	0.62
64	0.42	1.1	0.10
100	0.61	0.60	
115	0.27	0.35	

Table 23. Soil characteristics and degradation times of ethoprophos.

Soil	Temp. (°C)	% org. C	pH	CEC (meq/100 g)	% clay (<2 µm)	Moisture pF[1]	DT_{50} (days)	DT_{90} (days)	Remark
Humic sand 2.2	20	2.3	5.5	9.7	5.1	1.5	23	76	too dry
Sandy loam 2.3	20	1.3	6.5	9.5	8.3	3.0	25	85	-
Loamy silt	20	1.4	6.8	-	17	4.0	10	34	-

[1] pF values estimated by reviewer, based on pF-curves of representative soils

Confined roational crop study

A sandy loam soil was sprayed with [1-ethyl-^{14}C]ethoprophos as an EC formulation at a rate equivalent to 13.4 kg ai/ha (Wootton and Johnson, 1992). The specific activity of the test substance after dilution was 1.06 mCi/mmol with a radiochemical purity of 96.3% at application. Soil characteristics were pH 7.0, 0.41% om, CEC 17 meq/100 g; 6% clay, moisture holding capacity at 0.33 bar 32%. The test substance was incorporated into the top 10 cm of soil. The soil was placed outside in boxes inside a screened enclosure (Watsonville, CA, USA, 1989-1991), which was heated and covered with plastic during winter months, and left fallow for 30 to 365 days after treatment. Wheat (Anza), spinach (Polka) and radish (Cherry Belle) were planted at 30, 120 and 365 DAT for each crop. Immature and mature crops were harvested from each planting interval. Soil samples were collected at application, at each planting and at each harvest. The total radioactive residue in crops and soil was determined by combustion LSC (LOQ 0.01-0.13 mg/kg). Crop and soil samples were stored frozen for 1-648 days, then extracted successively with MeOH/water, MeOH and DCM. Remaining solids were hydrolysed sequentially with 0.1 M HCl and 0.1 M NaOH (reflux 30 min each). Extracts were analysed by reversed-phase HPLC with LSC detection (LOQ 0.01-0.11 mg/kg). Retention times were compared with those of known reference standards: the parent, mA, mJ, mN, and mO. HPLC results were confirmed by normal-phase TLC and/or GC-MS.

Crop development was normal for wheat and radish, but spinach planted at DAT 30, 120 and 365 was stunted as a result of the phytotoxicity of ethoprophos.

The total radioactive residue in soil is shown in Table 24 and ranged from 14 mg/kg at application to 7.8 mg/kg at 30 DAT, 1.4 mg/kg at 120 DAT, 0.88 mg/kg at 365 DAT and 0.77 mg/kg at 484 DAT. Dissipation of the TRR in soil was biphasic. An initial rapid decrease occurred in the first 90 days after treatment, so only little radioactivity remained in soil for uptake by rotated crops.

The total radioactive residue in crops is shown in Table 25 and was relatively high in all species in the 30 DAT rotational planting. Crops in the 120 DAT rotation generally showed TRR levels at about 10-25% of the same species at 30 DAT, except wheat straw and immature spinach. At 365 DAT, the TRR in rotational crops was generally an order of magnitude lower than in the 30 DAT crops. In all crops there was less total extractability over time. All crops harvested at an immature stage showed similar extractability, while mature crops showed different patterns of extractability.

Total extractability in mature wheat was generally lower than in mature spinach or mature radish. Part of the remaining solids could be hydrolysed by acid or alkaline treatment, but 1.9%–42% of the TRR remained fibre-bound, with the highest proportion in wheat chaff at 365 DAT.

Table 24. Distribution of radioactivity in extracts of soil.

Rotational Interval (days)	Sampling (DAT)	TRR (mg/kg eq)	MeOH/H_2O[1]	DCM	0.1 N HCl	0.1 N NaOH	Solids	Total
			(% of TRR)					
30 (application)	0	13	110	0.1	1.0	0.9	0.2	112
30 (planting)	30	7.8	72	0.1	13	8.5	1.5	95
30	84	1.1	50	0.8	6.7	22	9.5	89
30	132	0.54	14	0.2	11	39	22	86
30	169	0.96	23	0.7	6.6	29	14	73
120 (application)	0	15	33	0.2	5.9	5.2	1.2	46
120 (planting)	120	1.4	38	0.8	5.1	18	17	80
120	182	1.1	30	1.2	3.6	3.4	2.9	41
120	202	0.98	30	2.2	10	30	23	95
120	268	0.92	16	1.9	8.3	32	26	85
365 (application)	0	13	101	0.3	1.5	0.8	0.2	104
365 (planting)	365	0.88	10	2.1	5.1	21	22	61
365	399	0.66	11	1.0	17	28	31	88
365	406	0.63	10	0.6	9.0	24	4.5	49
365	426	0.78	8.6	2.3	6.0	16	13	46
365	428	0.67	8.4	1.5	9.9	49	22	92
365	484	0.77	8.0	0.0	9.3	48	27	93

[1] Combined MeOH and MeOH water extracts

Table 25. Distribution of radioactivity in extracts of rotational crops.

Sample	Planted (DAT)	Harvest (DAT)	TRR (mg/kg)	MeOH/H_2O[1]	DCM	0.1 N HCl	0.1 N NaOH	Solids	Total
				(% of TRR)					
Imm radish, foliage	30	65	15	72	1.2	1.7	10	4.1	89
Imm spinach, foliage	30	84	23	84	0.3	3.4	2.7	2.3	93
Imm wheat, forage	30	84	28	64	1.7	8.0	18	7.2	99
Mat radish, whole plant	30	84	4.3	85	1.2	3.1	6.4	6.1	102
Mat spinach, foliage	30	132	19	60	2.7	9.8	17	10	99
Mat wheat, straw	30	169	47	52	0.9	2.6	17	16	88
Mat wheat, grain	30	169	14	20	2.1	33	17	6.5	78
Mat wheat, chaff	30	169	41	48	1.6	7.5	22	20	99
Imm radish, foliage	120	182	1.6	59	1.7	13	9.4	6.0	89
Imm spinach, foliage	120	202	10	90	1.2	7.7	10	1.9	111
Imm wheat, forage	120	182	5.0	53	3.7	9.6	14	8.6	88
Mat radish, foliage	120	202	3.0	65	1.3	5.7	7.8	7.3	87
Mat radish, root	120	202	1.3	72	0.6	7.3	57	5.1	142
Mat spinach, foliage	120	268	3.0	70	1.6	3.3	8.3	9.6	93
Mat wheat, straw	120	268	38	56	2.2	2.8	1.5	19	82
Mat wheat, grain	120	268	5.0	26	2.1	0.7	2.2	25	56
Mat wheat, chaff	120	268	17	46	1.1	2.6	3.6	11	64
Imm radish, foliage	365	399	0.61	68	6.9	4.7	8.0	24	111
Imm spinach, foliage	365	426	0.87	68	3.1	6.1	9.8	6.2	93
Imm wheat, forage	365	406	0.61	60	2.6	3.2	22	11	99
Mat radish, foliage	365	406	1.2	36	1.5	2.7	11	1.5	53
Mat radish, root	365	406	0.19	41	5.3	7.8	24	11	89
Mat spinach, foliage	365	428	0.92	61	0.6	5.2	11	17	95
Mat wheat, straw	365	484	0.65	58	3.9	5.1	11	35	113
Mat wheat, grain	365	484	0.29	24	5.3	9.3	21	29	88
Mat wheat, chaff	365	484	0.50	54	2.9	13	14	42	125

imm: immature; mat: mature
[1] Combined MeOH and MeOH water extracts

Parent ethoprophos was the major compound identified in extracts of soil at all sampling times, except at 426 DAT where mJ was predominant (Table 26). Ethyl phosphate (mJ) was the primary product (0.14 mg/kg at 0 DAT) and remained relatively constant at 0.01 to 0.06 mg/kg throughout the study. The concentration of mA was very low in soil and was confirmed at only two samplings, 30 and 84 DAT.

Parent ethoprophos was present in extracts of immature and early maturing crops (radishes) at the 120 day as well as the 30 day rotational intervals (Table 27). No ethoprophos was found in the mature wheat or spinach planted at 120 days nor in any crops at 365 days. The major component of every crop sample was mJ, but mA was also found. A large number of unidentified compounds was found, some with levels above 10% of the TRR or 0.05 mg/kg eq. Hydrolysis of immature spinach extracts from the 120 day rotational interval (0.2 M HCl, 30 min) demonstrated that unknown compound 2 (12% of the TRR) and unknown compound 4 (8.5% of the TRR) were conjugates of ethyl phosphate (mJ). Isolated levels of unknown compounds 1, 3, and 5-18 were not sufficient to establish identity.

The major component in acid and base hydrolysates of crops and soil was the parent: 0.01 mg/kg in soil at DAT 132 and 0.13 mg/kg in mature wheat straw from the 120 day rotational interval. Most of the remainder was mN (0.02 mg/kg eq).

Mature wheat straw was selected for characterisation of bound residues. Plant material was sequentially treated to isolate extractable residues (50 mM phosphate buffer, pH 7, 10 min, ambient), starch (α-amylase, pH 7, 20 h, 30°C), protein (pronase E, pH 7.2, 16 h, 30°C), pectin (50 mM EDTA buffer, pH 4.5, 6 h, 80°C), lignin (glacial acetic acid/sodium chlorite, 4 h, 70°C), hemicellulose (24% potassium hydroxide, 24 h, 27°C), and cellulose (72% sulfuric acid, 4 h, ambient). Results showed general incorporation into cellular components: extractable 40% of the TRR, starch 7.7% of the TRR, protein 1.5% of the TRR, pectin 1.9% of the TRR, lignin 11% of the TRR, hemicellulose 14% of the TRR, cellulose 10% of the TRR and insoluble residue 22% of the TRR (overall recovery 105%).

Storage stability: Mature spiked radish showed no degradation of [^{14}C]ethoprophos after 648 days of storage, but results for other samples were not reported and degradation patterns from beginning and end of the study were not compared.

Conclusions: The total radioactive residue in soil decreased from 14 mg/kg to approximately 1 mg/kg in the first 90 days after treatment, so only little radioactivity remained in the soil for uptake by rotated crops. However, radioactive residues were found in all crop samples at all samplings, even though ethoprophos was not detected in plants after the 120-day rotational interval. The main product found in both soil and plants was ethyl phosphate (mJ).

The metabolism of ethoprophos in rotational crops appears to be, as before, by loss of an S-propyl group to give mA, then loss of the second propyl group to give mJ. The ethyl group can then be incorporated into plant cellular components.

Table 26. Metabolites in combined extracts[1] of soil.

Rotational interval (days)	DAT[1]	TRR (mg/kg eq)	parent (% of TRR)	mJ (% of TRR)	mA (% of TRR)	mO (% of TRR)	mN (% of TRR)	Other[2] (% of TRR)
30 (application)	0	13	96	1.1	nd	nd	nd	13
30 (planting)	30	7.8	40	nd	32	nd	nd	0.6
30	84	1.1	45	2.0	0.9	nd	nd	2.9
30	132	0.54	12	2.8	nd	nd	nd	nd
30	169	0.96	21	2.3	nd	nd	nd	0.3
120 (application)	0	15	16	17	0.1	0.1	0.1	0.4
120 (planting)	120	1.4	38	1.0	nd	0.3	nd	nd

Rotational interval (days)	DAT[1]	TRR (mg/kg eq)	parent (% of TRR)	mJ (% of TRR)	mA (% of TRR)	mO (% of TRR)	mN (% of TRR)	Other[2] (% of TRR)
120	182	1.1	28	1.8	nd	1.2	nd	nd
120	202	0.98	29	3.0	nd	0.5	nd	nd
120	268	0.92	14	4.3	nd	nd	nd	nd
365 (application)	0	13	88	12	0.1	0.5	0.1	0.5
365 (planting)	365	0.88	7.4	4.3	nd	0.8	nd	nd
365	399	0.66	8.4	3.8	nd	nd	nd	nd
365	426	0.78	1.8	7.3	nd	nd	nd	1.8

nd: <LOQ (0.001-0.005 mg/kg)
[1] combined MeOH/water, MeOH and DCM extracts.
[2] extractable radioactivity found in endogenous materials and /or minor unidentified products, 1-4 different compounds, each 0.1%-13% of the TRR or 0.01-1.7 mg/kg eq.

Table 27. Metabolites in combined extracts[1] of rotational crops.

Sample	Planted (DAT)	Harvest (DAT)	TRR (mg/kg eq)	parent (% of TRR)	mJ (% of TRR)	mA (% of TRR)	mO (% of TRR)	mN (% of TRR)	Other[2] (% of TRR)
Immature radish, foliage	30	65	15	18	22	14	nd	nd	19
Immature spinach, foliage	30	84	23	1.9	51	4.1	0.2	nd	27
Immature wheat, forage	30	84	28	6.5	31	nd	0.3	0.8	27
Mature radish, whole plant	30	84	4.3	7.6	24	21	0.2	0.3	32
Mature spinach, foliage	30	132	19	0.4	28	nd	nd	1.8	33
Mature wheat, straw	30	169	47	1.3	23	nd	0.6	nd	27
Mature wheat, grain	30	169	14	nd	21	nd	nd	nd	1.2
Mature wheat, chaff	30	169	41	0.4	36	nd	0.2	0.4	12
Immature radish, foliage	120	182	1.6	7.8	21	9.8	nd	nd	22
Immature spinach, foliage	120	202	10	5.2	34	nd	nd	2.5	50
Immature wheat, forage	120	182	5.0	4.9	33	10	nd	nd	8.6
Mature radish, foliage	120	202	3.0	3.7	24	18	nd	nd	21
Mature radish, root	120	202	1.3	5.1	29	nd	nd	nd	39
Mature spinach, foliage	120	268	3.0	nd	21	nd	nd	nd	50
Mature wheat, straw	120	268	38	nd	42	nd	0.4	nd	15
Mature wheat, grain	120	268	5.0	nd	25	0.7	nd	nd	2.5
Mature wheat, chaff	120	268	17	nd	40	nd	nd	nd	7.0
Immature radish, foliage	365	399	0.61	nd	6.6	nd	nd	nd	68
Immature spinach, foliage	365	426	0.87	nd	46	nd	nd	nd	23
Immature wheat, forage	365	406	0.61	nd	40	5.4	nd	nd	18
Mature radish, foliage	365	406	1.2	nd	18	6.2	0.8	1.3	12
Mature radish, root	365	406	0.19	nd	31	nd	nd	nd	14
Mature spinach, foliage	365	428	0.92	nd	42	nd	nd	nd	19
Mature wheat, straw	365	484	0.65	nd	31	nd	nd	nd	31
Mature wheat, grain	365	484	0.29	nd	18	nd	nd	nd	4.6
Mature wheat, chaff	365	484	0.50	nd	39	nd	nd	nd	18

nd: <LOQ (0.01-0.11 mg/kg, depending on sample)
[1] combined MeOH/water, MeOH and DCM extracts.
[2] extractable radioactivity found in endogenous materials and /or minor unidentified products, 2-8 different compounds per sample, each 0.1%-24% of the TRR or 0.05-2.8 mg/kg eq.

Field rotational crop study

Unlabelled ethoprophos was applied once as EC formulation before planting at an actual rate of 13.5 kg ai/ha in a volume of 224-279 l/ha, using a tractor-mounted broadcast sprayer (R008901, Norris,

1997). The formulation was incorporated into a sandy loam soil (pH 6.8-8.3; 1.5-2.0% om; 5-9% clay; CEC 8.7-9.7 meq/100g; 10%-16% moisture at 0.33 bar). Rotational crops included root vegetables (radish roots), leafy crops (radish leaves, red leaf lettuce, collards), cereals (winter wheat, spring wheat and sorghum), pulses/oilseeds (cow peas, wando peas, green peas, soya beans and mustard forage). Crops were planted in 1995-1996 at two US sites, California (CA) and North Carolina (NC), at 1, 4, 8 and 12 months after application. Rainfall was less than normal in California and greater than normal in North Carolina. In North Carolina, the cold and wet weather delayed the planting at the 8 months rotational interval to 10 months and mature wando peas were lost owing to the very cold winter. The crops were harvested at maturity or the specified growth stage. Spring wheat did not mature sufficiently for grain and straw to be sampled. Samples were stored at -10°C for 90-412 days until extraction. Extracts were stored for 0-11 days and analysed for ethoprophos and mA, using GC-FPD method 4, version 13. Samples containing the highest residues were analysed by GC-MS to confirm the presence of ethoprophos and mA. Results were not corrected for concurrent recoveries (63%-112% for the parent and 58%-99% for mA), nor for interferences (<0.01 mg/kg, except ethoprophos in radish roots 0.013 mg/kg).

Results: Residues of ethoprophos and mA in the rotational crop samples were below the LOQ of 0.01 mg/kg in all treated samples from both test sites except radish root and radish leaves (tops). Table 28 shows the average residues of ethoprophos and mA found in the radish samples. Because of matrix interferences in radish roots, the LOQ for ethoprophos should be increased to at least 0.013 x 10/3 = 0.05 mg/kg in radish roots. The presence of ethoprophos and mA in radish root and top was confirmed by GC-MS, but the levels measured by GC-MS were at least an order of magnitude lower than measured by GC-FPD. The crops were not washed before analysis so treated soil could adhere to the radishes. This soil may account for the residues found in the root crop.

Table 28. Average residues[1] of ethoprophos and mA in radish grown on ethoprophos treated soil in the USA.

Sample	Planting (DAT; date)	Harvest (DAT)	California		Planting (DAT; date)	Harvest (DAT)	North Carolina	
			Parent	mA			Parent	mA
Radish, root	31 17 July 95	32	0.018; 0.028; mean 0.023	0.030; 0.048; mean 0.039	31 23 June 95	34	0.015; 0.016; mean 0.016	<0.01 (2); mean 0.039
	119 13 Oct 95	35	<0.01; 0.011; mean 0.010	<0.01; 0.012; mean 0.011	120 20 Sept 95	57	<0.01 (2); mean <0.01	<0.01 (2); mean <0.01
	241 12 Feb 96	50	<0.01 (2); mean <0.01	<0.01 (2); mean <0.01	296[2] 14 Mar 96	60	<0.01 (2); mean <0.01	<0.01 (2); mean <0.01
	362 12 June 96	89	NA	NA	365 22 May 96	40	0.012; 0.014; mean 0.013	<0.01 (2); mean <0.01
Radish top	31 17 July 95	32	< 0.01 (2); mean <0.01	0.066; 0.13; mean 0.096	31 23 June 95	34	<0.01 (2); mean <0.01	<0.01 (2); mean <0.01
	119 13 Oct 95	35	< 0.01 (2); mean <0.01	0.022; 0.029; mean 0.026	120 20 Sept 95	57	<0.01 (2); mean <0.01	<0.01 (2); mean <0.01
	241 12 Feb 96	50	<0.01 (2); mean <0.01	<0.01 (2); mean <0.01	296[2] 14 Mar 96	60	<0.01 (2); mean <0.01	<0.01 (2); mean <0.01
	362 12 June 96	89	NA	NA	365 22 May 96	40	<0.01 (2); mean <0.01	<0.01 (2); mean <0.01

NA: not analysed

[1] residues were from duplicate field samples.

[2] Owing to unusually wet weather in North Carolina, crops had to be planted 10 instead of 8 months after treatment.

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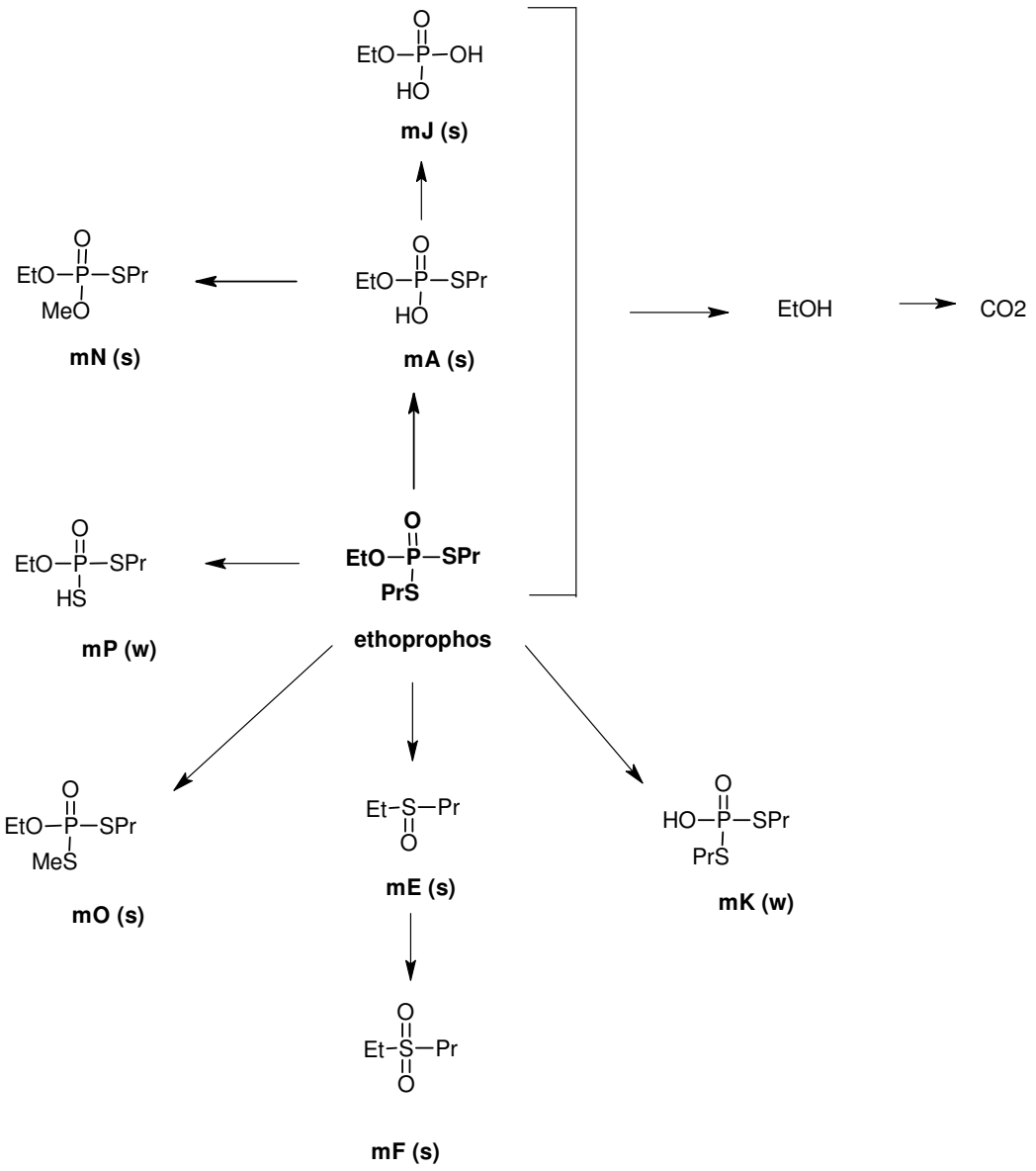

Figure 3. Proposed degradation pathways of ethoprophos in soil and water (Me = methyl; Et=ethyl; Pr=propyl, s=soil, w=water). The major route in soil is degradation to CO_2. Metabolites (mN and mO) were tentatively identified. See also footnote to Figure 1.

Environmental fate in water/sediment systems

The Meeting received information on hydrolysis and photolysis in water. These studies are summarized in physical and chemical properties. Information on biodegradability in water/sediment systems was submitted but was not relevant for this evaluation and was therefore not evaluated.

RESIDUE ANALYSIS

Enforcement methods for foodstuffs of plant and animal origin

The Meeting received information on enforcement and monitoring methods for the determination of parent ethoprophos in foodstuffs of plant and animal origin.

Dutch multi-residue method MRM-1

Ethoprophos was included in the list of 448 organochlorine, organophosphorus, pyrethroid and nitrogen-containing compounds that can be analysed using the Dutch multi-residue method MRM-1 (RIVM, 1996). This employs various extraction and clean-up modules and is suitable for foodstuffs of plant and animal origin. Quantification of ethoprophos was validated for non-fatty samples (<5% fat), which were extracted with ethyl acetate or acetone. Ethoprophos can be quantified by GC-NPD or GC-MS For lettuce, the recovery was 110% (RSD 9.7%, n=10) at 0.02 mg/kg and 102% (RSD 3.6%, n=10) at 0.12 mg/kg, using GC-MS (ion trap) as quantification technique. The LOQ for organophosphorus compounds is 0.01-0.05 mg/kg depending on the modules used.

German multi-residue method DFG-S8

In addition, ethoprophos was also included in the list of 121 organohalogen, organophosphorus or triazine compounds that can be analysed using the German multi-residue method DFG-S8 (DFG, 1987). The method is suitable for fruits , vegetables , herbs and honey. Samples were macerated with acetone followed by clean-up. Ethoprophos could be quantified by GC-ECD or GC-AFID. The reported LOQ for ethoprophos was 0.02 mg/kg. Recoveries above 70% are reported for ethoprophos in lettuce at 0.2 mg/kg and in green beans and mushrooms at 0.1 mg/kg.

German, multi-residue method DFG-S19

In the original version of DFG-S19 ethoprophos was not listed (DFG, 1987b). In the updated version of DFG-S19 ethoprophos was included (DFG, 1992). The method is suitable for foodstuffs of plant and animal origin. Samples were macerated with acetone/water followed by clean-up. Ethoprophos was quantified by GC-FPD. No validation results are published.

In addition, ethoprophos was also included in the list of organochlorine, organophosphorus, nitrogen containing and other pesticides that can be analysed using the extended revision of the German multi-residue method DFG-S19 (DFG, 1999). The method consists of different modules for extraction (E1-E9), clean-up (GPC, C1, C2) and detection (D1-D4). The method is suitable for foodstuffs of plant and animal origin. Ethoprophos quantification was validated for crops with high water content (water >70%, fat <2.5%, w/w), crops with low water content (water <70%, fat <2.5%, w/w) and °C with high fat content (fat >2.5%, ww).

For crops with high water content or °C with high fat content samples are extracted with acetone/water (2+1) followed by clean-up (E1, GPC). Ethoprophos is quantified by GC-FPD (D2) or GC-MS (D4). The mean recovery for unspecified °C and detection techniques was 80% (RSD 19%, n=20) at 0.05-0.30 mg/kg (2 laboratories).

For °C with low water content (samples were first soaked in water). The mean recovery for unspecified °C and unspecified detection techniques was 79% (RSD 12%, n=5) at 0.20 mg/kg (1 laboratory).

The extended revision of DFG-S19 (with slight modification) was independently validated for potatoes and tomatoes by another laboratory (Table 29) and was renamed method AR 274-01 (Dorn,

2001). Crops (50 g) were extracted and purified according to extraction module E1 and GPC clean-up. Further procedures were modified. The GPC eluate was fractionated on silica gel. Fractions containing ethoprophos were concentrated, diluted with toluene and analysed by GC-PFPD (Chrompack Sil-8 capillary column) using external standardisation. A confirmatory method using GC-MS (same column) was provided. The fragment ion m/z 158 was used for quantification and the fragment ions m/z 199 and m/z 139 for identification.

Table 29. Validation results for the determination of ethoprophos using GC-PFPD method AR 274-01.

Sample	LOQ reported mg/kg	Spike mg/kg	Confirm. ratio PFPD/MS	Recovery, % mean range	RSD	no	Control (mg/kg)	Linearity	Ref.
potato	0.01	0.01 0.10	0.87 0.90	87 77-97 84 73-91	10% 10%	5 5	<0.3LOQ (n=3)	6 single points; 0.01-0.75 ug/L, in toluene; r^2>0.99	Dorn, 2001 (ILV)
tomato	0.01	0.01 0.1	0.87 0.80	85 77-90 84 70-102	6% 16%	5 5	<0.3LOQ (n=3)	6 single points; 0.01-0.75 ug/L, in toluene; r^2>0.99	idem

USA, FDA multi-residue protocols PAM 1

Ethoprophos was tested through the USA FDA multiresidue protocols A, B, C, D and/or E as described in Pesticide Analytical Manual Volume 1 (PAM 1, 1989) (Ver Hey, 1991). Because all of the protocols were unsuccessful , Ethoprophos could not be determined by the USA FDA multi-residue protocols.

Method AR 271-01

Method AR 271-01 was proposed as an enforcement method for the determination of ethoprophos in milk, eggs, meat, fat and liver (Barbier, 2001).

Samples (25 g) were macerated with MeOH and filtered. For fatty °C such as fat and liver, lipids were removed by low-temperature precipitation (1.5 h at –20°C) followed by filtration. After concentration and addition of 10% NaCl, residues were partitioned into hexane. The hexane-phase was filtered through sodium sulfate and concentrated, before clean-up using a Florisil cartridge. The eluate was evaporated to dryness and redissolved in hexane. For fat this step was not necessary. Ethoprophos was quantified by GC-PFPD (semi-capillary column Rtx-1701 for milk, egg and beef meat, CP SIL 24 CB for fat and liver) using external standardisation. For milk, egg and beef meat GC-MS-MS (capillary CP Sil 8 CB, EI, isolation ion m/z=158, quantification m/z 94+114+30), and for fat and liver GC-PFPD with a different polarity column (VA-5) were used as confirmatory methods.

The method was independently validated by a different laboratory (Class, 2001). The following modifications were introduced: the CP SIL 24 CB column was used for all °C tested (milk, beef meat and fat) and the calibration was performed by external standardization using matrix-matched standards for beef meat and liver. The results are shown in Table 30.

Conclusion: The method is considered valid as an enforcement method for the determination of ethoprophos in the range 0.01-0.1 mg/kg in foodstuffs of animal origin (milk, eggs, meat, fat and edible offal).

Table 30. Validation results for the determination of ethoprophos using GC-MS method AR 271-01.

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean range	RSD	no	Control (mg/kg)	Linearity	Ref.
whole milk	0.01	0.01 0.10	87 71-112 89 81-101	19% 9%	5 5	<0.3LOQ (2)	6 single points; 0.02-0.1 mg/l; in hexane r^2>0.99	Barbier, 2001 (method validation)
whole egg	0.01	0.01 0.10	96 79-111 95 75-105	13% 13%	5 5	<0.3LOQ (2)	idem	idem
beef meat	0.01	0.01 0.10	84 66-107 88 68-110	19% 18%	5 5	<0.3LOQ (2)	idem	idem
pork fat	0.01	0.01 0.10	96 79-111 110 93-119	15% 10%	5 5	<0.3LOQ (2)	idem	idem
beef liver	0.01	0.01 0.10	84 81-87 79 70-92	3% 11%	5 5	<0.3LOQ (2)	idem	idem
milk	0.01	0.01 0.10	82 70-90 84 70-91	9% 10%	5 5	<0.3LOQ (2)	8 single points; 0.005-1.0 ug/L; in hexane; r^2>0.99	Class, 2001 (ILV)
beef meat	0.01	0.01 0.10	96 75-110 96 89-102	16% 6%	5 5	<0.3LOQ (2)	5 single points; 0.01-1.0 ug/L; matrix matched; r^2>0.99	idem
liver	0.01	0.01 0.10	77 50-96 82 73-93	26% 9%	5 5	<0.3LOQ (2)	5 single points; 0.01-1.0 ug/L; matrix matched; r^2>0.99	idem

Analytical methods for plant materials used in trials and studies

The Meeting received information on analytical methods for the determination of ethoprophos and mA in foodstuffs of plant origin as used in various studies (rotational crop, supervised residue trials, storage stability, processing and monitoring studies).

Method R-89-A (1966-1974)

Method R-89-A was used in trials on sugar cane (C032664), potato (R007982/C034085), cucumbers (C034085) and bananas (C034087). The method is based on extraction with hexane, clean-up on a Florisil column with MeOH as final eluent and determination of the parent by GC-MC. Table 31 shows the validation results.

Table 31. Validation results for the determination of ethoprophos using GC-MC method R-89-A.

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean range	RSD	no	Control (mg/kg)	Linearity	Ref.
Sugar cane stalks	0.02	0.02 0.03	94 85-100 98 90-106	8% -	4 2	<0.3LOQ (3)	not verified	C032664 (trial/processing) 1967 USA Anal. 1966-1970
Banana, whole	0.02	0.02 0.03	95 90-100 96 -	4.3% -	4 1	<0.3LOQ (3)	not verified	C034087 (trial) 1968-1969 Costa Rica; Côte d'Ivoire Anal. 1969
Cucumber, whole	0.02	0.02	98 90-100	5.1%	4	<0.02 (4)	not verified	C034085 (trial) 1969-1973 USA Anal 1969-73
Potato, whole	0.02	0.02 0.03	97 95-100 86 -	2.7% -	3 1	<0.02 (3)	not verified	R007982 (trial) 1969-1973 USA Anal 1969-74

GC-FPD, method 1 (1976-1984)

GC-FPD, method 1 is published (Hunt *et al.*, 1981), and was used in US trials on cucumbers (C032715), tomatoes (C032715) and potatoes (C033867). The method is based on extraction with hexane, clean-up on a silicic acid column using 10% acetone in n-hexane as final eluent and determination by GC-FPD (glass column, 15% Carbowax 20M, temperature 190°C). The method was validated for snap beans, tomato, cucumber, lettuce, onion, turnip root, turnip leaf and radish. The results for root and fruiting vegetables are shown in Table 32.

Table 32. Validation results for the determination of ethoprophos using GC-FPD method 1.

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean range	RSD	no	Control (mg/kg)	Linearity	Ref.
tomato	0.005	0.01 0.1	89 88-90 82 -	- -	2 1	-	not verified	C032715 (trial/ method validation) 1976 USA
cucumber	0.005	0.01 0.1	89 78-100 100 -	- -	2 1	-	not verified	C032715 (trial/ method validation) 1976 USA
turnip root	0.01	0.01 0.1	82 82-82 96 86-105	- ns	2 3	-	not verified	C032715 (method validation)
radish	0.005	0.01 0.1	108 - 105 -	- -	1 1	-	not verified	C032715 (method validation)
potatoes	0.01	0.5 2.5	92 - 100 -	- -	1 1	<0.3LOQ (2)	not verified	C033867 (trial) 1983 USA

GC-FPD, method 2 (1978)

In the analytical method used in Dutch trials on cucumbers (C034084) and tomato (C034084) crops were blended with sodium sulfate and hexane. The homogenate was filtered, evaporated to dryness and dissolved in hexane. Ethoprophos was determined by GC-FPD (glass, 10% DC200 + 15% QF1 (1+1) on chrom Q 80/100, temperature 190°C, phosphorus mode). Validation results from supervised residue trials are summarized in Table 33.

Table 33. Validation results for the determination of ethoprophos using GC-FPD method 2.

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean range	no	Control (mg/kg)	Linearity	Ref.
Cucumber	0.01	0.01 0.02 0.04 0.06 0.1 0.4	85 80-90 95 95-95 97 - 97 - 95 - 96 -	2 2 1 1 1 1	<0.3LOQ (7)	not verified	C034084 (trial/ method validation) Anal. Oct/Nov 78
Tomato	0.01	0.01 0.03 0.1	68 55-82 90 84-97 104 97-112	2 2 2	<0.3LOQ (5)	not verified	C034084 (trial/ method validation) Anal. Oct/Nov 78

Mobil GC method (1980-1981)

The Mobil GC method was used in supervised residue trials carried out in 1980 in Canada on cucumber (C032713). No description was available. Concurrent validation results are shown in Table 34.

Table 34. Validation results for the determination of ethoprophos using Mobil GC method.

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean range	no	Control (mg/kg)	Linearity	Ref.
Cucumber	0.01	0.1	99 94-104	2	<0.3LOQ (2)	not verified	C032713 (trial) 1980 Canada Anal. Aug 80
Cucumber	0.01	0.1	98 91-104	2	<0.3LOQ (1)	not verified	C032713 (trial) 1980 Canada Anal. Oct 81

GC-FPD, method MP-RE-08-83 (1983)

Method MP-RE-08-83, based on Mobil method MP 12-38, was used in Dutch trials on potatoes (R007979) and is based on extraction with hexane, clean-up (filtration) and determination by GC-FPD in the phosphorus mode (OV 17 column, temperature 200°C) (Rhone-Poulenc, 1983). Calibration was by 4 single external standards in the range 0.1-2.0 mg/l (mg/kg sample equivalent not stated). The method was validated for cucumber, maize (grains, whole plants), potatoes, and green tabacco. Validation results for potatoes are shown in Table 35.

Table 35. Validation results for the determination of ethoprophos using GC-FPD method MP-RE-08-83.

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean range	RSD	no	Control (mg/kg)	Linearity	Ref.
Potato	0.02	0.02 0.2	85 74-91 94 86-100	11% 7.6%	3 3	<0.02	4 single points, range 0.1-1.0 mg/l; linear by graph	R007979 (method validation)
Potato	0.02	0.02 0.2	94 - 95 -	- -	1 1	<0.02 (2)	not verified	R007979 (trial)

GC-FPD method 3 (1984-1987)

GC-FPD method 3 was used in Brazilian trials on tomato (C033859, banana (C033861/C033862) and *s*ugar cane (C033863/C033864). Only a summary description was available. Samples were extracted with n-hexane and passed through sodium sulfate. Ethoprophos was determined by GC-FPD (glass column, 5% SE-30 on Chromosorb WAW-DMCS 80-100 mesh, 150°C or160°C, phosphorus mode). The reported LOQ was 0.05 mg/kg. Recovery at 0.05 mg/kg was 98% for tomato, 97% for banana pulp, 111% for whole banana and 86% for *s*ugar cane stalks. No matrix interferences were found (<0.05 mg/kg, n=1 for each sample). Further details were not available.

Method 175 (1985-1991)

Method 175-1985 and modifications thereof were used in trials on sweet potatoes (C032642) and potatoes (R008006 and R008010) and in a storage stability study on broccoli, cabbage, dry peanut hay, and green and cured tobacco (R009168). Six different procedures (8.1-8.6) were developed depending on the sample. The method was based on extraction with hexane, clean-up (by silica gel or Florisil column, or partitioning into ACN) and determination by GC-FPD (phosphorus mode, 5% EGSS-X on 100/120 GCQ, 175°C for cole crops, 5% EGSS-X on 100/120 GCQ, 160°C or 10% DC-200 on 80/100 chrom WHP, 175°C for oily crops, 15% Carbowax 20M on 60/80 mesh GCP at 190°C or 10% DC-200 on 80/100 chrom WHP at 168°C for potatoes, 3% OV-17 on 80/100 GCQ, 180°C for tobacco, green and dry) (Perez *et al*., 1985).

Calibration was by external standardization in the range 0.1-2.0 mg/l in hexane (corresponding to 0.01-0.2 mg/kg).

Method 175-1990 was used in UK trials on potatoes (R008006). Modification of the 1985 method using clean-up on Florisil Sep-Pak with 15% ethyl acetate in toluene as final eluent. Ethoprophos was determined by GC-FPD (5% OV 101 column, temperature programme 140-190°C, phosphorus mode).

Method 175-1991 was used in other UK trials on potatoes (R008010). The chromatographic column was modified (glass OV-17 WCOT microbore capillary, temperature 150 - 210°C, phosphorus mode).

Table 36. Validation results for the determination of ethoprophos using GC-FPD method 175.

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean	range	RSD	no	Control (mg/kg)	Linearity	Ref.
cabbage	0.01	0.01	104	-	-	1	-	not verified	C032642/R009168 (method validation) 175-1985, procedure 8.1
broccoli	0.01	0.01	91	-	-	1	-	not verified	idem
peanut hay	0.01	0.01 0.02 0.05 0.1	110 84 87 92	- - - -	- - - -	1 1 1 1	-	not verified	C032642/R009168 (method validation) 175-1985, procedure 8.2
potato	0.01	0.01 0.05 0.1	87 90 77	- - -	- - -	1 1 1	-	not verified	C032642/R009168 (method validation) 175-1985, procedure 8.3
tobacco, green	0.01	0.02 0.05	99 94	- -	- -	1 1	-	not verified	C032642/R009168 (method validation) 175-1985, procedure 8.4
tobacco, dry	0.01	0.02 0.05	96 96	- -	- -	1 1	-	not verified	idem
sweet potato	0.01	0.01 0.1	90 104	80-100 98-109	- -	2 2	<LOQ (2)	not verified	C032642 (trial) Anal. 29 July 85 175-1985, procedure 8.3
peanut hay	0.01	0.05	96	86-101	7.4%	4	<0.3LOQ (4)	not verified	R009168 (storage stability) 175-1985, procedure 8.2
cabbage	0.01	0.05	102	92-109	8.6%	3	<0.3LOQ (3)	not verified	R009168 (storage stability) 175-1985, procedure 8.1
broccoli	0.01	0.05	98	92-105	6.0%	4	<0.3LOQ (4)	not verified	R009168 (storage stability) 175-1985, procedure 8.1
tobacco (green)	0.01	0.05	90	73-106	16%	5	<0.3LOQ (5)	not verified	R009168 (storage stability) 175-1985, procedure 8.4
tobacco (cured)	0.01	0.05	86	76-98	9.3%	5	<0.3LOQ (5)	not verified	R009168 (storage stability) 175-1985, procedure 8.4
potato	0.01	0.01 - 20[1]	92	77-101	ns	3	<LOQ (1)	single point 0.05 mg/l	R008006 (trial) Anal, 29 Jun 1990 175-1990
potato	0.01	0.01 0.1	79 96	- -	- -	1 1	<0.3LOQ (1)	single point 0.05 mg/l	R008010 (trial) Anal. 15 May 1991 175-1991

[1] Individual levels not shown in the study report

Method AR 52-87 (1987-2004)

Method AR 52-87 and modifications thereof were used in trials on potatoes (R007984, R007988, R008000, R007970, C013482, C015231, C019660, C019661), tomatoes (R008853, R008899, R016050, C016512, C023919), sweet peppers (R016050, R009798, C023543, C024789, C036690, C036691), strawberries (R008903, R008027), cucumbers (R004197, C025160, C036689), melons (R004456, C025152, C036692; C036693), a storage stability study on potatoes and tomatoes (R011312 and 02-120) and a processing study on potatoes (R016070). The method was based on extraction with MeOH, clean-up and determination by GC-FPD, GC-TSD (=GC-NPD), GC-PFPD, GC-MS or GC-MS-MS (Dupont and Soun, 1987, 1988, Maestracci, 1998e, Barbier, 2000, Meilland and Kieken, 2003, Bourgade and Rosati, 2003). The results are shown in Table 37.

Table 37. Validation results for the determination of ethoprophos using method AR 52-87.

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean	range	RSD	no	Control (mg/kg)	Linearity	Ref.
potato, whole	0.01	0.01 0.02 0.04	100 115 82	84-110 - -	12% - -	4 1 1	<0.01 (12)	3 single points; range 0.05-0.2 mg/l; in hexane; linear, by graph	R007984 (trial) 1986 Germany; analysis Mar 87; 1987: GC-FPD
potato, whole	0.01	0.01 0.04	96 100	- -	- -	1 1	<0.01 (2)	not verified	R007988 (trial) 1987 Germany analysis Jan 88 1988a: GC-FPD
potato, whole	0.01	0.01 0.02 0.06	96 87 87	- - -	- - -	1 1 1	<0.01 (20)	not verified	R008000 (trial) 1989 Germany anal. Mar 90 1990: GC-FPD
potato, whole	0.01	0.01 0.05 0.1 0.2	104 102 87 83	85-111 93-112 - -	12% - - -	4 2 1 1	<0.3LOQ - 0.0045 (8)	not verified	R007970 (trial/ method validation) 1995 UK anal. Mar 96 1996: GC-FPD
tomato	0.01	0.01 0.2	84 81	73-98 -	12% -	5 1	<0.01 (6)	5 single points; range 4-20 ug/L; in hexane; linear, r>0.999	R008853 (trial) 1996 ES Anal. Sept 96 1996b: GC-TSD
tomato	0.01	0.01 0.02 0.05	101 119 94	93-112 - 89-98	8.7% - -	4 1 2	<0.01 (8)	not verified	R008899 (trial) 1997 ES Anal Sept 97 1997: GC-FPD
tomato	0.01	0.01 0.02	79 78	- -	- -	1 1	<0.01 (2)	not verified	R008904 (trial) 1997 IT Anal. 1997: GC-FPD
plum	0.01	0.01 0.02 0.05	100 88 87	99-101 - 85-89	- - -	2 1 2	<0.01 (5)	not verified	C013119 (method validation) Anal. Sept 97 1997: GC-FPD
strawberry	0.01	0.02	88	-	-	1	<0.01 (2)	not verified	R008903 (trial) 1997 IT Anal. Oct 97 1997: GC-FPD
sweet pepper	0.01	0.01	88	-	-	1	<0.01 (2)	not verified	R016050 (trial) 1997 IT Anal Oct 97 1997: GC-FPD
potato	0.01	0.01 0.1	84 87	84-85 74-95	- 11%	2 5	<0.01 (13)	5 double or triple points; range 0.025-0.50 mg/l; in hexane r^2>0.99 (n=2)	R011312 (storage) Anal Mar-Dec 99 1997: GC-FPD

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean	range	RSD	no	Control (mg/kg)	Linearity	Ref.
cucumber	0.01	0.01 0.02 0.05	96 102 86	90-103 - 73-100	- - -	2 1 2	<0.01 (13)	6 single points; range 0.025-1.0 mg/l; in hexane; linear, by graph	R004197 (trial) 1998 ES Anal Sept 98 1998a: GC-FPD
melon, whole	0.01	0.01 0.025 0.10	107 98 92	- - -	- - -	1 1 1	<0.01 (3)	6 single points range 0.025-1.0 mg/l; in hexane; linear, by graph	R004456 (trial) 1998 ES Anal Dec 98 - Jan 99 1998a: GC-FPD
melon, peel	0.01	0.01 0.25	83 97	- -	- -	1 1	<0.01 (2)	idem	R004456 (trial) 1998 ES Anal Dec 98 - Jan 99 1998a: GC-FPD
melon, pulp	0.01	0.01 0.025	89 94	- -	- -	1 1	<0.01 (2)	idem	R004456 (trial) 1998 ES Anal Dec 98 - Jan 99 1998a: GC-FPD
strawberry	0.01	0.01 0.025 0.050	101 117 70	- - -	- - -	1 1 1	<0.01 (3)	5 single points; range 0.025-0.5 mg/l; in hexane; linear, by graph	R008027 (trial) 1998 IT Anal Dec 98- Jan 99 1998a: GC-FPD
green pepper	0.01	0.01 0.02 0.05 0.1	109 108 118 93	96-122 - - -	- - - -	2 1 1 1	<0.01 (5)	6 single points; range 0.025-1.0 mg/l; in hexane; linear, r^2>0.999	R009798 (trial) 1998 ES Anal Sept 98 - Feb 99 1998b: GC-FPD
potato, whole	0.005	0.005 0.1	84 84	72-105 75-100	9.6% 8.7%	15 14	<0.005 (13)	6 single points; range 0.003-0.1 mg/l; in hexane; linear, by graph	R016070 (trial/processing/ method validation) 1999 UK anal Dec 99-Mar00 1999: GC-FPD
potato, peel	0.005	0.005 0.1	78 68	- 64-72	- -	1 2	<0.005 (2)	idem	idem
potato, peeled	0.005	0.005 0.1	83 61	- -	- -	1 1	<0.005 (1)	idem	idem
potato, baked	0.005	0.005 0.1	75 82	- -	- -	1 1	<0.005 (1)	idem	idem
potato	0.01	0.01 0.1	101 95	97-104 88-101	3% 6%	5 5	<0.3LOQ (2)	6 single points; range 0.025-0.50 mg/l; in hexane; linear, R^2>0.999	C01520; Method validation 2000: GC-PFPD
grape	0.01	0.01 0.1	102 94	93-109 91-100	6% 4%	5 5	<0.3LOQ (2)	idem	idem
potato	0.01	0.01	106	100-110	5.0%	3	<0.01 (8)	6 single points; range 0.025-0.50 mg/l; in hexane; linearity not verified	C013482 (trial) 2000 France Anal Jan 2001 2000: GC-PFPD
potato	0.01	0.01	101	95-107	-	2	<0.01 (6)	6 single points; range 0.025-0.50 mg/l; in hexane; linear, R^2>0.999	C015231 (trial) 2000 Spain/Greece Anal Apr 2001 2000: GC-PFPD
tomato	0.01	0.01 0.02 0.04 0.1	77 102 70 98	70-88 - - 95-101	11% - - -	4 1 1 2	<0.01 (21)	6 single points range 0.025-1.0 mg/l; in hexane linear r^2>0.999 (n=2)	C016512 (trial) 2000 ES, IT Anal May-June 2001 2001a: GC-FPD
tomato	0.005	0.005 0.01 0.02 0.025 0.05	105 87 74 78 92	102-108 - - - 88-97	2.5% - - - -	5 1 1 1 2	<0.005 (30)	6 duplicate points range 0.01-0.5 mg/l; in hexane linear, r^2>0.999	C023919 (trial) 2001 ES, P Anal March 2002 2001a: GC-FPD
sweet pepper	0.005	0.005 0.01	76 71	72-80 -	4.4% -	4 1	<0.005 (18)	5 single point range 0.0125-0.2 mg/l;	C023543 (trial/method

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean	range	RSD	no	Control (mg/kg)	Linearity	Ref.
		0.015 0.05	71 90	- 87-94	- -	1 2		in hexane; linear, r^2>0.99	validation) 2001 FR, ES, I, GR Anal March 2002 2001a: GC-FPD
sweet pepper	0.005	0.005 0.01 0.02 0.025 0.05	78 71 72 73 94	75-85 - - - -	4.6% - - - -	7 1 1 1 1	<0.005 (36)	5 duplicate points range 0.0125-0.2 mg/l; in hexane; linear, r^2>0.99	C024789 (trial/method validation) 2001 ES, I Anal Mar 02 2001a: GC-FPD
potato	0.01	0.01	88	82-95	5.5%	6	<0.01 (12)	6 single points; range 0.020-0.50 mg/l; in hexane; linear: R^2>0.999	C019660 (trial/ method validation) 2001 FR, GR Anal Nov 2001 2001b: GC-PFPD
potato	0.005	0.005 0.005	84 91	65-94 75-111	19% 13%	3 15	<0.005 (41)	6 single points; range 0.020-0.50 mg/l; in hexane; linear: R^2>0.9999 (PFPD) R^2>0.99 (MS-MS)	C019661 (trial/ method validation) 2001 UK, DE, FR Anal Aug-Oct 2001 2001c: GC- PFPD/MS
cucumber	0.005	0.005 0.005 0.05	85 87 94	85-86 70-111 -	0.7% 14% -	3 - 1	<0.005 (52)	8 single points range 0.005-0.50 mg/l; in hexane; linear: R^2>0.9999 (TSD) R^2>0.999 (PFPD)	C025160 (trial/ method validation) 2001 FR, I, ES, P, GR Anal June 2002 2001d: GC- PFPD/TSD
melon, peel	0.005	0.005 0.05	79 86	70-95 -	10% -	8 1	<0.005 (9)	8 single points range 0.005-0.5 mg/l; in hexane; linear r^2>0.999 (n=2)	C025125 (trial/method validation) 2001 FR, I, ES, GR Anal July 2002 2001d: GC-TSD
melon, pulp	0.005	0.005 0.05	90 98	73-103 -	11% -	8 1	<0.005 (9)	idem	C025125 (trial/method validation) 2001 FR, I, ES, GR Anal July 2002 2001d: GC-TSD
potato	0.005	0.005 0.05	82 90	71-96 84-101	12% 8%	5 5	<0.3LOQ (2)	4 single points; range 0.02-0.2 ug/L; in hexane; linear, R^2>0.99	C028919; method validation; 2003a: GC-MS
tomato	0.005	0.005 0.05	84 88	75-90 79-101	8% 11%	5 5	<0.3LOQ (2)	idem	idem
lettuce	0.005	0.005 0.05	80 99	68-93 88-108	12% 9%	5 5	<0.3LOQ (2)	idem	idem
tomato	0.005	0.1	93	87-102	6%	5	<0.01 (4)	not verified	02-120 (storage stability) 2003a: GC-MS
potato	0.005	0.1	92	78-111	14%	6	<0.01 (4)	idem	idem
sweet pepper	0.005	0.005 0.05	102 74	101-104 71-78	- -	2 2	<0.3LOQ (1)	4 duplicate points range 0.02-0.2 ug/L in hexane; linear, R^2>0.99	C033190 (method validation) Anal. Apr/May 2003 2003b: GC-MS
melon	0.005	0.005 0.05	94 78	85-102 76-79	- -	2 2	<0.3LOQ (1)	idem	idem
cucumber	0.005	0.005 0.05	105 84	101-109 81-86	- -	2 2	<0.3LOQ (1)	idem	idem
lettuce	0.005	0.005 0.05	96 84	95-96 82-86	- -	2 2	<0.3LOQ (1)	idem	idem

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean	range	RSD	no	Control (mg/kg)	Linearity	Ref.
pepper	0.005	0.005 0.05	100 75	93-105 71-78	4.3% 5.0%	8 3	<0.005 (27)	5 duplicate points; range 0.02-0.25 ug/L; in hexane; R^2>0.99	C036690 (trial/method validation) 2002 FR, ES, I, GR Anal. Jul/Nov 2003 2003b: GC-MS
pepper	0.005	0.005 0.15 0.05	99 63 80	91-111 - 71-98	13% - 15%	4 1 4	<0.005 (18)	5 duplicate points; range 0.02-0.25 ug/L; in hexane; R^2>0.99	C036691 (trial/method validation) 2002 FR, ES, I Anal. June 2003 2003b: GC-MS
melon, whole	0.005	0.005 0.010 0.015 0.040 0.050	101 114 99 86 78	85-112 - - 85-88 76-79	11% - - - -	4 1 1 2 2	<0.005 (25)	5 duplicate points; range 0.02-0.25 ug/L; in hexane R^2>0.999	C036693 (trial) 2002 FR, ES, I Anal Aug-Sept 2003 2003b: GC-MS
melon, pulp	0.005	0.005 0.015 0.040	99 104 71	- 99-109 -	- - -	1 2 1	<0.005 (10)	idem	C036693 (trial) 2002 FR, ES, I Anal Aug-Sept 2003 2003b: GC-MS
cucumber	0.005	0.005 0.01 0.04 0.05	104 94 89 81	76-117 90-100 - 76-86	13% 5.9% - 6.2%	12 3 1 3	<0.005 (49)	5 single points; range 0.02-0.25 ug/L; in hexane; linearity not verified	C036689 (trial/method validation) 2002 FR, ES, I Anal. Sept-Oct 2003 2003b: GC-MS
melon, whole	0.005	0.005 0.05	89 76	79-102 -	13% -	3 1	<0.005 (4)	5 duplicate points; range 0.02-0.25 ug/L; in hexane; r^2>0.99	C036692 (trial/method validation) 2002 FR, ES, I Anal Oct 2003 2003b; GC-MS
melon, peel	0.005	0.005	92	90-94	2.1%	4	<0.005 (18)	idem	C036692 (trial) 2002 FR, ES, I Anal Oct 2003 2003b; GC-MS
melon, pulp	0.005	0.005	84	72-104	19%	4	<0.005 (18)	idem	C036692 (trial) 2002 FR, ES, I Anal Oct 2003 2003b; GC-MS

JFRL GC-FPD method (1988)

The analytical method used in Phillipine trials on bananas (peel and pulp, R011296) was based on extraction with acetone, clean-up and determination by GC-FPD (3% OV 17 on chromosorb WHP 80-100 mesh, 195°C, phophorus mode). Individual recoveries were not reported. The average recovery was 100% (0.01 mg/kg). Linearity was not reported. Proposed LOQ was 0.005 mg/kg and control samples were <LOQ (n=3).

GC-TSD method 1 (1988)

The analytical method used in a sugar cane processing study (C036561) was based on extraction with hexane, clean-up and determination by GC-TSD (5% OV-101 on chromosorb G, 160°C) (Brockelsby *et al*., 1988; Parthasarathy, 1989). Individual recoveries were not reported. Average recoveries were 89%-93% (0.02-0.05 mg/kg). Linearity and results for control samples were not reported. The reported LOQ was 0.01 mg/kg for sugar cane stalks, leaves and juice.

GC-FPD, method 4 (1991-)

The analytical method used in processing studies on *s*ugar cane (R016038) and potatoes (R007960), storage stability studies on *s*ugar cane commodities (R008872) and various other commodities (R008020), trials on cucumbers (R009784) and a field rotational crop study (R008901) was modified several times. The method is based on extraction of the parent and metabolite mA with MeOH, clean-up, derivatisation of metabolite A with diazomethane and determination by GC-FPD (Eng, 1992; Rhone-Poulenc, 1994a-e; Thiem, 1994). Only the validation results for the parent are shown in Table 38. The proposed LOQ was 0.005-0.01 mg/kg, but because brassica commodities and some batches of diazomethane contained compounds that interfered with quantification of the parent, the valid LOQ should be increased to at least 0.05 mg/kg.

Independent validation: In separate experiments, ethoprophos and metabolite mA were quantitatively recovered from resin/nuchar/attaclay (100%), GPC columns (98%-122%) and silica gel columns (84%-98%). Physical characteristics of GPC columns changed during several weeks of non-use and it is recommended to eliminate this step. In the ILV a DB-5 column (temperature 60-260°C) was used. The linear range was 7-25 pg injected instead of 5-200 pg as in the original method. An interference was found at the retention time of ethoprophos owing to impurities in the diazomethane used. Changes in GC conditions and GC columns did not resolve the problem, so ethoprophos was determined separately without the methylation step. This resulted in average matrix interferences of 0.076 mg/kg apparent ethoprophos, which is unacceptably high.

Method performance for ethoprophos and metabolite mA is generally better for crops of high to moderate moisture. The method will generally fail for mA if dry and oily crops are not hydrated before extraction. Chromatograms were characterized by numerous peaks which made interpretation difficult, especially for cruciferous plants (e.g. brassicas). Certain batches of diazomethane contained compounds that interfered with quantification of parent ethoprophos. Derivitization efficiency and precision for metabolite mA were not verified. Because of matrix interferences, the LOQ for parent ethoprophos should be increased to at least 0.05 mg/kg.

Table 38. Validation results for the determination of ethoprophos (parent) using GC-FPD method 4.

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean	range	RSD	no	Control (mg/kg)	Linearity	Ref.
cabbage	0.005	0.005	87	74-95	8.0%	7	<0.3LOQ-0.0028 (8)	6 single points; range 0.005-0.1 mg/l; in hexane linear; R2>0.98	R009735 (method validation) Anal Oct/Nov 91 Original version
		0.01	96	80-113	13%	7			
		0.05	99	85-107	8.1%	5			
		0.5	89	78-109	13%	5			
sugar cane, stalks	0.01	0.01	83	72-94	11%	6	0.0032 (1)	4 single points; range 5-50 ug/L; in iso-octane linear by graph	R016038 (method validation, processing study) Anal Feb 93 Version 3.0
		0.05	85	81-92	4.4%	6			
		0.5	88	84-91	3.0%	6			
sugar cane, bagasse	0.01	0.01	93	82-102	9.2%	6	<0.3LOQ (1)	idem	idem
		0.05	82	74-86	5.3%	6			
		0.5	87	85-90	8.1%	6			
sugar cane, sugar	0.01	0.01	104	96-114	7.5%	6	<0.3LOQ (1)	idem	idem
		0.05	103	97-108	3.7%	6			
		0.5	99	93-101	3.3%	6			
sugar cane, molasses	0.01	0.01	86	70-95	13%	6	<0.3LOQ (1)	idem	idem
		0.05	89	79-104	11%	6			
		0.5	96	90-101	5.0%	6			
sugar cane, syrup	0.01	0.01	99	84-120	15%	9	<0.3LOQ (1)	idem	idem
		0.05	96	85-105	7.8%	9			
		0.5	100	78-111	11%	9			
sugar cane, clarified juice	0.01	0.01	91	79-105	11%	6	<0.3LOQ (1)	idem	idem
		0.05	86	87-92	6.0%	6			
		0.5	95	86-99	5.8%	6			
sugar cane,	0.01	0.01	83	72-92	10%	5	0.0043 (1)	idem	idem

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean	range	RSD	no	Control (mg/kg)	Linearity	Ref.
mixed juice		0.05 0.5	91 98	80-104 91-102	8.8% 3.8%	6 6			
sugar cane, clarifier mud	0.01	0.01 0.05 0.5	100 87 93	89-107 79-95 83-100	8.3% 8.0% 7.5%	6 6 6	<0.3LOQ (1)	idem	idem
potato tubers	0.01	0.01 0.05 0.5	97 99 94	94-100 95-106 90-97	2.4% 4.2% 3.9%	6 6 6	<0.3LOQ (1)	4 single points; range 5-50 ug/L; in iso-octane linear by graph	R007960 (method validation, processing study) Anal Jul/Aug 93 Version 7.0
potato, dry peel	0.01	0.01 0.05	97 97	93-103 90-105	4.7% 5.4%	4 4	<0.3LOQ (1)	idem	idem
potato, chips	0.01	0.01 0.05	108 106	99-116 103-109	7.1% 2.7%	4 4	<0.3LOQ (1)	idem	idem
potato, wash water	0.01	0.01 0.05	94 99	90-98 96-102	3.7% 2.4%	4 4	<0.3LOQ (1)	idem	idem
lima bean pods	0.005	0.02 0.1	93 80	93-94 74-91	- 9.5%	2 4	0.065-0.088 (4)	5 single points range 7-25 pg injected; in iso-octane; r>0.98	C037530 (ILV) Anal 1994 Version 2.0, without methylation step
cabbage	0.02	0.2	100	95-104	4.5%	3	<0.3LOQ-0.016 (9)	5 single points; range not stated; in iso-octane; r^2>0.99	R008020 (method validation, storage stability) Anal. 1993-94 Version 3.0
potato tuber	0.02	0.2	99	95-104	4.8%	3	<0.3LOQ-0.018 (12)	idem	idem
pineapple bran	0.02	0.2	103	98-107	4.6%	3	<0.3LOQ-0.015 (12)	idem	idem
pineapple fruit	0.02	0.2	102	98-104	3.2%	3	<0.3LOQ-0.014 (11)	idem	idem
pineapple feed pulp	0.02	0.2	84	80-86	4.1%	3	<0.3LOQ-0.017 (10)	idem	idem
pineapple juice	0.02	0.2	102	92-110	9.0%	3	<0.3LOQ-0.016 (7)	idem	idem
peanut kernels	0.02	0.2	97	90-101	6.3%	3	<0.3LOQ-0.012 (12)	idem	idem
peanut meal	0.02	0.2	86	80-96	10%	3	<0.3LOQ-0.031 (9)	idem	idem
peanut vines	0.02	0.2	108	100-117	7.9%	3	<0.3LOQ-0.007 (9)	idem	idem
peanut hay	0.02	0.2	94	93-96	1.8%	3	<0.3LOQ-0.012 (10)	idem	idem
peanut hulls	0.02	0.2	114	110-117	3.1%	3	<0.3LOQ (9)	idem	idem
peanut refined oil	0.02	0.2	86	72-104	19%	3	<0.3LOQ-0.022 (9)	idem	idem
peanut crude oil	0.02	0.2	96	83-111	15%	3	<0.3LOQ-0.005 (8)	idem	idem
peanut soap stock	0.02	0.2	64	60-66	3.4%	9	<0.3LOQ-0.013 (13)	idem	idem
corn starch	0.02	0.2	100	94-106	6.0%	3	<0.3LOQ-0.011 (11)	idem	idem
corn fodder	0.02	0.2	112	109-116	3.1%	3	<0.3LOQ (11)	idem	idem
corn meal	0.02	0.2	99	98-100	1.0%	3	<0.3LOQ-0.014 (9)	idem	idem
corn grain	0.02	0.2	108	105-113	4.3%	3	<0.3LOQ-0.014 (13)	idem	idem
corn grain dust	0.02	0.2	85	81-91	6.5%	3	<0.3LOQ-0.015 (9)	idem	idem
corn forage	0.02	0.2	100	92-105	7.2%	3	<0.3LOQ (10)	idem	idem

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean	range	RSD	no	Control (mg/kg)	Linearity	Ref.
corn refined oil	0.02	0.2	78	72-81	6.7%	3	<0.3LOQ-0.014 (9)	idem	idem
corn crude oil	0.02	0.2	80	77-81	2.9%	3	<0.3LOQ-0.012 (9)	idem	idem
sugar cane stalks	0.005	0.2	86	73-96	13%	4	<0.3LOQ-0.041 (41)	5 single points 0.01-0.25 mg/l in iso-octane r^2>0.99	R008872 (method validation, storage stability) Anal 1994. Version 3.0
sugar cane molasses	0.005	0.2	87	78-96	9.2%	4	<0.3LOQ-0.051 (41)	idem	R008872 (method validation, storage stability) Anal 1994 Version 3.0
sugar cane refined sugar	0.005	0.2	97	93-100	3.1%	4	<0.3LOQ-0.12 (41)	idem	R008872 (method validation, storage stability) Anal 1994 Version 3.0
cucumber	0.01	0.01 0.05 0.5	89 89 90	86-92 87-92 84-95	2.4% 2.2% 4.9%	5 5 5	-	4 single points 15-150 pg injected in iso-octane; loglinear by graph	R009784 (method validation) Version 6.0
cucumber	0.01	0.01 0.05 0.5	95 95 99	87-108 82-106 97-101	5.8% 8.0% -	13 11 2	<0.01 (12)	4 single points 15-150 pg injected in iso-octane; r>0.99 (log-log)	R009784 (method validation/ trial/storage stab) Anal Oct 93/Feb 94 Version 6.0
field corn grain	0.01	0.01 0.05 0.5	96 94 90	90-98 91-97 88-96	3.1% 2.1% 3.2%	6 6 6	<0.3LOQ (1)	4 duplicate points 5-50 ug/L in iso-octane; linear graph (log-log)	R008901 (method validation) Anal May 94 Version 13.0
field corn forage	0.01	0.01 0.05 0.5	98 98 95	88-105 96-101 91-99	6.3% 2.0% 3.5%	6 6 6	<0.3LOQ (1)	idem	idem
field corn fodder	0.01	0.01 0.05 0.5	107 95 88	105-111 92-98 84-93	2.5% 2.3% 3.7%	6 6 6	<0.3LOQ (1)	idem	idem
collards	0.01	0.01 0.5	92 83	- -	- -	1 1	<0.01 (1)	4 duplicate points 5-50 ug/L in iso-octane r^2>0.98 (log-log)	R008901 (rotational crop study) Anal Aug-Nov 96 Version 13.0
pea forage	0.01	0.01 0.5	100 96	87-112 87-109	10% 10%	4 4	<0.01 (4)	idem	idem
pea seeds	0.01	0.01 0.5	80 76	71-85 75-78	9.7% -	3 2	<0.01 (3)	idem	idem
pea straw	0.01	0.01 0.5	82 76	77-90 74-79	8.8% 3.0%	3 3	<0.01 (3)	idem	idem
mustard forage	0.01	0.01 0.5	94 88	90-101 84-92	6.1% 4.5%	3 3	<0.01 (3)	idem	idem
radish roots	0.01	0.01 0.5	87 83	78-97 63-95	8.6% 13%	7 7	<0.01-0.013 (7)	idem	idem
radish tops	0.01	0.01 0.5	96 91	86-104 80-99	6.8% 6.2%	7 7	<0.01 (7)	idem	idem
red leaf lettuce	0.01	0.01 0.5	78 81	70-90 73-92	13% 13%	6 6	<0.01 (6)	idem	idem
wheat forage	0.01	0.01 0.5	96 90	92-102 83-98	4.7% 6.8%	4 4	<0.01 (4)	idem	idem
wheat grain	0.01	0.01 0.5	86 76	83-93 74-78	6.4% 2.6%	3 3	<0.01 (3)	idem	idem
wheat straw	0.01	0.01 0.5	86 78	82-93 73-84	6.5% 7.0%	3 3	<0.01 (3)	idem	idem

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean	range	RSD	no	Control (mg/kg)	Linearity	Ref.
sorghum forage	0.01	0.01 0.5	95 87	87-101 81-95	7.8% 8.0%	3 3	<0.01 (3)	idem	idem
sorghum grain	0.01	0.01 0.5	87 81	77-96 77-86	- -	2 2	<0.01 (2)	idem	idem
sorghum straw	0.01	0.01 0.5	88 81	77-96 77-86	- -	2 2	<0.01 (2)	idem	idem
soya bean forage	0.01	0.01 0.5	100 87	94-106 86-88	- -	2 2	<0.01 (2)	idem	idem
soya bean grain	0.01	0.01 0.5	89 82	- -	- -	1 1	<0.01 (1)	idem	idem
soya bean straw	0.01	0.01 0.5	80 74	- -	- -	1 1	<0.01 (1)	idem	idem

GC-NPD method 1 (1996)

GC-NPD method 1 (Capri *et al*., 1998) was used in Italian trials on tomato (R008029). Crops were blended with diatomaceous earth and ethyl acetate. After filtration, the extract was concentrated and ethoprophos was determined by GC-NPD (DB-5 column, 60-280°C). The reported LOQ was 0.01 mg/kg in tomato (fruit and plant), and the reported recoveries ± RSD 90% ± 13 for 1 ng and 90% ± 10% for 2 ng (equivalent mg/kg sample and individual values were not reported.

AOAC method 970.52

AOAC method 970.52 was used in a duplicate diet study carried out in the USA (Fenske *et al*., 2002), where residues <LOQ were found. Homogenised samples (20 g fruits or vegetables, 300 ml beverages, 100 ml dairy products) were extracted with ACN. The extract was washed with 30% aqueous sodium chloride and hexane. Water was added and residues were partitioned into DCM. Samples were concentrated and brought to 2 ml in hexane/acetone (1:1). Ethoprophos was determined using GC-PFPD (DB-1 column). Calibration was by external standardization at 3-5 concentration levels. Performance characteristics (n=3-6) were as follows.

- fresh fruits and vegetables: LOQ 0.005 mg/kg, mean recovery 77% at 0.025 mg/kg. This food group was represented by a mixture of equal portions of cored apples and peeled bananas.
- fruit juices and beverages: LOQ 0.033 mg/kg, mean recovery 91% at 0.067 mg/g, represented by a mixture of apple juice, grape juice and orange juice (with pulp).
- dairy products: LOQ 0.005 mg/kg, mean recovery 100% at 0.020 mg/kgs food, represented by whole milk.
- processed foods: LOQ 0.005 mg/kg, mean recovery 67% at 0.025 mg/kg, represented by a mixture of cookies, sugar pops, corn tortillas, bologna, corn chips, oatnut bread, macaroni and cheese.

Further details were not available.

Multi-residue GC method

The multi-residue GC method was used in a residue monitoring study carried out in Belgium, where no residues were found. The method is used for determination of organochlorine, organophosphorus, and nitrogen-containing pesticides in vegetables and fruits. Samples are extracted with petroleum etheracetone followed by liquid-liquid partitioning with water. Apolar pesticides are found in the petroleum ether-phase, polar pesticides are extracted from the aqueous layer with DCM. Analysis is by GC-ECD, GC-FPD or GC-TSD. Further details were not available.

Analytical methods for environmental studies

The Meeting received information on analytical methods for the determination of ethoprophos and mA in soil used in soil degradation and rotational crop studies. Various other methods for analysis of soil, air and water are not included, because the corresponding studies were not evaluated.

GC-FPD method 5 (1984)

GC-FPD method 5 was used in soil degradation study 1. Soil was extracted with MeOH. The MeOH extract was mixed with 10% (w/v) NaCl and partitioned into hexane. The hexane extract was filtered through anhydrous sodium sulfate and concentrated. Ethoprophos was determined by GC-FPD (10% OV101 on diatomite CQ (80/100 mesh), temperature 190°C, phosphorus mode). Calibration was by external standardization. Validation results are shown in Table 40.

Table 40. Validation results for the determination of ethoprophos using GC-NPD method 5.

Sample	LOQ reported mg/kg	Spike mg/kg	Recovery, % mean range	RSD	no	Control (mg/kg)	Linearity	Ref.
sandy clay loam sandy loam	-	0.53 1.1 5.3 14	84 78-89 93 90-96 84 79-90 90 86-95	- - - -	2 2 2 2	-	10 single points; range 0-5 mg/l in hexane; linear: r>0.999	R009121 (soil degradation) method validation

Rhone Poulenc method 172 (1984-1991)

Rhone Poulenc method 172 (Perette *et al*., 1984) is a modification of Mobil Chemical method 96-78 (25 Sept 1978). Dry soil is extracted with MeOH. The filtered MeOH extract is mixed with 10% aqueous NaCl and partitioned into hexane. The hexane extract is filtered through anhydrous sodium sulfate and concentrated. Ethoprophos is determined by GC-FPD (3% Silar 5CP on 80/100 GCQ or 3% OV-17, temperature 220°C, phosphorus mode). Calibration is by external standardization.

Validation results are shown in Table 41. In addition, samples were fortified with radiolabelled ethoprophos and analysed both by GC-FPD and LSC. Results were similar (ratio 0.88-1.1).

Method 172, version 1991, was used in soil degradation study 3 (R009121). The detection system was changed to GC-NPD (capillary OV-1, temperature programme 150-245°C).

Table 41. Validation results for the determination of ethoprophos using method 172.

Sample	LOQ reported mg/kg	Spike mg/kg	Ratio FPD/LSC mean range	Recovery, % mean range GC-FPD	RSD	no	Control (mg/kg)	Linearity	Ref.
loam sandy loam	0.01	0.01 0.1 1 10	1.1 0.95-1.1 1.0 0.88-1.1 1.0 0.94-1.1 1.0 0.91-1.1	107 97-115 100 91-107 100 91-107 91 82-98	5.8% 5.2% 6.8% 7.2%	7 8 5 5	-	6 single points; range 0.1-2.0 mg/l; in hexane; not verified	R009187 (method validation) original version
humic sand sandy loam loamy silt	0.01	0.01 0.05 0.1 0.25 0.50 1.0 5.0	-	88 - 90 88-91 91 - 91 - 94 - 92 - 80 -	- - - - - - -	1 2 1 1 1 1 1	<0.01 (3)	-	R009121 (soil degradation) version 1991

Stability of pesticide residues in stored analytical samples

The Meeting received data on the stability of residues in crops with high water content (pineapple, broccoli, cabbage, potatoes, sweet potatoes, tomato), dry crops with starch and protein (maize), dry crops with fat or oil, starch and protein (peanut), miscellaneaous crops (sugar cane, tobacco (green and cured)), processed commodities (pineapple juice, peanut and maize oil, maize starch, refined cane sugar) and feed items (pineapple bran and feed pulp, peanut hulls, meal, vines and dry hay, maize meal, forage, fodder, and grain dust, sugar cane molasses) stored frozen. Crops with high water and high acid content (citrus fruits) were not investigated.

Study 1. Broccoli, cabbage, dry peanut hay, and green and cured tobacco were spiked with ethoprophos at 0.05 mg/kg and stored at –20°C over a 9-18 months period (R009168, Perez, 1986, non-GLP). Sweet potatoes from a field trial (Ville Pratte, LA, USA) were treated with 10 kg ai/ha at lay-by (3 Aug 1984) and harvested after 101 days. They contained 0.06 mg/kg ethoprophos as incurred residues at initial analysis (259 days after harvest). Duplicate samples were analysed by method 175-1985 (procedures 8.1-8.4). Results were not corrected for concurrent recoveries (73%-109%), nor for interferences (<0.3 LOQ). They are shown in Table 42.

Table 42. Frozen storage stability of 0.05 mg/kg ethoprophos on various commodities (n=2) stored at –20°C.

Sample	Storage (months)	Ethoprophos remaining, % mean	range	Ethoprophos, concurrent recovery %
Broccoli	0	108	105-111	105
	6	76	69-82	99
	9	74	68-80	94
	12	56	54-58	92
Cabbage	0	107	104-108	104
	10	94	86-101	109
	12	84	84-84	92
Sweet potato[1]	0	100	0.058 mg/kg	-
	9	94	0.048-0.061 mg/kg	103
Peanut hay	0	91	90-92	96
	6	44	43-45	101
	9	42	40-44	101
	12	41	38-44	86
Tobacco green	0	90	84-96	84
	6	75	70-80	106
	9	113	106-120	73
	12	96	94-97	103
	18	92	88-96	84
Tobacco cured	0	82	82-82	84
	6	57	56-58	98
	9	92	90-94	76
	12	95	94-96	84
	18	61	54-68	86

[1] contained 0.058 mg/kg ethoprophos as incurred residues at initial analysis (259 days after harvest)

Study 2. Pineapple, cabbage, potato, peanut, maize, their processed products and their feed byproducts were spiked with either ethoprophos or mA at a concentration of 0.20 mg/kg (R008020, Ibrahim, 1995). Samples were stored for a period of 12 months. One set was stored at –5°C and another set at –20°C. Samples stored at –5°C were analysed first and if the residues were stable at this temperature, the set stored at –20°C was not analysed. Samples were analysed using GC-FPD, method 4, version

3.0. Results were not corrected for concurrent recoveries (37%-118%), but were corrected for matrix interferences (up to 0.031 mg/kg for ethoprophos and up to 0.007 mg/kg for mA). Results from the –20°C set are shown in Table 43.

Table 43. Frozen storage stability of 0.2 mg/kg ethoprophos or 0.2 mg/kg mA on various commodities (n=3) stored at –20°C or -5°C (pineapple juice).

Sample	Storage (months)	Ethoprophos remaining % mean	range	RSD	Ethoprophos, concurrent recovery %	mA remaining % mean	range	RSD	mA, concurrent recovery %
Pineapple fruit	0	85	70-97	16	95	75	72-81	7	80
	3	83	80-86	4	97	80	78-82	3	89
	6	83	81-85	3	91	76	75-77	2	85
	9	81	76-86	6	89	70	69-71	1	79
	12	62	57-69	10	75	67	64-70	5	79
Pineapple juice	0	97	94-102	5	93	90	86-93	4	89
(at -5°C)	3	93	76-103	16	97	92	90-95	6	96
	6	75	71-77	4	81	79	79-80	1	89
	9	99	90-106	8	113	83	80-86	4	96
	12	86	83-89	4	79	74	73-75	2	79
Pineapple bran	0	99	90-115	14	83	83	68-96	17	71
	3	70	62-78	11	91	57	55-60	5	86
	6	78	78-79	1	99	61	59-64	4	87
	9	81	76-87	7	104	55	48-60	12	84
	12	58	52-64	10	90	48	41-55	15	78
Pineapple feed pulp	0	118	110-127	7	116	84	80-86	4	88
	3	67	66-69	3	91	59	58-62	4	82
	6	73	67-78	8	91	61	58-64	5	84
	9	78	72-82	7	87	61	57-64	6	83
	12	55	52-59	7	87	50	46-53	7	69
Cabbage	0	85	71-93	14	82	87	86-91	2	86
	9	99	94-104	5	108	72	71-75	3	85
Potato	0	122	77-188	48	89	86	79-90	7	84
	2[1]	94	94-94	-	108	81	80-82	-	95
	3	78	65-94	19	90	78	75-80	3	91
	6	77	67-85	12	86	56	49-61	11	82
	9	95	92-100	4	101	55	53-56	3	79
	12	85	83-87	3	94	54	53-54	1	82
Peanut kernels	0	77	70-82	8	82	83	79-85	4	84
	1.5	78	76-81	3	90	91	90-92	1	89
	3	53	52-56	4	84	70	68-72	3	89
	6	48	47-51	5	71	68	67-68	1	72
	9	68	67-70	2	102	81	79-84	3	95
	12	69	66-73	5	84	75	75-75	0	83
Peanut crude oil	0	77	75-79	3	70	86	85-88	2	73
	6	78	73-83	6	78	63	60-65	4	68
Peanut refined oil	0	82	77-85	5	73	95	92-98	3	91
	3	81	80-83	2	89	81	80-83	2	89
	6	89	86-90	3	88	65	64-66	2	77
	9	80	74-84	7	85	59	52-64	11	80
	12	84	82-86	3	79	73	73-74	1	76
Peanut hull	0	94	90-100	6	92	86	86-87	1	90
	3	76	74-79	4	94	55	54-56	2	86
	6	72	69-73	3	95	42	40-45	7	84
	9	56	54-60	6	93	35	32-37	8	83
	12	61	57-64	6	89	34	30-39	14	77
Peanut meal[2]	0	95	93-100	5	93	81	80-84	3	81
	3	58	52-61	9	75	53	51-57	6	80
	6	48	40-54	15	83	39	37-41	5	71
	9	58	49-63	13	94	50	44-54	11	83
	12	50	46-53	7	96	43	42-43	1	79

Sample	Storage (months)	Ethoprophos remaining % mean	range	RSD	Ethoprophos, concurrent recovery %	mA remaining % mean	range	RSD	mA, concurrent recovery %
Peanut soapstock	0	61	61-62	1	63	72	72-73	1	74
	3	58	53-64	9	61	48	33-71	43	37
	6	64	59-69	8	72	76	60-99	26	111
Peanut vines	0	96	87-105	9	96	87	85-91	4	88
	3	91	87-98	7	100	29	28-30	3	91
	6	89	87-91	2	90	19	18-19	3	78
	9	89	85-92	4	91	13	12-15	11	78
	12	80	78-84	4	92	9	7-11	24	82
Peanut hay	0	94	91-99	5	93	90	87-93	3	91
	3	86	80-90	6	100	29	27-30	5	83
	6	76	73-80	5	93	17	16-18	6	78
	9	67	59-74	11	88	18	17-19	6	76
		68	68-68	0	83	17	16-18	6	78
	12	72	72-73	1	88	15	13-16	10	77
Corn grain	0	111	109-114	2	114	91	89-93	2	97
	1.5	94	90-99	5	108	54	48-60	11	88
	3	79	72-85	8	90	39	35-44	16	91
	6	85	81-88	4	97	35	35-36	2	81
	9	86	83-90	4	107	36	36-37	2	89
	12	112	77-171	46	97	37	28-48	27	75
		77	72-81	6	100	32	29-34	8	81
Maize starch	0	102	98-108	5	101	79	76-82	4	91
	3	115	106-125	8	106	28	26-31	9	77
	6	97	93-105	7	105	25	21-29	16	77
	9	104	99-108	4	118	21	19-24	13	69
	12	83	81-84	2	91	18	17-19	6	66
		85	83-87	2	92	19	17-21	11	58
Maize crude oil	0	71	69-73	3	72	81	80-83	2	80
	3	71	69-75	5	68	80	78-82	3	84
	6	70	66-73	5	74	68	67-69	2	75
Maize refined oil	0	69	65-75	7	70	81	79-84	3	84
	4	64	56-68	11	64	66	64-68	3	74
	6	80	77-81	3	72	61	60-62	2	71
	9	88	86-92	4	90	72	70-73	2	88
	12	82	80-87	5	83	73	71-75	3	82
Maize meal	0	104	103-105	1	91	89	88-89	1	80
	3	90	83-99	9	83	58	52-62	9	67
	6	104	100-112	6	105	68	63-74	8	88
	9	106	99-111	6	105	64	60-66	5	74
	12	90	89-91	1	95	54	53-54	1	67
Maize forage	0	95	89-102	7	92	85	83-88	3	84
	3	81	77-84	4	93	66	64-69	4	91
	6	82	81-84	2	86	55	53-56	3	75
	9	78	71-83	8	109	52	48-56	8	87
	12	74	67-81	10	93	51	45-55	10	75
Maize fodder	0	98	96-100	2	90	92	90-94	2	86
	1.5	81	76-86	6	91	67	65-70	4	87
	3	75	72-78	4	91	59	58-60	2	87
	6	86	83-90	4	98	56	54-58	4	83
	9	85	81-88	4	105	47	45-49	5	86
	12	74	67-81	10	93	51	45-55	10	75
		71	70-72	1	88	42	39-45	7	71
Maize grain dust	0	86	75-97	13	85	79	68-90	14	77
	3	79	72-83	8	90	66	63-68	4	85
	6	87	85-89	2	97	68	66-70	3	82
	9	85	75-92	11	113	61	54-68	12	88
	12	91	89-93	2	98	70	69-70	1	79

[1] Sample analysed in duplicate, not in triplicate
[2] Peanut meal control samples contained matrix interferences at 0.039 mg/kg ethoprophos eq.

Study 3. Samples of sugar cane and its processed commodities were spiked with either ethoprophos or mA at a concentration of 0.20 mg/kg (R008872, Eng, 1996) and stored at –20°C for 15 months. Triplicate samples were analysed using GC-FPD, method 4, version 3.0. Results were not corrected for concurrent recoveries (68%-105%), but were corrected for matrix interferences (<0.3 LOQ-0.12 mg/kg for ethoprophos, <0.3 LOQ for mA). Results are shown in Table 44.

Table 44. Frozen storage stability of 0.2 mg/kg ethoprophos or 0.2 mg/kg mA on sugar cane and its processed commodities (n=3) stored at –20°C.

Sample	Storage (days)	Ethoprophos remaining % mean	range	RSD	Ethoprophos, concurrent recovery %	mA remaining % mean	range	RSD	mA, concurrent recovery %
sugar cane	0	91	90-91	1	85	84	83-84	1	72
	44	73	70-76	4	95	77	73-79	4	87
	92	65	55-71	13	69	63	60-67	6	73
	167	80	75-87	8	93	74	73-76	2	79
	276	82	76-87	7	92	76	72-79	5	89
	358	73	62-91	22	81	67	62-74	9	91
	453	73	60-88	19	89	83	69-93	15	79
molasses	0	83	70-89	13	86	79	73-84	7	78
	44	86	75-94	12	88	88	80-93	8	87
	92	75	68-83	10	84	62	59-65	5	72
	166	86	74-94	12	81	74	63-83	14	91
	275	86	75-92	11	77	85	73-94	13	74
	357	109	104-113	4	91	96	73-108	21	103
	453	102	98-105	4	105	60	57-65	7	68
refined sugar	0	88	82-93	6	90	76	75-77	1	76
	44	89	86-92	3	95	71	67-73	5	74
	92	67	65-71	4	89	63	58-65	6	68
	163[1]	79	68-93	16	100	68	61-72	9	72
	276	92	88-96	4	97	87	86-87	1	83
	361	68	59-78	14	84	80	78-83	4	87
	451	81	72-88	10	84	82	75-89	9	93

[1] Apparent ethoprophos in control sample of refined sugar at 163 days of storage is 0.58 LOQ.

Study 4. Untreated potato samples were spiked with ethoprophos at 0.10 mg/kg and stored at –18°C for 9 months (Quintelas, 2000). Duplicate spiked samples were analysed using method AR 52-87, 1997, GC-FPD. Results were not corrected for concurrent recoveries (74%-95%), nor for interferences (<0.01, n=4). Results are shown in Table 45.

Table 45. Frozen storage stability of 0.1 mg/kg ethoprophos on potatoes (n=2) stored at –18°C.

Storage (months)	Remaining % mean	range	concurrent recovery % at 0.1 mg/kg
0	95	95-95	95
3	54	47-60	74
6	93	92-94	95
9	76	71-80	84

Study 5. Cucumbers in trial 93-0089 were treated with a single 13 kg ai/ha pre-planting soil EC application and three replicate field samples were harvested 69 days after treatment (Kowite, 1994a). The samples were stored for 105 days at -18°C and then analysed for the first time using GC-FPD method 3, 1994, version 6.0. Results were not corrected for interferences (<0.01 mg/kg) nor for concurrent recoveries (86%-98%). Samples were stored at -18°C for another 125 days (230 days since harvest). Results are shown in Table 46.

Although metabolite mA remained stable during the test period, no information is available for the first 105 days of storage. Therefore no conclusions can be drawn on overall storage stability.

Table 46. Frozen storage stability of incurred ethoprophos and metabolite mA in cucumbers stored at –18°C.

Storage (days)	mg/kg parent	mg/kg mA	% mA remaining	concurrent recovery % parent; mA
105	<0.01 (3); mean <0.01	0.047; 0.060; 0.078; mean 0.062	100[1]	89; 86
111	<0.01 (3); mean <0.01	0.058; 0.071; 0.080; mean 0.070	113	96; 89
230	<0.01 (3); mean <0.01	0.055; 0.061; 0.079; mean 0.065	105	98; 90

[1] % remaining set at 100% at 105 days of storage; storage stability for the first 105 days not known.

Study 6. Potato and tomato samples were fortified with ethoprophos at 0.10 mg/kg (Uceda, 2004). Duplicate spiked samples were stored at -18°C and analysed for ethoprophos at day 0, and 2, 12 and 19 months using method AR 52-87, 2003a, GC-MS. Results, uncorrected for concurrent recoveries (82%-111%) or interferences (<0.01, n=4) are shown in Table 46A.

Table 46A. Frozen storage stability of 0.1 mg/kg ethoprophos on potato and tomato stored at –18°C.

Sample	Storage period	Remaining % mean	range	Concurrent recovery % at 0.1 mg/kg
Potato	0 day	98	95-100	-
	2 months	88	78-84	82
	12 months	70	59-84	85, 78
	19 months	83	80-86	111
Tomato	0 day	88	87-89	-
	2 months	98	96-100	94
	12 months	96	91-101	94
	19 months	88	84-93	102

USE PATTERN

Ethoprophos is an organophosphorus insecticide and nematicide registered in over 58 countries for use on a wide variety of crops and field-grown ornamentals. The crops selected for the 2004 JMPR review encompass the ones, which represent the highest market segments worldwide (strawberry, banana, pepper, tomato, melon, cucumber, potato, sweet potato, and *s*ugar cane). Other uses of ethoprophos, not evaluated here, are on fruit trees (e.g. citrus, orange, lemon, grapefruit, apple, pear, peach, mulberry), fruit and vine crops, pistachios, olives, passion fruit, pineapple, tree tomato, radish, garlic, red onion, onion, aubergine, courgette, okra, baby marrows, butternuts, patti pans, head cabbage, cauliflower, endive, lettuce, spinach, artichokes, asparagus, leeks, peas, chickpeas, beans, green beans, French beans, snap beans, Lima beans, field beans, soya beans, peanuts, cotton, African oil palm, cereals (wheat, barley, rye, triticale, oats, spelt), sweet corn, maize (corn), field corn, rice, sorghum, coffee plants, grass, beets, sugar beets, tobacco, pine trees, horticulture (flowers, ornamentals, rose, chrysanthemum, carnation) and nurseries (fruit trees, olives, citrus).

Ethoprophos is a non-systemic, contact product to be used exclusively as a soil treatment. The use of any of the ethoprophos formulated products (GR, MG, EC, gel) must be followed by thorough soil incorporation (soil depth down to about 20 cm in some cases). Incorporation can be achieved either by watering-in (for banana for example) or by mechanical incorporation using suitable tillage equipment. The incorporation step is mandatory to enhance the effectiveness of the product as it is used to eradicate mainly soil-dwelling insects and nematodes.

Granular formulated products are applied either at pre-planting, or pre emergence or planting stages. For the crops for which a transplanting step is required (such as fruiting vegetables), ethoprophos is applied before or at the transplanting stage. For perennial crops such as banana and sugar cane, ethoprophos can be applied during the vegetative stages of the crops. Application of granular formulations is usually restricted to one application per growing cycle except banana to which the product can be applied twice a year. The granular product is applied either as a band or as an overall application.

Emulsifiable concentrates can be applied either at the pre-plant/planting stages (usually once) or post-planting/transplanting stages. In the latter case the liquid formulation is applied through the drip irrigation water, when the number of application can be up to 4 –5 per growing cycle depending on the crop.

Emulsifiable concentrate gel products are registered only in Mexico. The product is packaged as a water-soluble bag to be diluted in the proper amount of water before spraying using conventional ground equipment. Gel application is usually performed either at planting (potato) or post-planting (cucumber).

Tables 47 to 56 outline the current world-wide use patterns for ethoprophos. The manufacturer provided the GAP data in summarized form, as original labels and as English translations. No labels were available for Tunisia or Algeria, but they are the same as for Morocco. No labels were available for Ireland, but they are the same as for the UK.

For some crops ethoprophos is applied out either overall (broadcast over the entire surface) or as a band (also referred as row application). In the USA (except for banana/plantain) the maximum number of applications is restricted to 1 per year for the investigated crops. For band application, the dose rate per hectare can be expressed either on the entire surface area or the treated area. The calculation of the dose rate based upon the treated area is performed according to the label's instructions (bandwidth, row spacing) whenever possible. If overall or band is not specified on the label, the method of application is referred to as "soil treatment".

Application rates for bananas are given only as g ai/tree. For fruiting vegetables with edible peel (cucumber, sweet pepper, tomato) the PHI specified on the labels is either 30 days or 60 days. A PHI of 30 days does not seem relevant for a fruiting crop if the application is either pre-planting or at planting.

Table 47. Registered uses of ethoprophos on strawberries.

Country	Site	Formulation (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No	PHI (days)
Austria	F/I	GR 100	Soil treatment	6.0	na	ns	ns
Spain	F/I[1]	EC 200	Soil treatment (15 days before transplanting)	6.0	ns	1	60

F: open field; I: indoor, may be greenhouse or plastic cover;
na: not applicable, direct treatment with granular formulation
ns: not stated on label
[1] almost all commerical farms in Spain cultivate strawberries under plastic tunnels. On the label no distinction is made between indoor and outdoor crops (Barriere, 2004a)

Table 48. Registered uses of ethoprophos on bananas and plantains in the field.

Country	Formulation (g ai/kg; g ai/l)	Application method	Dose rate g ai/tree	Spray conc. kg ai/hl	No; (interval, days)	PHI (days)
Brazil	GR 100	Half moon around the stem	3.0	na	2	3

Country	Formulation (g ai/kg; g ai/l)	Application method	Dose rate g ai/tree	Spray conc. kg ai/hl	No; (interval, days)	PHI (days)
		(at beginning and end of rainy season)				
Cameroon	MG 100	Around the stem (0.50 m radius)	4.5 (57 kg ai/treated ha)	na	2-3; reapply every 4-6 months	ns
Central America[1]	GR 100; GR 150; EC 720	Soil treatment (at beginning of rainy season)	2.9-3.0	na/ns	1	30
Columbia	GR 50	Around the stem (0.75 m radius)	4.0 (23 kg ai/treated ha)	na	2; reapply every 6 months	ns
Columbia	GR 100	Around the stem (0.75 m radius)	3.0 (17 kg ai/treated ha)	na	2; reapply every 6 months	ns
Columbia	GR 110 Biodac	On the shoot about to sprout	3.3	na	3; reapply every 4 months	ns
Columbia	GR 150 Biodac	Around the stem (0.40 m radius)	3.0 – 3.8 (60-75 kg ai/treated ha)	na	3; reapply every 4 months	ns
Ecuador	GR 150 Biodac	Soil treatment	3.0	na	2 - 3	0
France	MG 100	Around the stem	4.0-4.5	na	ns	ns
Côte d'Ivoire	GR 200	Around the stem (0.30-0.40 m radius)	4.0-8.0 (80-283 kg ai/treated ha)	na	2-3	ns
Morocco*	GR 100	Overall application	5.0	na	ns	ns
Morocco	EC 200	Drip irrigation (during growing season: 1st at planting)	2.0 kg ai/ha (max 10 kg ai/ha)	ns	5 (7 days interval)	30
Peru	GR 150	Soil treatment	3.0 – 4.5	na	1	7
Philippines @	GR 100	Around the stem (0.75 m radius)	4.0 – 5.0 (23-28 kg ai/treated ha	na	2 (6 months)	ns
Portugal (Madeira)	GR 100	Around the stem (0.30 – 0.80 m radius)	2.0 – 4.5 (22-71 kg ai/treated ha)	na	2 (reapply every 6 months)	56
Spain[2]	EC 200	Drip irrigation	3.0 – 3.6	ns	1	60
Spain[2]	EC 200	Flood irrigation	5.0 – 6.0	ns	1	60
USA	GR 150	Around the stem (0.75 m radius)	6.0 (34 kg ai/treated ha)	na	2 (180)	ns
USA	EC 200	Around the stem (0.75 m radius)	5.8 (33 kg ai/treated ha)	ns	2 (180)	ns
Venezuela	GR 100	Around the stem (0.40 m radius)	4.0	na	2 - 3	30
Venezuela	GR 150	At sowing (in the plant hole) or around the stem for established crops	2.6-3.0	na	2-3	30

na: not applicable, direct treatment with granular formulation
ns: not stated on the label
*: no printed label or registration certificates available (confirmed by manufacturer)
@: There is no available commercial label for the Philippines, because the product is imported from the USA. Values listed in the Table are from the blueprint.
[1] Central America includes Guatemala, El Salvador, Honduras, Nicaragua, Costa Rica, Panama, Dominican Republic and Belize.
[2] Bananas are cultivated on a commercial basis in the Canary Islands. About 20% of the cultivated surface is under protected covers (plastic or mesh) while the remaining 80% is open field (Barriere, 2004a).

Table 49. Registered uses of ethoprophos on vegetables (without further specification).

Country	Site	Formulation (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No	PHI (days)
Austria	F/I	GR 100	Soil treatment	6.0	na	ns	ns
Algeria[1]*	I	GR 100	Soil treatment	5.0	na	2-3	ns

Country	Site	Formulation (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No	PHI (days)
			(application period ns)				
Cameroon	ns	MG 100	Overall application (pre planting/pre-transplanting)	4.5	na	1	ns
Cameroon	ns	MG 100	Band application[1] (pre planting / pre-transplanting)	- (4.5 kg ai/treated ha)	na	1	ns
Chile	F/I	EC 720	Overall application (pre planting)	3.6 – 8.6	ns	1	ns
France	F	EC 200	Overall application (10 days before planting upto planting)	4.0-10	0.50 – 1.7	1	ns
Greece	F	GR 100	Overall application (a few days before - at sowing/ 1 week before-at transplanting)	6.0 – 8.0	na	1	60
Greece	F	EC 720	Drip irrigation	7.2	ns	1	60
Morocco[1] *	ns	GR 100	Soil treatment (localised) (application period ns)	10	na	ns	ns
Tunisia[1] *	ns	GR 100	Soil treatment (application period ns)	5.0 - 10	na	ns	ns
Venezuela	F	GR 100	Band application (0.40-0.50 m wide) 1-3 weeks pre-planting	2.0-2.5	na	1	30

F: open field
I: indoor, may be greenhouse or plastic cover
na: not applicable, direct treatment with granular formulation
ns: not stated on label
* no printed label or registration certificates available (confirmed by manufacturer)
[1] Examples of vegetables, mentioned on label: peppers, cucurbits, cabbages.

Table 50. Registered uses of ethoprophos on cucumber.

Country	Site	Form. (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No (inter-val, days)	PHI (days)
Central America[1]	F	GR 100; GR 150; EC 720	Soil treatment (at planting)	2.0 – 4.2	na/ns	1	30
Italy	F/I	GR 100	Overall application (one week pre planting)	3.0 – 10	na	1	30
Italy	F/I	GR 100	Band application (one week pre planting)	- (3.0 – 10 kg ai/treated ha)	na	1	30
Italy	F	EC 172.9	Overall application (pre-sowing / pre-planting)	6.9 – 8.6	0.069-0.43	1	30
Italy	F	EC 172.9	Band application (pre-sowing / pre-planting)	- (6.9 – 8.6 kg ai/treated ha)	0.069-0.43	1	30
Côte d'Ivoire	ns	GR 200	Overall application (at planting / at transplanting)	6.0 – 12	na	1	ns
Côte d'Ivoire	ns	GR 200	Band application (width 0.35-0.65 m) (at planting / at transplanting)	- (6.0 – 12 kg ai/treated ha)	na	1	ns
Mexico	F	GR 150	Band application[2] (1 week before transplanting up to transplanting)	2.0 – 3.0	na	1	ns
Mexico	F	gel 720	Soil treatment (at planting)	2.2	ns	1	ns

Country	Site	Form. (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No (inter-val, days)	PHI (days)
Mexico	F	gel 720	Soil treatment (1st after seedtime until crop has 2 true leaves)	2.2	ns	1-2 (15-20)	ns
Portugal	F/I	GR 100	Overall application (pre planting)	8.0	na	1	56
Spain	F/I	GR 100	Overall application (pre-sowing or pre-transplanting)	6.0 – 8.0	na	1	60
Spain	F/I	EC 200	Soil treatment (15 days before planting/transplanting)	6.0	ns	1	60
Spain	F/I	EC 200	Drip irrigation (post transplanting)	0.6 (max total 6.0)	ns	1-10 (7-10)	60
USA	ns	GR 150	Band application[3] (pre planting/ at planting)	2.2 (12-15 kg ai/treated ha)	na	1	ns
USA	ns	EC 720	Band application[3] (pre planting/at planting	1.7 (9.7 – 12 kg ai/treated ha)	ns	1	ns

F: open field
I: indoor, may be greenhouse or plastic cover
na: not applicable, direct treatment with granular formulation
ns: not stated on the label
[1] Central America includes Guatemala, El Salvador, Honduras, Nicaragua, Costa Rica, Panama, Dominican Republic and Belize.
[2] Band 0.30-0.40 m wide, 1.5-2.0 m row spacing.
[3] Band 0.30-0.38 m wide, 2.1 m row spacing

Table 51. Registered uses of ethoprophos on sweet and chili peppers.

Country	Site	Form. (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No; (interval, days)	PHI (days)
Central America[1]	F	GR 100; GR 150; EC 720	Soil treatment (at planting)	2.0 – 4.2	na/ns	1	30
Italy	F/I	GR 100	Overall application (one week pre planting)	3.0 – 10	na	1	30
Italy	F/I	GR 100	Band application (one week pre planting)	- (3.0 – 10 kg ai/treated ha)	na	1	30
Italy	F	EC 172.9	Overall application (pre-sowing / pre-planting)	6.9 – 8.6	0.069-0.43	1	30
Italy	F	EC 172.9	Band application (pre-sowing / pre-planting)	- (6.9– 8.6 kg ai/treated ha)	0.069-0.43	1	30
Italy (green pepper)	F	EC 172.9	Drip irrigation (post transplanting)	1.7 – 3.5 (max total 8.6)	ns	3-4 (20-30)	30
Côte d'Ivoire*	F	GR 200	Overall/band application (at planting)	9.0	na	1	ns
Korea (red pepper)	F/I[2]	GR 50	Overall application (1 week before transplanting)	4.0-5.0	na	1	ns
Peru (chili pepper)	F	GR 150	Overall application (pre transplanting)	3.8 – 4.5	na	1	7
Portugal	F	GR 100	Overall application (pre planting)	8.0	na	1	56
Spain	F/I	GR 100	Overall application (pre-sowing/ pre-transplanting)	6.0 – 8.0	na	1	60
Spain	F/I	EC 200	Soil treatment (15 days before	6.0	ns	1	60

Country	Site	Form. (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No; (interval, days)	PHI (days)
			sowing/transplanting)				
Spain	F/I	EC 200	Drip irrigation (post transplanting)	0.6 (max. total 6.0)	ns	1-10 (7-10)	60
Thailand (pepper)	F	GR 100	Around the stem, followed by watering	40	na	1	ns

F: open field; I: indoor: may be greenhouse or plastic cover
na: not applicable, direct treatment with granular formulation
ns: not stated on the label
*: no printed label or registration certificates available (confirmed by manufacturer)
[1] Central America includes Guatemala, El Salvador, Honduras, Nicaragua, Costa Rica, Panama, Dominican Republic and Belize.
[2] In Korea, red peppers are cultivated both in open field and in vinyl houses.

Table 52. Registered uses of ethoprophos on tomatoes.

Country	Site	Formulation (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No; (interval, days)	PHI (days)
Central America[1]	F	GR 100; GR 150; EC 720	Soil treatment (at planting)	2.0 – 4.2	na/ns	1	30
Chile	F/I	EC 720	Overall application (pre planting)	3.6 – 8.6	ns	1	ns
Columbia	F/I	GR 50; GR 100	Band application (width 0.45-0.60 m) (pre planting until at transplanting)	6.8-9.0 (12.5–19 kg ai/treated ha)	na	1	ns
Columbia	F/I	GR 50; GR 100	Overall application (pre planting until at transplanting)	6.8 - 9.0	na	1	ns
Ecuador	F	EC 69.6	Soil treatment (1 week before transplanting)	0.56-0.70	ns	1	90
France	F	EC 200	Overall application (10 days before planting upto planting)	4.0-10	0.50 – 1.7	1	ns
Italy	F/I	GR 100	Overall application (one week pre planting)	3.0 – 10	na	1	30
Italy	F/I	GR 100	Band application (one week pre planting)	- (3.0 – 10 kg ai/treated ha)	na	1	30
Italy	F	EC 172.9	Overall application (pre-sowing / pre-planting)	6.9 – 8.6	0.069-0.43	1	30
Italy	F	EC 172.9	Band application (pre-sowing / pre-planting)	- (6.9 – 8.6 kg ai/treated ha)	0.069-0.43	1	30
Italy	F	EC 172.9	Drip irrigation (post transplanting)	1.7 – 3.5 (total max 8.6)	ns	3-4 (20-30)	30
Côte d'Ivoire	ns	GR 200	Overall application (at planting / at transplanting)	6.0 – 12	na	1	ns
Côte d'Ivoire	ns	GR 200	Band application (width 0.35-0.65 m) (at planting / at transplanting)	- (6.0 – 12 kg ai/treated ha)	na	1	ns
Morocco	F/I	EC 200	Drip irrigation (during growing season: 1st treatment 10 days before planting)	5.0 (1st treatment) 1.0 (later treatments) (total max 10)	ns	2-6 (5)	30
Peru	F	GR 150	Overall application (pre transplanting)	3.8 – 4.5	na	1	7
Portugal	F	GR 100	Overall application	8.0	na	1	56

Country	Site	Formulation (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No; (interval, days)	PHI (days)
			(pre planting)				
Spain	F/I	GR 100	Overall application (pre planting/pre-transplanting)	6.0 – 8.0	na	1	60
Spain	F/I	EC 200	Drip irrigation (during growing season: 1st treatment 15 days after transplanting)	0.8 – 2.0 (total max 6.0)	ns	several (15-20)	60
Venezuela	F	GR 100	Band application (0.40-0.50 m width) (1-3 weeks pre-planting)	2.0 – 2.5	na	1	30

F: open field
I: indoor, may be greenhouse or plastic cover
na: not applicable, direct treatment with granular formulation
ns: not stated on the label
[1] Central America includes Guatemala, El Salvador, Honduras, Nicaragua, Costa Rica, Panama, Dominican Republic and Belize.

Table 53. Registered uses of ethoprophos on melons.

Country	Site	Formulation (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No	PHI (days)
Central America[1] (watermelon)	F	GR 100; GR 150; EC 720	Soil treatment (at planting)	2.0 – 4.2	na/ns	1	30
Ecuador (cantaloupe)	F	GR 150 Biodac	Soil treatment (at planting/transplanting)	0.23 – 0.30 g ai/plant	na	1	ns
Italy (melon, watermelon)	F/I	GR 100	Overall application (one week pre planting)	3.0 – 10	na	1	30
Italy (melon, watermelon)	F/I	GR 100	Band application (one week pre planting)	- (3.0 – 10 kg ai/treated ha)	na	1	30
Italy (melon, watermelon)	F	EC 172.9	Overall application (pre-sowing / pre-planting)	6.9 – 8.6	0.069-0.43	1	30
Italy (melon, watermelon)	F	EC 172.9	Band application (pre-sowing / pre-planting)	- (6.9 – 8.6 kg ai/treated ha)	0.069-0.43	1	30
Côte d'Ivoire	ns	GR 200	Overall application (at planting / at transplanting)	6.0 – 12	na	1	ns
Côte d'Ivoire	ns	GR 200	Band application (width 0.35-0.65 m) (at planting/at transplanting)	- (6.0 – 12 kg ai/treated ha)	na	1	ns
Portugal	F	GR 100	Soil treatment (pre planting)	8.0	na	1	56
Peru (melon, watermelon)	F	GR 150	Overall application (pre transplanting)	3.8 – 4.5	na	1	7

F: open field
I indoor, may be greenhouse or plastic cover
na: not applicable, direct treatment with granular formulation
ns: not stated on the label
[1] Central America includes Guatemala, El Salvador, Honduras, Nicaragua, Costa Rica, Panama, Dominican Republic and Belize.

Table 54. Registered uses of ethoprophos on potatoes in the field.

Country	Formulation (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No	PHI (days)
Austria (seed potato)	GR 100	Overall application (at planting)	2.0 – 6.0	na	1	ns
Austria (seed potato)	GR 100	Band application (at planting)	2.5 – 3.0	na	1	ns
Belgium (ware potatoes)	MG 200	Overall application (pre planting)	4.0 – 6.0	na	1	ns
Brazil	GR 100	Application in the furrow, in the heap or both (at planting)	3.0	na	1	97
Central America[1]	GR 100; GR 150; EC 720	Soil treatment (at planting)	2.0 – 4.2	na/ns	1	30
Chile	EC 720	Overall application (pre planting)	3.6 – 10	0.72 – 2.5	1	ns
Chile	EC 720	Drip irrigation (pre planting)	3.6 – 5.8	ns	1	ns
Ecuador	GR 150 Biodac	Soil treatment (at planting)	1.1-2.2	na	2	45
France (ware, starch, seed potatoes)	MG 100	Overall application (pre planting)	6.0 – 10.0	na	1	ns
France (ware, starch, seed potatoes)	MG 100	Band application (pre planting)	2.0 (6.0 kg ai/treated ha)	na	1	ns
France	EC 200	Overall application (at planting)	6.0 – 10	0.75 – 1.7	1	ns
Greece	GR 100	Overall application (pre planting/at planting)	8 - 10	na	1	60
Greece	GR 100	Band application (plant covering stage)	2.5	na	1	60
Indonesia	GR 100	Around the planting hole (at planting)	2.0 – 4.0	na	1	ns
Ireland *	GR 100	Overall application (pre planting)	6.6-11	na	1	56
Ireland *	GR 100	Band application (pre planting)	4.0 – 6.0	na	1	56
Italy	GR 100	Overall application (one week pre planting)	3.0 – 10	na	1	90
Italy	GR 100	Band application (one week pre planting)	- (3.0 – 10 kg ai/treated ha)	na	1	90
Côte d'Ivoire	GR 200	Overall application (at planting / at transplanting)	6.0 – 12	na	1	ns
Côte d'Ivoire	GR 200	Band application (width 0.35-0.65 m) (at planting / at transplanting)	- (6.0 – 12 kg ai/treated ha)	na	1	ns
Korea	GR 50	Overall application (pre planting)	2.0 – 3.0	na	1	ns
Mexico	GR 150	In furrow (at planting)	3.4 – 4.5	na	1	ns
Mexico	gel 720	In furrow (at planting)	4.0 – 5.0	ns	1	ns
Netherlands	MG 200	Overall application (pre planting)	4.0-10	na	1	ns
Netherlands	MG 200	Band application (width 0.25-0.30 m) (at planting)	2.5	na	1	ns
Peru	GR 150	Overall application (1 week before planting / at planting)	3.0 – 4.0	na	1	7
Peru	GR 150	Band application (width 0.45-0.60 m)	6.8 (14-19 kg ai/treated	na	1	7

Country	Formulation (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No	PHI (days)
		(1 week before planting upto planting)	ha)			
Portugal	GR 100	Overall application (pre planting)	10	na	1	56
South Africa (Table, seed, chipping potatoes)	GR 150	Overall application (1-7 days before planting)	5.2 – 7.5	na	1	70
Spain	GR 100	Overall application (pre planting)	6.0 – 8.0	na	1	60
Thailand	GR 100	Overall application (1-7 days before planting)	6.2-12[2]	na	1	30
UK	GR 100	Overall application (pre planting)	6.6-11	na	1	56
UK*	GR 100	Band application (pre planting)	4.0 – 6.0	na	1	56
USA	GR 150; EC 720	Overall application (pre planting until before crop emergence)	4.5 – 13	na/ns	1	ns
USA	GR 150; EC 720	Band application (width 0.30, row spacing 0.91 m) (pre planting until before crop emergence)	3.4 (10 kg ai/treated ha)	na/ns	1	ns
Venezuela	GR 100	Band application (0.40-0.50 m wide) (1-3 weeks pre planting)	2.0 – 2.5	na	1	30

na: not applicable, direct treatment with granular formulation
ns: not stated on the label
*: no printed label or registration certificates available (confirmed by manufacturer)
[1] Central America includes Guatemala, El Salvador, Honduras, Nicaragua, Costa Rica, Panama, Dominican Republic and Belize.
[2] The dose rate of 10-19 kg product/rai was recalculated as 6.2-12 kg ai/ha assuming 1 rai = 1/6.25 = 0.16 ha.

Table 55. Registered uses of ethoprophos on sweet potatoes in the field.

Country	Formulation (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No	PHI (days)
USA	GR 150; EC 720	Band application (width 0.30-0.38 m; row spacing 1.1 m) (2-3 weeks before planting)	3.3 – 4.4 (9.3 - 16 kg ai/treated ha)	na	1	ns

na: not applicable, direct treatment with granular formulation
ns: not stated on the label

Table 56. Registered uses of ethoprophos on sugar cane in the field.

Country	Formulation (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No	PHI (days)
Central America[1]	GR 100; GR 150; EC 720	Soil treatment (at planting)	2.0 – 4.2	na/ns	1	30
Ecuador	GR 150 Biodac	Soil treatment (at planting)	2.2 – 4.5	na	1	45
Ecuador	EC 69.6	Soil treatment (at planting)	0.56-0.70	ns	1	300
Indonesia *	GR 100	Band application	1.0 – 2.0	na	1	ns

Country	Formulation (g ai/kg; g ai/l)	Application method	Dose rate kg ai/ha	Spray conc. kg ai/hl	No	PHI (days)
		(pre planting)				
Mexico	GR 150	In furrow (at planting)	3.9 – 5.0	na	1	ns
Mexico	GR 150	Band application (width 0.15-0.20 m) (2^{nd}-3^{rd} year crops)	3.9 – 5.0	na	1	60
USA	GR 150; GR 200 Lock 'n Load	Band application (width 0.30-0.38 m, row spacing 1.8 m^2) (at planting)	2.2-4.6 (10-27 kg ai/treated ha)	na	1	ns
Venezuela	GR 100	In furrow (at planting)	1.5 – 2.5	na	1	30

na: not applicable, direct treatment with granular formulation
ns: not stated on the label
*: no printed label or registration certificates available (confirmed by manufacturer)
[1] Central America includes Guatemala, El Salvador, Honduras, Nicaragua, Costa Rica, Panama, Dominican Republic and Belize
[2] Additional information from Barriere, 2004a

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on ethoprophos supervised field trials for:

Fruits	Table 57	Strawberry	EC - drip irrigation - indoor/outdoor
	Table 58	Banana	GR - soil treatment
Vegetables	Table 59	Cucumber	GR - soil treatment - indoor
	Table 60	Cucumber	GR - soil treatment - outdoor
	Table 61	Cucumber	EC - soil treatment - indoor
	Table 62	Cucumber	EC - soil treatment - outdoor
	Table 63	Cucumber	EC - drip irrigation - indoor
	Table 64	Melon	GR - soil treatment - outdoor
	Table 65	Melon	EC - drip irrigation - outdoor
	Table 66	Pepper	GR - soil treatment - indoor
	Table 67	Pepper	EC - drip irrigation - indoor/outdoor
	Table 68	Tomato	GR - soil treatment - indoor/outdoor
	Table 69	Tomato	EC - drip irrigation - indoor/outdoor
	Table 70	Potato	GR - soil treatment
	Table 71	Potato	EC - soil treatment
	Table 72	Potato, individual tubers	GR - soil treatment
	Table 73	Sweet potato	GR - soil treatment
Grasses	Table 74	*S*ugar cane stalks	GR - soil treatment
	Table 75	*S*ugar cane leaves	GR - soil treatment

Residue levels and application rates were reported as ethoprophos (parent) or as metabolite mA. When residues were not quantifiable, they are shown as below the reported LOQ (e.g. < 0.01 mg/kg). Residues, application rates and spray concentrations have been rounded to two figures. Residue data are recorded unadjusted for % recovery or for residue values in control samples. Residue values from the trials conducted according to GAP have been used for the estimation of maximum residue levels. These results are double underlined.

For most trials concurrent recoveries were reported to be within 70%-110% limits. Trials where no concurrent recoveries are reported or recoveries were outside these boundaries are indicated. For most trials control samples were reported to be below the LOQ. Trials where these exceeded the LOQ are indicated. Dates of analyses or duration of residue sample storage were also provided. For strawberry and banana the maximum storage period at -20°C is 9 months, for sugar cane it is 15

months and for tomato, pepper, cucumber, melon, potato and sweet potato it is 19 months. In none of the trials is this storage period exceeded. However, for some trials sample storage conditions are unknown, or samples were stored in temperatures other than -20°C.

Strawberry. Supervised trials on strawberries were carried out indoor or outdoor in the period 1996-1998 in Italy. Application was by drip irrigation with EC formulations throughout the growing season but before fruits had formed (Table 57).

Table 57: Ethoprophos residues in strawberries from supervised trials (indoor/outdoor) using drip irrigation with EC formulations.

Location, year, (variety)	Site	Form.	kg ai/ha	kg ai/hl	Water l/ha	No	Interval (days)	Last treatment	PHI (days)	parent (mg/kg)	Ref.
Igea Marina (Rn), Italy, 1997-98, (Dana)	G	EC	1.8	0.012	14880	4	30, 187, 21	22Apr; BBCH 67	30	<0.01 (2)	R008027, 97635BO1
Igea Marina (Rn), Italy, 1997-98, (Dana)	G	EC	3.5	0.024	14880	4	30, 187, 21	22 Apr; BBCH 67	30	<0.01 (2)	R008027, 97635BO1
Cesena, Forlì, Italy, 1996-97, (Dana)	F	EC	1.8	0.016	11284	4	31, 98, 32	15 Apr; BBCH 67	30	<0.01 (2)	R008903, 97654BO1
Cesena, Forlì, Italy, 1996-97, (Dana)	F	EC	3.5	0.031	11284	4	31, 98, 32	15 Apr; BBCH 67	30	<0.01 (2)	R008903, 97654BO1

BBCH 67: flowers fading: majority of petals fallen.
R008027. Barriere, 1999. GLP. No unusual climatic conditions. Plot size 34 m^2. Soil not stated. Irrigation treatment (band of 0.5 m) throughout the growing season but before fruits had formed. Fruit (1 kg) was harvested at maturity (BBCH 85). Samples were stored at -18°C for 7-8 months. Anal. method AR 52-87, 1998a, GC-FPD. Results were from duplicate trials. Results were not corrected for matrix interferences (<0.01 mg/kg, n=3) nor for concurrent recoveries (70%-117% at 0.01-0.05 mg/kg).
R008903. Maestracci, 1998d. GLP. No unusual weather conditions. Plot size 44 m^2. Soil not stated. Irrigation treatment (band of 0.5 m) throughout the growing season but before fruits had formed (BBCH 00 - BBCH 67). Fruit (1 kg) was harvested at maturity (BBCH 85). Samples were stored at -18°C for 5-6 months. Anal. method AR 52-87, 1997, GC-FPD. Results were from duplicate trials. Results were not corrected for matrix interferences (<0.01 mg/kg, n=1), nor for concurrent recoveries (88% at 0.02 mg/kg).

Banana. Supervised trials on bananas were carried out in the field in 1968-1969 in Côte d'Ivoire and Costa Rica, in 1988 in Brazil and 1987-1988 in the Philippines. One to four applications were made throughout the year by soil treatment with GR formulations (Table 58).

In the Costa Rica and Côte d'Ivoire trials concurrent recoveries were not reported and samples were stored in unknown conditions (probably at ambient or cool temperatures).

Table 58. Ethoprophos residues in banana fruit from supervised trials (outdoor) after soil treatment with GR formulations.

Location, year, (variety)	Form.	g ai/ tree	No	Interval (days)	Treatment dates; (harvest)	PHI (days)	parent (mg/kg)	Ref.
Abidjan, Côte d'Ivoire, 1968-1969, (ns)	GR	1x 10 1x 7.6	2	165	15 June; 27 Nov; (h: 18 Mar)	111	<0.02 (5)	C034087
San Jose, Costa Rica, 1968-1969, (ns)	GR	7.4	2	182	1 Oct 1 Apr (h: 1 Aug)	≥122[1]	<0.02	C034087
San Jose, Costa Rica, 1968-1969, (ns)	GR	7.3	2	182	22 Oct; 22 Apr (h: 20 Oct)	181	<0.02	C034087
San Jose, Costa Rica, 1968-	GR	6.8	3	123, 120	22 Oct; 22 Febr;	120	<0.02	C034087

Location, year, (variety)	Form.	g ai/ tree	No	Interval (days)	Treatment dates; (harvest)	PHI (days)	parent (mg/kg)	Ref.
1969, (ns)					22 June; (h: 20 Oct)			
San Jose, Costa Rica, 1968-1969, (ns)	GR	8.2	4	92, 90, 91	22 Oct; 22 Jan; 22 Apr; 22 July; (h: 20 Oct)	90	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	13.4	1	na	1 Febr; (h: 19 Apr)	77	<0.02 (2)	C034087
San Jose, Costa Rica, 1969, (ns)	GR	10.0	1	na	28 Mar; (h: 19 Apr)	22	<0.02 (2)	C034087
San Jose, Costa Rica, 1969, (ns)	GR	5.4	1	na	11 Apr; (h: 19 Apr)	8	<0.02 (2)	C034087
San Jose, Costa Rica, 1969, (ns)	GR	3.0	1	na	11 Apr (h: 24 May)	43	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	3.0	2	31	11 Apr 12 May (h: 24 May)	12	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	6.5	1	na	6 Febr (h: 24 May)	107	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	6.5	2	97	6 Febr 14 May (h: 24 May)	10	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	3.0	2	78	11 Apr 28 June (h: 26 July)	28	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	3.0	2	61	11 Apr 11 June (h: 26 July)	45	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	6.5	1	na	6 Febr (h: 26 July)	170	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	6.5	2	89	6 Febr 6 May (h: 26 July)	81	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	6.5	2	120	6 Febr 6 June (h: 26 July)	50	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	3.0	2	120	1 Febr 1 June (h: 1 Aug)	≥61[1]	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	6.0	2	181	6 Febr; 6 Aug (h: 17 Oct)	72	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	6.0	3	89, 92	6 Febr 6 May 6 Aug (h: 17 Oct)	72	<0.02	C034087
San Jose, Costa Rica, 1969, (ns)	GR	6.0	3	120, 122	6 Febr 6 June 6 Oct (h: 17 Oct)	11	<0.02	C034087
Sao Paulo, Brazil, 1988 (Nanicão)	GR	6.0	1	na	19 Nov; (h: 22, 25 Nov and 5 Dec)	3 6 13	<0.05 <0.05 <0.05	C033856/ C033857
Sao Paulo, Brazil, 1988 (Nanicão)	GR	12.0	1	na	19 Nov; (h: 22, 25 Nov and 5 Dec)	3 6 13	<0.05 <0.05 <0.05	C033856/ C033857

Location, year, (variety)	Form.	g ai/ tree	No	Interval (days)	Treatment dates; (harvest)	PHI (days)	parent (mg/kg)	Ref.
Tadeco, Philippines, 1987-88, (ns)	GR	2.5	3	60[1], 90[1]	Nov, Feb, May (h: 28 Jun)	>30[1]	<0.005[2]	R011296
Tadeco, Philippines, 1987-88, (ns)	GR	2.5	3	120[1] 120[1]	Sept, Jan, May (h: 28 Jun)	>30[1]	<0.005[2]	R011296
Tadeco, Philippines, 1987-88, (ns)	GR	2.5	3	60[1], 90[1]	Nov, Feb, May (h: 28 Jun)	>30[1]	<0.005[2]	R011296
Hijo, Philippines, 1987-88, (ns)	GR	3.0	2	150[1]	Dec, May (h: 28 Jun)	>30[1]	0.0060[2]	R011296
Evergreen, Philippines, 1987-88, (ns)	GR	3.0	3	180[1], 150[1]	June, Dec, May (h: 28 Jun)	>30[1]	0.011[2]	R011296

ns: not specified, na: not applicable
[1] only the month of application is stated so an exact PHI cannot be calculated.
[2] residue in the whole fruit calculated from the residues in the pulp and peel fractions assuming a weight ratio of 32% peel and 68% pulp, according to % edible portion in IESTI Table values for USA.
C034087. Mobil, 1969. **Non-GLP**. Weather conditions, plot size, soil type, treatment equipment, sampling procedures were not stated. Bananas (18 kg) were stored in unknown conditions for 8-13 days (probably at ambient or cool temperatures). Anal. method R-89-A. Replicate results were from replicate field trials. Results were not corrected for matrix interferences (<0.3LOQ, n=3). Concurrent recoveries were not reported.
C033856/C033857. Santana, 1989a/b. **Non-GLP**. Weather conditions, plot size and sampling procedures were not stated. Soil: hydromorphic. Application in the soil. Mature fruits were harvested, stored at -10°C for 180-190 days. Anal. method GC-FPD, method 3. Results were from combined samples of triplicate field trials. Results were not corrected for matrix interference (<0.05 mg/kg, n=1) nor for concurrent method recovery (111% at 0.05 mg/kg).
R011296. Dupont and Muller, 1988b. **Non-GLP.** Weather conditions, plot size, soil type and treatment procedures were not stated. Fruits were harvested from 4 trees with bunches ready for harvest. From each tree one finger was taken from hand number 2, 5 and 7. Fingers were only taken from the inner whorl. Samples (12 pieces) were separated into peel and pulp and analysed immediately (no storage). Anal. method JFRL GC-FPD. Results from Hijo and Evergreen, were the average of 2-3 analytical portions. Results were not corrected for matrix interference (<0.005 mg/kg, n=1) nor for concurrent method recovery (100% at 0.01 mg/kg).

Cucumber. Supervised trials on cucumbers were carried out in the field in 1969-1993 in the USA and indoors in 1978 in The Netherlands, 1980 in Canada, 1998 in Spain and 2001-2002 in Southern Europe (France, Italy, Spain, Greece, Portugal). Applications were made shortly before, at, or shortly after transplanting with overall or band soil treatment using GR formulations (Tables 59 and 60) or EC spray solutions (Tables 61 and 62). In addition, trials were carried out where applications were made throughout the growing season using drip irrigation with EC formulations (Table 63).

For the 1969-1971 US trials concurrent recoveries were not reported, and samples were stored in unknown conditions (probably at ambient or cool temperatures in some 1969-1971 US trials). For the 1976 US, 1978 Netherlands, and 1980 Canada trials the sample storage period was not stated. In trial 93-0087 (1993 US) control samples and treated samples were mislabelled or interchanged.

Results for metabolite mA are not reliable because the sample storage period exceeded the maximum storage time of 1 month in all trials.

Table 59. Ethoprophos residues in cucumbers from supervised trials (indoor) after overall soil treatment before planting or at transplanting with GR formulations.

Location, year, (variety)	Form.	kg ai/ha	No	Treatment time	PHI (days)	parent (mg/kg)	Ref.
Naaldwijk, The Netherlands 1978, (Stereo)	GR	7.5	1	4 Apr; pre-plant	35	<0.01 (2)	C034084

Location, year, (variety)	Form.	kg ai/ha	No	Treatment time	PHI (days)	parent (mg/kg)	Ref.
Dubbeldam, The Netherlands 1978, (Stereo)	GR	7.5	1	14 Apr; pre-plant	47	<0.01 (3)	C034084
Naaldwijk, The Netherlands 1978, (Stereo)	GR	10	1	4 Apr; pre-plant	35 42	<0.01 <0.01	C034084
Dubbeldam, The Netherlands 1978, (Stereo)	GR	10	1	14 Apr; pre-plant	47	<0.01 (3)	C034084
Naaldwijk, The Netherlands 1978, (Stereo)	GR	15	1	4 Apr; pre-plant	31 42	<0.01 <0.01	C034084
Dubbeldam, The Netherlands 1978, (Stereo)	GR	15	1	14 Apr; pre-plant	47	<0.01 (3)	C034084
Redcliff, Alberta, Canada, 1980, (Farbio)	GR	18	1	15 May; 1 d pre-transplant	ns	<0.01	C032713; ECPUA
Redcliff, Alberta, Canada, 1980, (Farbio)	GR	20	1	15 May; 2 d pre-transplant	ns	<0.01	C032713; ECPUA
Redcliff, Alberta, Canada, 1980, (Farbio)	GR	18	1	15 May; 1 d pre-transplant	ns	<0.01	C032713; Study 1
Redcliff, Alberta, Canada, 1980, (Farbio)	GR	20	1	15 May; 1 d pre-transplant	ns	<0.01	C032713; Study 1
Redcliff, Alberta, Canada, 1980, (Farbio)	GR	20	1	7 Aug; 2 d pre-plant	ns	<0.01	C032713; Study 2

ns: not specified
na: not applicable
C034084. De Wilde, 1978. **Non-GLP**. Weather conditions, plot size and soil type not stated. Broadcast soil treatment before planting. Formulation was mechanically incorporated into the soil. Fruit samples were picked just at the beginning of the production of crops. Sampling procedures and sample weights were not stated. Samples were stored at -20ºC (period not stated, but at least 5-6 months). In some cases, samples were from 2-3 replicate field trials. Anal. method GC-FPD, method 2. Results were not corrected for matrix interferences (<0.01 mg/kg, n=1), nor for concurrent method recovery (80%-97%, 0.01-0.4 mg/kg).
C032713. Howard, 1982. **Non-GLP**. Plot size 30 m^2. Soil sandy loam. Formulation was applied 1-2 days before transplanting, using a broadcast spreader followed by rototilling into a depth of 25 cm. Fruit samples were taken throughout the season and stored frozen (period not stated but at least 3 months (ECPUA and study 1) or 8 months (study 2). Anal. method unknown Mobil GC. Results were not corrected for matrix interferences (<0.01 mg/kg, n=1), nor for concurrent recoveries (91%-104% at 0.1 mg/kg).

Table 60. Ethoprophos residues in cucumber fruit from supervised trials (outdoor) after overall/band soil treatment 1-6 days before planting or at planting with GR formulations.

Location, year, (variety)	Form.	Method	kg ai/ha	No	Treatment date	PHI (days)	parent (mg/kg)	Ref. (storage)
Sanford (FL), USA, 1969, (ns)	GR	band; 0.30 m wide	2.2	1	25 Mar; at planting	51	<0.02	C034085 frozen, 22d
Sanford (FL), USA, 1969, (ns)	GR	band; 0.30 m wide	1.1	1	11 Sept; at planting	60	<0.02	C034085 cool, 4d
Sanford (FL), USA, 1969, (ns)	GR	band; 0.30 m wide	2.2	1	11 Sept; at planting	60	<0.02	C034085 cool, 4d
Hanover County (VA), USA, 1969, (ns)	GR	band; 0.46 m wide	3.4	1	21 May; 1 d pre-plant	48 - 51	<0.02 (2), mean <0.02 <0.02	C034085 cool, 2d frozen, 199d
Hanover County (VA), USA, 1969, (ns)	GR	overall	6.7	1	21 May; 1 d pre-plant	48 - 51	<0.02 (2), mean <0.02 <0.02	C034085 cool, 2d frozen, 199d

Location, year, (variety)	Form.	Method	kg ai/ha	No	Treatment date	PHI (days)	parent (mg/kg)	Ref. (storage)
Crystal Springs (MS), USA, 1969, (ns)	GR	overall	5.6	1	14 May; 9 d pre-plant	76	<0.02 (3); mean <0.02	C034085 frozen, 239d
Crystal Springs (MS), USA, 1970, (ns)	GR	overall	6.7	1	6 Apr; 17 d pre-plant	61	<0.02	C034085 cool, 132d
Sanford (FL), USA, 1970, (ns)	GR	band; 0.38 m wide	2.2	1	24 Mar; 2 d pre-plant	52	<0.02 (2); mean <0.02	C034085 cool, 31d
Hanover County (VA), USA, 1970, (ns)	GR	band; 0.46 m wide	3.4	1	12 May; 1 d pre-plant	56	<0.02	C034085 cool, 2d
Charleston (SC), USA, 1970, (ns)	GR	band; 0.91 m wide	4.5	1	7 Aug; 10 d pre-plant	73	<0.02	C034085 cool, 10d
Lafayette (LA), USA, 1970, (ns)	GR	band; 0.51 m wide	11	1	1 May; 6 d pre-plant	70	<0.02	C034085 frozen, 89d
Sanford (FL), USA, 1971, (ns)	GR	band; 0.38 m wide	1.1	1	10 Mar; at planting	69	<0.02	C034085 frozen, 132d
Sanford (FL), USA, 1971, (ns)	GR	band; 0.38 m wide	2.2	1	10 Mar; at planting	69	<0.02	C034085 frozen, 132d
Charleston (SC), USA, 1971, (ns)	GR	band; 0.61 m wide	4.5	1	17 July; 1 d pre-plant	81	<0.02	C034085 frozen, 182d
Clayton (NC), USA, 1976, (ns)	GR	overall	3.4	1	ns; pre-plant	58 62	<0.005 <0.005	C032715
Clayton (NC), USA, 1976, (ns)	GR	overall	6.7	1	ns; pre-plant	58 62	<0.005 <0.005	C032715
Clayton (NC), USA, 1976, (ns)	GR	overall	13	1	ns; pre-plant	58 62	<0.005 <0.005	C032715

ns: not specified
na: not applicable
C034085. Mobil, 1974. **Non-GLP**. Details of weather conditions, soil type, plot size and sampling were not available. Application as a band (width 0.30-0.50 m) or as an overall soil treatment, before or at planting. For some trials 2-3 replicate field samples were taken. Samples were stored frozen (temperature not stated) for 22-239 days or were stored for 2-132 days in unknown conditions before analysis (most likely at ambient or cooled conditions). Anal method R-89-A. Results were not corrected for matrix interferences (<0.02 mg/kg, n=4). **Concurrent recoveries were not reported.**
C032715. Hunt, 1981. **Non-GLP**. Four replicate residue trials, each subplot was 42 m^2. Soil loamy sand (pH 5.7, 0.5% om). Formulation was spread uniformly by hand and incorporated with a powered garden tiller to a depth of 13-15 cm. Information on treatment dates of cucumber are missing in the report. Samples were stored at -10°C (storage time not stated). Anal. method. GC-FPD, method 1. Each value represents the average of four replicate trials, individual values were however not shown. Results were not corrected for concurrent recoveries (78%-100% at 0.01-0.1 mg/kg). Information on matrix interferences is not available.

Table 61. Ethoprophos residues in cucumber fruit from supervised trials (indoor) after spray soil treatment with EC formulations (pre-planting and post-planting).

Location, year, (variety)	Form.	kg ai/ha	kg ai/hl	Water l/ha	No	Treatment date	PHI (days)	parent (mg/kg)	Ref.
33520 Bruges, Aquitane, S. France, 2001, (Defense)	EC	10	4.0	250	1	15 May; at planting	44 51 58 65	<0.005 <0.005 <0.005 <0.005	C025160 01R781-1
69360 Saint Symphorien d'Orzon, Rhone-Alpes, S. France, 2001, (Girola)	EC	10	1.7	600	1	13 Apr; at planting	28 33 40 49	<0.005 <0.005 <0.005 <0.005	C025160 01R781-2
40057 Cadriano (BO), Emilia Romagna, Italy, 2001, (Jazzer)	EC	10	2.5	400	1	8 June; at planting	34 41 47 55	<0.005 <0.005 <0.005 <0.005	C025160 01R781-3
44030 Pontegradela (Fe) Emilia Romagna, Italy, 2001, (Edona)	EC	10	2.0	500	1	19 July; 22 d post-planting	21 28 35 42	0.0090 <0.005 <0.005 <0.005	C025160 01R781-4
04007 El Zapillo Almeria, Andalusia,	EC	10	2.0	500	1	17 Aug; 2 d pre-plant	45 49	<0.005 <0.005	C025160 01R781-5

Location, year, (variety)	Form.	kg ai/ha	kg ai/hl	Water l/ha	No	Treatment date	PHI (days)	parent (mg/kg)	Ref.
Spain, 2001, (Tropico)							54 59	<0.005 <0.005	
58300 Esovalta, Macedonia, Greece, 2001, (Lubro)	EC	10	2.0	500	1	30 July; at planting	37 44 51 58	<0.005 <0.005 <0.005 <0.005	C025160 01R781-6
58300 Esovalta Pellas, Macedonia, Greece, 2001, (Gador)	EC	10	2.0	500	1	1 Aug; at planting	35 42 49 56	<0.005 <0.005 <0.005 <0.005	C025160 01R781-7
2520 Peniche, Ribatejo e Oeste, Portugal, 2001, (Jazzer)	EC	10	3.3	300	1	9 May; at planting	37 44 49 58	<0.005 <0.005 <0.005 <0.005	C025160 01R781-8
2520 Peniche, Ribatejo e Oeste, Portugal, 2001, (Torre)	EC	10	3.0	300	1	12 June; 1 d pre-plant	38 43 49 56	<0.005 <0.005 <0.005 <0.005	C025160 01R781-9

C025160. Davies, 2002c. GLP. Climatic conditions within greenhouses were within expected ranges. Soil loamy sand (1, pH 7.1, 3.1% om), sandy loam (2, pH7.4, 1.6% om), clay (3, 8, 9, pH 7.6-7.9, 0.75%-2.3% om), sand (4, pH 7.8, 1.7% om), sandy clay loam (5, 6, 7, pH 8.0-8.4, 0.84%-1.7% om). Spray application carried out with a boom sprayer. Samples were taken at the earliest possible harvest times and then at 7-day intervals. All harvested fruits had reached typical size and form (BBCH 72-81). Samples were stored at -18°C for 241-289 days (trial 5-7) or 291-392 days (trial 1-4 and 8-9). Anal. method AR 52-87, 2001d, GC-PFPD/TSD. Results were not corrected for matrix interferences (<0.005 mg/kg, n=41) nor for concurrent recoveries (70%-111% at 0.005 mg/kg).

Table 62. Ethoprophos residues in cucumber fruit from supervised trials (outdoor) after spray soil treatment before planting or at planting with EC formulations.

Location, year, (variety)	Form.	kg ai/ha	kg ai/hl	Water l/ha	No	Treatment date	PHI (days)	parent (mg/kg)	metabolite (mg/kg mA)	Ref.
Wharton, (TX), USA, 1993 (Straight Eight)	EC	13	5.3	243	1	10 June; at planting	55	<0.01 (3), mean <u>0.01</u>	<0.01 (3), mean <0.01	R009784 93-0085
Johnston, (NC), USA, 1993 (Poinsett #76)	EC	13	7.0	187	1	28 May; at planting	78	<0.01 (3), mean <u>0.01</u>	<0.01 (3), mean <0.01	R009784 93-0086
Wayne, (NC), USA, 1993 (Poinsett #76)	EC	13	6.6	196	1	3 May; at planting	53	<0.01 (3), mean <0.01	<0.01 - 0.013-0.019, mean 0.014	R009784 93-0087
Martin, (NC), USA, 1993 (Poinsett #76)	EC	13	6.6	198	1	6 May; at planting	57	<0.01 (3), mean <u>0.01</u>	<0.01 (3), mean <0.01	R009784 93-0088
Fresno (CA), USA, 1993 (Poinsett #76)	EC	13	7.0	187	1	16 Apr; at planting	69	<0.01 (3), mean <u>0.01</u>	0.054, 0.067, 0.079, mean 0.067	R009784 93-0089
Ottawa (MI), USA, 1993 (Marketmore 76)	EC	13	5.8	222	1	29 May; at planting	71	<0.01 (3), mean <u>0.01</u>	<0.01 (3), mean <0.01	R009784 93-0090
Ottawa (MI), USA, 1993 (Calypso)	EC	13	5.8	222	1	29 May; at planting	65	<0.01 (3), mean <u>0.01</u>	<0.01 (3), mean <0.01	R009784 93-0091
Walworth (WI), USA, 1993 (Marketmore 76)	EC	13	8.0	162	1	16 June; at planting	55	<0.01 (3), mean <u>0.01</u>	<0.01 (3), mean <0.01	R009784 93-0092
Dade (FL), USA, 1993 (Victory)	EC	13	4.6	280	1	22 Apr; 6 d pre-plant	69	<0.01 (3), mean <u>0.01</u>	<0.01 (3), mean <0.01	R009784 93-0093
Fayette (OH), USA, 1993 (Carolina)	EC	13	7.0	187	1	26 May; at planting	49	<0.01 (3), mean <u>0.01</u>	<0.01, 0.011, 0.020, mean 0.014	R009784 93-0094

R009784. Kowite, 1994a. GLP for analytical part only. No unusual weather conditions. Plot size 0.021-0.092 acres. Soil clay loam (85, 94, pH 5.9-6.4, 2.1%-3.8% om, 27%-39% clay), sandy loam (86-89, 93 pH 5.2-8.1, 0.83%-3.9% om, 6%-18% clay); loam (90-92, pH 6.0-7.0, 2.2% om, 16% clay); Broadcast soil treatment using a CO2 backpack sprayer, except in trial 93-0086 where a tractor with a broadcast boom sprayer was used. Samples were randomly collected by hand at normal crop maturity. Samples were stored frozen for 61-139 days. Anal. method GC-FPD, method 4, 1994, version 6.0. Results are the average of triplicate field samples, except in trial 93-0089 and 93-0094, where each field sample is the result of the average of 3 analytical portions (total of 9 results per trial). Results were not corrected for matrix interferences (<0.01 mg/kg) nor for concurrent recoveries (80%-108%). In one control sample from trial 93-0087 0.017 mg/kg mA was found. It is suspected that this sample is mis[l]abelled or switched with a treated sample (<0.01 mg/kg) from trial 93-0087.

Table 63. Ethoprophos residues in cucumbers from supervised trials (indoor) after drip irrigation post-planting or post-transplanting with EC formulations.

Location, year, (variety)	Form.	kg ai/ha	kg ai/hl	Water l/ha	No	Interval (days)	Treatment date	PHI (days)	parent (mg/kg)	Ref.
Almeria, Spain, 1998, (Crispina)	EC	0.78; 1.2; 2.0; 2.0;	na	na	4	8, 9, 11	11 May; 19 May; 28 May; 8 June	0 2 7 14	<0.01 (2) 0.038; 0.052 <0.01; 0.016 <0.01; 0.012	R004197 98641A1
Sevilla, Spain, 1998 (Darina)	EC	0.78; 1.2; 2.0; 2.0	na	na	4	20, 20, 16	25 Mar; 14 Apr; 4 May; 20 May	0 2 7 15	<0.01; 0.021 0.050; 0.075; 0.013; 0.016 <0.01 (2)	R004197 98641SE1
04740 La Mojonera, Almeria, Andalusia, Spain, 2002, (Trópico)	EC	1.9	0.006	30076	3	11, 14	26 Apr; 7 May; 21 May	0 3 7 11 15	0.0060 0.016 0.010 0.012 <0.005	C036689 02R781-5
04741 Cortijos de Marin, Roquetas, Andalucia, Spain, 2002, (Trópico)	EC	1.9	0.005	40000	3	13, 13	2 May; 15 May; 28 May	0 3 7 11 15	<0.005 <0.005 <0.005 <0.005 <0.005	C036689 02R781-6
69360 St. Symphorien d'Ozon, Rhone-Alpes, S. France, 2002, (Girola)	EC	1.9	0.032	6000	3	14, 11	19 Apr; 3 May; 14 May	0 3 7 11 16	<0.005 <0.005 <0.005 <0.005 <0.005	C036689 02R781-1
33520 Bruges, Aquitane, S. France, 2002 (Defense)	EC	1.9	0.071	2667	3	13, 14	21 May; 3 June; 17 June	0 3 7 11 15	<0.005 <0.005 <0.005 <0.005 <0.005	C036689 02R781-2
44030 Pontegradella (Fe) Emilia-Romagna, Italy, 2002, (Edona)	EC	1.9	0.014	13333	3	14, 14	10 May; 24 May; 7 June	0 3 7 11 15	0.0050 <0.005 <0.005 <0.005 <0.005	C036689 02R781-3
70056 Molfetta (BA) Puglia, Italy, 2002 (Saring)	EC	1.9	0.015	12500	3	14, 14	11 Oct; 25 Oct; 8 Nov	0 3 7 11 14	0.0090 0.040 <0.005 <0.005 <0.005	C036689 02R781-4

R004197. Richard and Yslan, 1999. GLP. No unusual climatic conditions. Plot size 8.8-15 m^2 (12-15 plants). Soil not stated. Formulation diluted to 100 ml (SE1) and 500 ml (A1) of water and this solution is spread on the area around the crops. Drip irrigation is provided to incorporate into the soil .Treatment at growth stages between BBCH 52-85. Samples were harvested at normal maturity (BBCH 82-88) at 12 pieces per sample. Samples were stored frozen at -18°C for 79-118 days. Anal method AR 52-87, 1998a, GC-FPD. Results were from duplicate field trials. Results were not corrected for matrix interferences (<0.01 mg/kg) nor for concurrent recoveries (73%-103% at 0.01-0.05 mg/kg).

C036689. Klein, 2004a. GLP. No unusual climatic conditions. Plot size 12-32 m^2. Soil: sandy loam (1-2, pH 7.1-7.6, 3.1%-8.4% om), sand (3, pH 7.8, 1.7% om); sandy clay (4, pH 7.7, 2.7% om); loamy sand (5, pH 8.3, 1.0% om); silt (6, pH 8.7, 0.17% om). Treatment at growth stages between BBCH 13-82 (3rd true leaf - maturity). Between 12-65 mature fruits were taken randomly from the centre of the plots. Samples were stored at -18°C for 223-272 days (02R781-4) or 366-443 days

(other trials). Anal. method AR 52-87, 2003b, GC-MS/GC-MS-MS. Results were not corrected for matrix interferences (<0.005 mg/kg, n=49) nor for concurrent recoveries (76%-117% at 0.005-0.05 mg/kg).

Melon. Supervised trials were carried out in the field or indoors in 1998 in Spain and 2001-2002 in Southern Europe (France, Italy, Spain, Greece, Portugal). Applications were made shortly before, at or shortly after transplanting with overall soil treatment using GR formulations (Table 64). In addition, trials were carried out where applications were made throughout the growing season using drip irrigation with EC formulations (Table 65).

Table 64. Ethoprophos residues in melons from supervised trials (outdoor) using overall soil treatment pre- planting/at planting/post-planting with GR formulations.

Location, year, (variety)	Form.	kg ai/ha	No	Treatment date	PHI (days)	parent (mg/kg)	Ref.
84800 Isle sur la Sorgue, Provence-Cote d'Azur, S. France, 2001, (Heliobel)	GR (FG)	10	1	27 Apr; 19 d post-planting	61 70 79	<0.005[2] <0.005[2] <0.005[2]	C025152 01R754-1
84800 Isle sur la Sorgue, Provence-Cote d'Azur, S. France, 2002 (Escrypto)	GR (FG)	10	1	28 May; 1 d pre-plant	63 69 76 83	<0.005[1] <0.005[1] <0.005[1] <0.005[1]	C036692 02R754-1
84840 Lamotte du Rhone, Provence-Cote d'Azur, S. France, 2002 (Anasta)	GR (FG)	10	1	17 June; 1 d pre-plant	58 67 74	<0.005[1] <0.005[1] <0.005[1]	C036692 02R754-2
70031 Andria (Ba) Puglia, Italy, 2001 (Proteo)	GR (FG)	10	1	12 June; at planting	62 72 78	<0.005[2] <0.005[2] <0.005[2]	C025152 01R754-2
70043 Molfetta, Bari, Puglia, Italy, 2002, (Proteo)	GR (FG)	10	1	6 May; 1 d pre-plant	61 67 74 84	<0.005[1] <0.005[1] 0.0055[1] <0.005[1]	C036692 02R754-3
46230 Alginet, Valencia, Spain, 2001, (Cantalup Rubens)	GR (FG)	10	1	25 Apr; at planting	54 64 75	<0.005[2] <0.005[2] <0.005[2]	C025152 01R754-4
41310 Brenes, Sevilla, Andalucia, Spain, 2001 (Sancho)	GR (FG)	10	1	28 May; 1 d pre-plant	67 77 87	<0.005[2] <0.005[2] <0.005[2]	C025152 01R754-6
46230 Alginet, Valencia, Spain, 2002, (Cantalup)	GR (FG)	10	1	14 Apr; at planting	68 75 84	<0.005[1] <0.005[1] <0.005[1]	C036692 02R754-4
57011 Prochoma, Thessaloniki, Macedonia, Greece, 2001, (Daniel)	GR (FG)	10	1	18 June; at planting	46 56 66	0.018[2] 0.010[2] <0.005[2]	C025152 01R754-5

na: not applicable

[1] residue in whole fruit calculated by the reviewer from the residues in the pulp and peel fractions assuming a weight ratio of 40% peel and 60% pulp, according to % edible portion in IESTI Table values for France.

[2] residue in whole fruit calculated from the residues in the actual peel and pulp fractions and the actual peel to pulp weight ratios; actual peel and pulp weights were however not given in the study reports.

C025125. Davies, 2002g. GLP. No unusual weather conditions. Plot size 18-80 m^2. Soil loam (1 and 6, pH 7.8-8.0, 0.74-2.0% om), sandy clay (2, pH 7.3, 2.5% om), clay loam (4-5, pH 8.1-8.6, 1.7%-1.8% om). Samples were harvested when full size and form was reached (BBCH 73-81). Samples were divided into peel and pulp and stored at -18°C for 302-380 days. Anal method AR 52-87, 2001d, GC-TSD. Results from plot 1R754-5 are the mean of two analytical portions. Results were not corrected for matrix interferences (<0.005, n=9) nor for concurrent recoveries (73%-103% at 0.005 mg/kg).

C036692. Klein, 2004d. GLP. No unusual weather conditions. Plot size 40-81 m^2. Soil clay loam (1 and 4, pH 7.8-8.6, 1.8%-2.1% om), sandy loam (2, pH 6.8, 3.0% om), sandy clay (3, pH 7.8, 2.5% om). Application by manual spreading followed by incorporation into the soil. Samples (12 pieces) were harvested when full size and form was reached (BBCH 71-89). Melons were sampled randomly from the centre of the plot. Samples were divided into peel and pulp, and stored at -18°C for 409-484 days. Anal method AR 52-87, 2003b, GC-MS. Results were not corrected for matrix interferences (<0.005, n=20) nor for concurrent recoveries (72%-107% at 0.005 mg/kg).

Table 65: Ethoprophos residues in melons from supervised trials (outdoor) after post-transplanting drip irrigation with EC formulations.

Location, year, (variety)	Form.	kg ai/ha	kg ai/hl	Water l/ha	No	Interval (days)	Treatment dates	PHI (days)	parent (mg/kg)	Ref.
Santa Ollala, Toledo, Spain, 1998 (Pinonet)	EC	0.078 0.12 0.20 0.20	na	na	4	20, 22, 21	23 June; 13 July; 4 Aug; 25 Aug (BBCH 81)	0 2 7 14	0.072, 0.25 0.036, 0.11 0.016, 0.025 0.013[1], 0.017[1]	R004456 98642M1
Sevilla, Spain, 1998 (Roché)	EC	0.078 0.12 0.20 0.20	na	na	4	19, 22, 20	10 June; 29 June; 21 July; 10 Aug (BBCH 87)	0 2 7 14	0.023, 0.064 <0.01, 0.015 0.024, 0.037 <0.01[1], <0.01[1]	R004456 98642SE1
46550 Albuixech, Valencia, Spain, 2002 (Sancho)	EC	1.9	0.043	4444	3	15, 14	23 May; 7 June; 21 June; (BBCH 71)	0 3 7 10 14	<0.005 0.023 <0.005 <0.005 <0.005[1]	C036693 02R787-5
41310 Brenes, Sevilla, Andalucia, Spain, 2002 (Regen Piel de Sapo)	EC	1.9	0.021	9149	3	14, 14	20 June; 4 July; 18 July; (BBCH 81)	0 14	<0.005 <0.005[1]	C036693 02R787-6
84840 Lamotte du Rhone, Provence-Cote d'Azur, S. France, 2002 (Indola)	EC	1.9	0.032	6024	3	14, 13	10 July; 24 July; 6 Aug (BBCH 81)	0 3 7 10 14	0.0094 0.012 0.0082 <0.005 <0.005[1]	C036693 02R787-1
84800 Isle sur la Sorgue, Provence Cote d'Azur, S. France, 2002 (Escrypto)	EC	1.9	0.038	5000	3	11, 13	8 July; 19 July; 1 Aug (BBCH 81)	0 14	0.013 0.0063[1]	C036693 02R787-2
40017 San Giovanni in Persiceto, Emilia-Romagna, Italy, 2002 (Calipso)	EC	1.9	0.038	5000	3	14, 14	20 May; 3 June; 17 June; (BBCH 81)	0 3 7 10 14	0.0074 0.019 0.034 0.029 0.014[1]	C036693 02R787-3
70056 Molfetta (BA), Puglia, Italy, 2002 (Proteo)	EC	1.9	0.015	12500	3	14, 14	13 June; 27 June; 11 July; (BBCH 73)	0 14	0.018 0.017[1]	C036693 02R787-4

BBCH 71-73: 1st - 3rd fruit on main stem has reached typical size and form)
BBCH 81-87: 10%-70% of fruits show typical fully ripe colour
[1] Residue in whole fruit calculated from the residues in the actual peel and pulp fractions and the actual peel to pulp weight ratios; actual peel and pulp weights were however not given in the study reports but were supplied by the company separately by e-mail.
For study report R004456 peel fractions were 20%-23% and pulp fractions were 77%-80%.
For study report C036693 peel fractions were 21%-47% and pulp fractions were 53%-79%.

R004456. Richard, 1999. GLP. No unusual weather conditions. Plot size 12 m^2 (6 plants). Soil not stated. Formulation diluted to 100 ml of water and this solution is spread on the area around the crops. Drip irrigation is provided to incorporate into the soil. Plants were treated post-planting throughout the growing season (BBCH 11- 87). Fruit (2-6 pieces) was sampled at maturity (BBCH 81-97). Samples were cut in quarters and stored at -18°C for 112-149 days. Anal method AR 52-87, 1998a, GC-FPD. Results were from duplicate trials. Results were not corrected for matrix interferences (<0.01 mg/kg, n=7) nor for concurrent recoveries (83%-107% at 0.01-0.25 mg/kg).

C036693. Klein, 2004e. GLP. No unusual weather conditions. Plot size 35-122 m^2. Soil silt loam (1, pH 7.1, 3.0% om), clay loam (2, pH 7.8, 2.1% om), clay (3, pH 7.6, 3.0% om), sandy clay (4, pH 7.8, 2.8%om), silt (5, pH 7.8, 6.3% om), loam (6, pH 7.8, 0.74% om). Drip irrigation. Plants were treated post-planting throughout the growing season (BBCH 29- 89). Fruits (12 pieces) were sampled randomly at maturity from the centre of the plots. Samples were divided into peel and pulp and stored for 378-447 days at -18°C. Anal. method AR 52-87, 2003b, GC-MS. Results were not corrected for matrix interferences (<0.005 mg/kg), nor for concurrent recoveries (71%-114% at 0.005-0.04 mg/kg).

Sweet pepper. Supervised trials on sweet and green peppers were carried out in the field or indoors in 1997-2002 in Southern Europe (France, Italy, Spain, Greece). Applications were made shortly before or at transplanting with overall soil treatment using GR formulations (Table 66). In addition, trials

were carried out where applications were made throughout the growing season using drip irrigation with EC formulations (Table 67).

There is no clear explanation for the unexpected residues shown in trial 01R784-4 (2001 Spain), although it was noted that the soil is this trial (gravelly silt) is very course in texture and has a high organic matter (3.2%). The soil has been laid to a shallow depth and the roots of these plants would not extend more than 4 cm into soil.

Table 66. Ethoprophos residues in sweet pepper fruit from supervised trials (indoor) using overall soil treatment pre-planting or at planting with GR formulations.

Location, year, (variety)	Form.	kg ai/ha	No	Treatment date	PHI (days)	parent (mg/kg)	Ref.
84800 Isla sur la Sorgue, Provence Cote d'Azur, S. France, 2001 (Sienor)	GR (FG)	10	1	6 Apr; 1 d pre-plant	62	<0.005	C023543 01R784-1
13160 Chateaurenard, Provence Cote d'Azur, S. France, 2001 (Volga)	GR (FG)	10	1	25 Apr; 1 d pre-plant	41 51 61	<0.005 <0.005 <0.005	C023543 01R784-2
47160 Villefranche du Queyran, Aquitaine, S. France, 2002 (Denver)	GR (FG)	10	1	30 Apr; 1 d pre-plant	56[1] 66 77	<0.005 <0.005 <0.005	C036690 02R784-1
47200 Marcellus, Aquitaine, S. France, 2002 (Elipari)	GR (FG)	10	1	11 Apr; 1 d pre-plant	67 83	<0.005 <0.005	C036690 02R784-2
33520 Bruges, Aquitaine, S. France, 2002 (Clovis)	GR (FG)	10	1	14 May; at planting	52 59 65	<0.005 <0.005 <0.005	C036690 02R784-3
70038 Terlizzi, Bari, Puglia, Italy, 2001 (Safari)	GR (FG)	10	1	24 Apr; at planting	77	<0.005	C023543 01R784-3
04710 St. M. del Aguila, El Ejido, Almeria, Andalucia, Spain, 2001 (Tajo)	GR (FG)	10	1	22 Aug; 2 d pre-plant	64 75	0.027 0.0070	C023543 01R784-4
58300 Stavrodomi, Pella, Macedonia, Greece, 2001 (Vaso)	GR (FG)	10	1	29 March; at planting	41 53 61	<0.005 <0.005 <0.005	C023543 01R784-5
58300 Stavrodomi, Pellas, Macedonia, Greece, 2002 (Raico)	GR (FG)	10	1	29 March; at planting	43 49 54 61	<0.005 <0.005 <0.005 <0.005	C036690 02R784-4
58300 Stavrodomi, Pellas, Macedonia, Greece, 2002 (Staborn)	GR (FG)	10	1	29 March; at planting	43 49 54 62	0.067 0.039 0.021 0.0070	C036690 02R784-5
58300 Stavrodomi, Pellas, Macedonia, Greece, 2002 (Raico)	GR (FG)	10	1	2 Apr; at planting	57 66	<0.005 <0.005	C036690 02R784-6

[1] Sample was immature at sampling (BBCH 63, 3rd inflorescence)

C023543. Davies, 2002d. GLP. No unusual climatic conditions. Plot size 10-41 m^2. Soil loam (1-2, pH 7.2-7.8, 2.9-3.0% om), sandy clay (3, pH 7.2, 23% om), silt (4, pH 7.9, 3.2% om), clay loam (5, pH 7.0, 1.5% om). Fruits were taken immature although they had reached their typical size and form (BBCH 71-89). Samples were stored at -18°C for 136-254d (trial 3-4) or 269-315 days (other trials). Anal. method AR 52-87, 2001a, GC-FPD. Results were not corrected for matrix interferences (<0.005, n=18) nor for concurrent recoveries (71%-87% at 0.005-0.05 mg/kg).

C036690. Klein, 2004b. GLP. No unusual climatic conditions. Plot size 18-67 m^2. Soil silty clay loam (1, pH 5.8, 1.5% om), silty clay (2, pH 7.9, 1.4% om), sandy loam (3, pH 7.1, 3.1% om), clay (4-5, pH 7.2-7.5, 2.2%-2.8% om), sandy clay (6, pH 7.4, 1.6% om). Manual spreading in France, spreader drop gravity in Greece. Results from the 2002 Between 12-80 fruits were sampled randomly from the centre of the plots. Samples were very often immature, but had reached typical size and form (BBCH 71-89), except where indicated. Samples were stored at -18°C for 357-555 days. Anal method AR 52-87, 2003b, GC-MS. Staborn samples are the mean of duplicate analytical sample portions. Results were not corrected for matrix interferences (<0.005 mg/kg) nor for concurrent recoveries (71%-105% at 0.005-0.05 mg/kg).

Table 67. Ethoprophos residues in pepper fruit from supervised trials (indoor/outdoor) after post-planting drip irrigation using EC formulations.

Location, year, (variety)	Site	Form.	kg ai/ha	kg ai/hl	Water l/ha	No	Interval (days)	Treatment dates	PHI (days)	parent (mg/kg)	Ref.
El Ejido, Almeria, Spain, 1998 (Roxy, green pepper)	G	EC	0.078 0.12 0.20 0.20	na	na	4	24, 22, 26	31 Aug; 24 Sept; 16 Oct; 11 Nov; (BBCH 81)	0 2 7 15	0.20, 0.24 0.18, 0.20 0.21, 0.23 0.22, 0.24	R009798 98640A1
Sevilla, Spain, 1998 (Italico, green pepper)	G	EC	0.078 0.12 0.20 0.20	na	na	4	21, 20, 20	4 Mar; 25 Mar; 14 Apr; 4 May (BBCH 79)	0 2 7 14	0.058, 0.097 0.039, 0.057 0.031, 0.069 0.032, 0.033	R009798 98640SE1
04710 St. M. del Aguila, El Ejido, Almeria, Andalucia, Spain, 2001 (Tajo, sweet pepper)	G	EC	2.5	0.0083	30000	3	15; 14	13 Nov; 28 Nov; 12 Dec; (BBCH 83)	0 7 15 22 30	0.026 0.018 0.021 0.013 0.0070	C024789 01R786-1
41720 Los Palacios, Sevilla, Andalucia, Spain, 2001 (Italico, sweet pepper)	G	EC	2.5	0.0095	26316	3	14; 14	30 May; 13 June; 27 June; (BBCH 81)	0 7 15 22 30	0.020 0.021 0.018 0.0080 0.0060	C024789 01R786-2
Bologna, Italy, 1997 (Corno Roso)	F	EC	1.8	0.014	12500	4	28, 28, 28	16 May; 13 June; 11 July; 8 Aug; (BBCH 77)	30	<0.01 (2)	R016050 97633BO1
Bologna, Italy, 1997 (Corno Roso)	F	EC	3.6	0.028	12500	4	28, 28, 28	16 May; 13 June; 11 July; 8 Aug; (BBCH 77)	30	<0.01 (2)	R016050 97633BO1
70056 Molfetta (BA) Puglia, Italy, 2001 (Eldorado, sweet pepper)	G	EC	2.5	0.0075	33333	3	14; 14	8 June; 22 June; 6 July; (BBCH 86)	0 7 15 21 30	<0.005 <0.005 <0.005 <0.005 <0.005	C024789 01R786-3
70038 Terlizzi, Puglia, Italy, 2001 (Safari, sweet pepper)	G	EC	2.5	0.014	17857	3	13; 15	3 July; 16 July; 31 July; (BBCH 81)	0 7 14 20 29	0.0070 0.0070 <0.005 <0.005 <0.005	C024789 01R786-4
70056 Molfetta, Puglia, Italy, 2001 (Valdo, sweet pepper)	G	EC	2.5	0.016	15625	3	14; 14	11 June; 25 June; 9 July; (BBCH 82)	0 7 15 22 30	0.023 0.016 <0.005 <0.005 <0.005	C024789 01R786-5
47160 St. Leon, Aquitaine, S. France, 2002 (Denver, sweet pepper)	G	EC	2.5	0.062	4000	3	14, 14	10 July; 24 July; 7 Aug; (BBCH 83)	0 16 30	0.065 0.032 0.0068	C036691 02R786-1
70054 Giovinazzo (BA) Puglia, Italy, 2002 (Safari, sweet pepper)	G	EC	2.5	0.026	9765	3	14, 14	28 May; 11 June; 25 June; (BBCH 84)	0 15 30	<0.005 <0.005 <0.005	C036691 02R786-2
04710 St. M. del Aguila, El Ejido, Andalucia, Spain, 2002 (Vergasa, sweet pepper)	G	EC	2.5	0.0083	30000	3	14, 14	25 Sept; 9 Oct; 23 Oct; (BBCH 81)	0 16 30	0.14 0.048 0.044	C036691 02R786-3

BBCH 71-79: 1st - 9th fruit on main stem has reached typical size and form),
BBCH 81-86: 10%-60% of fruits show typical fully ripe colour

R009798. Baudet and Yslan, 1999. GLP. No unusual climatic conditions. Plot size 6-9 m^2. Soil not stated. The formulation diluted in water (100 ml) was sprayed around each plant and thereafter the drip irrigation system was used to incorporate the product into the soil. Plants were treated post-planting at growth stages BBCH 16-81. Fruits (2 kg) were harvested when full size and form was reached (BBCH 79-87). Samples were stored at -18 C for 82-135 days. Anal. method AR 52-87, 1998b, GC-FPD. Results were from duplicate trials. Results were not corrected for matrix interferences (<0.01 mg/kg, n=6) nor for concurrent recoveries (93%-108% at 0.01-0.1 mg/kg).
C024789. Davies, 2002e. GLP. No unusual climatic conditions. Plot size 14-24 m^2. Soil: silt (1, pH 7.9, 3.2% om), sand (2, pH 6.5, 3.5% om), sandy clay (3-5, pH 6.8-7.8, 2.3%-2.6% om). Plants were drip irrigated post-planting at growth stages BBCH 71-84 (fruits fully formed). Fruits were harvested at maturity (BBCH 81-89). Samples were stored at -18°C for 74-271 days. Anal method AR 52-87, 2001a, GC-FPD. Results were not corrected for matrix interferences (<0.005, n=36) nor for concurrent recoveries (71%-94% at 0.005-0.05 mg/kg).
C036691. Klein, 2004c. GLP. No unusual climate conditions. Plot size 13-29 m^2. Soil clay loam (1, pH 6.8, 1.4% om), sandy clay (2, pH 6.9, 2.5% om), clay (3, pH 8.3, 1.5% om). Plants were treated post planting at growth stages BBCH 64-84 (4^{th} inflorescence - maturity). 12-20 fruits were sampled randomly from the centre of the plots at maturity (BBCH 81-89). Samples were stored frozen at -18°C for 207-233 days (02R786-3) or 280-356 days (other trials). Anal. method AR 52-87, 2003b, GC-MS. Sample at 0 daus from trial 02R786-3 is the mean of duplicate laboratory samples. Results were not corrected for matrix interferences (<0.005 mg/kg), nor for concurrent recoveries (71%-111% at 0.005-0.05 mg/kg).
R016050. Maestracci, 1998a. GLP. No unusual climate conditions. Plot size 40 m^2. Soil not stated. Plants were treated post-planting at BBCH 12-77. Irrigation water application with a 1 m band. Fruit (2 kg) was sampled at maturity (BBCH 87) and stored at -18 C for 1 month. Anal. method AR 52-87, 1997, GC-FPD. Results from duplicate trials were not corrected for matrix interferences (<0.01 mg/kg, n=2) nor for concurrent recoveries (88% at 0.01 mg/kg).

Tomato. Supervised trials on tomatoes were carried out indoors and outdoors in 1978 in The Netherlands, 1976 in the USA, 1984 in Brazil, 1996-2001 in Southern Europe (Spain, Italy, Portugal) . Applications were made shortly before or at transplanting with overall soil treatment using GR formulations (Table 68). In addition, trials were carried out where applications were made throughout the growing season using drip irrigation with EC formulations (Table 69).

In the 1978 Netherlands and 1976 US trials the sample storage period was not stated. In the 1996 Italy trials sample storage conditions were not reported.

Table 68. Ethoprophos residues in tomato fruit from supervised trials (indoor and outdoor) after overall soil treatment at pre-planting and post-planting using GR formulations.

Location, year, (variety)	Site	Form.	kg ai/ha	No	Appl. time	PHI (days)	parent (mg/kg)	Ref.
Moerkapelle; The Netherlands, 1978 (var ns)	G	GR	15	1	14 June; pre-plant	48	<0.01 (3)	C034084
Clayton (NC); USA, 1976 (Manapal)	F	GR	3.4	1	9 July; 4 d pre-plant	80 86	<0.005 <0.005	C032715
Clayton (NC); USA, 1976 (Manapal)	F	GR	6.7	1	9 July; 4 d pre-plant	80 86	<0.005 <0.005	C032715
Clayton (NC); USA, 1976 (Manapal)	F	GR	13	1	9 July; 4 d pre-plant	80 86	<0.005 <0.005	C032715
Sitio Morro Alto, Monte Mor, Brazil, 1984 (Santa Cruz)	F	GR	3.0	1	9 Apr; 8 d post-plant	53	<0.05	C033859
Sitio Morro Alto, Monte Mor, Brazil, 1984 (Santa Cruz)	F	GR	6.0	1	9 Apr; 8 d post-plant	53	<0.05	C033859

ns: not specified
na: not applicable
C034084. De Wilde, 1978. **Non-GLP**. Weather conditions, plot size and soil type not stated. Broadcast soil treatment before planting. Formulation was mechanically incorporated into the soil. Fruit samples were picked just at the beginning of the production of crops. Sampling procedures and sample weights were not stated. Samples were stored at -20ºC (period not stated, but at least 3-4 months). In some cases, samples were from triplicate field trials. Anal. method GC-FPD, method 2. Results were not corrected for matrix interferences (<0.01 mg/kg), nor for concurrent method recovery (55%-112%, 0.01-0.1 mg/kg).
C032715. Hunt, 1981. **Non-GLP**. Four replicate residue trials, each subplot was 42 m^2. Soil loamy sand (pH 5.7, 0.5% om). Formulation was spread uniformly by hand and incorporated with a powered garden tiller to a depth of 13-15 cm. Information on treatment dates of cucumber are missing in the report. Samples were stored at -10°C (storage time not

stated). Anal. method. GC-FPD, method 1. Each value represents the average of four replicate trials, individual values were however not reported. Results were not corrected for concurrent recoveries (82%-90% at 0.01-0.1 mg/kg). Information on matrix interferences is not available.
C033859. Fabi, 1984. **Non-GLP**. Weather conditions were not stated. Plot size 3 m^2. Soil clay. Mature fruits were harvested. Samples were stored at -10°C for 40 days. Anal. method GC-FPD, method 3. Results were from duplicate analytical portions of combined samples of triplicate field trials. Results were not corrected for matrix interference (<0.05 mg/kg) nor for concurrent method recovery (98% at 0.05 mg/kg).

Table 69. Ethoprophos residues in tomatoes from supervised trials (indoor and outdoor) using post-transplanting drip irrigation or band spraying using EC formulations.

Location, year, (variety)	Site	Form.	kg ai/ha	kg ai/hl	Water l/ha	No	Interval (days)	Treatment date	PHI (days)	parent (mg/kg)	Ref.
Puebla de Vicar, Almeria, Spain, 1996 (Daniela)	G	EC	1.3	na	na	1	na	26 Mar; mature	7 21 30	<0.01 (2) <0.01 (2) <0.01 (2)	R008853 96635A1
Puebla de Vicar, Almeria, Spain, 1996 (Daniela)	G	EC	2.0	na	na	1	na	26 Mar; mature	7 21 30	<0.01 (2) <0.01 (2) <0.01 (2)	R008853 96635A1
La Canada, Almeria, Spain, 1996 (Daniela)	G	EC	1.3	na	na	1	na	26 Mar; mature	7 21 30	<0.01 (2) <0.01 (2) <0.01 (2)	R008853 96635A2
La Canada, Almeria, Spain, 1996 (Daniela)	G	EC	2.0	na	na	1	na	26 Mar; mature	7 21 30	<0.01 (2) <0.01 (2) <0.01 (2)	R008853 96635A2
Roquetas, Almeria, Spain, 1997 (Brillante)	G	EC	2.0	na	na	3	42, 34	26 Febr; 9 Apr; 13 May (BBCH 82)	7 14 21 30	<0.01 (2) <0.01 (2) <0.01 (2) <0.01 (2)	R008899 97678A1
El Ejido, Alabama, Spain, 1997 (Daniela)	G	EC	2.0	na	na	3	43, 27	25 Febr; 9 Apr; 6 May; (BBCH 72)	7 14 21 30	<0.01 (2) <0.01 (2) <0.01 (2) <0.01 (2)	R008899 97678A2
41720 Los Palacios, Sevilla, Spain, 2000 (Von)	G	EC	2.5		19230	3	25, 24	18 Aug; 12 Sept; 6 Oct; (BBCH 82)	3 7 14 21	<0.01 <0.01 <0.01 <0.01	C016512 ESP0201
41720 Los Palacios, Sevilla, Andalucia, Spain, 2001 (Genaro)	G	EC	2.5	0.0095	26316	3	22, 26	9 May; 31 May; 26 June; (BBCH 87)	0 3 7 14 21	<0.005 <0.005 <0.005 <0.005 <0.005	C023919 01R782-1
04738 Puebla de Vicar, Almeria, Andalucia, Spain, 2001 Eldiez)	G	EC	2.5	0.012	20000	3	24, 26	18 June; 12 July; 7 Aug; (BBCH 82)	0 3 7 14 21	<0.005 <0.005 <0.005 <0.005 <0.005	C023919 01R782-2
Italy, 1996 (ns)	F	EC	4.3	ns	ns	2	14	14 Aug; 28 Aug;	58	<0.01	R008029
Italy, 1996 (ns)	F	EC	2.8	ns	ns	3	14, 14	14 Aug; 28 Aug; 11 Sept;	44	<0.01	R008029
Italy, 1996 (ns)	F	EC	2.1	ns	ns	4	14, 14, 12	14 Aug; 28 Aug; 11 Sept; 23 Sept	32	<0.01	R008029
Bologna, Italy, 1997 (Rio Grande)	F	EC	1.8	0.014	12500	4	28, 28, 28	16 May; 13 June; 11 July; 8 Aug; (BBCH 77)	30	<0.01 (2)	R008904 97632BO1
Bologna, Italy, 1997 (Rio Grande)	F	EC	3.6	0.028	12500	4	28, 28, 28	16 May; 13 June; 11 July;	30	<0.01 (2)	R008904 97632BO1

Location, year, (variety)	Site	Form.	kg ai/ha	kg ai/hl	Water l/ha	No	Interval (days)	Treatment date	PHI (days)	parent (mg/kg)	Ref.
								8 Aug; (BBCH 77)			
Igea Marina (Rn) Az. Cenci, Italy, 1997 (Rio Grande)	G	EC	1.8	0.010	17120	4	30, 21, 20	17 June; 17 July; 7 Aug; 27 Aug; (BBCH 72)	30	<0.01 (2)	R008904 97632BO2
Igea Marina (Rn) Az. Cenci, Italy, 1997 (Rio Grande)	G	EC	3.5	0.021	17120	4	30, 21, 20	17 June; 17 July; 7 Aug; 27 Aug; (BBCH 72)	30	<0.01 (2)	R008904 97632BO2
40057 Granarolo Emilia, Emilia-Romagna, Italy, 2000 (Arlette)	G	EC	2.5		24000	3	25, 25	20 Apr; 15 May; 9 June; (BBCH 81)	3 7 14 21	<0.01 <0.01 <0.01 <0.01	C016512 ITA0101
47814 Igea Marina, Emilia-Romagna, Italy, 2000 (Petula)	G	EC	2.5		18182	3	25, 24	12 May; 6 June; 30 June; (BBCH 81)	3 7 14 21	<0.01 <0.01 <0.01 <0.01	C016512 ITA0102
2585 Olhalvo, Ribatejo e Oeste, Portugal, 2001 (Indal)	G	EC	2.5	0.033	7532	3	27, 25	6 Apr; 3 May; 28 May; (BBCH 74)	0 3 7 14 21	<0.005 <0.005 <0.005 <0.005 <0.005	C023919 01R782-3
2520 Peniche, Ribatejo e Oeste, Portugal, 2001 (Judia)	G	EC	2.5	0.025	10000	3	27, 26	17 May; 13 June; 9 July; (BBCH 84)	0 3 7 14 22	<0.005 <0.005 <0.005 <0.005 <0.005	C023919 01R782-4

ns: not stated
na: not applicable
BBCH 72-77: 2nd - 7th fruit on main stem has reached typical size and form
BBCH 82-87: 20%-70% of fruits show typical fully ripe colour

R008853. Maestracci, 1996. GLP. No unusual climatic conditions. Plot size 27 m^2. Soil not stated. Formulation was applied in 100 ml water around the plant and was incorporated into the soil using the drip irrigation system. Application 196-198 days post-sowing, when plants were 2.5-3 m in height. Fruits (2 kg) were harvested at maturity. Samples were stored for 5-6 months at -20°C. Anal. method AR 52-87, 1996b, GC-TSD. Results were from duplicate trials. Results were not corrected for matrix interferences (<0.01 mg/kg, n=5), nor for concurrent recoveries (73%-98%).

R008899. Maestracci, 1998b. GLP. No unusual climatic conditions. Plot size 5-9 m^2. Soil not stated. Formulation was applied in 100 ml water around the plant and was incorporated into the soil using the drip irrigation system. Samples were treated post-planting throughout the growing season (BBCH 20-BBCH 82). Fruit (2 kg) was sampled at maturity (BBCH 82-89). Samples were stored for 4 months at -18°C. Anal. method AR 52-87, 1997, GC-FPD. Results were from duplicate trials. Results were not corrected for matrix interferences (<0.01 mg/kg, n=8) nor for concurrent recoveries (89%-119%).

R008904. Maestracci, 1998c. GLP. No unusual weather conditions (outdoor) or climatic conditions (indoor). Plot size 29-40 m^2. Soil not stated. Treatment throughout the growing season (BBCH 00-77). Irrigation water application in a band of 1 m wide (outdoor) or 0.5 m wide (indoor). Fruit (2 kg or 23 pieces) was sampled at maturity (BBCH 87) and stored at -8°C for 1-2 months. Anal. method AR 52-87, 1997, GC-FPD. Results were from duplicate trials. Results were not corrected for matrix interferences (<0.01 mg/kg, n=2) nor for concurrent recoveries (79%-78% at 0.01-0.02 mg/kg).

C016512. Hees, 2001b. GLP. No unusual climatic conditions. Plot size 20-33 m^2. Soil sand (ESP0201, pH 7.6, 1.2% om), clay (ITA0101, pH 8.0, 4.1% om), sandy clay loam (ITA0102, pH 8.4, 3.1% om). Application by drip irrigation throughout growing season (BBCH 51-81). Samples (12-24 pieces) were sampled at maturity. Samples were stored at -18°C for 214-233 days (Spain) or 313-353 days (Italy). Anal. method AR 52-87, 2001, GC-FPD. Results were not corrected for matrix interferences (<0.01 mg/kg, n=4) nor for concurrent recoveries (70%-102% at 0.01-0.04 mg/kg).

C023919. Davies, 2002f. GLP. No unusual climatic conditions. Plot size 12-44 m^2. Soil sand (1, pH 6.5, 3.5% om), silt loam (2, pH 7.8, 1.7% om), clay (3-4, pH 7.6-7.7, 0.75-1.4% om). Plants were treated throughout the growing season (BBCH 53-84) using drip irrigation. Fruits were harvested when they reached typical size and form (BBCH 74-89). Samples were stored at -18 °C for 190-263 days (trial 1, 2, 4) or 273-298 days (trial 3). Anal. method AR 52-87, 2001a, GC-FPD. Results were not corrected for matrix interferences (<0.005 mg/kg, n=6) nor for concurrent recoveries (74%-106%).

R008029. Capri *et al*., 1998. **Non-GLP**. Weather conditions not stated. Plot size 12 m^2. Soil loam (pH 8.0, 1.9% om, 20% clay). Tomatoes were grown under a polyethylene mulch. Application via drip irrigation (installed below the mulch) throughout the growing season. Sample size 1 kg. No information on storage. Anal. method GC-NPD, method 1. Results were not corrected for mean method recoveries (90%). Matrix interferences were not investigated

Potato. In supervised field trials on potatoes in 1969-1983 in the USA, in 1982-2001 in Northern Europe (The Netherlands, Germany, UK and Northern France), and in 2000-2001 in Southern Europe (Southern France, Spain and Greece) applications were made shortly before, at, or shortly after planting with overall or band soil treatment using GR or EC formulations (Tables 70 and 71).

For ware potatoes the normal harvest period is within 90 to 120 days post-application (either at planting or a few days pre-planting). Early maturing potatoes can be harvested before 90 days while late maturing ones (such as Russet Burbank or Maris Piper) are usually harvested after 120 days. The PHI is therefore very much dependent upon the crop variety.

In the 1969-1973 US trials concurrent recoveries were not reported. Samples from the 1989-1990 UK trials and some from the 1969-1973 US trials were partly stored in ambient and/or cool conditions. In the 1983 US trials samples were stored in unknown conditions

Three of the four 1995 UK trials suffered from abnormal weather conditions resulting in retarded growth of the tubers. Furthermore the LOQ should be increased to an unacceptably high level of 0.4 mg/kg, because residues were found in control samples (up to 0.096 mg/kg in trial GB4).

In some trials (GR formulation) individual tubers were analysed. The results are given in Table 72.

In the GB 1-GB5 trials (1995 UK), 2 composite field samples of 12 tubers each (from 3 plants each) were taken from the treated plots, together with 10 individual tubers.

In trial 99673GB4 (1999 UK), 2 composite field samples of 50 tubers each were taken together with 100 individual tubers. Average unit weights were 63.2 g (SD 27.3 g) and ranged from 17.7-85.1 g.

In trial 01R741-5 (2001, N. France) a composite field sample of 50 tubers was taken at PHI=101, together with 50 individually measured tubers. Average unit weights were 106 g (st.dev. 28 g) and ranged from 71 to 203 g.

Table 70. Ethoprophos residues in potato tubers from supervised trials (outdoor) after overall soil treatment or band application pre-planting/at planting using single applications of GR formulations.

Location, year, (variety)	Form.	Method	kg ai/ha	Growth stage at harvest	PHI (days)	Parent (mg/kg); individual, mean	Ref.
Dedemsvaart, The Netherlands 1982 (Procura)	GR 2070	Overall worked into soil	10	harvest	159	<0.02	R007979 227.84
Dedemsvaart, The Netherlands 1982 (Procura)	GR 2071	Overall; worked into soil	10	harvest	159	<0.02	R007979 227.84
Dedemsvaart, The Netherlands 1982 (Procura)	GR 2010	Overall; worked into soil	10	harvest	159	<0.02	R007979 227.84
5303-Hersel, Germany, 1986 (Granola N)	GR (FG) 6034	Overall; on the soil	10	70[2] 80[2] 90	91 113 133	<0.01 <0.01 <0.01	R007984 16250-87
5303-Hersel, Germany, 1986 (Granola N)	GR (FG) 5979	Overall; on the soil	10	70[2] 80[2] 90	91 113 133	<0.01 <0.01 <0.01	R007984 16250-87
2848-Langforden-Holtrup, Germany, 1986 (Bintje)	GR (FG) 6034	Overall; worked into soil	10	ns ns harvest	107 128 149	0.012 <0.01 <0.01	R007984 16250-87
2848-Langforden-Holtrup, Germany, 1986 (Bintje)	GR (FG) 5979	Overall; worked into soil	10	ns ns harvest	107 128 149	<0.01 <0.01 <0.01	R007984 16250-87
8069-Reichertshofen,	GR	Overall;	10	ns	98	0.044	R007984

Location, year, (variety)	Form.	Method	kg ai/ha	Growth stage at harvest	PHI (days)	Parent (mg/kg); individual, mean	Ref.
Bayern, Germany, 1986 (Granola)	(FG) 6034	worked into soil		ns 92	116 140	0.018 0.016	16250-87
8069-Reichertshofen, Bayern, Germany, 1986 (Granola)	GR (FG) 5979	Overall; worked into soil	10	ns ns 92	98 116 140	0.033 0.019 0.017	R007984 16250-87
4478-Dalum, Niedersachsen, Germany, 1986 (Mentor)	GR (FG) 6034	Overall; worked into soil	10	ns ns 85/87	98 119 140	0.010 <0.01 0.014	R007984 16250-87
4478-Dalum, Niedersachsen, Germany, 1986 (Mentor)	GR (FG) 5979	Overall; worked into soil	10	ns ns 85/87	98 119 140	<0.01 <0.01 <0.01	R007984 16250-87
2806 Ogten, Germany, 1987 (Indiva)	GR (FG)	Band; worked into soil	7.0[1]	harvest harvest	104 175	0.030; <0.01	R007988
4472 Haren, Germany, 1987 (Darwina)	GR (FG)	Band; worked into soil	4.7[1]	harvest	182	<0.01	R007988
4472 Haren, Germany, 1987 (Darwina)	GR (FG)	Band; worked into soil	4.7[1]	harvest	182	0.012	R007988
4472-Haren, Germany, 1989 (Elles)	GR (FG)	band	7.0	69[2] 79[2] 89[2] 99	86 128 146 183	<0.01 <0.01 <0.01 <0.01	R008000
4472-Haren, Germany, 1989 (Elles)	GR (FG)	band	7.0	79[2] 81[2] 99	128 146 183	<0.01 <0.01 <0.01	R008000
3102-Hermannsburg, Germany, 1989 (Cilena)	GR (FG)	band	7.0	68[2] 77[2] 89[2] 99	83 109 144 151	0.070 <0.01 <0.01 <0.01	R008000
3102-Hermannsburg, Germany, 1989 (Cilena)	GR (FG)	band	7.0	68[2] 77[2] 89[2] 99	83 109 144 151	0.010 0.015 0.012 <0.01	R008000
Vahlde, Germany, 1989, (Producent)	GR (FG)	overall; on the soil	7.0	ns ns ns	96[2] 152 201	0.034 0.017 <0.01	R008000
Drestedt, Germany, 1989 (Roxi)	GR (FG)	overall; on the soil	7.0	ns ns	154 177	0.02 <0.01	R008000
Vahlde, Germany, 1989 (Producent)	GR (FG)	overall; worked into soil	10	ns ns ns	96[2] 152 201	0.011 <0.01 <0.01	R008000
86368 Gersthofen, Bayern, Germany, 2001, (Bintje)	GR (FG)	Overall; worked into soil	11	BBCH62 BBCH75 BBCH93	81[2] 98 123	0.010 0.0076 <0.005	C019661 01R741-6
Margate, Kent, UK, 1989, (Desiree)	GR	Overall; worked into soil	11	harvest	136	<0.01	R008006 4500/2
Rufford, Lancashire, UK, 1989, (Wilja)	GR	Overall; worked into soil	11	fully formed	138	<0.01	R008006 4500/1
Wart Hill, Yorkshire, UK, 1990 (Pentland Dell)	GR	overall; worked into soil	33	ns	118	<0.01	R008010 5394/1
Weston on Trent, Derbyshire, UK, 1995 (Maris Bard)	GR	overall; worked into soil	11	BBCH625	75[2]	<0.01-0.017; mean 0.014	R007970 GB1
Weston on Trent,	GR	overall;	11	BBCH639	80[2]	<0.010 (2); mean	R007970

Location, year, (variety)	Form.	Method	kg ai/ha	Growth stage at harvest	PHI (days)	Parent (mg/kg); individual, mean	Ref.
Derbyshire, UK, 1995 (Wilia)		worked into soil				<0.010	GB2
Frodsham, Cheshire, UK, 1995 (Maris Bard)	GR	overall; worked into soil	11	BBCH601	70[2]	<0.01-0.050; mean 0.030	R007970 GB4
Albrighton, Shropshire, UK, 1995 (Dundrod)	GR	overall; worked into soil	11	BBCH501	71[2]	0.14-0.17; mean 0.16	R007970 GB5
Ongar, Essex, UK, 1999, (Desiree)	GR	Overall; worked into soil	11	BBCH65	85	<0.005, 0.005, mean 0.005	R016070 99673GB1
Roxwell, Essex, UK, 1999, (King Edwards)	GR	Overall; worked into soil	11	BBCH67	84	<0.005 (2); mean <0.005	R016070 99673GB2
Lineham, Wiltshire, UK, 1999, (Maris Peer)	GR	Overall; worked into soil	11	mature	85	<0.005 (2); mean <0.005	R016070 99673GB3
Beccles, Suffolk, UK, 1999, (Desiree)	GR	Overall; worked into soil	11	ns	84	0.009; 0.011; mean 0.010	R016070 99673GB4
Diss, Norfolk, UK, 1999, (Desiree)	GR	Overall; worked into soil	11	ns	84	<0.005(2); mean <0.005	R016070 99673GB5
Ely, Cambridgeshire, UK, 1999 (Maris Piper)	GR	Overall; worked into soil	11	mature	84	<0.005 (2); mean <0.005	R016070 99673GB6
Ely, Cambridgeshire, UK, 2001 (Maris Piper)	GR	Overall; worked into soil	11	BBCH61 BBCH47 BBCH49	79[2] 100 122	<0.005 <0.005 <0.005	C019661 01R741-1
Ely, Cambridgeshire, UK, 2001 (Maris Piper)	GR (FG)	Overall; worked into soil	55	BBCH61 BBCH49	79[2] 100	0.021, 0.032; mean 0.027 0.0054	C019661 01R741-1
Ely, Cambridgeshire, UK, 2001 (Maris Piper)	GR (FG)	Overall; worked into soil	11	BBCH65 BBCH47 BBCH48	81[2] 99 120	<0.005 <0.005 <0.005	C019661 01R741-2
Ely, Cambridgeshire, UK, 2001 (Maris Piper)	GR (FG)	Overall; worked into soil	55	BBCH65	81[2]	<0.005	C019661 01R741-2
Chelmsford, Essex, UK, 2001 (King Edwards)	GR (FG)	Overall; worked into soil	11	BBCH69 BBCH47 BBCH99	80[2] 101 119	<0.005 <0.005 <0.005	C019661 01R741-3
30 Aramon; S. France, 2000 (Venuska)	GR	Overall; worked into soil	10	BBCH41 BBCH48 BBCH48	62[2] 78 90	<0.01 (2); mean <0.01; <0.01 (2); mean <0.01 <0.01 (2); mean <0.01	C013482 00563AV1
11 Carcassone, S. France, 2000 (Sirtema)	GR	Overall; worked into soil	10	BBCH41 BBCH44 BBCH48	61[2] 80[2] 90	0.014, 0.029; mean 0.019 <0.01; 0.028; mean 0.019 <0.01 (2); mean <0.01	C013482 00563TL1
60480 St. Andre Farivillers, Picardie, N. France, 2001 (Bintje)	GR (FG)	Overall; worked into soil	11	BBCH69 BBCH48 BBCH49	77[2] 98 119	<0.005 <0.005 <0.005	C019661 01R741-4
51370 Thillois, Champagne-Ardenne; N. France, 2001, (Bintje)	GR (FG)	Overall; worked into soil	11	BBCH65 BBCH45 BBCH89	80[2] 101 122	0.0086 <0.005 <0.005	C019661 01R741-5
69380 Chazay d'Azergues; Rhone-Alpes, S. France, 2001, (Bintje)	GR (FG)	Overall; worked into soil	10	BBCH61 BBCH68 BBCH79 BBCH89	58[2] 70 80 91	0.042 <0.01 0.011 <0.01	C019660 01R755-1
46230 Alginet, Valencia, Spain, 2000, (Obelix)	GR; (FG)	Overall; on the soil	10	BBCH41 BBCH48	60[2] 88	<0.01 <0.01	C015231 ESP0101

Location, year, (variety)	Form.	Method	kg ai/ha	Growth stage at harvest	PHI (days)	Parent (mg/kg); individual, mean	Ref.
50100 Drepano-Kozani, Greece, 2000, (Spuda)	GR; (FG)	Overall; on the soil	10	BBCH43 BBCH48	59[2] 129	<0.01 <0.01	C015231 GRC0201
50100 Drepano-Kozani, Greece, 2001, (Aria)	GR	Overall; worked into soil	10	BBCH63 BBCH63	82[2] 92	<0.01 <0.01	C019660 01R755-2
Prosser (WA), USA, 1969 (Irish White)	GR	overall	2.2	ns	168	<0.02	R007982
Prosser (WA), USA, 1969 (Irish White)	GR	overall	4.5	ns	168	<0.02	R007982
Prosser (WA), USA, 1969 (Irish White)	GR	overall	6.7	ns	168	<0.02	R007982
Ashland (VA), USA, 1970 (Irish White)	GR	band; 0.46 m wide	3.4	ns	122	<0.02	R007982
Ashland (VA), USA, 1970 (Irish White)	GR	overall	6.7	ns	122	<0.02	R007982
Ashland (VA), USA, 1970 (Irish White)	GR	band; 0.46 m wide	3.4[3]	ns	87	<0.02	R007982
Prosser (WA), USA, 1970 (Irish White)	GR	overall	2.2	ns	165	<0.02	R007982
Prosser (WA), USA, 1970 (Irish White)	GR	overall	4.5	ns	165	<0.02	R007982
Hastings (FL), USA, 1971 (Irish White)	GR	Band, 0.46 m wide	3.4	ns	98	<0.02	R007982
Moscow (ID), USA, 1971 (Irish White)	GR	Band, 0.30 m wide	4.5	ns	110-112	<0.02	R007982
Moscow (ID), USA, 1971 (Irish White)	GR	Overall	9.0	ns	110-112	<0.02 (2); mean <0.02	R007982
Moscow (ID), USA, 1971 (Irish White)	GR	Band, 0.30 m wide	4.5[3]	ns	96-98	<0.02	R007982
Hastings (FL), USA, 1973 (Irish White)	GR	Band; 0.30-0.36 m wide	3.4	ns	91	<0.02	R007982
Hancock (WI), USA, 1983 (Russet Burbank)	GR (10G)	Band	13	ns	146	<0.01	C033867; 674883-258

Two digit BBCH codes: BBCH 41-48: 10%-80% of total final tuber mass reached); 48 is considered mature.
Three digit BBCH codes refer to nth flowering: BBCH 501: first individual buds of 1st inflorescence visible; BBCH 601: 10% of flowers of the 1st inflorescence open; BBCH 625: 50% of flowers of the 2nd inflorescence open, BBCH 639: end of flowering of 3rd inflorescence

[1] Band application: the dose refers to the overall surface and not to the treated surface

[2] Potatoes had not reached final maturity.

[3] Band application at the post-emergence stage (14 d post-planting in ID, 35 d post-planting in VA).

R007979. Muller and Buys, 1984. **Non-GLP**. Between application and harvest the rainfall was 228 mm (temperature not stated). Plot size 67 m^2. Soil: sandy soil (18% humus). Three different granular formulations were tested: CRD 82.2071 (20% ai, 78% pumice); CRD 82.2070 (20% ai, 70% sepiolite) and CRD 82.2010 (10% ai, 80% sepiolite). The formulation was worked into the soil with a rotary cultivator (depth not stated). Field samples (40 potatoes) were taken as follows: 5 rows; 2 plants per row; 4 potato tubers per plant; laboratory samples at random (20 potatoes each). Potato tubers were rapidly washed with distilled water, homogenised and stored for 3 months at -20ºC. Anal. method MP-RE-08-83. Results are the average of duplicate analytical portions. Results were not corrected for matrix interferences (<0.02, n=2) nor for concurrent recoveries (94%-95% at 0.02-0.2 mg/kg).

R007984. Dupont and Muller, 1987. **Non-GLP**. Details of climatic conditions were not given. Plot size 100-5000 m^2. Soil: Hersel: "LS" (1.2% org.C; pH = 6.2); Langförden-Holtrup = "h LS" (2.6% org. C, pH 5.0); Reichertshofen = sandy soil (3.0% org. C; pH 5.5); Dalum = "sandmischcultur" (3.5% org. C, pH 5.5). Two experimental formulations were tested with 20% (w/w) ai: Exp 6034 with 78% pumice and Exp 5979 with 70% sepiolite. Formulation was either spread onto the soil at the time of ridging (Hersel), worked into the soil for 10-15 cm with a rotary cultivator (Langförden-Holtrup), for 8-10 cm with a drill and a seed harrow (Reichertshofen) or with a drill and deep cultivator (Dalum). Field samples (2-200 kg) were reduced to 2 kg laboratory samples. Samples were washed and frozen either as whole tubers or as cut tubers at -19ºC for 1-4 months, then blended and stored at –20ºC for another 3-4 months. Anal method AR 52-87, 1987a, GC-FPD. Results were not corrected for matrix interferences (<0.01 mg/kg, n=12) nor for concurrent recoveries 82%-115% (0.01-0.04 mg/kg).

R007988. Dupont and Muller, 1988a. **Non-GLP**. Details of climatic conditions were not given. Plot size 25 - 420 m^2. Soil: Haren = sandy soil; Ogten = "lS" (2.75% organic carbon; pH 5.5). Formulation was worked into the soil before, during or post-planting. Unwashed field/laboratory samples (2 kg) were frozen as whole tubers at -20ºC for 1-4 months. Samples were blended and kept frozen at –20ºC for another 1-2 months. Results are the average of two analytical portions. Anal. method AR 52-87, 1988a, GC-FPD. Results were not corrected for matrix interferences (<0.01 mg/kg, n=2) nor for concurrent recoveries 96%-100% (0.01-0.04 mg/kg).
R008000. Dupuis and Muller, 1990. **Non-GLP**. Details of weather conditions were not given. Plot size 480-10000 m^2. Soil, Haren = sandy soil, Hermannsburg = lS (1.0% org. C, pH 5.2), Vahlde and Drestedt not stated. Formulation was either spread onto the soil (Vahlde, Drestedt) or worked into the soil with a drill and a cultivator (Vahlde) or was worked into the soil during planting and ridging (Haren, Hermannsburg). Laboratory samples (2kg) were either brushed or brushed and washed and cut in pieces, and kept at -18 C for 3-7 months, then blended and kept frozen at -20 C for 2-3 months. Anal. method AR 52-87, 1990, GC-FPD. Results were not corrected for matrix interferences (<0.01 mg/kg, n=15) nor for concurrent recoveries (87%-96% at 0.01-0.06 mg/kg).
C019661. Davies, 2002b. GLP. No unusual weather conditions. No rain within 24 h of application. Plot size 86-105 m^2. Soil: peat (pH 6, 15% om) trials 1 and 2, clay loam (pH 6.5-8.1, 2-4% om) for trial 3, 4, 5 and sandy loam (pH 6.9, 2.3% om) for trial 6. Manual spreading or by hand with pepper pot. Brushed potatoes. Field samples of 50 tubers. Samples were stored at -18°C for 14-112 days. Anal. method AR 52-87, 2001c, GC-PFPD/MS. Results are the means of 1-3 replicate analytical portions. Trial 01R741-3, PHI=79 days duplicate field samples. Results were not corrected for matrix interferences (<0.005 mg/kg, n=41) nor for concurrent recoveries 75%-111% (0.005 mg/kg).
R008006. Brockelsby *et al*., 1991a. **Non-GLP**. Weather conditions: more dry and hot than usual. Plot size 480 m^2 (Margate) or 24 rows of 200 m (Rufford). Soil: SCL (Margate) or LS (Rufford). Field samples (5 kg) were stored at ambient temperature for 7-13 days and thereafter at 4°C for 7 days. Tubers were washed to remove loose soil and stored at -20°C for 270 days. Anal method 175-1990. Results are the average of two replicate analytical portions. Results were not corrected for matrix interferences (<0.01 mg/kg, n=1), nor for concurrent recoveries (77%-102% at 0.01-20 mg/kg).
R008010. Brockelsby *et al*., 1991b. **Non-GLP**. No unusual weather conditions. No rainfall 24 h after application. Plot size 11 m^2. Soil sandy loam. Application by hand pepper pot. Field samples of 5 kg. Samples were stored 1 day at ambient temperature, followed by 7 days at 4°C and thereafter for 268 days -18°C. Potatoes were washed before analysis. Anal method 175-1991. Results were not corrected for matrix interferences (<0.3LOQ, n=1), nor for concurrent recoveries (79%-96% at 0.01-0.1 mg/kg).
R007970. King, 1996. GLP. Weather conditions: rainfall below average. Plot size 60 m^2. Soil (ADAS 85 system): sandy clay loam (GB1, GB2) or silty loam (GB4, GB5). Experimental formulation EXP 05806A on a sepiolite basis. Formulation was worked into the soil using a penumatic granule applicator. Two composite field samples of 12 tubers each (from 3 plants each) were taken and adhering soil was removed. Samples were stored at -18°C for 231-275 days. Anal. method AR 52-87, 1996a, GC-FPD. Residues were not corrected for matrix interferences (<0.01 mg/kg and **0.096 mg/kg in GB4 trial**) nor for concurrent recoveries (83%-112% at 0.01 mg/kg).
R016070. Venet, 2000. GLP. No rain at planting. No unusual weather conditions. Plot size 40-50 m^2. Application by pepper pot and incorporation into soil. Field samples consisted of 50 potatoes, brushed. Samples from GB3 and GB4 plots were stored at ambient temperature for 3-21 days until dispatch and stored frozen thereafter at -18°C for 101-214 days. Anal. method AR 52-87, 1999, GC-FPD. Results are the average of duplicate field samples. Residues were not corrected for matrix interferences (<0.005 mg/kg, n=13) nor for concurrent recoveries (72%-105% at 0.005-0.1 mg/kg).
C013482. Gateaud, 2001. GLP. No unusual weather conditions. No rain at application. Plot size 45-48 m^2. Soil not specified. Application was incorporated into the soil with a harrow or rotary spade barrow (rotavator). Brushed potatoes, 1-2 kg samples. Samples were stored at -18°C for 217-266 days. Anal. method AR 52-87, 2000, GC-PFPD. Results are the average of duplicate field samples. Residues were not corrected for matrix interferences (<0.01 mg/kg, n=8) nor for concurrent recoveries (100%-110% at 0.01 mg/kg).
C015231. Hees, 2001a. GLP. No unusual weather conditions. Rainfall within 6 hours of treatment in Greek trial, no rainfall at treatment for Spanish trial. Plot size at least 45-75 m^2. Soil clay loam (pH 6.5-8.6, 1.3-1.8% om). Manual spreading. Randomly sampled, 15 tubers per field sample. Earth was removed. Samples were stored at -18°C for 259-351 days. Anal. method AR 52-87, 2000, GC-FPFD. Results were not corrected for matrix interferences (<0.01 mg/kg, n=6) nor for concurrent recoveries (95%-107% at 0.01 mg/kg).
C019660. Davies, 2002a. GLP. No unusual weather conditions. No rainfall within 24 h after application. Plot size 36-60 m^2. Soil clay loam (pH 6.5-6.8, 1.3-1.8% om). Manual spreading. Earth removed. Samples were stored frozen for 84-112 days at -18°C. Anal. method AR 52-87, 2001b, GC-PFPD. Results were not corrected for matrix interferences (<0.005 mg/kg, n=12) nor for concurrent recoveries (90%-95% at 0.01 mg/kg).
R007982/C034085. Mobil, 1973, 1974. **Non-GLP**. Details of weather conditions, soil, plot size and sampling were not available. Samples were stored frozen for 36-235 days or 1-34 days in unknown (cooled/ambient) conditions before analysis. Anal. method R-89-A. Results were not corrected for matrix interferences (<0.02 mg/kg, n=3). **Concurrent recoveries were not reported.**
C033867. Guyton, 1984. **Non-GLP**. Weather conditions not reported. Plot size 4 rows of 7.6 m. Soil: silt loam (0.6% om, pH 6.5-7.5). Application as a 12 inch band (4.5 kg ai/ha, equivalent to 13.5 kg ai/ha broadcast rate), using a tractor-mounted granule applicator. Samples from 4 replicate plots were combined as one sample (2.2 kg). Samples were stored for 161-162 days (**storage conditions not stated**). Anal. method GC-FPD, method 1. Results were not corrected for matrix interferences (<0.3LOQ, n=2), nor for concurrent recoveries (92%-100% at 0.5-2.5 mg/kg).

Table 71. Ethoprophos residues in potato tubers from supervised trials (outdoor) using EC formulations.

Location, year, (variety)	kg ai/ha	kg ai/hl	No	Method; treatment time	Growth stage at harvest	PHI (days)	parent (mg/kg)	Ref.
Auburn (AL), USA, 1973 (White Irish)	9.0	ns	1	overall- (1 Febr); at planting	ns	133	<0.02	R007982
Prosser (WA), USA, 1983 (Russet Burbank)	14	ns	1	overall- (7 Apr); 6 d pre-planting	ns	146	<0.01	C033867; 354683-401
Parma (ID), USA, 1983, (Russet Burbank)	6.7[1]	ns	2	overall; 22Apr (at planting) and band application at 14 June (54 d post-planting)	ns	105	<0.01	C033867; 351183-403

[1] First application was overall at 6.7 kg ai/ha, the second application a band application (width 0.305 m) at a dose rate of 3.4 kg ai/ha (equivalent to 6.7 kg ai/treated ha).

R 007982/C034085. Mobil, 1973, 1974. **Non-GLP**. Details of weather conditions, soil, plot size and sampling were not available. Samples were stored frozen for 36 days. Anal. method R-89-A. Results were not corrected for matrix interferences (<0.02 mg/kg, n=3). Concurrent recoveries were not reported.

C033867. Guyton, 1984. **Non-GLP**. Plot size 315-360 sqft. Soil: silt loam, <1.0-2.0% om, pH 6.5-7.5. Application by CO2 sprayer. Samples from 5 replicate plots combined in one sample (2.2 kg) and stored for 161-162 days (storage conditions not stated). Anal. method GC-FPD, method 1. Results were not corrected for matrix interferences (<0.3LOQ, n=2), nor for concurrent recoveries (92%-100% at 0.5-2.5 mg/kg).

Table 72. Ethoprophos residues in individual potato tubers from supervised trials (outdoor) after overall soil treatment or band application pre-planting /at planting using overall GR formulations worked into soil.

Location, year, (variety)	kg ai/ha	No	Growth stage at harvest	PHI (days)	parent (mg/kg); individual	Ref.
Weston on Trent, Derbyshire, UK, 1995 (Maris Bard)	11	1	BBCH625	75	<0.01 (6x), 0.012, 0.015, 0.025, 0.037	R007970 GB1
Weston on Trent, Derbyshire, UK, 1995 (Wilia)	11	1	BBCH639	80	<0.01 (10x)	R007970 GB2
Frodsham, Cheshire, UK, 1995 (Maris Bard)	11	1	BBCH601	70	<0.01 (2x), 0.011, 0.017, 0.018, 0.019, 0.026, 0.027, 0.051, 0.23	R007970 GB4
Albrighton, Shropshire, UK, 1995 (Dundrod)	11	1	BBCH501	71	<0.01 (2x), 0.017, 0.048, 0.055, 0.068, 0.071, 0.090, 0.093, 0.32	R007970 GB5
Beccles, Suffolk, UK, 1999, (Desiree)	11	1	ns	84	<0.005 (12x), 0.005 (4x), 0.006 (9x), 0.007 (8x), 0.008 (7x), 0.009 (9x), 0.010 (2x), 0.011 (5x), 0.012 (6x), 0.013 (3x), 0.014 (7x), 0.015 (2x), 0.016 (4x), 0.017, 0.018 (5x), 0.020, 0.021 (2x), 0.022, 0.023, 0.024 (2x), 0.026, 0.030, 0.036, 0.038, 0.045 (2x), 0.049, 0.056, 0.076	R016070 99673GB4
51370 Thillois, Champagne-Ardenne; N. France, 2001, (Bintje)	11	1	BBCH45	101	<0.005 (48x), 0.005, 0.007	C019661 01R741-5

Sweet potato. Supervised field trials on sweet potatoes were carried out in 1984 in the USA. Applications were as a band at or shortly after planting with GR formulations (Table 73). In all the trials samples were stored in unreported conditions.

Table 73. Ethoprophos residues in sweet Centennial potato tubers from supervised trials (outdoor) after band application using GR formulations.

Location, year,	kg ai/ha	kg ai/hl	No	Treatment time	PHI (days)	parent (mg/kg)	Ref.
Ville Pratte, (LA),	3.4	2.4	1	3 Aug; 37 d post planting at	101	<0.01	C032642

Location, year,	kg ai/ha	kg ai/hl	No	Treatment time	PHI (days)	parent (mg/kg)	Ref.
USA, 1984				lay-by			201784-201
Ville Pratte, (LA), USA, 1984	5.0	3.6	1	3 Aug; 37 d post planting at lay-by	101	0.014	C032642 201784-201
Bunkie, (LA), USA, 1984	3.4	na	2	10 May (at planting); 15 June (36 d post-planting at lay-by)	123	<0.01	C032642 201784-200
Bunkie, (LA), USA, 1984	5.0	na	1	15 June; 36 d post planting at lay-by	123	<0.01	C032642 201784-200

C032642. Guyton, 1985. **Non-GLP**. Weather conditions not stated. Plot size ns (Bunkie) or 0.4-0.8 ha (Ville Pratte). Soil sandy loam (Bunkie) or ns (Ville Pratte). Application volume 140 l/ha (water) for Ville Pratte. Random field samples (1.5 kg each). Samples were stored for 259-286 days, storage conditions not stated. Anal. method 175-1985. Results were not corrected for matrix interferences (<0.01 mg/kg), nor for concurrent recoveries (80%-109% at 0.01-0.1 mg/kg).

Sugar cane. Supervised trials on sugar cane were carried out in the field in 1965-1969 in the USA, in 1988-1989 in India and 1987 in Brazil. Applications were carried out in the open furrow at planting or post-planting using GR formulations. Results were available for stalks and leaves (Tables 74 and 75).

In the 1965-1969 US trials concurrent recoveries were not reported. In the 1965-1969 USA and 1988-1989 India trials samples were stored in unreported conditions.

Table 74. Ethoprophos residues in sugar cane stalks from supervised trials (outdoor) with an application in the open furrow at planting or post-planting using GR formulations.

Location, year, (variety)	Method	kg ai/ha	No	Treatment date	PHI (days)	parent (mg/kg)	Ref.
Baton Rouge (LA), USA, 1965-66 (ns)	ns	6.7	1	30 Nov 1965; at planting	305	<0.02	C032664
Belle Glade (FL), USA, 1966-67 (ns)	ns	4.2	1	25 Febr 1966; at planting	324	<0.02	C032664
Belle Glade (FL), USA, 1966-67 (ns)	ns	8.4	1	25 Febr; 1966 at planting	324	<0.02	C032664
Belle Glade (FL), USA, 1966-67 (ns)	ns	17	1	25 Febr 1966; at planting	324	<0.02	C032664
Baton Rouge (LA), USA, 1967-68 (ns)	ns	2.2	1	18 Oct 1967; at planting	384	<0.02	C032664
Belle Glade (FL), USA, 1967-68 (ns)	ns	11	1	25 Oct 1967; at planting	320	<0.02	C032664
Belle Glade (FL), USA, 1967-68 (ns)	ns	4.5	1	30 Nov 1967; at planting	320	<0.02	C032664
Belle Glade (FL), USA, 1968 (ns)	ns	5.6	1	16 Feb 1968; at planting	242	<0.02	C032664
Baton Rouge (LA), USA, 1968-69 (ns)	ns	4.5	1	3 Oct 1968; at planting	371	<0.02	C032664
Jalgaon, Maharastra, India, 1988-89	band	1.0	1	3 Febr 1988; at planting	384	<0.01 (3)	C036561
Jalgaon, Maharastra, India, 1988-89	band	2.0	1	3 Febr 1988; at planting	384	<0.01 (3)	C036561
Jalgaon, Maharastra, India, 1988-89	band	3.0	1	3 Febr 1988; at planting	384	<0.01 (3)	C036561
Paulinia, Brazil, 1987 (NA 5679)	band	3.0	1	7 Aug; post planting, height 2.2 m	32 47 62	<0.01 <0.01 <0.01	C033863/ C033864
Paulinia, Brazil, 1987 (NA 5679)	band	6.0	1	7 Aug; post planting, height 2.2 m	32 47 62	0.01 <0.01 <0.01	C033863/ C033864

C032664. Mobil, 1971. **Non-GLP**. Weather conditions, plot size, soil, treatment and sampling procedures were not stated. Plants were divided into stalks and leaves and stored in unspecified conditions (ambient, cool) for 6-221 days. Anal. method R-89-A. Some samples were the average of 2-4 laboratory samples. Results were not corrected for matrix interferences (<0.02 mg/kg). Concurrent recoveries were not reported.

C036561. Parthasarathy, 1989. **Non-GLP**. No unusual weather conditions. Plot size not stated. Soil black clay. Sugar canes and leaves were taken at maturity. Storage conditions were not stated. Anal. method GC-TSD method 1. Results were from triplicate trials. Results were not corrected for matrix interferences (<0.01 mg/kg, n=1) nor for concurrent recoveries (89%-93% at 0.02-0.05 mg/kg).
C033863/C033864. Fabi, 1987a/b. **Non-GLP**. Weather conditions were not reported. Soil clay. Four replicate fields, 20 m^2each. Individual results for the replicate fields were not reported. Samples were harvested at maturity. Samples were stored at -10°C for 28-53 days. Anal. method GC-FPD, method 3. Results were not corrected for matrix interferences (<0.01 mg/kg, n=1) nor for concurrent recoveries (86% at 0.05 mg/kg).

Table 75. Ethoprophos residues in sugar cane leaves from supervised trials (outdoor) with an application in the open furrow at planting using GR formulations.

Location, year, (variety)	Method	kg ai/ha	No	Treatment time	PHI (days)	parent (mg/kg)	Ref.
Belle Glade (FL), USA, 1967-68 (ns)	ns	11	1	25 Oct 1967; at planting	320	<0.02	C032664
Belle Glade (FL), USA, 1967-1968 (ns)	ns	4.5	1	30 Nov 1967, at planting	320	<0.02	C032664
Belle Glade (FL), USA, 1968 (ns)	ns	5.6	1	16 Feb 1968, at planting	242	<0.02	C032664
Jalgaon, Maharastra, India, 1988-89	band	1.0	1	3 Febr 1988; at planting	384	<0.01 (3)	C036561
Jalgaon, Maharastra, India, 1988-89	band	2.0	1	3 Febr 1988; at planting	384	<0.01 (3)	C036561
Jalgaon, Maharastra, India, 1988-89	band	3.0	1	3 Febr 1988; at planting	384	<0.01 (3)	C036561

C032664. Mobil, 1971. **Non-GLP**. Weather conditions, plot size, soil, treatment and sampling procedures were not stated. Plants were divided into stalks and leaves. Samples were stored in unspecified conditions (ambient, cool) for 6-10 days. Anal. method R-89-A. Samples were the average of 2-4 laboratory samples. Results were not corrected for matrix interferences (<0.02 mg/kg). Concurrent recoveries were not reported.
C036561. Parthasarathy, 1989. **Non-GLP**. No unusual weather conditions. Plot size not stated. Soil black clay. Sugar canes and leaves were taken at maturity. Storage conditions were not stated. Anal. method GC-TSD method 1. Results were from triplicate plots. Results were not corrected for matrix interferences (<0.01 mg/kg, n=1) nor for concurrent recoveries (89%-93% at 0.02-0.05 mg/kg).

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

The Meeting received information on the fate of residues during commercial storage of bananas (Dupont and Muller, 1988b).

The effect on residues of storage for fruit ripening at 7 days at 10°C followed by 8 days at 20°C were investigated. Samples were immediately analysed using method JFRL GC-FPD. Results were not corrected for matrix interference (<0.005 mg/kg) nor for concurrent method recovery (100% at 0.01 mg/kg). They are shown in Table 76.

Only the two trials where residues were found at harvest were considered suitable for evaluation. Storage had no effect on the residues in banana fruit which were 80%-130% of the original residue levels.

Table 76. Ethoprophos residues in banana fruit[1] from supervised trials (indoor/outdoor) in the Philippines after soil treatment with GR formulations and storage at two temperatures.

Location, year, (variety)	kg ai/ha	No	Interval	DAT	parent (mg/kg)	% initial	Ref.
Tadeco, 1987-88, (ns)	2.5	3	60^2, 90^2	$>30^2$	<0.005	-	R011296

Location, year, (variety)	kg ai/ha	No	Interval	DAT	parent (mg/kg)	% initial	Ref.
				+7+8[3]	<0.005	-	
Tadeco, 1987-88, (ns)	2.5	3	120[2] 120[2]	>30[2] +7+8[3]	<0.005 <0.005	- -	R011296
Tadeco, 1987-88, (ns)	2.5	3	60[2], 90[2]	>30[2] +7+8[3]	<0.005 <0.005	- -	R011296
Hijo, 1988, (ns)	3.0	2	150[2]	>30[2] +7[3] +7+8[3]	0.0060 0.0057 0.0050	- 95% 83%	R011296
Evergreen, 1988, (ns)	3.0	3	180[2], 150[2]	>30[2] +7[3] +7+8[3]	0.011 0.014 0.012	- 127% 109%	R011296

[1] Residue in the whole fruit calculated from the residues in the pulp and peel fractions assuming a weight ratio of 32% peel and 68% pulp, according to % edible portion in IESTI Table values for USA.
[2] Only the month of application was stated, so an exact interval and PHI value could not be calculated.
[3] Harvested bananas were stored for 7 days at +10°C and 8 days at +20°C for fruit ripening.
R011296. Dupont and Muller, 1988b. **Non-GLP.** Fruits were harvested from 4 trees with bunches ready for harvest. From each tree one finger was taken from hand number 2, 5 and 7. Fingers were only taken from the inner whorl. When ready (day 0, +7, +8), samples (12 pieces) were separated into peel and pulp and analysed immediately. Anal. method JFRL GC-FPD. Results from Hijo and Evergreen were the average of 2-3 analytical portions. Results were not corrected for matrix interference (<0.005 mg/kg) nor for concurrent method recovery (100% at 0.01 mg/kg).

In processing

The Meeting received information on the fate of incurred residues of ethoprophos during the processing of potatoes and *s*ugar cane.

Potatoes

Study 1. Ethoprophos (EC formulation) was applied at an actual dose rate of 65 kg ai/ha (5 times label rate) as a broadcast spray using ground equipment in one trial in Texas, USA in 1993 (R007960, Kowite, 1994b). The applied product was incorporated into the soil (5-10 cm depth) on the day after the application. Triplicate potato samples (136 kg each) were harvested 110 days after treatment. Each sample was washed and split into two for commercial flake and chip processing on a laboratory scale. The time interval between harvest and processing was 15-17 days (at -10°C).

Chip processing. Potatoes were peeled and sliced. The slices were washed with warm water (50°C–57°C) to remove free starch, then fried in oil at 180–190°C for 90 seconds. After draining and salting, the chips were packaged and stored at -10°C for 29-44 days.
Flake processing. Potatoes were steam-peeled (in a pilot plant), scrubbed with a Hobart Peeler to remove the loosened peel and cut into slabs. The slabs were washed in cold water, pre-cooked at 70–72°C for 20 minutes and steam cooked at 100°C for about 45 minutes. The cooked slabs were mashed, mixed with food additives and dried into a thin sheet in a single drum drier. The dried potato sheets were broken by hand into large flakes and hammer-milled into finished flakes which were packaged and stored at -10°C for 29-44 days.

Samples were analysed for ethoprophos and mA, using GC-FPD, method 4, version 7.0, which is considered valid for potatoes. Neither raw potatoes nor processed fractions (washed tubers, wash water, peeled tubers, wet peel, dry peel, flakes, chips) contained residues (<0.01 mg/kg ethoprophos and <0.01 mg/kg metabolite mA). Results were not corrected for concurrent recoveries (78%-101% at 0.05 mg/kg, n=2 for each sample), nor for interferences (<0.3LOQ, n=1 for each sample). No processing factors could be calculated.

Study 2. Ethoprophos (GR formulation) was applied as a broadcast at a dose rate of 11 kg ai/ha in two trials in the UK in 1999 (GB3 in Wiltshire and GB5 in Norfolk; R016070, Venet, 2000) and

incorporated into the soil before planting. Tuber samples were harvested 84–85 days after planting. Duplicate field samples (5 kg) were taken from each trial. Potatoes were wiped to take off the adhering soil and divided into 1.2 kg fractions for processing.

Peeling. Potatoes were peeled and both the raw peeled potatoes and raw peel were analysed.
Microwave baked potatoes. Unpeeled potatoes were put in a glass dish without water, covered with a glass lid and microwaved for 10 min at 900 W.

Samples from theGB3 plots were stored in ambient temperature for 3 days until dispatch and stored frozen at -18°C for 101- 214 days. Raw and processed samples were analysed using method AR 52-87, 1999, GC-FPD. Residues were found in potato peels: 0.022 and 0.062 mg/kg (average 0.042 mg/kg) in trial GB3 (variety Maris Peer) and 0.009 and 0.011 mg/kg (average 0.010 mg/kg) in trial GB5 (variety Desiree) but were undetected in potatoes or raw agricultural commodities and processed samples (peeled potato, baked potato) (<0.005 mg/kg ethoprophos). Results were not corrected for concurrent recoveries (61%-105%), nor for interferences (<LOQ).

Table 77. Residues in processed potato fractions (all values: mean of duplicates).

Trial, variety	Peel		Peeled potatoes		Tubers	Baked potatoes
	Residues (mg/kg)	Weight (g)	Residues (mg/kg)	Weight (g)	Re-calculated residues (mg/kg)	Residues (mg/kg)
99673GB3, Maris Piper	0.042	3.4	< 0.005	115	0.0061	< 0.005
99673GB5, Desiree	0.010	3.5	< 0.005	42	0.0054	< 0.005

No meaningful processing factors could be calculated, but it can be tentatively concluded that the residue concentrates in the peel, not in the pulp.

Sugar cane

Study 1. Ethoprophos (GR formulation) was applied at a dose rate of 6.7 kg ai/ha at planting in a trial in Belle Glade, Florida, USA, in 1966-1967 (Mobil, 1971). Stalks were harvested 1 year after application. A two-tonne sugar cane batch was processed into bagasse, mixed juice, clarified juice, mud, syrup, raw sugar and molasses according to commercial practices in a pilot plant.

Sugar processing. The cane was crushed and milled with water in a milling factory, giving bagasse and mixed juice. The extracted mixed juice was transferred to a pilot plant. Phosphoric acid (80 mg/l) was added to the cold juice to ensure proper liming and uniform clarification. Liming was carried out under cold condition (pH 6.8 -7.2). The juice was then heated to 100°C. Separan AP-30 (2 ppm, a carboxy-amide type poly-electrolyte) was added to the hot juice before settling to ensure good quality for the subsequent crystallization. The hot juice was left to settle in an open clarifier, yielding clarified juice and mud. After settling, the clarified juice was transferred to an evaporator feed tank and evaporated to syrup. In the crystallization stage, the syrup was boiled to make grain (grain strike). A footing of grain is left in the pan for a sugar strike, which was completed with syrup. The resultant massecuite is transferred to the centrifuge where a small amount of water was added. The products were sugar and molasses. Raw and processed samples were stored for 7 months under unreported conditions.

Samples were analysed for ethoprophos using method R-89-A. Concurrent validation results were not reported. Ethoprophos treatment did not lead to any quantifiable residues (<0.02 mg/kg) in the raw agricultural commodity or its processed fractions. No processing factors could be calculated.

Study 2. Ethoprophos (GR formulation) was applied as a band in the furrows at planting at a dose rate of 1.0, 2.0 and 3.0 kg ai/ha in Jalgaon, Maharastra, India, in 1988 (C036561, Parthasarathy, 1989). The sugar canes were harvested 384 days after application. Juice from crushing half of the harvested

stalks was collected. Further processing details were not available. Storage conditions for raw and processed samples were not reported.

Samples were analysed for ethoprophos using GC-TSD method 1. Matrix interferences and concurrent validation results were not reported. There were no quantifiable residues (<0.01 mg/kg) in the stalks or juice and no processing factors could be calculated.

Study 3. Ethoprophos (GR formulation) was applied over the open furrows containing the *s*ugar cane seed pieces at a dose rate of 40 kg ai/ha (9.0 x label rate) in one trial in Louisiana, USA, in 1990-1991 (R016038, Kowite, 1994c), and the furrows were then covered with soil. The *s*ugar canes (2700 kg) were harvested 14 months later. A 2700 kg batch was processed one day after harvest into bagasse, mixed juice, clarified juice, clarifier mud, syrup, molasses, and sugar according to commercial practices in a pilot plant.

Processing was as in study 1, except that the mixed juice was limed to pH 7.0-7.4 and the added polyelectrolyte was Zuclar 2000. Samples were stored for 455-464 days at -10°C and analysed in triplicate for ethoprophos and mA, using GC-FPD, method 4, version 3.0. Results were not corrected for concurrent recoveries (69%-109%), nor for interferences (up to 0.0043 mg/kg ethoprophos; <0.3 LOQ metabolite mA). The exaggerated dose rate did not lead to any quantifiable residues (<0.01 mg/kg) of either ethoprophos or mA in the raw agricultural commodity or its processed fractions, and no meaningful processing factors could be calculated.

Residues in the edible portion of food commodities

The Meeting received information on the distribution of residues in the peel and pulp fractions of bananas and melons.

For all trials concurrent recoveries were reported to be within 70%-110% limits and control samples were reported to be below the LOQ.

Banana. Supervised field trials were conducted in 1985 in Brazil and in 1987-1988 in the Philippines. The soil was treated one to three times throughout the year with GR formulations. Samples were analysed immediately. The distribution of residues between peel and pulp is shown in Table 78.

From the two trials where quantifiable residues were found at harvest it can be tentatively concluded that ethoprophos tends to concentrate in the pulp fraction of bananas.

Table 78. Distribution of ethoprophos residues in banana peel and pulp from supervised trials after soil treatment with GR formulations.

Location, year, (variety)	g ai/tree	No	Interval (days)	Treatment dates (harvest)	PHI (days)	Sample	parent (mg/kg)	Ref.
Paulinia, Brazil, 1985 (Nanicão)	6.0	1	na	26 Jan (h: 11 Feb)	16	Pulp	<0.05	C033861/ C033862
Paulinia, Brazil, 1985 (Nanicão)	12.0	1	na	26 Jan (h: 11 Feb)	16	Pulp	<0.05	C033861/ C033862
Tadeco, Philippines, 1987-88, (ns)	2.5	3	60[1], 90[1]	Nov, Feb, May (h: 28 Jun)	>30[1]	Pulp Peel	<0.005 <0.005	R011296
Tadeco, Philippines, 1987-88, (ns)	2.5	3	120[1] 120[1]	Sept, Jan, May (h: 28 Jun)	>30[1]	Pulp Peel	<0.005 <0.005	R011296
Tadeco, Philippines, 1987-88, (ns)	2.5	3	60[1], 90[1]	Nov, Feb, May (h: 28 Jun)	>30[1]	Pulp Peel	<0.005 <0.005	R011296
Hijo, Philippines,	3.0	2	150[1]	Dec, May	>30[1]	Pulp	0.0065	R011296

Location, year, (variety)	g ai/tree	No	Interval (days)	Treatment dates (harvest)	PHI (days)	Sample	parent (mg/kg)	Ref.
1987-88, (ns)				(h: 28 Jun)		Peel	<0.005	
Evergreen, Philippines, 1987-88, (ns)	3.0	3	180[1], 150[1]	June, Dec, May (h: 28 Jun)	>30[1]	Pulp Peel	0.013 0.0075	R011296

[1] only month of application is stated, so an exact interval and PHI value cannot be calculated.

C033861/C033862. Fabi, 1985a/b. **Non-GLP**. Weather conditions, plot size and sampling procedures were not stated. Soil clay. Manual application in the soil. Mature fruits were harvested and analysed immediately. Anal. method GC-FPD, method 3. Results were from duplicate analytical portions of combined samples of triplicate field trials. Results were not corrected for matrix interference (<0.05 mg/kg, n=1) nor for concurrent method recovery (97% at 0.05 mg/kg).

R011296. Dupont and Muller, 1988b. **Non-GLP.** Fruits were harvested from 4 trees with bunches ready for harvest. From each tree one finger was taken from hand number 2, 5 and 7. Fingers were only taken from the inner whorl. Samples (12 pieces) were separated into peel and pulp and analysed immediately. Anal. method JFRL GC-FPD. Results from Hijo and Evergreen were the average of 2-3 analytical portions. Results were not corrected for matrix interference (<0.005 mg/kg, n=1) nor for concurrent method recovery (100% at 0.01 mg/kg).

Melon. Supervised field trials were carried out in 1998 in Spain and in 2001-2002 in Southern Europe (France, Italy, Spain and Greece). Applications were made shortly before, at, or shortly after transplanting with overall soil treatment using GR formulations, or throughout the growing season using drip irrigation with EC formulations. The distribution of residues between peel and pulp is shown in Tables 79 and 80.

From the six trials where residues were found at harvest it can be concluded that ethoprophos is present in both the peel and pulp. Generally the peel fractions contained slightly higher residues. Residues could have been affected by sub-optimal storage conditions, because in the 2001-2002 trials the maximum storage period of 9 months was exceeded.

Table 78. Distribution of ethoprophos residues in melon peel and pulp from supervised trials (outdoor) using overall soil treatment with GR formulations.

Location, year, (variety)	Form.	kg ai/ha	No	PHI (days)	Sample	parent (mg/kg)	Ref.
84800 Isle sur la Sorgue, Provence-Cote d'Azur, S. France, 2001, (Heliobel)	GR (FG)	10	1	61 61 70 70 79 79	Peel Pulp Peel Pulp Peel Pulp	<0.005 <0.005 <0.005 <0.005 <0.005 <0.005	C025152 01R754-1
70031 Andria (Ba) Puglia, Italy, 2001 (Proteo)	GR (FG)	10	1	62 62 72 72 78 78	Peel Pulp Peel Pulp Peel Pulp	<0.005 <0.005 <0.005 <0.005 <0.005 <0.005	C025152 01R754-2
46230 Alginet, Valencia, Spain, 2001, (Cantalup Rubens)	GR (FG)	10	1	54 54 64 64 75 75	Peel Pulp Peel Pulp Peel Pulp	<0.005 <0.005 <0.005 <0.005 <0.005 <0.005	C025152 01R754-4
57011 Prochoma, Thessaloniki, Macedonia, Greece, 2001, (Daniel)	GR (FG)	10	1	46 46 56 56 66 66	Peel Pulp Peel Pulp Peel Pulp	0.022 0.015 0.012 0.008 <0.005 <0.005	C025152 01R754-5
41310 Brenes, Sevilla, Andalucia, Spain, 2001 (Sancho)	GR (FG)	10	1	67 67 77 77	Peel Pulp Peel Pulp	<0.005 <0.005 <0.005 <0.005	C025152 01R754-6

Location, year, (variety)	Form.	kg ai/ha	No	PHI (days)	Sample	parent (mg/kg)	Ref.
				87	Peel	<0.005	
				87	Pulp	<0.005	
84800 Isle sur la Sorgue, Provence-Cote d'Azur, S. France, 2002 (Escrypto)	GR	10	1	63	Peel	<0.005	C036692 02R754-1
				63	Pulp	<0.005	
				69	Peel	<0.005	
				69	Pulp	<0.005	
				76	Peel	<0.005	
				76	Pulp	<0.005	
				83	Pulp	<0.005	
				83	Peel	<0.005	
84840 Lamotte du Rhone, Provence-Cote d'Azur, S. France, 2002 (Anasta)	GR	10	1	58	Peel	<0.005	C036692 02R754-2
				58	Pulp	<0.005	
				67	Peel	<0.005	
				67	Pulp	<0.005	
				74	Peel	<0.005	
				74	Pulp	<0.005	
70043 Molfetta, Bari, Puglia, Italy, 2002, (Proteo)	GR	10	1	61	Peel	<0.005	C036692 02R754-3
				61	Pulp	<0.005	
				67	Peel	<0.005	
				67	Pulp	<0.005	
				74	Peel	0.0063	
				74	Pulp	<0.005	
				84	Peel	<0.005	
				84	Pulp	<0.005	
46230 Alginet, Valencia, Spain, 2002, (Cantalup)	GR	10	1	68	Peel	<0.005	C036692 02R754-4
				68	Pulp	<0.005	
				75	Peel	<0.005	
				75	Pulp	<0.005	
				84	Peel	<0.005	
				84	Pulp	<0.005	

C025125. Davies, 2002g. GLP. Samples were harvested when full size and form was reached (BBCH 73-81) and divided into peel and pulp. Samples were stored at -18°C for 302-380 days. Anal method AR 52-87, 2001d, GC-TSD. Results from plot 1R754-5 are the means of two analytical portions.
C036692. Klein, 2004d. GLP. Samples (12 pieces) were harvested when full size and form was reached (BBCH 71-89), divided into peel and pulp and stored at -18°C for 409-484 days. Anal method AR 52-87, 2003b, GC-MS. Results were not corrected for matrix interferences (<0.005, n=20) nor for concurrent recoveries (72%-107% at 0.005 mg/kg).

Table 80. Distribution of ethoprophos residues in melon peel and pulp from supervised trials (outdoor) after post-transplanting drip irrigation with EC formulations.

Location, year, (variety)	kg ai/ha	kg ai/hl	Water l/ha	No	PHI (days)	Sample	parent (mg/kg)	Ref.
Sta Ollala, Toledo, Spain, 1998 (Pionet)	0.078	na	na	4	14	Pulp	<0.01, 0.011	R004456 98642M1
	0.12				14	Peel	0.022, 0.046	
	0.20							
	0.20							
Sevilla, Spain, 1998 (Roché)	0.078	na	na	4	14	Pulp	<0.01, <0.01	R004456 98642SE1
	0.12				14	Peel	<0.01, <0.01	
	0.20							
	0.20							
84840 Lamotte du Rhone, Provence-Cote d'Azur, S. France, 2002 (Indola)	1.9	0.032	6024	3	14	Peel	<0.005	C036693 02R787-1
					14	Pulp	<0.005	
84800 Isle sur la Sorgue, Provence Cote d'Azur, S. France, 2002 (Escrypto)	1.9	0.038	5000	3	14	Peel	0.0070	C036693 02R787-2
					14	Pulp	0.0056	
40017 San Giovanni in Persicet, Emilia-Romagna, Italy, 2002 (Calipso)	1.9	0.038	5000	3	14	Peel	0.012	C036693 02R787-3
					14	Pulp	0.015	
70056 Molfetta (BA), Puglia, Italy, 2002 (Proteo)	1.9	0.015	12500	3	14	Peel	0.021	C036693 02R787-4
					14	Pulp	0.015	

Location, year, (variety)	kg ai/ha	kg ai/hl	Water l/ha	No	PHI (days)	Sample	parent (mg/kg)	Ref.
46550 Albuixech, Valencia, Spain, 2002 (Sancho)	1.9	0.043	4444	3	14 14	Peel Pulp	<0.005 <0.005	C036693 02R787-5
41310 Brenes, Sevilla, Andalucia, Spain, 2002 (Regen Piel de Sapo)	1.9	0.021	9149	3	14 14	Peel Pulp	<0.005 <0.005	C036693 02R787-6

R004456. Richard, 1999. GLP. Fruit (2-6 pieces) was sampled at maturity (BBCH 81-97). Samples were cut in quarters and stored at -18°C for 112-149 days. Anal method AR 52-87, 1998a, GC-FPD. Results were from duplicate trials. Results were not corrected for matrix interferences (<0.01 mg/kg, n=7) nor for concurrent recoveries (83%-107% at 0.01-0.25 mg/kg).
C036693. Klein, 2004e. GLP. Fruits (12 pieces) were sampled randomly at maturity from the centre of the plots and divided into peel and pulp and stored for 378-447 days at -18°C. Anal. method AR 52-87, 2003b, GC-MS. Results were not corrected for matrix interferences (<0.005 mg/kg), nor for concurrent recoveries (71%-114% at 0.005-0.04 mg/kg).

RESIDUES IN ANIMAL COMMODITIES

Direct animal treatments

No data submitted.

Farm animal feeding studies

No data submitted.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The Meeting received information on duplicate diet studies of pre-school children in Washington State, USA and a monitoring study of food commerially available in Belgium.

Ethoprophos residues in the diets of pre-school children in Washington State, USA

Twenty-four hour duplicate diets were collected in 1998 from seven children living in the Seattle metropolitan area and six children living in Chelan and Douglas agricultural counties in Central Washington, which include a substantial proportion of orchards (Fenske *et al*., 2002). Children with high potential OP pesticide exposure based on combined urinary dialkyl phosphate (DAP) levels from previous studies were targeted for participation in the study. The average age was 3.9 years (range 2.5-5.5 years) and the average weight 16.8 kg (range 13.4-22.7 kg). Ten girls and three boys were enrolled. The samples were collected from each child in the summer and again in the autumn. A total of 88 individual food category samples was collected and analysed for 15 organophosphorus pesticides including ethoprophos. Food items were frozen at -20°C for 2 months. Samples were analysed using AOAC method 970.52. Results were not corrected for concurrent mean method recoveries (67%-100%). Ethoprophos was not present at quantifiable levels either in processed food samples or in any of the dairy samples.

Ethoprophos residues in fresh vegetables, fruits, and other selected food items in Belgium

A monitoring study was carried out in Belgium in the period April 1991-March 1993 (Dejonckheere *et al*., 1996). Selection of food commodities was based on their relative importance in the Belgian food diet. The fruits surveyed were citrus fruits (oranges, lemons), pome fruits (apples, pears), stone fruits (nectarines, peaches, cherries, plums), small fruits (currants, strawberries, grapes) and tropical fruits (pineapples, bananas, kiwifruit). The vegetables were bulb vegetables (onions), brassica

vegetables (cauliflower, Brussels sprouts), fruiting vegetables (cucumbers, melons, peppers, tomatoes, mushrooms), leafy vegetables (endive, spinach, Belgian endive (witloof), lamb's lettuce), legume vegetables (beans, peas), root and tuber vegetables (radishes, carrots, salsify, potatoes), stalk and stem vegetables (leeks), fresh herbs (celery leaves, parsley). Other items of special interest or importance were coffee beans, wheat flour, rice, tea, drinking water, wine, and bran. Samples were obtained from wholesale markets, stores, auction halls, and retail outlets according to procedures described by the inspection services. Sampling times were spread evenly over the 2-year period and the sampling frequency and number were tailored towards the active substances and crop combinations that were expected to result in residues. Pesticide monitoring includes the survey of all active ingredients in all samples, including ethoprophos. For ethoprophos a multi-residue GC method was used. No ethoprophos residues were found in the 3698 samples.

NATIONAL MAXIMUM RESIDUE LIMITS

MRLs were reported by the manufacturer (Barriere, 2004b). At present only national MRLs exist and no European MRLs have been granted for ethoprophos. In all the countries listed, the residue in plants is defined as the parent compound.

Country	Sample	MRL (mg/kg)
Republic of Korea	Strawberry	0.02
Brazil	Banana	0.05
Costa Rica	Banana	0.02
France	Banana	0.01
Germany	Banana	0.02
Honduras	Banana	0.02
Israel	Banana	0.02
Kenya	Banana	0.02
Korea	Banana	0.02
Nicaragua	Banana	0.02
Panama	Banana	0.02
USA	Banana	0.02
Croatia	Cucumber	0.02
Indonesia	Cucumber	0.2
Italy	Cucumber	0.02
Republic of Korea	Cucumber	0.02
USA	Cucumber	0.02
Republic of Korea	Pepper	0.02
Austria	Potato	0.02
Belgium	Potato	0.02
Brazil	Potato	0.05
France	Potato	0.01
Germany	Potato	0.02
Ireland	Potato	0.02
Italy	Potato	0.02
Kenya	Potato	0.02
Republic of Korea	Potato	0.02
Mexico	Potato	0.02
The Netherlands	Potato	0.02
Spain	Potato	0.02
USA	Potato	0.02
Germany	Sweet Potato	0.02
USA	Sweet Potato	0.02
Costa Rica	*S*ugar cane	0.02
Honduras	*S*ugar cane	0.02
Nicaragua	*S*ugar cane	0.02
Panama	*S*ugar cane	0.02
USA	*S*ugar cane	0.02

APPRAISAL

Ethoprophos, a nematicide and soil-insecticide, was evaluated for residues in 1984 and 1987. The toxicology of ethoprophos was reviewed within the periodic review programme by the 1999 JMPR. Ethoprophos was listed as a priority by the the CCPR at its Thirtieth Session (Alinorm 99/24 App VII) for for periodic review of residues by the 2001 JMPR. The manufacturer requested postponement of the residue evaluation.

The Meeting received information on identity; metabolism and environmental fate; analysis of residues; use pattern; residues resulting from supervised trials on strawberry, banana, cucumber, melon, pepper, tomato, potato, sweet potato and sugar-cane; fate of residues during storage and in processing; residues in food in commerce or at consumption; and national maximum residue limits.

Metabolism

Animals

The Meeting received information on the fate of [1-ethyl-^{14}C]ethoprophos in rats, lactating goats and laying hens dosed orally.

Studies on metabolism in laboratory animals (rats) were evaluated by the WHO Expert Group of the 1999 JMPR, which concluded that ^{14}C-ethoprophos is rapidly and virtually completely absorbed, metabolized and excreted after oral administration to rats. The main route of excretion was urine (51–56%), but significant proportions were excreted in expired air (about 15%) and faeces (10–14%). Little radiolabel was found in tissues at 168 h, representing less than 2.5% of the dose, and the highest concentrations were found in excretory organs (liver, kidneys and lungs). There was no evidence that bioaccumulation would occur after repeated doses. Ethoprophos was metabolized by dealkylation of one or both *S*-propyl groups, followed by conjugation.

Lactating goats given feed containing ^{14}C-ethoprophos at a concentration of 32 ppm excreted 78% of the administered radiolabel in urine (including cage rinse), 3.6% in faeces (including the gastrointestinal tract and contents) and 1.7% in milk; 3.9% of the administered dose was found in tissues. During the 7-day dosing period, 2% of the applied radiolabel was found in expired air. The highest concentration of radioactive residues was found in liver (8.8 mg/kg), while kidney contained 0.93 mg/kg, milk 0.49 mg/kg, muscle 0.095 mg/kg and fat 0.051 mg/kg. The total recovery of the administered dose was 88%.

The majority of the radiolabel in liver and kidney remained in the post-extraction solids, and enzyme and acid digests of these solids co-chromatographed with amino acid standards. Radiolabelled amino acids can be formed by hydrolysis of ethoprophos to ethanol and subsequently to acetaldehyde, acetate, acetyl coenzyme A and amino acids (tricarboxylic acid cycle). Thin-layer chromatography of the polar liver extract showed three radioactive spots, representing 1.1%, 1.4% and 0.45 % of the total radioactive residues (TRR). The first spot co-chromatographed with *O*-ethyl-*S*-propyl phosphorothioate and ethyl phosphate, while the other two spots did not co-chromatograph with any of the reference markers used. The parent compound was not found. Radioactivity in the kidney extract was not characterized.

Most of the radioactivity in muscle was released from the post-extracted solids by acid or base treatment, while that in fat was distributed approximately equally between the extracted and unextracted fractions. The radiolabel in the post-extracted solids could be released by enzyme digestion. No further characterization of muscle or fat fractions was attempted owing to the low levels of radioactivity.

The residue levels in milk reached a plateau on the first day of treatment, with an average level over days 0–7 of 0.49 mg/kg (maximum, 0.68 mg/kg). The radioactivity in the chloroform extract of milk (55% TRR) co-chromatographed with standards of the fatty acids palmitic acid, oleic acid and stearic acid, which were poorly resolved. Radiolabelled fatty acids can be formed by hydrolysis of ethoprophos to ethanol. No parent compound was found.

When laying hens were given feed containing ^{14}C-ethoprophos at a concentration of 2.1 ppm for 7 days, 48% of the total administered radioactivity was recovered in excreta (including the gastrointestinal tract and contents), 1.0% in egg whites, 9.3% in egg yolks, 3.6% in expired volatiles and 3.2% in tissues and blood. The total recovery of the administered radioactivity was 64%. The highest concentration of radioactive residues was found in liver, at 1.2 mg/kg, followed by kidney at 0.42 mg/kg; 0.069 mg/kg radioactive residue was found in fat and 0.010 mg/kg in muscle. A maximum residue level of 0.64 mg/kg was found in egg yolk and 0.029 mg/kg in egg white.

As in goats, most of the radioactivity in liver and kidney remained in the post-extracted solids. Enzyme and acid digests of these solids co-chromatographed with amino acid standards. Thin-layer chromatography of the polar extract of liver contained three radioactive zones, representing 1.9%, 0.95% and 2.0% TRR. The first zone contained *O*-ethyl-*S*-propyl phosphorothioate or ethyl phosphate, the second zone did not co-chromatograph with any of the reference markers used, and the third zone co-chromatographed with *O*-ethyl-*O*-methyl-*S*-propyl phosphorothioate or *O*-ethyl-*S*-methyl-*S*-propyl phosphorodithioate. No parent compound was found.

Most of the radioactivity in muscle was released from the post-extracted solids by acid or base treatment, while that in fat was present mainly in the organic extract. The radiolabel could be released from the post-extracted solids by enzyme digestion. No further characterization of muscle or fat fractions was attempted owing to the low levels of radioactivity.

The radioactive residue level reached a plateau in egg whites on the third day of treatment, but no plateau was reached in egg yolks during the 7-day treatment. The average concentrations found were 0.021 mg/kg in egg whites (average over days 3–7; maximum, 0.029 mg/kg) and 0.30 mg/kg in egg yolks (average over days 0–7; maximum, 0.64 mg/kg). In egg yolks, 84% was extractable in hexane and 11% in chloroform. The hexane fraction of egg yolks co-chromatographed with the fatty acids palmitic, myristic, oleic and stearic acid, which were poorly resolved. No parent compound was found.

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

Plants

The Meeting received information on the fate of ethoprophos labelled with ^{14}C in the ethyl or the propyl group after soil treatment before planting of pulses or oil seeds (French beans), cereals (maize), root and tuber vegetables (potatoes) and leafy crops (cabbage).

In a greenhouse, *French bean* bedding plants (variety Contender) were planted in clay pots filled with steam-sterilized soil treated with [α-^{14}C-ethyl]- or [α-^{14}C-propyl]ethoprophos. The compound was applied as a granule formulation at 14.3 mg ai/kg soil. The plants were grown for 63 days and were sampled at weekly intervals from day 7 onwards. The residue levels in soil extracts decreased with time, while the total residues in the bean plants increased with time, from 2.2% of the total applied radioactivity to 13% with the ethyl label and from 0.58% to 8.3% with the propyl label between days 7 and 63. Mainly extractable residues were found early in the study, while unextracted residues predominated (> 57%) from day 21 onwards. In mthanol:water extracts of the bean plants, the main compounds were *O*-ethyl-*S*-propyl phosphorothioate and ethyl phosphate. In dichloromethane extracts, the main compounds were the parent (maximum, 13%) and ethyl propyl sulfide (maximum, 9.2%). The amount of parent compound decreased with time after application and contributed < 10% from day 28 onwards. Minor amounts of propyl disulfide, ethyl propyl sulfoxide (plus methyl propyl sulfoxide) and ethyl propyl sulfone (plus methyl propyl sulfone) were present at some sampling times.

In a greenhouse, *maize seeds* were planted in clay pots filled with steam-sterilized soil treated with [α-^{14}C-ethyl]- or [β-^{14}C-propyl]ethoprophos. Ethoprophos was applied as a granule formulation at 14.3 mg ai/kg soil. Maize plants were grown for 100 days and were sampled at 10-day intervals from day 18 onwards. The residue levels in soil extracts were constant, while those in maize plants increased from 0.96% of the applied radiolabel to 74% for the ethyl label and from 0.26% to 34% with the propyl label between days 18 and 100. Most of the extractable residues in the maize plants

were found early in the study, while unextracted residues predominated (> 67%) from day 38 onwards. In methanol:water extracts of the maize plants, the main compounds were *O*-ethyl-*S*-propyl phosphorothioate and ethyl phosphate. In dichloromethane extracts, the main compounds were the parent (maximum, 40% TRR) and ethyl propyl sulfide (maximum, 7.6% TRR). The amount of parent compound decreased over time and contributed < 10% from day 48 onwards. Small amounts of propyl disulfide, ethyl propyl sulfoxide (plus methyl propyl sulfoxide) and ethyl propyl sulfone (plus methyl propyl sulfone) were present at some sampling times. The ethyl label was found mainly on ethyl phosphate.

In a second study on *maize*, silt loam was treated with [1-ethyl-^{14}C]ethoprophos (emulsifiable concentrate formulation) at a rate of 13 kg ai/ha in plastic-lined wooden boxes placed in the field. The actual concentration in the soil was 10 mg ai/kg. The application mixture was incorporated to a depth of 10 cm. Sweet maize seeds (variety Early extra sweet) were planted 3 days after soil treatment and were sampled at the green forage stage (soil, whole plant), at maturity (shanks, husks, silks, grain, empty cobs) and at the fodder stage (soil, senescent stalks without cobs). The TRR was 2.2 mg/kg in maize forage, 0.27 mg/kg in maize cobs, 0.25 mg/kg in grain, 0.79 mg/kg in husks and 1.4 mg/kg in fodder. Most of the TRR in these matrices was solvent-extractable. Acid or base hydrolysis released a further 6–14% TRR from forage, grain, cobs and fodder; however, 13% TRR in forage and 40% TRR in grain, cobs and fodder remained unextracted. Ethyl phosphate was the main metabolite detected in green forage, grain and fodder (10%, 35% and 8.9%, respectively). Parent ethoprophos and its metabolite *O*-ethyl-*S*-propyl phosphorothioate were also present in small amounts in forage and fodder. The extracts of forage and fodder further tentatively contained < 1% each of *O*-ethyl-*O*-methyl-*S*-propyl phosphorothioate and *O*-ethyl-*S*-methyl-*S*-propyl phosphorodithioate.

Silt loam was treated with [1-ethyl-^{14}C]ethoprophos (emulsifiable concentrate formulation) at a rate of 13 kg ai/ha in plastic-lined wooden boxes placed in the field. The actual concentration in the soil was 15 mg ai/kg. The mixture was incorporated to a depth of 10 cm. *Potatoes* (variety Kenebeck) were planted 3 days after soil treatment, and soil and plants were sampled at the 'new potato' stage and at maturity. The TRR was 0.24–0.54 mg/kg in tubers and 1.1–3.8 mg/kg in vines. Most of the TRR was extracted with aqueous methanol. Acid or base hydrolysis solubilized a further 17% of the radioactivity in the vines, while 31% TRR in vines and 23% TRR in tubers remained unextracted. In both vines and the tubers, the main metabolite was ethylphosphate (12% and 38% TRR, respectively). Parent ethoprophos, *O*-ethyl-*S*-propyl phosphorothioate and *O*-ethyl-*O*-methyl-*S*-propyl phosphorothioate (the latter tentatively) were present in small amounts in the vines but were not detected in tubers.

To determine the nature of the unextracted residues in potatoes, sandy loam was treated with [1-ethyl-^{14}C]ethoprophos (emulsifiable concentrate formulation) at a dose rate of 13 kg ai/ha in plastic-lined wooden boxes placed in the field. The mixture was incorporated to a depth of 10 cm; the actual concentration in the soil was 5.9 mg ai/kg. Potatoes (minituber variety Kennebec) were planted 3 days after soil treatment and were harvested 118 days (new potato tubers) or 167 days after treatment (mature potatoes). The TRR and extractability were comparable with those in the first study. A sequential extraction scheme showed that 41% TRR in new potato tubers consisted of solvent-extractable residues, 11% TRR was present in starch, 8.5% TRR in protein, 4.4% TRR in pectin, 3.7% TRR in lignin, 8.2% in hemicellulose and 8.8% TRR in cellulose. The unextracted radioactive residue associated with starch was shown to be ^{14}C-glucose.

Silt loam was treated with [1-ethyl-^{14}C]ethoprophos (emulsifiable concentrate) at a rate of 11 kg ai/ha in plastic-lined wooden boxes placed in the field. The actual concentration in the soil was 7.6 mg ai/kg. The mixture was incorporated to a depth of 7.6 cm. *Cabbage* bedding plants (variety Stonehead) were planted 2 days after soil treatment, and soil and plants were sampled at the leafy stage and at maturity. The TRR was 16 mg/kg in leafy cabbage and 3.1 mg/kg in head cabbage. Most of the TRR was extractable, and ethylphosphate was the main metabolite found in both leafy and head cabbage extracts (21% and 24%, respectively). Ethoprophos and *O*-ethyl-*S*-propyl phosphorothioate were present at 0.3–4% in both types of cabbage, and *O*-ethyl-*O*-methyl-*S*-propyl phosphorothioate and *O*-ethyl-*S*-methyl-*S*-propyl phosphorodi-thioate were tentatively identified at 0.4–1.7%. A

supplementary characterization study showed that most of the unextractable radioactive residues in cabbage were incorporated into plant structural components, mainly in lignin (38%).

The metabolism of ethoprophos in plants appears to be qualitatively similar to that in animals; however, the toxicologically significant metabolites *O*-ethyl-*O*-methyl-*S*-propyl phosphorothioate and *O*-ethyl-*S*-methyl-*S*-propyl phosphorodithioate were tentatively identified in hen liver, maize green forage and fodder, potato vines and cabbage heads, but not in rats or goats.

Environmental fate

Soil

The Meeting received information on aerobic degradation in soil and studies on rotational crops (confined and field).

The route and rate of degradation of [1-^{14}C-propyl]ethoprophos was investigated in three studies in different soils under aerobic conditions in the dark at 10 °C and 20–25 °C. On the basis of an application rate of 10.5 kg ai/ha in the field, the test substance was applied at a nominal concentration of 10–14 mg ai/kg dry weight of soil. The main degradation product in soil under aerobic conditions was $^{14}CO_2$, which accounted for 54–60% of the applied radioactivity after 90 days at 22–25 °C and 43–50% after 110 days at 10 °C. Most of the radioactivity in the extracts was associated with unchanged ethoprophos, representing 90–94% on day 0 and 7.2–9.4% on day 90 at 22 °C. One major metabolite was identified as *O*-ethyl-*S*-propyl phosphorothioate (maximum, 3.6–7.9% of the applied radioactivity); two minor metabolites were *O*-ethyl-*O*-methyl-*S*-propyl phosphorothioate (maximum, 0.7%) and *O*-ethyl-*S*-methyl-*S*-propyl phosphorodithioate (maximum, 0.3%). The half-life of ethoprophos at ambient temperature was 10–25 days, while that at 10 °C was two to three times longer.

In a study of a confined rotational crop, a sandy loam soil was sprayed with [1-ethyl-^{14}C]ethoprophos as an emulsifiable concentrate at a rate equivalent to 13.4 kg ai/ha and thus incorporated into the top 10 cm of soil. The soil was placed in boxes inside a screened enclosure, which was heated and covered with plastic during the winter months. The soil was left fallow for 30–365 days after treatment. *Wheat* (variety Anza), *spinach* (variety Polka) and *radish* (variety Cherry Belle) were each planted 30, 120 and 365 days after treatment, and immature and mature crops were harvested at each planting interval. Soil samples were collected at application, at each planting and at each harvest. The TRR in rotational crops was generally much lower after a plant-back interval of 365 days than that after a plant-back interval of 30 days; e.g. mature wheat straw contained a radioactive residue level of 47 mg/kg after a plant-back interval of 30 days and 0.65 mg/kg after a plant-back interval of 365 days. Crops harvested when immature showed similar extractability, while the total extractability from mature wheat was generally lower than that from mature spinach or radish. Some of the remaining solids could be hydrolysed by acid or alkaline treatment; however, 1.9–42% TRR remained unextractable, with the highest portion in wheat chaff 365 days after treatment.

Parent ethoprophos was present in extracts of immature and early maturing crops (radish) at both the 120-day and the 30-day plant-back interval. The parent compound was not found in mature wheat or spinach at the 120-day plant-back interval or in any crop at the 365-day plant-back interval. The main component in each crop matrix was ethyl phosphate, but *O*-ethyl-*S*-propyl phosphorothioate was also found. Many unidentified compounds were found, some at levels > 10% TRR or 0.05 mg/kg. After hydrolysis of immature spinach extracts from the 120-day plant-back interval, two of the unknown compounds (12% and 8.5% TRR) were found to be conjugates of ethyl phosphate. The levels of the remaining unknown compounds were not sufficient for structural identification. The main component in acid and base hydrolysates of the crops was the parent compound (0.13 mg/kg in mature wheat straw at the 120 day plant-back interval). Most of the remaining radiocarbon was associated with *O*-ethyl-*O*-methyl-*S*-propyl phosphorothioate (0.02 mg/kg). Unextractable residues were characterized in mature wheat straw. General incorporation into cellular components was 40% TRR in extractable residues, 7.7% TRR in starch, 1.5% TRR in protein, 1.9% TRR in pectin, 11%

TRR in lignin, 14% TRR in hemi-cellulose, 10% TRR in cellulose and 22% TRR in insoluble residue; the overall recovery was 105%.

In a field study of rotational crops, unlabelled ethoprophos was applied once as an emulsifiable concentrate to sandy loam before planting at an actual rate of 13.5 kg ai/ha. The rotational crops were root vegetables (radish roots), leafy crops (radish leaves, red leaf lettuce, collards), cereals (forage, grain and straw from winter wheat, spring wheat and sorghum) and pulses or oil seeds (forage, grain and straw from cow peas, wando peas, green peas and soya beans and mustard forage). The crops were planted 1, 4, 8 and 12 months after application at two sites. Sample extracts were analysed for ethoprophos and *O*-ethyl-*S*-propyl phosphorothioate by gas chromatography with flame photometry detection. The residue levels were below the LOQ of 0.01 mg/kg in all treated samples from both test sites, except in radish root and radish leaves. The highest level of parent compound found in radish root was in samples taken at the plant-back interval of 31 days with harvest 32 days after planting, at 0.023 mg/kg; in the same samples, the highest level of *O*-ethyl-*S*-propyl phosphorothioate was 0.039 mg/kg. The presence of ethoprophos and *O*-ethyl-*S*-propyl phosphorothioate in radish root and tops was confirmed by gas chromatography–mass spectrometry but at levels at least an order of magnitude lower than those measured by gas chromatography with flame photometry detection.

Methods of analysis

The Meeting received information on enforcement and monitoring methods for the determination of ethoprophos in foodstuffs of plant and animal origin and on the analytical methods used in studies of rotational crops, supervised trials and studies of storage stability, processing and monitoring for determination of ethoprophos and the metabolite *O*-ethyl-*S*-propyl phosphorothioate in foodstuffs of plant origin.

Five enforcement methods were submitted. Ethoprophos can be determined by the Dutch multi-residue method MRM-1 (validated for non-fatty matrices, quantification by gas chromatography with nitrogen–phosphorus or mass spectrometry detection; LOQ, 0.01–0.05 mg/kg) and with the German multi-residue methods DFG-S8 (validated for fruits and vegetables, quantification by gas chromatography with electron capture or alkali flame ionization detection; LOQ, 0.02 mg/kg) and DFG-S19 (validated for foodstuffs of plant and animal origin, quantification with gas chromatography with flame photometry, mass spectrometry or PFP detection, depending on the module used; LOQ, 0.01 mg/kg). Ethoprophos could not be determined by the multi-residue protocols of the US Food and Drug Administration. Method AR 271-01 was proposed as an enforcement method for determination of ethoprophos in milk, egg, meat, fat and liver and is considered valid in the range 0.01–0.1 mg/kg (quantification by gas chromatography with flame photometric detection).

All the methods used in the various studies were based on extraction with hexane, methanol, acetone, ethyl acetate, acetonitrile or petroleum ether:acetone, followed by a clean-up and determination by gas chromatography with MC, flame photometry, nitrogen–phosphorus, flame photometric, mass spectrometry, electron capture or tandem mass spectrometry detection. The LOQs ranged from 0.005 mg/kg to 0.05 mg/kg, 0.01 mg/kg being the most common.

Stability of residues in stored analytical samples

The Meeting received data on the stability of residues in crops with a high water content (pineapple, broccoli, cabbage, potato, sweet potato, tomato), in dry crops with starch and protein (maize), in dry crops with fat or oil, starch and protein (peanut), in special cases (sugar-cane, tobacco (green, cured)), in processed commodities (pineapple juice, peanut crude oil, peanut refined oil, maize crude oil, maize refined oil, maize starch, refined cane sugar) and in feed remains (pineapple bran, pineapple feed pulp, peanut hulls, peanut meal, peanut vine, dry peanut hay, maize meal, maize forage, maize fodder, maize grain dust, sugar-cane molasses) stored frozen. Crops with a high water and a high acid content (citrus fruits) were not investigated.

The freezer storage stability of ethoprophos depends on the matrix. Parent ethoprophos was found to be stable at –20 °C for a maximum of 9 months in broccoli and pineapple fruit, but for at least 9–12 months in other crops with a high water content (cabbage, sweet potato, potato, peanut vine, maize forage). In another study, the parent compound was stable for at least 19 months in tomato and potato. It was stable for at least 12 months in dry crops with starch and protein (maize grain) and for a maximum of 12 months in tobacco and peanut nutmeat. Ethoprophos was not stable in peanut hay. Ethoprophos and *O*-ethyl-*S*-propyl phosphorothioate were stable at –20 °C for at least 15 months in sugar-cane and its processed commodities. No general conclusions can be drawn for processed commodities and remains.

The results showed that, in general, *O*-ethyl-*S*-propyl phosphorothioate is not stable at –20 °C for < 1 month, although longer storage times are possible for some crops.

Definition of the residue

Ethoprophos is metabolized rapidly in rats and livestock and was not found in edible tissues. In metabolism studies with labelled compounds, most of the radioactivity was found to be incorporated into natural components, such as fatty acids and amino acids. Low levels of *O*-ethyl-*S*-propyl phosphorothioate or ethyl phosphate were identified in goat and hen liver, and *O*-ethyl-*O*-methyl-*S*-propyl phosphorothioate and *O*-ethyl-*S*-methyl-*S*-propyl phosphorodithioate were tentatively identified in hen liver at low levels. The main route of metabolism in livestock is hydrolysis of the P–S bond, yielding *O*-ethyl-*S*-propyl phosphorothioate and propyl sulfide, with hydrolysis of *O*-ethyl-*S*-propyl phosphorothioate to ethyl phosphate; the ethyl moiety can be split off and become incorporated into natural components like amino acids and fatty acids.

Although ethoprophos is not found in edible tissues, the Meeting agreed that, in the absence of a better indicator, the parent should be considered the compound of interest in animal commodities, both for enforcement and for dietary risk assessment. The log octanol–water partition coefficient (P_{ow}) of 2.99 indicates that the residue is not fat-soluble.

The main route of metabolism is similar in plant and animals, although other routes differ. Propylsulfide in plants can react with a parent molecule to yield ethylpropyl sulfide and propyl disulfide, while propylsulfide is methylated in rats.

In edible plant parts (mature maize grain, potato and cabbage), the major residue is ethyl phosphate, which is considered not to be toxicologically relevant and is thus not included in the residue definition for dietary risk assessment. Furthermore, ethyl phosphate is formed by several other organophosphate pesticides (e.g. parathion) and can therefore not be used for enforcement purposes. Ethylpropyl sulfide, which was found in amounts similar to the parent compound in French beans, was not found in rats; however, it behaves similarly to methylpropyl sulfide, which was detected in rats. It is not expected that this metabolite will be toxicologically significant.

Possible candidates for the residue definition are the parent, *O*-ethyl-*S*-propyl phosphorothioate, *O*-ethyl-*O*-methyl-*S*-propyl phosphorothioate and *O*-ethyl-*S*-methyl-*S*-propyl phosphorodithioate.

As reported by the 1999 JMPR, *O*-ethyl-*S*-propyl phosphorothioate, *O*-ethyl-*O*-methyl-*S*-propyl phosphorothioate and *O*-ethyl-*S*-methyl-*S*-propyl phosphorodithioate were tested for toxicity and for their ability to inhibit cholinesterase activity in female rats given single oral doses. The last two metabolites had approximately the same cholinergic toxicity as the parent compound, while the first was less toxic than the parent. As *O*-ethyl-*S*-propyl phosphorothioate is less toxic than the parent compound in rats, is rapidly converted to ethyl phosphate and is not found in mature maize grain, potato tubers or mature cabbage heads, the Meeting decided not to include this metabolite in either residue definition. The two remaining metabolites were not detected in mature maize grain or potato tubers but were tentatively identified in mature cabbage heads. These metabolites were also tentatively identified in animal feedstuffs (maize forage and fodder), although they were not identified in rats. It is possible that the molecules are artefacts formed during extraction with methanol. In view

of the low levels found in the metabolism studies, the Meeting decided not to include *O*-ethyl-*O*-methyl-*S*-propyl phosphorothioate or *O*-ethyl-*S*-methyl-*S*-propyl phosphorodithioate in either residue definition.

Definition of the residue for compliance with MRLs and for estimating dietary intake: ethoprophos, for both plant and animal commodities.

Results of supervised residue trials on crops

Supervised trials were available for stawberry, banana, cucumber, melon, pepper, tomato, potato and sugar-cane, but none were provided for the remaining commodities that currently have a Codex level (CXL). Therefore, the Meeting decided to withdraw the current recommendations for beetroot, cabbage head, gherkin, grape, lettuce head, maize, maize fodder, onion bulb, peanut, peanut fodder, pea (pods and succulent or immature seeds), pineapple, pineapple fodder, pineapple forage, soya bean and soya bean fodder.

Berries and other small fruit

Strawberry

Ethoprophos is registered in Austria and Spain for use on strawberry with granule and emulsifiable concentrate formulations at the pre-planting or planting stages. Four trials on strawberry were conducted in Italy in 1996–98 at two sites. Application was by drip irrigation with emulsifiable concentrates throughout the growing season but before the fruits had formed. Although drip irrigation is usually the critical GAP and no residues were detected in the trials, the application rate stated on the available labels was 6 kg ai/ha, while that used in the trials was only 1.8–3.5 kg ai/ha: None of the trials was conducted according to GAP.

The Meeting agreed that the available data were insufficient to estimate a maximum residue level for ethoprophos in strawberry.

Assorted tropical and sub-tropical fruits minus inedible peel

Banana

Trials on bananas were reported to the Meeting from Brazil (GAP: 3.0 g ai/tree, two applications, 3-day PHI), Costa Rica (GAP for Central America: 2.9–3.0 g ai/tree, one application, 30-day PHI), Côte d'Ivoire (GAP: 4.0–8.0 g ai/tree, two to three applications, PHI not specified) and the Phillipines (GAP: 4.0–5.0 g ai/tree, two applications, PHI not specified).

In one trial in the Côte d'Ivoire, the residue levels in banana were below the LOQ (< 0.02 mg/kg).

None of the 20 Costa Rican trials was conducted according to GAP in Central America, as 15 involved overdosing, 14 involved more than one treatment or residues were measured at a PHI of < 30 days. As residue levels above the LOQ were not measured in any of the trials, the Meeting decided that the six trials with a PHI of ≤ 30 days could be considered for estimating the MRL. The residue levels in banana were < 0.02 mg/kg in all six trials.

The two trials in Brazil did not comply to GAP (overdosing, with only one application), and no residues were found. The five trials in the Philippines were also not conducted according to GAP (underdosing). In two of the trials, residue levels of 0.0065 mg/kg and 0.013 mg/kg were found in pulp.

The Meeting decided to combine the results of the trial in the Côte d'Ivoire and of the six trials in Costa Rica to estimate the maximum residue level for banana. The levels in all seven trials were < 0.02 mg/kg. The Meeting agreed to withdraw the previously recommended maximum residue level for banana of 0.02* mg/kg and to replaced it by a recommendation of 0.02 mg/kg. The Meeting estimated an STMR and a highest residue level for ethoprophos in banana of 0.02 mg/kg.

Fruiting vegetables, cucurbits

Cucumber

Indoor trials on cucumber in which soil received overall treatment before planting or at transplanting with a granule formulation were reported from Canada and The Netherlands. No GAP was reported for either country. In the five Canadian trials, conducted according to US GAP (12–15 kg ai/ha), the residue levels were < 0.01 mg/kg. In four of the six Dutch trials conducted according to Italian, Portuguese or Spanish GAP (3–10 kg ai/ha, 30–60-day PHI), the residue levels in cucumber were < 0.01 mg/kg.

Seventeen outdoor trials on cucumber, with overall soil treatment with a granule formulation before planting or at transplanting, were reported from the USA. In the five conducted according to US GAP, the residue levels were < 0.005 and < 0.02 (four) mg/kg.

Nine indoor trials on cucumber in which soil received spray treatment with emulsifiable concentrate formulations pre- and post-planting were reported from southern Europe (France, Greece, Italy, Portugal and Spain). The trials were evaluated against Spanish GAP (6.0 kg ai/ha, one application, 60-day PHI). All the trials involved overdosing. In one trial in which ethoprophos was applied after planting, an actual residue level of 0.0090 mg/kg was found at 21 days PHI; however, all trials at the correct PHI showed residue levels of < 0.005 mg/kg.

Ten outdoor trials on cucumber in which soil received spray treatment with emulsifiable concentrate formulations before or at planting were reported from the USA. All the trials were conducted according to US GAP, but the results of one trial was excluded from evaluation as the samples were purportedly mislabelled. The residue levels were < 0.01 (nine) mg/kg.

Eight indoor trials on cucumber in which soil was treated with emulsifiable concentrate formulations by drip irrigation after planting or transplanting were reported from southern Europe (France, Italy and Spain). The trials complied with Spanish GAP (0.6 kg ai/ha, 1–10 applications, maximum total of 6 kg ai/ha, 60-day PHI), except that the latest PHI for which residue levels were reported was 14–15 days. On these days, the residue levels were < 0.005 (six), < 0.01 and 0.012 mg/kg.

The Meeting concluded that, irrespective of the method of application and the site (indoors or outdoors), the residue levels would not be expected to exceed the enforcement LOQ of 0.01 mg/kg. The Meeting agreed to withdraw the previously recommended maximum residue level for cucumber of 0.02* mg/kg and to replace it by a recommendation of 0.01 mg/kg. The Meeting estimated an STMR and a highest residue level for ethoprophos in cucumber of 0.01 mg/kg.

Melon

Nine outdoor trials on melon involving overall soil treatment with granule formulations before, at and after planting were reported from southern Europe (France, Italy and Spain). The trials were compared with Portuguese GAP (8 kg ai/ha, 56-day PHI). The residue levels were < 0.005 (seven), 0.0055 and 0.010 mg/kg. The levels in melon pulp (edible portion) were $\underline{< 0.005}$ (eight) and 0.012 mg/kg.

Eight outdoor trials on melon involving post-transplanting drip irrigation with emulsifiable concentrate formulations were reported from southern Europe (France, Italy and Spain); however, there is no GAP for drip irrigation on melon in southern Europe.

On the basis of the trials of overall soil treatment, the Meeting agreed to withdraw the previously recommended maximum residue level for melon, except watermelon, of 0.02* mg/kg and to replace it by a recommendation of 0.02 mg/kg. The Meeting estimated an STMR of 0.005 mg/kg and a highest residue level of 0.012 mg/kg for ethoprophos in the edible portion of melon.

Fruiting vegetables other than cucurbits

Pepper

Eleven indoor trials on sweet pepper involving overall soil treatment with granule formulations before or at planting were reported from southern Europe (France, Greece, Italy and

Spain). The trials were evaluated against Spanish GAP (6.0–8.0 kg ai/ha, one application, 60-day PHI). The residue levels were: < 0.005 (nine), 0.007 and 0.027 mg/kg.

A further 12 trials from southern Europe on green and sweet pepper involved application of ethoprophos as an emulsifiable concentrate formulation by post-planting drip irrigation. Ten could be evaluated against Italian GAP (1.7–3.5 kg ai/ha, three to four applications, 30-day PHI). The residue levels were: < 0.005 (four), < 0.01 (two), 0.006, 0.0068, 0.007 and 0.044 mg/kg. Two trials on green pepper yielded higher residue levels, but the latest sampling was at a PHI of 14–15 days.

The Meeting decided to combine the results of all the trials, yielding residue levels, in ranked order, of: < 0.005 (13), < 0.01 (two), 0.006, 0.0068, 0.007 (two), 0.027 and 0.044 mg/kg.

The Meeting agreed to withdraw the previously recommended maximum residue level for pepper of 0.02* mg/kg and to replace it by a recommendation of 0.05 mg/kg for sweet pepper. The Meeting estimated an STMR of 0.005 and a highest residue level of 0.044 mg/kg for ethoprophos on sweet peppers.

Tomato

Six trials on tomato fruit involving overall soil treatment with granule formulations before or after planting were reported from Brazil (two, no GAP), The Netherlands (indoors) and the USA (three, no GAP). The dose used in the Dutch trial was twice that of Spanish GAP, but no residue level above the LOQ was found (< 0.01 mg/kg).

In 20 trials in southern Europe on tomato fruit, ethoprophos was applied as an emulsifiable concentrate formulation by post-planting drip irrigation or band spraying. The 13 trials conducted according to Italian GAP (1.7–3.5 kg ai/ha, three to four applications, total maximum of 8.6 kg ai/ha, 30-day PHI) or Spanish GAP (0.8–2.0 kg ai/ha, several applications, total maximum of 6 kg ai/ha, 60-day PHI) yielded residue levels of < 0.005 (four) and < 0.01 (nine) mg/kg.

On the basis of the trials conducted in southern Europe, the Meeting estimated a maximum residue level of 0.01* mg/kg, an STMR of 0.005 mg/kg and a highest residue level of 0.01 mg/kg for ethoprophos on tomato.

Root and tuber vegetables

Potato

The results of 62 trials were available in which ethoprophos was applied to potatoes after overall soil treatment or band application with granule formulations before or at planting. Ware potatoes are normally harvested within 90–120 days after application at or a few days before planting. Early maturing potatoes can be harvested before 90 days, while late maturing ones (such as Russet Burbank or Maris Piper varieties) are usually harvested after 120 days. The PHI therefore depends on the crop variety. On most labels, no PHI is indicated, as treatment is made before or at planting, and the potatoes are harvested when they are ready. In trials in which the time of maturity of the potataoes was not indicated, the residue level measured at the shortest PHI was used for evaluation.

Three Dutch trials were evaluated against Dutch GAP (overall application, pre-planting: 4–10 kg ai/ha; band application at planting, 2.5 kg ai/ha), all yielding < 0.02 mg/kg. In 19 German trials evaluated against Dutch GAP, the residue levels were: < 0.01 (10), 0.0076, 0.012 (two), 0.014, 0.016, 0.017 (two), 0.02 and 0.03 mg/kg.

Three of four trials in the United Kingdom in 1995 suffered from abnormal weather conditions, resulting in retarded growth of the tubers. As residues were found in control samples (up to 0.096 mg/kg in one trial), these trials were excluded from evaluation. The remaining 14 trials in the United Kingdom could not be evaluated against that country's GAP (overall application, pre-planting: 6.6–11 kg ai/ha; band application pre-planting, 4.0–6.0 kg ai/ha; 56-day PHI) because the PHI was longer. Eleven of the trials could be evaluated against Dutch GAP, yielding residue levels of: < 0.005 (seven), 0.005 and < 0.01 (three) mg/kg.

Five French trials could be compared to French GAP (overall application, pre-planting: 6–10 kg ai/ha), yielding residue levels of: < 0.005 (two), < 0.01 (two) and 0.011 mg/kg.

One Spanish trial was evaluated against Spanish GAP (overall application, pre-planting: 6–8 kg ai/ha), yielding a residue level of < 0.01 mg/kg.

Two Greek trials could not be compared with Greek GAP (overall application, pre- or at planting: 8–10 kg ai/ha; 60-day PHI) because of the specified PHI. When they were evaluated against Spanish GAP, the residue levels were < 0.02 mg/kg in both.

Fourteen trials in the USA with a granule formulation were compared with US GAP (pre-planting until prior to crop emergence: overall application, 4.5–13 kg ai/ha; band application, 10 kg ai/treated ha = 3.4 kg ai/ha). In the 12 that complied with GAP, the residue levels were: < 0.01 and < 0.02 (11) mg/kg. In three trials in the USA with an emulsifiable concentrate formulation, which complied with US GAP, the residue levels were < 0.01 (two) and < 0.02 mg/kg.

The Meeting decided to combine the residue levels from all the studies, yielding, in ranked order: < 0.005 (nine), 0.005, ≤ 0.01 (19), < 0.02 (17), 0.0076, 0.011, 0.012 (two), 0.014, 0.016, 0.017 (two), 0.02 and 0.03 mg/kg. The Meeting estimated a maximum residue level of 0.05 mg/kg, an STMR of 0.01 mg/kg and a highest residue level of 0.03 mg/kg.

For assessing the risk to consumers of short-term intake, the possible residue level in single units is more important than the average residue level in a lot, which is the residue level in a representative composite sample. The concept of a variability factor was introduced to describe the relationship between the level in a high-residue unit and the typical or average level in the whole batch. The concept was refined to a more precise definition: the residue level in the 97.5th percentile unit divided by the mean residue level for the lot. There is a relation between the number of data from field trials, the proportion (percentile) of the population covered and the confidence level. The 2003 Meeting determined a method for calculating the variability factor on the basis of probabilities of random sampling from a population, making no assumptions as to the type of distribution.

In four of the trials on potato, residue levels were measured in individual units. Two were among the trials conducted in the United Kingdom in 1995 that were considered unreliable (see above). In a trial in France in 2001, 48 of 50 samples had undetectable residues, making the result unsuitable for calculation of a variability factor. In the fourth trial, conducted in the United Kingdom in 1999, 88 of 100 samples contained finite residue levels, so that a variability factor could be calculated. Applying the method referred to above to the 100 individual values available and using the 97.5th percentile in the calculation, the best estimate of the variability factor is 4.1 when the 12 data points below the LOQ are assumed to be at the LOQ, and 4.2 when those values are assumed to be 0. The 95% confidence limits on these estimates are 2.63 – > 5.6 and 2.75 – > 5.6, respectively. The Meeting decided to use the default variability factor of 3 in calculating the short-term intake of ethoprophos, as this value was within the confidence interval of the calculated factor, and the default factor was based on a much larger database.

Sweet potato

The Meeting received the results of four trials on sweet potato in the USA, three of which complied to US GAP (3.3–4.4 kg ai/ha). The residue levels were < 0.01 (two) and 0.014 mg/kg. Three trials is insufficient for recommending a maximum residue level, but the Meeting decided to extrapolate the data on potato to sweet potato, because GAP is similar for the two crops.

On the basis of the trials on potato, the Meeting estimated a maximum residue level of 0.05 mg/kg, an STMR of 0.01 mg/kg and a highest residue level of 0.03 mg/kg for sweet potato.

Grasses for sugar or syrup production

Sugar-cane

Fourteen trials were available in which ethoprophos in granule formulations was applied to sugar-cane in the open furrow at planting. Of these, nine trials from the USA complied to US GAP (band application: 2.2–4.6 kg ai/ha; 10–27 kg ai/treated ha). In all cases, the residue level was below the LOQ (< 0.02 mg/kg). Three trials in India were evaluated against Indonesian GAP (band

application, pre-planting: 1.0–2.0 kg ai/ha), yielding residue levels of < 0.01 mg/kg. The two trials in Brazil with application after planting had no matching GAP.

The Meeting decided to combine the results of the trials in India and the USA, yielding residue levels, in ranked order, of: < 0.01 (three) and < 0.02 (nine) mg/kg. The Meeting estimated a maximum residue level of 0.02 mg/kg, an STMR of 0.02 mg/kg and a highest residue levelof 0.02 mg/kg for ethoprophos on sugar-cane.

Miscellaneous fodder and forage crops (group 052)

Sugar-cane leaves

In the three trials on sugar-cane in India, the residue levels in leaves were < 0.01 mg/kg. In three of the trials in the USA, the residue levels in leaves were < 0.02 mg/kg.

The Meeting estimated an STMR and a highest residue level of 0.02 mg/kg for ethoprophos on sugar-cane forage.

Fate of residues during processing

The Meeting received information on the fate of residues during commercial storage of bananas. After successive storage at 10 °C and 20 °C for fruit ripening, the residue level remained within 80–130% of the original level.

The Meeting received information on the fate of incurred residues of ethoprophos during the processing of potatoes and sugar-cane.

In the first study on potato, the raw agricultural commodity and the processed fractions (washed tubers, wash water, peeled tuber, wet peel, dry peel, flakes, chips) did not contain residues (< 0.01 mg/kg ethoprophos and < 0.01 mg/kg *O*-ethyl-*S*-propyl phosphorothioate). In the second study, no residues were found (< 0.005 mg/kg ethoprophos) in the raw agricultural commodity or in processed fractions (peeled and baked potato). Nevertheless, residues were found in potato peel, at 0.022 and 0.062 mg/kg (average, 0.042 mg/kg) in variety Maris Peer and 0.009 and 0.011 mg/kg (average, 0.010 mg/kg) in variety Desiree. As the raw agricultural commodity did not contain residues, no processing factors for potato could be calculated; however, it can be concluded tentatively that the residue concentrates in peel and not in potato pulp.

After treatment with ethoprophos at planting, a 2-t batch of sugar-cane was processed into bagasse, mixed juice, clarified juice, mud, syrup, raw sugar and molasses according to commercial practices in a pilot plant. No quantifiable residues (< 0.02 mg/kg) were found in the raw agricultural commodity or its processed fractions. In a second study, in which ethoprophos was applied at planting, no residues (< 0.01 mg/kg) were detected in sugar-cane stalks or juice. Even when an exaggerated dose rate was used, in a third study, no residues (< 0.01 mg/kg) were found in stalks, bagasse, mixed juice, clarified juice, clarifier mud, syrup, molasses or sugar. Therefore, no processing factors for sugar-cane could be calculated.

The Meeting also received information on the distribution of residues in peel and pulp fractions of banana and melon. The results of two trials on banana in which residues were found at harvest indicate that ethoprophos tends to concentrate in the pulp fraction of banana. The results of six trials on melon in which residues were found at harvest indicate that ethoprophos is present in both peel and pulp fractions. Generally, the peel fractions contained slightly higher residue levels.

Residues in animal commodities

Dietary burden of farm animals

The Meeting estimated the dietary burden of ethoprophos residues in farm animals from the diets listed in Appendix IX of the *FAO Manual*. Only one feed commodity from each Codex

Commodity Group was used, in this case potato culls (group VR). Calculation from highest residue values provides the concentrations in feed suitable for estimating MRLs for animal commodities, while calculation from the STMR values for feed is suitable for estimating STMR values for animal commodities. In the case of processed commodities, the STMR-P value is used for both intake calculations.

On the basis of a highest residue value of 0.03 mg/kg and 20% dry matter in potato culls, the maximum contribution of residue to the dietary burden would be 0.11 mg/kg for beef cattle given feed containing 75% potato culls and 0.06 mg/kg for dairy cattle given feed containing 40% potato culls.

On the basis of an STMR of 0.01 mg/kg and 20% dry matter, the mean dietary burden of beef cattle given feed containing 75% potato culls would be 0.038 mg/kg, and that of dairy cattle given feed containing 40% culls would be 0.02 mg/kg.

Maximum residue levels

The results of the metabolism study in lactating goats given feed containing 32 ppm ethoprophos indicate that no residues are to be expected in mammalian commodities at a maximum dietary burden of 0.11 mg/kg. As laying hens are not exposed to ethoprophos, no maximum residue levels for poultry commodities are required.

The Meeting estimated a maximum residue level of 0.01* mg/kg in mammalian meat, offal and milks, and STMR and highest residue values of 0.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below 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: ethoprophos.

COMMODITY		RECOMMENDED MRL, mg/kg		STMR or STMR-P mg/kg	HR or HR-P, mg/kg
CCN	Name	New	Previous		
FI 0327	Banana	0.02	0.02*	0.02	0.02
VR 0574	Beetroot	W	0.02*		
VB 0041	Cabbages, head	W	0.02*		
VC 0424	Cucumber	0.01	0.02*	0.01	0.01
MO 0105	Edible offal (mammalian)	0.01*	-	Liver 0 kidney 0	Liver 0 kidney 0
VC 0425	Gherkin	W	0.02*		
FB 0269	Grapes	W	0.02*		
VL 0482	Lettuce, Head	W	0.02*		
GC 0645	Maize	W	0.02*		
AS 0645	Maize fodder	W	0.02*		
AF 0645	Maize forage	W	0.02*		
MM 0095	Meat (from mammals other than marine mammals)	0.01*	-	Muscle 0 fat 0	Muscle 0 fat 0
VC 0046	Melons, except watermelon	0.02	0.02*	0.005	0.012
ML 0106	Milks	0.01*	-	0	
VA 0385	Onion, Bulb	W	0.02*		
SO 0697	Peanut	W	0.02*		
AL 0697	Peanut fodder	W	0.02*		
VP 0063	Peas (pods and succulent=immature seeds)	W	0.02*		
VO 0051	Peppers	W	0.02*		
VO 0445	Peppers, sweet	0.05	-	0.005	0.044

COMMODITY		RECOMMENDED MRL, mg/kg		STMR or STMR-P mg/kg	HR or HR-P, mg/kg
CCN	Name	New	Previous		
FI 0353	Pineapple	W	0.02*		
AM 0353	Pineapple fodder	W	0.02*		
AV 0353	Pineapple forage	W	0.02*		
VR 0589	Potato	0.05	0.02*	0.01	0.03
VD 0541	Soya bean (dry)	W	0.02*		
AL 0541	Soya bean fodder	W	0.02*		
GS 0659	Sugar cane	0.02	-	0.02	0.02
VR 0508	Sweet potato	0.05	-	0.01	0.03
VO 0448	Tomato	0.01*	-	0.005	0.01

DIETARY RISK ASSESSMENT

Long-term intake

The IEDIs of ethoprophos, on the basis of the STMRs estimated for 11 commodities, for the five GEMS/Food regional diets represented 5–10% of the maximum ADI (0–0.0004 mg/kg bw), see Annex 3. The Meeting concluded that the long-term intake of residues of ethoprophos resulting from uses that have been considered by JMPR is unlikely to present a public health concern.

Short-term intake

The IESTIs for ethoprophos were calculated for 11 food commodities for which maximum residue levels had been estimated and for which consumption data were available. The results are shown in Annex 4.

The IESTI represented 0–1% of the ARfD (0.05 mg/kg bw) for the general population and 0–3% of the ARfD for children. The Meeting concluded that the short-term intake of residues of ethoprophos resulting from uses that have been considered by the JMPR is unlikely to present a public health concern.

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